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Author
Mutlu, Zafer

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Crystal Growth and Phase Engineering of Two-Dimensional Metal Chalcogenides

A Dissertation submitted in partial satisfaction of the requirements for the degree of

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in

Materials Science and Engineering

by

Zafer Mutlu

December 2016

Dissertation Committee:
Dr. Cengiz S. Ozkan, Chairperson
Dr. Sandeep Kumar
Dr. Elaine D. Haberer
Dr. Mihri Ozkan
The Dissertation of Zafer Mutlu is approved:

                                                                                      Committee Chairperson

University of California, Riverside
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The text and figures in this dissertation, in part or in full, are a reprint of the material as it appears in the following publications:

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The co-author Cengiz S. Ozkan Lake, listed in the above publications directed and supervised the research which forms the basis for this dissertation. The remaining co-authors listed provided technical expertise and support as collaborators.
ABSTRACT OF THE DISSERTATION

Crystal Growth and Phase Engineering of Two-Dimensional Metal Chalcogenides

by

Zafer Mutlu

Doctor of Philosophy, Graduate Program in Materials Science and Engineering
University of California, Riverside, December 2016
Dr. Cengiz S. Ozkan, Chairperson

The ability to grow crystals of desired dimensions is an important aspect of the design of new functional materials. The crystals grown in two dimensions enable successful and efficient modification of a wide range of physical, electronic and structural properties tailored for smaller and more efficient electronics, optoelectronics, valleytronics, and spintronic applications. The control of phases in crystals is also an additional element in the design of functional materials. Two-dimensional (2D) atomic crystals can crystallize in a variety of crystal phases, which possess distinct properties. Therefore, identifying approaches for controlling dimension and crystal phase is essential for tuning the properties of 2D materials to specific applications.

Herein, various unique methods of producing 2D atomic layered metal chalcogenide crystals (LMCs) including growth of group VI transition metal dichalcogenides (TMDs) by chalcogenization of pre-deposited metal-containing precursors, and phase-engineered growth of group IV LMCs by vapor-phase reaction of metal oxide and chalcogen powders are demonstrated. Scanning transmission electron
microscopy (STEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), optical microscopy, Raman spectroscopy, photoluminescence (PL) spectroscopy, ultraviolet photoelectron spectroscopy (UPS), X-ray photoemission spectroscopy (XPS), and X-ray diffraction (XRD) are all notable experimental techniques used to characterize these various materials. The experimental results are corroborated by density functional theory (DFT) calculations.
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Chapter 1 Introduction

Layered metal chalcogenides (LMCs) belong to a broader class of van-der-Waal (vdW) materials that have been the subject of intense research. Examples of vdW materials include graphene [1], hexagonal boron nitride (h-BN) [2], transition metal dichalcogenides (TMDs) [3], metal halides [4], phosphorene [5], germanene [6], silicene [7] and transition metal carbides and carbonitrides (MXenes) [8]. These materials and their heterostructures have been used to investigate a wide range of devices including field-effect transistors (FETs) [9], PN junctions [10], photodetectors [11], supercapacitors [12], spin FETs [13], photovoltaics [14], thermoelectrics [15]. This family of materials also provides the opportunity for the following physical phenomena to be studied at low dimensions: Dirac fermions [1], valley and spin physics [16], superconductivity [17], commensurate and incommensurate charge density waves (CDW) [18], excitons and trions [19], itinerant magnetism [20], Lifshitz transitions [21] and Mott transitions [22].

The performance of these devices and the physical phenomena studied are quantitatively different from the properties demonstrated by these materials in their bulk form.

The electronic, thermal, optoelectronic and mechanical properties of the bulk LMCs can change in beneficial ways when they are reduced to a few monolayers or single monolayer in thickness. Examples of such changes include an increase in the photoluminescence (PL) intensity by 3 orders of magnitude when bulk MoS$_2$ is confined to a single monolayer and variations in the thermal conductivity by up to 2 orders of magnitude between the basal and cross-plane axis of conduction. The sensitivity of the properties of LMCs to changes in dimensionality, polytypism, strain and elemental
composition and the ability to vertically stack these materials to create heterostructures have resulted in a resurgence in research interest in this family of materials.

Studies on LMC materials can be found dating back to the 1950s. The first report on earth abundant MoS$_2$ dates back to 1953 with intercalation studies on bulk MoS$_2$. [23] The metallic and semi-metallic LMCs were the focus of several studies in the 1970s with the identification of superconducting and CDW phenomena in these materials. This was complemented by the emergence of electronic structure calculations of a number of LMC compounds which were used to explain the observed phenomena. The first studies of transistor type structures using the LMC were first conducted on the metallic LMCs to investigate CDW phenomena and other correlated phenomena. [24] In 2004, the first top gated thin film WSe$_2$ transistor was fabricated [25], with the proposal of applying LMCs for flexible electronics. This was followed by transport studies on MoS$_2$ and TaS$_2$ nanopatches by Ayari et al. [26] in 2007. The first experimental investigations of transport in monolayer MoS$_2$ were published in 2010 by Radisavljevic et al. [9], and the number of publications on this family of materials has been rapidly increasing ever since.

Changes in the properties of LMCs are driven by qualitative changes in the electronic and phononic dispersion of the materials. Alignment of monolayers with respect to each other and the surrounding dielectric environment can also lead to changes in the electronic, optical and thermal properties. Current research on the LMCs family of compounds is focused on understanding the fundamental properties of these materials and their heterostructures.
In this chapter, an overview of some of the experimental and theoretical investigations of these properties, synthesis of LMCs and their heterostructures and possible emerging applications that can be derived from vertically and horizontally stacked vdW compounds is provided.

1.1 Brief properties of 2D LMCs

In their bulk form, these vdW materials are covalently bonded along the basal plane of the monolayer, and the individual monolayers are held together via weak vdW forces perpendicular to the basal plane.

