STRUCTURE AND OPTICAL PROPERTIES OF TRANSITION METAL DICHALCOGENIDES (TMDs) – MX₂ (M = Mo, W & X = S, Se) UNDER HIGH PRESSURE AND HIGH TEMPERATURE CONDITIONS

by

Nirup Bandaru

Bachelor of Technology in Electrical Engineering
J.N.T. University, Hyderabad, India
May 2006

Master of Science in Electrical Engineering
University of Nevada, Las Vegas
December 2008

A dissertation submitted in partial fulfillment of the requirements for the

Doctor of Philosophy - Electrical Engineering
Department of Electrical and Computer Engineering
Howard R. Hughes College of Engineering
The Graduate College

University of Nevada, Las Vegas
May 2015
We recommend the dissertation prepared under our supervision by

Nirup Bandaru

entitled

**Structure and Optical Properties of Transition Metal Dichalcogenides (TMDS) – MX2 (M=MO, W & X = S, SE) Under High Pressure and High Temperature Conditions**

is approved in partial fulfillment of the requirements for the degree of

**Doctor of Philosophy in Engineering - Electrical Engineering**

Department of Electrical Engineering

Rama Venkat, Ph.D., Committee Co-Chair
Ravhi S. Kumar, Ph.D., Committee Co-Chair
Clemens Heske, Ph.D., Committee Co-Chair
Venkatesan Muthukumar, Ph.D., Committee Member
Ke-Xun Sun, Ph.D., Committee Member
Thomas Hartmann, Ph.D., Graduate College Representative
Kathryn Hausbeck Korgan, Ph.D., Interim Dean of the Graduate College

May 2015
ABSTRACT

Structure and Optical properties of Transition Metal Dichalcogenides (TMDs) – MX$_2$ (M = Mo, W & X = S, Se) under High Pressure and High Temperature conditions

by

Nirup Bandaru

Dr. Rama Venkat, Examination Committee Chair
Professor of Electrical and Computer Engineering
University of Nevada, Las Vegas

Dr. Ravhi S Kumar, Examination Committee Co-Chair
Professor of Physics and Astronomy
University of Nevada, Las Vegas

Dr. Clemens Heske, Examination Committee Co-Chair
Professor, Materials Chemistry
Department of Chemistry and Biochemistry

Layered structured materials such as transition metal dichalcogenides (TMDs) have gained immense interest in recent times due to their exceptional structural, electrical and optical properties. Recent studies show semiconducting TMDs such as MX$_2$ (M= Mo, W
& X = S, Se) could be used as potential shock absorbing material, which has resulted in extensive studies on structural stability of these materials under the influence of high pressure. Understanding the structural stability of transition metal dichalcogenides (TMDs) such as MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$ under high pressure has been very challenging due to contradicting observations and interpretations reported in the past. Hence, the main objective of this work is to study the crystal structure and optical properties of bulk MX$_2$ at high hydrostatic pressures up to 51 GPa using a diamond anvil cell with synchrotron radiation in addition to high pressure Raman spectroscopic and high temperature X-ray diffraction (XRD) experiments. Crystal structures of MX$_2$ materials are observed to be stable up to 500 °C with nonlinear thermal coefficients of expansion. Results of high pressure experiments show a pressure induced isostructural hexagonal distortion to a 2H$_a$-hexagonal $P6_3/mmc$ phase, in MoS$_2$ around 26 GPa as predicted by theoretical calculations reported earlier. No pressure induced phase transformation is observed in other MX$_2$ (MoSe$_2$, WS$_2$, WSe$_2$). A semi empirical model based on the energy of interaction of bond electrons is proposed to explain the observed inconsistency between MoS$_2$ and other TMDs studied. Using this model, it is shown that except MoS$_2$, no other MX$_2$ within the scope of this study undergoes pressure induced phase transition in the pressure range 0 – 50 GPa. High pressure Raman results show continuous red shifts in dominant vibrational modes with increase in pressure in MX$_2$. Additionally, emergence of a new peak, namely ‘d - band’ associated with 2H$_a$ structure in MoS$_2$ supports the observation of a isostructural phase transition in high pressure X-ray diffraction experiments. In addition to the studies on bulk MoS$_2$ material, thin film
(approximately 100 nm thicknesses) is successfully fabricated via DC magnetron sputtering system and sulfurization technique.
ACKNOWLEDGEMENTS

I would like to acknowledge each and every person involved either directly or indirectly to my work described in this dissertation. I would like to dedicate this work to my parents, sister and brother for their constant inspiration and encouragement. My sincere gratitude to my advisor Dr. Rama Venkat, who always trusted my abilities and encouraged me to perform better with his invaluable guidance and thoughts all throughout my budding years at UNLV. I would like to express my gratefulness towards my co-advisor Dr. Ravhi Kumar for his valuable suggestions and supervision, which have been very instrumental in molding me into a good experimentalist. Also, I would like to thank Dr. Clemens Heske my co-advisor for his precious counsels.

I would like to acknowledge Dr. Thomas Hartmann for help in high temperature experiments and also for accepting my invitation to be a graduate college representative. I would like to thank Dr. Ke-Xun Sun, and Dr. Venkatesan Muthukumar, for their time in reviewing my dissertation and also for been part of my dissertation committee members. I would also like to express my sincere gratitude towards Stanley Goldfarb for his time and effort put in building the 3 gun sputtering system and more importantly educating me to become a skilled professional in vacuum technology. I thank Dr. Minghua Ren and Dr. Oliver Tschauner for help in Scanning Electron Microscopy (SEM) and shock experiments. I would also like to express gratitude to all the students (Brandon Blackstone, Frankie, Aldo, Makram, Jorge, Stryder) and my fellow researchers at HiPSEC, especially Jason Baker, Daniel Antonio, and Daniel Sneed for their every ready helping nature. I acknowledge HIPSEC and NNSA for funding this project. Also, I would like to express
my gratitude towards APS beamline scientists and support staff for their help. Also, would like to acknowledge NSTec for their funding.

Finally I would like to thank my friends Deepak, Rana, Anupam, Nandu, Sriky, Uppi, Ajay, Sriman, my roomies (Aravind, Kranthi, Karthik, Sandeep, Avinash, Dilip, Sai, Naveen etc.), Apt #70, Rebel Cricket Club (RCC) and many more to name for most enduring memories of my life in Las Vegas, in particularly at UNLV.
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CHAPTER 1

INTRODUCTION

The transition metal dichalcogenides (TMDs) belong to a class of layered compounds represented generally as MX$_2$, where M is a transition-metal atom from the group IV, V, or VI columns of the periodic table and X is one of the chalcogens, Sulfur, Selenium or tellurium. In recent times, these materials have fascinated research community due to their diverse physical, electrical and optical properties. Electrically, TMDs encompass a wide range of properties, like from being an insulator (HF$_2$) to semiconductors (MoS$_2$), to metallic (NbS$_2$). Today there are more than sixty available TMDs including various combinations of polytypes and polymorphs. The scope of the present work is limited to understanding the structural and optical properties of semiconducting TMDs (MX$_2$) under high pressure, where M is either molybdenum or tungsten and X is either sulfur or selenium [1, 2].

Structurally TMDs (MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$) crystallize in hexagonal layered configuration, in which a plane of metallic atoms (Mo or W) are bonded and sandwiched between two chalcogen (S or Se) planes, to form a slab, “X-M-X”. Within each slab, the atoms are held together by strong covalent bonds with very limited ionic nature. Repeated stacking of these slabs in the c-axis direction gives rise to the observed hexagonal structure as shown in the Figure 1.1. But, between the adjoining slabs at the interface, the interactions are weak and attractive through van der Waals forces. By the virtue of these weak van der Waals forces, the slabs slide over each other upon application of shear
stress, resulting in low friction and phenomenal lubricating properties and thus, establishing TMDs as widely used dry lubricant agents in commercial, especially, aerospace engineering fields. TMDs serve multiple purposes, when used as a supplement to liquid lubricants; they not only enhance the loading capability of the heavy machinery, but also reduce frictional losses due to surface contacts. Even though structurally TMDs resemble graphene but unlike graphene, which has low or no bandgap (0 to 0.25 eV), MX₂ exhibit finite band gap, 1.20-1.35 eV. This makes them as promising materials similar to Si for making a transistor and other electronic device applications, which operate at room temperature [3 - 9].

Figure 1.1 Atomic arrangement of metal and chalcogen atoms in a hexagonal structured TMD
By varying the stacking sequence of consecutive X-M-X layers sandwiching along the hexagonal c-axis different polytypes, 1T, 2H, and 3R, could be achieved. In this abbreviated notation of polytypes, the integer indicates the number of X-M-X layers per unit cell along the c-axis and the letters T, H, and R denote trigonal, hexagonal, and rhombohedral symmetries, respectively [10]. Under ambient conditions most of TMDs crystallize to 2Hc structure as shown in the Figure 1.2.

![Figure 1.2 Graphical representation atomic arrangements in a MoS2 - 2Hc type unit cell](image)

1.1 Motivation

1.1.1 High pressure studies of bulk materials

Similar to temperature (T), pressure (P) is an important thermochemical parameter inducing a change in physical, chemical and structural characteristics of
Historically high pressure studies are carried out to study rocks and minerals that make up the deep interior earth and other planets. Thus, a high pressure study is considered as an apt tool in condensed matter physics, for understanding the evolution of matter from relatively less dense state to a highly packed new chemical state. Unlike temperature, whose effect is reflected in the variation of kinetic energy of atoms, high pressure, on the other hand, alters atomic bonds and bond energy, by constraining atoms closer together in a smaller volume. Thus, high pressure serves as a powerful probe of atomic interactions and chemical bonding.

The most naturally found assembly of MX$_2$ unit cell is 2H$_c$ - hexagonal structure, belonging to P6$_3$/mmc space symmetry group. Though both structural and chemical forms of MX$_2$ under ambient conditions have been studied extensively [11 - 14], but very little is known about their high pressure phases. Of late, both experimentalists and theoreticians have hypothesized the existence of anonymous high pressure phase in MoS$_2$ between 20 – 30 GPa but, surprisingly nothing conclusive had been reported. The maximum pressure achieved in the high pressure studies relating to MX$_2$ materials is 38 GPa. Since MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$ all belong to the same symmetry group; with similar lattice constants, one would expect similar high pressure phases in all these materials at different pressure range. Also, recent high pressures studies have proved that MX$_2$ materials have excellent shock absorbing ability and constant efforts are in progress to use them as potential anti shock materials. The aim of this work is to extend experimental studies to understand the high pressure properties of MX$_2$ materials beyond 30 GPa. Diamond Anvil Cell (DAC) is used for applying pressure to the samples and structural information of the samples under high pressures is determined via *in-situ*
powder X-ray diffraction through the DAC at Advanced Photon Source (APS), Chicago. Besides, high pressure Raman spectroscopy experiments were performed in order to correlate the phase transitions, with the high pressure x-ray diffraction results. Additionally, high temperature powder x-ray diffraction experiments were performed to understand the effect of temperature on the crystal structure stability.

1.1.2 Thin film processing

As mentioned earlier MX₂ are a class of hexagonal layered materials with strong in-plane covalent and weak out-of-plane van der Waals bonds respectively, thus enabling exfoliation to form two dimensional structures (Thin Films). Size shrinking, i.e., moving from bulk to thin films, may result in several fundamental properties such as structural, optical, band gap (E_g) and electrical conductivity of the materials.

In order to explore thin film properties of these materials, an effort was made to synthesize and calibrate individual metallic (Mo and W) thin films via DC sputtering system, a home-built three gun sputtering unit. Subsequently, as deposited metallic films were sulfurized to form respective sulfides. Preliminary high pressure studies on exfoliated MoS₂ thin films and limited resulted is reported.

1.2 Dissertation Outline

The remainder of this dissertation is arranged into six chapters including this chapter. Chapter two provides a detailed literature review and key concepts relating to these materials discussed above. Chapter three includes details of experimental set up used in this study. Chapter four provides details of the procedure employed in synthesizing thin films. Chapter five provides results and discussion section on the high pressure and high
temperature studies on the bulk materials. Conclusions and future plan of action are discussed in Chapter six.
CHAPTER 2

BACKGROUND MATERIAL

In this chapter, the essential theoretical backgrounds of the physical and chemical properties of TMDs of interest are summarized. In the first half of the chapter structural stability and optical behavior of the bulk TMDs under various extreme conditions such as high pressure and temperature are discussed along with relevant recent studies. In the second part, physics of thin film fabrication followed by literature review of the recent scientific developments attained in the two dimensional (2-D) arena of TMDs are discussed.

2.1 Transition metal dichalcogenides (TMDs)

Today there are at least sixty (60) TMDs in number, with two thirds of them assuming layered structure. Compounds of TMDs exhibit wide range of electrical properties such as from being an insulator (HF₂) to semiconductor (MoS₂) to semi metallic (NbS₂), depending upon the type of polytypes and the number of d electrons. In particular, TMDs compounds based on molybdenum and tungsten have attracted enormous interests due to their semiconducting behavior, perceived from the wide band gaps ranging from visible to as far as near infrared regions [1 -10]. Thus, the primary emphasis of the present work is devoted in studying the structural stability of Mo and W TMDs (MoS₂, MoSe₂, WS₂, and WSe₂ (Figure 2.1) under high pressure and high temperature conditions. Additionally, high pressure Raman studies were performed to
complement any pressure induced phase transition observed in high pressure X-ray diffraction studies.

2.2 Crystal Structure and Physical Properties of TMDs

As mentioned earlier, transition metal dichalcogenides, MX$_2$ (M, Transition metal either Mo or W; X, Chalcogen, S, Se) are group of layered compounds formed by stacking of slabs (X-M-X) in the direction of c-axis. Each slab constitutes of array of transition metal (M) atoms sandwiched between two layers of chalcogens (S) as shown in the Figure 2.2. Within slabs the layers are held together by strong intralayer covalent bonds whereas, between slabs the interactions are weak and thus, are held loosely by van der Waals forces. Due this weak interlayer bonding, layers slides over each other upon application of shear stress, causing low friction and thus, enabling TMDs to be used excellent dry lubricant properties. Recent studies show that MX$_2$ can be used as potential shock absorbing material, which has resulted in extensive studies on structural stability of these materials under the influence of high pressure. Moreover, MoS$_2$ and WS$_2$ are used as catalysts for desulfurization of crude oil in refineries [15].
Figure 2.1 Image of the periodic table with arrows pointing to groups VIB (transition metal) and VIA (chalcogens) under this review.

Figure 2.2 Drawing representing atomic array of hexagonal layered metallic and chalcogen atoms in MX2, TMDs.
In layered hexagonal structure every metal atom is always surrounded by six chalcogen atoms. This yields two possible structures, trigonal prismatic and octahedral. In trigonal prismatic structure, the two chalcogenide planes in a slab are stacked directly above each other forming trigonal interstices for metal atoms ($D_{3h}$ point group, honeycomb motif). Octahedral interstices ($D_{3d}$ point group, centered honeycomb motif) are formed for metal atoms, when the chalcogen planes are slightly disorientated [16] as shown in the Figure 2.3.

