The relations between Van Der Waals and covalent forces in layered crystals

Chaturvedi, Apoorva

2017

Chaturvedi, A. (2017). The relations between Van Der Waals and covalent forces in layered crystals. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/69485>

<https://doi.org/10.32657/10356/69485>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**THE RELATIONS BETWEEN VAN DER WAALS AND
COVALENT FORCES IN LAYERED CRYSTALS**

CHATURVEDI APOORVA

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2016

**THE RELATIONS BETWEEN VAN DER WAALS AND
COVALENT FORCES IN LAYERED CRYSTALS**

CHATURVEDI APOORVA

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2016

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

5th August 2016
Date

A rectangular box containing a handwritten signature in blue ink. The signature appears to be 'A. Chaturvedi'.

.....
(CHATURVEDI APOORVA)

Abstract

With the advent of graphene that propels renewed interest in low-dimensional layered structures, it is only prudent for researchers' world over to develop a deep insight into such systems with an eye for their unique "game-changing" properties. An absence of energy band gap in pristine graphene makes it unsuited for logic electronics applications. This led academia to turn their attention towards structurally similar semiconducting counterparts of graphene, layered transition metal dichalcogenides (LTMDs). Prominent in them, MoS₂, WSe₂ shows tuning of physical properties including band gap with reduced thickness and even an indirect to direct band gap transition when reduced to monolayer. In general, layered compounds are more sensitive to weak bonds (van der Waals forces) than to strong bonds (covalent bonds).

From the perspective of materials science, a novel method for rapid synthesis of thin few layer LTMD crystals has been proposed and developed in-house to complement other existing methods. In this a domestic microwave oven is re-engineered to hold two concentric quartz tubes with inner quartz tube sealed with metal and non-metal powders. The synthesis was achieved by plasma that was formed inside the inner sealed quartz tube heated by plasma surrounding the sealed ampoule. Several compounds (MoS₂, WS₂, MoSe₂, WSe₂ and ReS₂) belonging to layered transition metal dichalcogenides family has been synthesized. Their phase-pure and highly crystalline nature has been confirmed through characterization. The special aspect of the synthesis is the few layer thin nature of the obtained compound that is also confirmed by atomic force microscopy. It has been proposed through this work that such synthesis is practically applicable to other similar metal-nonmetal compounds as long as nonmetal vapor pressure reaches a value required for plasma generation.

Another aspect of the current project is the synthesis of large high quality bulk single crystal of layered transition metal that till today proved to be the bed rock of fundamental electronic and optoelectronic research. Several compounds (MoS₂,

WS₂, etc.) and their alloys and similar new layered systems were successfully grown and their growth conditions are optimized for the available setup. As discussed earlier, interplay between strong and weak bonds plays an important role in the physical properties of such compounds, one of them being anisotropy. While traditionally every layered material has out-of-plane anisotropy on account of their sensitivity to van der Waals forces, there is less explored member of LTMD family that has both in-plane and out-of-plane anisotropy as well as insensitivity towards weak forces (vdW forces). This and its covalent bond (strong bond) substitution and resulting alloy properties are investigated in detail.

After successful synthesis of the compounds, structural, optoelectronic anisotropy is demonstrated. ReS₂ shows highly anisotropic polarization dependent response from 1.55 eV to 2.41 eV. Further its FET has an on/off ratio of 10⁵ and mobility of 18 and 40 cm²V⁻¹s⁻¹ at room and low temperature respectively. Its layer independent direct band is utilized for photodetector devices with high responsivity of 10³ A/W that depicts its intrinsic optical anisotropy and could be utilized as a linear dichroism media for sensitive detection of polarized light. In addition, the alloy ReSSe is both isostructural and anisotropic like ReS₂ besides being direct bad gap. In the end as an example of real application of that as an electrode of lithium ion battery has been proposed. Earth-abundant dichalcogenides in the form of SnS₂ is used as an anode material for lithium-ion battery with LiMn₂O₄ cathode.

Acknowledgements

Every scientific work is an amalgam of ideas, execution and people. This work is accomplished on the above principles. So it becomes prudent for the author to highlight and acknowledge the contribution and support given by different people.

At the very beginning, I would like to thank my supervisor, Professor Christian Kloc for his patient guidance, kind supervision, invaluable hands-on training and constant motivation. His unadulterated views on the aspects of fundamental research allows me to broaden my horizon in terms of scientific approach and research methodology. With utmost sincerity, I would like to whole-heartedly thank him for allowing me to learn, work and explore creative ideas without which this work would not be achievable

A vibrant research group and a healthy working environment always contribute to improve the efficiency of research. In this respect, author finds himself fortunate to be associated with gifted individuals and highly experienced researchers as a member of Crystal Growth Laboratory research group. Many fruitful discussions, enhancement of knowledge and sharing of in-house technological know-how took place during the course of Ph.D. I would like to thank my former group members Dr. Shuanglong Feng, Dr. Ming Lin Toh, Dr. Du Kezhao and Dr. Tan Ke Jei. I would also like to thank my current group members Dr. Jiang Hui, Dr. Peng Hu and Dr., Zhang Keke.

Next, I would like to thank my collaborators, Dr. Fucai Liu, Dr. Xuexia He, Dr. Chaoliang Tan as well as their supervisors A/P Dr. Liu Zheng and Professor Zhang Hua for allowing us to explore joint creative ideas leading to novel results.

I would also like extend my gratitude to Assoc. Professor Alex Yan Qingyu and Assoc. Professor Zhang Qichun for serving on my thesis advising committee, besides giving very useful recommendations. In addition to this I would like to thank the technical and administrative staff of MSE to help us with issues of equipment handling, technical details, safety trainings, course-work guidelines and submission deadlines.

Apart from the scientific journey inside the confines of the laboratory, the course duration would also be cherished for the time spent with friends here in NTU for their love, support and understanding. I would like to thank Ankur, Ankit, Anurag, Ayan, Deepak, Govind, Gurudayal, Prince, Rajiv, Sudhanshu, Sujit, Varun, Venkat, Vipin , Vishal and Yogesh.

Lastly, I am thankful to my family members to encourage me to pursue higher degree and always act as an unwavering pillar of support during the tough times. This dissertation is a tribute to them for their belief in me.

Table of Contents

Abstract	i
Acknowledgements	iii
Table of Contents	v
Table Captions	xi
Figure Captions	xiii
Abbreviations	xxiii
 Chapter 1 Introduction.....	 1
1.1 Hypothesis	2
1.2 Objectives and Scope	5
1.3 Dissertation Overview	5
1.4 Findings and Outcomes	7
References	9
 Chapter 2 Literature Review	 13
2.1 Overview	14
2.2 Early Developments in LTMDs	15
2.3 Renaissance in Layered Materials.....	16
2.4 Two-dimensional Transition Metal Dichalcogenides	17
2.4.1 Atomic Structure of TMDs	19
2.4.2 Electronic Properties of LTMDs.....	20

2.4.3	Optical Studies of LTMDs.....	21
2.4.4	Synthesis Practices in LTMDs.....	23
2.4.5	Field-Effect Transistors and Optoelectronic Applications of LTMDs	26
2.5	Topics Addressed in this Work	29
	References.....	30
Chapter 3	Experimental Methodology	47
3.1	Rationale for selection of Materials	48
3.1.1	Layered Transition Metal Dichalcogenides (LTMDs)	48
3.1.2	Significance of Single Crystal	49
3.2	Typical Experimental Procedure.....	49
3.3	Vapor Phase Single Crystal Growth	50
3.3.1	Chemical Vapor Transport (CVT) Method.....	51
3.3.2	Physical Vapor Transport (PVT) Method.....	52
3.4	Microwave-Induced-Plasma(MIP) Assisted Synthesis of LTMD Thin Crystals ...	53
3.5	Device Fabrication and Measurement for ReS ₂ Crystals.....	54
3.6	Device Fabrication and Measurement for ReSSe Crystals	56
3.7	General Materials Characterizations	57
3.7.1	Thin LTMD Crystal Materials Characterization.....	57
3.7.2	Bulk Single Crystal Materials Characterization	57
	References.....	58
Chapter 4	Vapor Transport Growth of Bulk LTMD Single Crystals	61
4.1	Introduction	62
4.2	Bulk Single Crystal Synthesis	62

4.2.1	Ampoule Preparation and Crystal Growth.....	63
4.3	Materials Characterization of the Synthesized LTMD Crystals	64
4.4	Outcomes and Conclusions	68
	References.....	68
Chapter 5 Microwave-Induced-Plasma Assisted Synthesis of Thin Layered Transition Metal Dichalcogenides Crystals – WS₂, MoS₂, WSe₂, MoSe₂ and ReS₂...		69
5.1	Introduction	70
5.2	Brief Overview of Current Practices for the synthesis of LTMDs and Motivation for Development of New Method	70
5.3	Experimental Setup and Process Details of the Novel Method	72
5.4	Investigation into Synthesized Compounds by the Novel Method	73
5.5	Mechanism Discussion and Advantages Over Other Similar Processes for the Novel Method	78
5.6	Outcomes and Conclusions	80
	References.....	80
Chapter 6 Rhenium Dichalcogenides – True Anisotropic 2D Materials		85
6.1	Introduction	86
6.2	Synthesis of ReS ₂ , ReSe ₂ and ReSSe Bulk Single Crystals.....	87
6.3	Optical, SEM/EDX and P-XRD Characterizations of ReX ₂ Crystals.....	88
6.4	TEM Imaging of ReS ₂ Crystals	94
6.5	AFM Imaging of micro-mechanically exfoliated ReX ₂ flakes	96
6.6	Thickness-dependent Raman Spectroscopy of exfoliated ReX ₂ flakes	97
6.6.1	Rhenium Disulfide (ReS ₂)	97
6.6.2	Rhenium Sulfo-selenide (ReSSe)	99

6.7	Study of Anisotropic Optoelectronic Properties of Rhenium Disulfide (ReS_2)....	100
6.7.1	ARPES and Polarization Dependent Absorption Measurement	100
6.7.2	Electronic Transport Properties of Few Layer ReS_2 FET	103
6.7.3	Photoresponse Properties of Few Layer ReS_2 Photodetector Device	105
6.8	Study of Optoelectronic Properties of Rhenium Sulfo-selenide (ReSSe).....	109
6.9	Outcomes and Conclusions	115
	References.....	116
Chapter 7 Tin Disulfide – Promising “Cousin” of LTMD Family		123
7.1	Introduction	124
7.2	Tin Disulfide Synthesis	124
7.3	Materials Characterization	125
7.4	Thickness Dependent Raman Spectroscopy of Cleaved SnS_2 Crystals	129
7.5	SnS_2 as Negative Electrode in Lithium Ion Battery (LIB).....	130
7.5.1	Electrode Fabrication and Cell Assembly.....	131
7.5.2	Performance of Half and Full-Cell Assembly	131
7.6	Outcomes and Conclusions	136
	References.....	136
Chapter 8 Conclusions and Recommendations.....		139
8.1	Conclusions	140
8.2	Future Recommendations.....	141
	References.....	143
Appendix A Tin Disulfide Single Crystal Data		145

Appendix B Electrochemical performance of LiMn_2O_4 in Half-Cell Assembly	146
Appendix C ReS_2 Phototransistor Data	147
List of Publications	149

Table Captions

Table 2.1   Review of electronic character of LTMDs

Table 4.1   List of all the synthesized compounds with their single crystal growth parameters.
First temperature represents source and second the growth zone temperature

Table A.1   Tin Disulfide (SnS_2) Single Crystal Data from Single Crystal XRD

Figure Captions

Figure 2.1 Structure of a typical layered transition metal dichalcogenides (LTMD) compound

Figure 2.2 Few prominent members of layered compound family

Figure 2.3 Expanse of layered transition metal dichalcogenides depicted over the periodic table by full and partially colored elements. On the right (colored in yellow), are the choice for chalcogen atom that could be combined with different transition metals (in color). The fully colored transition metal depicts the homogeneous layered structure of their chalcogenides while the partially colored transition metal symbolize the non-layered nature of some of its dichalcogenides compounds

Figure 2.4 Two main coordination geometry found in a single sandwich-type monolayer of LTMDs, trigonal prismatic (left) and octahedral (right)

Figure 2.5 (a) Mechanism of light absorption and subsequent photoluminescence process (PL), (b) Raman scattering process. In figure (a), $h\omega$ represents incident light energy, $h\omega$ is the emitted light energy in the PL process, VBM stands for valence band maximum and CBM stands for conduction band maximum. In figure (b), $h\omega_q$ represents emitted phonon's energy during Raman scattering process. E_0 is the ground energy state

Figure 2.6 A temperature dependent study of MoSe₂ monolayer's PL spectra. The temperature range is from 15 K to 295 K. The spectra are plotted in the energy range of 1.52-1.68 eV. Trionic and excitonic transitions could be attributed to the peaks at 1.62 eV and at 1.65 eV respectively

Figure 2.7 (a) Exfoliation through sonication in organic solvent, (b) Exfoliation via lithium intercalation and the corresponding STEM and AFM images, (c) CVD growth of MoS₂ from solid S and MoO₃ precursor and the optical image of the product, (d) CVD growth of MoS₂ from a solid layer of Mo on SiO₂ exposed to S vapour and the optical image of the product

Figure 2.8 (a) Comparative study of field-effect mobility and on/off ratios of semiconductors, (b) Study of field-effect mobility vs band gap for semiconductors used for photovoltaic applications

Figure 2.9 Transport measurement of CVD MoS₂ top-gate FETs, (a) $I_d - V_d$ (output characteristics) curve, (b) $I_d - V_g$ (transfer characteristics) curve, (c) field-effect-mobility extraction from back-gate device

Figure 2.10 (a) Expected line-up of metal Fermi level with the electronic bands of MoS₂ flake if only the difference of the electron affinity of MoS₂ and the work function of the corresponding metal is considered. (b) The cartoon of expected transfer characteristics based on (a). (c) Transfer characteristics of back-gated 6-nm-thick MoS₂ transistor with Sc, Ti, Ni, and Pt metal contacts. The inset shows the actual line-up based on the experimental data

Figure 2.11 (a) Schematic of a MoS₂ photodetector device, (b) its time-domain photoresponse

Figure 2.12 (a) Electroluminescence mapping, (b) combined absorption, electroluminescence and photoluminescence spectra of monolayer MoS₂ with Cr/Au metal contacts

Figure 3.1 Depiction of the availability of LTMDs by the combination of transition metals and chalcogen atoms and their versatile electronic character. *Note:* Tin is added to this family due to the structural and physical similarities of its disulfides and diselenides with that of LTMDs

Figure 3.2 A typical experimental flow followed during the course of this thesis from synthesis, characterization, device fabrication to possible applications

Figure 3.3 Description of the cyclic process of chemical vapor transport in a closed system, (a) Typical temperature profile, (b) Products at different stages and zones

Figure 3.4 A schematic of the field-effect device prepared for electronic transport measurement

Figure 3.5 Typical I_d - V_g curve obtained from a FET device for a range of V_g

Figure 4.1 An illustration of a typical two-zone furnace and temperature profile across sealed ampoule inside the furnace

Figure 4.2 Optical images of some of the selected crystals grown *via* vapor transport

Figure 4.3 (a,b) SEM images, **(c)** EDX spectrum of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ microflakes. Inset in **(c)** is the elemental ratio obtained from the EDX spectrum, **(d)** XRD pattern of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ microflakes. The standard diffraction peaks of MoS_2 (JCPDS #00-009-0312) and MoSe_2 (JCPDS #00-017-0887) are inserted as references

Figure 4.4 (a,b) SEM images and **(c)** EDX spectrum of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ flakes. Inset in **(c)** is the elemental ratio obtained from the EDX spectrum. **(d)** XRD pattern of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ flakes. The standard diffraction peaks of MoS_2 (JCPDS #00-009-0312) and WS_2 (JCPDS #00-008-0237) are inserted as references

Figure 5.1 A schematic of the process flow setup for the synthesis of few-layer transition metal dichalcogenide (TMDC) nanosheets

Figure 5.2 SEM Micrographs of synthesized compounds showing hexagonal morphology. Starting from top-left (in clockwise direction), WS_2 , MoS_2 , WSe_2 , ReS_2 and MoSe_2 . The scale bar shown in the bottom right corner of each micrograph represents 100 nm except for the ReS_2 micrograph, with a scale bar of 1 μm

Figure 5.3 Powder X-ray diffraction (P-XRD) pattern of as-grown samples along with their corresponding standard powder diffraction ICSD file from the database. Starting from top-left (in clockwise direction): WS_2 , MoS_2 , WSe_2 , ReS_2 and MoSe_2

Figure 5.4 Atomic force microscopic images and section height analysis of as-grown samples, starting from the top: WS_2 , MoS_2 and ReS_2

Figure 5.5 Raman response of as-grown samples. Peak positions indicate the phase presence and few-layer nature of WS_2 , MoS_2 , WSe_2 , MoSe_2 and ReS_2

Figure 5.6 Selected area electron diffraction (SAED) patterns (above) and high-resolution transmission electron microscopy (HR-TEM) images (below) of individual WS₂ (left) and MoS₂ (right) crystals

Figure 5.7 Stage-wise mechanism of the synthesis process inside the vacuum-sealed ampoule, (a) The beginning of the process with no plasma generation, (b) the ignition of non-metal (chalcogen) plasma inside the ampoule heated by the outer tube plasma (not shown in this drawing), (c) direct reaction between metal element and non-metal (chalcogen), (d) few-layer thick crystals of TMDCs formed due to the heat of synthesis reaction

Figure 6.1 Optical Image of as-grown ReS₂ crystal

Figure 6.2 (a) SEM images of single crystals of ReS₂ grown via CVT, (b) corresponding EDX analysis with semi-quantitative stoichiometric data

Figure 6.3 P-XRD pattern of ReS₂ crystal indexed with the ICSD file no. 75459

Figure 6.4 Simulated structure of atomic arrangement of ReS₂ in spatial arrangement based on ICSD file no. 75459. Yellow atoms represent sulfur and grey denotes rhenium

Figure 6.5 2D isotropy vs 2D anisotropy between members of LTMDs. A zig—zag diamond-like chain (shown in green) is along the b-axis showing Re-Re clusters

Figure 6.6 Optical image of as-grown ReSe₂ crystals (left) and SEM image of the single crystals grown *via* CVT (right)

Figure 6.7 Semi-quantitative EDX analysis with rough stoichiometric data (left) and P-XRD pattern of ReSe₂ crystals indexed with the ICSD file no. 81813 (right)

Figure 6.8 Simulated structure of atomic arrangement of ReSe₂ in spatial arrangement based on ICSD file no. 81813. Green atoms represent selenium and grey denotes rhenium. A distortion in the structure is on the account of asymmetric Re-Re chains along the b-axis

Figure 6.9 Optical image of as-grown ReSSe crystals (left) and SEM image of the single crystals grown *via* CVT (right)

Figure 6.10 Semi-quantitative EDX analysis with rough stoichiometric data (left) and P-XRD pattern of ReSSe crystals indexed with the ICSD file no. 81815 (right)

Figure 6.11 Simulated structure of atomic arrangement of ReSSe in spatial arrangement based on ICSD file no. 81815. Grey atoms represent rhenium and partial yellow and partial green atoms denotes sulfur and selenium respectively

Figure 6.12 Low resolution TEM images of ultrasonicated ReS₂ crystals diluted in ethanol (left), the circular portion is captured at a higher resolution in the next image (right) by keeping focus on the sharp edges meeting at the corner

Figure 6.13 High resolution TEM (HRTEM) images with the electron beam direction normal to the basal plane and representation of 001 and 010 axes on the sample (left), and corresponding selected area electron diffraction pattern (SAED) centered on [001] zone axis (right)

Figure 6.14 Optical image of mechanically exfoliated ReS₂ crystals in SiO₂/Si substrate

Figure 6.15 (a) Height (thickness) scan of the linear region on the ReS₂ flakes highlighted in (b) and monolayer thickness (height) is observed to be 0.9 nm, **(b)** AFM image of ReS₂ flake used for height (thickness) scan. A white linear region is ear-marked for analysis

Figure 6.16 Optical image of mechanically exfoliated ReSSe crystals in SiO₂/Si substrate

Figure 6.17 (a) An AFM image of ReSSe flake with the selected line profile shown in (b) highlighted by black line, **(b)** The line profile of the ReSSe flakes highlighted in (a) and height of monolayer as 0.76 nm

Figure 6.18 A comparative Raman spectra of rhenium disulfide (ReS₂) indicating negligible or no change in the signal while moving down from bulk (blue), few layer (red) right till the monolayer (green) sample. This is usually attributes to weak interlayer coupling. Apart from many minor peaks, two prominent peaks at 150 cm⁻¹ and 210.5 cm⁻¹ are the one that corresponds to the in-plane (E_{2g}) and mostly out-of-plane (A_{1g}-like) vibration modes, respectively

Figure 6.19 Similar to ReS₂, ReSSe flakes shows similar Raman spectra behavior with changing thickness from monolayer to bulk with thicknesses ranging from monolayer to five layers, and bulk samples. Prominent peaks at 135, 200, 230 and 390 cm⁻¹ are clearly observed

Figure 6.20 A plot between position of prominent peaks (135, 200, 230 and 390 cm⁻¹) and number of layers of ReSSe sample shows the layer-independent nature owing to weak inter-layer interactions

Figure 6.21 Investigation of anisotropy in ReS₂ through ARPES. (a) Undistorted hexagonal Brillouin zone of ReS₂. The band dispersion along Γ -M1 (b) and Γ -M2 (c) with their momentum locations marked in (a). The differences between (b) and (c) indicate that the six-fold symmetry of the hexagonal Brillouin zone is broken due to lattice distortion

Figure 6.22 The optical image of the ReS₂ flake utilized for polarization dependent absorption studies. It's thickness is 12 nm and rotation along b axis is depicted through angle definition

Figure 6.23 Polarization dependent absorption studies ReS₂ flake shown in figure 6.22. (a) Polarization angle (with respect to b-axis of the crystal structure) dependent absorption spectrum, (b) Sinusoidal function – like behavior (black line) is observed when absorption is plotted against polarization angle for different photo energies (2.41, 1.96, and 1.58 eV, respectively)

Figure 6.24 Characteristic curves for few layer ReS₂ field effect transistor based on a 3 nm ReS₂ flake as shown in the optical image (inset of (a), scale bar 10 μ m) (a) Room temperature transistor output transfer curve depicts n-type behavior with low contact resistance. (b) A mobility of 18 cm²V⁻¹s⁻¹ is deduced from the linear (red) and log (black) scale plots of the transfer curve with an on/off ratio of about 10⁵. (c) Temperature dependent study of I_d-V_g transfer curve for the ReS₂ transistor with a drain voltage of 0.1 V (d) Temperature dependent study of the field effect mobility as a function of temperature extracted from (c). With a decrease in temperature, mobility gradually increases. The inset of (d) shows the power law fitting of the data. This indicates the dominant electron-phonon scattering at higher temperature

Figure 6.25 Optoelectronic characterization of the ReS₂ device, (a) 3D schematic view of the photodetection device. The light is illuminated on the ReS₂ channel, and the light polarization is controlled by the half wave plate, which is used for the linear dichroism detection later, (b) Under the different intensity of green light illumination, A plot of photocurrent response for different drain voltage is generated. (c) Similarly, dependence of photocurrent on the intensity of incident illumination is plotted for various drain voltages (1 V (blue), 2 V (green) and 3 V (red) respectively). This also satisfies the power law behavior and depicted by black line. (d) A graphical illustration for different illumination and bias conditions and resultant device band diagrams (E_F , Fermi level; E_C , Conduction band; E_V , Valence band). Schottky barrier is formed at the device-contact interface. On illumination, electron-hole pairs are generated and separated by the applied drain voltage, generating photocurrents, (e) A plot of photoresponsivity with respect to intensity of light is generated based on the data obtained in (c) for drain voltages of 1 V (blue), 2 V (green), and 3 V (red), respectively

Figure 6.26 Polarization sensitive photoresponse studies of ReS₂, (a) 2D plot of dependence of photocurrent on the value of drain bias for different polarization light illuminations. (b) Polarization angle dependence photocurrent for different drain biases. The power law curve (black line) fits with the obtained data. (c) A polar coordinate plot depicting near similar behavior between the photocurrent with drain bias of 1 V (red square) and absorption (green circle) measured under different polarization angle of green light. The blue line is an extension of the sinusoidal function fitting results. This behavior conclusively exhibits the intrinsic linear dichromatic response of ReS₂

Figure 6.27 Absorption spectrum of ReS₂ (red), ReSSe (green) and ReSe₂ (blue)

Figure 6.28 Characteristic curves for few layer ReSSe field effect transistor based on a 3 nm ReSSe flake as shown in the optical image (inset of (b), scale bar 10 μ m) (a) I_d - V_d curve shows near-linear dependence at a low drain voltage indicating a small Schottky barrier between the metal contact and the channel, (b) I_d - V_g curve exhibits n-type behavior with a drain voltage of 1 V, 3 V, and 5 V. (c) I_d - V_d curve and (d) I_d - V_g curve at different temperatures. The drain voltage first increases when the temperature decreases from 300 K, and then decreases when the temperature falls below 240 K. The inset of panel (c) shows

the drain–current change as a function of temperature at a gate voltage of 30 V. The inset of panel (d) shows the temperature dependence of the mobility deduced from the I_d – V_g curve

Figure 6.29 (a) Dependence of photocurrent on the value of drain voltage for different intensities of incident light. (b) A logarithmic plot for dependence of photocurrent on intensity of light for drain voltages of 1 V, 3 V, and 5 V. The power-law fits are depicted by solid lines. The value of exponent on power law is 0.73. (c) A plot of drain voltage dependence of photocurrent for different excitation wavelengths. The inset shows the photocurrent at a drain voltage of 4 V as a function of excitation wavelength, (d) Photoresponsivity as a function of the light intensity as deduced from panel (b)

Figure 6.30 (a) I_d – V_d curve of the ReSSe field-effect transistor, with and without illumination, (b) Photocurrent as a function of gate voltage. The photo-current is deduced by taking the difference of the drain currents with and without illumination. The photocurrent can be strongly modulated by the gate voltage

Figure 7.1 A typical setup and temperature profile for vapor transport growth of single crystals in a two-zone furnace. One zone that contains the starting materials (source zone) is at a comparatively higher temperature (ΔT) to other zone (growth zone) where single crystals are formed

Figure 7.2 Optical images of tin disulfide (SnS_2) single crystalline flakes

Figure 7.3 EDAX of the as-grown SnS_2 single crystals

Figure 7.4 P-XRD pattern of SnS_2 single crystal (P-3 m1, $a=3.6215(8)$ Å and $c=5.856(3)$ Å) on a background-less sample holder

Figure 7.5 Simulated structure of tin disulfide (SnS_2) obtained from CIF file (Single Crystal XRD)

Figure 7.6 Indexed Selected Area Electron Diffraction Pattern (SAED) of SnS_2 crystals ultra-sonicated in ethanol solvent

Figure 7.7 Raman spectrum of SnS_2 single crystal

Figure 7.8 (a) Typical galvanostatic charge-discharge curves of Li/SnS₂ cell between 5-800 mV vs. Li at current density of 65 mA g⁻¹. Inset: Differential capacity profile, **(b)** Plot of capacity vs. cycle number. Filled and open symbols correspond to the charge and discharge, respectively

Figure 7.9 (a) Typical galvanostatic charge-discharge curves of (I) Li/LiMn₂O₄, (II) Li/SnS₂, (III) LiMn₂O₄/SnS₂ cells recorded in the second cycle at current density of 65 mA g⁻¹. The full-cell capacity is calculated based on the anode mass loading. **(b)** Cycling profiles of LiMn₂O₄/SnS₂ cell with coulombic efficiency

Figure 7.10 Cleaved crystal of SnS₂ on SiO₂/Si substrate with different thickness shown through color contrast (yellow/pink represents thicker portion while blue/green represents thinner portion)

Figure 7.11 Thickness dependent Raman spectra of cleaved SnS₂ crystals. Prominent A_{1g} mode at 313 cm⁻¹ is insensitive to thickness although intensity decreases on decreasing thickness. N3 is the thickest region of the sample and N1 is the thinnest region of the sample (as observed under optical microscope)

Figure 8.1 A schematic of the measurement setup used for THz-TDS of two-dimensional layered materials

Abbreviations

2D	Two-dimensional
3D	Three-dimensional
LTMDs	Layered Transition Metal Dichalcogenides
LMDs	Layered Metal Dichalcogenides
FET	Field Effect Transistors
PVT	Physical Vapor Transport
CVT	Chemical Vapor Transport
TMDCs	Transition Metal Dichalcogenides
SPM	Scanning Probe Microscopy
AFM	Atomic Force Microscopy
STM	Scanning Tunneling Microscope
PVD	Physical Vapor Deposition
CVD	Chemical Vapor Deposition
PL	Photoluminescence
VBM	Valence Band Maximum
CBM	Conduction Band Maximum
STEM	Scanning Tunneling Electron Microscopy
s-TMDC	Semiconducting-Transition Metal Dichalcogenides
LEDs	Light Emitting Diodes
PPC	Persistent Photoconductivity
P-XRD	Powder X-Ray Diffraction
SC-XRD	Single Crystal X-Ray Diffraction
SEM	Scanning Electron Microscopy
EDX	Energy-dispersive X-ray spectroscopy
TEM	Transmission Electron Microscopy
MIP	Microwave Induced Plasma
ARPES	Angle-Resolved Photoemission Spectroscopy
HER	Hydrogen Evolution Reaction
DSSC	Dye Sensitized Solar Cell

MW	Microwave
RF	radio-frequency
DBD	Dielectric Barrier Discharge
AC	Alternating Current
DC	Direct Current
EA	Electric Arc
SAED	Select Area Electron Diffraction
HR-TEM	High-Resolution Transmission Electron Microscopy
BP	Black Phosphorus
ICSD	Inorganic Crystal Structure Database
EDC	Energy Distribution Curves
CMOS	Complementary Metal Oxide Semiconductor
vdW	Van der Waals
LIB	Lithium Ion Battery
SEI	Solid Electrolyte Interface
ICL	Irreversible Capacity Loss
TAB-2	Teflonized Acetylene Black
EC	Ethylene Carbonate
DMC	Di-methyl Carbonate

Chapter 1

Introduction

Graphene brought a renaissance in the field of van der Waals solids (layered materials) in the way physicist, materials scientists, chemists, electrical and electronics engineer perceive them. From applications, such as lubricants and intercalation (battery), it starts assuming pivotal position in new-age ultra-low dimension semiconducting devices and related applications. On the similar lines, structurally similar layered transition metal dichalcogenides (LTMDs) with semiconducting behavior have established themselves as the most promising family of the broad class of layered materials. The focus of this work is on the growth, characterization, device fabrication and application of relatively newer member of this family such as ReS_2 and SnS_2 apart from developing novel methods to produce these materials (LTMDs). While studying the above-mentioned materials, emphasis is given on exploring the role of in-plane strong bonds (covalent bonds) and out-of-plane weak bonds (van der Waals forces) in constituting their intrinsic properties both individually and with mutual interaction. Few highlights of this work are investigations into unusual in-plane anisotropy and development of novel method for synthesis of layered materials. Later in this chapter, a small synopsis discussing the presentation of the content in the thesis is reported. Lastly, the findings and outcomes of the project are summarized.

1.1 Hypothesis

For years, layered compounds fascinated physicists, chemists and materials scientists alike first with regards to their two-dimensional crystalline order and later with its quasi two-dimensional structure and related properties. The former was widely debated in the academia during the early years [1]. Once a generic understanding about these materials (layered compounds) has been developed, focus shifted to identifying such compounds and their optimum synthesis route. This allows people to understand their structural and physical properties in detail. One of the primary aspect of such compounds was the presence of strong (covalent) and weak (van der Waals) bonds in an orderly fashion, i.e. covalently bonded layers (a-b plane) stacked or held loosely by van der Waals forces (c-axis). Such structural arrangement gives rise to anisotropy of structural and physical properties in these compounds. These compounds are essentially quasi-two-dimensional systems, and, thus, some physical properties in such structures may exhibit a two-dimensional behavior. Traditionally they were found suitable as excellent lubricants due to the ease of sliding of the layers over one another.

In addition, the van der Waals “spaces” between them can be utilized to introduce “foreign” atoms and some organic molecules between the layers forming the intercalation compounds. These intercalation compounds exhibit significant changes in a wide variety of properties as compared to the non-intercalated materials. The process of intercalation is reversible, and thus such layered compounds may be used, e.g., as cathodes in rechargeable high-energy-density batteries, in which the cell reaction is the reversible intercalation of the layered crystals.

Recently (in 2004), the layered compounds family experienced a renaissance of sorts with the realization of an atom thick layer of graphite (graphene) by the scotch-tape technique [2,3]. Further study and investigation revealed “game-changing” properties on account of truly two-dimensional nature of graphene. Its ultra-high mobility coupled with anomalous quantum Hall effect and massless Dirac Fermions propelled it as an ideal candidate for real-world applications [4–11].

In spite of the above, the biggest drawback of graphene is the absence of energy band gap which makes it incompatible with the logic electronics with low-power applications. Several attempts were undertaken thereafter to open up a band gap in graphene by studying bilayer graphene, functionalized graphene, reduced graphene oxide, etc. but not without compromising on the pristine properties of graphene including ultra-high mobility.[12–18] This roadblock in the development of low-dimensional logic electronics puts into limelight some of the inorganic analogues of graphene such as transition metal chalcogenides, metal halides, transition metal oxides and tri-oxides, oxy-chalcogenides and III-V layered semiconductors.[19] The availability of band gap coupled with relative stability of their few and monolayer counterparts makes them attractive for a plethora of applications. In addition, some of the group VI transition metal dichalcogenides (MoS_2 , WSe_2) undergo indirect-to-direct band gap transition when cleaved to monolayer [20].