Each monolayer can be stacked in a number of different configurations in the LMC compounds. For each of these stacking configurations, the monolayers cleave along the plane of the chalcogen atom. Each monolayer is hexagonally packed. A single metal chalcogenide monolayer is approximately 3Å to 5Å thick and the vdW gap between the adjacent planes of chalcogen atoms varies between 3Å to 4Å. The electronegativity of the chalcogen atom in a LMC compound and its coordination (octahedral vs. trigonal prismatic) determines the metal-chalcogen bond lengths. Prior studies have shown the octahedral coordination is preferred when intra-layer bonding is ionic, which leads to maximum separation distance between the negatively charged chalcogens. When intra-layer bonding is more covalent, the trigonal prismatic coordination is preferred which leads to maximum overlap between the metal and chalcogen atom. [27] Each metal chalcogenide has a preferred ground state stacking order. The layered nature of these compounds means alternate stacking orders can be achieved by overcoming an energy
barrier that is unique to each material, either through charge transfer intercalation or controlled synthesis methods.

The electrical and optical properties of LMCs cover a wide spectrum based on the coordination of the metal atom and the filling of the d-orbital. Trigonal prismatic coordination of the transition metal atoms in LMC compounds result in degenerate $a_1$ ($d_z^2$), $e$ ($d_{x^2-y^2}$, $xy$) and $e'$ ($d_{xz}$, $d_{yz}$) orbitals with a gap between the $a_1$, $e$ and $e'$ group of orbitals. Octahedral coordination of the metal atom results in degenerate $e_g$ ($d_{z^2}$, $x^2-y^2$) and $t_{2g}$ ($d_{yz}$, $xz$, $xy$) orbitals. When the d-orbital of the LMC compound is fully occupied, the material is a semiconductor. Partial occupation of the d-orbital leads to either semi-metallic or metallic behavior. The electronic and structural properties of the LMCs have been summarized in Table 1.1.

Research into monolayer and few-layer MoS$_2$ and other LMCs was popularized by the first demonstrations of the indirect to direct gap transition in MoS$_2$ through the use of PL experiments by Mak et al. [28] and Splendiani et al. [29]. The band gap of bulk MoS$_2$ increases from 1.29 eV to 1.8 eV when thinned down to a single monolayer. This phenomenon is explained by the orbital composition of the different high symmetry points in the group VI TMDs. The large contribution of the $p_z$ orbitals of the S atoms at the $\Gamma_v$ valley results in the largest interlayer coupling greatest sensitivity to the presence of adjacent layers. The $K_v$ valley, with no $d_z^2$ or $p_z$ components has very weak interlayer coupling and, therefore, is insensitive to the presence of adjacent layers. When two monolayers are brought together, the $\Gamma_v$ valleys of the two layers couple and split. In bulk MoS$_2$, the interlayer distance is approximately 3.12 Å and the energy splitting at $\Gamma_v$ is
approximately 600 meV. When two group VI dichalcogenide monolayers are brought into close proximity the interlayer coupling causes the Γ$_v$ valley to rise above the K$_v$ valley which drives the direct to indirect gap transition when the film thickness increases above a monolayer. Recent angle-resolved photoemission spectroscopy (ARPES) measurements on MoS$_2$, MoSe$_2$ and WSe$_2$ [30] [31] [32] have confirmed this shift of the valence band at Γ as the origin of the indirect to direct crossover as a function of film thickness in the group VI TMDs. The sensitivity of these valleys to variations in interlayer coupling and film thickness can lead to changes in degeneracy and barrier heights which can affect the performance of devices formed with heterostructures of the group VI TMDs. Recent ab-initio studies have demonstrated the near degeneracy of the conduction band K$_c$ and Λ$_c$ valleys as the film thickness increases above four monolayers. [33] The K$_c$ valley is three fold degenerate and the Λ$_c$ valley is six fold degenerate.
Table 1.1: Electronic and material properties of different LMCs. The bandgaps for the monolayer structures are from ab-initio theoretical (T) results, the bulk bandgaps and lattice constants are from experimental data (E). Cited references are included in square parentheses.

<table>
<thead>
<tr>
<th>Stacking Order</th>
<th>Electronic Characteristics</th>
<th>Lattice Constant (Å)</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Group V TMDs:</strong> VS₂, VSe₂, NbS₂, NbSe₂, TaS₂, TaSe₂</td>
<td>Metal, superconducting, CDW</td>
<td>3.18 - 3.47 [77]</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Group VI TMDs:</strong> MoS₂, MoSe₂, MoTe₂, WS₂, WSe₂</td>
<td>Semiconducting</td>
<td>3.15 - 3.28 [78][79][80]</td>
<td>Bulk: 1.09 - 1.35 (E) [78][79][80]</td>
</tr>
<tr>
<td><strong>Group III metal chalcogenides</strong> GaS, GaSe, GaTe, InS, InSe</td>
<td>α, β</td>
<td>Semiconducting</td>
<td>3.58 - 4.00 [82][83][84][85]</td>
</tr>
</tbody>
</table>

There is an increasing effort to identify new LMCs beyond the group IV to VI TMDs. Examples of new low-dimensional layered chalcogenides that have been synthesized are the group III (gallium, indium) chalcogenides, tin sulfides and selenides. [34] [35] [36] [37] [38] Confining these materials to few-monolayers and a monolayer leads to the emergence of new phenomena and possible application spaces in which these materials can be adopted.

When the group III sulfides, selenides and tellurides are confined from their bulk structure to a single monolayer the parabolic dispersion of the valence band edge at Γ is deformed into a 'Mexican-hat' dispersion. [21] [39] [40] The presence of a 'Mexican-hat'
dispersion results in a Fermi-ring of states which can lead to novel phenomena including a $1/\sqrt{E}$ singularity in the two-dimensional (2D) density of states. [41] [42] This singularity in the density of states can lead to novel correlated phenomena such as itinerant magnetism, superconductivity and also have practical implications such as enhanced thermo-electric response [40] [42] [43] and photo response [44].

In addition to obtaining an understanding of the intrinsic properties of the LMC compounds in their monolayer limit, it is also necessary to understand how these properties change when heterostructures are formed between LMCs and other vdW or non-vdW materials. This includes but is not limited to changes in material properties as the film thickness of the material increases and approaches the bulk limit, interfaces formed between different vdW materials and interfaces between LMCs and metal contacts. Each of these interfaces can either have perfect alignment or be rotationally misaligned. Prior studies have shown rotational faults in bilayer graphene or heterostructures between graphene, and other vdW materials can either decouple the two layers [45] [46], increase contact resistance [47] [48], affect thermal conductivity [49] and modulate the intrinsic Fermi velocity of graphene [46][50]. Thus, a similar understanding of interfaces formed between LMC compounds is necessary.