The type of coordination preferred by the materials depends upon the nature of the bond formed between the metal and chalcogen atoms. Typically, octahedral coordination is preferred for ionic compounds and in contrast, trigonal prismatic coordination is preferred for covalently bonded compounds. Different polymorphs can be obtained by changing the slab stacking sequences such as AbA/BaB and BcB/AcA, where capital and lower case letters denote chalcogen, S and metal, M atoms. The stacking sequence of the most commonly featured polymorphs of $MX_2$ are shown in the Tabular column 1 [17, 18].
Figure 2.3 Graphical illustrations of a) Trigonal Prismatic Structure and b) Octahedral Structure
Table 2.1 Metallic coordination and stacking sequence of the most commonly found polytypes of TMDs

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<th>Space Group Symmetry</th>
<th>Metal Coordination</th>
<th>Stacking Sequence</th>
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<tr>
<td>1T</td>
<td>P3m1</td>
<td>Octahedral</td>
<td>AbC</td>
</tr>
<tr>
<td>2H&lt;sub&gt;a&lt;/sub&gt;</td>
<td>P6&lt;sub&gt;3&lt;/sub&gt;/mmc</td>
<td>Trigonal Prismatic</td>
<td>BcB AcA</td>
</tr>
<tr>
<td>2H&lt;sub&gt;b&lt;/sub&gt;</td>
<td>P6&lt;sub&gt;3&lt;/sub&gt;/mmc</td>
<td>Trigonal Prismatic</td>
<td>BcB AbA</td>
</tr>
<tr>
<td>2H&lt;sub&gt;c&lt;/sub&gt;</td>
<td>P6&lt;sub&gt;3&lt;/sub&gt;/mmc</td>
<td>Trigonal Prismatic</td>
<td>BaB AbA</td>
</tr>
<tr>
<td>3R</td>
<td>R&lt;sub&gt;3&lt;/sub&gt;m</td>
<td>Trigonal Prismatic</td>
<td>BcB CaC AbA</td>
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</tbody>
</table>

A simplified nomenclature is used in describing different phases of the material as shown in Table 2.1. In this abbreviated notation of polytypes used, the integer indicates the number of layers (X-M-X) encompassed in a unit cell along the c-axis direction and the capital letter T,H,R denote the trigonal, hexagonal, and rhombohedral symmetries, respectively. Although polytypes belonging to the same point symmetry group as in the case of 2H<sub>a</sub>, 2H<sub>b</sub>, and 2H<sub>c</sub>, there exists a finite difference in the physical, electrical, and optical properties displayed by these polytypes. This variance in the properties is attributed to dissimilar stacking of layered hexagonal array of metal and chalcogen atoms within each slab as indicated by the letters, ‘A, B, C, a,b,c’ in the Table 2.1 [19, 20]. Under ambient pressure and temperature conditions, MX<sub>2</sub> crystallize in 2H<sub>c</sub> structure and in total have six atoms per unit cell, with two metal atoms and four chalcogen atoms as shown in the Figure 2.4.

TMDs of interest (MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub>) share striking similarities not only in terms of crystal structure but also in terms other properties such as lattice constant,
bulk electronic bandgap, thermal stability etc. Detailed comparisons of physical and electronic properties of MX₂ are presented in Table 2.2.

Figure 2.4 Pictorial representation of 2Hₖ type MX₂ unit cell
Table 2.2 List of physical, electronic and optical properties of various TMDs of interest

[21 - 23]

<table>
<thead>
<tr>
<th>Property</th>
<th>MoS$_2$</th>
<th>MoSe$_2$</th>
<th>WS$_2$</th>
<th>WSe$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (Kg/m$^3$)</td>
<td>5060</td>
<td>6980</td>
<td>7500</td>
<td>9200</td>
</tr>
<tr>
<td>Molecular Wt.(g/mol)</td>
<td>160.07</td>
<td>253.892</td>
<td>247.98</td>
<td>341.782</td>
</tr>
<tr>
<td>Crystal Structure Type (Ambient Conditions)</td>
<td>2H$_c$</td>
<td>2H$_c$</td>
<td>2H$_c$</td>
<td>2H$_c$</td>
</tr>
<tr>
<td>Lattice parameters $a$ &amp; $c$ (Å)</td>
<td>3.16</td>
<td>3.28</td>
<td>3.15</td>
<td>3.28</td>
</tr>
<tr>
<td>Melting Point ($^0$C)</td>
<td>1185</td>
<td>&gt;1250</td>
<td>1250</td>
<td>&gt;1250</td>
</tr>
<tr>
<td>Electronic Bulk Indirect Band gap (eV)</td>
<td>1.23-1.29</td>
<td>1.09</td>
<td>1.35</td>
<td>1.20</td>
</tr>
<tr>
<td>Electronic Monolayer direct Bandgap (eV)</td>
<td>1.90</td>
<td>1.56</td>
<td>2.1</td>
<td>1.73</td>
</tr>
<tr>
<td>Predominant Bulk Raman Peaks (cm$^{-1}$)</td>
<td>$A_{1g} = 409$</td>
<td>$A_{1g} = 244$</td>
<td>$A_{1g} = 421$</td>
<td>$A_{1g} = 251$</td>
</tr>
<tr>
<td></td>
<td>$E^{'+}2g = 383$</td>
<td>$E^{'+}2g = 286$</td>
<td>$E^{'+}2g = 356$</td>
<td>$E^{'+}2g = 248$</td>
</tr>
</tbody>
</table>

2.3 High Pressure Studies

Similar to temperature (T), pressure (P) is an important thermodynamically parameter used to probe condensed matter. Historically, high pressure studies were considered to be marginal relative to temperature studies, due to lack of high quality measurements,
economic feasibility, and great disagreement between theoretical and experiment results etc. After 1960s, significant developments were achieved in Diamond Anvil cells (DAC), large volume cells (LVC) in combination with state of art synchrotron facilities. Also, recent developments in the theoretical physics, especially in the field of condensed matter have led to better understandings of experimental results.

High pressure, which is another form of stress, can be applied either quasi statically via using DACs or dynamically by means of shock waves. In either case, atoms inside the matter under pressure are driven closer to each other and subsequently, leading to effects such as reduced volume coupled with bond shortening (inter atomic distances), bond bending, atomic rearrangement etc. as shown in the Figure 2.5. Effects of atomic reordering under high pressure are obvious and drastic such as formation of new chemical phases which are hard and dense, solidified form of liquids and gases etc. Thus, high pressure studies are crucial in understanding the process of synthesizing novel solid phase materials, which are dense and hard in nature [24 – 26]. In fact materials, which are typically insulators at ambient conditions, tend to behave as metals under sufficiently high pressure, a phenomenon known as Mott’s transition. For example, in silicon and germanium, transition from semiconductor to metal takes place at sufficiently high pressures. Unlike temperature, whose effect is reflected in the variation in kinetic energy of atoms, contrary to that, high pressure alters atomic bonds and bond energy by constraining atoms closer together in a smaller volume. To sum it up, high pressure serves as a powerful probe of atomic interactions and chemical bonding [27, 28].
Figure 2.5 Pictorial representation of effect of pressure on intra and inter molecular bonds [28]

In layered compounds such as TMDs, there exists a differential compression rates between intermolecular bonds and intramolecular bonds thus, leading to significant anisotropic behavior. Fundamentally under high pressure, all TMDs undergo structural
transition that is., from electrically insulating nature to semiconductor or metal transition. Hence, knowledge of high pressure behavior provides a thorough understanding of rules governing the material properties such as type atom–atom interaction, atomic bonding, and bond strength. Also these high pressure studies enable us to design new theoretical models for forecasting physical and chemical properties under ultra-high pressures.

2.4 Review of High Pressure Structural Studies on bulk TMDs

High pressure investigation of transition metal dichalcogenides (TMDs) plays a vital role in understanding the fundamentals of condensed matter and their applications. The following section is a review of the recent high pressure studies on MX$_2$ materials.

2.4.1 Molybdenum Sulfide (MoS$_2$)

Several studies, including both theoretical and experimental, have been carried out in order to understand the effect of extreme external pressure on the crystal structure of MoS$_2$. At ambient conditions, MoS$_2$ crystallizes in 2H$_c$ crystal structure with lattice parameters, $a = 3.159(8)$ Å and $c = 12.298(3)$ Å with Mo atoms at Wyckoff position 2(c) and S atoms at 4(f), respectively [29]. Recently Aksoy et al. [11] performed Energy Dispersive X-ray Diffraction (EDXRD) of MoS$_2$ under pressures up to 38.8 GPa. They reported anomalous behavior in the volume versus pressure data between the pressures range 20.5 and 28.9 GPa and suggested a possible electronic or structural phase transition with limited distortion of the parent 2H$_c$ structure. Also they observed discontinuities in evolution of lattice parameters in the same pressure range. A bulk modulus value of 53.4 ±1 GPa, by fitting a third order Birch-Murnaghan Equation of State (EOS) to the P-V data was also reported.
Recently, Hromadova et al. [30] employed *ab initio* calculation and metadynamics simulations, on 2H\(_c\)-MoS\(_2\) structure to predict the structural behavior under high pressure conditions. Their results predicted a possible isostructural phase transition from 2H\(_c\) to 2H\(_a\) in the pressure range 20 to 30 GPa. Additionally, the results indicated that the layered hexagonal semiconducting MoS\(_2\) undergoes a Mott’s transition, i.e., transition from semiconductor to semimetal, in the same pressure range. Based upon the calculated enthalpies for the two polymorphs, 2H\(_c\) and 2H\(_a\), a new high pressure phase (2H\(_a\)) at pressure point, P = 20 GPa is predicted (with new lattice parameters, \(a = 3.080\) Å and \(c = 10.754\) Å with Mo atoms at 2(b) and S atoms at 4(f) Wyckoff position). Additionally, it was inferred that the 2H\(_a\) phase is less anisotropic than the initial parent phase, 2H\(_c\).

Hromadova et al. [30] theoretically calculated (\(hkl\)) reflections which correlated well with experimentally determined (\(hkl\)) locations [30]. It is reported that the pressure induced onset of the new phase 2H\(_a\), is strongly associated with the appearance of new (104) reflection and a much stronger (102) reflection. Further, the vanishing of 2H\(_c\) phase is indicated by the disappearance of (105) reflection and the drop in intensity of (103) reflection. Interestingly, it was also predicted that around same pressure range 20 – 30 GPa, MoS\(_2\) would undergo an electronic transition.

Recent high pressure studies by, Nayak et al. [31] and Chi et al. [32] have also reinforced the argument that MoS\(_2\) will undergo both structural and electronic phase transition between 20 – 30 GPa.
2.4.2 Molybdenum Selenide (MoSe$_2$)

MoSe$_2$ crystalizes in 2H$_c$ crystal structure under ambient pressure and temperature conditions with lattice parameters, $a = 3.288(4)$ Å and $c = 12.920(2)$ Å with W atoms at Wyckoff position 2(c) and Se atoms at 4(f), respectively [33]. High pressure x-ray diffraction experiments conducted by Aksoy et al. [12] on bulk WSe$_2$ for pressures up to 35.9 GPa have concluded no phase transformation in the pressure range. Similar to MoS$_2$, it was observed that c-direction is more compressible than the a-direction. The reported bulk modulus is 45.7 ±0.3 GPa.

Based up on the predicted phase transition in bulk MoS$_2$, Riflikov et al. [34] anticipated a similar behavior in MoSe$_2$ around 28 GPa. However, theoretical simulations by the same group proved that, MoSe$_2$ does not undergo any structural phase transition, but rather experience an electronic transition around 28 GPa.

2.4.3 Tungsten Sulfide (WS$_2$)

Similar to other MX$_2$, under ambient conditions WS$_2$ crystalizes into 2H$_c$ crystal structure with lattice parameters, $a = 3.181(5)$ Å and $c = 12.513(8)$ Å with W atoms at Wyckoff position 2(c) and S atoms at 4(f), respectively [35]. Selvi et al. [13] conducted EDXRD of WS$_2$ up to 25.5 GPa. No phase transformation was reported in the pressure range. The reported bulk modulus in the pressure range up to 25.5 GPa of 61 ±1 GPa, by fitting a third order Birch-Murnaghan Equation of State (EOS) to the obtained P-V data. Additionally, it was also observed that the 2H$_c$- WS$_2$ was more compressible along c-axis than a-axis.
2.4.4 Tungsten Selenide (WSe$_2$)

Under ambient conditions WSe$_2$ crystalizes in 2H$_c$ crystal structure with lattice parameters, $a = 3.282(7)$ Å and $c = 12.937(3)$ Å with W atoms at Wyckoff position 2(c) and Se atoms at 4(f), respectively [36]. Aksoy et al. [14] conducted high pressure x-ray diffraction of WSe$_2$ up to 35.8 GPa. With no pressure induced phase transition observed in the pressure range, the reported bulk modulus is 72 ± 1 GPa. Also, it was found that the c-direction was significantly more compressible than the a-direction.

2.5 Review of High Pressure Raman Studies on bulk TMDs

Materials under sufficient pressure undergo a change in atomic bonds and angles resulting in corresponding change in local vibrational modes. By monitoring these modes as function of applied pressure one can determine any pressure induced phase transformations. Hence, Raman spectroscopy is a complementary tool to X-ray diffraction technique in determining any pressure induced phase transitions [37]. Use of Raman spectroscopy for materials under high pressure is productive only if the materials under study are Raman active. Fortunately due to its layered 2H structure MX$_2$ are non-linear compounds and hence, are Raman active.

The compounds representing the MX$_2$ structure type are isomorphic and are crystallizing with space group $P6_3/mmc$. Since MoS$_2$ is a nonlinear molecule and there are six atoms per unit cell (N=6) and hence, 3N-6 = 12, normal modes of vibration exits at the center of hexagonal Brillouin zone and given by the following equation.

$$\Gamma = A_{1g} + 2A_{2u} + 2B_{2g} + B_{1u} + E_{1g} + 2E_{1u} + 2E_{2g} + E_{2u}$$

(2.1)
Of the aforementioned twelve (12) modes, A$_{1g}$, E$_{1g}$, E$_{2g}^1$, and E$_{2g}^2$ are Raman active and the remaining are infrared absorption and acoustic modes. In plane, E$_{2g}^1$, and out of plane, A$_{1g}$, are the two most commonly studied internal molecular modes under pressure. The two external modes, namely rigid modes, E$_{1g}$, E$_{2g}^2$ are associated with movement of the layers [38]. In the present work we limit our study to two internal modes of vibrations. Figure 2.5 provides a graphical representation of Raman active modes for MX$_2$ type TMDs.

Figure 2.6 Graphical representation of active Raman modes of layered TMDs
2.5.1 Molybdenum Sulfide (MoS$_2$)

The prominent active Raman vibrational modes of MoS$_2$ are A$_{1g}$ at 408.5 cm$^{-1}$, and at E$_{2g}^{(1)}$ at 383.4 cm$^{-1}$. Evolution of Raman modes under pressure was first reported by Bagnall et al. [39]. But this work was just limited to 5 GPa. Bagnall et.al observed that for low pressures both, the in plane, E$_{2g}^{(1)}$ and out of plane, A$_{1g}$ modes red shift with the increase in pressure. Further, it was noticed that the A$_{1g}$ mode had higher pressure gradient than E$_{2g}^{(1)}$ mode. This effect was explained to be due to the fact that the A$_{1g}$ mode is compressional along the c-axis which is known to decrease with pressure at much faster rate than the a-axis. Additionally, the authors successfully used the low pressure Raman data and the model proposed by Bromley et al. [40] to determine the compressive force constants between metal-chalcogen and chalcogen-chalcogen atoms.

Sugai et al. [38] and Bhatt et al. [41] extended the high pressure Raman studies of MoS$_2$ up to 18 GPa and 12 GPa, respectively. It was observed that evolution of Raman modes namely, E$_{2g}^{(1)}$ and A$_{1g}$ under pressure was in good agreement with the previous studies [38 - 41] and no pressure induced transition were observed. Also, Sugai et al. [38] observed that the rigid layer mode E$_{2g}^{(2)}$, redshifts with increase in pressure. Bromley’s proposed model was used by Sugai et al. [38] and Bhatt et al. [41] to determine the corresponding compressive force constants and Gruneisen constants. It is worth to mention that Bhatt et al [4] performed high pressure Raman analysis of single crystals grown via vapor transport technique, (which is similar to chemical vapor deposition (CVD)) using a mixture of 16:3:1 methanol-ethanol-water as the pressure transmitting medium.
Livneh et al. [42] extended the Raman studies up to 31 GPa. They observed a new band, namely, “d” band on the higher energy side of \(E_{2g}^{(1)}\) peak approximately around 19 GPa. In fact, the energy of newly emerged “d” band coincides with the \(E_{2g}^{(1)}\) energy of \(2H_a\) phase calculated by Hromadova et al. [30].