This suitability of inorganic layered compounds and the gradual development of their synthesis methods allows researchers over the world to study their optical, transport, and structure-sensitive properties and employ them in applications ranging from field-effect transistors, logic integrated circuits, light emitting diodes, multi-purpose chemical sensing and bio-detection.[21–32] Even though the available catalogue of inorganic layered 2D materials family is not completely explored, new and novel layered materials are in process to contribute and expand the horizons of imaginations of what these materials can achieve. Lately, academia also started pioneering attempts to “club” two or more such materials in a single integrated system to harness their hybrid functionalities in devices such as light harvesting, light generations, all 2D materials flexible electronics, Ohmic contacts for integrated circuits, etc. [33–37].

While moving forward it is also pretty important to understand the fundamental phenomena at work in these material systems that allow them to have special properties and usage in high-end applications.

The family of 2-D layered materials are relatively more sensitive to weak bonds than strong bonds when it comes to change in structure (thickness) sensitive properties. We need to

closely inspect the confinement effects, stacking or inter-layer coupling energy and the resulting transition of optical band gap or an absence of it. Owing to the disparity and the different nature of layered dichalcogenides, they could be divided into two groups for the purpose of the current work:

- a) Robust or structure (thickness) independent, e.g. ReS₂, SnS₂, Black Phosphorus.
- b) Sensitive or thickness dependent, e.g. MoS₂, WSe₂ and WS₂.

In both the groups, the transition or relative absence of it is dependent on a key factor of magnitude of interlayer coupling energy. While MoS₂ and similar members have a coupling energy of order of few hundred meV for conventional 2 X 2 cell, weakly stacked SnS₂ and ReS₂ have a coupling energy of an order less per unit cell [38]. This could be ascribed to the negligible overlap of molecular orbitals in the latter resulting in decoupled units (single layer) which makes the bulk behaves as if it is a single layer. From the perspective of materials science, following points were probed in this work:

- 1) Preparation of weakly stacked members of layered dichalcogenides family
- 2) Development of new methods for efficient synthesis of LTMDs.
- 3) Their optical band gap behavior with thickness variation
- 4) The behavior of their individual layers (monolayers) as isotropic and anisotropic
- 5) Application of their intrinsic properties in devices.

Above described properties of layered compounds allows formulation of a hypothesis that almost all physical properties are anisotropic described by both weak and strong bonds. Therefore, while in 3D materials doping and defect describe the extrinsic properties of bulk samples, in 2D materials these two parameters are not sufficient. An additional parameter, modification of crystal composition and structure on van der Waals spaces, needs to be controlled. On one hand, such additional tuning possibility make 2D materials more complex, on the other control of both strong – covalent and weak van der Waals positions is a chance to utilization of 2D behavior typical only to 2D materials. Moreover, not all 2D crystals structures are similar. While MoS₂, WS₂ and many more show strong anisotropy

along c-axis and isotropy in the ab-plane, other like ReS_2 are anisotropic not only along the c axis but in addition they show strong anisotropic behavior in ab-plane also. It should have unexplored consequences in absence of coupling energy between the layers and possibility to form new artificial compounds based on materials like ReS_2 .

1.2 Objective and Scope

The objective of this project is to grow high quality crystalline compounds of layered metal dichalcogenides (LMDs) family, their intercalation with inorganic/organic species (elements and compounds), investigation of their physical and chemical properties to enable understanding of high-performance applications such as field effect transistors (FET), photovoltaics, energy storage and light harvesting, etc. The detailed scope is listed below:

1. Growth and intercalation of large high quality single crystals of LTMDs from gas phase *via* Physical Vapor Transport (PVT) or Chemical Vapor Transport (CVT).
2. Synthesis of thin crystals of LTMDs and similar compounds through in-house microwave assisted plasma process. It also includes optimization, scaling – up and better understanding of the current system with respect to morphological control, reaction time, etc.
3. Investigation of optoelectronic properties of crystals, especially transport properties through few-layer field effect transistor (FET) and optical properties.
4. Investigations of intrinsic two-dimensional in-plane anisotropic materials and the resultant variations in properties on account of it.
5. Presentation of synthesized compounds as viable alternatives to currently practiced materials in applications (e.g. battery, photodetector, etc.).

1.3 Dissertation Overview

Chapter 2 presents the historical advances in the family of layered materials in general and two dimensional materials in particular. The chapter discusses the basic structural attributes of the layered materials, the properties arising from it and historical application usages.

The recent renewed interest is reviewed in detail to understand the challenges and opportunities available in the field of layered materials. Further, anisotropic two-dimensional layered materials with lower symmetry are discussed that identify with the work carried out in this thesis that were not explored earlier.

Chapter 3 describes the methodology to synthesize LTMDs and related layered materials both via traditional vapor transport growth method as well as novel microwave plasma method developed for rapid synthesis of thin LTMD crystals. It also describes the experimental scheme followed during the course of this thesis work and various materials characterizations techniques used and optoelectronic measurements performed to study the materials properties.

Chapter 4 discusses all the single crystal growth of the layered compounds that are synthesized via vapor transport growth (CVT or PVT). Their starting materials, growth conditions, experimental setup and physical characterizations were discussed. In addition to pristine stoichiometric compounds, alloys were also synthesized as an attempt to tune properties based on alloy composition. Some new two-dimensional compounds other than LTMDs with attractive future possibilities were also synthesized and characterized.

Chapter 5 introduces and explores the development of a novel method for the synthesis of few layer thin crystals of LTMDs. In this, few-layer thin crystals of WS_2 , MoS_2 , WSe_2 , MoSe_2 and ReS_2 were synthesized via the microwave-induced-plasma-assisted method. The synthesis was accomplished in plasma that was formed inside sealed quartz ampoules heated by plasma surrounding the sealed ampoule. Powder X-ray diffraction, Raman spectroscopy and Transmission Electron Microscopy indicate thin crystals of high quality. The novel method is rapid, reproducible and environmentally friendly. It is applicable to practically every direct reaction between metals and nonmetals if the nonmetal vapor pressure can reach a pressure of a few torr, which is required for plasma formation inside a sealed ampoule.

In chapter 6, a unique member, rhenium disulfide (ReS_2) of LTMD family has been explored by focusing on its intra-layer anisotropic property apart from usual out-of-plane anisotropy present in all the other layered compounds. This occurs on account of its distorted structure and weak inter-layer coupling. Rhenium dichalcogenides series being isostructural and single phase in nature provides a new candidate for composition-dependent band gap engineering and their tunable properties coupled with in-plane anisotropy makes it an attractive proportion. This and other rhenium based dichalcogenides (alloys) materials has been probed in detail to study their structural, electronic and optical anisotropy and their possible usage in niche applications.

Chapter 7 describes another special compound SnS_2 . Its earth-abundant nature makes it attractive to explore for variety of applications. Another aspect that sets it apart from the other TMDCs is the lack of optoelectronic band structure transition which is common for this family. Here an attempt is made to propose the high-crystalline SnS_2 as an anode material for Li-ion Battery and methods that could be useful in optimizing its performance are discussed.

Chapter 8 summarizes and concludes the thesis work and lists the recommendations for future directions.

1.4 Findings and Outcomes

The following are the findings, outcomes and originality of this work

- Large, high quality bulk single crystals of LTMDs have been synthesized by means of vapor-phase transport growth method that are considered gold-standard for any compound with near-ideal properties. These could be utilized as a platform for fundamental optoelectronic research both at bulk and few or monolayer level.
- A new novel method has been developed for the synthesis of LTMDs. This method utilizes the concept of microwave-induced-plasma to assist and ignite plasma inside a sealed quartz tube for synthesis to occur. This method is rapid, reproducible and

environmentally friendly. While optimizing the system we found that the system could be utilized for virtually every material/compound where the non-metal component could reach the required vapor pressure to ignite plasma and synthesis to occur. This method provides a new approach for the synthesis of LTMDs for follow-up applications such as catalysis for hydrogen evolution reaction, etc.

- A new but unique member of LTMD family, ReS_2 has been synthesized and its intra-layer anisotropy is characterized in detail. Based on that its optical and electronic anisotropy is observed. ReS_2 also exhibits direct band gap both in bulk and few or monolayer form.
- For thin few layer sample of ReS_2 , anisotropic response in a wide range from 1.55 eV (800 nm) to 2.41 eV (450 nm) with respect to crystal orientation are observed for polarization dependent absorption studies.
- Few-layer thick ReS_2 field-effect mobility (n-type) of $18 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with an on/off ratio of 10^5 is recorded that could be increased to as high as $40 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ by lowering the temperature up to 77K.
- Optical anisotropy of ReS_2 is utilized to study the polarization dependence of photoresponse which is found to be following a similar pattern as that of absorption studies. Also the photoreponsivity is as high as 10^3 A/W at low intensity of light.
- Composition dependent band-gap engineering is employed for rhenium based chalcogenide alloy ReSSe as they are isostructural and single phase to both ReS_2 and ReSe_2 . The prepared alloy crystal is structurally and optoelectronically characterized to present it as viable alternative for low cost devices. In addition, these alloys also exhibit direct band gap through their thicknesses with in-plane anisotropy.
- Few layer thick ReSSe field effect mobility (n-type) of $3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with an on/off ratio of 10^5 is recorded. Due to alloying and higher defect concentration, their mobility

below 240 K decreases on account of charged impurity scattering becoming dominant.

- A healthy photoresponse of 8 A/W at 1 V is also recorded for the few layer photodetector device of ReSSe.
- Earth-abundant dichalcogenides in the form of SnS₂ is used as an anode material for lithium-ion battery with LiMn₂O₄ cathode. It shows meager capacity fade upon cycling irrespective of half-cell or full-cell configuration. The full cell is capable of working in the potential of ~3.64 V.

References

- [1] N.D. Mermin, Crystalline order in two dimensions, *Phys. Rev.* 176 (1968) 250–254.
- [2] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V. V Khotkevich, S. V Morozov, et al., Two-dimensional atomic crystals., *Proc. Natl. Acad. Sci. U. S. A.* 102 (2005) 10451–3.
- [3] K.S. Novoselov, A.K. Geim, S. V Morozov, D. Jiang, Y. Zhang, S. V Dubonos, et al., Electric Field Effect in Atomically Thin Carbon Films, *Sci.* 306 (2004) 666–669.
- [4] K.S. Novoselov, A.K. Geim, S. V Morozov, D. Jiang, M.I. Katsnelson, I. V Grigorieva, et al., Two-dimensional gas of massless Dirac fermions in graphene, *Nature.* 438 (2005) 197–200.
- [5] Y. Zhang, Y.-W. Tan, H.L. Stormer, P. Kim, Experimental observation of the quantum Hall effect and Berry's phase in graphene, *Nature.* 438 (2005) 201–204.
- [6] E.H. Hwang, S. Adam, S. Das Sarma, Carrier Transport in Two-Dimensional Graphene Layers, *Phys. Rev. Lett.* 98 (2007) 186806.
- [7] A.K. Geim, K.S. Novoselov, The rise of graphene, *Nat Mater.* 6 (2007) 183–191.
- [8] K.I. Bolotin, K.J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, et al., Ultrahigh electron mobility in suspended graphene, *Solid State Commun.* 146 (2008) 351–355.
- [9] J.-H. Chen, C. Jang, S. Xiao, M. Ishigami, M.S. Fuhrer, Intrinsic and extrinsic performance limits of graphene devices on SiO₂, *Nat Nano.* 3 (2008) 206–209.
- [10] A.H. Castro Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov, A.K. Geim, The electronic properties of graphene, *Rev. Mod. Phys.* 81 (2009) 109–162.

- [11] F. Schwierz, Graphene transistors, *Nat Nano.* 5 (2010) 487–496.
- [12] T. Ohta, A. Bostwick, T. Seyller, K. Horn, E. Rotenberg, Controlling the Electronic Structure of Bilayer Graphene, *Sci.* 313 (2006) 951–954.
- [13] E. V Castro, K.S. Novoselov, S. V Morozov, N.M.R. Peres, J.M.B.L. dos Santos, J. Nilsson, et al., Biased Bilayer Graphene: Semiconductor with a Gap Tunable by the Electric Field Effect, *Phys. Rev. Lett.* 99 (2007) 216802.
- [14] Q. Yan, B. Huang, J. Yu, F. Zheng, J. Zang, J. Wu, et al., Intrinsic Current–Voltage Characteristics of Graphene Nanoribbon Transistors and Effect of Edge Doping, *Nano Lett.* 7 (2007) 1469–1473.
- [15] J.B. Oostinga, H.B. Heersche, X. Liu, A.F. Morpurgo, L.M.K. Vandersypen, Gate-induced insulating state in bilayer graphene devices, *Nat Mater.* 7 (2008) 151–157.
- [16] X. Wang, Y. Ouyang, X. Li, H. Wang, J. Guo, H. Dai, Room-Temperature All-Semiconducting Sub-10-nm Graphene Nanoribbon Field-Effect Transistors, *Phys. Rev. Lett.* 100 (2008) 206803.
- [17] Y. Zhang, T.-T. Tang, C. Girit, Z. Hao, M.C. Martin, A. Zettl, et al., Direct observation of a widely tunable bandgap in bilayer graphene, *Nature.* 459 (2009) 820–823.
- [18] X. Li, X. Wang, L. Zhang, S. Lee, H. Dai, Chemically Derived, UltrasMOOTH Graphene Nanoribbon Semiconductors, *Sci.* 319 (2008) 1229–1232.
- [19] A.D. Yoffe, Layer Compounds, *Annu. Rev. Mater. Res.* 3 (1973) 147–170.
- [20] K.F. Mak, C. Lee, J. Hone, J. Shan, T.F. Heinz, Atomically Thin MoS₂: A New Direct-Gap Semiconductor, *Phys. Rev. Lett.* 105 (2010) 136805.
- [21] G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, M. Chhowalla, Photoluminescence from Chemically Exfoliated MoS₂, *Nano Lett.* 11 (2011) 5111–5116.
- [22] B. Radisavljevic, a Radenovic, J. Brivio, V. Giacometti, A Kis, Single-layer MoS₂ transistors., *Nat. Nanotechnol.* 6 (2011) 147–50.
- [23] L. Liu, S.B. Kumar, Y. Ouyang, J. Guo, Performance Limits of Monolayer Transition Metal Dichalcogenide Transistors, *IEEE Trans. Electron Devices.* 58 (2011) 3042–3047.
- [24] S. Ghatak, A.N. Pal, A. Ghosh, Nature of Electronic States in Atomically Thin MoS₂

- Field-Effect Transistors, *ACS Nano*. 5 (2011) 7707–7712.
- [25] B. Radisavljevic, M.B. Whitwick, A. Kis, Integrated Circuits and Logic Operations Based on Single-Layer MoS₂, *ACS Nano*. 5 (2011) 9934–9938.
- [26] Z. Yin, H. Li, H. Li, L. Jiang, Y. Shi, Y. Sun, et al., Single-Layer MoS₂ Phototransistors, *ACS Nano*. 6 (2012) 74–80.
- [27] S. Kim, A. Konar, W.-S. Hwang, J.H. Lee, J. Lee, J. Yang, et al., High-mobility and low-power thin-film transistors based on multilayer MoS₂ crystals, *Nat Commun*. 3 (2012) 1011.
- [28] W. Choi, M.Y. Cho, A. Konar, J.H. Lee, G.-B. Cha, S.C. Hong, et al., High-Detectivity Multilayer MoS₂ Phototransistors with Spectral Response from Ultraviolet to Infrared, *Adv. Mater*. 24 (2012) 5832–5836.
- [29] O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, A. Kis, Ultrasensitive photodetectors based on monolayer MoS₂, *Nat Nano*. 8 (2013) 497–501.
- [30] R.S. Sundaram, M. Engel, A. Lombardo, R. Krupke, A.C. Ferrari, M. Steiner, Electroluminescence in Single Layer MoS₂, *Nano Lett*. 13 (2013) 1416–1421.
- [31] W. Zhu, T. Low, Y.-H. Lee, H. Wang, D.B. Farmer, J. Kong, et al., Electronic transport and device prospects of monolayer molybdenum disulphide grown by chemical vapour deposition, *Nat Commun*. 5 (2014) 3087.
- [32] D. Jariwala, V.K. Sangwan, L.J. Lauhon, T.J. Marks, M.C. Hersam, Emerging Device Applications for Semiconducting Two-dimensional Transition Metal Dichalcogenides, *ACS Nano*. 8 (2014) 1102–1120.
- [33] A.K. Geim, I. V Grigorieva, Van der Waals heterostructures., *Nature*. 499 (2013) 419–25.
- [34] O. Lopez-Sanchez, E.A. Llado, Light Generation and Harvesting in a van der Waals Heterostructure, *ACS Nano*. 8 (2014) 3042–3048.
- [35] H. Fang, C. Battaglia, C. Carraro, S. Nemsak, B. Ozdol, J.S. Kang, et al., Strong interlayer coupling in van der Waals heterostructures built from single-layer chalcogenides., *Proc. Natl. Acad. Sci. U. S. A*. 111 (2014) 6198–6202.
- [36] C.-H. Lee, G.-H. Lee, A.M. van der Zande, W. Chen, Y. Li, M. Han, et al., Atomically thin p–n junctions with van der Waals heterointerfaces, *Nat. Nanotechnol*. 9 (2014) 676–681.

- [37] X. Hong, J. Kim, S.-F. Shi, Y. Zhang, C. Jin, Y. Sun, et al., Ultrafast charge transfer in atomically thin MoS₂/WS₂ heterostructures, *Nat. Nanotechnol.* 9 (2014) 682–686.
- [38] S. Tongay, H. Sahin, C. Ko, A. Luce, W. Fan, K. Liu, et al., Monolayer behaviour in bulk ReS₂ due to electronic and vibrational decoupling., *Nat. Commun.* 5 (2014) 3252.

Chapter 2

Literature Review

This chapter presents the historical advances in the family of layered materials in general and two dimensional materials in particular. The chapter discusses the basic structural attributes of the layered materials, the properties arising from it and historical application usages. The recent renewed interest is reviewed in detail to understand the challenges with regards to synthesis, device fabrications and integration into real world applications. This presents an opportunity to explore new members apart from well-established members to fully understand the interplay between strong and weak bonds as well as the impact of nature (magnitude) of such bonds on shaping the electronic band structure and other intrinsic material properties. Further, anisotropic two-dimensional layered materials with lower symmetry are discussed that is the focus of the work carried out in this thesis that were not explored earlier.

2.1 Overview

Research and development in non-conventional materials is often proceeded by the necessity emanated in the form of imminent exhaustion of resources (fossil fuels), environmental concerns (greenhouse gas emissions) and cost-ineffective mass utilization of the prevailing technology [1,2]. The optoelectronic industry needs high quality, flexible, and consequently thin direct band gap semiconductor materials in order to realize devices in situations where standard silicon chips and commercial materials cannot work due to expense and geometry. So far research has focused on organic materials [3,4] because of their potentially low cost. But their poor mobility has prompted several groups to look for inorganic alternatives [5,6] i.e. layered materials. Layered materials such as the family of layered transition metal dichalcogenides (LTMDs) and graphite have desired physical properties and chemical stability. In addition, wide range of electronic and optical properties of the layered materials with large ranges of band gap values provide prospectives in diverse applications. Another noticeable aspect of such compounds is their changing behavior with changing dimensionality i.e. monolayer or few layer thick samples and bulk (many layers) samples. In fact, monolayers of MoS₂ exhibited direct band gap of 1.8 eV but much lower mobility, compared to its bulk (indirect band gap, 1.20 eV) in the same transistor architecture [7,8]. Similarly, graphene, the monolayer of layered graphite shows exceptionally high mobility of 200000 cm²/V-s but no energy band gap (E_g) [9].

Lately, LTMDs assume equal significance if not more owing to their subtle advantages (band gap, availability in nature, etc.), over monolayer graphite (graphene) both in bulk and reduced dimensionality. These materials are characterized by strong bonding within the layer and weak (van der Waals) interactions between the layers (figure 2.1).

Figure 2.1: Structure of a typical layered transition metal dichalcogenides (LTMD) compound

The strong anisotropy of the crystal structure influences many of their physical and chemical properties. The layered transition metal dichalcogenides (LTMDs) are the most widely investigated of the layered materials with regard to their structural, electronic and optical properties. Thus, availability of such crystalline material for technological purposes (single crystal, Nano-sheets, etc.) assumes greater significance as a crucial factor for the development of advanced technologies as well as breakthrough in applied and basic sciences.

2.2 Early developments in LTMDs

Even before the successful isolation of graphene in 2004 [10], LTMD compounds kept the research world fascinated with them for a large part of last five decades. The motivations for scientists, ranges from structural and electronic anisotropy for electronic transport measurements [11] to the insertion (intercalation) of guest species in the “van der Waals space” between the layered materials with exotic properties such as high T_c superconductivity, magnetic properties and as storage materials (battery, supercapacitor, etc.) [12–19]. Due to the sliding nature of the individual layers they were also often employed as solid lubricants in tribological applications [20–24]. In the metallic members of this family, prominent being TaS₂, TaSe₂ and NbSe₂, phenomena such as charge density waves and super lattices were observed by various groups [25]. In the early years, the major portion of the research was focused on finding the optimum route to synthesize high purity single crystal of the LTMD compounds which was carried extensively by Nitsche and co-workers from late 1950's to early 1960's [26–31]. Later Schafer described the vapor transport growth of such compounds in detail with thermodynamic and kinetics parameters [32–35], thus establishing it as a standard method for the synthesis of high purity bulk single crystal of LTMDs. After this, researchers start studying the bulk physical properties of these systems and observed anisotropy [36–42] analogous with what was reported very early for layered graphite [43]. Additionally, the presence of weak bonds between the layers allow them to cleave the bulk crystals along the basal plane through its thickness. Although much research on few or monolayer counterpart of LTMDs have been done only very recently, the studies on very thin crystals of LTMDs were reported several times

exploring low-dimensional layered structures [44,45]. One of the reasons for slow progress could be the non-availability of nanoscale characterization techniques such as scanning probe microscopy (SPM), atomic force microscopy (AFM), etc. [46,47]. These techniques took as late as early 1990's to be hands-on and commercially available after the pioneering work by two IBM scientists, Dr. Binnig and Dr. Rohrer in 1981 in inventing the scanning tunneling microscope (STM) [48]. In fact, an isolated layer of MoS₂ supported on alumina was reported as early as 1986 by Joensen et al. [49]. One can imagine the plateaued nature of research in LTMDs from late 1980's to early 2000's with the fact that it took another 25 years to have single layer MoS₂ transistors [50]. In the pre-graphene (before 2004) era much of the research on LTMDs was focused on bulk material properties of the LTMD family and tuning of physical properties through intercalation of inorganic and organic species between the layers or through substitutional doping and alloying of the pristine materials. Even then researchers have discussed such quasi-two dimensional structures and the special properties they might have in atomically thin range. Recent developments would be discussed in the next section.

2.3 Renaissance in Layered Materials

In 2004, a watershed moment arrived in the field of layered materials with the isolation of single layer of graphite (graphene) by a simple scotch tape technique by Novoselov et al. [10]. Since then several “game-changing” physical properties of graphene such as massless Dirac Fermions, half-integer and anomalous quantum Hall effect, ballistic transport with ultra-high mobility, superior mechanical strength, etc. have been reported [9,51–62]. Although discovery of graphene does provide a new perspective for the investigation of layered compounds at low-dimensions but gapless electronic energy band structure proves to be its biggest drawback. This rendered its unsuitability for applications such as logical gate electronics or in low-power applications. In a bid to overcome this shortcoming, efforts were made to structurally manipulate graphene to open up a narrow band gap in it but it led to deterioration of other existing impressive pristine physical properties [51,63–68]. Simultaneously, such revelations brought back other established layered compounds in the same discourse. The prominent members of this graphene-analogue layered family

are chalcogenides (Bi_2Se_3), oxides (MoO_3), nitrides ($h\text{-BN}$), metal phosphotrisulfides (FePS_3), oxychlorides, halides and transition metal dichalcogenides (figure 2.2). The facile and almost universal nature of the proposed mode of preparation (scotch-tape technique) for few or monolayer sample from bulk samples also played a part in expanding the horizons beyond graphene.

Figure 2.2: Few prominent members of layered compound family

While exploring the graphene-analogues, emphasis is given on the stability of its mono or few layer form and preferably semiconducting nature of its electronic band structure. On this count, layered transition metal dichalcogenides (LTMDs) are the most suited member of this family [50,69–71]. Their monolayer counterpart experience direct band transition from their indirect bulk counterparts. Also, their amicable band gap range falling between near infrared to visible range, and their superior performance compared with graphene as a candidate for logic electronic and optoelectronic applications propped them at the forefront of two-dimensional/low-dimension revolution in layered compounds [50,69–111].

2.4 Two-dimensional Transition Metal Dichalcogenides

In the period of last 10 years, more specifically post 2010, a deluge of studies is reported

on 2D LTMDs and still continuing till today [10,112], initial attempts to prepare large area monolayer samples were attempted through physical vapor deposition (PVD) [111] and later chemical vapor deposition (CVD) [113–122]. In comparison to graphene, CVD synthesis of LTMDs uses solid precursors and very narrow homogeneity range to work with. Despite such tight requirements of thermodynamic parameters, it has now developed into an almost standard method and successful growth have been reported with a quality comparable to micro-mechanically exfoliated flakes [86,87,117]

The unique physical properties of 2D LTMDs have also been deeply explored. In 2010, K.F. Mak et al. [8] reported the indirect-to-direct transition of the band gap as MoS_2 evolves from bulk to the monolayer form; and C. Lee et al. [123] reported the anomalous behaviors of the Raman spectroscopy of mono-, bi- and few-layer MoS_2 . Various theoretical studies [124–132] showed that many-body effects, including the electron-electron interaction and the electron-hole interaction, are of great importance in 2D LTMDs; that is, both the electron self-energies and the exciton binding energies should be considered in describing the electronic band structure of 2D TMDs correctly. The existence of tightly bound excitons [8,70] and multi-excitons [133–137] with relatively large binding energies in 2D TMDs was then discovered, making the optical world of 2D closely coupled with the "exciton" concept, which is rarely mentioned in 3D optoelectronics. Later on, four research groups reported at the same time that the two electron valleys with different spins in TMD materials can be selectively activated by their excitation using the circularly polarized light [138–141]; based on this, they proposed the novel type of electronics - called valleytronics which can be potentially used in high-performance digital signal processing and even quantum computing. More recently, K. F. Mak et al. observed the valley Hall Effect [142] in monolayer MoS_2 , which is the first non-magnetic-field-involved quantum Hall Effect discovered so far.

With such outstanding properties, 2D TMDs have been quite attractive to electrical engineers as well. The first transport measurement on atomic thin TMDs was done by the A. Geim's group and co-workers and reported in 2005 [112], in which MoS_2 and NbSe_2 monolayers were probed at room temperature with tunable conductivity measurements

using an external electric field. In 2010, a group of researchers from EPFL, Switzerland led by Andres Kis and S. Salahuddin's and co-workers situated at University of California, Berkeley published their path-breaking works on the experimental demonstration [50] and theoretical prediction [71], respectively, of monolayer MoS₂ field effect transistors (FETs). Soon after that, more groups joined this rapidly growing field of 2D semiconductors, and more potential applications with 2D TMDs were proposed, including logic integrated circuits [50,71–89], photodetectors [90–98], light-emitting devices [99, 101, 103, 105, 107, 108, 143], multi-purpose chemical sensing and bio-detection [144–148].

2.4.1 Atomic Structure of TMDs

The family of TMDs is composed of nearly 40 different compounds [149]. As shown in the periodic table in figure 2.3, the highlighted transition metal and chalcogen chemical elements are the elements that are predominately crystalized into layered structures. The half colored elements can form layered dichalcogenides as well, but the same constituents can also form other crystal structures as that interesting phase transitions can occur. For example, NiS₂ is found to have a pyrite structure but NiTe₂ is a layered compound.

H	MX ₂ M = Transition metal X = Chalcogen																He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La - Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac - Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

Figure 2.3: Expanse of layered transition metal dichalcogenides depicted over the periodic table by full and partially colored elements. On the right (colored in yellow), are the choice for chalcogen atom that could be combined with different transition metals (in color). The fully colored transition metal depicts the homogeneous layered structure of their chalcogenides while the partially colored transition metal symbolize the non-layered nature of some of its dichalcogenides compounds [149]

The unit cell of LTMDs consists of 1 transition metal atom and 2 chalcogen atoms.

Accordingly, the general chemical formula is denoted by MX_2 , in which M and X stand for the transition metal and the chalcogen element, respectively. Each layer of MX_2 is three-atoms thick, with 1 transition metal layer sandwiched between 2 chalcogen layers. The monolayer atomic structure can be either trigonal prismatic (e.g. MoS_2 , NbS_2 ,) or octahedral (e.g. HfS_2 , PtS_2), as shown in figure 2.4.

Figure 2.4: Two main coordination geometry found in a single sandwich-type monolayer of LTMDs, trigonal prismatic (left) and octahedral (right) [149]

2.4.2 Electronic Properties of LTMDs

Depending on the configuration of the IVB-VIB transition metal and chalcogen elements, the physical properties of LTMDs vary significantly. Table 2.1 summarizes the basic electronic properties of the TMD family. The dichalcogenides are wide bandgap semiconductors when the metal elements are from Group IVB and VIB, and narrow bandgap semiconductors when the metal elements are from Group VIIB and VIII, whereas the Group VB dichalcogenides are metallic materials, and some of them are superconducting at low temperature. The electronic and optical properties depend strongly on the thickness of the TMDs, especially when they are less than 5 nm thick. If we take MoS_2 as an example, the optical bandgap can be varied from 1.2 eV to 1.9 eV when going from the bulk to the monolayer. MoS_2 with a thickness of more than 2 layers is an indirect band gap semiconductor, whereas it becomes a direct band gap semiconductor when thinned down to a monolayer. Other unique properties of monolayer or few-layer MoS_2 include a large excitonic binding energy, abundance of multi-excitons, strong electron-exciton interactions, dielectric-screened charge impurity scatterings, etc. All these phenomena in thin MoS_2 and other TMDs can be attributed to the quantum confinement effect, which is discussed later.

Table 2.1: Review of electronic character of LTMDs

Semiconducting	Metallic → Superconducting	Metallic
TiS ₂ , TiSe ₂ and TiTe ₂	NbS ₂ and NbSe ₂	NbTe ₂
HfS ₂ , HfSe ₂ and HfTe ₂	TaS ₂ and TaSe ₂	TaTe ₂
ZrS ₂ , ZrSe ₂ and ZrTe ₂	PdTe ₂	VS ₂ , VSe ₂ and VTe ₂
MoS ₂ , MoSe ₂ and MoTe ₂		PtTe ₂
WS ₂ , WSe ₂ and WTe ₂		
ReS ₂ and ReSe ₂		
PdS ₂ and PdSe ₂		
PtS ₂ and PtSe ₂		

2.4.3 Optical Studies of LTMDs

In direct band gap semiconductors, electrons in the valence bands can be easily excited to the conduction bands by incident photons, and the excess carriers can also recombine, passing the excess energies to photons, as shown in figure 2.5 (a). The former process can be probed by light absorption measurements, and the latter process can be probed by photoluminescence (PL) measurements. If lattice vibrations or phonons are involved in the optical transitions, the generated photon can have a lower energy than the incident photon, and the energy difference is related to a specific phonon mode. This inelastic light scattering is called Raman scattering (see figure 2.5 (b)).

Figure 2.5 (a) Mechanism of light absorption and subsequent photoluminescence process (PL), (b) Raman scattering process. In figure (a), $\hbar\omega_0$ represents incident light energy, $\hbar\omega$ is the emitted light energy in the PL process, VBM stands for valence band maximum and CBM stands for conduction band maximum. In figure (b), $\hbar\omega_q$ represents emitted phonon's energy during Raman scattering process. E_0 is the ground energy state

In 2D semiconducting TMDs, light-generated electrons and holes tend to attract each other due to the strong Coulomb interactions between them. This can be modeled by the concept of the exciton, which is the combination quasiparticle state of an electron and an hole. In addition, multi-excitons, such as trions and bi-excitons, are observable in 2D TMDs even at room temperature [133–137]. Figure 2.6 shows the PL spectra of monolayer MoSe₂ in the energy range from 1.52 to 1.68 eV for temperatures between 15 K and 295 K (room temperature). From these results we can clearly see the evolution of the exciton and trion peaks as a function of temperature, and how the peaks are separated at low temperature and are merged into a single peak with some asymmetry at room temperature.

Figure 2.6: A temperature dependent study of MoSe₂ monolayer's PL spectra. The temperature range is from 15 K to 295 K. The spectra are plotted in the energy range of 1.52-1.68 eV. Trionic and excitonic transitions could be attributed to the peaks at 1.62 eV and at 1.65 eV respectively

2.4.4 Synthesis Practices in LTMDs

Realization of graphene in 2004 [10] caught the fancy of the field of silicon-based electronics that were in pursuit of relentless miniaturization. The game-changing possibilities of two-dimensional or ultra-thin semiconductors coupled with the absence of band gap [10,57,60,150,151] leads the researchers to transition metal dichalcogenides (TMDC). Being similar in structure (layered) and with wide range of electronic properties (low to wide band gap semiconductors) makes it suitable for digital electronics, unlike graphene. Its isolation in monolayers, subsequent stability and direct band gap in visible

range of electromagnetic spectrum points towards its suitability for digital electronics and optoelectronics. Bulk TMDCs are found in several structural polytypes depending on the stacking order of layers [152], while single layers of TMDCs are found in two polymorphs, depending on the position of chalcogen with respect to the metal element in the X-M-X structure. The TMDC monolayer polytypes can be either trigonal prismatic (D_{3h} point group, honey-comb motif) or octahedral (D_{3d} point group, centered honey-comb motif) also referred to as 2H (1H for a monolayer) and 1T respectively [149,152], as shown in figure 2.4. 2H is the more pre-dominant, although chemical processing results in 1T transformation [153]. The synthesis of TMDC nanosheets is generally divided into two approaches: the top-down and the bottom-up method.