The self-passivated surfaces of the LMCs, in principle, enable atomically sharp interfaces to be engineered. vdW epitaxy was proposed as an approach to achieve atomically sharp quantum well structures between vdW materials that are highly lattice mismatched. [51] Prior photoemission spectroscopy experiments demonstrated the possibility of achieving different band alignments in a number of bulk LMC
heterostructures grown using vdW epitaxy. [52] Type-II (staggered) band alignments were shown to form in bulk MoS$_2$/SnSe$_2$, WSe$_2$/SnSe$_2$ SnS$_2$/MoS$_2$. Type-III (broken gap) alignments occur in SnSe$_2$/MoTe$_2$, SnS$_2$/MoTe$_2$ and SnSe$_2$/GaSe. For the broken gap alignments, the valence band (conduction band) offsets for these heterostructures were measured to be 0.94 eV (0.92 eV), 1.72 eV (0.55 eV) and 0.83 eV (1.82 eV) respectively. A number of theoretical calculations have examined the natural band alignments and offsets between different monolayers of the LMCs. [53] [54] Type-III band alignments were predicted to occur between monolayers of Mo and W selenides and tellurides (MoTe$_2$, MoSe$_2$, WSe$_2$, WTe$_2$) and zirconium and hafnium sulfides and selenides (ZrS$_2$, ZrSe$_2$, HfS$_2$, HfSe$_2$). The valence band offset between MoS$_2$ and WS$_2$ is 386 meV, and the conduction band offset is 310 meV. The type-II alignment formed between monolayer MoS$_2$/WS$_2$ was investigated using PL spectroscopy. Future calculations and experimental investigations of band alignments formed between few-layer LMCs will have to account for quantum dipoles, which can lead to alterations in the conduction and valence band offsets. [52] [55] Broken gap alignments are beneficial for next-generation broken gap heterojunction tunnel field effect transistor (TFET) devices that utilize monolayers or few-layers of the LMCs or post-CMOS excitonic devices.

Interfaces between monolayers and few-layers of LMC compounds and the metal contacts used to fabricate vdW FET devices is a major bottleneck that impedes the transfer characteristics in these devices. A number of comprehensive experimental and theoretical studies have recently demonstrated the natural band lineup between the group VI TMDs and a variety of metal work functions. [56] [57] However, experimental studies
have shown that this simplified picture is insufficient to predict the ideal metal contact that would lead to an Ohmic contact with ultra-thin LMC transistors. The ultra-thin geometry of these devices leads to Fermi level pinning which alters the predicted alignment of the metal work function with the conduction and valence band of the LMCs. Das et al. [58] investigated the n-type transfer characteristics between a 10 nm film of MoS$_2$ interfaced with metals that have a variety of work functions (WF); Nickel (WF=5.0 eV), Platinum (WF=5.9 eV), Scandium (WF=3.5 eV) and Titanium (WF=4.3 eV). For each of these metals, the Schottky barrier (SB) height was measured to be approximately 150 meV, 230 meV, 30 meV and 50 meV respectively. The n-type transfer characteristics observed with a high work function metal such as nickel and platinum was identified as evidence of Fermi level pinning. [58] Based on these extracted SB heights, scandium was identified as an optimum contact for n-type transport.

The sensitivity of the band edges in the LMC compounds to interlayer interactions also introduces the possibility of tuning the electronic properties of the group VI TMDs using strain, intercalation and engineering layered heterostructures. Using a two-point bending apparatus and PL experiments it was shown uniaxial strain up to 1.51% in bilayer WSe$_2$ induces an indirect to direct gap transition. [59] This was explained with the use of density functional theory (DFT) calculations to be due to the near degeneracy (50 meV) of the K$_c$ and $\Sigma_c$ valleys of the conduction band. This indirect to direct band gap transition is less likely to occur at similar strain levels in the other group VI TMDs given the larger offset between K$_c$ and the nearest conduction band edge.
Applying pressure to the LMCs also results in quantitative changes in the crystal structure and electronic structure. Recent diamond anvil cell experiments on bulk MoS$_2$ demonstrated a structural distortion followed by an insulating to metal transition at a pressure of 19 GPa. [60] This equates to the c/a lattice-parameter ratio of bulk MoS$_2$ decreasing from its equilibrium value of 3.89 to 3.675.

The ability to manipulate the electrical and optical properties of these LMCs through mechanical strain and pressure is possible due to the robust mechanical properties of the LMCs. Measurements of the stiffness and breaking strength of monolayer MoS$_2$ using atomic force microscopy (AFM) demonstrate an in-plane stiffness of 270 +/- 100 GPa and a of 15 +/- 3 Nm$^{-1}$ which occurs at an effective strain between 6 and 11%. [61] Although these values are lower than the fundamental Young's modulus of 1000 GPa and breaking strength of 130 GPa for monolayer graphene, they are superior in value to commonly used substrates for flexible electronics such as polymide and polydimethylsiloxane (PDMS). This would suggest LMCs are suitable candidates for flexible electronics. [62]

Future studies on such heterostructures would have to take into account effects such as lattice mismatch which can lead to misorientation between the two atomic planes and heterostructures formed with few-layer films of the LMCs. The electronic and vibrational properties of the LMCs are sensitive to proximity of adjacent monolayers. In addition to strain, pressure and interlayer spacing, misorientation of one monolayer with respect to another can affect the fundamental properties of these materials. Given the surge of interest in heterostructures formed with dissimilar or similar layered materials,
such devices are often formed by layer by layer growth or mechanical stacking. These approaches are known to lead to naturally misoriented interfaces.

Recent experiments have studied changes in the electronic and vibrational properties of 'folded' and misoriented bilayer MoS$_2$. [63][64][65] The electronic structure of the misoriented bilayer remains indirect with no evidence of the individual layers being completely decoupled. Instead, the indirect bandgap between the twisted bilayers was shown by PL measurements to increase as a function of twist angle by up to 140 meV. Steric effects between the adjacent layers of S atoms are predicted by DFT calculations to lead to repulsion between the individual monolayers and increase the interlayer separation. This in turn leads to a downward shift in the valence band at $\Gamma$ and an increase in the indirect bandgap. Since the orbital composition and location of the band extrema are the same for the bilayers of the other group VI TMDs, similar behavior of the electronic structure with rotation can be expected.