2.5.2 Molybdenum Selenide (MoSe₂)

Energy corresponding to the two predominant Raman modes of MoSe₂ are \(A_{1g}\) at 244 cm⁻¹ and at \(E_{2g}^{(1)}\) at 286 cm⁻¹. Single crystal MoSe₂ Raman analysis was performed by Bhatt et al [41] for pressures up to 16 GPa. The intensity of \(E_{2g}^{(1)}\) mode is comparatively lesser than that of the \(A_{1g}\) mode and at relatively higher pressures, the intensity of \(E_{2g}^{(1)}\) was observed to be in the order equivalent to the background noise. No anomalies were observed except the reduced intensities accompanied by peak broadening upon increase in external pressure.

2.5.3 Tungsten Sulfide (WS₂)

The prominent Raman active vibrational modes of WS₂ are \(A_{1g}\) at 420 cm⁻¹, and at \(E_{2g}^{(1)}\) at 352 cm⁻¹. Bhatt et al [41] reported single crystal Raman analysis of WS₂ for pressure up to 19.4 GPa. It is reported that both in-pane, \(E_{2g}^{(1)}\) and out of plane, \(A_{1g}\) modes shift continuously to higher wavelengths, accompanied by reduced intensities and peak broadening with increase in pressure. No structural transformation was reported in the investigated pressure range.

2.5.4 Tungsten Selenide (WSe₂)

Under ambient conditions the two active Raman modes of WSe₂ are \(A_{1g}\) at 251 cm⁻¹, and at \(E_{2g}^{(1)}\) at 248 cm⁻¹. These two modes are very close to each other and hence, a shoulder is noticed in the Raman spectroscopy under ambient pressure conditions by
Bhatt et al. [41]. Raman analysis was performed on single crystal WSe$_2$, and the maximum pressure attained during the experiments was 19 GPa. There were no aberrations noticed in the evolution of modes with increase in applied pressure other than the red shift of the modes themselves.

2.6 Review of High Temperature Structural Studies on bulk TMDs

Unlike the effect of pressure, where atoms are constrained to a small volume; heating causes atomic arrangement of materials to span and thus, increasing the unit cell volume. In molecular solids when viewed from a microscopic scale, increasing temperature means adding more kinetic energy to the individual atoms which subsequently results in overall increase in energy of the system, given by $(KE_{avg} = \frac{3}{2}kT)$, where $k$ is Boltzmann constant and $T$ is the temperature. Unlike in gaseous phase, the atoms in molecular solids are held together by bonds and hence, have very restricted motions such as bond stretching, bending, torsion etc. as shown in the Figure 2.7 with increase in temperature. But, at sufficiently high energy these molecular motions reach a critical point beyond which the material assumes different physical form (phase) to accommodate the extra energy provided via heat. This phenomenon, change in phase with respect to temperature is termed as a phase transition. Phase transitions are characterized by discontinuity in the thermochemical properties of matter such as structural, electrical, optical etc. In today’s world where almost all electronic gadgets are made of semiconducting/metallic materials, whose properties are very sensitive to heat exposure, it is very imperative to have an insight on the exact temperature range where the phase transition occurs. Though there
are various established methods to identify temperature induced the phase transitions, XRD technique stands out to be one of the most prominent due to its versatility [43 - 45].

Figure 2.7 Graphical representation of various effects associated with chemical bonds w.r.t increase in temperature

TMDs discussed above are most commonly used dry lubricants in industrial and aerospace engineering applications. Also, recent technological advancements have encouraged the use of two dimensional structures (2D) of TMDs in digital applications such as FETs (Field Effect Transistors), phototransistors, photodiode etc. [46 - 48]. Hence, it is imperative to understand the effect of temperature on structural stability of TMDs
and the following section provides a brief evaluation of previous high temperature studies on bulk TMDs.

Mahalawy et al. [49] experimentally determined the structural stability of MoS$_2$, MoSe$_2$, and WSe$_2$ compounds for temperatures ranging from room temperature to 800 °C through powder XRD. The powdered samples were enclosed in a vacuum sealed container. Though there was no phase transformations observed in the temperature range, it was noticed that all materials oxidize around 550 °C due to presence of finite oxygen levels in the vacuum container. The coefficient of thermal expansion of these materials were found be nonlinear.

Bhushan et al. [50] have reported that tribology compounds of interest MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$ are thermally stable for temperatures up to 1185 °C.

2.7 Thin Film Fabrication of Transition Metal Dichalcogenides

In this section physics of formation of thin films are discussed followed by brief review of the recent developments in thin film TMDs of interest.

2.7.1 Physics of Thin Film Formation

A solid material is said to be in thin film form when it is built up, as a thin layer on a solid support, called substrate, by controlled condensation of the individual atomic, molecular, or ionic species, either directly by a physical process or through a chemical process [51].

Thin films are different from bulk materials in the following ways.

- Thin films are not fully dense
- Have a two dimensional (2-D) structure
- Strongly influenced by surface and interface effects
- Subject to stress, from lattice misfits with the substrate or difference in thermal characteristics between thin film and substrate exhibit different defect structure.

Thin film deposition process mainly involves the following three steps:

- Emission of atomic, molecular, or ionic particles from source (target) either through heat or physical sputtering by the other atomic species.
- Transport of these emitted particles to the substrate, which can be either directed or through vacuum.
- Condensation of particles on substrate, either directly or through a chemical reaction to form a solid deposit.

Formation of thin film takes place via nucleation and growth, details of which are presented below.

- The particles on impinging the substrate lose enough thermal energy to stay physically on the surface of the substrate. These adsorbed particles are known as adatoms. Typically, in this case the adatoms are attached to the surface through Van der Waal type bonding which has energies less than 0.3eV [52].
- The adatoms move over the surface by hopping from one location to another with help of thermal energy known as surface migration. During this process they interact with the other adatoms to form bigger clusters.
- These adatoms being thermodynamically unstable tend to desorbs depending upon the deposition parameters such as flux rate and temperature. If the adatom
reaches a stable cluster before getting desorbed, it enlarges the cluster.

- Since these clusters critical nuclei are less mobile and thermally stable than individual adatoms they tend to remain at the locations where they are formed and grow in size and numbers. These are called islands [52].

- In order to reduce the surface area these small islands start fusing with each other to form bigger islands, known as agglomeration [52].

- These large islands continue to grow leaving behind channels or holes of exposed substrate leading to the formation of thin film.

![Figure 2.8 Simplified model of thin film deposition](image)

2.7.2 Factors Affecting Thin Film Formation

The following affect the formation of thin films.

- Deposition techniques

- Type of material to be deposited
• Substrate properties, which determine the amount of adhesion between the substrate and target atoms and the lattice misfits between the thin film and substrate.
• Surface irregularities of the substrate
• Rate of deposition and
• Medium of deposition such as argon gas, or vacuum.

2.7.3 Deposition Techniques
There are many ways to deposit a specimen as a thin film. The most commonly used one are Vapor deposition techniques. Vapor deposition techniques can be broadly divided into two categories:

• Physical Vapor Deposition (PVD) and
• Chemical Vapor Deposition (CVD)

Physical vapor deposition (PVD) is a vaporization coating technique, which involves transfer of solid material from the source to the substrate on an atomic level in a vacuum. The level of vacuum should be such that the mean free path of the target molecules is greater than the chamber dimensions and the distance from source to the substrate [51, 52]. Furthermore physical vapor deposition technique can be classified as:

• Thermal Evaporation and
• Sputtering

Thermal Evaporation
Thermal evaporation known, as vacuum evaporation is one of the most widely used deposition techniques. As the name suggests, this technique consists of vaporization of
the solid material by thermally heating the raw material above its melting temperature and then, condensing it onto a cooler substrate to form thin film. An electric resistance heater in the form of tungsten filament or a boat is used to heat the source material. This process is carried out in vacuum so that the material in the form of vapor reaches the substrate without scattering against any other gas atoms and also to avoid the presence of impurities. Molecular Beam Epitaxy (MBE) is a sophisticated form of thermal evaporation [51, 52].

Sputtering

Sputtering is a PVD process in which the target atoms or molecules are ejected by bombarding the solid material with energetic and non-reactive ions. Usually argon gas (Ar) is used for bombarding the target. These ions upon impinging the solid material transfer energy and momentum to the target atoms, which condense on a substrate to form thin film. There should be enough ions, i.e., Ar plasma inside the deposition chamber in order to sustain the sputtering process [51].

Sputtering process is characterized by a parameter called sputter yield (S).

\[ S = \frac{\text{number of ejected target atoms}}{\text{number incident (Ar) ions}} \]

Sputtering yield (S) depends upon:

- Type of sputtering employed
- Mass and energy of sputtering gas atoms
- Target materials which include the mass and binding energy of target atoms
- Geometry of the deposition chamber
Using magnetron sputtering, in which a magnetic field is used to yield multiple sputtering events by the ions, can enhance sputtering yield.

Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) is a process by which solid thin films are deposited on substrate by reacting vapor or liquid phase chemicals that contain the constituents of thin film. The main difference between CVD and PVD is that in PVD the target material is in solid form where as in CVD it can be either a liquid or a gas. A pictorial representation illustrating the difference between CVD and PVD is shown in Figure 2.9

Figure 2.9 Pictorial representations illustrating the differences between CVD and PVD

2.7.4 Thin film deposition of TMDs

Some of the most commonly used methods for depositing thin film TMDs are sputtering, (either direct sputtering of metal dichalcogenides or sputtering of respective metallic films followed by sulfurization/selenization) Molecular Beam Epitaxy (MBE), Atomic layer Deposition (ALD), Chemical bath deposition etc. MBE and ALD are
variants of PVD and CVD techniques as described in the previous section. Although, there are several techniques available for the deposition of transition metal dichalcogenides films, the thin film properties are extremely sensitive to the choice of technique employed. Nevertheless, no single deposition technique can cover all the desired aspects, such as cost of equipment, reproducibility, economy of chemicals, deposition conditions and nature of deposit etc. [53 - 55].

2.8 Review of recent studies on Transition Metal Chalcogenide (TMDs) Thin Films

Two dimensional (2D) TMDs exhibit very unusual optical and electronic properties in contrast to their 3D structures. In this section, previous and current studies on thin film properties of MX$_2$ are presented.

Several recent theoretical and experimental studies have shown that MX$_2$ materials undergo gradual transition in nature of the band gap exhibited, from indirect in bulk form to direct in mono or few layers. Quantum confinement effect and the resulting change in electronic distributions have ascribed to create these dramatic changes in the band structure of thin films. Sizeable band gap of MX$_2$ materials has encouraged researchers to develop new optoelectronic and photovoltaic devices [46 - 48]. Recently Radisavljevic et al. [56] have synthesized low power consumption single layer MoS$_2$ channel MOSFET with carrier mobility as high as 200 cm$^2$V$^{-1}$S$^{-1}$, and relatively high on/off ratio at room temperature. Also, Lee et al. [57] have recently demonstrated atomically thin flexible and transparent MoS$_2$ field-effect transistor (FET) to which has reasonable carrier mobility. Also their results showed that these ultra-thin FETs could operate at voltages as high as 10 V. The use of few or mono layers of MoS$_2$ have enabled the researchers to overcome
the channel induced effects such as, reduced mobility, low on/off ratio etc. Apart of tunable band gap, 2D structures of MX$_2$ in general exhibit excellent optical and vibrational properties. Photoluminescence (PL) studies on single layer and few layers of MoS$_2$ transistor by Sundaram et al. [58] have demonstrated the potential use of 2D MoS$_2$ structures for detecting and emitting electromagnetic light in the visible spectrum. Splendiani et al. [59] have also confirmed emergence of strong PL peak in mono or few layers of MoS$_2$, which are completely absent in bulk. Recently, Sanchez et al. [60] have fabricated a phototransistor using few layers of MoS$_2$ to detect green and red light. Investigations by Li et al. [61] and Lee et al. [62] have shown Raman modes in ultra-thin MoS$_2$ flakes to continuous evolution with thickness due to reduced coupling between electronic transition energies and phonons. The in-plane mode, E$_{2g}^{(1)}$ red shifts while the other out-of plane mode, A$_{1g}$ blue shifts. They also concluded that the energy difference between these modes, approximately 18 cm$^{-1}$ could be used for reliable identification of monolayer MoS$_2$. Very recently Wu et al. [63] have reported piezotronics application of atomically thin MoS$_2$ films. It is shown that odd number of atomically thin MoS$_2$ films can be used to convert subjected to strain energy to considerable amount piezo electric voltage. Interestingly, the same phenomenon was absent in bulk due to opposite orientations of the adjacent atomic layers.

Since both MoS$_2$ and WS$_2$ belong to same family of compounds, similar kind of studies were performed on WS$_2$ thin films. Hwang et al. [64] have realized room temperature 2D WS$_2$ Schottky-barrier Field Effect Transistor (FET) ambipolar behavior with reasonably high ($\sim 10^5$ x) on/off current ratio. Zhao et al. [65] have demonstrated mechanical exfoliated WS$_2$ films to exhibit strong thickness dependent absorption and
emission properties. Studies on evolution of vibrational modes of few layers and mono
layers of WS$_2$ by Berkdemir et al. [66] have revealed that softening of $A_{1g}$ mode and
prominent presence of $E_{12g}^1$ mode with decreasing number of WS$_2$ layers.

Lu et al. [67] have synthesized monolayer to few layers of MoSe$_2$ thin film by
selenization of MoO$_3$ vapor on SiO$_2$ substrate. Compositions of the films were
characterized by EDS (Energy Dispersive X-ray Spectroscopy) and Raman analysis. The
measured electron transport properties highlight the potential application of MoSe$_2$ thin
films in nanoelectronics etc. Das et al. [68] have reported to atomic layer thick, high
mobility transparent thin Film Transistors (TFTs) device using bilayers of tungsten
selenide (WSe$_2$) as junction channel. The stated performance characteristics of the device
are remarkable with respect to temperature of operation, mobility, ON/OFF ratio etc.
CHAPTER 3

EXPERIMENTAL TECHNIQUES AND SETUP

In this chapter, details of the various experimental techniques used for studying the structural stability of TMDs under extreme pressure and temperature conditions are presented. Theoretical backgrounds behind each experimental methodology are also provided.

3.1 X-ray Diffraction

X-rays used for material studies are electromagnetic radiation of wavelength 0.2 to 2.5 Å, which is about the same size as an atom and comparable to lattice constants in crystals. X-rays enable us to probe crystalline structure and chemical composition of materials and thin films. Each crystallized solid has a unique X-ray diffraction pattern representing its structure type and Laue symmetry, which can be used to determine the crystal structure [69].

The unit cell of any compound can be determined by analyzing the diffracted X-ray intensities in accordance with the Bragg's law and the reflex conditions related to crystal system and Bravais lattice type. Equation 3.1 is Bragg’s law, where $d’$ is the interplanar distance, $\theta$ is the angle of incidence with respect to the plane, $\lambda$ is the wavelength of the incident beam, and $n$ is the order of diffraction. As per Bragg's law, depending upon the path difference between the two reflected beams from two different planes, they either add up constructively or destructively resulting in an intensity pattern on detector plates.
\[ n(\lambda) = 2d \sin(\theta) \]

A schematic diagram depicting X-ray diffraction from crystal planes with interplanar distance (d) is shown Figure 3.1 [70].

![Schematic diagram of X-ray diffraction](image)

Figure 3.1 Schematic diagram of X-ray diffraction from crystal planes with interplanar distance (d) and angle of incidence of \( \theta \) [70]

3.1.1 Powder X-ray Diffraction

In a powder x-ray diffraction experiment, the diffraction pattern is obtained from polycrystalline powder. The sample is very finely grounded in to powder of small size particles (1-10 µm) and consists of large number of ordered crystallites with many
random orientations. An X-ray beam hitting the sample will be diffracted by crystallites at the lattice planes \((d_{hkI})\) with different orientation in to various directions forming a cone of diffracted beam as determined by Bragg’s law. Every lattice plane with different d-spacing in the crystal gives rise to a Debye-Scherrer cone (rings) diffraction pattern as shown in the Figure 3.2. Each concentric diffraction rings on the detector plate correspond to a different crystal plane

![Debye-Scherrer cones corresponding to planes with various interplanar distances, d, in powder X-ray Diffraction](image)

Figure 3.2 Debye-Scherrer cones corresponding to planes with various interplanar distances, d, in powder X-ray Diffraction [71]

The mechanical assembly that makes up the sample holder, detector and the associated accessories is referred to as goniometer as shown in the Fig.3.3. For \(\theta-2\theta\) scan mode, the X-ray source is stationary, the sample moves by the angle \(\theta\) and simultaneously the detector has to be rotated by \(2\theta\) to capture the diffracted beam by
Bragg’s law. If the Bragg angle is $\theta$, then the angle between the direction of the incident beam and diffracted beam is $2\theta$.