(a) Top-down methods

This consists of methods such as micro-mechanical cleavage of parent bulk crystal using scotch-tape technique, liquid exfoliation *via* intercalation, ultra-sonication, etc. The first method of micro-mechanical cleavage is very basic in nature that involves using adhesive tapes applied to substrate [8,10,50,123,154–156] and optically identified by light interference [157,158]. Although it produces high purity and clean flakes but the method is not scalable. On that account liquid phase exfoliation either through organic solvent [159] or through intercalation of ionic species [49,153,160–163] (figure 2.7 (a), (b)) becomes prominent for scalable operations. In the above, Li-ion exfoliation is preferred as it results in high yield monolayers. The only drawback is the non-ambient nature of Li^+ compounds and its increasing value makes it an unattractive proportion.

Figure 2.7 (a) Exfoliation through sonication in organic solvent, (b) Exfoliation via lithium intercalation and the corresponding STEM and AFM images, (c) CVD growth of MoS₂ from solid S and MoO₃ precursor and the optical image of the product, (d) CVD growth of MoS₂ from a solid layer of Mo on SiO₂ exposed to S vapour and the optical image of the product

(b) Bottom-up methods

Chemical Vapor Deposition (CVD) on metal substrates [164] and epitaxial growth of wafer-scale synthesis [165] of graphene allows large-scale device fabrication [166–168]. Similarly, for synthesizing thin dichalcogenides such as MoS₂, CVD involving heating of solid precursors have been employed. In one method, sulfur powder and MoO₃ powder is vaporized and co-deposited on a nearby substrate [113,169] as shown in figure 2.7 (c). In another method, a thin layer of Mo metal deposited onto a wafer heated with solid sulfur [118] as shown in figure 2.7 (d). Although the thickness of the product is dependent on the thickness or concentration of initial precursor but the same could not be said for precise control of large areas. A further optimization and work is required in this direction for it to be workable for other dichalcogenides and for uniform large films.

Another important aspect about having TMDC nanosheets is the inherent advantages it provides over other competing technological materials in terms of field-effect mobility and on/off ratio as higher value of latter ($> 10^3$) with highest possible mobility (figure 2.8 (a))

are pre-requisite for digital electronics applications. In addition to it, its band gap is near to Shockley-Quessier optimum (~ 1.3 eV) and high mobilities (figure 2.8 (b)) make it attractive for high-efficiency photovoltaic devices [170]. This and other applications will be discussed in detail in next section.

Figure 2.8: (a) Comparative study of field-effect mobility and on/off ratios of semiconductors, (b) Study of field-effect mobility vs band gap for semiconductors used for photovoltaic application [170]

2.4.5 Field-Effect-Transistors and Optoelectronic Applications of LTMDs

Owing to the presence of the band gap, MoS_2 field effect transistors (FETs) were proposed to have a high on/off ratio, which has not been achieved on graphene FETs, so that MoS_2 FETs can potentially be used in nanoscale logic electronics [50,71–89,171–175]. MoS_2 can be made into good n-type FETs, with a field-effect mobility of $190 \text{ cm}^2/\text{Vs}$ and an on/off ratio of 10^9 (see figure 2.9) [171]. Based on such achievements, several typical logic circuits were fabricated, such as inverters, NAND gates, random access memories and ring oscillators [84,171]. P-type MoS_2 FETs are difficult to realize, because both exfoliated and CVD MoS_2 are naturally n-type doped, and the work functions of most of the commonly used contact metals are pinned near the conduction band edge [77], as shown in figure 2.10. However, if we look into MoSe_2 or WSe_2 with lower band gaps, it is possible to shift the Fermi level to the p-type side with a gate bias, and thus both n-type and p-type FETs, or

even bipolar FETs can be made [172–175].

Figure 2.9: Transport measurement of CVD MoS₂ top-gate FETs. [171], (a) $I_d - V_d$ (output characteristics) curve, (b) $I_d - V_g$ (transfer characteristics) curve, (c) field-effect-mobility extraction from back-gated device

Figure 2.10: (a) Expected line-up of metal Fermi level with the electronic bands of MoS₂ flake if only the difference of the electron affinity of MoS₂ and the work function of the corresponding metal is considered. (b) The cartoon of expected transfer characteristics based on (a). (c) Transfer characteristics of back-gated 6-nm-thick MoS₂ transistor with Sc, Ti, Ni, and Pt metal contacts. The inset shows the actual line-up based on the experimental data [77]

The direct band gap nature makes LTMDs promising to be used in high-performance optoelectronics as well, such as photodetectors, light-emitting diodes (LEDs) and so on [90–101,103–105,107–110,143,176]. The structure of a MoS₂ photodetector is quite similar to that of a MoS₂ FET, as shown in figure 2.11 (a). When shining a laser onto the device, more electrons and holes are generated, leading to either a large photocurrent when the source-drain voltage is 0, or a large photoconductivity when the voltage is not 0. figure 2.11 (b) plots the time domain photocurrent responses with different working biases applied to the MoS₂-based photodetectors. It was reported that the photoresponsivity could be as high as 880 A/W at an excitation wavelength of 561 nm [93]. According to M. Buscema et al. [94], the photocarriers in MoS₂ are mainly generated around MoS₂/metal interfaces. The consequent photoresponse results from the photo-thermoelectric effect, rather than from the commonly observed photovoltaic effect in bulk semiconductors [94]. The effect of persistent photoconductivity (PPC) is also widely reported [95,96], which may originate from the deep trap states in MoS₂. Similar studies on the photoresponse of monolayer WS₂ have been done as well [98]. The mechanism of light emission in LEDs is basically the electroluminescence effect occurring in a MoS₂ diode. Due to its direct band gap nature, excited electrons and holes in semiconductor TMD monolayers can be easily recombined radiatively, and thus emitting light [99]. Earlier research has shown a strong photoluminescence in monolayer MoS₂; the observation of electroluminescence was first reported for MoS₂/metal and MoS₂/p-Si heterojunctions [99,103]. Figure 2.12 shows the electroluminescence observed near the MoS₂/Au Schottky junction as well as the photoluminescence and absorption spectra. The wavelength of the emitted light is at around 680 nm [99]. More recently, three research groups [105,107,143] reported gate tunable WSe₂ p-n diodes, which give better performance in both light emission and photodetection. Heterojunctions of different TMDs have also been studied [100–103], with better rectifying behavior and improved efficiency of the photon-to-electron or the electron-to-photon transitions. Researchers believe that the TMD family would eventually provide a feasible solution for high performance optoelectronics either integrated with silicon integrated circuits or fabricated on flexible substrates.

Figure 2.11: (a) Schematic of a MoS₂ photodetector device, (b) its time-domain photoresponse [93]

Figure 2.12: (a) Electroluminescence mapping, (b) combined absorption, electroluminescence and photoluminescence spectra of monolayer MoS₂ with Cr/Au metal contacts [99]

2.5 Topics Addressed in this Work

In light of the topics covered in this literature review, relatively newer and lesser explored members of LTMDs (ReX₂, SnS₂, etc.) will be systematically studied and employed for applications in this particular work. As clear from the overview of the low-dimensional

layered transition metal dichalcogenides (LTMDs) current research, molybdenum disulfide (MoS_2) has established itself as the front-runner in LTMD family and other members need to show distinct or comparable properties to be an attractive addition to the ever-expanding 2D catalogue. The candidates for new 2D materials vary from nanostructured graphene off-shoots (composites, reduced oxide, etc.), [177] graphene analogues like silicene, germanene and boronene [178–182] to oxy-chalcogenides, III-V layered compounds, etc. This family can include almost all the compounds having layered lattice structure. One such compound is black phosphorus that could be obtained for atomically thin range, and is commonly known as phosphorene. It comes with several advantage in the form of direct band gap of 0.3 eV, intra-layer anisotropic structure and properties [183–192]. The problem with phosphorene is its lack of environmental stability in spite of all its positive points [193]. Thus, a similar intra-layer anisotropically structured dichalcogenide material rhenium disulfide (ReS_2) that is also reported for its monolayer-like behavior in bulk owing to its vibrational and electronic decoupling [194]. would be studied and compared with it. In addition, ReS_2 possess direct band gap through its thicknesses.

Another focus of the current work is the development of the novel synthesis methods for generating low-dimension thin LTMD crystals over and above the existing methods. Each of the synthesis techniques discussed above either is un-scalable (micro-mechanical exfoliation) or fundamentally alter the material (liquid-phase solution phase exfoliation). Further bottom-up methods are still in their development stage and often requires dealing with volatile precursor. Based on this, a novel method is proposed and developed in-house for rapid, reproducible, high quality synthesis of thin few-layer LTMD crystals that may find usage in applications where the availability of a suitable material is holding back the promise of 2D materials.

References

- [1] AzoNano, New Materials Making Photovoltaic Devices Cost Efficient, *AzoNano*. (2016) 2. <http://www.azonano.com/news.aspx?NewsID=7272> (accessed May 22, 2016).
- [2] E. Bucher, Photovoltaic power, *Phys. Technol.* 17 (1986) 152.

- [3] S.R. Forrest, The path to ubiquitous and low-cost organic electronic appliances on plastic, *Nature*. 428 (2004) 911–918.
- [4] D.J. Gundlach, Y.Y. Lin, T.N. Jackson, S.F. Nelson, D.G. Schlom, Pentacene organic thin-film transistors-molecular ordering and mobility, *IEEE Electron Device Lett.* 18 (1997) 87–89.
- [5] X. Duan, C. Niu, V. Sahi, J. Chen, J.W. Parce, S. Empedocles, et al., High-performance thin-film transistors using semiconductor nanowires and nanoribbons, *Nature*. 425 (2003) 274–278.
- [6] D.B. Mitzi, L.L. Kosbar, C.E. Murray, M. Copel, A. Afzali, High-mobility ultrathin semiconducting films prepared by spin coating, *Nature*. 428 (2004) 299–303.
- [7] R. Coehoorn, C. Haas, R.A. de Groot, Electronic structure of MoSe₂, MoS₂ and WSe₂. II. The nature of the optical band gaps, *Phys. Rev. B*. 35 (1987) 6203–6206.
- [8] K.F. Mak, C. Lee, J. Hone, J. Shan, T.F. Heinz, Atomically Thin MoS₂: A New Direct-Gap Semiconductor, *Phys. Rev. Lett.* 105 (2010) 136805.
- [9] K.I. Bolotin, K.J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, et al., Ultrahigh electron mobility in suspended graphene, *Solid State Commun.* 146 (2008) 351–355.
- [10] K.S. Novoselov, A.K. Geim, S. V Morozov, D. Jiang, Y. Zhang, S. V Dubonos, et al., Electric Field Effect in Atomically Thin Carbon Films, *Sci.* 306 (2004) 666–669.
- [11] J.A. Wilson, A.D. Yoffe, The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties, *Adv. Phys.* 18 (1969) 193–335.
- [12] F.R. Gamble, J.H. Osiecki, M. Cais, Intercalation complexes of Lewis bases and layered sulfides: a large class of new superconductors, *Sci.* 174 (1971) 493–497.
- [13] M.S. Whittingham, *Chemistry of intercalation compounds: Metal guests in chalcogenide hosts*, 1978.
- [14] M.S. Whittingham, Lithium Batteries and Cathode Materials, *Chem. Rev.* 104 (2004) 4271–4302.
- [15] R.H. Friend, The electronic and magnetic properties of transition metal dichalcogenide intercalation complexes, *Physica B+C*. 117-118. (1983) 593–598.
- [16] E.A. Mersegila, Transition Metal Dichalcogenides and Their Intercalates, *Int. Rev.*

- Phys. Chem.* 3 (1983) 177–216.
- [17] B.G. Silbernagel, The Physical Properties of Layered Dichalcogenides and their Intercalation Compounds, *Mater. Sci. Eng.* 31 (1977) 281–288.
- [18] A.D. Yoffe, Electronic Properties of Intercalate Complexes of Layer Type Transition Metal Dichalcogenides, in: J.V. Acrivos, N.F. Mott, A.D. Yoffe (Eds.), *Phys. Chem. Electrons Ions Condens. Matter*, Volume 130, Springer Netherlands, 1984: pp. 437–458.
- [19] R.H. Friend, A.D. Yoffe, Electronic properties of intercalation complexes of the transition metal dichalcogenides, *Adv. Phys.* 36 (1987) 1–94.
- [20] H.E. Sliney, Solid lubricant materials for high temperatures - a review, *Tribol. Int.* 15 (1982) 303–315.
- [21] M.R. Hilton, R. Bauer, S. V. Didziulis, M.T. Dugger, J.M. Keem, J. Scholhamer, Structural and tribological studies of MoS₂ solid lubricant films having tailored metal-multilayer nanostructures, *Surf. Coatings Technol.* 53 (1992) 13–23.
- [22] L. Rapoport, Y. Bilik, Y. Feldman, M. Homyonfer, S.R. Cohen, R. Tenne, Hollow nanoparticles of WS₂ as potential solid-state lubricants., *Nature*. 387 (1997) 791–3.
- [23] M. Chhowalla, G.A. Amaratunga, Thin films of fullerene-like MoS₂ nanoparticles with ultra-low friction and wear, *Nature*. 407 (2000) 164–167.
- [24] C. Donnet, A. Erdemir, Solid lubricant coatings: recent developments and future trends, *Tribol. Lett.* 17 (2004) 389–397.
- [25] J.A. Wilson, F.J. Di Salvo, S. Mahajan, Charge-density waves and superlattices in the metallic layered transition metal dichalcogenides, *Adv. Phys.* 24 (1975) 117–201.
- [26] R. Nitsche, The growth of single crystals of binary and ternary chalcogenides by chemical transport reactions, *J. Phys. Chem. Solids*. 17 (1960) 163–165.
- [27] R. Nitsche, H.U. Bolsterli, M. Lichtenstriger, Crystal Growth by Chemical Reactions-I, *J. Phys. Chem. Solids*. 21 (1961) 199–205.
- [28] R. Nitsche, D. Richman, Crystal Growth by Chemical Transport Reactions II: Equilibrium Measurements in the System Cadmium Sulfide-Iodine, *Zeitschrift Für Elektrochemie, Berichte Der Bunsengesellschaft Für Phys. Chemie*. 66 (1962) 709–716.
- [29] R. Nitsche, Proceedings in international conference on crystal growth, Boston, *J.*

- Phys. Chem. Solids Suppl.* 1 (1961) 215.
- [30] D.L. Greenaway, R. Nitsche, Preparation and optical properties of group IV–VI₂ chalcogenides having the CdI₂ structure, *J. Phys. Chem. Solids*. 26 (1965) 1445–1458.
- [31] R. Nitsche, *Crystal Growth*, Pergoman Oxford, 1967.
- [32] H. Schafer, Chemische Transportreaktionen. Der Transport anorganischer Stoffe über die Gasphase und seine Anwendung. Monographie Nr. 76 zu „Angewandte Chemie“ und „Chemie-Ingenieur-Technik“. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Weinheim/Bergstr., *Zeitschrift Für Elektrochemie, Berichte Der Bunsengesellschaft Für Phys. Chemie*. 66 (1962) 885.
- [33] H. Schafer, *Chemical Transport Reactions*, 1964th ed., Academic Press Inc. New York, 1964.
- [34] H. Schafer, F. Wehmeier, M. Trenkel, Chemical Transport with sulfur as a transport agent, *J. Less-Common Met.* 16 (1968) 290–291.
- [35] H. Schäfer, T. Grofe, M. Trenkel, The chemical transport of molybdenum and tungsten and of their dioxides and sulfides, *J. Solid State Chem.* 8 (1973) 14–28.
- [36] a. a. Al-Hilli, B.L. Evans, The preparation and properties of transition metal dichalcogenide single crystals, *J. Cryst. Growth*. 15 (1972) 93–101.
- [37] W.Y. Liang, Optical anisotropy in layer compounds, *J. Phys. C Solid State Phys.* 6 (1973) 551.
- [38] A.A. Balchin, Growth and the Crystal Characteristics of Dichalcogenides having Layer Structures, in: F. Levy (Ed.), *Crystallogr. Cryst. Chem. Mater. with Layer. Struct., Physics an*, 1976: pp. 1–50.
- [39] R.M.A. Lieth, J.C.J.M. Terhell, Transition Metal Dichalcogenides, in: R.M.A. Lieth (Ed.), *Prep. Cryst. Growth Mater. with Layer. Struct.*, Volume 1, Springer Netherlands, 1977: pp. 141–223.
- [40] S.K. Srivastava, B.N. Avasthi, Layer type tungsten dichalcogenide compounds : their preparation , structure , properties and uses, *J. Mater. Sci.* 20 (1985) 3801–3815.
- [41] W.Y. Liang, Physics and Chemistry of Layered Compounds, in: J.L. Beeby, P.K. Bhattacharya, P.C. Gravelle, F. Koch, D.J. Lockwood (Eds.), *Condens. Syst. Low*

- Dimens.*, Springer US, Boston, MA, 1991: pp. 677–693.
- [42] A.D. Yoffe, Electronic properties of some chain and layer compounds, *Chem. Soc. Rev.* 5 (1976) 51–78.
- [43] K.S. Krishnan, N. Ganguli, Large Anisotropy of the Electrical Conductivity of Graphite, *Nature*. 144 (1939) 667–667.
- [44] R.F. Frindt, Single Crystals of MoS₂ Several Molecular Layers Thick, *J. Appl. Phys.* 37 (1966) 1928.
- [45] W.M.R. Divigalpitiya, S.R. Morrison, R.F. Frindt, Thin oriented films of molybdenum disulphide, *Thin Solid Films*. 186 (1990) 177–192.
- [46] G. Binnig, H. Rohrer, C. Gerber, E. Weibel, 7 X 7 Reconstruction on Si(111) Resolved in Real Space, *Phys. Rev. Lett.* 50 (1983) 120–123.
- [47] G. Binnig, C.F. Quate, C. Gerber, Atomic Force Microscope, *Phys. Rev. Lett.* 56 (1986) 930–933.
- [48] G. Binnig, H. Rohrer, C. Gerber, E. Weibel, Tunneling through a controllable vacuum gap, *Appl. Phys. Lett.* 40 (1982) 178.
- [49] P. Joensen, R.F. Frindt, S.R. Morrison, Single-layer MoS₂, *Mater. Res. Bull.* 21 (1986) 457–461.
- [50] B. Radisavljevic, a Radenovic, J. Brivio, V. Giacometti, A Kis, Single-layer MoS₂ transistors., *Nat. Nanotechnol.* 6 (2011) 147–50.
- [51] T. Ohta, A. Bostwick, T. Seyller, K. Horn, E. Rotenberg, Controlling the Electronic Structure of Bilayer Graphene, *Sci.* 313 (2006) 951–954.
- [52] M.S. Reis, Oscillating magnetocaloric effect on graphenes, *Appl. Phys. Lett.* 101 (2012) 222405.
- [53] A.K. Geim, K.S. Novoselov, The rise of graphene, *Nat Mater.* 6 (2007) 183–191.
- [54] Y. Ding, Y. Wang, J. Ni, L. Shi, S. Shi, W. Tang, First principles study of structural, vibrational and electronic properties of graphene-like MX₂ (M=Mo, Nb, W, Ta; X=S, Se, Te) monolayers, *Phys. B Condens. Matter.* 406 (2011) 2254–2260.
- [55] K.S. Novoselov, V.I. Fal'ko, L. Colombo, P.R. Gellert, M.G. Schwab, K. Kim, A roadmap for graphene., *Nature*. 490 (2012) 192–200.
- [56] X. Du, I. Skachko, A. Barker, E.Y. Andrei, Approaching ballistic transport in suspended graphene, *Nat Nano.* 3 (2008) 491–495.

- [57] F. Schwierz, Graphene transistors, *Nat Nano.* 5 (2010) 487–496.
- [58] J.-H. Chen, C. Jang, S. Xiao, M. Ishigami, M.S. Fuhrer, Intrinsic and extrinsic performance limits of graphene devices on SiO₂, *Nat Nano.* 3 (2008) 206–209.
- [59] A. Pospischil, M. Humer, M.M. Furchi, D. Bachmann, R. Guider, T. Fromherz, et al., CMOS-compatible graphene photodetector covering all optical communication bands, *Nat Phot.* 7 (2013) 892–896.
- [60] A.H. Castro Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov, A.K. Geim, The electronic properties of graphene, *Rev. Mod. Phys.* 81 (2009) 109–162.
- [61] T. Mueller, F. Xia, P. Avouris, Graphene photodetectors for high-speed optical communications, *Nat Phot.* 4 (2010) 297–301.
- [62] L. a. Ponomarenko, a. K. Geim, a. a. Zhukov, R. Jalil, S. V. Morozov, K.S. Novoselov, et al., Tunable metal–insulator transition in double-layer graphene heterostructures, *Nat. Phys.* 7 (2011) 958–961.
- [63] Y. Zhang, T.-T. Tang, C. Girit, Z. Hao, M.C. Martin, A. Zettl, et al., Direct observation of a widely tunable bandgap in bilayer graphene, *Nature.* 459 (2009) 820–823.
- [64] E. V Castro, K.S. Novoselov, S. V Morozov, N.M.R. Peres, J.M.B.L. dos Santos, J. Nilsson, et al., Biased Bilayer Graphene: Semiconductor with a Gap Tunable by the Electric Field Effect, *Phys. Rev. Lett.* 99 (2007) 216802.
- [65] J.B. Oostinga, H.B. Heersche, X. Liu, A.F. Morpurgo, L.M.K. Vandersypen, Gate-induced insulating state in bilayer graphene devices, *Nat Mater.* 7 (2008) 151–157.
- [66] X. Li, X. Wang, L. Zhang, S. Lee, H. Dai, Chemically Derived, Ultrasoft Graphene Nanoribbon Semiconductors, *Sci.* 319 (2008) 1229–1232.
- [67] X. Wang, Y. Ouyang, X. Li, H. Wang, J. Guo, H. Dai, Room-Temperature All-Semiconducting Sub-10-nm Graphene Nanoribbon Field-Effect Transistors, *Phys. Rev. Lett.* 100 (2008) 206803.
- [68] Q. Yan, B. Huang, J. Yu, F. Zheng, J. Zang, J. Wu, et al., Intrinsic Current–Voltage Characteristics of Graphene Nanoribbon Transistors and Effect of Edge Doping, *Nano Lett.* 7 (2007) 1469–1473.
- [69] K.F. Mak, C. Lee, J. Hone, J. Shan, T.F. Heinz, Atomically Thin MoS₂: A New Direct-Gap Semiconductor, *Phys. Rev. Lett.* 105 (2010) 136805.

- [70] G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, M. Chhowalla, Photoluminescence from Chemically Exfoliated MoS₂, *Nano Lett.* 11 (2011) 5111–5116.
- [71] Y. Yoon, K. Ganapathi, S. Salahuddin, How Good Can Monolayer MoS₂ Transistors Be?, *Nano Lett.* 11 (2011) 3768–3773.
- [72] L. Liu, S.B. Kumar, Y. Ouyang, J. Guo, Performance Limits of Monolayer Transition Metal Dichalcogenide Transistors, *IEEE Trans. Electron Devices.* 58 (2011) 3042–3047.
- [73] H. Liu, A.T. Neal, P.D. Ye, Channel Length Scaling of MoS₂ MOSFETs, *ACS Nano.* 6 (2012) 8563–8569.
- [74] G.-H. Lee, Y.-J. Yu, X. Cui, N. Petrone, C.-H. Lee, M.S. Choi, et al., Flexible and Transparent MoS₂ Field-Effect Transistors on Hexagonal Boron Nitride-Graphene Heterostructures, *ACS Nano.* 7 (2013) 7931–7936.
- [75] D. Lembke, A. Kis, Breakdown of High-Performance Monolayer MoS₂ Transistors, *ACS Nano.* 6 (2012) 10070–10075.
- [76] A. Dankert, L. Langouche, M.V. Kamalakar, S.P. Dash, High-Performance Molybdenum Disulfide Field-Effect Transistors with Spin Tunnel Contacts, *ACS Nano.* 8 (2014) 476–482.
- [77] S. Das, H.-Y. Chen, A.V. Penumatcha, J. Appenzeller, High Performance Multilayer MoS₂ Transistors with Scandium Contacts, *Nano Lett.* 13 (2013) 100–105.
- [78] S. Ghatak, A.N. Pal, A. Ghosh, Nature of Electronic States in Atomically Thin MoS₂ Field-Effect Transistors, *ACS Nano.* 5 (2011) 7707–7712.
- [79] S. Kim, A. Konar, W.-S. Hwang, J.H. Lee, J. Lee, J. Yang, et al., High-mobility and low-power thin-film transistors based on multilayer MoS₂ crystals, *Nat Commun.* 3 (2012) 1011.
- [80] J. Pu, Y. Yomogida, K.-K. Liu, L.-J. Li, Y. Iwasa, T. Takenobu, Highly Flexible MoS₂ Thin-Film Transistors with Ion Gel Dielectrics, *Nano Lett.* 12 (2012) 4013–4017.
- [81] X. Zou, J. Wang, C.-H. Chiu, Y. Wu, X. Xiao, C. Jiang, et al., Interface Engineering for High-Performance Top-Gated MoS₂ Field-Effect Transistors, *Adv. Mater.* 26 (2014) 6255–6261.

- [82] J. Yoon, W. Park, G.-Y. Bae, Y. Kim, H.S. Jang, Y. Hyun, et al., Highly Flexible and Transparent Multilayer MoS₂ Transistors with Graphene Electrodes, *Small*. 9 (2013) 3295–3300.
- [83] B. Radisavljevic, M.B. Whitwick, A. Kis, Integrated Circuits and Logic Operations Based on Single-Layer MoS₂, *ACS Nano*. 5 (2011) 9934–9938.
- [84] H. Wang, L. Yu, Y.-H. Lee, Y. Shi, A. Hsu, M.L. Chin, et al., Integrated Circuits Based on Bilayer MoS₂ Transistors, *Nano Lett.* 12 (2012) 4674–4680.
- [85] L. Yu, Y.-H. Lee, X. Ling, E.J.G. Santos, Y.C. Shin, Y. Lin, et al., Graphene/MoS₂ Hybrid Technology for Large-Scale Two-Dimensional Electronics, *Nano Lett.* 14 (2014) 3055–3063.
- [86] H. Liu, M. Si, S. Najmaei, A.T. Neal, Y. Du, P.M. Ajayan, et al., Statistical Study of Deep Submicron Dual-Gated Field-Effect Transistors on Monolayer Chemical Vapor Deposition Molybdenum Disulfide Films, *Nano Lett.* 13 (2013) 2640–2646.
- [87] W. Zhu, T. Low, Y.-H. Lee, H. Wang, D.B. Farmer, J. Kong, et al., Electronic transport and device prospects of monolayer molybdenum disulphide grown by chemical vapour deposition, *Nat Commun*. 5 (2014).
- [88] S. Najmaei, M. Amani, M.L. Chin, Z. Liu, A.G. Birdwell, T.P. O'Regan, et al., Electrical Transport Properties of Polycrystalline Monolayer Molybdenum Disulfide, *ACS Nano*. 8 (2014) 7930–7937.
- [89] T. Roy, M. Tosun, J.S. Kang, A.B. Sachid, S.B. Desai, M. Hettick, et al., Field-Effect Transistors Built from All Two-Dimensional Material Components, *ACS Nano*. 8 (2014) 6259–6264.
- [90] W. Choi, M.Y. Cho, A. Konar, J.H. Lee, G.-B. Cha, S.C. Hong, et al., High-Detectivity Multilayer MoS₂ Phototransistors with Spectral Response from Ultraviolet to Infrared, *Adv. Mater.* 24 (2012) 5832–5836.
- [91] Z. Yin, H. Li, H. Li, L. Jiang, Y. Shi, Y. Sun, et al., Single-Layer MoS₂ Phototransistors, *ACS Nano*. 6 (2012) 74–80.
- [92] H.S. Lee, S.-W. Min, Y.-G. Chang, M.K. Park, T. Nam, H. Kim, et al., MoS₂ Nanosheet Phototransistors with Thickness-Modulated Optical Energy Gap, *Nano Lett.* 12 (2012) 3695–3700.
- [93] O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, A. Kis, Ultrasensitive

- photodetectors based on monolayer MoS₂, *Nat Nano.* 8 (2013) 497–501.
- [94] M. Buscema, M. Barkelid, V. Zwiller, H.S.J. van der Zant, G.A. Steele, A. Castellanos-Gomez, Large and Tunable Photothermoelectric Effect in Single-Layer MoS₂, *Nano Lett.* 13 (2013) 358–363.
- [95] W. Zhang, J.-K. Huang, C.-H. Chen, Y.-H. Chang, Y.-J. Cheng, L.-J. Li, High-Gain Phototransistors Based on a CVD MoS₂ Monolayer, *Adv. Mater.* 25 (2013) 3456–3461.
- [96] K. Roy, M. Padmanabhan, S. Goswami, T.P. Sai, G. Ramalingam, S. Raghavan, et al., Graphene-MoS₂ hybrid structures for multifunctional photoresponsive memory devices, *Nat Nano.* 8 (2013) 826–830.
- [97] W. Zhang, C.-P. Chuu, J.-K. Huang, C.-H. Chen, M.-L. Tsai, Y.-H. Chang, et al., Ultrahigh-Gain Photodetectors Based on Atomically Thin Graphene-MoS₂ Heterostructures, *Sci. Rep.* 4 (2014) 3826.
- [98] N. Perea-López, A.L. Elías, A. Berkdemir, A. Castro-Beltran, H.R. Gutiérrez, S. Feng, et al., Photosensor Device Based on Few-Layered WS₂ Films, *Adv. Funct. Mater.* 23 (2013) 5511–5517.
- [99] R.S. Sundaram, M. Engel, A. Lombardo, R. Krupke, A.C. Ferrari, M. Steiner, Electroluminescence in Single Layer MoS₂, *Nano Lett.* 13 (2013) 1416–1421.
- [100] R. Cheng, D. Li, H. Zhou, C. Wang, A. Yin, S. Jiang, et al., Electroluminescence and Photocurrent Generation from Atomically Sharp WSe₂/MoS₂ Heterojunction p–n Diodes, *Nano Lett.* 14 (2014) 5590–5597.
- [101] C.-H. Lee, G.-H. Lee, A.M. van der Zande, W. Chen, Y. Li, M. Han, et al., Atomically thin p–n junctions with van der Waals heterointerfaces, *Nat. Nanotechnol.* 9 (2014) 676–681.
- [102] M. Furchi, A. Pospischil, F. Libisch, Photovoltaic effect in an electrically tunable van der Waals heterojunction, *arXiv* 1403.2652(2014) 4785–4791.
- [103] O. Lopez-Sanchez, E.A. Llado, Light Generation and Harvesting in a van der Waals Heterostructure, *ACS Nano.* 8 (2014) 3042–3048.
- [104] P. Rivera, J.R. Schaibley, A.M. Jones, J.S. Ross, S. Wu, G. Aivazian, et al., Observation of long-lived interlayer excitons in monolayer MoSe₂–WSe₂ heterostructures, *Nat Commun.* 6 (2015) 6242.