In addition, the electronic, optical and mechanical properties of the LMCs, the intrinsic vibrational and thermal conductivity properties of these materials are being studied. [66][67][68] The in-plane thermal conductivity of suspended and supported monolayer and few-layer MoS$_2$ was measured experimentally using Raman thermometry technique. The thermal conductivity of suspended and supported MoS$_2$ is 34.5 W/mK and increases to 52 W/mK for the few-layer sample. This is in good agreement with theoretical predictions of the thermal conductivity in free-standing monolayers of MoS$_2$. Anisotropy in the intra-layer and inter-layer bonding of the LMCs also leads to anisotropic thermal conductivity properties. The cross-plane thermal conductivity of the
layered TMDs was experimentally measured to be approximately 1 W/mK, which was attributed to the weak vdW bonds perpendicular to the strong covalent intra-layer bonding.

A number of LMCs also exhibit competing instabilities which can lead to new collective ground states. Examples of such instabilities include ferromagnetic, superconductivity and charge density wave phases. Although no experimental demonstrations of ferromagnetism have yet been observed in the LMCs, a number of theoretical predictions have been put forth for emergent ferromagnetic order either through dilute magnetic doping of LMCs or in electrostatically doped III-VI compounds that fulfill the Stoner criteria for magnetism. [69][70][71] The group V dichalcogenides (TaS$_2$, TaSe$_2$, NbS$_2$, NbSe$_2$, VSe$_2$) and TiSe$_2$ have complex phase diagrams that undergo either charge density wave and/or superconducting phase transitions. [18] Recent studies have begun to explore the effect of dimensionality on these phase diagrams. [72][73][74][75][76] A number of studies have shown the charge density wave transition temperatures can be tuned as a function film thickness, itinerant ferromagnetism can be induced by electron doping monolayer and few-layer LMCs and competing phase transitions can be suppressed.

1.2 Synthesis

To access the properties of the LMCs discussed in Section 1.1 and enable their integration in devices requires methods for controllable synthesis of atomic thick LMCs of both large-area and high quality. In this section, the recent progress made in the synthesis of the LMCs, e.g., MoS$_2$, MoSe$_2$, WS$_2$, WSe$_2$, GaS, GaSe, InSe, and SnS$_2$ and
their heterostructures with vertical and lateral interfaces, e.g., WS$_2$/MoS$_2$, and WSe$_2$/MoSe$_2$ is overviewed.

Various methods have been used to synthesize LMCs. The first isolation of monolayer MoS$_2$, was successively reported by Mak et al. [28] using scotch tape, otherwise referred to as mechanical exfoliation (ME). This led to the isolation of other monolayer to few-layer LMCs e.g., MoSe$_2$ [86], WS$_2$ [87], WSe$_2$ [88], GaS [89] [90], GaSe [34], and InSe [91] [92], which were isolated based from bulk counterparts. Although mechanical exfoliation is impractical [93] [94] for large-scale applications of LMCs due to low throughput and lack of control over layer thickness, it is still the method of choice to explore and prototype novel properties and new device concepts. Liquid-phase exfoliation which involves ion intercalation or solvent-based exfoliation, is an alternative to mechanical exfoliation. It has been also used to produce a variety of LMCs. [95] [96] [97] The liquid phase exfoliation is promising for integration of LMCs into large-scale solution-based or printable electronics. [95]

In addition to mechanical or liquid exfoliation, a few unconventional techniques such as laser thinning [98], thermal annealing [99] [100] [101], gas-assisted etching [102] and plasma etching [103] have been reported to produce 2D LMCs. Castellanos-Gomez et al. [98] demonstrated synthesis of monolayer MoS$_2$ from bulk MoS$_2$ by laser sublimation of the upper layers via heat induced laser absorption. Monolayer or few-layer MoS$_2$ films were obtained by heating multilayer MoS$_2$ in air [99], oxygen [100] or in an argon environment [101], which led to the top-most layers being etched. Chemical dry-etching of MoS$_2$ multilayer flakes down to monolayer was also reported by using XeF$_2$ as
a gaseous reactant. [102] Using a plasma etching technique, Liu et al. [103] demonstrated etching of thick MoS\(_2\) sheets down to monolayer with lower surface roughness under Ar\(^+\) plasma irradiation. The aforementioned methods are likely to provide novel insights into engineering the geometry of LMCs for specific applications. However, these techniques are still inhibited defect formation, incomplete sublimation or pinhole creation. [104] [105]

Apart from the above-mentioned synthetic techniques, very recently, chemical vapor deposition (CVD) techniques have shown great promise to produce high-quality 2D LMCs with controllable flake size and thickness. Several research groups have reported CVD growth of atomically thin 2D LMCs, with the focus on MoS\(_2\), MoSe\(_2\), WS\(_2\) and WSe\(_2\). For example, typical CVD growth of MoS\(_2\) involves sulfurization/decomposition of their corresponding pre-deposited thin metal films [106] [107] [108] [109] [110] and vapor phase reaction/deposition of gaseous metal and chalcogen feedstocks [111] [112] [113] [114] [115] [116] [117]. WS\(_2\) layers have also been grown by sulfurization of pre-deposited W [110] [118] or WO\(_3\) [119] [120] films, and reaction of elemental S and W-based powders [121] [122] [123] [124]. CVD has also been explored using Se powder (or pellet) and MoO\(_3\) powder as the reactants, yielding monolayer to few-layer triangular MoSe\(_2\) islands. [125] [126] [127] [128] The recent demonstration [129] of the p-type transistor behaviors in exfoliated monolayer WSe\(_2\) flakes has triggered extensive interest on the production of large-scale intrinsically p-type monolayer LMCs for realizing complementary digital logic applications. Monolayer
WSe$_2$ flakes have been mainly produced by gas-phase reaction of WO$_3$ and Se powders [130] [131] or vapour phase transport of WSe$_2$ powder [132] [133] [134].

GaSe is an emerging 2D material with novel electronic and optoelectronic properties discussed in Section 1.1. Recent reports have demonstrated the possibility of the synthesis of large-scale monolayer and few-layer GaSe flakes by using CVD-based approaches. Lei et al. [35] showed the growth large-scale few-layer GaSe crystals with the thickness down to 2 nm on SiO$_2$/Si by a vapor phase transport method using GaSe powders as precursor and GaSe flakes as seeds. By using a vdW method, Zhou et al. [135] synthesized monolayer and few-layer GaSe p-type nanoplates, with the lateral size of up to tens of micrometers on a flexible mica substrate. Most recently, Li et al. [136] reported on the synthesis of monolayer and thicker 2D GaSe crystals, with a lateral size up to $\sim 60$ μm, on SiO$_2$/Si substrates using GaSe crystals and Ga$_2$Se$_3$ powder as source materials.