![Diagram of Bragg's law](image)

**Figure 3.3** Graphical representation of $\theta$ -2$\theta$ scan, Goniometer assembly

### 3.1.2 Synchrotron X-ray Diffraction

High purity (99%) powders of MoS$_2$, WS$_2$, MoSe$_2$, and WSe$_2$ with average particle size less than 2 $\mu$m were obtained from Sigma - Aldrich®. The samples were loaded in a 150 $\mu$m hole of a Symmetric type diamond anvil high pressure cell in a rhenium gasket chamber with ruby grains for pressure measurement. The culet size of the diamonds was 300 $\mu$m and the rhenium gaskets were indented to 50 $\mu$m (average) for drilling. Helium gas was used as the pressure transmitting medium for MoSe$_2$, WS$_2$, and WSe$_2$. In the case of MoS$_2$, Ne gas was used as pressure transmitting medium. High pressure experiments were performed at the high resolution powder diffraction beam line at Sector 16 BM - D of HPCAT at the Advanced Photon Source (APS). A monochromatic x-ray beam from a
double crystal branching monochromatic was focused to a size of 5 x 15 µm using Kirkpatrick-Baez mirrors. A MAR-345 imaging plate was used in the experiments to obtain high quality powder diffraction patterns from the samples. An incident monochromatic x-ray beam of wavelength of \( \lambda = 0.424603 \) Å was used for the experiments. The detector distance was calibrated by collecting a CeO\(_2\) standard. Due to the weak x-ray scattering signal from the sample, longer exposure time of about 5 minutes was necessary to improve the signal to noise ratio. The Debye-Scherrer rings recorded by the MAR imaging plate were, then, integrated using the Fit2D software to obtain one dimensional intensity versus diffraction angle plot [72]. The diffraction patterns were then analyzed with JADE 7.0 commercial software program and Rietveld refinement was carried out using Rietica (LHPM) software package for obtaining structural information [73]. The pressure at the sample site was determined by measuring the shift of the R1 fluorescence line of ruby with an online system at HPCAT and fitting with the standard ruby pressure scale [74]. High pressures were generated using Diamond Anvil Cell at room temperature which is described in the next section. Figure 3.4 illustrates a hutch layout in sector 16-BMD at APS.
Figure 3.4 *In-situ* high pressure powder XRD experiment set up in sector16 BMD, APS

3.2 Diamond Anvil Cell (DAC)

The Diamond Anvil Cell (DAC) is the most versatile and popular device used for generating hydrostatic high pressure. Intrinsic properties of diamond such as hardness and transparent to x-rays and light have enabled researchers to carry out variety of optical studies under high reach pressures up to 400 GPa. The assembly of the DAC is shown in Figure 3.4. Sample under study is placed between the two opposing cutlet faces of a fine quality diamonds with size of the cutlet face approximately 300 µm. Since pressure is applied force per unit area and even a modest force applied to the flat surfaces of the two opposed diamond anvils will generate very high pressure on the small cutlet face. Since, diamond is one of the hardest materials on earth and any poor alignment in cutlet faces will eventually lead to crushing of diamonds. Routine experimental assembly consists of a thin metallic foil called gasket made of either rhenium, or steel, with a hole drilled through it, typically 100-150 µm in diameter, is placed between two diamond cutlets. The
use of gasket serves two purposes: one providing a sample chamber and the other preventing the diamonds from crushing each other. The sample, a pressure gauge and a pressure transmitting medium are placed in the hole in this metal gasket which is sealed by pushing the cutlet faces together [75, 76]. Although there are various types of DAC available, the one used in our experiments was the Symmetric type DAC as shown in the Figure 3.5.

Even though, the pressure applied in a DAC is uniaxial, the use of a pressure transmitting medium enables the sample to be subjected to hydrostatic pressure. The medium chosen should not react with the sample or interfere with the measurement. However, the medium can be liquid, solid or a gas. The pressure media are 4:1 Methanol/Ethanol ratio or silicone gel or inert gases, He or Ne. Also the medium should retain its hydrostatic properties at elevated pressures as high as 50 GPa and use of gaseous medium was appropriate [77]. In all our experiments Helium gas was used as pressure transmitting medium except for the MoS$_2$ sample, where Ne gas was used.
The pressure measurements inside the cell are carried out by reading the pressure exerted on the pressure gauge, ruby grains placed next to the sample. The sample chamber assembly along with ruby grains and pressure media is shown in the Figure 3.4. Ruby has two distinct fluorescence emission lines, $R_1$ and $R_2$, which shifts linearly to higher wavelength values under compression [76]. By reading the amount of shift in $R_1$ line relative to ambient conditions, pressure inside the sample chamber can be estimated. Tiny NaCl crystal grains, whose equation of state (EOS) is very well studied under high pressure, is also used as an alternate to ruby grains for pressure determination.
Figure 3.6 Photograph of a Symmetric Type DAC along with cell screw fittings

Figure 3.7 Snapshot of sample chamber containing sample along with pressure medium and ruby grains
Figure 3.8 Snapshot of R₁ and R₂ lines of ruby grains used for pressure measurement in a DAC [76]

3.3 Raman Spectroscopy

3.3.1 Theory

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source. Unlike in Rayleigh scattering, which is elastic in nature, during inelastic scattering, the frequency of impinging photons (monochromatic light) changes upon interaction with a sample. In absorption, the photons of a particular frequency (ν₀) (laser source) are absorbed by the sample and then reemitted. Characteristically, the frequency of the reemitted photons is either shifted up or down in comparison with original frequency, and this particular phenomenon is called
the Raman Effect as shown in the Figure 3.9. This change in frequency provides vital information about vibrational, rotational energies in molecules, which are very unique in nature and thus, provide molecular fingerprint. Samples can be in the form of solids (powder, particles, thin films etc.), liquid, and gases [78 - 80].

Raman scattering was first discovered by Sir C.V. Raman and K.S. Krishnan in liquids [81]. Classically, Raman effect is based on change in polarizability ($\alpha$) of the molecule due to an interaction with light. Monochromatic light such as laser beam is an electromagnetic (EM) wave which upon interaction with the sample induces a time-varying dipole moment ($P(t)$) which deforms the molecules. The scattered light by the sample can be considered to be radiation from the induced dipole moment, $P(t) = \alpha E(t)$ where $E(t) = E_0 \cos (\nu_0 t)$ is the electric field associated with the incident radiation, $\nu_0$ is the frequency of the incident EM radiation, and $\alpha$ is the polarizability of the sample. Due to periodic deformation caused by the EM radiation, molecules start vibrating with characteristic frequency $\nu_i$. On an average, one in a million photons undergoes an inelastic scattering. And hence, detecting them is practically impossible, unless special measures are taken [82].
3.3.2 Instrumentation

In this section the experimental setup for the Raman spectroscopy is briefly described. A block diagrammatic representation of a typical Raman system is shown in the Figure 3.10. There are four key components to a Raman spectroscopy system:

1. Monochromatic light source (Laser Beam), Filter, Beam Splitters
2. Optics system
3. Gratings and Filters
4. Detector (Photodiode array, CCD).

1. Monochromatic light source (Laser Beam): Monochromatic laser beam in the ultraviolet (UV), visible (Vis) or near infrared (NIR) range is normally used to illuminate a sample. An Ar–ion laser is most commonly used excitation source. A notch filter stationed in the downstream is used to filter out unwanted frequencies due to dispersion.
etc. Usually two or more notch filters are employed to obtain a very high quality laser beam (Monochromatic). Filtered laser beam from notch filter enter into a beam splitter, where the incident beam is split in two identical beams. These identical beams are diverted toward the sample and the detector respectively. Intensity of the laser beam can be modulated by changing the power setting of the laser source.

2. Optics system: In this stage, an interference filter coupled with collimator is used to transmit the essential band to the sample. Typically, interference filter has nearly zero coefficient of absorption for all wavelengths of interest. Typical spot size of the focused laser beam is 0.5 μm.

3. Gratings and Filters: Scattered light from the sample is collected at this stage. Once more a series of notch filters along with holographic gratings are used to eliminate stray light. Purpose of using holographic gratings is to reduce light dispersion caused by the manufacturing defects in the ruled gratings.

4. Detector (Photodiode array, CCD): Historically, photomultiplier tubes (PMT) were used as detectors. However, use of PMT has become obsolete due to their substantial longer data acquisition time. Nowadays, more and more often researchers use multi-channel detectors like Photodiode Arrays (PDA) or, more commonly, a Charge-Coupled Devices (CCD) to detect the Raman scattered light. Sensitivity and performance of modern CCD detectors are rapidly improving. In many cases CCD is becoming the detector of choice for Raman spectroscopy.
3.3.3 High Pressure Raman Experiments

Raman experiments were performed with an Ar-ion laser using an excitation wavelength of 514.5 nm operating at 100 mW. The spectra through the diamond anvil cell were recorded with an ISA Jobin-Yvon U1000 double-grating spectrometer equipped with a charge coupled device (CCD) detector (ISA Spectrum One) with an effective resolution of 2 cm\(^{-1}\). The sample was loaded in a 150 μm hole of a Symmetric Mao-type diamond anvil high pressure cell in a stainless steel gasket chamber with ruby
grains for pressure measurement. The culet size of the diamonds was 300 μm, and the steel gaskets were indented to 50 μm for drilling. A 4:1 methanol and ethanol mixture was used as the pressure transmitting medium in all TMDs of interest excluding WS$_2$. In the case of WS$_2$, Helium gas was used as the pressure transmitting medium. Pressure at the sample site was determined by the standard ruby fluorescence method. The pressure dependence of the active vibrational Raman modes of MX$_2$ was monitored upon increasing pressure at ambient temperature.

Figure 3.11 Snapshot of the Raman set up at UNLV
3.4 High Temperature Powder X-ray Diffraction

High temperature powder x-ray diffraction was performed to understand the effect of heating on the crystal structure stability of TMDs. High resolution Bruker D8 Advance Vario powder x-ray diffractometer with Cu Kα₁ incident radiation (λ = 1.54063 Å) was used for conducting the experiment. The powder sample was loaded into a (corundum) sample holder at ambient pressure conditions and heated up to 500 °C gradually. Snapshot of high temperature powder XRD module along with the ceramic capsule is shown in the Figure 3.12. Diffraction patterns at selected temperatures were collected at six different temperatures 25 °C (ambient), 100 °C, 200, 300 °C, 400 °C, 500 °C, under air. The obtained diffraction patterns were later analyzed by the same software programs used for analyzing high pressure data at HPCAT.
3.5 Energy Dispersive X-ray Diffraction Spectroscopy (EDS)

EDS is a technique used for determining the elemental composition of the specimen. The EDS analysis system works as an integrated feature of a Scanning Electron Microscope (SEM), and cannot operate on its own without the latter. In EDS, the specimen to be analyzed is placed inside the SEM and bombarded with an electron beam. The bombarding electrons collide with the electrons of the specimen atoms, knocking
some of them off in the process. During this process, an electron from outer electronic shell eventually occupies lower electronic shell vacated by an ejected inner shell electron. However, during this transition from high energy state to low energy state, the difference of energy between the two states is radiated as X-ray. Furthermore, the atom of every element releases X-rays with unique energy and hence wavelength during this process. Thus, by measuring the energy present of X-rays released by a specimen during electron beam bombardment, the identity of the atom from which the X-ray was emitted can be established, which is very useful in determining the composition of each element in a compound [83]. Compositions of the as grown molybdenum sulfide films were obtained using a JOEL electron probe microanalyzer (EPMA) model JXA-8900 equipped with scanning electron microscope model JSM-5610, a photograph of which is shown in Figure 3.13.
3.6 Shock compression of TMDs

Additionally, MoS$_2$ and WS$_2$ samples were subjected to shock waves by compressing their powders into a recovery chamber with rhenium driver and flyer. A single stage light gas gun was used to launch the flyer onto the target chamber containing the sample under study. By matching the impedance of the reverberative shock compression, the measured the shock pressure in the rhenium driver for MoS$_2$ and WS$_2$ was 28 and 30 GPa, respectively. The estimated peak shock pressures in the respective compounds were 8 and 10 GPa. Previously reported isothermal bulk modulus and $K_o$ [84] was used for estimating the material specific parameters such as $C$ and $S$. The recovery chamber remained intact during the experiment. High resolution powder x-ray diffraction was
performed on the recovered sample at Sector 16 BM - D of HPCAT at the Advanced Photon Source. A MAR-345 imaging plate was used in the experiments to obtain high quality powder diffraction patterns from the samples. An incident monochromatic x-ray beam of wavelength of $\lambda = 0.424602$ Å for the experiments was used. The detector distance was calibrated by collecting the diffraction pattern of a CeO$_2$ standard under high pressure diffraction experiments.
CHAPTER 4

THIN FILM FABRICATION

In this chapter, the physics of sputtering followed by a brief description of various components of home built three gun sputtering system used for growing metallic sulfides (MoS\textsubscript{2}) are presented. Also, discussed are the results of Field Emission Scanning Electron Microscopy (FE-SEM), EDS and Raman spectroscopy used for calibrating and characterizing as grown sulfides film.

4.1 Sputtering

Sputtering is a process whereby atoms are ejected from the surface of a target material when bombarded with sufficiently high energy particles created via plasma. Ever since its introduction sputtering mechanism has become a dominant technique for depositing metallic films/contacts in IC fabrication. As mentioned earlier in chapter 2, sputtering is one of the variants of physical vapor deposition (PVD). Contrary to traditional form of PVD that is evaporation method, sputtering has the following advantages [51, 52].

Advantages of sputtering over evaporation process:

- Better control over the deposition rate
- Uniformly thin metallic films over large wafers can be accomplished.
- Precision control of alloy composition of deposited thin films.
- Improved grain size, step coverage, and adhesion.
- Many depositions per single target and
- Deposition of non-metallic films possible.

4.1.1 Physics of sputtering process

There are four stages to a sputter process as shown in the Figure 4.1. 1) Ions are produced and directed at the target material to be deposited, 2) these sufficiently high energy ions knock off atoms from the surface of the target material, by breaking the target chemical bonds, 3) fraction of the ejected atom are transported to the substrate as ad atoms and 4) these ad atoms condense and form a thin film. Sputter yield (number of target atoms ejected per incident ion), of the sputtering process depend upon number of things such as, direction of the incident ions, the target material, mass of the ions, and their energy. In recent times, a modified version of sputtering known as DC magnetron is used for achieving higher yield rates [51, 52].

![Figure 4.1 Schematic illustration of sputter deposition process involving Argon gas ions](image-url)
In general, DC (direct current) voltage is applied to the cathode w.r.t. to the anode for sputter deposition of metallic films. But, for depositing nonmetallic or semiconducting films, RF (Radio Frequency) sputter deposition is employed.

4.2 Three Gun Sputtering system

Figure 4.2 illustrates graphical representation of home built three gun sputtering system with all the major components. A typical sputtering system consists of the following modules as shown in the Fig 4.2.

1) Sample preparation and Load lock chamber
2) Sputter chamber (Main Chamber) – where substrate and sputter source reside
3) Vacuum pumps
4) Power supplies (dc or rf)
5) Sputtering gas and flow controllers
6) Monitoring equipment and accessories
1) Sample Preparation and Load lock chamber: Microscopic glass slides cut into 0.5”x1” in dimension were chosen as substrate for growing thin film. The substrates were cleaned with deionized water and ethanol in an ultrasonic bath for 10 minutes each respectively. The substrates were later placed inside load lock chamber using portable glove box so as to avoid any contamination etc. Inside load lock chamber the samples were dried by heating the chamber in nitrogen gas ambience. Subsequently, the load lock chamber was pumped down to a vacuum level as high as $10^{-7}$ torr using a combination of diaphragm and turbo molecular
pump. A manual gate valve (GV) was used to isolate the load lock chamber and the main sputter chamber.