- [105] B.W.H. Baugher, H.O.H. Churchill, Y. Yang, P. Jarillo-Herrero, Optoelectronic devices based on electrically tunable p-n diodes in a monolayer dichalcogenide, *Nat Nano.* 9 (2014) 262–267.
- [106] A. Pospischil, M.M. Furchi, T. Mueller, Solar-energy conversion and light emission in an atomic monolayer p-n diode, *Nat Nano.* 9 (2014) 257–261.
- [107] J.S. Ross, P. Klement, A.M. Jones, N.J. Ghimire, J. Yan, M. G., et al., Electrically tunable excitonic light-emitting diodes based on monolayer WSe₂ p-n junctions, *Nat Nano.* 9 (2014) 268–272.
- [108] Y.J. Zhang, T. Oka, R. Suzuki, J.T. Ye, Y. Iwasa, Electrically switchable chiral light-emitting transistor., *Sci.* 344 (2014) 725–8.
- [109] M.-L. Tsai, S.-H. Su, J.-K. Chang, D.-S. Tsai, C.-H. Chen, C.-I. Wu, et al., Monolayer MoS₂ Heterojunction Solar Cells, *ACS Nano.* 8 (2014) 8317–8322.
- [110] D. Jariwala, V.K. Sangwan, C.-C. Wu, P.L. Prabhumirashi, M.L. Geier, T.J. Marks, et al., Gate-tunable carbon nanotube–MoS₂ heterojunction p-n diode, *Proc. Natl. Acad. Sci.* 110 (2013) 18076–18080.
- [111] S. Wu, C. Huang, G. Aivazian, J.S. Ross, D.H. Cobden, X. Xu, Vapor–Solid Growth of High Optical Quality MoS₂ Monolayers with Near-Unity Valley Polarization, *ACS Nano.* 7 (2013) 2768–2772.
- [112] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V. V Khotkevich, S. V Morozov, et al., Two-dimensional atomic crystals., *Proc. Natl. Acad. Sci. U. S. A.* 102 (2005) 10451–3.
- [113] Y.-H. Lee, X.-Q. Zhang, W. Zhang, M.-T. Chang, C.-T. Lin, K.-D. Chang, et al., Synthesis of Large-Area MoS₂ Atomic Layers with Chemical Vapor Deposition, *Adv. Mater.* 24 (2012) 2320–2325.
- [114] Y.-H. Lee, L. Yu, H. Wang, W. Fang, X. Ling, Y. Shi, et al., Synthesis and Transfer of Single-Layer Transition Metal Disulfides on Diverse Surfaces, *Nano Lett.* 13 (2013) 1852–1857.
- [115] Y. Shi, W. Zhou, A.-Y. Lu, W. Fang, Y.-H. Lee, A.L. Hsu, et al., van der Waals Epitaxy of MoS₂ Layers Using Graphene As Growth Templates, *Nano Lett.* 12 (2012) 2784–2791.
- [116] X. Wang, H. Feng, Y. Wu, L. Jiao, Controlled Synthesis of Highly Crystalline MoS₂

- Flakes by Chemical Vapor Deposition, *J. Am. Chem. Soc.* 135 (2013) 5304–5307.
- [117] X. Ling, Y.-H. Lee, Y. Lin, W. Fang, L. Yu, M.S. Dresselhaus, et al., Role of the Seeding Promoter in MoS₂ Growth by Chemical Vapor Deposition, *Nano Lett.* 14 (2014) 464–472.
- [118] Y. Zhan, Z. Liu, S. Najmaei, P.M. Ajayan, J. Lou, Large-Area Vapor-Phase Growth and Characterization of MoS₂ Atomic Layers on a SiO₂ Substrate, *Small.* 8 (2012) 966–971.
- [119] Y. Yu, C. Li, Y. Liu, L. Su, Y. Zhang, L. Cao, Controlled Scalable Synthesis of Uniform, High-Quality Monolayer and Few-layer MoS₂ Films, *Sci. Rep.* 3 (2013) 1866.
- [120] X. Wang, Y. Gong, G. Shi, W.L. Chow, K. Keyshar, G. Ye, et al., Chemical Vapor Deposition Growth of Crystalline Monolayer MoSe₂, *ACS Nano.* 8 (2014) 5125–5131.
- [121] M. Okada, T. Sawazaki, K. Watanabe, T. Taniguchi, H. Hibino, H. Shinohara, et al., Direct Chemical Vapor Deposition Growth of WS₂ Atomic Layers on Hexagonal Boron Nitride, *ACS Nano.* 8 (2014) 8273–8277.
- [122] J.-K. Huang, J. Pu, C.-L. Hsu, M.-H. Chiu, Z.-Y. Juang, Y.-H. Chang, et al., Large-Area Synthesis of Highly Crystalline WSe₂ Monolayers and Device Applications, *ACS Nano.* 8 (2014) 923–930.
- [123] C. Lee, H. Yan, L. Brus, T. Heinz, J. Hone, S. Ryu, Anomalous lattice vibrations of single-and few-layer MoS₂, *ACS Nano.* 4 (2010) 2695–700.
- [124] G. Berghäuser, E. Malic, Analytical approach to excitonic properties of MoS₂, *Phys. Rev. B.* 89 (2014) 125309.
- [125] A. Ramasubramaniam, Large excitonic effects in monolayers of molybdenum and tungsten dichalcogenides, *Phys. Rev. B.* 86 (2012) 115409.
- [126] F. Hüsler, T. Olsen, K.S. Thygesen, How dielectric screening in two-dimensional crystals affects the convergence of excited-state calculations: Monolayer MoS₂, *Phys. Rev. B.* 88 (2013) 245309.
- [127] T. Cheiwchanamangij, W.R.L. Lambrecht, Quasiparticle band structure calculation of monolayer, bilayer, and bulk MoS₂, *Phys. Rev. B.* 85 (2012) 205302.
- [128] D.Y. Qiu, F.H. da Jornada, S.G. Louie, Optical Spectrum of MoS₂: Many-Body

- Effects and Diversity of Exciton States, *Phys. Rev. Lett.* 111 (2013) 216805.
- [129] A. Molina-Sánchez, D. Sangalli, K. Hummer, A. Marini, L. Wirtz, Effect of spin-orbit interaction on the optical spectra of single-layer, double-layer, and bulk MoS₂, *Phys. Rev. B.* 88 (2013) 45412.
- [130] T.C. Berkelbach, M.S. Hybertsen, D.R. Reichman, Theory of neutral and charged excitons in monolayer transition metal dichalcogenides, *Phys. Rev. B.* 88 (2013) 45318.
- [131] H.-P. Komsa, A. V Krashenninnikov, Effects of confinement and environment on the electronic structure and exciton binding energy of MoS₂ from first principles, *Phys. Rev. B.* 86 (2012) 241201.
- [132] J. Feng, X. Qian, C.-W. Huang, J. Li, Strain-engineered artificial atom as a broad-spectrum solar energy funnel, *Nat Phot.* 6 (2012) 866–872.
- [133] K.F. Mak, K. He, C. Lee, G.H. Lee, J. Hone, T.F. Heinz, et al., Tightly bound trions in monolayer MoS₂, *Nat Mater.* 12 (2013) 207–211.
- [134] J.S. Ross, S. Wu, H. Yu, N.J. Ghimire, A.M. Jones, G. Aivazian, et al., Electrical control of neutral and charged excitons in a monolayer semiconductor, *Nat Commun.* 4 (2013) 1474.
- [135] K. He, N. Kumar, L. Zhao, Z. Wang, K.F. Mak, H. Zhao, et al., Tightly Bound Excitons in Monolayer WSe₂, *Phys. Rev. Lett.* 113 (2014) 26803.
- [136] A. Chernikov, T.C. Berkelbach, H.M. Hill, A. Rigosi, Y. Li, O.B. Aslan, et al., Exciton Binding Energy and Nonhydrogenic Rydberg Series in Monolayer WS₂, *Phys. Rev. Lett.* 113 (2014) 76802.
- [137] E.J. Sie, A.J. Frenzel, Y.-H. Lee, J. Kong, N. Gedik, Intervalley biexcitons and many-body effects in monolayer MoS₂, *Phys. Rev. B.* 92 (2015) 125417.
- [138] K.F. Mak, K. He, J. Shan, T.F. Heinz, Control of valley polarization in monolayer MoS₂ by optical helicity, *Nat Nano.* 7 (2012) 494–498.
- [139] H. Zeng, J. Dai, W. Yao, D. Xiao, X. Cui, Valley polarization in MoS₂ monolayers by optical pumping, *Nat Nano.* 7 (2012) 490–493.
- [140] T. Cao, G. Wang, W. Han, H. Ye, C. Zhu, J. Shi, et al., Valley-selective circular dichroism of monolayer molybdenum disulphide, *Nat Commun.* 3 (2012) 887.
- [141] S. Wu, J.S. Ross, G.-B. Liu, G. Aivazian, A. Jones, Z. Fei, et al., Electrical tuning

- of valley magnetic moment through symmetry control in bilayer MoS₂, *Nat Phys.* 9 (2013) 149–153.
- [142] K.F. Mak, K.L. McGill, J. Park, P.L. McEuen, The valley Hall effect in MoS₂ transistors, *Sci.* 344 (2014) 1489–1492.
- [143] A. Pospischil, M.M. Furchi, T. Mueller, Solar-energy conversion and light emission in an atomic monolayer p-n diode., *Nat. Nanotechnol.* 9 (2014) 257–61.
- [144] F.K. Perkins, A.L. Friedman, E. Cobas, P.M. Campbell, G.G. Jernigan, B.T. Jonker, Chemical Vapor Sensing with Monolayer MoS₂, *Nano Lett.* 13 (2013) 668–673.
- [145] D.J. Late, Y.-K. Huang, B. Liu, J. Acharya, S.N. Shirodkar, J. Luo, et al., Sensing Behavior of Atomically Thin-Layered MoS₂ Transistors, *ACS Nano.* 7 (2013) 4879–4891.
- [146] H. Li, Z. Yin, Q. He, H. Li, X. Huang, G. Lu, et al., Fabrication of Single- and Multilayer MoS₂ Film-Based Field-Effect Transistors for Sensing NO at Room Temperature, *Small.* 8 (2012) 63–67.
- [147] Q. He, Z. Zeng, Z. Yin, H. Li, S. Wu, X. Huang, et al., Fabrication of Flexible MoS₂ Thin-Film Transistor Arrays for Practical Gas-Sensing Applications, *Small.* 8 (2012) 2994–2999.
- [148] C. Zhu, Z. Zeng, H. Li, F. Li, C. Fan, H. Zhang, Single-Layer MoS₂-Based Nanoprobes for Homogeneous Detection of Biomolecules, *J. Am. Chem. Soc.* 135 (2013) 5998–6001.
- [149] M. Chhowalla, H.S. Shin, G. Eda, L.-J. Li, K.P. Loh, H. Zhang, The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets., *Nat. Chem.* 5 (2013) 263–75.
- [150] D. Jariwala, V.K. Sangwan, L.J. Lauhon, T.J. Marks, M.C. Hersam, Carbon nanomaterials for electronics, optoelectronics, photovoltaics, and sensing, *Chem. Soc. Rev.* 42 (2013) 2824–2860.
- [151] D. Jariwala, A. Srivastava, P.M. Ajayan, Graphene Synthesis and Band Gap Opening, *J. Nanosci. Nanotechnol.* 11 (2011) 6621–6641.
- [152] N.V. Podberezskaya, S.A. Magarill, N.V. Pevukhina, S.V. Borisov, Crystal Chemistry of Dichalcogenides MX₂, *J. Struct. Chem.* 42 (2001) 654–681.
- [153] G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, M. Chhowalla,

- Photoluminescence from Chemically Exfoliated MoS₂, *Nano Lett.* 11 (2011) 5111–5116.
- [154] N. Alem, R. Erni, C. Kisielowski, M.D. Rossell, W. Gannett, A. Zettl, Atomically thin hexagonal boron nitride probed by ultrahigh-resolution transmission electron microscopy, *Phys. Rev. B.* 80 (2009) 155425.
- [155] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, et al., Emerging photoluminescence in monolayer MoS₂, *Nano Lett.* 10 (2010) 1271–5.
- [156] S. Bertolazzi, J. Brivio, A. Kis, Stretching and Breaking of Ultrathin MoS₂, *ACS Nano.* 5 (2011) 9703–9709.
- [157] M.M.B. and B.R. and J.S.H. and S.S. and H.B. and A. Kis, Visibility of dichalcogenide nanolayers, *Nanotechnology.* 22 (2011) 125706.
- [158] H. Li, G. Lu, Z. Yin, Q. He, H. Li, Q. Zhang, et al., Optical Identification of Single- and Few-Layer MoS₂ Sheets, *Small.* 8 (2012) 682–686.
- [159] J.N. Coleman, M. Lotya, A. O'Neill, S.D. Bergin, P.J. King, U. Khan, et al., Two-dimensional nanosheets produced by liquid exfoliation of layered materials, *Sci.* 331 (2011) 568–571.
- [160] R. Bissessur, J. Heising, W. Hirpo, Toward Pillared Layered Metal Sulfides. Intercalation of the Chalcogenide Clusters Co₆Q₈(PR₃)₆ (Q = S, Se, and Te and R = Alkyl) into MoS₂, *Chem. Mater.* 8 (1996) 318–320.
- [161] M. Osada, T. Sasaki, Exfoliated oxide nanosheets: new solution to nanoelectronics, *J. Mater. Chem.* 19 (2009) 2503–2511.
- [162] Z. Zeng, Z. Yin, X. Huang, H. Li, Q. He, G. Lu, et al., Single-layer semiconducting nanosheets: high-yield preparation and device fabrication., *Angew. Chem. Int. Ed. Engl.* 50 (2011) 11093–7.
- [163] M.B. Dines, Lithium Intercalation via n-Butyllithium of the Layered Transition Metal Dichalcogenides, *Mater. Res. Bull.* 10 (1975) 287–292.
- [164] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, et al., Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils, *Sci.* 324 (2009) 1312–1314.
- [165] J.H. and W.A. de H. and E.H. Conrad, The growth and morphology of epitaxial multilayer graphene, *J. Phys. Condens. Matter.* 20 (2008) 323202.
- [166] Y. Wu, K.A. Jenkins, A. Valdes-Garcia, D.B. Farmer, Y. Zhu, A.A. Bol, et al., State-

- of-the-Art Graphene High-Frequency Electronics, *Nano Lett.* 12 (2012) 3062–3067.
- [167] Y. Wu, Y. Lin, A.A. Bol, K.A. Jenkins, F. Xia, D.B. Farmer, et al., High-frequency, scaled graphene transistors on diamond-like carbon, *Nature*. 472 (2011) 74–78.
- [168] Y.-M. Lin, A. Valdes-Garcia, S.-J. Han, D.B. Farmer, I. Meric, Y. Sun, et al., Wafer-Scale Graphene Integrated Circuit, *Sci.* 332 (2011) 1294–1297.
- [169] S. Balendhran, J.Z. Ou, M. Bhaskaran, S. Sriram, S. Ippolito, Z. Vasic, et al., Atomically thin layers of MoS₂ via a two step thermal evaporation-exfoliation method, *Nanoscale*. 4 (2012) 461–466.
- [170] D. Jariwala, V.K. Sangwan, L.J. Lauhon, T.J. Marks, M.C. Hersam, Emerging Device Applications for Semiconducting Two-dimensional Transition Metal Dichalcogenides, *ACS Nano*. 8 (2014) 1102–1120.
- [171] H. Wang, L. Yu, Y.H. Lee, W. Fang, A. Hsu, P. Herring, et al., Large-scale 2D electronics based on single-layer MoS₂ grown by chemical vapor deposition, *Electron Devices Meet. (IEDM), 2012 IEEE Int.* (2012) 4.6.1–4.6.4.
- [172] A. Allain, A. Kis, Electron and Hole Mobilities in Single-Layer WSe₂, *ACS Nano*. 8 (2014) 7180–7185.
- [173] H.-J. Chuang, X. Tan, N.J. Ghimire, M.M. Perera, B. Chamlagain, M.M.-C. Cheng, et al., High Mobility WSe₂ p- and n-Type Field-Effect Transistors Contacted by Highly Doped Graphene for Low-Resistance Contacts, *Nano Lett.* 14 (2014) 3594–3601.
- [174] M. Tosun, S. Chuang, H. Fang, A.B. Sachid, M. Hettick, Y. Lin, et al., High-Gain Inverters Based on WSe₂ Complementary Field-Effect Transistors, *ACS Nano*. 8 (2014) 4948–4953.
- [175] B. Chamlagain, Q. Li, N.J. Ghimire, H.-J. Chuang, M.M. Perera, H. Tu, et al., Mobility Improvement and Temperature Dependence in MoSe₂ Field-Effect Transistors on Parylene-C Substrate, *ACS Nano*. 8 (2014) 5079–5088.
- [176] M.M. Furchi, A. Pospischil, F. Libisch, J. Burgdörfer, T. Mueller, Photovoltaic Effect in an Electrically Tunable van der Waals Heterojunction, *Nano Lett.* 14 (2014) 4785–4791.
- [177] S. Stankovich, D.A. Dikin, G.H.B. Dommett, K.M. Kohlhaas, E.J. Zimney, E.A. Stach, et al., Graphene-based composite materials, *Nature*. 442 (2006) 282–286.

- [178] P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M.C. Asensio, et al., Silicene: Compelling Experimental Evidence for Graphenelike Two-Dimensional Silicon, *Phys. Rev. Lett.* 108 (2012) 155501.
- [179] C.-C. Liu, W. Feng, Y. Yao, Quantum Spin Hall Effect in Silicene and Two-Dimensional Germanium, *Phys. Rev. Lett.* 107 (2011) 76802.
- [180] A. Fleurence, R. Friedlein, T. Ozaki, H. Kawai, Y. Wang, Y. Yamada-Takamura, Experimental Evidence for Epitaxial Silicene on Diboride Thin Films, *Phys. Rev. Lett.* 108 (2012) 245501.
- [181] Z. Ni, Q. Liu, K. Tang, J. Zheng, J. Zhou, R. Qin, et al., Tunable Bandgap in Silicene and Germanene, *Nano Lett.* 12 (2012) 113–118.
- [182] A. O'Hare, F. V Kusmartsev, K.I. Kugel, A Stable “Flat” Form of Two-Dimensional Crystals: Could Graphene, Silicene, Germanene Be Minigap Semiconductors?, *Nano Lett.* 12 (2012) 1045–1052.
- [183] M. Buscema, D.J. Groenendijk, G.A. Steele, H.S.J. van der Zant, A. Castellanos-Gomez, Photovoltaic effect in few-layer black phosphorus p-n junctions defined by local electrostatic gating, *Nat Commun.* 5 (2014).4651
- [184] V. Tran, R. Soklaski, Y. Liang, L. Yang, Layer-controlled band gap and anisotropic excitons in few-layer black phosphorus, *Phys. Rev. B.* 89 (2014) 235319.
- [185] L. Li, Y. Yu, G.J. Ye, Q. Ge, X. Ou, H. Wu, et al., Black phosphorus field-effect transistors, *Nat Nano.* 9 (2014) 372–377.
- [186] X. Wang, A.M. Jones, K.L. Seyler, V. Tran, Y. Jia, H. Zhao, et al., Highly anisotropic and robust excitons in monolayer black phosphorus, *Nat Nano.* 10 (2015) 517–521.
- [187] A.S. Rodin, A. Carvalho, A.H. Castro Neto, Strain-Induced Gap Modification in Black Phosphorus, *Phys. Rev. Lett.* 112 (2014) 176801.
- [188] F. Xia, H. Wang, Y. Jia, Rediscovering black phosphorus as an anisotropic layered material for optoelectronics and electronics, *Nat Commun.* 5 (2014) 4458.
- [189] M. Buscema, D.J. Groenendijk, S.I. Blanter, G.A. Steele, H.S.J. van der Zant, A. Castellanos-Gomez, Fast and Broadband Photoresponse of Few-Layer Black Phosphorus Field-Effect Transistors, *Nano Lett.* 14 (2014) 3347–3352.
- [190] N. Youngblood, C. Chen, S.J. Koester, M. Li, Waveguide-integrated black

- phosphorus photodetector with high responsivity and low dark current, *Nat Phot.* 9 (2015) 247–252.
- [191] J. Qiao, X. Kong, Z.-X. Hu, F. Yang, W. Ji, High-mobility transport anisotropy and linear dichroism in few-layer black phosphorus, *Nat Commun.* 5 (2014) 4475.
- [192] H. Liu, A.T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tománek, et al., Phosphorene: An Unexplored 2D Semiconductor with a High Hole Mobility, *ACS Nano.* 8 (2014) 4033–4041.
- [193] J.O. Island, G. a Steele, S.J. van der Z. Herre, A. Castellanos-Gomez, Environmental instability of few-layer black phosphorus, *2D Mater.* 2 (2015) 11002.
- [194] S. Tongay, H. Sahin, C. Ko, A. Luce, W. Fan, K. Liu, et al., Monolayer behaviour in bulk ReS₂ due to electronic and vibrational decoupling., *Nat. Commun.* 5 (2014) 3252.

Chapter 3

Experimental Methodology

This chapter describes the methodology to synthesize layered transition metal dichalcogenides (LTMDs) and related layered materials both via tradition vapor transport growth method as well as novel microwave plasma method developed for rapid synthesis of thin layered transition metal dichalcogenides crystals. It also describes the experimental flow followed during the course of this thesis work and various materials characterizations techniques used and optoelectronic measurements performed to study the materials properties.

3.1 Rational for Selection of Materials:

3.1.1 Layered Transition Metal Dichalcogenides (LTMDs)

Among the many layered compounds identified after the pioneering work on graphene[1,2], layered transition metal dichalcogenides (LTMDs) found to be the most versatile (ranging from metallic to semiconducting to superconducting), easily accessible (facile synthesis, scalable generation and commercially available) and stable in ambient atmosphere (figure 3.1). Their structural anisotropy arises from in-plane strong bonds and inter-planar weak van der Waals forces, which enables them to have unique properties that are sensitive to the thickness of the material (sample). In addition to this, introduction of inorganic or organic species in the van der Waals spaces (intercalation) may results in tuning of optoelectronic properties.

Group	M	X	Character
4	Ti, Hf, Zr	S, Se, Te	Semiconducting ($E_g = 0.2 \sim 2$ eV)
5	V, Nb, Ta	S, Se, Te	Narrow band metals or semimetals
6	Mo, W	S, Se, Te	Sulfides and Selenides are semiconducting. Tellurides are semietallic.
7	Tc, Re	S, Se, Te	Small gap semiconductors.
10	Pd, Pt	S, Se, Te	Sulfides and Selenides are semiconducting. Tellurides are metallic. PdTe ₂ is superconducting.
14	Sn	S, Se	Sulfides are indirect and Selenides are direct band gap semiconductors.

Figure 3.1: Depiction of the availability of LTMDs by the combination of transition metals and chalcogen atoms and their versatile electronic character. *Note:* Tin is added to this family due to the structural and physical similarities of its disulfides and diselenides with that of LTMDs

In this work, the synthesis of variety of LTMDs have been realized (WSe_2 , MoSe_2 , NbSe_2 , ReS_2 , ReSe_2 , SnS_2 , WS_2 , several LTMD alloys with $\text{M}_1\text{yM}_21-\text{yX}_2$ or $\text{MX}_1\text{yX}_22-\text{y}$ distribution) and also ternary layered compounds of MPX_3 form. Later it is narrowed down to select compounds for detailed study *viz.* tin disulfide (SnS_2), rhenium disulfide (ReS_2) and rhenium dichalcogenides alloys (ReSSe) on account of their special place in LTMD family as described in the previous chapters.

3.1.2 Significance of Single Crystal

With the growing importance of mono or few-layer dimension of layered materials, many methods have been devised to directly generate thin high quality few-layer samples for measurement and device fabrication. The developments in this direction are still in their nascent stage but each of those methods comes with either a compromise in quality of sample or limited in application. On the contrary, single crystal growth of LTMDs by vapor transport is a well-established method to synthesize high-quality bulk single crystal that could be utilized as-grown or by exfoliating them to mono or few-layer thickness by scotch tape method [1]. In addition to single crystal growth, a novel method has been proposed and developed for synthesis of high quality few-layer thick crystals of LTMDs in large quantities by microwave-plasma assisted method.

3.2 Typical Experimental Procedure

Figure 3.2 shows the flowchart of typical experimental procedures followed in this thesis work. In the present work we have synthesized LTMDs with both traditional methods vapor-phase single crystal growth as well as in-house developed method. Later the synthesized products were characterized thoroughly, either exfoliated or tested in bulk electric transport and other optoelectronic properties and applications.

Figure 3.2: A typical experimental flow followed during the course of this thesis from synthesis, characterization, device fabrication to possible applications

3.3 Vapor-Phase Single Crystal Growth

From vapor phase, good quality crystal can be obtained. The vapor transport technique is used to grow thin crystals. Majority of TMDCs with MX_2 formula is insoluble in water and are having comparatively higher melting points. In this case, crystallization from the vapor phase has various advantages over other growth techniques [3]. These advantages result mostly from:

- (i) The lower processing temperature involved-as the melting temperatures of TMDC compounds are higher, melt growth process is very difficult to be handled.

- (ii) Physical vapor transport act as a purification process [4] because of difference in vapor pressure of native elements and impurities.
- (iii) Most solid-vapor interface exhibit higher interfacial morphological stability [5–7] during the growth process because of their low atomic roughness [8] and consequently the pronounced growth rate anisotropy.

Vapor transport method is classified into two classes:

1. Chemical Vapor Transport (CVT) method and
2. Physical Vapor Transport (PVT) or Sublimation method

3.3.1 Chemical Vapor Transport (CVT) Method

A large number of layered compounds have been grown by this technique [9–22]. There are various theoretical attempts available in literature [23–28] that have shown that it is possible to grow crystals up to several centimeters using this technique under well-controlled nucleation [23].

CVT technique mainly relies on a chemical reaction between the source material to be crystallized and transporting agent. The reaction product is volatile and can be transported in the vapor phase at temperature well below the melting point of the compound. Transportation occurs between two zones having different temperatures as shown in figure 3.3. Usually the starting reaction occurs at a higher temperature and is reversed at the low temperature to deposit crystals of the compound at the most favorable crystalline sites. Initially random deposition occurs until seed crystals are formed. Thereafter growth preferentially occurs on these seeds and large single crystals are formed.

Figure 3.3: Description of the cyclic process of chemical vapor transport in a closed system, (a) Typical temperature profile, (b) Products at different stages and zones; A_x is metallic species, B_y is non-metallic species and I_2 is iodine element.

3.3.2 Physical Vapor Transport (PVT) Method

Although CVT technique gives very large size crystals, it has been observed that crystals grown by the CVT method usually incorporate small amount of the transporting agent, which may remain as an active impurity and affect the measured properties. In some cases, for example $ZrSe_2$ grown using I_2 , the transport agent remains strongly absorbed on the surface or incorporated between the layers and becomes difficult to remove it completely [29]. In order to avoid contamination by the transport agent Al Hilli and Evans [27] and Agarwal and coworkers [29] used the direct vapor transport method (without transporting agent). Their work showed that it is possible to grow fairly large crystals of LTMDs (Layered transition metal dichalcogenides) and their solid solutions.

The reaction-taking place to form AB compounds can be given as:

One of the elements has lower melting point. So, it vaporizes at lower temperature. This vapor reacts with powder of other elements at high temperature forming the compound.

In both CVT and PVT techniques, the transport rate depends on several factors:

- (1) Difference in equilibrium pressure at different temperatures,
- (2) Diffusion coefficient of gases,
- (3) Cross- sectional area and length of the reaction tube [9].

At low pressure and small ampoule diameter diffusion is the only important transport mechanism. As the pressure or the diameter is increased, convection current setup by the thermal gradient rapidly becomes more important. Broadly speaking, an optimum transport occurs when reaction is not far from equilibrium (Gibbs Free Energy, $\Delta G \rightarrow 0$). Also, rate of transport must not exceed rate of rate of growth of seeds.

3.4 Microwave-Induced-Plasma(MIP) Assisted Synthesis of LTMD Thin Crystals

Microwave-Induced-Plasma(MIP) synthesis has been carried out as a form of rapid synthesis method for variety of compounds such as oxides, nitrides, carbides, graphene, diamond and chalcogenides. As mentioned earlier in several reports, solid-state synthesis of LTMDs were not realized by plain microwave exposure of the starting materials (metal powder as bulk metal comes with a disadvantage of drastic electric discharge) [30]. To overcome this, microwave synthesis methods either include addition of a susceptor as a heat source or addition of a large quantity of metal powder to provide the “thermal runaway” necessary to drive microwave reaction. The method including susceptor is prone to contamination of the final product whereas quantity of metal powder for different reactions and systems may prove to be a barrier [31].

In addition to these, another method that involves exposure of reactants to microwave-induced plasma (MIP) has been employed to improve the microwave dielectric heating. Although MIP method looks convincing and a preferred method in the scientific community of all the three methods, it also comes with its own drawbacks. Volatile

reactants or products may evaporate the reactor on exposure to plasma heating reaching temperatures in excess of 1000 °C via ion bombardment. Moreover, the microwave solid-state synthesis methods of chalcogenides/dichalcogenides by direct combination of the appropriate elemental powders are limited and others involving microwave are solution-based processes. This puts an onus on materials scientists to improve and simplify over the above methods specially for scientifically and technological important compounds LTMDs and other similar layered quasi-2D compounds.

Keeping this in mind, an in-house method has been developed for rapid synthesis of few-layer thick transition metal dichalcogenides by the direct combination of transition metal and chalcogen powder. The setup is designed on the principle of MIP but differs from other setups in a manner that the process utilized an outer primary argon plasma to generate a secondary inner plasma of the chalcogen starting material. The unique aspect of this process is that unlike the previous MIP synthesis methods, the reactants never come in direct contact of external plasma. The reactants are secured inside an evacuated quartz tube throughout the process. As such volatile, hazardous reactants and products could be handled easily without the impediments of toxic reactants or a trade-off in the quality of end product on account of inclusion of impurities. The process, principle and product will be described further in detail in Chapter 5.

3.5 Device Fabrication and Measurement for ReS₂ Crystals

Thickness of the thin flake was measured by Asylum Research Cypher S Atomic Force Microscopy (AFM) in tapping mode. Raman spectrum characterization was performed using Witec confocal Raman system under 532 nm laser excitation. HRTEM image was obtained using FEI Tecnai F20 system. The ARPES experiments were carried out at Beamline 5–4 of the Stanford Synchrotron Radiation Lightsource (SSRL) of Slac National Accelerator Laboratory using 25 eV photons with a base pressure better than 5×10^{-11} Torr. Absorption spectrum was characterized by Jasco MSV-5200 microscopic spectrophotometer. A field-effect-transistor (FET) has been prepared to study the electronic transport characteristics of ReS₂. Thin flakes of 3 nm thickness were exfoliated

on SiO_2/Si (SiO_2 layer thickness = 285 nm) substrate. A schematic of the prepared device is shown in figure 3.3 The electrodes were patterned via photolithography, followed by thermal evaporation of Cr/Au (5/50 nm) and subsequent lift-off process. Electric characterization was performed by using the Agilent B1500 semiconductor parameter analyzer. Low temperature measurement was performed in a probe station cooled by liquid nitrogen.

Figure 3.4: A schematic of the field-effect device prepared for electronic transport measurement

Important parameters can be deduced from field-effect transistor (FET) device, prominent being nature of charge carriers (n or p type), threshold voltage and the field effect mobility of charge carriers and temperature effect on mobility. The field-effect mobility could be estimated from the linear region in the I_d - V_g curve (figure 3.5) by using the equation (below):

Figure 3.5: Typical I_d - V_g curve obtained from a FET device for a range of V

$$\mu = \frac{dI_d}{dV_g} \times \frac{L}{WC_iV_d}$$

L is the channel length,

W is the channel width, and

C_i is the capacitance between the channel and the back gate per unit area ($C_i = \epsilon_0\epsilon_r/d$; ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity, and d is the thickness of SiO_2 layer),.

Same device is used to measure the photoresponse without any gate bias applied to it. The photoresponse was measured using a semiconductor green laser as the illumination source, in the ambient condition. Light power dependence of the photoresponse was performed by tuning the light power while keeping the light polarization unchanged. Polarization dependence of the photoresponse was carried out by rotating the polarization of the light using a half wave plate and a polarizer, while keeping the light power unchanged throughout the measurement.

3.6 Device Fabrication and Measurement for ReSSe Crystals

The thickness of the ReSSe flakes was measured by atomic force microscopy (AFM, Cypher S). Raman measurements were performed using a Witec system in a backscattering configuration. The excitation was provided by visible laser light ($\lambda = 532 \text{ nm}$) through a 100 $\times$ objective (NA = 0.95). To avoid laser-induced modification or ablation of samples, all spectra were recorded at low power levels. Optical absorption spectra were measured using a Jasco MSV-5200 microscopic spectrophotometer.

As described in the section earlier, FET device has been prepared. Thin flakes of ReSSe crystals were exfoliated on SiO_2/Si substrate. The electrodes [Ti/Au (5/50 nm)] were then patterned using standard photolithography, electron-beam metal deposition, and lift-off. All the electronic and optoelectronic characterization was performed in a probe station under vacuum conditions at room temperature, and recorded by using an Agilent 1500A semiconductor analyser. The light excitation was provided by diode pumped solid state

lasers operated in continuous wave mode with wavelengths of 405 nm, 532 nm, 633 nm, and 670 nm.

3.7 General Materials Characterization

General materials characterization techniques were used extensively throughout this thesis work for both the bulk single crystals synthesized through vapor transport growth and novel microwave plasma method synthesized thin LTMD crystals.

3.7.1 Thin LTMD Crystal Materials Characterization

Powder X-ray diffraction (P-XRD) data of the thin crystals were obtained with a Bruker D8 advance diffractometer ($\text{CuK}\alpha=1.5406\text{\AA}$ radiation at 45kV, 30mA). The 2θ range is from 10° to 80° with a step size of 0.0238968° and a dwell time of 1.2 seconds per step. SEM imaging of thin crystals was done using the SEM JSM – 7600, JEOL. Elemental distributions over the crystal surfaces were studied by an energy-dispersive X-ray analysis provided semi-quantitative compositional information. AFM imaging of thin crystals was done through c-Atomic Force Microscope, Asylum Research. TEM imaging of thin crystals was performed using Energy Filtered Carl Zeiss TEM, LIBRA® 120. Micro-Raman spectroscopy analysis of thin crystals was performed using Renishaw System 2000 (excitation wavelength 514 nm and laser spot size $\sim 2\text{ }\mu\text{m}$).

3.7.2 Bulk single crystal material characterization

Optical imaging of the single crystals was obtained using the Leica M205C optical microscope. Image processing was performed using the Leica LAS software. SEM imaging of the single crystal was taken using the SEM JSM – 6360, JEOL. Elemental distributions over the crystal surfaces were studied by an energy-dispersive X-ray analysis provided semi-quantitative compositional information. Powder X-ray diffraction (P-XRD) data of the single crystals were obtained with a Bruker D8 advance diffractometer ($\text{CuK}\alpha=1.5406\text{\AA}$ radiation at 45kV, 30mA). The 2θ range is from 10° to 80° with a step

size of 0.0238968° and a dwell time of 1.2 seconds per step. Single Crystal X-ray diffraction (SC-XRD) data of the synthesized crystals were collected using Bruker SMART APEX II single crystal diffractometer (X-ray radiation, Mo $K\alpha$, $\lambda = 0.71073 \text{ \AA}$).