Lower temperature processes such as molecular beam epitaxy (MBE) and atomic layer deposition (ALD) are possible alternatives to CVD. MBE at very low vacuum and controlled deposition rates can produce epitaxial LMCs [31] [137]. Recently, Zhang et al. [31] has successively grown epitaxial MoSe$_2$ films with various thickness by MBE and studied the transition from indirect to direct band gap in monolayer films by using ARPES. In addition to MBE, ALD has attracted increasing interest in the growth of large-scale ultrathin LMC materials. Song et al. [138] demonstrated the wafer-scale synthesis of WS$_2$ nanosheets on SiO$_2$ substrates via sulfurization of WO$_3$ thin films by using plasma-enhanced ALD using WH$_2$(iPrCp)$_2$ as W precursor. The growth of
monolayer to multilayer MoS$_2$ film was demonstrated by ALD based on self-limiting reactions of molybdenum hexacarbonyl (MoCl$_5$) and H$_2$S at 300 °C on a sapphire wafer. [139] The post annealing of the as-deposited MoS$_2$ films further improved its crystallinity. Furthermore, Jin et al. [140] reported on the growth of MoS$_2$ by ALD using MoCl$_5$ and dimethyldisulfide (C$_2$H$_6$S$_2$) as Mo and S precursors at 100 °C. The crystallinity of the as-grown amorphous MoS$_2$ films was observed to improve on annealing at 900 °C. Although current production status is still in a nascent stage due to poor crystallinity, small grain size and low throughput [138] [139] [140], ALD can be a possible approach to achieve large-scale production of 2D LMCs with precise with thickness control.

In parallel with the recent advances in the synthesis of LMCs, the stacking of various 2D layered materials in vertical and lateral directions is being explored for device applications. Layer-by-layer stacking of 2D LMCs could be achieved by using mechanical transfer techniques. [142] [141] [143] For instance, vertically stacked WS$_2$/MoS$_2$ heterostructures were deposited on SiO$_2$/Si substrates from CVD-grown WS$_2$ and MoS$_2$ monolayers using conventional PDMS stamping method. [141] However, the use of transfer techniques to vertically stack layers with contamination-free interfaces is challenging. Furthermore, building lateral heterostructures with atomically sharp interfaces remains a major challenge.

CVD-based approaches [10] [144] [145] haven been proven to produce vertical and in-plane heterostructures with atomically clean and sharp interfaces. Gong et al. [10] demonstrated the growth of vertical and lateral WS$_2$/MoS$_2$ heterostructures by a CVD set-
up using W, MoO₃ and S powders with the addition of Te. By lowering the temperature, they showed that WS₂ layers preferentially grow laterally from MoS₂ monolayers whereas vertical heterostructures dominate at high temperatures. In a subsequent study, Huang et al. [146] reported the synthesis of the in-plane MoSe₂-WSe₂ heterojunctions without the addition of Te. More choices of 2D LMCs building blocks and their combinations are expected in the near future.

CVD synthesis of LMCs leads to polycrystalline films with a variety of grain boundary topologies. Grain boundaries are a source of scattering for electrons and phonons. Hence, understanding grain and grain boundary characteristics in CVD grown LMCs is essential to improve the characteristics of transistors that adopt these materials. Recently, high-resolution transmission electron microscopy (HR-TEM) methods have been used to examine the morphology of the grains and their boundaries in MoS₂ islands. [116] The coalescence of the grains leads to the formation of grain boundaries consisting of 5- and 7-membered rings. Coalescence of grain boundaries can also occur with overgrowth. Prior studies [116] have shown there is a competition between the formation of conventional grain boundaries and the overlapped grain boundaries. However, a clear on the degree of lattice orientation mismatch in the two grains was not observed. Zande et al. [111] demonstrated that CVD grown single crystal and polycrystalline triangular MoS₂ grains contain both tilt and mirror twin boundaries containing 8- and 4- membered rings. MoS₂ grain boundaries strongly affect the PL and slightly alter the in-plane electrical conductivity. The mirror twin boundaries lead to the strong PL quenching and
improved in plane conductivity whereas the tilt boundaries lead to the strong PL enhancement and the lower conductivity.

To fully utilize 2D LMCs’ potential to 2D materials-based electronic devices, p- and n-type doping is required. In this regard, considerable efforts have been recently devoted to developing new doping strategies. Laskar et al. [147] demonstrated p-type conductivity in few-layer MoS$_2$ films with a hole density of $3.1\times10^{20}$ cm$^{-3}$ using Nb as a substitutional impurity on the Mo site. The Nb-doped MoS$_2$ films were grown by sulfurization of the thin films deposited using electron beam evaporation in the sequence of Mo/Nb/Mo. In another study [148], p-type conduction in the exfoliated MoS$_2$ flakes with a hole density of $\sim 3\times10^{19}$ cm$^{-3}$ was demonstrated by substitutional Nb doping. The Nb-doped MoS$_2$ crystals were grown by a chemical vapor transport (CVT) method using iodine as the transport agent. Comprehensive theoretical studies [149] have investigated the thermodynamics of doping single monolayers of the LMCs. Substitutional doping of Mo atoms by Nb introduces minimal change to the metal-chalcogen bond length since the atomic number of Nb (41) is one less than the atomic number of Mo (42). Using DFT calculations it was shown 4% Nb doping introduces a hole defect state approximately 150 meV below the valence band edge of monolayer MoS$_2$. [149] Future studies of substitutional doping in LMC compounds will require the exploration of alternative p- and n-type dopants combined with theoretical studies of thermodynamic ground state, phase diagrams and kinetics of dopant atoms in a given LMC.