2) Sputter Chamber: Sputtering chamber consist of a sample stage along with sputter sources and Inficon quartz crystal monitor as shown in the Figure 4.2. With the notion that, only two sputter sources (or sputter gun) needed for our experimental work, the existing three gun sputtering system was slightly modified to a two gun sputtering system. A fused silica view port (VP) was attached to the vacant third sputter source slot, which in turn was connected to a camera so as to capture plasma ignition, movement and rotation of sample stage etc. as shown in the Figure 4.2. Each sputter source encloses a metallic circular disc of material to be deposited known as target material. In this work, we limited our scope to the following 2 inch metallic targets (99.9% purity from Plasmaaterials, Inc. USA), molybdenum (Mo) and tungsten (W). Further, the access to each sputter source is controlled by manually open/close shutter mechanism. The average measured source to the sample stage distance is 6.5625 inches.

3) Vacuum pumps: Vacuum technology is an important aspect of the semiconductor technology. Many materials and device fabrication processes are carried out under vacuum conditions. This includes sputtering, ion implantation; plasma etching, chemical vapor deposition, and other fabrication processes. The deposition of electronic thin film materials is done under high vacuum conditions for many reasons, including 1) to increase the mean free path of the dislodged atoms which results in a higher sputtering yield, 2) to eliminate all reactive gases that would react with deposited atoms and cause impurities in the film, and 3) to reduce the
vapor pressure of the deposited material which in turn lowers the evaporation temperature of the deposited material. Vacuum is defined as a region in which the total pressure of all gases is significantly below that of atmospheric pressure. In practice, a vacuum is usually created by eliminating atmospheric gases from a process chamber. The level of vacuum needed depends on the type of process or application. Usually, for applications such as sputtering process, vacuum level as high as $3 \times 10^{-8}$ torr is desired.

As seen from the Figure 4.2 a manual gate valve (GV) separates the main chamber from the high vacuum pumping mechanisms. Before turning on the high vacuum pumps, the main chamber and forline were pumped down to less than 1 mtorr ($1 \times 10^{-3}$ torr) using just the mechanical pump. As soon as the pressure readings at the back end of turbo and molecular drag pumps reached to a sufficiently low level (less than 1 mtorr), the gate valve (GV) bridging the main chamber and high vacuums pumps was opened and thus, enabling all the three pumps to be connected in series and there by leading to an exponential boost in the effective pumping speed of the system. On an average within less than 2 hours of pumping time the measured pressure inside main chamber reached to as low as $10^{-7}$ torr, which was more than the designed maximum vacuum level, $1 \times 10^{-8}$ torr and thus, indicating presence of contaminants. Usually heavy molecules such as hydrocarbons and water vapor get trapped on the surface of the inner walls (stainless steel) of the main chamber, whose presence will compromise the integrity of the deposited thin films. By employing a process called bake out the effect of impurities was minimized. Bake-out is a process which involves heating
the inner walls of the main chamber to elevated temperatures consequently providing sufficient energy to the trapped molecules to escape the adhesive van der Waals forces and therefore accelerates the process of outgassing. In our experimental set-up set of heater lamps located underneath the sample stage was used to bake-out the system to temperatures as high as 60 – 80 °C (measured via IR portable temperature instrument). Additionally, a cryopump, located on the either side of the main chamber was used in conjunction with bake-out process to eliminate substantial traces of water contamination. Cryopumps offers higher water pumping speeds than regular turbo pumps. The final base pressure achieved was 3x10⁻⁸ torr.

4) Power Supplies: Advanced energy MDX 1K series, dc power supply was used to power the sputter sources. It is worth mentioning that sputtering is a highly inefficient process, where in 70% of the power is dissipated as heat in the target head (sputter source) and another 25% is consumed in generating secondary electrons and photons. Overheating of sputter targets could be lead to warpage, delamination of the copper backing plate attached to the target or even target melting and hence, during deposition process a mixture of deionized water and coolant is constantly pumped through the sputter sources to prevent any. Additionally, the same coolant lines were wrapped around the turbo pump, molecular drag pump and quartz crystal monitor to avoid any malfunctioning of the respective instruments due to overheating effects.

5) Sputtering gas and flow controllers: Sputter efficiency (yield) is determined by the choice of sputter gas and the pressure range of operation employed. However,
the choice of gases used for non-reactive sputtering process (as in the case of our experiments) limits the selection of gases to only noble gases. Hence, Argon (Ar) gas (99.999% pure) is generally the most commonly used one, as it is easily available (cost effective) and also has a mass quite comparable to that of most common elemental metals. Mass flow controllers coupled with metering valve (Swagelok) provides precision control over Ar flow rate.

6) Monitoring equipment and accessories: The variations in the pressure inside the vacuum chamber are very broad and hence, varieties of pressure gauges are installed for recording the pressure reading. In our sputtering system, three kinds of gauges, namely, Convectron gauge, hot and cold ionization gauges, and a capacitance manometer gauge were used as shown in the Fig 4.2. Also, a quadrupole residual gas analyzer (RGA) is used to measure the individual partial pressures of gases present inside the main chamber. RGA aids in identifying all gas species (including impurity gases such as water, hydrocarbon etc.) present inside a high vacuum chamber by ionizing, separating, identifying, and measuring the quantity of each. Fig 4.3 is a typical RGA spectrum of the main chamber recorder for the base pressure of $3 \times 10^{-8}$ torr.
Figure 4.3 Snapshot of a typical RGA spectrum taken at base pressure $3 \times 10^{-8}$ torr with

$\text{H}_2\text{O}$, $\text{N}_2$ and $\text{O}_2$ traces
4.3 Deposition procedure

Growth of molybdenum sulfide (MoS$_2$) thin films is a two stage process 1) deposition of molybdenum (Mo) thin film and 2) sulfurization technique.

1) Deposition of Mo thin films: Metallic molybdenum (Mo) thin films were prepared using DC magnetron sputtering, with the base pressure of the system maintained at 3x10$^{-8}$ torr. Depositions were carried out at 100 W, DC power in the presence of Ar gas at a pressure of 2 mtorr. On an average the deposition times were limited to 13 minutes so as to achieve the desired thickness of 100 nm (Standard Deviation ±13 nm). Moreover, during deposition the sample stage was continuously rotated at 5 rpm for better uniformity of the deposited film.
Thickness calibration of as deposited Molybdenum thin films was performed with the help of Inficon quartz crystal monitor in combination with Field Emission Scanning Electron Microscope (FE-SEM). Crystal monitors uses a quartz crystal microbalance (QCM) sensor, which calculates the mass per unit area by measuring the change in the frequency of a quartz crystal sensor onto which some of the sputtered material deposits. The resonance of the crystal is modified proportional to the amount and type of deposited atoms on the surface of the acoustic resonator. The measurement is actually a function of change of mass and therefore the procedure mandates basic information of the material such as type and density. Rate of deposition is determined by taking the first derivative of the shift in resonator frequency. However, since the sensor and the actual substrate are in different locations, they do not receive the same amount of deposition as shown in the Fig 4.5. Therefore, the user must perform a calibration and assign a “tooling factor”. Thus, in this study, deposition of molybdenum films was carried out by setting the tooling factor of QCM to its default value, 100%. For the purpose of calibration, the deposition time was changed to 30 minutes with the remaining all parameters kept unchanged.
Figure 4.5 a) Top view of QCM, sample stage and substrate inside a sputter chamber
b) Snapshot of as deposited Mo thin film via dc sputtering
Cross sectional imaging of as deposited Mo film revealed the actual thickness of the film as shown in the Figure 4.6. As observed from the Figure 4.5 it is obvious that there is a definite variation in thickness of Mo films along the width of the sample and hence, average value was considered. Adjustments were made to the tooling factor by comparing the actual measured thickness (average) with that of the apparent thickness displayed on the QCM screen. The final corrected tooling factor was determined to be 169% for molybdenum (Mo) target. Additionally, same set of experiments and calculations were carried out multiple times to demonstrate process reproducibility capability. Maximum standard deviation measured in the deposited thin film is ± 13 nm.

Figure 4.6 Cross-sectional image of as deposited Mo film captured using FE-SEM
2) Sulfurization: Sulfurization one of the most commonly used process for growing transition metal dichalcogenides such as MoS$_2$, WS$_2$ etc. [86]. As deposited Mo films obtained from sputtering process were placed inside a long fused silica tube along with some flakes of sulfur powder. The tube was flushed with Ar gas several times before eventually outgassed using a miniature diaphragm pump (pressure inside quartz tube approximately 1 mtorr). Subsequently, the tube was air tight sealed and heated to a temperature of 450°C for 60 minutes. At 445°C sulfur boils to form highly energetic vapor phase sulfur molecules which chemically interact with Mo film to form respective sulfide, MoS$_2$. This process is very similar to chemical process deposition (CVD) except that it is being performed inside a sealed quartz tube. Figure 4.7 provides a quick glance of various steps involved in growing MoS$_2$ thin film.

Figure 4.7 Graphical representation of various steps involved during growth process of MoS$_2$ film
4.4 EDS and Raman results

To confirm the growth of sulfide film, MoS$_2$, a series of spectroscopy experiments were performed. Firstly, EDS results proved that the grown films indeed contains molybdenum and sulfur atoms in the required stoichiometry (Note that reading from substrate has been ignored). Secondly, Raman spectroscopy of the as grown sulfide film showed presence of two distinctive and dominant peaks ($A_{1g}$ and $E^{(1)}_{2g}$) around same energy level as opposed to the bulk MoS$_2$ sample as shown in the Figure 4.8 and thus, suggesting that the grown film are undeniably MoS$_2$. From the above two observations we finally conclude that we have successfully built a 3 gun sputtering system for growing transition metal dichalcogenides films.
Figure 4.8 EDS (Upper Panel) and Raman spectroscopy (Lower) results of as grown MoS$_2$ thin film
CHAPTER 5

RESULTS AND DISCUSSIONS

In this chapter the results of high pressure powder X-ray diffraction and Raman spectroscopy of bulk TMDs are provided. Also, discussed is the proposed first order semi–empirical model to explain the observed phase transition in TMDs. In the latter half of the chapter, results of high temperature powder XRD of bulk TMDs materials are discussed.

5.1 Effect of pressure on structural stability of bulk TMDs

As mentioned in the chapter 3, in-situ high pressure experiments were performed at the high resolution powder diffraction beam line at Sector 16 BM - D of HPCAT at the Advanced Photon Source (APS). Results of the high pressure structural data are presented in the following sections.

5.1.1 Pressure induced structural transition in MoS$_2$

The evolution of diffraction patterns with increasing pressure is shown in Figure 5.1. As displayed in Figure 5.1, the diffraction patterns look similar up to 23 GPa except for a gradual shift in peak position towards larger 2$\theta$ values caused by decreasing lattice planar distances. But for pressures around 20 GPa, a new line, next to the (006) lattice plane, emerges corresponding to d-spacing of 1.774 Å ($2\theta$=13.75$^\circ$). Emergence of this line is accompanied by the increase in intensities of the (102) lattice plane and drop in the intensities of the (103) and (105) lines. Further, beyond 26 GPa, it is found that the intensities of the major peaks located at 2$\theta$ = 9.2$^\circ$ and 9.47$^\circ$, and d$_{hkl}$ =2.647 Å and 2.572
Å, respectively, decreased noticeably. In addition, the intensity of the new diffraction peak (102) increased consistently with increasing pressure up to 51 GPa. These changes may suggest the presence of another phase which emerges around 20 GPa, in addition to the parent structure (2Hc – hexagonal, P63/mmc). These changes are also observed in previous studies [11, 30] but however, are not conclusive to be explained by a structural transition. To the best of our knowledge, there are no previous conclusive experimental reports on the nature of the MoS₂ crystal structure under extreme pressure conditions above 26 GPa. Even though a possible electronic or structural phase transition with partial distortion around the same pressure point is suspected by Aksoy et al. [11], they did not provide any further details. Later, a theoretical study on structural stability of MoS₂ by Hromadova et al. indicated a possible structural distortion to a 2Ha type hexagonal phase [30]. Structural refinement at low pressures was carried out assuming presence of only 2Hc phase, with Mo and S atoms positioned at 2(b), 4(f) (z = 0.6118) Wyckoff’s positions, respectively. But for pressures around 20 GPa and beyond, a two phase fitting was carried out as suggested by Hromadova et al. [30]. The refined atomic positions for Mo and S atoms for both for the phases, 2Hc and 2Ha are 2(b), 4(f) (z = 0.6350(1)) and 2(c), 4f (z = 0.9155(7)), respectively. These results are presented in the Table 5.1 and are in excellent agreement with Hromadova [30]. As most of the other diffraction peaks corresponding to the parent phase (2Hc – hexagonal structure, P63/mmc) survived during compression, possible presence of mixed phase region is postulated. Our results agree well with the structural distortion predicted by the ab initio calculations [30]. Hence, from our observations, it can be inferred that under high pressure the crystal structure undergoes a partial distortion resulting in change in atomic positions,
particularly that of Mo atoms. In other words, presence of isostructural $2H_a$ phase due to change in Wyckoff’s position of Mo atoms from 2(c) to 2(b) under high pressure is indicated. Previous theoretical studies performed by Gundelli et al. [86] on a similar compound (FeS$_2$) suggests pressure induced phase transitions more likely for larger $c/a$ ratios and smaller the chalcogen-metal-chalcogen bond angles. Since MoS$_2$ has a high $c/a$ ratio and bond angle less than 90°, the observed phase transitions at elevated pressures in our experiments is consistent.

The analysis of high pressure X-ray diffraction data is indicating that the presence of $2H_a$ crystal structure resulted in successful indexing of all diffraction peaks in the X-ray pattern. The lattice parameters as a function of pressure are shown in Figure 5.2. It is observed from inset in Fig 5.2 that the initial rate of change of lattice constants, $\frac{d(c/c_0)}{dp}$ and $\frac{d(a/a_0)}{dp}$ is rapid and gradually slows down with the increase in pressure up to 23 GPa. In fact, the rate of change of lattice parameter, ‘c’ is higher than that of ‘a’, which suggests that the nature of compression is anisotropic along the c axis. But around the pressure point 26 GPa, interestingly a significant change in the evolution of lattice parameters, particularly lattice constant ‘a’ is observed. The sign of the slope changes from negative to positive and thus, indicating an increase in ‘a’ at that point. Above 26 GPa, the slope of the path traced by the parameter, ‘a’ is different and lower than the initial slope for pressure below 26 GPa. In contrast, the rate of change of lattice constant, ‘c’ with pressure increases rapidly for pressures beyond 26 GPa and hence, suggesting sharp decrease in lattice parameter ‘c’. Since the change in lattice constants at various
pressure points is beyond their calculated individual maximum error bars, the dispersion in data clearly implies a phase transition. The aforementioned inferences are consistent with the earlier reports [11, 30] and strongly suggest that the presence of mixed phase region containing both 2H_c and 2H_a for pressure beyond 17 GPa, with 2H_c as the dominant phase.