References

- [1] K.S. Novoselov, A.K. Geim, S. V Morozov, D. Jiang, Y. Zhang, S. V Dubonos, et al., Electric Field Effect in Atomically Thin Carbon Films, *Sci.* 306 (2004) 666–669.
- [2] K.S. Novoselov, A.K. Geim, S. V Morozov, D. Jiang, I. V Grigorieva, S. V Dubonos, et al., Two-dimensional gas of massless Dirac fermions in Graphene, *Nature*. 438 (2005) 197.
- [3] C.-H. Su, Y.-G. Sha, Growth of wide band gap II-VI compound semiconductors by physical vapor transport, *Curr. Top. Cryst. Growth Res.* 2 (1995) 401–433.
- [4] R. Lauck, G. Müller-Vogt, Vapour transport of impurities in semi-closed ampoules, *J. Cryst. Growth*. 74 (1986) 513–519.
- [5] A.A. Chernov, Stability of faceted shapes, *J. Cryst. Growth*. 24 (1974) 11–31.
- [6] F. Rosenberger, M.C. Delong, D.W. Greenwell, J.M. Olson, G.H. Westphal, Constitutional supersaturation revisited, *J. Cryst. Growth*. 29 (1975) 49–54.
- [7] R.-F. Xiao, J.I.D. Alexander, F. Rosenberger, Growth morphology with anisotropic surface kinetics, *J. Cryst. Growth*. 100 (1990) 313–329.
- [8] J. Chen, N. Ming, F. Rosenberger, On the atomic roughness of solid–vapor interfaces: Significance of many-body interactions, *J. Chemcial Phys.* 84 (1986) 2365–2375.
- [9] H. Schafer, *Chemical Transport Reactions*, 1964th ed., Academic Press Inc. New York, 1964.
- [10] R. Nitsche, *Crystal Growth*, Pergoman Oxford, 1967.
- [11] S. Srivastava, T. Mandal, B. Samantaray, Studies on layer disorder, microstructural parameters and other properties of tungsten-substituted molybdenum disulfide, $\text{Mo}_{1-x}\text{W}_x\text{S}_2$, *Synth. Met.* 90 (1997) 135–142.
- [12] L.H. Brixner, Preparation and Properties of the Single Crystalline AB_2 -Type Selenides and Tellurides of Niobium, Tantalum, Molybdenum and Tungsten *, *Joural Inorg. Nucl. Chem.* 24 (1962) 257–263.

- [13] R. Nitsche, The growth of single crystals of binary and ternary chalcogenides by chemical transport reactions, *J Phys. Chem. Solids*. 17 (1960) 163–165.
- [14] R. Nitsche, H.U. Bolsterli, M. Lichtenstriger, Crystal Growth by Chemical Reactions-I, *J. Phys. Chem. Solids*. 21 (1961) 199–205.
- [15] R. Nitsche, Proceedings in international conference on crystal growth, Boston, *J. Phys. Chem. Solids Suppl.* 1 (1961) 215.
- [16] R.F. Lever, Multiple Reaction Vapor Transport of Solids, *J. Chemcial Phys.* 37 (1962) 1078.
- [17] R.F. Lever, Transport of Solid through the Gas Phase Using a Single Heterogeneous Equilibrium, *J. Chemcial Phys.* 37 (1962) 1174.
- [18] G. Mandel, Vapor transport of solids by vapor phase reactions, *J. Phys. Chem. Solids*. 23 (1962) 587–598.
- [19] G. Mandel, Multiple reactions and the vapor transport of solids, *J. Chem. Phys.* 37 (1962) 1178.
- [20] T.A. and T. Nishinaga, Transport Reaction in Closed Tube Process, *Jpn. J. Appl. Phys.* 4 (1965) 165.
- [21] E. Kaldis, R. Widmer, Nucleation and growth of single crystals by chemical transport—I cadmium-germanium sulphide, *J. Phys. Chem. Solids*. 26 (1965) 1697–1700.
- [22] E. Kaldis, Nucleation and growth of single crystals by chemical transport—II zinc selenide, *J. Phys. Chem. Solids*. 26 (1965) 1701–1705.
- [23] K.G. Weil, H. Schäfer: Chemische Transportreaktionen. Der Transport anorganischer Stoffe über die Gasphase und seine Anwendung. Monographie Nr. 76 zu „Angewandte Chemie” und „Chemie-Ingenieur-Technik”. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Weinheim/Bergstr. 1962. 142 Seiten mit 44 Abbildungen. Preis: Kart. DM 16,80, *Zeitschrift Für Elektrochemie, Berichte Der Bunsengesellschaft Für Phys. Chemie*. 66 (1962) 885.
- [24] H. Schäfer, T. Grofe, M. Trenkel, The chemical transport of molybdenum and tungsten and of their dioxides and sulfides, *J. Solid State Chem.* 8 (1973) 14–28.
- [25] A. Aruchamy, H. Berger, F. Levy, Photoelectronic properties of the p-type layered trichalcogenophosphates FePS₃ and FePSe₃, *J. Solid State Chem.* 72 (1988) 316–

323.

- [26] A. Aruchamy, H. Berger, F. Lévy, Photoelectrochemical Investigation of n- and p-Doped Nickel Phosphorous Trisulfide (NiPS_3), *J. Electrochem. Soc.* 136 (1989) 2261–2265.
- [27] A. A. Al-Hilli, B.L. Evans, The preparation and properties of transition metal dichalcogenide single crystals, *J. Cryst. Growth.* 15 (1972) 93–101.
- [28] H. Wiedemeier, A.G. Sigai, Vapor transport and crystal growth in the mixed system MnS-MnSe , *J. Cryst. Growth.* 6 (1969) 67–71.
- [29] A. Aruchamy, M.K. Agarwal, Materials Aspects of Layered Semiconductors for Interfacial Photoconversion Devices, in: A. Aruchamy (Ed.), *Photoelectrochem. Photovoltaics Layer. Semicond.*, Springer Netherlands, Dordrecht, 1992: pp. 319–347.
- [30] J. Ouerfelli, S.K. Srivastava, J.C. Bernède, S. Belgacem, Effect of microwaves on synthesis of MoS_2 and WS_2 , *Vacuum.* 83 (2008) 308–312.
- [31] V.D. Szabó, S. Schlabach, Microwave Plasma Synthesis of Materials—From Physics and Chemistry to Nanoparticles: A Materials Scientist's Viewpoint, *Inorganics* . 2 (2014).

Chapter 4

Vapor Transport Growth of Bulk LTMD Single Crystals

In this chapter, all the single crystal growth of the layered compounds that are synthesized via vapor transport growth (CVT or PVT) has been compiled. Their starting materials, growth conditions, experimental setup and physical characterizations were discussed. In addition to pristine stoichiometric compounds, alloys were also synthesized as an attempt to tune properties based on alloy composition. Some new two-dimensional compounds other than LTMDs with attractive future possibilities are also synthesized and characterized.

4.1 Introduction

Single crystals come with its inherent advantages. For instance, in lasing application, optimum laser output and quality is attributed to the low defect density, exceptional spectroscopic and thermal intrinsic properties in single crystalline medium [1]. Conversely, in the microelectronics, drastic increases in the carriers' lifetime and diffusion length are accredited to larger grain sizes [2], characteristics of higher crystallinity. The minute concentration of grain boundaries and impurities in high quality single crystals minimizes charge trapping and scattering related processes that improve the charge transport and optical properties [3].

Additionally, single crystals of TMDCs allows greater versatility in studying the electronic structure, charge transfer in intercalated species and band gap engineering which may propel a certain application that might be previously under-utilized in the absence of suitable material. Here in this section, single crystal growth of LTMDs would be discussed as well as their alloys. Even some new ternary two-dimensional compound of the form of metal-phosphorous sulfide of the form of MPX_3 have been grown and could be utilized for applications in the future.

4.2 Bulk Single Crystal Synthesis

Transition metal precursors were used in the form of molybdenum powder (99.995%, Alfa Aesar), tungsten powder (99.95%, Alfa), tin shots (99.999%, Alfa), niobium powder (99.8%, STREM Chemicals), rhenium powder (99.99%, STREM Chemicals) in the single crystal growth. For chalcogen, sulfur powder (99.9995%, Alfa) and selenium shots (99.999+ %, Alfa) were used. For chemical vapor transport (CVT) technique, sublimed grade iodine shots were used as transport agent. WSe_2 , WS_2 , $NbSe_2$, NbS_2 , ReS_2 , $ReSe_2$, etc. had been grown *via* CVT using iodine as transport agent and SnS_2 and $SnSe_2$ crystals *via* PVT. Crystal growth took place in two-zone furnace. Several transition metal dichalcogenides alloys have been grown and used in applications for collaborative work.

4.2.1 Ampoule Preparation and Crystal Growth

A total mass of around 3 grams of stoichiometric mass of starting materials were placed in one end sealed quartz tube of 150 mm length and 13 mm diameter. For CVT synthesis, few milligrams of iodine shots as transport agent were introduced. The open end of the quartz tube was then connected to rotary-turbo molecular pump via flange vacuum connector and the system was evacuated to 10^{-6} torr and subsequently sealed. The quartz ampoules were placed in the furnace zone and suitable temperature gradient and set points as indicated in figure 4.1.

Figure 4.1: An illustration of a typical two-zone furnace and temperature profile across sealed ampoule inside the furnace

Referring to binary phase diagrams and surveying through literatures had predetermined temperature set point values of the synthesis. The set point condition was set below the melting point in the phase diagram in the compound for the formation of materials. The two zones of furnace for convenience are usually named as source zone (T2) and growth zone (T1). T2 is always at a little higher temperature than T1, and it's the region where the starting material is placed while crystalline product is obtained at T1. ΔT ($T_2 - T_1$) should not be abruptly large as it adversely affects crystal growth. The temperature of the furnace is slowly increased up to the set point to avoid any explosion of the sealed ampoule on account of highly exothermic nature of the reaction between the starting materials. In the current work, several attempts were made to identify the optimum thermal parameters in the current setup to grow large crystals. The average time to grow single crystals of the order of mm size requires at least 12-14 days.

4.3 Materials Characterization of the Synthesized LTMD Crystals

A variety of single crystals of the LTMD family members have been successfully grown and characterized (figure 4.2(a-i)). Multiple synthesis parameters have been employed to ascertain the ideal growth condition such as growth temperature and temperature gradient. Crystals of transition metal dichalcogenides could be noted to be two-dimensional and flat layered in nature. This indicates that growth along the a-b planes is much more rapid than along the c-direction. Cleaving the layered crystals with a razor blade along the 2-D layer or using sticky tapes exposes clean, flat surfaces. These flat clean surfaces will be ideal for measurements of intrinsic electrical and optical properties.

Figure 4.2: Optical images of some of the selected crystals grown *via* vapor transport

In an attempt to further expand the layered two-dimensional library further, new family of two-dimensional material MPX_3 were grown as could be seen in figure 4.2(g-i) that shares the same physical attributes as those of LTMDs. Initial studies suggest wide band gap range

in this family with weak stacking like ReS_2 that may lead to range of optoelectronic properties and as a unit of artificial two-dimensional heterostructures [4]. A list of all the crystals grown during the course of this work has been compiled in table 4.1.

The SEM imaging was also performed on the synthesized materials to confirm the optical observations and to evaluate the stoichiometry of the sample. Small thickness in the c-direction as compared to the dimensions on 2D-planes observed, similar to the instance of the optical images. It has been reported by several researchers that it is possible to alloy the stoichiometric LTMDs by either substituting transition metal sites or by having substitution at the chalcogen sites [5]. On the same line, prominent LTMD such as MoS_2 were alloyed and characterized as shown in figure 4.3.

Figure 4.3: (a,b) SEM images, (c) EDX spectrum of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ microflakes. Inset in (c) is the elemental ratio obtained from the EDX spectrum, (d) XRD pattern of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ microflakes. The standard diffraction peaks of MoS_2 (JCPDS #00-009-0312) and MoSe_2 (JCPDS #00-017-0887) are inserted as references [6] value of x for this data is 0.68. Reproduced by permission. Copyright 2016, Wiley-VC

As shown in figure 4.3, chalcogen sites in pristine MoS_2 have been substituted by selenium atoms giving $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ alloy with the value of x tuned from 0 to 1. All the peaks of the XRD pattern can be indexed to the MoS_2 with some shifts, indicating the single-crystalline nature the prepared alloy $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ crystals.

Figure 4.4: (a,b) SEM images and (c) EDX spectrum of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ flakes. Inset in (c) is the elemental ratio obtained from the EDX spectrum. (d) XRD pattern of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ flakes. The standard diffraction peaks of MoS_2 (JCPDS #00-009-0312) and WS_2 (JCPDS #00-008-0237) are inserted as references [6]. Reproduced by permission. Copyright 2016, Wiley-VCH

In another scenario, transition metal site has been substituted by tungsten atom as shown in figure 4.4. Similar tuning of composition is found in $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ crystals and the phase purity of single crystal as was in $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ crystals. A collaborative work was carried out using these same crystal to report their metallic 1T monolayer counterparts and their performance for hydrogen evolution reaction (HER) and as an electrode in dye sensitized solar cell (DSSC) [6].

Table 4.1: List of all the synthesized compounds with their single crystal growth parameters. First temperature is source and second the growth zone temperature

S.No.	Compound's Name	Growth Temperatures
1.	Cobalt Phospho-sulfide (CoPS_3)	650-600 $^{\circ}\text{C}$
2.	Hafnium Diselenide (HfSe_2)	950-900 $^{\circ}\text{C}$
3.	Hafnium Ditelluride (HfTe_2)	700-800 $^{\circ}\text{C}$
4.	Hafnium Sulfo-selenide ($\text{HfS}_x\text{Se}_{2-x}$)	950-900 $^{\circ}\text{C}$
5.	Iron Phospho-sulfide (FePS_3)	750-700 $^{\circ}\text{C}$
6.	Manganese Phospho-sulfide (MnPS_3)	650-600 $^{\circ}\text{C}$
7.	Molybdenum Diselenide (MoSe_2)	1080-1020 $^{\circ}\text{C}$
8.	Molybdenum Disulfide (MoS_2)	1080-1020 $^{\circ}\text{C}$
9.	Molybdenum Ditelluride (MoTe_2)	1020-970 $^{\circ}\text{C}$
10.	Molybdenum Sulfo-selenide ($\text{MoS}_x\text{Se}_{2-x}$)	1000-950 $^{\circ}\text{C}$
11.	Molybdenum-tungsten Disulfide ($\text{Mo}_x\text{W}_{1-x}\text{S}_2$)	1000-950 $^{\circ}\text{C}$
12.	Nickel Phospho-sulfide (NiPS_3)	750-700 $^{\circ}\text{C}$
13.	Niobium Diselenide (NbSe_2)	950-900 $^{\circ}\text{C}$
14.	Niobium Disulfide (NbS_2)	950-900 $^{\circ}\text{C}$
15.	Niobium Ditelluride (NbTe_2)	900-850 $^{\circ}\text{C}$
16.	Rhenium Diselenide (ReSe_2)	1060-1000 $^{\circ}\text{C}$
17.	Rhenium Disulfide (ReS_2)	1060-1000 $^{\circ}\text{C}$
18.	Rhenium Sulfo-selenide (ReSSe)	1060-1000 $^{\circ}\text{C}$
19.	Tantalum Diselenide (TaSe_2)	970-920 $^{\circ}\text{C}$
20.	Tantalum Disulfide (TaS_2)	950-900 $^{\circ}\text{C}$
21.	Tin Diselenide (SnSe_2)	750-700 $^{\circ}\text{C}$
22.	Tin Disulfide (SnS_2)	680-630 $^{\circ}\text{C}$
23.	Titanium Diselenide (TiSe_2)	700-670 $^{\circ}\text{C}$
24.	Tungsten Diselenide (WSe_2)	1010-960 $^{\circ}\text{C}$
25.	Tungsten Disulfide (WS_2)	1000-950 $^{\circ}\text{C}$
26.	Tungsten Ditelluride (WTe_2)	1020-970 $^{\circ}\text{C}$

4.4 Outcomes and conclusions

We successfully synthesized variety of large high quality LTMD crystals that could act as a platform for almost all kinds of fundamental optoelectronic research both at the bulk and a few or monolayer level. We also explored the possibility of alloying the pristine LTMD compounds that could be used for tuning of intrinsic properties. With a view point of materials science, new family of layered two-dimensional materials, MPX_3 have been grown and will be studied in detail in future.

References

- [1] D. Sangla, I. Martial, N. Aubry, J. Didierjean, D. Perrodin, F. Balembois, et al., High power laser operation with crystal fibers, *Appl. Phys. B.* 97 (2009) 263–273.
- [2] G. Mathian, H. Amzil, M. Zehaf, J.P. Crest, E. Psaila, S. Martinuzzi, et al., Dependence of electronic properties of polysilicon grain size and intragrain defects, *Solid. State. Electron.* 26 (1983) 131–141.
- [3] J.T. Heath, C.-S. Jiang, H. Moutinho, M. Al-Jassim, Investigation of Charge Trapping at Grain Boundaries in Polycrystalline and Multicrystalline Silicon Solar Cells, *MRS Online Proc. Libr. Arch.* 1268 (2010) 1268–EE07–10 (6 pages).
- [4] K. Du, X. Wang, Y. Liu, P. Hu, M.I.B. Utama, C.K. Gan, et al., Weak Van der Waal Stacking, Wide-Range Band Gap and Raman Study on Ultrathin Layers of Metal Phosphorus Trichalcogenides, *ACS Nano.* (2015) 1738-1743.
- [5] H.-P. Komsa, A. V. Krashennnikov, Two-Dimensional Transition Metal Dichalcogenide Alloys: Stability and Electronic Properties, *J. Phys. Chem. Lett.* 3 (2012) 3652–3656.
- [6] C. Tan, W. Zhao, A. Chaturvedi, Z. Fei, Z. Zeng, J. Chen, et al., Preparation of Single-Layer $MoS_{2x}Se_{2(1-x)}$ and $Mo_xW_{1-x}S_2$ Nanosheets with High-Concentration Metallic 1T Phase, *Small.* 12 (2016) 1866–1874.

Chapter 5

Microwave-Induced-Plasma Assisted Synthesis of Thin Layered Transition Metal Dichalcogenides Crystals – WS₂, MoS₂, WSe₂, MoSe₂ and ReS₂.

Few-layer thin crystals of WS₂, MoS₂, WSe₂, MoSe₂ and ReS₂ were synthesized via the microwave-induced-plasma-assisted method. The synthesis was accomplished in plasma that was formed inside sealed quartz ampoules heated by plasma surrounding the sealed ampoule. Powder X-ray diffraction, Raman spectroscopy and Transmission Electron Microscopy indicate thin crystals of high quality. The proposed method is rapid, reproducible and environmentally friendly. It is applicable to practically every direct reaction between metals and nonmetals if the nonmetal vapor pressure can reach a pressure of a few torr, which is required for plasma formation inside a sealed ampoule.

5.1 Introduction

Several vapor phase routes have been employed for the realization of materials (elements and compounds) to either form powders or nanoparticles [1–11]. The underlying principle of vapor phase reactions is the chemical reaction of vaporized chemical compounds or precursors in a gaseous environment. Once evaporated, individual atoms or molecules collide resulting in particle formation by homogeneous nucleation. Further growth occurs by condensation of vapor molecules or atoms on existing particles [12–14]. Collision and coalescence occur throughout the process to generate the materials. As evident, these desired reactions comprising of collisions and coalescence require energy supply. This energy requirement is channeled by either thermal source (high temperature, flame, laser), or by a plasma (microwave (MW), radio-frequency (RF), dielectric barrier discharge (DBD), alternating current (AC), direct current (DC), induction or electric arc (EA)).

The advantage of using microwave energy or microwave-induced-plasma (MIP) is, that higher degrees of ionization and dissociation can be obtained, compared to other types of electrical excitation [15]. This higher ionization and dissociation reduces the activation energy and enhances the kinetics to initiate a chemical reaction. A low operating temperature as compared to standard thermal reactions is advantageous as it lowers the dimensions of synthesized product. Considering the thrust of today's research of rapid synthesis of high quality low-dimensional materials (specially graphene-like compounds such as layered transition metal dichalcogenides), above described advantages could be put to good use for synthesis. In the sections, ahead, a brief overview of the other practices, need to improvise over them and the in-house developed method will be discussed in detail.

5.2 Brief Overview of Current Practices for the Synthesis of LTMDs and Motivation for Development of New Method

Over the last few years, the two-dimensional materials (noticeably, graphene and transition metal dichalcogenides) enjoyed unprecedented attention due to their proclaimed “game-changing” properties and the promise of their wide use for device fabrication [16–18].

However, closer inspection reveals that the special properties are attributed not to the long studied bulk forms of these materials but mostly to crystalline, few-layer thin or even monolayer samples. Therefore, extensive research has been conducted on two-dimensional samples. Few-layer thin and monolayer crystalline samples are obtained easily by mechanical “tape” exfoliation, which results in very high-quality samples for research purposes, but this method is unsuitable for scale-up or mass production. Therefore, it is imperative to increase the output of few-layer thin sample production and synthesize such materials in large quantities without compromising the quality, which in turn is responsible for its properties. Large quantities of thin samples are mostly obtained through solution exfoliation methods [19–21]. However, solvent contamination of the huge surface areas is a problem.

Fundamentally, transition metal dichalcogenides (TMDCs) are not compatible with the classical synthesis methods used for the mass production of semiconductors. For example, large amounts of widely-used binary semiconductors, such as GaAs and Bi₂Sb₃, are obtained by melting high-purity elements or high-temperature synthesis. In the case of TMDCs, the very high melting temperatures of transition metals (Mo, W) and the low melting temperatures with high vapor pressures of non-metals (S, Se, Te) make direct synthesis difficult. Thus, the high-temperature reaction between high purity, solid metals heated at one end and the vapors of non-metals at the second sealed quartz ampoule, controlled by temperature, is opted. By this method, high-quality polycrystalline materials or even large single crystals have been obtained, though in amounts of a few grams with a total growth time of several days.

Here, we developed a rapid synthesis of few-layer transition metal dichalcogenide (TMDCs) nanosheets *via* the microwave-induced-plasma-assisted method. In contrast to the unsuccessful plasma synthesis reported in [22], we improve the microwave coupling of plasma inside the ampoules and use an outside plasma to heat the starting materials during synthesis and crystal growth. This method avoids the contact of the material with any solvent or other reagents, resulting in high-quality thin layers. Few flagship members, such as WS₂, MoS₂, WSe₂, MoSe₂ and ReS₂ of this family (TMDCs) have been successfully

synthesized by this method, and further characterization confirms their morphology, dimensions, stoichiometry and resultant phases.

5.3 Experimental Setup and Process Details of the Novel Method

Stoichiometric quantities of pure elements in powder form were taken as starting materials and were vacuum-sealed in quartz ampoules (transition metals and chalcogens were used without further purification, as received from either Sigma Aldrich Singapore or Alfa-Aesar Singapore). For a typical synthesis, we used approximately 1.5 g of starting material with 2-3 wt% of extra chalcogen in a quartz ampoule (13 mm outer diameter and 100 mm length). The ampoule was placed in the second quartz tube (19 mm outer diameter) that went through the re-engineered microwave oven possessing input and output holes for this evacuated outer quartz tube. A schematic of the setup is shown in figure 5.1. The quartz tube was connected to the gas in-flow on one end and the gas out-flow on the other. The gas flow arrangement was connected to a vacuum oil pump to evacuate air from the quartz tube. The whole synthesis process was carried out for 60 minutes, though we did not optimize the time duration. We suppose that an even shorter time is reasonable.

Figure 5.1: A schematic of the process flow setup for the synthesis of few-layer transition metal dichalcogenide (TMDC) nanosheets

5.4 Investigation into Synthesized Compounds by the Novel Method

To understand the morphology of the product, scanning electron microscopy images of the synthesized products were taken. One of the important features noticed in the micrographs (figure 5.2) is the presence of micrometer-sized, almost hexagonal stacked flakes (sheets) with sub-100 nm cross-sectional dimension (thickness). To further investigate phases of the obtained product, powder X-ray diffraction (PXRD) was carried out to ascertain the desired phases as well as any residual amount of starting materials left inside the product. The PXRD did confirm the presence of the desired phases (TMDCs), as shown in figure 5.3. The sharp diffraction peaks also indicate high crystallinity of the synthesized materials. The thickness of individual as-grown flakes (sheets) was determined through atomic force microscopy (AFM). The results shown in figure 5.4 pointed to a height variation of individual flakes (sheets) from 2-20 nm. Such thin TMDC samples may find use in a plethora of applications, such as optical or optoelectronic materials, either directly for device preparation or the achievement of individual monolayers after additional sonication [23].

Figure 5.2: SEM Micrographs of synthesized compounds showing hexagonal morphology. Starting from top-left (in clockwise direction), WS_2 , MoS_2 , WSe_2 , ReS_2 and MoSe_2 . The scale bar shown in the bottom right corner of each micrograph represents 100 nm except for the ReS_2 micrograph, with a scale bar of 1 μm

Figure 5.3: Powder X-ray diffraction (P-XRD) pattern of as-grown samples along with their corresponding standard powder diffraction ICSD file from the database. Starting from top-left (in clockwise direction): WS₂, MoS₂, WSe₂, ReS₂ and MoSe₂

Figure 5.4: Atomic force microscopic images and section height analysis of as-grown samples, starting from the top: WS₂, MoS₂ and ReS₂

In addition, Raman spectroscopy (figure 5.5) has been performed on the samples as Raman signals were found to be highly responsive to the thickness of the layered materials [24]. In MoS₂ and WS₂, the peak shifts E_{2g}^1 and A_{1g} indicate few-layer thickness [25–27]. For WSe₂, the single maxima and a very weak signal near 308 cm⁻¹, which could be attributed to the B_{2g} mode, are the evidence for few-layer thickness [25,28–31]. The Raman signal of ReS₂ in figure 5.5 shows thickness independent behavior due to the weak interlayer

interactions [32]. The selected area electron diffraction (SAED) patterns and high-resolution transmission electron microscopy (HR-TEM) images (figure 5.6) of the synthesized compounds reveal the hexagonal symmetry for WS_2 and MoS_2 (194-P6₃/mmc space group) and the high quality of the crystals.

Figure 5.5: Raman response of as-grown samples. Peak positions indicate the phase presence and few-layer nature of WS_2 , MoS_2 , WSe_2 , MoSe_2 and ReS_2

Figure 5.6: Selected area electron diffraction (SAED) patterns (above) and high-resolution transmission electron microscopy (HR-TEM) images (below) of individual WS₂ (left) and MoS₂ (right) crystals

5.5 Mechanism Discussion and Advantages Over Other Similar Processes for the Novel Method

The principal feature of the proposed method is the presence of two separated compartments: the first one inside the tube connected to the low-pressure gas flow, where the outer plasma has been formed; and the second one inside of the sealed ampoule. Plasma forms in the outer quartz tube as soon as the pressure of the argon flow is reduced to a few torr. The sealed quartz ampoule contains a mixture of elements used for synthesis. Due to the vacuum inside the cold sealed ampoule, plasma was not formed there even when plasma was lit in the outer tube (figure 5.7(a)). Once the argon plasma from the outer tube starts heating the ampoule and its constituents, the vapor pressure of the non-metal (S, Se) increases. At some temperatures characteristic to equilibrium vapor pressures of non-metals, the vapor pressure in the ampoule reaches a few torr, and the secondary plasma is ignited inside the ampoule (figure 5.7(b)). Plasma formed from non-metal vapor is reactive enough to cause the chemical reaction between the metal (W, Mo or other metal) and the non-metal. Such a reaction is strongly exothermic. Therefore, the temperature of solid materials drastically increases, resulting in the spontaneous reaction between the metal and the chalcogen powder (figure 5.7(c)). Such a solid-state reaction is rather rapid (30 to 60 mins.). The secondary plasma acts as a reacting species/catalyst for the formation of compounds. The high reaction temperature (achieved) causes evaporation of the compounds and formation of small but very thin crystalline flakes of TMDCs (figure 5.7(d)). The stoichiometry of the forming compounds can be regulated in the range of homogeneity of the respective binary system before sealing the ampoule. During the synthesis of all the compounds, additional chalcogen constituents (2-3 wt%) were added above the stoichiometric quantities to supplement the consumption of chalcogen by the secondary plasma inside the ampoule.

In the last two decades, several microwave-induced-plasma-assisted synthesis methods of TMDCs have been reported [33]. In 1998, Vollath and co-workers demonstrated nano-crystalline MoS₂ and WS₂ through microwave plasma in a CVD process [9,34–36]. Ouerfelli et al. reported irregular plasma generation and the lack of reaction between W (or

Mo) and S by simple microwave exposure of elements inside a sealed ampoule [22]. This indicates that the presence of an external primary argon plasma and later ignition of secondary plasma inside the ampoule are integral for successful synthesis of TMDC thin crystals.

Figure 5.7: Stage-wise mechanism of the synthesis process inside the vacuum-sealed ampoule, (a) The beginning of the process with no plasma generation, (b) the ignition of non-metal (chalcogen) plasma inside the ampoule heated by the outer tube plasma (not shown in this drawing), (c) direct reaction between metal element and non-metal (chalcogen), (d) few-layer thick crystals of TMDCs formed due to the heat of synthesis reaction

More recently, plasma-assisted synthesis has been attempted to synthesize TMDC thin films on various substrates [37–41]. However, in contrast to our method, an open tube with a flow of poisonous gases, such as H₂S or H₂Se, over highly heated metals has been used.

5.6 Outcomes and Conclusions

In summary, few-layer TMDC nanosheets of WS₂, MoS₂, WSe₂, MoSe₂ and ReS₂ were synthesized *via* the microwave-induced-plasma-assisted method. The transition metal dichalcogenide compounds were synthesized from elements that already are commercially available in high purity. The samples were characterized by powder X-ray diffraction, field-emission scanning electron microscopy, atomic force microscopy, micro-Raman spectroscopy and transmission electron microscopy, and their range of thickness (2-20 nm) in the as-grown state was found to be in good accordance with the standard data.

Once a plasma of S, Se or similar elements is formed, it easily reacts with the metal heated by an outside plasma, and the heat of the reaction (exothermic reaction) supports the direct reaction and crystal growth. The method presented here is proven for a number of TMDCs. Moreover, due to the lack of any other components, except elements that form desired compounds, this synthesis is applicable to practically every direct reaction between a metal and a nonmetal if the nonmetal vapor pressure can reach the few torr required for plasma formation inside a sealed ampoule. We believe that this method can be used for numerous tellurides, arsenides, phosphides or antimonites without any modifications. We also used it to successfully lead selenide (PbSe) synthesis in the same mode that has been described here.

References

- [1] R.W. Siegel, S. Ramasamy, H. Hahn, L. Zongquan, L. Ting, R. Gronsky, Synthesis, characterization, and properties of nanophase TiO₂, *J. Mater. Res.* 3 (1988) 1367–1372.
- [2] A. Gurav, T. Kodas, T. Pluym, Y. Xiong, Aerosol Processing of Materials, *Aerosol Sci. Technol.* 19 (1993) 411–452.
- [3] S.E. Pratsinis, S. Vemury, Particle formation in gases: A review, *Powder Technol.* 88 (1996) 267–273.
- [4] H. Hahn, Gas phase synthesis of nanocrystalline materials, *Nanostructured Mater.*

- 9 (1997) 3–12.
- [5] Y. Chen, N. Glumac, B.H. Kear, G. Skandan, High rate synthesis of nanophase materials, *Nanostructured Mater.* 9 (1997) 101–104.
- [6] B.H. Kear, N.G. Glumac, Y.-J. Chen, G. Skandan, Flame Synthesis of Nanophase Oxide Powders, *Part. Sci. Technol.* 15 (1997) 174.
- [7] G. Skandan, Y.-J. Chen, N. Glumac, B.H. Kear, Synthesis of oxide nanoparticles in low pressure flames, *Nanostructured Mater.* 11 (1999) 149–158.
- [8] B. Rellinghaus, D. Lindackers, M. Köckerling, P. Roth, E.F. Wassermann, The Process of Particle Formation in the Flame Synthesis of Tin Oxide Nanoparticles, *Phase Transitions.* 76 (2003) 347–354.
- [9] D. Vollath, Plasma synthesis of nanopowders, *J. Nanoparticle Res.* 10 (2008) 39–57.
- [10] B.M. Kumfer, K. Shinoda, B. Jeyadevan, I.M. Kennedy, Gas-phase flame synthesis and properties of magnetic iron oxide nanoparticles with reduced oxidation state, *J. Aerosol Sci.* 41 (2010) 257–265.
- [11] S.E. Pratsinis, Aerosol-based technologies in nanoscale manufacturing: from functional materials to devices through core chemical engineering, *AIChE J.* 56 (2010) 3028–3035.
- [12] B. Schwade, P. Roth, Simulation of nano-particle formation in a wall-heated aerosol reactor including coalescence, *J. Aerosol Sci.* 34 (2003) 339–357.
- [13] B. Giesen, H.R. Orthner, A. Kowalik, P. Roth, On the interaction of coagulation and coalescence during gas-phase synthesis of Fe-nanoparticle agglomerates, *Chem. Eng. Sci.* 59 (2004) 2201–2211.
- [14] H.-R.P. and W.B. and H.M. and H. Seifert, Formation of nanoparticles in flames; measurement by particle mass spectrometry and numerical simulation, *Nanotechnology.* 16 (2005) S354.
- [15] R.G.B. and M.R.W. and C.F. Weissfloch, Generation of large volume microwave plasmas, *J. Phys. E.* 6 (1973) 628.
- [16] K.S. Novoselov, A.K. Geim, S. V Morozov, D. Jiang, Y. Zhang, S. V Dubonos, et al., Electric Field Effect in Atomically Thin Carbon Films, *Sci.* 306 (2004) 666–669.