Fang et al. [129] have reported the chemical p-doping of monolayer WSe$_2$. NO$_2$ molecules were absorbed on both the WSe$_2$ channel and contacts of the FETs, leading to
lower the metal contact resistance. In a similar study [150], n-doping of few-layer MoS$_2$ and WSe$_2$ layers with high motilities was shown by molecular adsorption of potassium (K) vapor. Electron doping by K vapor leads to lower contact resistance and high motilities. Yang et al. [151] reported a chlorine (Cl) molecular doping technique for MoS$_2$ and WS$_2$, which leads to high electron-doping density, thus a significant reduction of Schottky barrier width. Two recent studies demonstrated the chemical doping of few-layer MoS$_2$ [152] and monolayer WS$_2$ [153] by using tetrafluoro-tetracyanoquinodimethane (F$_4$TCNQ) as a p-type dopant. It was shown that the more F$_4$TCNQ adsorption, the more electrons withdraw from MoS$_2$ and WS$_2$, resulting in significant PL enhancement in the layers.

Molecular chemistry was first applied to LMC compounds to study intercalation chemistry. It is now well known that the ion based intercalation of the group VI TMDs induces structural or phase transformations, which leads to a concomitant change in their electronic structure [154] [155] [156] Intercalation of Li ions causes MoS$_2$’s crystalline structure to change from the stable semiconducting 2H-MoS$_2$ to the meta-stable metallic 1T-MoS$_2$ phase. The electron transfer from Li to the MoS$_2$ structure was identified as the driving mechanism for this structural change. The 2H and 1T phases can be identified by Raman spectroscopy. While both 1T-MoS$_2$ and 2H-MoS$_2$ show Raman active A$_{1g}$ and E$_{2g}$ modes at 380 cm$^{-1}$ and 410 cm$^{-1}$, 1T-MoS$_2$ results in additional Raman active modes at 160 cm$^{-1}$, 230 cm$^{-1}$ and 330 cm$^{-1}$. [157] However, since the 1T phase is meta-stable, it gradually converts to the trigonal prismatic coordination over time. [155] [156] This phase transformation from trigonal prismatic to octahedral coordination in MoS$_2$ is
currently being explored as a platform to engineer low-resistance contacts for field-effect transistor devices utilizing the group VI TMDs. [157] [158]

Alternatively, intercalation of zero-valence ions into LMCs compounds preserves the morphology and structure of the host material. [159] Such an approach can be used to engineer the interlayer coupling between the individual layers of LMC compounds.

1.3 Characterization Methods

A variety of different characterization methods, such as Raman spectroscopy [160], PL spectroscopy [120], AFM [107], STM [137], TEM [106], ARPES [31], second harmonic generation [SHG] [161], X-ray photoelectron spectroscopy (XPS) [162] and X-ray diffraction (XRD) [109] have been used to study the structure and properties of LMCs.

In this section, an overview of a limited number of spectroscopy and measurement techniques that have been crucial to characterize the structural, electrical, optical and vibrational properties of few-layer LMCs is provided.

Raman measurements are a useful technique to understand the stacking order, interlayer coupling and thickness of Raman measurements on registered bulk and few-layer metal chalcogenides demonstrate two primary Raman modes, the $A_{1g}$ out of plane and $E_{2g}$ in plane Raman modes. These two distinct peaks that correspond to the in-plane and out of plane vibrational modes are the most intense peaks in the Raman spectra of these materials, determined by the selection rules of the Raman active vibrational modes. When LMCs, such as MoS$_2$ and MoSe$_2$ are reduced to a single monolayer there are quantitative shifts in the Raman spectra. [86] The in-plane $E_{2g}$ mode frequency increases
and the $A_{1g}$ out of plane mode frequency decreases as the film thickness is reduced to a single monolayer. These modes have also been shown to be sensitive to changes in stacking order and misorientation between monolayers. Raman modes due to two-phonon modes have also been observed in single- and few-layer LMC. These shifts in the out of plane Raman mode frequency as a function of film thickness indicates the sensitivity of these materials to sample thickness, interlayer coupling, rotation and stacking.

TEM, in particular, has proven to be an excellent tool for the characterization of 2D materials at the atomic level. Recent advances in the TEM techniques, such as selected-area electron diffraction (SAED) [115], bright-field conventional TEM (BF-CTEM) [111] and high-angle annular dark field scanning TEM (ADF-STEM) [106], have shown that the layer number and stacking order can be quantitatively determined, and the individual atoms in a layer can be visualized. In a recent report on the growth and structural characterization of MoS$_2$, George et al. [106] showed that monolayers as well as bi- and triple-layers of MoS$_2$ can be identified by using high-angle annular dark-field scanning TEM (HAADF-STEM).

In addition to TEM, ARPES has enabled direct observation of the Fermi surface and underlying electronic structure of 2D LMCs. Prior studies have shown [31] [30] the thickness-dependent electronic band structures of LMCs can be experimentally determined using ARPES. Zang et al. [137] directly measured the electronic band structure of MoSe$_2$ using ARPES.
1.4 Applications

The current application space of LMCs and their heterostructures ranges from next generation electronic [165] and optoelectronic devices [11] beyond the technology road map, flexible electronics [62], piezoelectronics [166] and energy storage and conversion [167].

Research into electronic devices that utilize LMC materials as the active material are driven by the search for new materials that would scale beyond the international technology roadmap for semiconductors (ITRS). The semiconducting LMC compounds have an inherent advantage over traditional CMOS materials at dimensions beyond the scaling roadmap (< 5 nm). The larger effective masses of the LMCs (~0.4 to 0.5 m₀, m₀ is the free electron mass) provide a higher density of states and hence a higher drive current while simultaneously having a low direct tunneling current which lowers the off-state leakage current at channel lengths below 5nm. [168] The robust mechanical properties of LMC compounds combined with mobilities that vary between 1 cm²/Vsec and 100 cm²/Vsec make them suitable candidates for future flexible electronics.

2D LMCs with high surface-to-volume ratio, flexibility, high sensing ability, robust photoluminescence and good electrical conductivity have emerged as new promising materials for chemical sensors and biosensors. [169] The interaction with an analyte changes the charge transport properties of atomically thick LMC materials as an active channel in a FET configuration, so the electrical properties are correspondingly changed upon exposure. In addition to sensing based on changes in electrical properties, LMCs also provide an alternative avenue for sensing based on light emission. [170] The
charge transfer upon physisorption of the analyte leads to changes in the PL emission efficiencies. Application of gate bias and exposure to light have been found to enhance device sensing performance. [171] LMC materials can be also potentially adopted for biosensing applications. More recently, MoS$_2$ has been successfully used as a sensing material for the detection of DNA and small molecules on the basis of its high fluorescence quenching ability and different affinity toward ssDNA versus dsDNA. [172]

Along with their interesting catalytic properties, LMCs hold great promise as catalysts for hydrogen evolution reaction (HER) in which hydrogen is produced through the process of electrocatalytic or photocatalytic water reduction. LMCs provide large edge to volume ratio and greater density of edge sites for high catalytic performance. The edge sites of 2D layers with unsaturated coordination atoms and dangling bonds could serve as active sites for hydrogen bonding. Several studies [173] [174] have demonstrated high catalytic activity in MoS$_2$ which emerges as a low-cost alternative material to the traditional HER catalysts such as Pt, and Pd. Metallic T phase of MoS$_2$ was found to be a more active HER catalyst than semiconducting 2H-MoS$_2$. [175] The possibility of tuning the HER activity of LMCs through phase selection, engineering, nanostructuring and alloying is expected to further increase the substantial advantages of 2D layers for their catalytic applications.