Assuming the hexagonal 2H_c phase for all the pressure range 0 – 51 GPa, the unit cell volume as a function of pressure was calculated and is shown in Figure 5.2. It is observed that the unit cell volume decreases gradually upon increase in pressure and no volume collapse was observed (Change is slope of P-V curve indicates a new phase formation, 2H_a). A third order Birch-Murnaghan equation of state (EOS) was used for fitting the P-V data. The maximum error between the calculated and observed pressure values is 0.66 GPa and 1.06 GPa for third and second order B-M EOS fits, respectively. The obtained third and second order bulk module are B_0 = 70±5 GPa (B'_0 = 4.5±0.5) and B_0 = 79± 2 GPa (B'_0= 4.0±0.5). The difference between the calculated second and third order bulk modulus can be ascribed due to fixed B'_0 in case of the former. The bulk modulus obtained in our studies agrees well with the bulk modulus reported by Aksoy et al. [11].
Table 5.1 Rietveld refinement parameters at 2 GPa and 20 GPa for MoS$_2$

<table>
<thead>
<tr>
<th></th>
<th>2 GPa</th>
<th>20 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$2H_c$</td>
<td>$2H_c$</td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.1504(6)</td>
<td>3.0389(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>12.016(4)</td>
<td>11.101(4)</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>103.2(8)</td>
<td>88.7(8)</td>
</tr>
<tr>
<td>Mo (x,y,z)</td>
<td>(1/3,2/3,1/4)</td>
<td>(1/3,2/3,1/4)</td>
</tr>
<tr>
<td>S (x,y,z)</td>
<td>(1/3,2/3,0.6118(9))</td>
<td>(1/3,2/3,0.6350(1))</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>3.4%</td>
<td>5.5%</td>
</tr>
</tbody>
</table>
Figure 5.1 Representative synchrotron powder x-ray diffraction patterns at various pressures for MoS$_2$. The calculated (continuous line), Symbols (data), difference and phase markers obtained from Rietveld refinement are plotted in the figure for 2 GPa and 20 GPa.
Figure 5.2 Pressure versus volume of the lattice cell plot for MoS$_2$. The dotted line is the fit with Birch-Murnaghan equation of state. The inset shows the variation of cell normalized cell parameters as a function of pressure. The error bars are smaller than the size of the symbols.
5.1.2 Structural stability of MoSe$_2$ under high pressure

Figure 5.3 shows the evolution of diffraction patterns of bulk MoSe$_2$ as a function of pressure up to 43 GPa. Preliminary observations indicate gradual shift in peak positions to larger 2θ values with the increase in applied pressure as shown in the Figure 5.3. Further, upon detailed analysis of x-ray patterns, it is noticed that the intensity of the diffraction line (004) increases with the increase in pressure and correspondingly, the intensity of the peak (103) decreases monotonically with increase in compressive force. Additionally, the intensity of (109) peak increases steadily for pressures up to 13 GPa and drops for pressure beyond 13 GPa. Furthermore, the peak associated with (106) reflection at ambient grows into a substantial peak at higher pressures beyond 13 GPa. In the pressure range of study from 0 to 43 GPa, no new peaks emerged and none of the peaks vanished and thus, suggesting no phase transformation in the bulk MoSe$_2$ structure. Unlike in MoS$_2$, where isostructural phase transition, 2H$_c \rightarrow$ 2H$_a$, was observed for pressures between 20 – 30 GPa, MoSe$_2$ structure (2H$_c$) did not exhibit such a phase transition. The absence of structural transition was recently attributed to the higher enthalpy of formation of 2H$_a$ phase compared to that of 2H$_c$ phase in MoSe$_2$ in the pressure range of this study by Riflikova et. al. [34]. Besides, Riflikova et. al. [34] has proposed that electronic transitions could take place in the bulk MoSe$_2$ for compressive forces in the range of 20 – 30 GPa. Our results are in good agreement with the previous studies by Riflikova et. al [34] and Aksoy et al. [12].

Assuming MoSe$_2$ to exhibit 2H$_c$ phase for the entire pressure range, the variation of cell parameters with pressure along with Pressure-Volume (P-V) data are shown in the Figure 5.4. Similar to all other layered compounds, the lattice parameters (‘a’ and ‘c’) in
MoSe$_2$ undergoes differential strains under compression as evident from the Figure 5.4. In fact, it is observed that the structure is more compressive along the c-axis than the a-axis. The pressure – volume data for 2H$_c$ phase of MoSe$_2$ was fitted using the third order Birch-Murnaghan equation of state given by:

$$P = \frac{3}{2} B_0 [(V_0/V)^{7/3} - (V_0/V)^{5/3}] \times \{1 + 3/4(B_0' - 4) \times [(V/V_0)^{-2/3} - 1]\}$$

(5.1)

where $B_0$ is the bulk modulus and $B_0'$ is the pressure derivative. Using least squares fitting, $B_0 = 67 \pm 6$ GPa and $B_0' = 4.6 \pm 0.4$ were obtained. From Figure 5.4, it is observed that the unit cell volume decreases gradually upon increase in pressure without any sudden collapse.
Figure 5.3 Representative Synchrotron powder x-ray diffraction patterns at various pressures for MoSe$_2$

Comparing the current results with the previously studies by Aksoy et al. [12], it is observed that there is an obvious difference between our results for $B_0$ and $B_0'$ and theirs. The reported bulk modulus and its pressure derivative by Aksoy et al. [12] are $45.7 \pm 0.3$ GPa and $11.6 \pm 0.1$, respectively. The discrepancy between the results in the obtained bulk moduli can be attributed to use of different pressure derivatives, $B_0'$. Besides, studies
by Lee et al. [87] and Hofmeister [88] proved the existence of strong correlation between $B_0$ and $B_0'$ for any physically realizable system. Further, Hofmeister [88] proved that pressure derivative of values beyond the range of 3.8 – 8.0 will result in physically unrealistic potentials and are inappropriate for finding EOS. Thus, we assume that $B_0' = 11.6 \pm 0.1$ reported in ref [12] is probably unreasonable. In addition to the aforementioned reasons, choice of pressure transmitting medium used in DAC plays a significant role in determining EOS of a system. Aksoy et al. [12] used methanol and ethanol mixture as a pressure medium, which eventually loses its hydrostatic nature for pressure beyond 12 GPa. In contrast, in our work, helium gas (He) was used which keeps the pressure inside the DAC hydrostatic.
Figure 5.4 Pressure versus volume plot for MoSe$_2$. The dotted line is the fit with Birch-Murnaghan equation of state. The inset shows the variation of cell normalized cell parameters as a function of pressure. The error bars are smaller than the size of the symbols.
5.1.3 Structural stability of WS$_2$ under high pressure

Figure 5.5 shows diffraction patterns of WS$_2$ as a function of pressure up to 52 GPa. It is observed that the peak positions shift continuously to higher 2θ values due to continuous decrease of interplanar spacing under applied pressure. As illustrated in the Figure 5.5 for the entire pressure range, no new peaks emerged and none of the existing ones disappeared, thus, suggesting no pressure induced phase transformation, which inconsistent with Selvi et al. [13]. The pressure dependency of unit cell parameters of WS$_2$ is shown in the inset in Figure 5.5.

As the hexagonal 2H$_c$ structure persists for the entire pressure range of 0 – 52 GPa, the unit cell volume and lattice parameters of WS$_2$ as a function of pressure were calculated based on the $P6_3/mmc$ structure and is shown in the Figure 5.6. It is observed that the unit cell volume decreases gradually upon increase in pressure without any sudden collapse. A third order Birch-Murnaghan equation of state was used for fitting the P-V data. The bulk modulus was obtained as $B_0 = 63\pm5$ GPa ($B'_0 = 6.5\pm0.1$). The bulk modulus obtained in our studies agrees well with the bulk modulus reported earlier [13]. As observed from the Figure 5.6 at the highest pressure point achieved, 52 GPa, the change along c-axis is around 13.5 %, which is almost twice the change along a-axis (7%). This suggests that the c-direction is more compressible than the a-direction due to anisotropic reduction in inter layer spacing, S-S planes, which are held together by weak Van der Waals forces. It is also interesting to compare the high pressure x-ray diffraction results on WS$_2$ with the structural analogue MoS$_2$, which has been investigated recently by our group [89]. The MoS$_2$ compound is found to undergo a pressure induced structural distortion from the ambient pressure 2H$_c$ type hexagonal phase to a high pressure 2H$_a$ type
phase as predicted by theory [30]. Co-existence of both phases was observed in MoS$_2$ above 20 GPa. Such a distortion was not observed in the x-ray diffraction results obtained for WS$_2$. Comparing the bulk modulus values of both compounds, WS$_2$ is found to be relatively softer and more compressible compared to MoS$_2$. Further theoretical investigations are necessary to understand the compression mechanism in these compounds.

Figure 5.5 Representative Synchrotron powder x-ray diffraction patterns at various pressures for WS$_2$
Figure 5.6 Pressure versus volume plot for WS$_2$. The dotted line is the fit with Birch-Murnaghan equation of state. The inset shows the variation of cell normalized cell parameters as a function of pressure. The error bars are smaller than the size of the symbols.
5.1.4 Structural stability of WSe\textsubscript{2} under high pressure

Figure 5.7 shows the evolution of diffraction patterns of bulk WSe\textsubscript{2} as a function of applied hydrostatic pressure up to 50 GPa. As seen in the case of other TMDs of interests, the peak positions in WSe\textsubscript{2} move to higher 2θ values gradually with increase in the applied compressive force. Upon further analysis, it is observed that the intensities of the dominant peaks such as (100), (103), and (203) drop with increase in pressure. Besides, it is noticed that reflections such as (104), (006) evolve with increase in applied pressure. Moreover, due to non-linear peak shift w.r.t to the applied pressure, diffractions lines corresponding to the peaks (106), (110), and (008) move closer. At 16 GPa, these three reflection lines merge together form a peak with three shoulders as shown in the Figure 5.7. Additionally, no new peaks were detected suggesting absence of any pressure induced phase transformation, which is consistent with the observation of Selvi et al. [14].

Assuming WSe\textsubscript{2} to exist in 2H\textsubscript{c} phase for the entire pressure range 0-50 GPa, the variation of lattice parameters and unit cell volume as a function of pressure was calculated using X-ray diffraction data, as shown in the Figure 5.8. As observed from the figure, it is clear that there is no sudden collapse in the unit cell volume. A third order Birch-Murnaghan equation of state was used for fitting the P-V data. The obtained bulk modulus is, $B_0 = 46\pm6$ GPa ($B'_0 = 7.8\pm0.9$). The bulk modulus obtained in our studies agrees well with the bulk modulus reported earlier [14]. It is important to point out that the calculated bulk modulus and its pressure derivative differ from the values reported by Selvi et al. [14]. The deviation in the obtained bulk moduli can be attributed to the fact that the pressure transmitting media used in two studies are different. In this work, helium
gas was used as opposed to methanol and ethanol mixture used by Selvi et al. [14].

Besides, from the Fig 5.8 inset, it is noticed that the normalized ‘c’ lattice parameter exhibits higher compressibility relative to the ‘a’ lattice parameter indicating that the material experiences anisotropic strains under pressure.

Figure 5.7 Representative Synchrotron powder x-ray diffraction patterns at various pressures for WSe$_2$
Figure 5.8 Pressure versus volume plot for WSe$_2$. The dotted line is the fit with Birch-Murnaghan equation of state. The inset shows the variation of cell normalized cell parameters as a function of pressure. The error bars are smaller than the size of the symbols.
5.2 Semi empirical modeling of structural stability of TMDs under pressure

In the following section, based on the observed experimental data, a model for predicting the phase transition in TMDs of interest under high pressure conditions is proposed. In this first order approximation model, effects such as bond hybridizations, delocalization of electronic states and other quantum effects etc. are ignored. The role and significance of these ignored effects should be studied and understood.

Transition metal dichalcogenides (TMDs) considered under current study belong to a group of layered compounds with generic chemical formula MX$_2$, where M is a transition metal (Mo, W) atom and X is one of the chalcogens, S, Se. Structurally most of TMDs crystallize to layered hexagonal, 2H$_c$ structure under ambient conditions. Pictorially, the 2H$_c$ structure can be viewed as a stack of X-M-X, which are loosely coupled together by weak Van der Waals forces. Within each slab, hexagonal arrays of metal and chalcogen atoms are bonded by strong covalent bonds as shown in the Figure 5.9.
5.2.1 Bond Polarization

Usually, depending upon the difference in electronegativities ($\Delta E$) of the atoms involved in covalent bond, the bonds can be broadly classified into non-polarized and polarized covalent bonds. Suppose if the difference in electronegativity is zero, $\Delta E = 0$ as in the case of the H-H bonding in H$_2$ diatomic molecule, then it is considered to be a non-polarized covalent bond and in this case of pure covalent bond, the electron cloud is equally shared between the bonding atoms and hence, the centroid of the electron density lies at the center of the bond. If $\Delta E \neq 0$ then the electron cloud density is not equally
distributed between the two atomic nuclei but, is distorted towards the more electronegative atom and hence, resulting in creation of a polarized covalent bond. With the effect of polarization, though covalent bonds are not ionic, a dipole moment is created between the bonding atoms due to creation of partial positive (+$$\delta$$) and negative charges (−$$\delta$$) on either side of the bond. Also, the centroid of the bond (electron density) is shifted more towards the electronegative atom [90 - 93]. Figure 5.10 provides a graphical representation of polarization of covalent bond. Ionic compounds such as in NaCl have a electro-negativity difference of two.

By the virtue of their place in the periodic table, next to the halides, chalcogens such as S and Se have relatively high electronegativities when compared to that of Mo and W metals. Elemental and net molecular electro-negativities of interest are provided in Table 5.2. From the Table 5.2, it is obvious that MoS$_2$ has the highest electronegativity difference ($$\Delta$$E), followed by MoSe$_2$, WS$_2$, and WSe$_2$. This implies that the Mo-S bond in MoS$_2$ is relatively more polarized and directional when compared to that of others, but much less polarized compared with NaCl. Thus, for all these four compounds in the first order approximation, it can be assumed that the electron clouds that participate in the covalent bond are at the center of the bond.
Table 5.2 List of elemental electro-negativities and electro-negative difference in various TMDs

<table>
<thead>
<tr>
<th></th>
<th>Element</th>
<th>E (Pauling Scale)</th>
<th>Molecule</th>
<th>$\Delta E = E_{Ch} - E_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mo</td>
<td>2.16</td>
<td>MoS$_2$</td>
<td>0.42</td>
</tr>
<tr>
<td>2</td>
<td>S</td>
<td>2.58</td>
<td>MoSe$_2$</td>
<td>0.39</td>
</tr>
<tr>
<td>3</td>
<td>Se</td>
<td>2.55</td>
<td>WS$_2$</td>
<td>0.22</td>
</tr>
<tr>
<td>4</td>
<td>W</td>
<td>2.36</td>
<td>WSe$_2$</td>
<td>0.19</td>
</tr>
</tbody>
</table>

5.2.2 Effect of Pressure: Observations and Proposed Model

In general, under high pressure atoms in molecular solids experience a constant compressive force, dynamically pushing neighboring atoms closer to each other and thus, reducing the volume of the unit cell. A similar behavior was observed in the case of MX$_2$. 

Figure 5.10 Graphical representation of a) Non - polarized bond b) Polarized bond
materials of concern in this study when subjected to high pressures in the range of 0 – 50 GPa. But, due to the anisotropic structural make up of these materials, it was noticed that the change in unit cell parameters under pressure was asymmetrical. In other words lattice parameters such as ‘a’ and ‘c’ (in hexagonal structure type) undergo varying levels of strain. Figure 5.11 shows an example of variation of the inter layer anion-anion distance, $d_{x-x}$, for all the four compounds as a function of applied hydrostatic pressure. Actual experimental data are represented with colored symbol and the dotted lines represent curve fitted data.

![Graph showing variation of interlayer distance as a function of pressure](image)

Figure 5.11: Variation of Interlayer distance, $d_{x-x}$ in TMDs as a function of applied pressure

From Figure 5.11, it is observed that under ambient conditions the interlayer distance, $d_{x-x}$ is lowest for MoS$_2$. Also, it is observed that the interlayer distance for all the four materials decrease monotonically with the increase in applied hydrostatic pressure.
Analysis of the x-ray diffraction data shows that MoS$_2$ undergoes a phase change from 2H$_c$ to 2H$_a$ at around 20 GPa. A pictorial depiction of 2H$_a$ and 2H$_c$ is shown in Figure 5.12. This is also confirmed to be true by other researchers [11, 30, and 34]. Additionally, it is observed that the other three materials do not show any phase transformation in the pressure range of the experiments (0 to 50 GPa).