- [17] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V. V Khotkevich, S. V Morozov, et al., Two-dimensional atomic crystals., *Proc. Natl. Acad. Sci. U. S. A.* 102 (2005) 10451–3.
- [18] Q.H. Wang, K. Kalantar-Zadeh, A. Kis, J.N. Coleman, M.S. Strano, Electronics and optoelectronics of two-dimensional transition metal dichalcogenides., *Nat. Nanotechnol.* 7 (2012) 699–712.
- [19] J.N. Coleman, M. Lotya, A. O'Neill, S.D. Bergin, P.J. King, U. Khan, et al., Two-dimensional nanosheets produced by liquid exfoliation of layered materials., *Sci.* 331 (2011) 568–571.
- [20] V. Nicolosi, M. Chhowalla, M.G. Kanatzidis, M.S. Strano, J.N. Coleman, Liquid Exfoliation of Layered Materials, *Sci.* 340 (2013) 1226419–1226419.
- [21] K.R. Paton, E. Varrla, C. Backes, R.J. Smith, U. Khan, A. O'Neill, et al., Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids., *Nat. Mater.* 13 (2014) 624–30.
- [22] J. Ouerfelli, S.K. Srivastava, J.C. Bernède, S. Belgacem, Effect of microwaves on synthesis of MoS₂ and WS₂, *Vacuum.* 83 (2008) 308–312.
- [23] D. Jariwala, V.K. Sangwan, L.J. Lauhon, T.J. Marks, M.C. Hersam, Emerging Device Applications for Semiconducting Two-dimensional Transition Metal Dichalcogenides, *ACS Nano.* 8 (2014) 1102–1120.
- [24] C. Lee, H. Yan, L. Brus, T. Heinz, J. Hone, S. Ryu, Anomalous lattice vibrations of single-and few-layer MoS₂, *ACS Nano.* 4 (2010) 2695–700.
- [25] H. Zeng, G.-B. Liu, J. Dai, Y. Yan, B. Zhu, R. He, et al., Photoluminescence emission and Raman response of monolayer MoS₂, MoSe₂, and WSe₂, *Opt. Express.* 21 (2012).
- [26] A. Berkdemir, H.R. Gutiérrez, A.R. Botello-Méndez, N. Perea-López, A.L. Elías, C.-I. Chia, et al., Identification of individual and few layers of WS₂ using Raman Spectroscopy, *Sci. Rep.* 3 (2013) 1755.
- [27] P. Hu, J. Ye, X. He, K. Du, K.K. Zhang, X. Wang, et al., Control of Radiative Exciton Recombination by Charge Transfer Induced Surface Dipoles in MoS₂ and WS₂ Monolayers, *Sci. Rep.* 6 (2016) 24105.
- [28] H. Terrones, E. Del Corro, S. Feng, J.M. Poumirol, D. Rhodes, D. Smirnov, et al.,

- New first order Raman-active modes in few layered transition metal dichalcogenides., *Sci. Rep.* 4 (2014) 4215.
- [29] H. Li, Q. Zhang, C.C.R. Yap, B.K. Tay, T.H.T. Edwin, A. Olivier, et al., From bulk to monolayer MoS₂: Evolution of Raman scattering, *Adv. Funct. Mater.* 22 (2012) 1385–1390.
- [30] C. Ataca, M. Topsakal, E. Akt, S. Ciraci, A Comparative Study of Lattice Dynamics of Three- and Two-Dimensional MoS₂, *J. Phys. Chem. C.* 115 (2011) 16354–16361.
- [31] Y. Ding, Y. Wang, J. Ni, L. Shi, S. Shi, W. Tang, First principles study of structural, vibrational and electronic properties of graphene-like MX₂ (M=Mo, Nb, W, Ta; X=S, Se, Te) monolayers, *Phys. B Condens. Matter.* 406 (2011) 2254–2260.
- [32] Y. Feng, W. Zhou, Y. Wang, J. Zhou, E. Liu, Y. Fu, et al., Raman vibrational spectra of bulk to monolayer ReS₂ with lower symmetry, *Phys. Rev. B.* 92 (2015) 054110.
- [33] H.J. Kitchen, S.R. Vallance, J.L. Kennedy, N. Tapia-Ruiz, L. Carassiti, A. Harrison, et al., Modern microwave methods in solid-state inorganic materials chemistry: From fundamentals to manufacturing, *Chem. Rev.* 114 (2014) 1170–1206.
- [34] D. Vollath, D. V Szabo, Synthesis of nanocrystalline MoS₂ and WS₂ in a microwave plasma, *Mater. Lett.* 35 (1998) 236–244.
- [35] D. V Szabo, D. Vollath, Morphological Characterisation of Nanocrystals with Layered Structures, *NanoStructured Mater.* 12 (1999) 597–600.
- [36] D. Vollath, D. V Szabo, Nanoparticles from Compounds with Layered Structures, *Acta Mater.* 48 (2000) 953–967.
- [37] D.J. Brooks, R.E. Douthwaite, Microwave-induced plasma reactor based on a domestic microwave oven for bulk solid state chemistry, *Rev. Sci. Instrum.* 75 (2004) 5277–5279.
- [38] D.J. Brooks, R. Brydson, R.E. Douthwaite, Microwave-induced-plasma-assisted synthesis of ternary titanate and niobate phases, *Adv. Mater.* 17 (2005) 2474–2477.
- [39] T. Suriwong, T. Thongtem, S. Thongtem, Direct energy gap of Sb₂Te₃ synthesised by solid-state microwave plasma, *Micro Nano Lett.* 6 (2011) 170.
- [40] C. Ahn, J. Lee, H.U. Kim, H. Bark, M. Jeon, G.H. Ryu, et al., Low-Temperature Synthesis of Large-Scale Molybdenum Disulfide Thin Films Directly on a Plastic Substrate Using Plasma-Enhanced Chemical Vapor Deposition, *Adv. Mater.* 27

(2015) 5223–5229.

- [41] M. O'Brien, K. Lee, R. Morrish, N.C. Berner, N. McEvoy, C.A. Wolden, et al., Plasma assisted synthesis of WS₂ for gas sensing applications, *Chem. Phys. Lett.* 615 (2014) 6–10.

Chapter 6

Rhenium Dichalcogenides – True Anisotropic 2D Materials

In this chapter, a unique member, rhenium disulfide (ReS_2) of LTMD family has been explored by focusing on its intra-layer anisotropic property apart from usual out-of-plane anisotropy present in all the other layered compounds. This occurs on account of its distorted structure and weak inter-layer coupling. Rhenium dichalcogenides series being isostructural and single phase in nature provides a new candidate for composition-dependent band gap engineering and their tunable properties coupled with in-plane anisotropy makes it an attractive proportion. This and other rhenium based dichalcogenides (alloys) materials has been probed in detail to study their structural, electronic and optical anisotropy and their possible usage in niche applications.

The findings of this chapter has been substantially published in F. Liu, S. Zheng, X. He, A. Chaturvedi, J. He, W.L. Chow, et al., Highly Sensitive Detection of Polarized Light Using Anisotropic 2D ReS_2 , Adv. Funct. Mater. 26 (2016) 1169–1177 (Reproduced with permission. Copyright 2016, Wiley-VCH) and F. Liu, S. Zheng, A. Chaturvedi, V. Zolyomi, J. Zhou, Q. Fu, et al., Optoelectronic properties of atomically thin ReSSe with weak interlayer coupling, Nanoscale. 8 (2016) 5826–5834 (Reproduced by permission of The Royal Society of Chemistry).

6.1 Introduction

Discovery of graphene in 2004, altered the landscape of two-dimensional (2D) materials on account of fascinating physical properties and futuristic applications in nanoelectronics, optoelectronics, and valleytronics [1–10]. Layered compound graphite's single unit, graphene made up of carbon atoms arranged in a honey-comb lattice, has shown extremely high mobilities,[11,12] a high Young's modulus,[13] and excellent thermal conductivity [14]. Although graphene has several excellent properties, zero band gap inhibits its usage in modern day electronics and optoelectronics. This has led the researchers to look elsewhere for structurally similar but semiconducting 2D materials. Presence of direct band gaps and strong absorption in layered transition metal dichalcogenides (LTMDs) makes them attractive for electronics and optoelectronics applications among the available catalogue of 2D semiconductors [15–19]. More recently, black phosphorus (BP), one of the allotropes of phosphorus shows a direct band gap independent of thickness and the band gap value that ranges from ~ 0.3 eV in bulk sample to ~ 1.7 eV in a monolayer [20,21]. In addition to a direct band gap, a mobility value of up to $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature adds to its impressive physical properties [22,23]. Such material attributes present an opportunity for its utilization in broadband photo- detectors, solar cells, and digital electronics [24,25]. Till now, majority of 2D semiconductors (MoS_2 , WSe_2) shows intra-layer isotropy i.e. in a-b plane while having inter-layer anisotropy (c-direction). Interestingly BP's structure shows an structural in-plane anisotropy in addition to out-of-plane anisotropy that could lead to a totally new perspective of looking at such materials and conceptualize them in new optoelectronic devices [26–28]. A concern with regards to its environmental stability in practical applications reduces its general viability [29]. A research in a direction of identifying similar air-stable 2D materials having intra-layer (in-plane) anisotropy and other related functional aspects that would open up unexplored technological paradigms.

Other than black phosphorus (BP), a member of now well established family of layered transition metal dichalcogenides (LTMDs), rhenium dichalcogenides (ReX_2) emerges as a promising candidates for the study of intra-layer anisotropy. ReS_2 forms a distorted 1T structure with triclinic symmetry (figure 6.4, 6.5) [30]. The Peierls distortion of the

1T structure results in buckled S layers and zigzag Re chains along one of the lattice vectors (b-axis) in the plane. In turn layer-plane assumes anisotropic nature with respect to the optical and electrical properties [31]. A demonstration of anisotropy in electrical conductivity of ReS₂ has been reported with the help of ReS₂ based integrated inverter [32]. It has also been reported that bulk ReS₂ exhibits electronic and vibrational decoupling or weaker inter-layer coupling. Thus, their response *via* Raman spectrum remains same irrespective of sample thickness or number of layers [33].

In addition to the special pristine properties of Re dichalcogenides (ReX₂) that makes them promising materials for novel optoelectronic devices and related applications. An ability to tune or control the band gap is vital for realizing efficient photovoltaics and optoelectronics devices. This provides immediate motivation to device ways to engineer layered transition dichalcogenides' (LTMDs) band gap. Few of the techniques practiced to achieve this includes either having a strained structure or an artificially stacked heterostructure combining different available 2D materials to engineer their band gap [34–37]. In comparison, a more primitive and established approach of having alloy semiconductors (composition-dependent) has also found acceptance even for layered transition meta dichalcogenides (LTMDs) family and the same has been reported for the band gap engineering of molybdenum (Mo) and tungsten (W) based dichalcogenides alloys [38–40]. Such flexibility of alloying these materials provides opportunity to investigate change in other properties such as spin-orbit coupling in addition to band gap [41].

6.2 Synthesis of ReS₂, ReSe₂ and ReSSe Bulk Single Crystals

CVT technique as described in Chapter 4 is also employed here to grow bulk single crystals of rhenium disulfide (ReS₂), rhenium diselenide (ReSe₂) and rhenium sulfo-selenide (ReSSe) alloy. The stoichiometric ratio between sulfur (S) and selenium (Se) in ReSSe alloy is chosen as 1:1 for this work.

Rhenium powder (Alfa Aesar, ~22 mesh, 99.999%, Puratronic®), sulfur pieces (Alfa Aesar, 99.999%, Puratronic®) and selenium shots (Alfa Aesar, 1-3mm, 99.999%, Puratronic®) were used for the synthesis of rhenium disulfide (ReS₂) and subsequent

crystal growth. Stoichiometric amounts of rhenium, sulfur and/or selenium were sealed in quartz ampoules with an internal pressure in the range of 10^{-5} to 10^{-6} torr. In addition to the elemental constituents, iodine (2mg/cc) was also incorporated inside the tube as a transport agent. The sealed tubes were then subjected to two-zone horizontal tube furnace as shown in figure 4.1.

For all three compounds, a common synthesis scheme is followed. Various attempts have been made to identify the optimum conditions for the growth of these compounds. Initially, the source zone (Zone I) was kept at 900 °C and the growth zone (Zone II) at 1000 °C for 120 hours. This was done to allow the constituents to react completely as well as prevent the nucleation of large number of crystal seeds. Instead few large crystals would be formed in the subsequent growth process. After this, the temperature of Zone I was gradually increased to 1060 °C while the growth zone remains at 1000 °C. This arrangement continued for next 360 hours. Further, the temperatures of both the zones were lowered to room temperature and ampoules were taken out to obtain single crystals for characterization and measurements.

6.3 Optical, SEM/EDX and P-XRD Characterizations of ReX_2 Crystals

Figure 6.1: Optical Image of as-grown ReS_2 crystal

The as-grown bulk crystal is shown in figure 6.1. and a large edge (b-axis) and a short edge (a-axis) is evident on the plate-like structure. Later, the sample is characterized

via SEM with the image depicting the distorted structure of ReS_2 is distinctly visible (figure 6.2(a)). Following up on it a semi-quantitative EDX analysis has been performed which shows a rough stoichiometry of 1:2 for ReS_2 .

Figure 6.2: (a) SEM images of single crystals of ReS_2 grown via CVT, (b) corresponding EDX analysis with semi-quantitative stoichiometric data

P-XRD patterns of the CVT products were collected to check for presence of precursors or by-products and completion of CVT. The P-XRD studies were performed on background-less sample holders such that the flat, 2D bulk crystallites orientate perpendicular to the face of the sample holder. In this way, strong diffraction peaks in the $(0\ 0\ l)$ direction were detected and the low diffraction peaks from other planes are masked as shown in figure 6.3.

Figure 6.3: P-XRD pattern of ReS₂ crystal indexed with the ICSD file no. 75459

This also illustrates preferred growth sites in basal extension, flat plate-like morphology and highly single crystalline nature of the product. The compound matched with the help of ICSD file no. 75459 is rhenium disulfide and in the P-1 phase (triclinic symmetry and distorted CdI₂ structure). Additionally, no precursor or by-product is detected suggesting complete CVT synthesis. The rhenium and sulfur atomic arrangements in rhenium disulfide have been simulated using Diamond 3.0 program. In figure 6.4, tri-layers (X-M-X) are separated *via* van der Waals gaps.

Figure 6.4: Simulated structure of atomic arrangement of ReS₂ in spatial arrangement based on ICSD file no. 75459. Yellow atoms represent sulfur and grey denotes rhenium

While depicting the structure of ReS_2 it is important to highlight its unique in-plane anisotropy in comparison to other members of LTMDs. Other than rhenium dichalcogenides, all the other LTMDs are usually isotropic within the layer thus devoid of anisotropic oriented properties at atomically thin 2D range. This anisotropy is the result of movement of rhenium atom within one anion-metal-anion layer giving three short and three long Re-S bonds and three significantly short Re-Re distances. This results in the formation of Re_4 clusters connected to each other along the b direction by Re-Re bonds. A comparison of the structural anisotropy is shown in figure 6.5 [42].

Figure 6.5: 2D isotropy vs 2D anisotropy between members of LTMDs. A zig—zag diamond-like chain (shown in green) is along the b-axis showing Re-Re clusters

Later based on the thorough investigations it was reported that the whole series of $\text{ReS}_{2-x}\text{Se}_x$ single crystals were shown to be single phase and isostructural [43]. As a logical conclusion similar rhenium dichalcogenides were synthesized and characterized for further investigations and are reported ahead.

Figure 6.6: Optical image of as-grown ReSe_2 crystals (left) and SEM image of the single crystals grown *via* CVT (right)

Similar procedure was followed to first obtain rhenium diselenide mm-scale high quality crystals (figure 6.6) and later their phase, morphology and composition (figure 6.7) were examined that agrees with the standard data. Powder diffraction files are indexed to ICSD file no. 81813 and a simulated structure has been generated to understand the structural similarity with ReS_2 and clustering of Re-Re chains.

Figure 6.7: Semi-quantitative EDX analysis with rough stoichiometric data (left) and P-XRD pattern of ReSe_2 crystals indexed with the ICSD file no. 81813 (right)

Figure 6.8: Simulated structure of atomic arrangement of ReSe_2 in spatial arrangement based on ICSD file no. 81813. Green atoms represent selenium and grey denotes rhenium. A distortion in the structure is on the account of asymmetric Re-Re chains along the b-axis

Although ReSe_2 is similar to ReS_2 , the work ahead in this chapter is devoted to few layer flakes of pristine ReS_2 flakes and rhenium dichalcogenides alloys. Keeping this in mind, an alloy with 1:1 (S/Se) ratio has been prepared and discussed ahead.

Figure 6.9: Optical image of as-grown ReSSe crystals (left) and SEM image of the single crystals grown *via* CVT (right)

With the motive of exploring band-gap engineering and single phase isostructural nature of $\text{ReS}_{2-x}\text{Se}_x$ series discussed in previous sections, an attempt was made using similar synthesis parameters to obtain rhenium sulfo-selenide (ReSSe) alloy single crystals for studying their optoelectronic applications. Single crystals were obtained *via* CVT and are shown in figure 6.9 (left) and their SEM images (right). The crystalline quality of the crystals obtained were found slightly inferior although the phase purity and composition is at par with pristine compounds (ReS_2 , ReSe_2). The same could be observed from semi-quantitative EDX analysis (figure 6.10(left)) and P-XRD data where reflections other than $(0\ 0\ l)$ are also visible (figure 6.10 (right)). The P-XRD data is indexed with ICSD file no. 81815. Simulated structure (figure 6.11) from the same file shows structural similarity comprising of distortion of CdI_2 structure and formation of Re-Re chains with either of the pristine compounds (ReS_2 , ReSe_2).

Figure 6.10: Semi-quantitative EDX analysis with rough stoichiometric data (left) and P-XRD pattern of ReSSe crystals indexed with the ICSD file no. 81815 (right)

Figure 6.11: Simulated structure of atomic arrangement of ReSSe in spatial arrangement based on ICSD file no. 81815. Grey atoms represent rhenium and partial yellow and partial green atoms denotes sulfur and selenium respectively

6.4 TEM Imaging of ReS₂ Crystals

The detailed atomic arrangement of ReS₂ crystals was investigated using High Resolution Transmission Electron Microscopy (HRTEM). Samples were prepared by dispersing small crystallites of ReS₂ in ethanol via ultrasonication and then drop casting it on copper grid. A crystalline flake is visible from the low resolution TEM image with sharp edges meeting at around 120° angle consistent with previous characterization (figure 6.12 (left)) and

corresponding higher resolution by keeping the area of interest near the sharp edges meeting at the corner (figure 6.12 (right)).

Figure 6.12: Low resolution TEM images of ultrasonicated ReS₂ crystals diluted in ethanol (left), the circular portion is captured at a higher resolution in the next image (right) by keeping focus on the sharp edges meeting at the corner

Figure 6.13 (left) shows the top view of the along the $[0\ 0\ 1]$ zone axis, normal to the basal plane, where the Re chains can be clearly seen. The corresponding diffraction pattern is shown in figure 6.13 (right). It is interesting to note that the intensity of the $(hk0)$ diffraction spots are higher in intensity compared to those from the $(hk0)$ planes, owing to an anisotropic ordering of the Re atoms, with small in-plane displacements from the equilibrium positions.

Figure 6.13: High resolution TEM (HRTEM) images with the electron beam direction normal to the basal plane and representation of 001 and 010 axes on the sample (left), and corresponding selected area electron diffraction pattern (SAED) centered on $[001]$ zone axis (right)

6.5 AFM Imaging of micro-mechanically exfoliated ReX₂ flakes

One of the advantages of having high quality single crystals is to be able to exfoliate them on a desired substrate with a control on the number of layers to identify the thickness of a monolayer or to just check any thickness dependent property. Scotch tape based mechanical exfoliation method was used to peel thin flakes from bulk crystal with the motivation of thinning it down to mono or few layer that could be utilized for thickness measurement and later for device fabrication (figure 6.14 & figure 6.16). Atomic Force Microscopy has been identified as a hands on technique for looking at the topography at nanoscale structures which in turn provides thickness information. Same is used here for both ReS₂ and ReSSe crystals.

Figure 6.14: Optical image of mechanically exfoliated ReS₂ crystals on SiO₂/Si substrate [44]. Adapted with permission. Copyright 2016, Wiley-VCH.

Figure 6.15: (a) Height (thickness) scan of the linear region on the ReS₂ flakes highlighted in (b) and monolayer thickness (height) is observed to be 0.9 nm, (b) AFM image of ReS₂ flake used for height (thickness) scan. A white linear region is ear-marked for analysis [44]. Reproduced with permission. Copyright 2016, Wiley-VCH.

ReS₂ monolayer by the above technique comes out to be 0.9 nm and is consistent with its distorted structure (figure 6.15 (a), (b)). The same is carried out for ReSSe and the monolayer thickness comes out to be 0.76 nm (figure 6.17 (a), (b))

Figure 6.16: Optical image of mechanically exfoliated ReSSe crystals in SiO₂/Si substrate [45]. Reproduced by permission of The Royal Society of Chemistry.

Figure 6.17:(a) An AFM image of ReSSe flake with the selected line profile shown in (b) highlighted by black line, (b) The line profile of the ReSSe flakes highlighted in (a) and height of monolayer as 0.76 nm [45]. Reproduced by permission of The Royal Society of Chemistry.

6.6 Thickness-dependent Raman Spectroscopy of exfoliated ReX₂ flakes

Raman spectroscopy is a powerful tool for studying phonons in 2D materials. To study the Raman spectrum of the ReX₂ flakes of different thicknesses, a scotch tape based mechanical exfoliation method was used to peel thin flakes from bulk crystal onto degenerately doped silicon wafer covered with 285 nm SiO₂ [5].

6.6.1 Rhenium Disulfide (ReS₂)

As shown in figure 6.18; the Raman spectra for a monolayer, few layers and bulk (3nm) of ReS₂, 15 vibrational modes (100–400 cm⁻¹ range) were observed. These modes are

associated with fundamental Raman modes (A_{1g} , E_{2g} , and E_{1g}) which are coupled to each other as well as to acoustic phonons. The plotted spectra vary significantly from TMDs with higher hexagonal symmetries [46,47], demonstrating the structural anisotropy of ReS_2 . The major peaks at 150 and 210.5 cm^{-1} corresponds to in plane (E_{2g}) and mostly out of plane (A_{1g} -like) vibration modes. The position of the respective peaks are slightly different from the reported one, which can be attributed to different excitation laser wavelengths (488 nm) reported the literature [48], and the excitation wavelength used in this study (532 nm). As the thickness of the bulk ReS_2 is reduced down to monolayer, the main Raman peaks show very small change due to weak interlayer coupling in ReS_2 . This result is in good agreement with previously reported Raman shifts [33].

Figure 6.18: A comparative Raman spectra of rhenium disulfide (ReS_2) indicating negligible or no change in the signal while moving down from bulk (blue), few layer (red) right till the monolayer (green) sample. This is usually attributes to weak interlayer coupling. Apart from many minor peaks, two prominent peaks at 150 cm^{-1} and 210.5 cm^{-1} are the one that corresponds to the in-plane (E_{2g}) and mostly out-of-plane (A_{1g} -like) vibration modes, respectively [44]. Reproduced with permission. Copyright 2016, Wiley-VCH.

6.6.2 Rhenium Sulfo-selenide (ReSSe)

Raman spectra of ReSSe flakes; monolayer to five layers, and bulk ReSSe is presented as collated spectra in figure 6.19. Regardless of the thickness more than ten peaks were observed in the scan range from 100 cm^{-1} to 450 cm^{-1} . The peak counts in ReSSe were higher than those found in TMDs with higher crystal symmetries [45] which can be attributed to low crystal symmetry and are associated with fundamental Raman modes coupled to each other and to acoustic phonons. The prominent Raman peaks positions are at 135 , 200 , 230 and 390 cm^{-1} . The relatively broad peaks of ReSSe might be due to lower quality of the alloy when compared with the parent ReS_2 or ReSe_2 compounds. By plotting the position of main Raman peak with respect to layer thickness; figure 6.20, it was observed that the peak positions of the Raman spectra are independent of layer thickness. There were no significant differences between the Raman spectra of monolayer and bulk ReSSe. By these an argument for weak lattice vibrations between the adjacent layers in ReSSe can be attributed to the weak interlayered interaction energy be presented [33], though one should note that the relationship between the interlayer binding energy and phonon modes is nontrivial.

Figure 6.19: Similar to ReS_2 , ReSSe flakes shows similar Raman spectra behavior with changing thickness from monolayer to bulk with thicknesses ranging from monolayer to five layers, and bulk samples. Prominent peaks at 135 , 200 , 230 and 390 cm^{-1} are clearly observed [45]. Adapted by permission of The Royal Society of Chemistry.

Figure 6.20: A plot between position of prominent peaks (135, 200, 230 and 390 cm^{-1}) and number of layers of ReSSe sample shows the layer-independent nature owing to weak inter-layer interactions [45]. Reproduced by permission of The Royal Society of Chemistry.

6.7 Study of Anisotropic Optoelectronic Properties of Rhenium Disulfide (ReS_2)

6.7.1 ARPES and Polarization Dependent Absorption Measurements

The M points in Brillouin zone are distinctive for Layered Transition Metal Di-chalcogenides (LMTDs) with a perfect in-plane hexagonal lattice due to LMTDs six fold symmetry, as shown in figure 6.21a. Due to this, similar electronic dispersion is found between Γ -M1 and Γ -M2. Similar symmetry is not observed in ReS_2 since lattice distortion breaks the original symmetry making M1 and M2 different. Angle-resolved photoemission spectroscopy (ARPES) measurements are evaluated to study the electronic band dispersion across Γ -M1 and Γ -M2, respectively.

The electronic structures are enhanced by applying the second derivation on the energy distribution curve (EDC), as shown in figure 6.21(b, 6.21(c) with respect to their M location as shown in figure 6.21(a). In agreement with theoretical calculations [33], dissimilar bandgap dispersion across Γ -M1 and Γ -M2 are observed.

Figure 6.21: Investigation of anisotropy in ReS₂ through ARPES. (a) Undistorted hexagonal Brillouin zone of ReS₂. The band dispersion along Γ -M1 (b) and Γ -M2 (c) with their momentum locations marked in (a). The differences between (b) and (c) indicate that the six-fold symmetry of the hexagonal Brillouin zone is broken due to lattice distortion [44]. Reproduced with permission. Copyright 2016, Wiley-VCH.

Material which have exhibited structural anisotropy always have exhibited associative optical and/or electrical anisotropy. To prove that ReS₂ does also exhibit associative anisotropies, its in-plane optical anisotropy is studied by measuring the polarization dependence of the absorption spectra of cleaved ReS₂ thin flake on a quartz substrate. Orientation of crystal used for the measurement is shown in the optical image, figure 6.22. A positive increase in the absorption is observed when the polarization angles are varied from 0° to 90° along the b-axis. Similar trend is observed over large range of absorption wavelength; from 1.55 eV (800 nm) to 2.76 eV (450 nm) as shown in figure 6.23(a). The enhancement can be attributed to improved transmission of light from ultrathin ReS₂ layer. This result is an improvement in electrical anisotropy in comparison with previously reported for bulk samples, where the variation is observed in a small range around the band edge [49,50].

There is an unmet need to improve the polarization sensitivity of photodetector to improve efficiency in visible to near infrared spectrum. Our material presents itself as a unique candidate to improve polarization efficiency due to its broadband anisotropic absorption. The absorption is plotted as a function of polarization angle; figure 6.23(b), and fitted with a sinusoidal function which is similar to the band-edge absorption and

Raman spectra spectrum change in anisotropic materials [49,51].

In-plane anisotropy of ReS₂ can be attributed to the field-induced polarization of the lattice leading to displacements of the lattice atoms, and consequently affects the electronic states of the solids [52]. The peak observed near band edge is related to the exciton absorption [53], which is polarization dependent. By rotating the polarization from perpendicular to parallel along the b-axis direction as shown in figure 6.22, shifts exciton absorption from 1.51 to 1.48 eV. This polarization dependence of exciton absorption of ReS₂ makes it an excellent candidate to be used for wavelength and polarization sensitive luminescent applications.

Figure 6.22: The optical image of the ReS₂ flake utilized for polarization dependent absorption studies. It's thickness is 12 nm and rotation along b axis is depicted through angle definition [44]. Reproduced with permission. Copyright 2016, Wiley-VCH

Figure 6.23: Polarization dependent absorption studies ReS₂ flake shown in figure 6.22. **(a)** Polarization angle (with respect to b-axis of the crystal structure) dependent absorption spectrum, **(b)** Sinusoidal function – like behavior (black line) is observed when absorption is plotted against polarization angle for different photon energies (2.41, 1.96, and 1.58 eV, respectively) [44]. Reproduced with permission. Copyright 2016, Wiley-VCH.

6.7.2 Electronic Transport Properties of Few Layer ReS₂ FET

Electronic properties of a material define the performance of photo detection, which can be quantified by studying the transport performances of atomically thin ReS₂. By this an extended argument for photodetector performance can be formulated.

Transport performance of the ReS₂ was studied using fabricated field effect transistors (FETs). The device was fabricated using the photo-lithography and Cr/Au (5/50 nm) electrodes were deposited using the high vacuum thermal evaporator. Conduction channels were fabricated along the b-axis direction to study the polarization dependence of ReS₂ FET device. As shown in figure 6.24(a), the output characteristics of the 3 nm thick ReS₂ FET is an obvious n-type semiconducting behavior. The linear I_d – V_d curve under low drain voltage indicates negligible Schottky barrier at the ReS₂ and Cr/Au interfaces. As shown in figure 6.24(b), varying the gate voltage from –30 to 30 V with 0.1 V drain voltage, the channel switched from “off” state to “on” state. Also, an increase in drain current by a factor of 10^5 was observed. The measured “on/off” ratio is four orders of magnitude larger than reported for graphene and is comparable to recently reported in MoS₂ device [54]. The field-effect mobility was estimated from the linear region in the I_d – V_g curve (V_g from 10 to 30V) by using the equation

$$\mu = [(dI_d \times dV_g) \times (L/WC_i V_d)]$$

L is the channel length, W is the channel width, and C_i is the capacitance between the channel and the back gate per unit area ($C_i = \epsilon_0 \epsilon_r / d$; ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity of the dielectric, and d is the thickness of SiO_2 layer).

At room temperature, the mobility is $18 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, with $L=6.2 \mu\text{m}$, $W=1.7 \mu\text{m}$, and $d=285 \text{ nm}$. The mobility of ReS_2 is comparable to exfoliated MoS_2 layers. [54–56].

Figure

6.24:

Characteristic curves for few layer ReS_2 field effect transistor based on a 3 nm ReS_2 flake as shown in the optical image (inset of (a), scale bar 10 μm) (a) Room temperature transistor output transfer curve depicts n-type behavior with low contact resistance. (b) A mobility of $18 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is deduced from the linear (red) and log (black) scale plots of the transfer curve with an on/off ratio of about 10^5 . (c) Temperature dependent study of I_d - V_g transfer curve for the ReS_2 transistor with a drain voltage of 0.1 V (d) Temperature dependent study of the field effect mobility as a function of temperature extracted from (c). With a decrease in temperature, mobility gradually increases. The inset of (d) shows the power law fitting of the data. This indicates the dominant electron-phonon scattering at higher temperature [44]. Reproduced with permission. Copyright 2016, Wiley-VCH.

Experiments were designed to understand the relationship between the mobility and

temperature to study the reason for limited mobility in ReS₂. As shown in figure 6.24(c), (d); when the temperature was decreased from room temperature to 100 K the mobility of ReS₂ increased monotonically up to 40 cm² V⁻¹ s⁻¹ because of weak electron-phonon scattering at low temperature [57]. As shown in the inset of figure 6.24(d), the temperature dependence is fitted with power law

$$\mu \propto T^{\gamma},$$

The exponent γ is about 1.1, which depends on the dominant phonon scattering mechanism and is comparable to reported for bilayer MoS₂ [58], is smaller than that of monolayer MoS₂ and predicted theoretical calculation [57,59]. Variations in the apparent phonon damping factor may be explained by charged impurity scattering and homo-polar phonon quenching [58], the origin of the observed γ in our work is still unclear. To have a theory for γ more detailed experimental and theoretical calculation need to be researched at temperature much lower than used in these thesis. It can be further hypothesized that by combining the measurements with the Hall mobility measurement, will help to fully understand the scattering mechanism ReS₂ but also optimizing the device performance many ReS₂ like 2D materials.

6.7.3 Photoresponse Properties of Few Layer ReS₂ Photodetector Device

It is expected that direct band gap nature of ReS₂ will lead to high absorption coefficient and efficient electron–hole pair generation under photoexcitation, a crucial requirement for a high-performance photodetector in an optoelectronic device. The argument was assessed by studying the photo-response properties of atomically thin ReS₂ (≈ 3 nm) in a two-terminal device geometry using a green semiconductor laser (2.4 eV) as the illumination source (figure 6.25(a)). The photoresponse is investigated under different wavelength excitations and the corresponding data is compiled in Appendix C, figure C.1. The device shows good response irrespective of the wavelength of lights used. As shown in figure 6.25(b) which plots the photocurrent as a function of drain bias, by increasing the light power the photocurrent becomes stronger. The light power dependence of photocurrent was extracted at different drain voltages; plotted in figure 6.25(c), satisfies a simple power law relation

$$I_{ph} \propto P^\alpha,$$

where I_{ph} is the photocurrent, P is the light power, respectively.

The index of power law α is 0.3. The values may be due to complex processes involved in carrier generation, trapping, and electron–hole recombination in the semiconductor [60].