1.5 Grand Challenges and Opportunities

The current focus of research on 2D LMCs is on establishing the fundamental properties of these materials and their heterostructures. These efforts are driven by the hope that amongst this large family of compounds is a solution for next generation low
power electronics, high capacity energy storage and conversion and broadband optical devices. The LMCs also provide a platform to study fundamental condensed matter phenomena such as superconductivity and charge density waves at low dimensions. This combination of applied and fundamental research with this family of materials is still in its infancy. The first paper on a monolayer MoS$_2$ transistor appeared in 2011 and the field has been growing ever since. The combined effort on the growth of new layered materials, advances in the fabrication of pristine heterostructures and sophisticated theoretical predictions based on ab-initio theory suggest that further developments in the field are forthcoming that would lead to the adoption of LMCs in practical applications and also provide a platform to explore exotic physical phenomena.

### 1.6 Thesis Outline

This dissertation focuses on the various unique methods of producing 2D atomic LMC crystals including growth of group VI transition metal dichalcogenides by chalcogenization of pre-deposited metal-containing precursors, and phase-engineered growth of group IV LMCs by vapor-phase reaction of metal oxide and chalcogen powders. STEM, SEM, AFM, optical microscopy, Raman spectroscopy, PL spectroscopy, ultraviolet photoelectron spectroscopy (UPS), XPS, energy dispersive X-ray spectroscopy (EDX), and XRD are all notable experimental techniques used to characterize these various materials, and the experimental results are corroborated by density functional theory (DFT) calculations.

In chapter 2, we developed a seed-assisted CVD approach for the growth of 2D WS$_2$ crystals and its alloys with MoS$_2$ on SiO$_2$/Si substrates using hydrothermally
synthesized WO₃ seeds. This method produces highly crystalline semiconductor WS₂ crystals with a bandgap of 1.94 eV in monolayer form. PL spectroscopy measurements in conjunction with ab-initio DFT calculations show that bulk WS₂ undergoes a transition from an indirect bandgap to a direct one in monolayer limit. We also showed that the modification of the band gap is possible by changing the composition of Mo and W in MoS₂-WS₂ heterogeneous layers, pointing to creating a range of bandgap values by alloying 2D semiconductors.

In chapter 3, we demonstrated the large-area growth of atomically thin WS₂ films via sulfurization of the pre-deposited W-based films on SiO₂/Si substrates. The fundamental morphologic, electronic, optical and chemical properties of the pre-deposited W-based films and WS₂ films were investigated using various microscopy and spectroscopy techniques. We showed that the WS₂ films show laser power dependent PL characteristics, where the PL peak shifts toward lower photon energy, and its intensity increases with laser power. Moreover, we introduced a simple method to etch WS₂ films with well-oriented triangular pits with a preferential edge termination.

In chapter 4, the phase-selective growth of 2D tin sulfides (SnS₂ and SnS) is demonstrated. Highly crystalline hexagonal SnS₂ and orthorhombic SnS crystals were synthesized on SiO₂ substrates by a simple vapor-phase method using SnO₂ and S as the source materials. The structural, vibrational, and electronic properties of each phase are studied by both experimental characterizations and ab-initio DFT calculations.

In chapter 5, we reported on the growth of 2D SnS₂ nanowalls (NWs) by a facile vapor-phase synthesis method on insulator substrates such as SiO₂/Si and MgO using
SnO$_2$ and S powders as precursors. The fundamental properties of the SnS$_2$ NWs were studied by using various techniques. The results suggested that the grown films are highly crystalline SnS$_2$ with an open network structure constituted of interconnected NWs.

In chapter 6, we demonstrated the synthesis of few-layer MoSe$_2$ films in arbitrary shapes and patterns on SiO$_2$ wafers by rapid thermal processing (RTP) and Raman laser annealing of the stacked elemental layers, which are deposited using electron beam evaporation in the sequence of Mo/Se/Mo. The morphology and microstructure of the films were characterized by AFM and SEM. Compositional and electronic structure analysis of the films were done by XPS, PL spectroscopy and Raman spectroscopy.

References


Chapter 2 Seed-Assisted CVD Synthesis of 2D WS\textsubscript{2} and MoS\textsubscript{2}-WS\textsubscript{2}

Abstract

Atomically thin WS\textsubscript{2} crystals were synthesized on SiO\textsubscript{2}/Si substrates via chemical vapor deposition (CVD) with the assistance of hydrothermally synthesized WO\textsubscript{3} seeds. This seed-assisted CVD approach allows production of highly crystalline semiconductor WS\textsubscript{2} with a bandgap of 1.94 eV in monolayer form. Photoluminescence (PL) spectroscopy measurements in conjunction with ab-initio density functional theory (DFT) calculations showed that bulk WS\textsubscript{2} undergoes a transition from an indirect bandgap to a direct one in monolayer limit. We also synthesized heterogeneous systems of MoS\textsubscript{2} and WS\textsubscript{2} and characterized them by Raman and PL spectroscopy measurements. The DFT calculations verify the modification of the band gap by changing the composition of Mo and W in MoS\textsubscript{2}-WS\textsubscript{2} heterogeneous layers, pointing to creating a range of bandgap values by alloying two-dimensional (2D) semiconductors.