![Diagram of 2H$_a$ and 2H$_c$]

Figure 5.12 Structural description of MoS$_2$ unit cells, 2H$_a$ and 2H$_c$ type

Though 2H$_a$ is a polymorph of 2H$_c$ structure with a characteristic variation in stacking of hexagonal arrays of metal (Mo) and chalcogen (S) atoms as shown in Figure 5.12, the difference in structure and atomic interactions between the polymorphs are identified as follows.
1. In $2H_c$ structure, Mo atom from the top layer is above S atom in the bottom layer, whereas in $2H_a$ arrangement, Mo atom from the top layer is above Mo atom in the bottom layer.

2. Inter-layer S-S Van der Waal bond distances stay the same, but the orientation changes.

3. The covalent bond interaction distance (Mo-S) between the top and bottom layers is much closer in $2H_c$ compared to $2H_a$ as illustrated in the Figure 5.13 and 5.14.

4. The inter-layer covalent bond electronic clouds interaction in $2H_a$ is more shielded by the two inter-layer S nuclei in between than in $2H_c$ structure where the electronic clouds interact much more directly.

5. This results in less repulsive interaction energy in $2H_a$ than in $2H_c$.

6. The covalent bond electronic clouds are closer to anion in $2H_c$ - MoS$_2$ compared to all other materials due to larger difference in the electronegativity ($\Delta E$) (see Fig 5.13).

7. Assuming that the centroid of the covalent bond electronic clouds to be in the middle of the bond ($\Delta E =0$), the centroid-centroid distance, $D_{c1-c2}$ (as shown in Figure 5.15) was calculated using trigonometry for all materials as a function of pressure and shown in Figure 5.16.

8. $D_{c1-c2}$ is the smallest for MoS$_2$ for the whole pressure ranges.

9. On set of phase transition from $2H_c$ to $2H_a$ occurs in MoS$_2$ when $D_{c1-c2}$ reaches $2.208(4)$ Å corresponding to 20 GPa.
10. For all other materials, $D_{c1-c2}$, has not reached this critical value for repulsive electrostatic energy for the whole pressure range of the experiment.

11.

**MoS$_2$ - 2H$_c$ Type Unit Cell**

- $-\delta$, $+\delta$ : Bond Polarization.
- $d_{s1,s2}$: Interlayer distance between centroids of electronic cloud of each MoS$_2$ molecule.

Figure 5.13 Graphical representation of covalent bond electron cloud interaction in MoS$_2$

2H$_c$ type unit cell
-δ, +δ: Bond Polarization.

\(d_{s1-s2}\): Interlayer distance between centroids of electronic cloud of each MoS\(_2\) molecule.

Figure 5.14 Graphical representation of covalent bond electron cloud interaction in MoS\(_2\)

2H\(_a\) type unit cell
**2H\textsubscript{c} Unit Cell Structure**

M – Metal (Mo or W)

X – Chalcogen (S or Se)

d\textsubscript{X1-X2} - Interlayer X – X distance

d\textsubscript{M,X} – Metal to Chalcogen covalent bond length

θ: X – M – X bond angle

α : Interlayer X – M – X bond angle

D\textsubscript{M,X} – Interlayer Metal to Chalcogen distance

● - Electron Cloud Centroid

D\textsubscript{c1-c2} - Interlayer Centroid – Centroid Distance

**Trigonometry Calculations:**

\[
\alpha = \frac{180^\circ - \theta}{2}
\]

*Using law of Cosines to the \( \Delta^e \) with \( \alpha \), the unknown distance, \( D_{M-Ch} \) is:*

\[
D_{c1-c2} \cong D_{M-X} = \sqrt{(d_{M-X})^2 + (d_{X1-X2})^2 - 2d_{M-X}D_{X1-X2}Cos(\alpha)}
\]

Figure 5.15 Illustration of various bond angles, bond length; inter layer distances and trigonometry calculations for the proposed model in 2H\textsubscript{c} – MoS\textsubscript{2} unit cell
Figure 5.16 $D_{c1-c2}$ values calculated using experimental data of atom-atom distances and angles using trigonometry for all materials over the pressure range of 0 - 50 GPa. Symbols represent the experimental data and the curves are fitted using exponentials given by equation (5.2)

Based on the observations 1 to 10, the following model for the phase transition is proposed. As the hydrostatic pressure increases, atoms are squeezed together increasing repulsive electro-static energy of interaction between the covalent bonds in adjacent layers in the 2H$_c$ structure. When the centroid-centroid distance, $D_{c1-c2}$, reaches 2.208(4) Å, at around 20 GPa in MoS$_2$, the repulsive electrostatic energy reaches a level such that it is higher than the energy of the molecule when it adopts 2H$_a$ structure. At this juncture, molecular system is in highly energetic and unstable state and subsequently, leading to atomic rearrangement to form energetically stable, 2H$_a$ type structure. The reason for lowering of this energy is that the covalent bond electron clouds interaction are shielded by S anion nuclei in 2H$_a$ compared 2H$_c$ (compare Figure 5.13 and 5.14). This reduces the
repulsive electrostatic energy in 2H$_a$ compared to 2H$_c$. Thus, MoS$_2$ undergoes the phase transition at around 20 GPa.

The critical value of parameter, $D_{c1-c2}$ for phase transition is 2.208(4) Å given that the electro-negativities ($\Delta E$) are not very different for all these materials. In the pressure range of the experiments, this parameter does not reach this critical value for MoSe$_2$, WS$_2$ and WSe$_2$ (Figure 5.16). In other words, the covalent bond electron cloud repulsive interaction energy is less than that of energy required to form 2H$_a$ structure even at the highest pressures attained in the experiments. That is why there is no 2H$_c$ to 2H$_a$ phase transition observed in these materials.

By means of curve fitting the experimental data of $D_{c1-c2}$ versus $P$ (GPa) to the form as shown in the equation (5.2) and also assuming no other effects causes the phase transition, the predicted pressure range for $D_{c1-c2}$ to reach critical value (2.208 Å) were obtained as listed in the Table 5.3. From the Table 5.3, it can be concluded that compressive forces of the order of minimum 90 GPa is required to cause any pressure induced phase transition in these materials and which is well beyond the highest pressure attained in this study (50 GPa). And hence, we do not observe any phase transformation in these materials.

$$D_{c1-c2} = ae^{bP} + ce^{dP}$$  \hspace{1cm} (5.2)

where $a$, $b$, $c$ and $d$ are constants and $P$ is the applied pressure in GPa. List of constants are tabulated in the Table 5.4.
Table 5.3 Pressure range (calculated using equation (5.2) in which the $2H_c$ to $2H_a$ phase transition occurs for WS$_2$, MoSe$_2$ and WSe$_2$

<table>
<thead>
<tr>
<th>S.no</th>
<th>TMD</th>
<th>Pressure Range (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>WS$_2$</td>
<td>90 - 100</td>
</tr>
<tr>
<td>2</td>
<td>MoSe$_2$</td>
<td>110 - 120</td>
</tr>
<tr>
<td>3</td>
<td>WSe$_2$</td>
<td>170 - 180</td>
</tr>
</tbody>
</table>

Table 5.4 List of constants for equation (5.2) used for curve fitting the experimental data

<table>
<thead>
<tr>
<th>S.no</th>
<th>TMD</th>
<th>$a$ (Å)</th>
<th>$b$ (1/GPa)</th>
<th>$c$ (Å)</th>
<th>$d$ (1/GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MoS$_2$</td>
<td>0.03481</td>
<td>-0.0961</td>
<td>2.241</td>
<td>-0.00096</td>
</tr>
<tr>
<td>2</td>
<td>WS$_2$</td>
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<td>2.589</td>
<td>-0.00146</td>
</tr>
<tr>
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<td>MoSe$_2$</td>
<td>0.07799</td>
<td>-0.1937</td>
<td>2.743</td>
<td>-0.00192</td>
</tr>
<tr>
<td>4</td>
<td>WSe$_2$</td>
<td>0.13210</td>
<td>-0.0967</td>
<td>2.695</td>
<td>-0.00113</td>
</tr>
</tbody>
</table>
5.3 High pressure Raman spectroscopy results

As mentioned in the chapter 3, *in-situ* high pressure Raman measurements were conducted at room temperature using a symmetric diamond anvil cell (DAC) with 300 μm culet anvils at HiPSEC (High Pressure Science and Engineering Center) facility, UNLV. Results and their interpretations of the high pressure Raman spectroscopy of MX$_2$ are presented in this section.

5.3.1 High pressure Raman results of MoS$_2$

MoS$_2$ belongs to D$^4_{6h}$ ($P6_3/mmc$) space group and is iso-symmorphic isomorphic with MoSe$_2$, WS$_2$, and WSe$_2$. Since MoS$_2$ is a nonlinear molecule and there are six atoms per unit cell (N=6) and hence, 3N-6 = 12, normal modes of vibration exits at the center of hexagonal Brillouin zone and given by the following equation:

\[
\Gamma = A_{1g} + 2A_{2u} + 2B_{2g} + B_{1u} + E_{1g} + 2E_{1u} + 2E_{2g} + E_{2u}
\]  

(5.3)

Of the 12 modes, $A_{1g}$, $E_{1g}$, $E_{1}^{2g}$, and $E_{2}^{2g}$ are Raman active and the remaining are Infrared absorption and acoustic. In plane, $E_{1}^{2g}$, and out of plane, $A_{1g}$, are the two most commonly studied internal molecular modes under pressure. The two external modes, namely, rigid modes, $E_{1g}$, $E_{2g}^2$ are associated with movement of the layers. In the present work, we limit our study to two internal modes of vibrations. Under ambient pressure conditions, the energy corresponding to the two internal lattice vibrations are, $E_{1}^{(1)}_{2g}$ at 383.4 cm$^{-1}$, and $A_{1g}$ at 408.5 cm$^{-1}$, respectively. The observed pressure dependence of these modes is shown in the Figure 5.18. It is observed that both $E_{1}^{(1)}_{2g}$ and $A_{1g}$ modes red shift with increase in applied hydrostatic pressure. Further, from the data, it can be
inferred that the initial rate of shift of vibrational frequencies is rapid with pressure, but for pressures above 5 GPa, the rate of increase decreases. Moreover, it is observed from plot that both the modes more or less vary linearly with pressure and are in good agreement with the data of Bangall et al. [39] and Sugai et al. [38].

Interestingly for pressures between 17 to 26 GPa, when both the phases, \(2H_c\) and \(2H_a\) are proposed to co-exist (see X-ray diffraction results in section 5.1.1) the one of the Raman modes, i.e., in plane, \(E^{(1)}_{2g}\) peak broadens significantly along with reduced intensity. Further, in the background, a new peak is observed to emerge at around 26 GPa, corresponding to 432 cm\(^{-1}\) wave number and it is suspected that this is due to the presence of another phase, \(2H_a\) along with the original \(2H_c\) phase. Also recent studies by Tsachi Livneh et. al. [42] confirmed the existence of this new peak namely,’d band’ between the 19 to 31 GPa pressure range as shown in the Figure 5.17 and Figure 5.18. On the other hand, \(A_{1g}\), out of plane Raman mode red shifts systematically as expected [38, 39] with significant reduction in the peak intensity and peak broadening. These observations are consistent with the proposed emergence of a second MoS\(_2\) phase, \(2H_a\) between 17 to 26 GPa (based on the X-ray diffraction results presented in section 5.1.1), with original \(2H_c\) phase being the dominant one.
Figure 5.17 Pressure dependence of the Raman active vibrational modes $A_{1g}$ and $E^{(1)}_{2g}$ in MoS$_2$ bulk.
5.3.2 High pressure Raman results of MoSe$_2$

Similar to MoS$_2$, bulk MoSe$_2$ also crystallize with a layered, non-linear 2H structure and hence, is expected to be Raman active. Bulk MoSe$_2$ has two prominent internal Raman modes, in plane mode, E$_{2g}^{(1)}$ at 287 cm$^{-1}$ and out of plane mode, A$_{1g}$ at 241 cm$^{-1}$, respectively. But due to relatively low intensity of the E$_{2g}^{(1)}$ mode coupled with the experimental limitation, the Raman results yielded presence of only A$_{1g}$ mode at 241 cm$^{-1}$. Figure 5.19 (top) shows the variation of the out of plane mode, A$_{1g}$ as function of applied pressure. From the figure, it is clear that the A$_{1g}$ mode moves to higher wavelengths (red shifts) with increase in compressive force (hydrostatic pressure). Besides, it is observed that the rate at which the A$_{1g}$ mode red shifts decreases gradually with increase in pressure as shown in the Figure 5.19 (bottom). Maximum rate of shift in peak position is
observed at pressure point 1 GPa. With no anomalies observed except the reduced intensity of the A\textsubscript{1g} mode up on increase in compressive stress, high pressure Raman results indicate that bulk MoSe\textsubscript{2} does not undergo any pressure induced phase transitions. Our results are in good agreement with previously published data [38, 41].
5.3.3 High pressure Raman results of WS$_2$

For a nonlinear molecule such as WS$_2$, the number of Raman active modes is given by, $3N-6$, where $N$ is the number of atoms in the compound. WS$_2$ exhibits three Raman modes as expected and these three modes are represented as in-plane, $E_{1g}$, $E^{(1)}_{2g}$ and out of plane $A_{1g}$ along with rigid layer mode, $E^{(2)}_{2g}$, respectively, as shown in the Figure 5.20. Out of these modes, WS$_2$ consists of two active internal Raman vibrational modes, $E^{(1)}_{2g}$ at 355 cm$^{-1}$, in plane and $A_{1g}$ at 421 cm$^{-1}$, out of plane, respectively. The observed pressure dependence of these modes is shown in the upper panel of Figure 5.21. In this plot, at each pressure point, the data set used for plotting was normalized with respect to the $E^{(1)}_{2g}$ peak value. From the plot, it can be seen that both $E^{(1)}_{2g}$ and $A_{1g}$ modes red shift accompanied by peak broadening with increase in applied hydrostatic pressure. Strangely, the intensity of $E^{(1)}_{2g}$, in plane mode drops considerable relative to out of plane mode, $A_{1g}$ with the increase in pressure. Though, the cause for this behavior is unclear, it is suspected that a second order electronic transition may cause such changes without explicit structural re-arrangement. As seen from the Figure 5.21, the pressure response of peak position shift of $A_{1g}$ mode almost twice that of $E^{(1)}_{2g}$, which is attributed to the higher compression along c-axis direction. Moreover, with the absence of any anomaly in the observed behavior of the vibration modes under pressure combined with high pressure X-ray diffraction results discussed in the section 5.1.3, it is inferred that the material WS$_2$ does not under go any phase transformation under static high pressures. Our results are in good agreement with reported data [41].
Figure 5.20 Pictorial representations of active Raman modes of layered TMD, WS$_2$
Figure 5.21 Pressure dependence of the Raman active vibrational modes, $A_{1g}$ and $E^{(1)}_{2g}$ in WS$_2$ compound
5.3.4 High pressure Raman results of WSe$_2$

WSe$_2$ belongs to a family of layered non–linear compounds similar to that of WS$_2$ and hence, has two active Raman modes, namely, in plane, $E^{(1)}_{2g}$ and out of plane, $A_{1g}$ mode, respectively. At ambient pressure condition, these two dominant modes are clustered close to each other, thus forming a peak with a shoulder as shown in the Figure 5.22. The observed pressure dependence of these modes is shown in the upper panel of Figure 5.22. The plot is obtained by normalizing each data point with respect to the $A_{1g}$ peak intensity for the corresponding pressure points. From the plot, it is observed that both modes, $E^{(1)}_{2g}$ and $A_{1g}$ red shift, i.e., to move to higher wave number with increases in applied pressure. Besides, it is observed that the distance of separation between the two modes increases gradually with the increase in pressure, due to difference in the rate of change of peak positions of the two modes as shown in the Figure 5.22 (lower panel). Moreover, the intensity of the peaks of the two modes increases and become distinct with increase in pressure. Further work has to be performed to study this unusual behavior. With no irregularities found, high pressure Raman results suggests no phase induced transition in WSe$_2$, which is consistent with the x-ray diffraction data of section 5.1.4. Our results are consistent with previous studies [41].
Figure 5.22 Pressure dependence of the Raman active vibrational modes, $A_{1g}$ and $E^{(1)}_{2g}$, in WS$_2$ compound
5.3.5 Lattice Dynamics in TMDs

In the following section high pressure Raman data in conjunction with the high pressure X-ray diffraction data is used to determine the lattice dynamics of TMDs such as intralayer force constants between metal-ligand ($\gamma$) and ligand-ligand ($\beta$) as shown in the Figure 5.23. Though various models have been proposed in the past [40, 93, 94] to explain the lattice dynamics in TMDs, in the present work, Born-von Karman model proposed by Bromley [40] is adopted. Bromley’s model is built under the notion that the interactions between atoms in MoS$_2$ compound are restricted to its nearest neighbor. In other words, analysis of single sandwich layer of MoS$_2$ is sufficient enough to determine relationship between the frequency ($\omega$) of optical phonons and force constants, $\gamma$ and $\beta$, given as follows:

$$\omega^2(E_{2g}^{1}) = \frac{3\gamma sin^2 \theta}{\mu} \quad (5.4)$$

$$\omega^2(A_{1g}) = \frac{3\gamma cos^2 \theta + 2\beta}{m_2} \quad (5.5)$$

where $\mu$ is the reduced mass, $\mu = \frac{2m_1 m_2}{m_1 + m_2}$ and $m_1$ and $m_2$ are the masses of the molybdenum atom and sulphur atom, respectively.