The process for the photocurrent generation can be explained by a simplified energy band diagram as illustrated in figure 6.25(d). The charge transfer through Fermi level tuning between the interface of metal electrodes and ReS_2 channels results in band bending leading to formation of Schottky type barriers and depletion layers. Under illumination with the photon energy greater than the energy gap of the semiconductor, electron–hole pairs get excited by absorbing light and are laterally separated by the applied drain bias, leading to the generation of photocurrent. The response of photodetector is proportional to the rate of incident beams of photons, which is consistent with the result shown in figure 6.25(c). The time dependent photoresponse of the ReS_2 device is analyzed by recording the current change as a function of mechanically modulation the intensity of the incoming light as shown in Appendix C, figure C.2.

Photoresponsivity (R), defined as the ratio between the intensity of generated photocurrent to that of the incident light, is a critical parameter for designing a photodetector. Photoresponsivity values are deduced from the data in figure 6.25 (c) at different bias voltages and plotted in figure 6.25 (e) respectively. Photoresponsivity of 10^3 A W^{-1} was achieved for the device at low intensity of light which. The recorded value is several order of magnitude higher than that of graphene-based photodetectors [2], three orders of magnitude higher than that of black phosphorus [24], and comparable with the best value of reported MoS_2 -based photodetectors [61]. A sub-linear dependence of the photoresponse was observed upon tuning the light power. The presence of the trap states either in the channel or at the interface between ReS_2 and the

underlying SiO_2 layer may be responsible for the reduction of the photoresponsivity at higher light power [61].

Figure 6.25: Optoelectronic characterization of the ReS₂ device, (a) 3D schematic view of the photodetection device. The light is illuminated on the ReS₂ channel, and the light polarization is controlled by the half wave plate, which is used for the linear dichroism detection later, (b) Under the different intensity of green light illumination, A plot of photocurrent response for different drain voltage is generated. (c) Similarly, dependence of photocurrent on the intensity of incident illumination is plotted for various drain voltages (1 V (blue), 2 V (green) and 3 V (red) respectively). This also satisfies the power law behavior and depicted by black line. (d) A graphical illustration for different illumination and bias conditions and resultant device band diagrams (E_F , Fermi level; E_C , Conduction band; E_V , Valence band). Schottky barrier is formed at the device-contact interface. On illumination, electron-hole pairs are generated and separated by the applied drain voltage, generating photocurrents, (e) A plot of photoresponsivity with respect to intensity of light is generated based on the data obtained in (c) for drain voltages of 1 V (blue), 2 V (green), and 3 V (red), respectively [44]. Reproduced with permission. Copyright 2016, Wiley-VCH.

It is expected that the structure anisotropy induces linear dichroism in ReS₂. This forms a basis for characterization of polarization sensitive detection of ReS₂ photodetector. The polarization of the illuminated light is controlled by combining one half wave plate and a polarizer. Figure 6.26(a) shows the evolution of photocurrent as a function of polarization angle of a linear polarizer. It was observed that by changing the polarization angle of the light and keeping the incident power constant, the change in the photocurrent is striking. The photocurrent with the incident light polarized along the b-axis; defined as 90° in figure 6.22, is much stronger than that perpendicular to the b-axis; defined as 0°. This is a strong evidence that demonstrates the polarization dependent absorption and resulting photocurrent detection via linear dichroism. The photocurrents under drain voltages of 1, 2, and 3 V as a function of incident light polarization angle; shown in figure 6.26(b), can be perfectly fitted by a sinusoidal function. In addition, the photocurrent and absorption has a similar dependence on the incident light polarization, as shown in figure 6.26(c), plotted in polar coordination. This experimental result serves as a strong proof that the intrinsic polarization dependency of the photoresponse originates from ReS₂ itself. This result also indicates that as the incident light in different polarization states passes through the anisotropic ReS₂ experiences a varying absorption, directly reflecting the intrinsically anisotropic nature of the crystal structure. As seen in the spectra, the absorption varies over wide wavelength range which can essentially extend the polarization sensitive photodetection from visible to near infrared. Compared to the reported polarization sensitive device based on a wire-grid polarizer relying on nanofabrication processes [62], our device demonstrations prove that atomically thin ReS₂ can be used as a potential intrinsic linear dichroic media with high responsivity for practical integrated optical applications.

Figure 6.26: Polarization sensitive photoresponse studies of ReS₂, (a) 2D plot of dependence of photocurrent on the value of drain bias for different polarization light illuminations. (b) Polarization angle dependence photocurrent for different drain biases. The power law curve (black line) fits with the obtained data. (c) A polar coordinate plot depicting near same behavior between the photocurrent with drain bias of 1 V (red square) and absorption (green circle) measured under different polarization angle of green light. The blue line is an extension of the sinusoidal function fitting results. This behavior conclusively exhibits the intrinsic linear dichroic response of ReS₂ [44]. Reproduced with permission. Copyright 2016, Wiley-VCH.

6.8 Study of Optoelectronic Properties of Rhenium Sulfo-selenide (ReSSe)

With respect to the discussion in section 6.1, an effective strategy with regards to composition dependent alloying of pristine semiconductor compounds are imperative in establishing the versatility of the material. To follow this approach already synthesized large high-quality ReSSe alloy bulk single crystals (as described in section 6.2, 6.3. and 6.4) are utilized for the preparation of electronic and optoelectronic devices. Prior to exfoliation, absorption spectrum of the ReSSe bulk alloy crystals are recorded and compared with that of pristine crystals of ReS₂ and ReSe₂ (figure 6.27). In all three

compounds, stable exciton states are observed at room temperature on account of their large exciton binding energy. From the same data, band gap engineering of ReX_2 alloy series is evident from the fact that the exciton peak of ReSSe alloy lies at 1.39 eV which is between the exciton peak value of 1.51 eV for ReS_2 and that of 1.32 eV for ReSe_2 .

Figure 6.27: Absorption spectrum of ReS_2 (red), ReSSe (green) and ReSe_2 (blue) [45]. Reproduced by permission of The Royal Society of Chemistry

Thin flakes of about 3 nm thickness are obtained *via* micro-mechanical exfoliation (as described in section 6.5). To study the electronic properties, a field-effect transistor (FET) was fabricated using the exfoliated flakes of ReSSe alloy. An optical image with the section height analysis of channel is shown in the inset of figure 6.28 (b). The I_d – V_d and I_d – V_g curves of the device were measured as shown figure 6.28(a), (b). The I_d – V_d data exhibit a slight superlinear behavior at low drain bias, which suggests that the electrons are injected through Schottky barrier at the metal–semiconductor interface. The transfer characteristic measured at three different drain biases, $V_d = 1$ V, 3 V and 5 V, respectively as shown in figure 6.28(b). The device shows a typical n-type behavior with on/off ratio at $V_d = 1$ V larger than 10^5 , similar to the reported on/off ratios for MoS_2 , WS_2 , and WSe_2 devices, and is explained by the large band gaps. The mobility of the ReSSe device is deduced by fitting the linear range in the transfer curve from $V_g = 20$ V to $V_g = 50$ V. The mobility is calculated to be $3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, using the equation

$$\mu = dI_d/dV_g \times (L/WC_iV_d),$$

where L is the channel length, W is the channel width, and C_i is the capacitance between the channel and the back gate per unit area ($C_i = \epsilon_0 \epsilon_r/d$, where ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity of dielectric medium, and d is the thickness of the SiO_2 layer).

The mobility of our device is comparable to the other reported values for established compounds such as GaS and MoS_2 [63]. Transistors having bottom-gate architecture are always prone to the existence of either trap or impurity states at the SiO_2/Si surface which can degrade the carrier mobility of the device on account of scattering due to charged impurities. Higher values of mobility are expected to be achieved from ReSSe-based devices with the optimization of the bottom-gate dielectric layer in terms due to better control of impurities or traps [56]. One of the defining features of the rhenium dichalcogenides and their alloys are the in-plane structural, electronic and optical anisotropy. This is exhibited by the in-plane axis-dependent behavior of conductivity (separate device is prepared for this experiment). Consequently, an anisotropic mobility values are obtained for b-axis and a-axis as 2.6 and 1.4 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ respectively.

Figure 6.28: Characteristic curves for few layer ReSSe field effect transistor based on a 3 nm ReSSe flake as shown in the optical image (inset of (b), scale bar 10 μm) (a) I_d – V_d curve shows near-linear dependence at a low drain voltage indicating a small Schottky barrier between the metal contact and the channel, (b) I_d – V_g curve exhibits n-type behavior with a drain voltage of 1 V, 3 V, and 5 V. (c) I_d – V_d curve and (d) I_d – V_g curve at different temperatures. The drain voltage first increases when the temperature decreases from 300 K, and then decreases when the temperature falls below 240 K. The inset of panel (c) shows the drain–current change as a function of temperature at a gate voltage of 30 V. The inset of panel (d) shows the temperature dependence of the mobility deduced from the I_d – V_g curve [45]. Reproduced by permission of The Royal Society of Chemistry.

To investigate the transport properties of the ReSSe transistor, temperature dependency measurements from room temperature down to 100 K and the corresponding characteristic curves are plotted; figure 6.28(c), (d) show the temperature dependent transfer and output curves respectively. As the temperature decreases from room

temperature, there is an initial increase in the drain current initially followed by gradual decrease. The temperature dependence of the drain current and the mobility is shown in the inset of figure 6.28(c), (d), respectively. The temperature dependence is characterized by a peak at 240 K, below which we observe a decrease of current mobility as the temperature decreases continuously till 100 K. This behavior is consistent with the mobility being limited by scattering from charged impurities [57]. Increasing the temperature above 240 K results in strong decrease in the mobility from its peak value. This decrease is attributed to electron-phonon scattering becoming a dominant scattering mechanism at higher temperatures.

The photoresponse properties of devices based on few-layer ReSSe were also investigated under vacuum condition by monitoring the photocurrent change under an applied drain voltage as function of incident light power and wavelength. The photocurrent changes as a function of the drain voltage with a gate voltage of 0 V, under excitation by different intensities of light is shown in figure 6.29(a). When the device is illuminated with an excitation wavelength of 532 nm and a low optical power of 3 mW cm^{-2} , the device generates an expected photocurrent. The photocurrent increases gradually as the driving drain voltage increases. Figure 6.29(b) shows the light-power dependence of the photocurrent, which can be expressed by a simple power law, on a log–log scale. The nonlinear behavior of light-power dependency arises due to complex processes of electron–hole generation, trapping, and recombination within the semiconductor. Photoresponsivity (R), which is the ratio of the generated photocurrent to the incident optical power is a critical parameter to assess the photodetector. Photoresponsivity is extracted from figure 6.29(b) and plotted in figure 6.29(d). At low illumination intensities, the device reaches a photoresponsivity of 8 A W^{-1} , which is more than an order of magnitude higher than widely studies graphene photodetectors as well as the BP phototransistors [64]. The high photoresponsivity makes ReSSe a promising material for applications in optoelectronic devices.

Broadband photoresponse is important for a photodetection device. When the photon energy of the incident light is greater than the band gap of the active material, the carriers can be excited and generate photocurrent under the applied drain voltage. As shown in figure 6.29(c), by reducing the wavelength of the incident light there is an enhancement in the photocurrent. This can be attributed to the absorption coefficient

being higher at short wavelength than at long wavelength. As light is absorbed by the channel increases it leads to generation of more electron–hole pairs which further contributes to increase of the photocurrent produced by short-wavelength excitation. Because the gap of the ReSSe sample is around 1.39 eV, the device can be used over a wide range, from near infrared to ultraviolet.

Figure 6.29: (a) Dependence of photocurrent on the value of drain voltage for different intensities of incident light. (b) A logarithmic plot for dependence of photocurrent on intensity of light for drain voltages of 1 V, 3 V, and 5 V. The power-law fits are depicted by solid lines. The value of exponent on power law is 0.73. (c) A plot of drain voltage dependence of photocurrent for different excitation wavelengths. The inset shows the photocurrent at a drain voltage of 4 V as a function of excitation wavelength, (d) Photoresponsivity as a function of the light intensity as deduced from panel (b) [45]. Reproduced by permission of The Royal Society of Chemistry.

The gate voltage can be used to modulate the Schottky barrier at the interface between the electrode and channel materials. Also, photoresponse is highly sensitive to Schottky barriers. So we investigated the gate-voltage modulation of photocurrent generation using a 532 nm laser illumination with light power fixed at 100 mW cm^{-2} . Figure 6.30(a) shows the drain-current changes as a function of gate voltage with and without illumination. By subtracting the dark current from the drain current generated under illumination, we can clearly see the gate modulation of the photocurrent (figure 6.30(b)), which is attributed to the reduced Schottky barrier when a large, positive gate voltage is applied.

Figure 6.30: (a) I_d - V_d curve of the ReSSe field-effect transistor, with and without illumination, (b) Photocurrent as a function of gate voltage. The photo-current is deduced by taking the difference of the drain currents with and without illumination. The photocurrent can be strongly modulated by the gate voltage [45]. Reproduced by permission of The Royal Society of Chemistry.

6.9 Outcomes and Conclusions

The electronic and photoresponse properties of atomically thin ReS_2 obtained by mechanical exfoliation method was investigated. Electron mobility upto $40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was attained with an “on/off” ratio of 10^5 . The device also shows a good photoresponse with a photoresponsivity of 10^3 A W^{-1} .

The linear dichroic photodetector device based on anisotropic ReS_2 is demonstrated, which is ascribed to the polarization sensitive absorption induced by crystal’s structure anisotropy. The environmental stability and unique physical properties like weak interlayer coupling and linear dichroism observed in ReS_2 when coupled with high

flexibility afforded by 2D materials [65], allows us with new degree of freedom to manipulate electronic and optoelectronic properties.

Based on the results of this section, there exist new and exciting opportunities for developing novel integrated optical and optoelectronic device applications for polarization detection. The advantage of the simple transistor architecture reported here allows the polarization dependent phototransistor to be used as part of a circuit, for example, as part of a complementary inverter or ring oscillator. Recent progress in growth of 2D materials and heterostructure, [66–68] should allow the creation of arrays of micrometer - scale devices, as well as integration with CMOS electronics and ultimate thin light polarization detection devices based on anisotropic ReS₂ and other 2D materials [61,69].

Atomically thin ReSSe have also been studied for its electronic and photoresponsive properties. A n-type few-layered ReSSe transistor was fabricated and its electron mobility was measured to be around $3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Due to direct bandgap behavior of ReSSe; few-layered ReSSe photosensitive devices exhibits very high photoresponsivity, up to 8 A W^{-1} . This when couple with large area material preparation methods such as liquid scale exfoliation and chemical vapor deposition, the composition dependent bandgaps of ReSSe alloy make it an excellent substrate for design of low-cost and efficient optoelectronic devices.

References

- [1] K.F. Mak, K.L. McGill, J. Park, P.L. McEuen, Valleytronics. The valley Hall effect in MoS₂ transistors., *Sci.* 344 (2014) 1489–92.
- [2] T. Mueller, F. Xia, P. Avouris, Graphene photodetectors for high-speed optical communications, *Nat Phot.* 4 (2010) 297–301.
- [3] K.S. Novoselov, V.I. Fal'ko, L. Colombo, P.R. Gellert, M.G. Schwab, K. Kim, A roadmap for graphene., *Nature.* 490 (2012) 192–200.
- [4] K.S. Novoselov, A.K. Geim, S. V Morozov, D. Jiang, Y. Zhang, S. V Dubonos, et al., Electric Field Effect in Atomically Thin Carbon Films, *Sci.* . 306 (2004) 666–669.
- [5] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V. V Khotkevich, S. V

- Morozov, et al., Two-dimensional atomic crystals., *Proc. Natl. Acad. Sci. U. S. A.* 102 (2005) 10451–3.
- [6] A. Pospischil, M. Humer, M.M. Furchi, D. Bachmann, R. Guider, T. Fromherz, et al., CMOS-compatible graphene photodetector covering all optical communication bands, *Nat Phot.* 7 (2013) 892–896.
- [7] K. Roy, M. Padmanabhan, S. Goswami, T.P. Sai, G. Ramalingam, S. Raghavan, et al., Graphene-MoS₂ hybrid structures for multifunctional photoresponsive memory devices, *Nat Nano.* 8 (2013) 826–830.
- [8] F. Schwierz, Graphene transistors, *Nat Nano.* 5 (2010) 487–496.
- [9] H. Zeng, J. Dai, W. Yao, D. Xiao, X. Cui, Valley polarization in MoS₂ monolayers by optical pumping, *Nat Nano.* 7 (2012) 490–493.
- [10] W.J. Yu, Z. Li, H. Zhou, Y. Chen, Y. Wang, Y. Huang, et al., Vertically stacked multi-heterostructures of layered materials for logic transistors and complementary inverters, *Nat Mater.* 12 (2013) 246–252.
- [11] X. Du, I. Skachko, A. Barker, E.Y. Andrei, Approaching ballistic transport in suspended graphene, *Nat Nano.* 3 (2008) 491–495.
- [12] D. R., Y. F., MericI., LeeC., WangL., SorgenfreiS., et al., Boron nitride substrates for high-quality graphene electronics, *Nat Nano.* 5 (2010) 722–726.
- [13] C. Lee, X. Wei, J.W. Kysar, J. Hone, Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene, *Sci.* (80-.). 321 (2008) 385–388.
- [14] A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, et al., Superior Thermal Conductivity of Single-Layer Graphene, *Nano Lett.* 8 (2008) 902–907.
- [15] T. Georgiou, R. Jalil, B.D. Belle, L. Britnell, R. V Gorbachev, S. V Morozov, et al., Vertical field-effect transistor based on graphene-WS₂ heterostructures for flexible and transparent electronics, *Nat Nano.* 8 (2013) 100–103.
- [16] Y. Gong, J. Lin, X. Wang, G. Shi, S. Lei, Z. Lin, et al., Vertical and in-plane heterostructures from WS₂/MoS₂ monolayers, *Nat Mater.* 13 (2014) 1135–1142.
- [17] Y. Yoon, K. Ganapathi, S. Salahuddin, How Good Can Monolayer MoS₂ Transistors Be?, *Nano Lett.* 11 (2011) 3768–3773.
- [18] X. Hong, J. Kim, S.-F. Shi, Y. Zhang, C. Jin, Y. Sun, et al., Ultrafast charge transfer in atomically thin MoS₂/WS₂ heterostructures, *Nat. Nanotechnol.* 9 (2014) 682–686.
- [19] K.F. Mak, C. Lee, J. Hone, J. Shan, T.F. Heinz, Atomically Thin MoS₂: A New

- Direct-Gap Semiconductor, *Phys. Rev. Lett.* 105 (2010) 136805.
- [20] A.S. Rodin, A. Carvalho, A.H. Castro Neto, Strain-Induced Gap Modification in Black Phosphorus, *Phys. Rev. Lett.* 112 (2014) 176801.
- [21] V. Tran, R. Soklaski, Y. Liang, L. Yang, Layer-controlled band gap and anisotropic excitons in few-layer black phosphorus, *Phys. Rev. B.* 89 (2014) 235319.
- [22] H. Liu, A.T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tománek, et al., Phosphorene: An Unexplored 2D Semiconductor with a High Hole Mobility, *ACS Nano.* 8 (2014) 4033–4041.
- [23] L. Li, Y. Yu, G.J. Ye, Q. Ge, X. Ou, H. Wu, et al., Black phosphorus field-effect transistors, *Nat Nano.* 9 (2014) 372–377.
- [24] N. Youngblood, C. Chen, S.J. Koester, M. Li, Waveguide-integrated black phosphorus photodetector with high responsivity and low dark current, *Nat Phot.* 9 (2015) 247–252.
- [25] M. Buscema, D.J. Groenendijk, G.A. Steele, H.S.J. van der Zant, A. Castellanos-Gomez, Photovoltaic effect in few-layer black phosphorus p-n junctions defined by local electrostatic gating, *Nat Commun.* 5 (2014) 4651.
- [26] X. Wang, A.M. Jones, K.L. Seyler, V. Tran, Y. Jia, H. Zhao, et al., Highly anisotropic and robust excitons in monolayer black phosphorus, *Nat Nano.* 10 (2015) 517–521.
- [27] F. Xia, H. Wang, Y. Jia, Rediscovering black phosphorus as an anisotropic layered material for optoelectronics and electronics, *Nat Commun.* 5 (2014) 4458.
- [28] J. Qiao, X. Kong, Z.-X. Hu, F. Yang, W. Ji, High-mobility transport anisotropy and linear dichroism in few-layer black phosphorus, *Nat Commun.* 5 (2014) 4475.
- [29] J.O. Island, G. a Steele, S.J. van der Z. Herre, A. Castellanos-Gomez, Environmental instability of few-layer black phosphorus, *2D Mater.* 2 (2015) 11002.
- [30] H.H. Murray, S.P. Kelty, R.R. Chianelli, Structure of Rhenium Disulfide, *Inorg. Chem.* 33 (1994) 4418–4420.
- [31] D. Wolverson, S. Crampin, A. Kazemi, Raman Spectra of Monolayer, Few-Layer and Bulk ReSe₂: an Anisotropic Layered Semiconductor, *ACS Nano.* (2014).
- [32] E. Liu, Y. Fu, Y. Wang, Y. Feng, H. Liu, X. Wan, et al., Integrated digital inverters based on two-dimensional anisotropic ReS₂ field-effect transistors, *Nat*

- Commun.* 6 (2015) 6991.
- [33] S. Tongay, H. Sahin, C. Ko, A. Luce, W. Fan, K. Liu, et al., Monolayer behaviour in bulk ReS₂ due to electronic and vibrational decoupling., *Nat. Commun.* 5 (2014) 3252.
- [34] J. Feng, X. Qian, C.-W. Huang, J. Li, Strain-engineered artificial atom as a broad-spectrum solar energy funnel, *Nat Phot.* 6 (2012) 866–872.
- [35] Y.Y. Hui, X. Liu, W. Jie, N.Y. Chan, J. Hao, Y.-T. Hsu, et al., Exceptional Tunability of Band Energy in a Compressively Strained Trilayer MoS₂ Sheet, *ACS Nano.* 7 (2013) 7126–7131.
- [36] M. Ghorbani-Asl, S. Borini, A. Kuc, T. Heine, Strain-dependent modulation of conductivity in single-layer transition-metal dichalcogenides, *Phys. Rev. B.* 87 (2013) 235434.
- [37] H.-P. Komsa, A. V Krasheninnikov, Electronic structures and optical properties of realistic transition metal dichalcogenide heterostructures from first principles, *Phys. Rev. B.* 88 (2013) 85318.
- [38] A. Kutana, E.S. Penev, B.I. Yakobson, Engineering electronic properties of layered transition-metal dichalcogenide compounds through alloying, *Nanoscale.* 6 (2014) 5820–5825.
- [39] H. Li, X. Duan, X. Wu, X. Zhuang, H. Zhou, Q. Zhang, et al., Growth of Alloy MoS_{2x}Se_{2(1-x)} Nanosheets with Fully Tunable Chemical Compositions and Optical Properties, *J. Am. Chem. Soc.* 136 (2014) 3756–3759.
- [40] Y. Chen, J. Xi, D.O. Dumcenco, Z. Liu, K. Suenaga, D. Wang, et al., Tunable Band Gap Photoluminescence from Atomically Thin Transition-Metal Dichalcogenide Alloys, *ACS Nano.* 7 (2013) 4610–4616.
- [41] G. Wang, C. Robert, A. Suslu, B. Chen, S. Yang, S. Alamdari, et al., Spin-orbit engineering in transition metal dichalcogenide alloy monolayers, *ArXiv E-Prints.* 6 (2015) 1–9.
- [42] J. V Marzik, R. Kershaw, K. Dwight, A. Wold, Photoelectronic properties of ReS₂ and ReSe₂ single crystals, *J. Solid State Chem.* 51 (1984) 170–175.
- [43] C. Ho, Y. Huang, P. Liao, K. Tiong, Crystal structure and band-edge transitions of ReS_{2-x}Se_x layered compounds, *J. Phys. Chem. Solids.* 60 (1999) 1797–1804.
- [44] F. Liu, S. Zheng, X. He, A. Chaturvedi, J. He, W.L. Chow, et al., Highly Sensitive Detection of Polarized Light Using Anisotropic 2D ReS₂, *Adv. Funct. Mater.* 26 (2016) 1169–1177.

- [45] F. Liu, S. Zheng, A. Chaturvedi, V. Zolyomi, J. Zhou, Q. Fu, et al., Optoelectronic properties of atomically thin ReSSe with weak interlayer coupling, *Nanoscale*. 8 (2016) 5826–5834.
- [46] A. Berkdemir, H.R. Gutiérrez, A.R. Botello-Méndez, N. Perea-López, A.L. Elías, C.-I. Chia, et al., Identification of individual and few layers of WS₂ using Raman Spectroscopy, *Sci. Rep.* 3 (2013) 1755.
- [47] H. Li, Q. Zhang, C.C.R. Yap, B.K. Tay, T.H.T. Edwin, A. Olivier, et al., From bulk to monolayer MoS₂: Evolution of Raman scattering, *Adv. Funct. Mater.* 22 (2012) 1385–1390.
- [48] T. Fujita, Y. Ito, Y. Tan, H. Yamaguchi, D. Hojo, A. Hirata, et al., Chemically exfoliated ReS₂ nanosheets, *Nanoscale*. 6 (2014) 12458–12462.
- [49] C.H.H. and Y.S.H. and K.K.T. and P.C. Liao, In-plane anisotropy of the optical and electrical properties of layered ReS₂ crystals, *J. Phys. Condens. Matter*. 11 (1999) 5367.
- [50] G. Dresselhaus, Optical Absorption Band Edge in Anisotropic Crystals, *Phys. Rev.* 105 (1957) 135–138.
- [51] S. Zhang, J. Yang, R. Xu, F. Wang, W. Li, M. Ghufraan, et al., Extraordinary Photoluminescence and Strong Temperature/Angle-Dependent Raman Responses in Few-Layer Phosphorene, *ACS Nano*. 8 (2014) 9590–9596.
- [52] G. Weiser, Modulation spectroscopy on anisotropic systems, *Surf. Sci.* 37 (1973) 175–197.
- [53] C.H. Ho, P.C. Liao, Y.S. Huang, K.K. Tiong, Temperature dependence of energies and broadening parameters of the band-edge excitons of ReS₂ and ReSe₂, *Phys. Rev. B*. 55 (1997) 15608–15613.
- [54] B. Radisavljevic, a Radenovic, J. Brivio, V. Giacometti, a Kis, Single-layer MoS₂ transistors., *Nat. Nanotechnol.* 6 (2011) 147–50.
- [55] W. Liu, J. Kang, D. Sarkar, Y. Khatami, D. Jena, K. Banerjee, Role of Metal Contacts in Designing High-Performance Monolayer n-Type WSe₂ Field Effect Transistors, *Nano Lett.* 13 (2013) 1983–1990.
- [56] B. Chamlagain, Q. Li, N.J. Ghimire, H.-J. Chuang, M.M. Perera, H. Tu, et al., Mobility Improvement and Temperature Dependence in MoSe₂ Field-Effect Transistors on Parylene-C Substrate, *ACS Nano*. 8 (2014) 5079–5088.
- [57] B. Radisavljevic, A. Kis, Mobility engineering and a metal–insulator transition in monolayer MoS₂, *Nat Mater.* 12 (2013) 815–820.

- [58] B.W.H. Baugher, H.O.H. Churchill, Y. Yang, P. Jarillo-Herrero, Intrinsic Electronic Transport Properties of High-Quality Monolayer and Bilayer MoS₂, *Nano Lett.* 13 (2013) 4212–4216.
- [59] K. Kaasbjerg, K.S. Thygesen, K.W. Jacobsen, Phonon-limited mobility in n-type single-layer MoS₂ from first principles, *Phys. Rev. B.* 85 (2012) 115317.
- [60] H. Kind, H. Yan, B. Messer, M. Law, P. Yang, Nanowire Ultraviolet Photodetectors and Optical Switches, *Adv. Mater.* 14 (2002) 158–160.
- [61] O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, A. Kis, Ultrasensitive photodetectors based on monolayer MoS₂, *Nat Nano.* 8 (2013) 497–501.
- [62] S. Ura, H. Sunagawa, T. Suhara, H. Nishihara, Focusing grating couplers for polarization detection, *J. Light. Technol.* 6 (1988) 1028–1033.
- [63] P. Hu, L. Wang, M. Yoon, J. Zhang, W. Feng, X. Wang, et al., Highly Responsive Ultrathin GaS Nanosheet Photodetectors on Rigid and Flexible Substrates, *Nano Lett.* 13 (2013) 1649–1654.
- [64] M. Buscema, D.J. Groenendijk, S.I. Blanter, G.A. Steele, H.S.J. van der Zant, A. Castellanos-Gomez, Fast and Broadband Photoresponse of Few-Layer Black Phosphorus Field-Effect Transistors, *Nano Lett.* 14 (2014) 3347–3352.
- [65] D. Akinwande, N. Petrone, J. Hone, Two-dimensional flexible nanoelectronics, *Nat Commun.* 5 (2014) 5678.
- [66] G.H. Han, N.J. Kybert, C.H. Naylor, B.S. Lee, J. Ping, J.H. Park, et al., Seeded growth of highly crystalline molybdenum disulphide monolayers at controlled locations, *Nat. Commun.* 6 (2015) 6128.
- [67] Z. Liu, L. Ma, G. Shi, W. Zhou, Y. Gong, S. Lei, et al., In-plane heterostructures of graphene and hexagonal boron nitride with controlled domain sizes, *Nat Nano.* 8 (2013) 119–124.
- [68] K. Kang, S. Xie, L. Huang, Y. Han, P.Y. Huang, K.F. Mak, et al., High-mobility three-atom-thick semiconducting films with wafer-scale homogeneity, *Nature.* 520 (2015) 656–660.
- [69] H.-M. Li, D. Lee, D. Qu, X. Liu, J. Ryu, A. Seabaugh, et al., Ultimate thin vertical p–n junction composed of two-dimensional layered molybdenum disulfide, *Nat Commun.* 6 (2015) 6564.

Chapter 7

Tin Disulfide – Promising “Cousin” of LTMD Family

Tin Disulfide (SnS_2) assumes a unique position in transition metal dichalcogenides (TMDC) family on account of tin(Sn) being a non-transition metal but the compound tin disulfide, structurally and physically similar to other real TMDC members (MoS_2 , WSe_2 , etc.). Therefore, it has been often grouped within the TMDC family. Its earth-abundant nature makes it attractive to explore for variety of applications. Here an attempt is made to propose the high-crystalline SnS_2 as an anode material for Li-ion battery and methods that could be useful in optimizing its performance are discussed.

7.1 Introduction

Transition metal dichalcogenides (TMDC) has attracted renewed interest with the discovery of graphene [1] in 2004 and accompanied new avenues opened up in low-dimensional systems [2–5]. Transition metal dichalcogenides (*i.e.*, MX_2 , where $\text{M} = \text{Mo}, \text{W}$ and $\text{X} = \text{S}, \text{Se}, \text{Te}$) belongs to the family of layered materials, whose crystal structures are built up of covalently bonded X-M-X single-layers that are loosely held by weak van der Waals (vdW) forces [6]. Each single layer consists of two X atom layers and a layer of metal atoms sandwiched between two layers of chalcogens. Previous studies revealed that MX_2 has a band gap of $1.1 \sim 2.0$ eV [7–9], for example in MoS_2 , there is a transition from an indirect band gap (1.2 eV) in the bulk to a direct band gap (1.8 eV) in single-layer. This has attracted interest in a variety of fields, including energy storage, catalysis, solar cell, sensing devices, and electronic devices. Similarly, other members of this class of material could be utilized for numerous applications as they are earth-abundant and sometimes exist in the form of minerals (molybdenite, MoS_2) are worth to investigate. One such material is tin disulfide (SnS_2), which exhibit CdI_2 structure (octahedral co-ordination) and assumes various polytypes (different stacking arrangement of individual layers) [10]. Although SnS_2 is not a TMDC but due to its similar structure and ultra-flat nature, it has been often clubbed while discussing the TMDC family. Previously, SnS_2 has been investigated as a promising material for photovoltaic applications [11]. In addition, intercalation of organic molecules into SnS_2 single crystal has been demonstrated as a prototype for inorganic-organic hybrid for efficient photovoltaic applications [12]. The layered nature of such compounds allow them to be utilized as storage materials also.

7.2 Tin Disulfide Synthesis

Single crystals of SnS_2 were grown based on the principle of closed growth physical vapor transport (CG-PVT). The process follows the sequence of vaporization-transport-solidification. In this method a closed tube (ampoule) with the polycrystalline sample is placed inside a two-zone tube furnace in an arrangement where the polycrystalline compound is at a higher temperature (T_1) and the target or other end at relatively low temperature ($T-\Delta T$). This creates the thermal gradient that allows transport of the evaporated species to the colder end (T_2) and subsequent solidification.

Tin shots (3 mm (0.1 in), 99.999%, metal basis) and sulfur pieces (Puratronic®, 99.9995%, metal basis) were purchased from Alfa-Aesar as starting materials. The materials in stoichiometric proportion were sealed in quartz ampoules with an inner pressure of 10^{-5} Torr. The ampoules were placed in two-zone furnace by initially keeping both the zones at 680 °C for around 48 hours for complete reaction between the starting materials to give polycrystalline compound. The ampoules were then subjected to a two-zone temperature profile of 680 to 630 °C for a period of 14 days as shown in figure 7.1. A typical ampoule used for the growth was having dimensions in the order of a diameter of 13 mm and length of 150 mm. Owing to the exothermic nature of the synthesis reaction and the constituents involved (*viz.* sulfur and tin), the temperatures were raised in a phased and gradual manner to avoid any explosion inside the furnace. On the completion of the process, crystals were carefully transferred from the ampoule for their subsequent characterization. LOBA 2-Zone furnace from REETZ GmbH, was used to grow single crystal of tin disulfide. The average rate of increase of temperature was approximately 5 K min.⁻¹.