In the present work, Bromley’s model has been extended to other TMDs such as WS$_2$ and WSe$_2$ in determining respective lattice dynamics. Using pressure and frequency data from high pressure Raman experiments along with calculated angle ‘$\theta$’ from high pressure X-ray diffraction; we estimated the force constants, $\gamma$ and $\beta$ from the equations (5.4) and (5.5).
Figure 5.23 2H$_c$ Unit Cell Structure

M – Metal (Mo or W)
X – Chalcogen (S or Se)

$\theta$: M – X – X bond angle

$\alpha$: Intralayer X – M – X bond angle

$\gamma$, Force constant in x direction (In plane)

$\beta$, Force constant in 2b direction (Out of plane)

$\beta_1$, Force constant in g direction (Out of plane)

From $\Delta^\alpha$ with $0, \theta = 90 - \alpha/2$

Figure 5.23 2H$_c$ – Unit cell of MX$_2$ showing the orientation of various force constants

Figure 5.24 shows the variation of force constants as function of applied pressure. From the Figure it is clear that the value of force constants increases gradually with increase in applied pressure and moreover, the intralayer metal (M) – ligand (Ch) bonding ($\gamma$) is stronger than the intralayer ligand – ligand ($\beta$) bonding. Thus, reinforcing the fact that the bond formed between metal – ligand, is covalent bond involving ‘s’ and ‘p’ orbital hybridization from the respective metal and ligand atoms. Besides, it noticed
that the metal - ligand bond is highest in the case of MoS$_2$ and lowest for WSe$_2$. Our results are in good agreement with the reported values [41]. Forces constants for MoSe$_2$ compound could not obtained due to unavailability of information on, in plane, $E^{(1)}_{2g}$ Raman mode. Also, we could not evaluate interlayer force constant, $\beta_1$ due to absence of information on $E^{(2)}_{2g}$, rigid mode (approximately less than 100 cm$^{-1}$).

Figure 5.24 Variation of force constants as a function of pressure. The error bars are smaller than the size of the symbols

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5.4 Structural stability at high temperatures

As cited in the chapter 3, in-situ high temperature powder X-ray diffraction experiments were performed using high resolution Bruker D8 Advance Vario powder x-ray diffractometer with Cu Kα1 incident radiation (λ = 1.54063 Å) at UNLV. Results of high temperature powder XRD of bulk TMDs of interest are presented in the following section.

5.4.1 High Temperature XRD of bulk MoS\textsubscript{2}

Powder X-ray diffraction patterns for MoS\textsubscript{2} samples at ambient and at temperatures in the range of 100 °C to 500 °C are shown in the Figure 5.25. At ambient conditions, MoS\textsubscript{2} crystalizes in the hexagonal space group \textit{P6}_3/mmc. The XRD patterns collected showed the sample in a single phase and the lattice parameter were refined to a = 3.159(8) Å and c = 12.298(3) Å. From the Figure 5.25, it is clear that upon heat treatment, the relative 2θ position of the diffraction peaks remained virtually unchanged with respect to temperatures up to 500 °C. The additional weak peaks (less than 5%) in the temperature dependent XRD pattern may be due to surface oxidation of the sample due to residual air in the ampule (approximately 1 torr) since the predominant lines showed no changes upon increasing temperature. This leads us to the conclusion that the crystal structure of MoS\textsubscript{2} is stable up to 500 °C under ambient pressure conditions. This result is in good agreement with the earlier work [50]. Further, it was noticed that for temperatures above 500 °C, MoS\textsubscript{2} oxidizes to form MoO\textsubscript{3}, evident from the emergence of diffraction lines associated with MoO\textsubscript{3}. Our results are in good agreement with the previously published data [49]. Interestingly, at sufficiently high temperatures around 700 °C, the oxide, MoO\textsubscript{3} under vacuum decomposes (high vapor pressure) and we could not recover the sample.
from the sample cell container. It was observed that the initial Wyckoff’s positions of Mo and S atoms at 2c and 4f, respectively remained unperturbed with increase in the temperature up to 500 °C.

Figure 5.25 X-ray diffraction patterns of MoS$_2$ at ambient and elevated temperatures.

The top panel shows the measured and the calculated MoS$_2$ pattern using Rietveld structure refinement at ambient temperature. The unit cell is displayed; the large solid spheres represent Mo, and smaller spheres represent S atoms.
5.4.2 High Temperature XRD of bulk MoSe$_2$

Figure 5.26 illustrates powder XRD pattern of bulk MoSe$_2$ as a function of temperature. Just as MoS$_2$, under ambient conditions the XRD pattern of MoSe$_2$ showed presence of single phase hexagonal space group $P6_3/mmc$ structure as seen in the Figure 5.26. Refined ambient lattice parameters were $a = 3.286$ (3) Å and $c = 12.920$ (5) Å. From the Figure 5.26, it is clear that the effect of heating on the relative position of prominent peaks is negligible for temperatures as high as 400 $^\circ$C. Moreover, it is observed that the intensities of prominent peaks drop considerably with the increase in temperature. For temperatures beyond 500 $^\circ$C, emergence of two new peaks was noticed roughly around 27° (2θ) & 37° (2θ), respectively. Persistence of these peaks even at elevated temperatures suggests that the new diffractions lines are connected to the chemical compound MoO$_3$. Molybdenum oxide is formed due to chemical reaction (oxidation) between metallic molybdenum and finite amount of oxygen traces present inside the sample chamber even under vacuum (approximately 1 torr). Yet again, for temperatures beyond 700 $^\circ$C, the oxides evaporated due to high vapor pressure MoO$_3$ under vacuum and hence, we could not recover the sample after the experiment. From the aforementioned discussion, it can be concluded that MoSe$_2$ crystal structure is stable for temperatures up to 400 $^\circ$C and our results are in good agreement with earlier studies [49].
Figure 5.26 X-ray diffraction patterns of MoSe$_2$ at ambient and elevated temperatures

Figure 5.27 X-ray diffraction patterns of WS$_2$ at ambient and elevated temperatures
5.4.3 High Temperature XRD of bulk WS$_2$

The results of high temperature XRD data analysis of WS$_2$ showed presence of single phase hexagonal space group $P6_3/mmc$ structure under ambient conditions. The obtained refined lattice parameters were $a = 3.158$ (6) Å and $c = 12.375$ (8) Å. Figure 5.3 shows the diffractions patterns of WS$_2$ at selected temperatures including ambient temperature. From Figure 5.27, it is obvious that the relative 2θ positions of different diffraction planes remain unperturbed upon heating to as high as 500 °C. Also it can be inferred that the emergence of weak and superfluous peaks (less than 5 %) at elevated temperatures is due to the surface oxidation of the sample. Besides, we did not notice any perceptible change in the prominent reflections planes positions upon heating. Based upon the above observations, we conclude that the WS$_2$ crystal structure is very stable up to 500°C under ambient pressure conditions, which is in good agreement with the earlier work [49]. For temperatures beyond 500 °C, the sulfide oxidizes to WO$_3$ as noticed indirectly through the drop in intensity of the (002) peak ($\sim$13 °2θ). Unlike MoO$_3$, WO$_3$ oxide has relative low vapor pressure under vacuum and hence, the peaks associated with WO$_3$ were persistent for temperatures as high as 700 °C in vacuum.

5.4.4 High Temperature XRD of bulk WSe$_2$

Figure 5.28 illustrates evolution of X-ray diffraction pattern of bulk WSe$_2$ sample as a function of temperature. The obtained ambient lattice parameters were $a = 3.280$ (7) Å and $c = 12.911$ (3) Å. The 2θ positions of the dominant diffraction peaks are intact, except that there is significant drop in the corresponding intensities for temperatures as low as 400 °C. Similar to MoSe$_2$, for temperatures 500 °C and beyond the diffraction lines associated with WSe$_2$ disappear indicating oxidation of the sample at higher
temperature in presence of traces of oxygen inside the sample cell. Due to low vapor pressure of WO$_3$ oxide, the diffraction associated with oxidized sample persists for temperatures as high as 700 $^\circ$C in vacuum.

![X-ray diffraction patterns of WSe$_2$ at ambient and elevated temperatures](image)

Figure 5.28 X-ray diffraction patterns of WSe$_2$ at ambient and elevated temperatures

5.4.5 Coefficients of thermal expansion

Figure 5.29 and 5.30 illustrate variation of lattice parameters ‘a’ and ‘c’ as a function of temperature. From the figures it is obvious that the unit cell expands upon heating and hence, increase in unit volume is expected. Also, noticed is that the coefficients of thermal expansion for individual compounds vary nonlinearly. The observed results were in excellent agreement with the reported data [49].
Figure 5.29 Variation of cell parameter, ‘a’ as a function of temperature. The error bars are smaller than the size of the symbols.
Figure 5.30 Variation of cell parameter, ‘c’ as a function of temperature. The error bars are smaller than the size of the symbols.
5.5 Dynamic compression and static compression

Recent studies have reported that MoS$_2$ and WS$_2$ as exceptional shock absorbers [11, 13]. In order to examine the effect of shock on their crystal structure, we have compared the x-ray diffraction data collected for the shocked MoS$_2$ and WS$_2$ sample with the corresponding static high pressure data and previous reports [84]. Interestingly, the results showed no evidence for a phase transformation in MoS$_2$ and WS$_2$ when subjected to shock pressure up to 8 and 10 GPa respectively. Our shock compression experiments further ascertain that the stability of these compounds and are in good agreement with the reported data [11, 13].

5.6 Summary

To sum it up, high pressure in-situ angle dispersive powder x-ray diffraction using synchrotron radiation along with high pressure Raman analysis were performed on powder TMDs (MoS$_2$, MoSe$_2$, WS$_2$, WSe$_2$) samples to determine the effect of pressure on crystal structure stability. Pressure-Volume (P-V) relationship and cell parameters were obtained as a function of pressure. A semi empirical model was proposed to predict phase transitions in TMDs under high pressure. In addition, X-ray diffraction experiments performed at high temperatures on bulk to determine the effect heating on crystal structure stability. Based on our experiments we conclude the following,

- Except in MoS$_2$, there was no phase transformation observed in other TMDs of interest under pressure as high as 50 GPa.
MoS$_2$ undergoes a pressure induced structural distortion around 20 GPa from the 2H$_c$ phase to a 2H$_a$ type hexagonal phase as predicted by theoretical simulations. Both phases co-exist up to 51 GPa.

Successfully developed a first order semi empirical model for predicting phase transition in bulk TMDs. Further, it is predicted that except MoS$_2$ no other TMDs of interest undergoes iso structural phase transition under high pressure for pressures up to 50 GPa.

From the Raman spectroscopy, we notice that in the case of MoS$_2$, a new mode (in the background), namely ‘d band’ pertaining to 2Ha phase structure emerges next to the already existing in plane vibrational mode, E$^{(1)}_{2g}$ between 17 and 26 GPa, which further reinforces our observation in high pressure diffraction experiments.

High pressure Raman spectroscopy results of MoSe$_2$, WS$_2$ and WSe$_2$ demonstrated consistent red shift of the two predominant Raman active modes, A$_{1g}$ and E$^{(1)}_{2g}$ under compression.

High temperature XRD results established that the ambient crystal structure, 2H$_c$ hexagonal phase of MX$_2$ (M = Mo or W and X = S or Se) is very stable up to 500 $^\circ$C. Besides, the coefficients of thermal expansion were found exhibit nonlinear behavior as a function of temperature.

Structural analysis of shock subjected MoS$_2$ and WS$_2$ showed no significant changes relative to that of ambient pressure conditions and our results indicate it may be a good shock absorber.
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

_In-situ_ high pressure X-ray diffraction in conjunction with high pressure Raman spectroscopy were performed on bulk transition metal dichalcogenides (TMDs), MX\(_2\) (M = Mo or W and X = S or Se) to determine their crystal structure stability under high pressure. Except MoS\(_2\), the remaining TMDs under review, MoSe\(_2\), WS\(_2\), WSe\(_2\) were found to be stable for pressures up to 50 GPa. Pressure induced isostructural phase transition (2H\(_c\) to 2H\(_a\)) was observed in bulk MoS\(_2\) between 17 – 30 GPa. A first order semi empirical model based on energy of interaction between bonding electrons has been proposed to explain the observed distinctive behavior of MoS\(_2\) under high pressure compared to the other TMDs. High pressure Raman results showed continuous red shifts in dominant vibrational modes with increase in pressure. Additionally, emergence of a new peak, namely ‘d - band’ associated with 2H\(_a\) structure in MoS\(_2\) reinforces the observation of a isostructural phase transition observed in high pressure X-ray diffraction experiments. Results of high temperature X-ray diffraction demonstrated structural stability of TMDs for temperatures up to 500 °C. Also, it is observed that the coefficients of thermal expansions of individual TMDs vary nonlinearly as a function of temperature. Furthermore, the diffraction data obtained for the shocked samples of MoS\(_2\) and WS\(_2\) to pressures 8 GPa and to 11GPa respectively were found to be structurally resilient. In addition to studies on bulk material, MoS\(_2\) thin film (approximately 100 nm thicknesses)
was fabricated and characterized via DC magnetron sputtering system and sulfurization technique.

6.2 Future recommendations

The following are few recommendations for possible future research in this area:

- High pressure band gap ($E_g$) and resistance measurements for added information on the materials properties under pressure.
- Extending the pressure regime to 150 GPa in high pressure studies of bulk crystal MX$_2$ to see if the predictions made by the semi-empirical model are true.
- Including the effects such as bond hybridization, delocalization of electrons, quantum effect etc. in to the semi-empirical model to see the effect of these additions on the predicted results.
- Performing high temperature X-ray diffraction in either H$_2$ or N$_2$ ambience to avoid any surface oxidation.
- Depositing thicker MoS$_2$ and TMD films so that the exfoliated thin films could be characterized using X-ray diffraction experiment and high pressure Raman scattering experiments.
- Understanding pressure induced transitions in these materials using the first principle calculations.
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CURRICULUM VITA

Graduate College
University of Nevada, Las Vegas
Nirup Bandaru

Degrees:
Bachelor of Engineering, Electrical Engineering, 2006
Jawaharlal Nehru Technological University, Hyderabad, India

Master of Science, Electrical Engineering, 2008
University of Nevada, Las Vegas

Publications and Conferences:

Dissertation Title: Structural stability of bulk transition metal dichalcogenides (TMDs), MX$_2$ (M = Mo or W and X = S or Se) under high pressure and temperature.

Dissertation Examination Committee:

Co - Chairperson, Dr. Rama Venkat, Ph.D.
Co - Chairperson, Dr. Ravhi S. Kumar, Ph.D.
Co - Chairperson, Dr. Clemens Heske, Ph.D
Committee Member, Dr. Ke-Xun Sun, Ph.D.
Committee Member, Dr. Venkatesan Muthukumar, Ph.D.
Graduate College Representative, Dr. Thomas Hartmann, Ph.D.