Figure 7.1: A typical setup and temperature profile for vapor transport growth of single crystals in a two-zone furnace. One zone that contains the starting materials (source zone) is at a comparatively higher temperature (ΔT) to other zone (growth zone) where single crystals are formed

7.3 Materials Characterization

Tin disulfide (SnS_2) single crystalline platelets of various sizes were obtained as shown in figure 7.2. SEM/EDX measurements were performed to investigate the preservation of the stoichiometric arrangement between the reacting elements in the resulting

compound. The data as shown in figure 7.3 reveals near-perfect stoichiometric ratio indicating purity of the product. The P-XRD pattern reveals preferred orientation ($00l$ peaks) on account of the ultra-flat 2D nature of SnS_2 platelets that was further amplified with the help of background-less sample holder that allows the platelets and the holder to be in the same plane (zero error correction). The typical P-XRD pattern is shown in figure 7.4 where all the peaks belonged to the SnS_2 (P-3 m1).

Figure 7.2: Optical images of tin disulfide (SnS_2) single crystalline flakes

Figure 7.3: EDX of the as-grown SnS_2 single crystals

Figure 7.4: P-XRD pattern of SnS_2 single crystal (P-3 m1, $a=3.6215(8)$ Å and $c=5.856(3)$ Å) on a background-less sample holder

SC-XRD was also performed on obtained crystals to ascertain its polytypes, since SnS_2 possesses many different polytypes [10]. The cif file generated by collecting all the diffraction data suggested the formation of P-3 m1 polytypes with the unit cell with values of $a = 3.6215(8)$ Å and $c = 5.856(3)$ Å (Appendix A, table A.1). A simulated structure of the above cif file was generated with the help of Diamond 3.2 program and is shown in figure 7.5. To further detail out the structure at atomic level, select area electron diffraction (SAED) data was collected through transmission electron microscopy (TEM) and the pattern was indexed accordingly to reveal the trigonal arrangement of the atoms in SnS_2 single crystal (figure 7.6).

Figure 7.5: Simulated structure of tin disulfide (SnS_2) obtained from CIF file (Single Crystal XRD)

Raman spectroscopy was performed on the as synthesized crystals in order to confirm the crystal structure of SnS_2 and eliminate the presence of any other binary phases like SnS , Sn_2S_3 . Figure 7.7 shows the Raman spectrum of the as synthesized crystals and only one intense peak was observed at 313 cm^{-1} which corresponds to the A_{1g} vibration mode of SnS_2 [13].

Figure 7.6: Indexed Selected Area Electron Diffraction Pattern (SAED) of SnS_2 crystals ultra-sonicated in ethanol solvent

Figure 7.7: Raman spectrum of SnS_2 single crystal

7.4 Thickness Dependent Raman Spectroscopy of Cleaved SnS₂ Crystals

Raman spectroscopic technique has emerged as one of the most efficient tool to do preliminary examination of any layered two dimensional materials to identify any change in vibrational modes on account of increase or decrease in the sample thickness (number of layers). Similar operation has been employed for SnS₂ to observe its Raman spectra. Crystal flakes obtained from the method described in section 7.2 were mechanically exfoliated on an SiO₂ coated Si substrate with scotch-tape technique [2]. The exfoliated crystals with different thickness were taken and identified under optical microscope (figure 7.10). Raman spectra were collected on the samples. The interesting observation from the Raman spectra is the layer-independent nature of the prominent peak (A_{1g}) for different number of layers (figure 7.11), although the intensity is higher for higher thickness sample. The spectra were consistent and reproducible for the samples having similar thickness thus providing a method to identify the thickness of SnS₂ flakes accurately.

Figure 7.10: Cleaved crystal of SnS₂ on SiO₂/Si substrate with different thickness shown through color contrast (yellow/pink represents thicker portion while blue/green represents thinner portion)

Figure 7.11: Thickness dependent Raman spectra of cleaved SnS_2 crystals. Prominent A_{1g} mode at 313 cm^{-1} is insensitive to thickness although intensity decreases on decreasing thickness. N3 is the thickest region of the sample and N1 is the thinnest region of the sample (as observed under optical microscope)

The layer-independent nature could be attributed to the orbital composition that is insensitive to both interlayer coupling and confinement (if any). Also the fact that there is no signature transition from indirect to direct band gap on going down to monolayer confirms its vibrational and electronic homogeneity through the thicknesses [29].

7.5 SnS_2 as Negative Electrode in Lithium Ion Battery (LIB)

An attempt has been made to employ SnS_2 single crystal as negative electrode for Li-ion battery (LIB) applications for first time owing to the phase purity. Since, Sn-based materials are promising for LIB applications owing to its high theoretical capacity ($\sim 645 \text{ mAh g}^{-1}$) compared with conventional graphite ($\sim 372 \text{ mAh g}^{-1}$), comparable working potential (~ 0.1 and $\sim 0.25 \text{ V vs. Li}$ for graphite and Li_xSn , respectively) and high current performance [14–18]. Unfortunately, the huge volume variation upon alloying/de-alloying reaction is the prime issue for such Sn-based anodes [19]. We believe the presence of sulfide in SnS_2 during metallic reaction (Sn^0) results the formation of amorphous Li_2S which is expected to uphold volume variation for certain

extends during charge-discharge process [20]. An effort has been made to thoroughly investigate the suitability of SnS_2 as an anode for LIB applications. Therefore, in addition to the routine work with metallic Li in half-cell assembly, full-cell is also fabricated with spinel LiMn_2O_4 cathode for first time. An electrochemical pre-lithiation is adopted for SnS_2 to overcome the irreversible capacity loss (ICL) observed during the first cycle. Emphasis is also given on the purity of the material (uniform phase) and as a result high-quality, high-purity single crystalline SnS_2 grown through physical vapor transport (PVT) were used [21].

7.5.1 Electrode Fabrication and Cell Assembly

For the formulation of composite electrode, the single crystals were crushed in to fine powders and subsequently blended using 10% of Super P and 10% of teflonized acetylene black (TAB-2) using ethanol. The slurry has been placed over a 200 mm^2 stainless steel mesh (Goodfellow, UK) and dried in a vacuum oven for overnight before conducting cell assembly. Half-cells were fabricated (Li/SnS_2 or $\text{Li}/\text{LiMn}_2\text{O}_4$) with metallic Li and composite electrode in the coin-cell (CR 2016) assembly was separated by microporous separator (Whatman, Cat. No. 1825 047, UK). 1 M LiPF_6 in ethylene carbonate (EC)/di-methyl carbonate (DMC) mixture (Selectipure LP30, Merck KGaA, Germany) was used as electrolyte. Mass loading has been adjusted for cathode with respect to the anode loading by keeping the aforementioned conductive additive and binder ratio. Before fabricating the full-cell with LiMn_2O_4 cathode, the SnS_2 was pre-lithiated by cycling between 5–800 mV vs. Li in Swagelok fittings for two cycles. After the completion cycling and it was dismantled and paired with LiMn_2O_4 cathode in the presence of new separator and fresh electrolyte in CR 2016 coin-cell assembly with balanced mass loadings. Galvanostatic cycling profiles were recorded for both half-cells and full-cell assemblies using Arbin battery (2000) tester in ambient temperature conditions.

7.5.2 Performance of Half and Full-Cell Assembly

Li-storage properties of the SnS_2 single crystals (crushed) were investigated in half-cell assembly between 5 to 800 mV vs. Li at current density of 65 mA g^{-1} . Corresponding charge-discharge profiles are given in figure 7.8. Apparent to note the multiple events

in the first discharge process, for example at ~ 1.95 V *vs.* Li a prominent plateau observed which is associated with the Li-intercalation in to SnS_2 . Since, a mol of SnS_2 is able to accommodate 2 mole of Li (Li_2SnS_2) without much deviation in the crystal structure [22,23]. The Li-insertion process occurred in two stages at ~ 1.95 and ~ 1.65 V *vs.* Li which is clearly evidenced from the galvanostatic discharge process and corroborated with differential capacity profile (figure 7.8(a) Inset) [24].

Figure 7.8: (a) Typical galvanostatic charge-discharge curves of Li/SnS₂ cell between 5-800 mV vs. Li at current density of 65 mA g⁻¹. Inset: Differential capacity profile, (b) Plot of capacity vs. cycle number. Filled and open symbols correspond to the charge and discharge, respectively

In the present case, 1.83 mole of Li is intercalated in to the crystal structure of SnS₂ (Li_{1.83}SnS₂). The prominent plateau at ~1.3 V vs. Li is associated with the destruction of Li_{1.83}SnS₂ phase and subsequent formation of Sn⁰ and amorphous Li₂S. A kink like region at ~0.7 V vs. Li corresponds to the decomposition of the electrolyte solution. Similarly, the monotonous curve at ~0.25 V vs. Li is attributed to the Li_xSn reversible alloy formation. Except this alloying reaction, rests of the reaction are irreversible in the subsequent cycles according to the following reaction mechanism,

Upon cathodic scan, the peak potential at ~0.45 V vs. Li is ascribed to the de-alloying reaction which is clearly seen from the differential capacity profile (figure 7.8(a) inset).

The upper cut-off potential is restricted to 800 mV *vs.* Li for preventing the further oxidation of Sn^0 in to $\text{Sn}^{2+}/\text{Sn}^{4+}$ and allows for alloying/de-alloying reaction only [25,26]. The half-cell delivered the capacity of ~ 1705 and ~ 542 mAh g^{-1} for first discharge and charge, respectively. The irreversible capacity of ~ 1163 mAh g^{-1} is noted and it is common for the case of Sn based materials. In addition, the decomposition of electrolyte solution certainly consumes more amounts of Li in irreversible manner for the formation of solid electrolyte interface (SEI) cannot be ruled out for excess capacity. Though, the SnS_2 is prepared *via* crystal growth with phase pure nature, but only the reversible capacity of ~ 542 mAh g^{-1} noted instead ~ 645 mAh g^{-1} (theoretical capacity). Upon cycling capacity fading is noted, for example the cell retained $\sim 71\%$ of initial reversible capacity after 30 cycles. There are few reasons like (i) unstable SEI formation, (ii) pulverization of the electrode because of the huge volume variation upon alloying/de-alloying and (iii) aggregation of Sn^0 nanoparticulates during charge process are believed for the fade in capacity upon cycling. Carbon coating or preparing composite with inactive matrix elements are the best ways to improve the electrochemical profiles of Sn based materials. Although single crystalline SnS_2 is experiencing capacity fade in half-cell configuration, but compatibility with commercial cathodes is worth investigating and it is crucial for constructing practical Li-ion cells.

In this line, we made an attempt to construct the full-cell assembly with well-known spinel LiMn_2O_4 cathode. As noted above, a huge ICL is noted in the first discharge and overcome the said issue is necessary before fabricating the full-cell. Hence, an electrochemical pre-lithiation was conducted for SnS_2 in half-cell configuration in Swagelok fittings for two galvanostatic cycles. This electrochemical pre-lithiation certainly beneficial in two ways, first to ensure the reversible capacity obtained from the half-cell assembly and overcome the ICL observed in the first discharge. After the two cycles, the cycled SnS_2 electrode were carefully taken from the Swagelok fittings and placed with LiMn_2O_4 cathode under the optimized mass loadings (anode to cathode ratio is fixed at 1:4.74, 4 mg: 18.9 mg) in coin-cell assembly by filling fresh electrolyte as well. The anode to cathode mass ratio has been calculated based on the second discharge capacity of SnS_2 (~ 554 mAh g^{-1}) in half-cell assembly at Swagelok fittings and first discharge capacity of cathode, LiMn_2O_4 (~ 117 mAh g^{-1}). Similar kind of high cathode mass loading has been already described by Tarascon *et al.*, [27,28] for

conversion type CoO and Co_3O_4 anodes when paired with LiCoO_2 and LiMn_2O_4 . The $\text{LiMn}_2\text{O}_4/\text{SnS}_2$ cell delivered the capacity of ~ 509 and $\sim 403 \text{ mAh g}^{-1}$ at current density of 65 mA g^{-1} (based on anode loading) for first charge and discharge, respectively (figure 7.9(a)) with working potential of $\sim 3.64 \text{ V}$. After electrochemical treatment, still the full-cell is experiencing the ICL of $\sim 106 \text{ mAh g}^{-1}$ which is mainly because of the decomposition of the fresh electrolyte filled during the fabrication of the full-cell. Also, the small ICL observed from the cathode, LiMn_2O_4 cannot be ruled out.

Figure 7.9: (a) Typical galvanostatic charge-discharge curves of (I) $\text{Li}/\text{LiMn}_2\text{O}_4$, (II) Li/SnS_2 , (III) $\text{LiMn}_2\text{O}_4/\text{SnS}_2$ cells recorded in the second cycle at current density of 65 mA g^{-1} . The full-cell capacity is calculated based on the anode mass loading. (b) Cycling profiles of $\text{LiMn}_2\text{O}_4/\text{SnS}_2$ cell with coulombic efficiency.

The charge-discharge curves are exact replica of the electrochemical profiles of SnS_2 in half-cell assembly. Except in the first cycle ($\sim 79\%$), the coulombic efficiency is substantially improved in the subsequent cycles ($>90\%$) which is clearly evident from figure 7.9(b). Capacity fading is also noted for the full-cell, $\text{LiMn}_2\text{O}_4/\text{SnS}_2$ and retains $\sim 65\%$ of initial reversible capacity after 60 cycles. The anode, SnS_2 is responsible for the fade in capacity upon cycling, since LiMn_2O_4 is very stable in the half-cell assembly (Appendix B, figure B.1). This preliminary study clearly revealed the possibility of using SnS_2 single crystals as potential anode in LIB applications. Further studies are in progress to improve the electrochemical performance of SnS_2 single crystals.

7.6 Outcomes and Conclusions

We successfully synthesized high quality single crystals of tin disulfide (SnS_2) through physical vapor transport (PVT). We have done thorough investigation through different materials characterization techniques to ascertain phase purity and morphology of the grown material. As a possibility to explore the storage performance of SnS_2 we prepared both half and full cell assembly that are comparatively higher than the once reported for graphene. The presence of high ICL value is one of the drawbacks of SnS_2 as anode material but initial performance and the promise of high theoretical capacity coupled with its earth-abundant nature are attractive enough to optimize its performance in future. We also explored the Raman spectra of SnS_2 samples having different thicknesses and its insensitive nature of it.

References

- [1] K.S. Novoselov, A.K. Geim, S. V Morozov, D. Jiang, Y. Zhang, S. V Dubonos, et al., Electric Field Effect in Atomically Thin Carbon Films, *Sci.* . 306 (2004) 666–669.
- [2] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V. V Khotkevich, S. V Morozov, et al., Two-dimensional atomic crystals., *Proc. Natl. Acad. Sci. U. S. A.* 102 (2005) 10451–3.
- [3] Y. Zhang, Y.-W. Tan, H.L. Stormer, P. Kim, Experimental observation of the quantum Hall effect and Berry’s phase in graphene, *Nature*. 438 (2005) 201–204.
- [4] K.S. Novoselov, A.K. Geim, S. V Morozov, D. Jiang, M.I. Katsnelson, I. V Grigorieva, et al., Two-dimensional gas of massless Dirac fermions in graphene, *Nature*. 438 (2005) 197–200.
- [5] C. Lee, X. Wei, J.W. Kysar, J. Hone, Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene, *Sci.* 321 (2008) 385–388.
- [6] J.A. Wilson, A.D. Yoffe, The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties, *Adv. Phys.* 18 (1969) 193–335.
- [7] K.K. Kam, B.A. Parkinson, Detailed photocurrent spectroscopy of the semiconducting group VIB transition metal dichalcogenides, *J. Phys. Chem.* 86 (1982) 463–467.
- [8] K.F. Mak, C. Lee, J. Hone, J. Shan, T.F. Heinz, Atomically Thin MoS_2 : A New Direct-Gap Semiconductor, *Phys. Rev. Lett.* 105 (2010) 136805.

- [9] B. Radisavljevic, A Radenovic, J. Brivio, V. Giacometti, A Kis, Single-layer MoS₂ transistors., *Nat. Nanotechnol.* 6 (2011) 147–50.
- [10] C.R. Whitehouse, A.A. Balchin, Polytypism in Tin Disulphide, *J. Cryst. Growth.* 47 (1979) 203–212.
- [11] B.A. Parkinson, Dye sensitization of van der Waals surfaces of tin disulfide photoanodes, *Langmuir.* 4 (1988) 967–976.
- [12] M.L. Toh, K.J. Tan, F.X. Wei, K.K. Zhang, H. Jiang, C. Kloc, Intercalation of organic molecules into SnS₂ single crystals, *J. Solid State Chem.* 198 (2013) 224–230.
- [13] D.W. and S.J. and J.Y. Harbec, Raman active modes of the layer crystal SnS_{2-x}Se_x, *J. Phys. C Solid State Phys.* 13 (1980) L125.
- [14] I.A. Courtney, J.R. Dahn, Electrochemical and In Situ X-Ray Diffraction Studies of the Reaction of Lithium with Tin Oxide Composites, *J. Electrochem. Soc.* 144 (1997) 2045–2052.
- [15] I.A. Courtney, J.R. Dahn, Key Factors Controlling the Reversibility of the Reaction of Lithium with SnO₂ and Sn₂BPO₆ Glass, *J. Electrochem. Soc.* 144 (1997) 2943–2948.
- [16] A.D.W. Todd, P.P. Ferguson, M.D. Fleischauer, J.R. Dahn, Tin-based materials as negative electrodes for Li-ion batteries: Combinatorial approaches and mechanical methods, *Int. J. Energy Res.* 34 (2010) 535–555.
- [17] R.A. Huggins, Lithium alloy negative electrodes, *J. Power Sources.* 81–82 (1999) 13–19.
- [18] V. Aravindan, Y.-S. Lee, S. Madhavi, Research Progress on Negative Electrodes for Practical Li-Ion Batteries: Beyond Carbonaceous Anodes, *Adv. Energy Mater.* 5 (2015) 1–43.
- [19] C.-M. Park, J.-H. Kim, H. Kim, H.-J. Sohn, Li-alloy based anode materials for Li secondary batteries, *Chem. Soc. Rev.* 39 (2010) 3115–3141.
- [20] N.-S. Choi, Y. Yao, Y. Cui, J. Cho, One dimensional Si/Sn - based nanowires and nanotubes for lithium-ion energy storage materials, *J. Mater. Chem.* 21 (2011) 9825–9840.
- [21] S.K. Arora, D.H. Patel, M.K. Agarwal, Vapour growth of SnS₂ single crystals, *J. Cryst. Growth.* 131 (1993) 268–270.
- [22] J. Morales, C. Perez-Vicente, J.L. Tirado, Chemical and electrochemical lithium

- intercalation and staging in 2H-SnS₂, *Solid State Ionics*. 51 (1992) 133–138.
- [23] I. Lefebvre-Devos, J. Olivier-Fourcade, J.C. Jumas, P. Lavela, Lithium insertion mechanism in SnS₂, *Phys. Rev. B*. 61 (2000) 3110–3116.
- [24] T. Momma, N. Shiraishi, A. Yoshizawa, T. Osaka, A. Gedanken, J. Zhu, et al., SnS₂ anode for rechargeable lithium battery, *J. Power Sources*. 97–98 (2001) 198–200.
- [25] V. Aravindan, J. Sundaramurthy, E.N. Kumar, P.S. Kumar, W.C. Ling, R. von Hagen, et al., Does carbon coating really improves the electrochemical performance of electrospun SnO₂ anodes?, *Electrochim. Acta*. 121 (2014) 109–115.
- [26] V. Aravindan, K.B. Jinesh, R.R. Prabhakar, V.S. Kale, S. Madhavi, Atomic layer deposited (ALD) SnO₂ anodes with exceptional cycleability for Li-ion batteries, *Nano Energy*. 2 (2013) 720–725.
- [27] F. Badway, I. Plitz, S. Grugeon, S. Laruelle, M. Dollé, A.S. Gozdz, et al., Metal Oxides as Negative Electrode Materials in Li-Ion Cells, *Electrochem. Solid-State Lett.* 5 (2002) A115–A118.
- [28] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.-M. Tarascon, Searching for new anode materials for the Li-ion technology: time to deviate from the usual path, *J. Power Sources*. 97–98 (2001) 235–239.
- [29] Y. Huang, E. Sutter, J.T. Sadowski, M. Cotlet, O.L. a Monti, D. a Racke, et al., Tin Disulfide - An Emerging Layered Metal Dichalcogenide Semiconductor: Materials Properties and Device Characteristics., *ACS Nano*. (2014).

Chapter 8

Conclusion and Recommendations

This chapter summarizes the work carried out as part of this thesis. The approach followed for the same has been briefly described. Novel outcomes of the work were discussed with respect to the contemporary research in the field of two-dimensional materials. It also indicates the importance of work from materials science perspective of synthesis-characterization-property-application route. In the end possibilities of the future follow-up work from this thesis has been listed.

8.1 Conclusions

The focal point of this work is synthesizing large high-quality single crystals of layered transition material dichalcogenides (LTMDs), obtaining few or monolayer morphologies from them and their optoelectronic characterization. Another thrust of the work is to develop methods to attain thin LTMD crystals having “special” properties that would be rapid, reproducible and of comparable quality to the ones synthesized with existing methods.

In line with above, using vapor transport technique (both PVT or CVT), large high quality bulk single crystals of variety of LTMD compounds of MX_2 formula are synthesized. They are characterized for phase purity through materials characterization techniques (P-XRD, SEM-EDX, TEM, etc.). The crystals synthesized in this work proved to be the starting point of every device fabrication and characterization carried out later. Even the few-layer samples micro-mechanically exfoliated from bulk single crystal have near-ideal structures and properties. Although, the technological aspect of synthesis has advanced leaps and bounds in terms of getting large area growth of monolayer samples of graphene and LTMDs on desired substrates and getting better day by day. But the ever-expanding canvas of 2D materials need to inquire about new binary, ternary or in some case quaternary layered materials to improve our understanding of layered 2D materials further and to add to exhibit additional properties that may add to the versatility of such materials. The starting point of this has always been pure single crystals that could be cleaved down to thin samples for investigations of their into properties. Once the material is established as a promising candidate, only then the necessary motivation for the development of technology comes in to picture that leads to methods such as CVD, epitaxial growth, hetero-structures, etc. Also for the fundamental electronics and optoelectronic research, pure exfoliated samples are a pre-requisite that are often obtained through scotch-tape exfoliation of bulk crystals. Liquid phase exfoliation and other similar preparation methods always leads to some form of degradation of properties on account of surface contamination.

In addition to the synthesis, exploring new unique members within the 2D LTMD family is the most interesting aspect of current low dimensional 2D materials. On the similar lines, this work tried to explore rhenium-based chalcogenide materials (ReS_2 , ReSSe , etc.). and present them as a viable alternative for existing materials for detection

of polarized light. This work emphasized the fact that the intrinsic intra-layer anisotropy or the two-dimensional anisotropy present in the rhenium compounds is responsible for first, structural anisotropy that leads to optical and electronic anisotropy and in turn linear dichroism. The uniqueness of rhenium disulfide lies in the fact that other prominent members of the family (MoS_2 , WSe_2 , etc.) are intrinsically isotropic within the layer or they have a lack of 2D anisotropy. Also, the direct band gap nature of rhenium-based chalcogenide compounds irrespective of sample thickness herald well for optoelectronic and photovoltaic applications. Thus, one can safely label ReS_2 – like compounds are true-anisotropic materials. Based on earlier reports that suggest that $\text{ReS}_x\text{Se}_{2-x}$ alloys are isostructural and single phase with both ReS_2 and ReSe_2 . This allows us to investigate composition dependent band gap engineering in ReSSe alloy. These also found to be direct band gap and anisotropic. This presents an interesting two-dimensional alloy series to work with for photovoltaic and optoelectronic applications. The novel study carried out on ReS_2 and ReSSe in this work would open doors for many follow-up works in future.

On identifying the importance of low-dimension few layer morphology of layered materials and in particular LTMDs, an innovative method to complement other existing techniques have been developed in-house. The method uses re-engineered domestic microwave oven to induce plasma in a closed quartz jacket that induces a non-metal plasma that reacts with metal powder. The crystals synthesized with this method have been characterized by several techniques and found to be highly crystalline, thin-layered and phase-pure. This novel method provides an alternative approach for closed system synthesis of LTMDs. It is rapid and reproducible and could be utilized for applications such as catalyst for photocatalytic hydrogen evolution reaction, etc.

8.2 Future Recommendations

With respect to the current work following future recommendations are made in various domains that could be followed to further broaden the 2D horizon in general.

- Technology: In the materials synthesis aspect, new methods as well as new class of 2D materials could be studied, prominent being MPX_3 ($\text{M} = \text{Fe, Mn, Ni, Cd, Zn}$ and $\text{X} = \text{S, Se}$) and $\text{M}_1\text{M}_2\text{X}_z$ (M_1, M_2 are metals and X is a chalcogen atom) class of materials. In this MPX_3 class of materials have been reported recently and found to

be weakly-stacked and having a wide band gap range of 1.3 to 3.5 eV [1]. The same materials have only been grown through CVT method, even in this work. The new microwave plasma method could be employed to synthesize such ternary layered compounds for their easy availability.

- **Property Modulation:** In spite of the fact that the intrinsic property of 2D LTMDs and other layered materials is quite useful and interesting, a better control over them for different parameters in electronics, optoelectronics and related applications would take them near to the real devices. For that to happen, researchers need to dwell over tuning of their physical properties (band gap, defects, etc.) with respect to external stimuli (gate bias, temperature control, etc.). Further an old but effective technique of intercalation in which introduction of foreign materials between the layers alters its physical properties and may represent an alternative approach to prepare van der Waals heterostructures [2].
- **Applications:** Interesting properties of compounds such as that of LTMDs always encourages academia to try them in applications. Its layered nature and ability to intercalate lithium between the layers put them as a candidate for electrode in lithium ion batteries. They could also be utilized as a catalyst in hydrogen evolution reaction where the plane edges and later with some surface treatment even the plane found to be active sites for catalysis to occur [3]. Devices such as sensors and photodetectors could be prepared from few or monolayer samples for integrated electronics.
- **Terahertz Time-Domain Spectroscopy (THz-TDS):** Recently THz-TDS emerged as an impressive technique to explore the electronic and optical properties of low-dimensional materials (2D materials and heterostructures). One of the main factors that could make it useful for atomically thin layered materials because of a sub-pico second scale time range, an energy content range of 0.41 to 41.36 meV and a chemical temperature of 47.6 K. Majority of semiconducting charge transfer processes occur within these regime and THz-TDS as a technique can provide direct evidence of the same. Additionally, this technique does not require any external stimuli for measurement as in the case of traditional techniques such as

photoluminescence, etc. Most of the time transport properties measurement of semiconducting materials are limited by the employed technique (field-effect-transistor, hall measurement, etc.) as there is always an additional interface between the sample and the contact. On the contrary, THz-TDS is not dependent on the efficiency of any contact at all. Thus, THz-TDS could prove to be a powerful tool as non-invasive, non-contact and sensitive method to extract intrinsic material properties of pristine as well as heterostructures 2D materials that would provide an insight in optimizing various electronic and optoelectronic devices based on them [4]. Several materials, old and new synthesized during this thesis (ReS_2 , SnS_2 , etc.) are under investigation through this technique. A schematic of the measurement setup is shown below (figure 8.1).

Figure 8.1: A schematic of the measurement setup used for THz-TDS of two-dimensional layered materials

References

- [1] K. Du, X. Wang, Y. Liu, P. Hu, M.I.B. Utama, C.K. Gan, et al., Weak Van der Waal Stacking, Wide-Range Band Gap and Raman Study on Ultrathin Layers of Metal Phosphorus Trichalcogenides, *ACS Nano*. (2015) 1738-1743.
- [2] A.K. Geim, I. V Grigorieva, Van der Waals heterostructures., *Nature*. 499 (2013) 419–25.
- [3] H. Li, C. Tsai, A.L. Koh, L. Cai, A.W. Contryman, A.H. Fragapane, et al.,

Activating and optimizing MoS₂ basal planes for hydrogen evolution through the formation of strained sulphur vacancies, *Nat Mater.* 15 (2016) 48–53.

- [4] P.U. Jepsen, D.G. Cooke, M. Koch, Terahertz spectroscopy and imaging – Modern techniques and applications, *Laser Photon. Rev.* 5 (2011) 124–166.

APPENDIX A: SnS₂ Single Crystal Data

Table A.1: Tin Disulfide (SnS₂) Single Crystal Data from Single Crystal XRD

Bond precision:	Sn- S = 0.0040 Å		Wavelength=0.71073	
Cell:	a=3.6215(8)		b=3.6215(8)	c=5.856(3)
	alpha=90		beta=90	gamma=120
Temperature:	293 K			
	Calculated	Reported		
Volume	66.51(5)	66.52(4)		
Space group	P -3 m 1	P -3 m 1		
Hall group	-P 3 2"	-P 3;-2"		
Moiety formula	S ₂ Sn	?		
Sum formula	S ₂ Sn	S ₂ Sn ₁		
Mr	182.83	182.80		
Dx,g cm-3	4.565	4.564		
Z	1	1		
Mu (mm-1)	10.786	10.785		
F000	82.0	82.0		
F000'	81.61			
h,k,lmax	5,5,8	5,5,8		
Nref	97	98		
Tmin,Tmax				
Tmin'				
Correction method= Not given				
Data completeness= 1.010		Theta(max)= 29.900		
R(reflections)= 0.0490(98)		wR2(reflections)= wR= 0.0784(98)		
S = 5.880	Npar= 7			

APPENDIX B: Electrochemical performance of LiMn_2O_4 in Half-Cell Assembly

Figure B.1: Electrochemical performance of LiMn_2O_4 in half-cell assembly between 3.5-4.3 V vs. Li at current density of 65 mA g^{-1} , plot of discharge capacity vs. Cycle number. Inset: typical Charge-discharge curves

APPENDIX C: ReS₂ Phototransistor Data

Figure C.1: The wavelength dependence of photocurrent generation for ReS₂ phototransistor. The device is excited by 405 nm, 532 nm, and 633 nm light and recording the photocurrent change with a fixed light power, respectively. The device shows good photoresponse under all the wavelength excitation. Inset shows the wavelength dependence of photocurrent under drain voltage of 2 V. The photocurrent increases gradually with decreasing the wavelength. The bandgap of ReS₂ is about 1.5 eV (820 nm). In principle, the phototransistor should have a photoresponse from 820 nm to short wavelength range.

Figure C.2: Dynamical photoresponse of ReS₂ phototransistor. The photocurrent change by mechanically switching the light illumination on and off. The device shows very stable saturated photocurrent after cycles of light on and off, indicating the stability and reliability of the device. By fitting the time resolved photocurrent change using biexponential function, two time constants can be obtained. These two processes indicate that different mechanisms are attributed to the photocurrent generation. The fast and slow time constants of the photocurrent rise process are 98 ms and 1.9 s, respectively

List of Publications

1. **A. Chaturvedi**, C. Kloc et al. Rapid Synthesis of Transition Metal Dichalcogenides Few-layer Thin Crystals by Microwave-induced-plasma Assisted Method, *J. Cryst. Growth*, 2016, 450, 140-147.
2. **A. Chaturvedi**, C. Kloc et al. Synthesis of SnS₂ single crystals and its Li-storage performance with LiMn₂O₄ cathode, *Appl. Mater. Today*, 2016, 5, 68-72.
3. F. Liu, **A. Chaturvedi** et al. Highly Sensitive Detection of Polarized Light Using Anisotropic 2D ReS₂, *Adv. Funct. Mater.*, 2015, 26(8), 1169.
4. F. Liu, **A. Chaturvedi** et al. Optoelectronic properties of atomically thin ReSSe with weak interlayer coupling, *Nanoscale*, 2016, 8, 5826.
5. K. Du, **A. Chaturvedi** et al. Plasma-enhanced microwave solid-state synthesis of cadmium sulfide: reaction mechanism and optical properties, *Dalton Transactions*, 2015, 44, 13444.
6. C. Tan, **A. Chaturvedi*** et al. Preparation of Single-Layer MoS_{2x}Se_{2(1-x)} and Mo_xW_{1-x}S₂ Nanosheets with High-Concentration Metallic 1T Phase, *Small*, 2016, 12(14), 1866.
7. V. Chaudhary, **A. Chaturvedi** et al. Magnetocaloric properties and critical behavior of high relative cooling power FeNiB nanoparticles, *J. Appl. Phys.* 2014, 116(16), 163918.
8. V. Chaudhary, **A. Chaturvedi** et al. Fe-Ni-Mn nanoparticles for magnetic cooling near room temperature, *IEEE Magnetism Letters* 2014, 5, 1-4.

Conferences

1. **A. Chaturvedi**, M.L. Toh, C. Kloc, Intercalation of organic donors and acceptors into 2D SnS₂, 18th International Symposium on Intercalation Compounds, Strasbourg, France, 2015. (Oral).
2. **A. Chaturvedi**, C. Kloc, Layered Transition Metal Dichalcogenides (Growth, Properties and Applications), 6th MRS-S Conference on Advanced Materials, Singapore 2014. (Poster Presentation).
3. V. Chaudhary, **A. Chaturvedi** et al. Magnetocaloric behavior of Fe-Ni-Mn nanoparticles, Magnetism Symposium 2014-Celebrating 50th Anniversary of IEEE Magnetism Society (MSSC50), Singapore, 2014.

4. V. Chaudhary, **A. Chaturvedi** et al. High relative cooling power iron based magnetocaloric nanoparticles, 6th International Conference on Magnetic Refrigeration at Room Temperature (Thermag VI), Vancouver, Canada, 2014.

* → Equal Contribution