2.1 Introduction

2D layered transition metal dichalcogenides (TMDs), especially WS\textsubscript{2}, have become the focus of intense scientific interest due to their exotic physical properties and exciting prospects for a variety of applications. [1, 3] TMDs exhibit a large variety of electronic behaviors such as semiconductivity, superconductivity or charge density waves. [4-6]

Layered semiconductor WS\textsubscript{2}, with an indirect bandgap of 1.48 eV in bulk form and a direct band gap of 1.94 eV in monolayer form, exhibits tunable electronic properties allowing for the realization of advanced optoelectronic devices, transistors and
valley polarization devices, etc. [7-10] The WS$_2$ bulk unit cell belongs to the hexagonal space group P6$_3$/mmc with lattice parameters of a=3.1532 Å and c=12.323 Å, and each WS$_2$ monolayer contains an individual layer of W atoms with a 6-fold coordination symmetry, which are hexagonally packed between two trigonal atomic layers of S atoms. [11]

Scientists and researchers around the world have been racing to discover and engineer methods for the reliable synthesis of 2D materials. Although the isolation of atomically thin 2D flakes from their bulk crystals through exfoliation is still the method choice for fundamental studies, it is impractical for large scale applications due to the size limitations of the produced flakes. [12]

CVD has been considered to be one of the most promising approaches for large scale production of 2D materials. [13, 14] Typical CVD synthesis of atomically thin WS$_2$ films includes sulfurization of W or WO$_3$ films, which are pre-deposited on the substrates by using sputtering, e-beam deposition, thermal evaporation or atomic layer deposition (ALD) methods, or vapor phase reaction of elemental S and WO$_3$ powders at high temperatures. [15-17]

Recently, Orofeo et al. have reported on the synthesis of few-layers WS$_2$ films by sulfurization of magnetron sputtered W films. [15] The synthesis of monolayer to few-layer WS$_2$ nanosheets has been demonstrated through sulfurization of an ALD WO$_3$ film. [18] Zang et al. have presented the synthesis of atomically thin WS$_2$ triangular flakes on sapphire via low-pressure CVD reaction of WO$_3$ and S. [19] However, to date, no studies have examined the role of the seeding in the synthesis of WS$_2$. 
Here, we have developed a seed-assisted CVD procedure for the synthesis of 2D atomically thin WS\textsubscript{2} and MoS\textsubscript{2}-WS\textsubscript{2} heterogeneous layers using WO\textsubscript{3} nanoplates (NPs) as nucleation promoters. The morphological, optical and electronic properties of the synthesized layers have been characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), optical microscopy, Raman spectroscopy and PL spectroscopy. Ab-initio DFT calculations have been performed to evaluate the electronic band structures.

2.2 Experimental Section

2.2.1 Materials Synthesis

WO\textsubscript{3} NPs were synthesized by a simple hydrothermal process and used as the precursor for WS\textsubscript{2} growth. 0.16 gr of sodium tungstate dehydrate (Na\textsubscript{2}WO\textsubscript{4}∙2H\textsubscript{2}O) was first dissolved in 2 mL of deionized (DI) water and 10 mL of nitric acid (HNO\textsubscript{3}) aqueous solution under magnetic stirring. The light yellow aqueous solution obtained after continuous 2 h of vigorous stirring was transferred to a 45 mL teflon-lined autoclave. The autoclave was sealed and kept at 180 °C for 2 h. The final product was washed with DI water several times and dried in a vacuum at 100 °C for 5 h. Si substrates with a thermally deposited 300 nm thick SiO\textsubscript{2} layer were cleaned in successive ultrasonic baths of acetone and isopropanol (IPA) for 30 min each.

WO\textsubscript{3} NPs were dispersed on SiO\textsubscript{2}/Si substrate, and the substrate was placed face-down above a polished quartz boat containing 0.5 mg of WO\textsubscript{3} powder. The WO\textsubscript{3}-coated substrate with the boat was then located at the center of heating zone. A ceramic boat containing 100 mg of S was located upstream where S starts evaporating when the
temperature of the center of the tube is 525 °C. The furnace was pumped down to 0.1 Torr in order to remove the air and then stabilized at 20 Torr with an Ar flow of 200 sccm. Next, the center of heating zone was heated to 525 °C, then to 850 °C with ramping rates of 10 °C /min and 5 °C /min, respectively. The furnace was kept at 850 °C for 15 min, and then naturally cooled down to room temperature (RT).

For the synthesis of MoS$_2$-WS$_2$, the same experimental set-up and the recipe were used. The WO$_3$ NPs were also employed as nucleation promoters. The only difference was the use of 0.5 mg of MoO$_3$ powder instead of WO$_3$.

2.2.2 Materials Characterization

Raman and PL spectra were collected using a 532 nm laser (<2 mW excitation power, 100x objective lens) at RT. The thickness measurements were performed by AFM in tapping mode. Microstructural analysis was done by SEM.

2.2.3 DFT Calculations

Our calculations were based on first-principles DFT using the projector augmented wave method as implemented in Vienna ab-initio simulation package (VASP). The screened Heyd-Scuseria-Ernzerhof (HSE) hybrid functional was employed for this study. A Monkhorst-Pack scheme was adopted to integrate over the Brillouin zone with a k-mesh 9 x 9 x 1 (8 x 8 x 4) for monolayer and bulk structure. A plane-wave basis kinetic energy cutoff of 280 eV was used. The lattice constant for monolayer WS$_2$ structure was obtained from a volume optimized bulk 2H-WS$_2$ structure. The atomic coordinates for monolayer structure were optimized at this fixed lattice constant. Spin-orbit coupling (SOC) was included self-consistently within the band structure.
calculations for monolayer WS$_2$. For the HSE calculations, 25% short-range exact Hartree-Fock exchange was used with the Perdew-Burke-Ernzerhof (PBE) correlation. The HSE screening parameter, $\mu$, was empirically set to 0.5 (1/Å) for bulk 2H-WS$_2$ and 0.26 (1/Å) for monolayer WS$_2$. For the Mo$_{1-x}$W$_x$S$_2$ system, the calculations were conducted using the PBE GGA approximation of DFT as implemented in the software package VASP. A (5x5x1) Mo$_{1-x}$W$_x$S$_2$ monolayer supercell was setup using the volume optimized bulk lattice constant of WS$_2$ (3.179 Å). The following values of $x$ were used: 0.0, 0.12, 0.20, 0.32, 0.40, 0.56, 0.60, 0.80 and 1.0. For each of these supercell structures the positions of the W atoms were randomly placed. Following a structure optimization of each supercell, the electronic band structure was calculated for each concentration of W atoms. For each structure, the bandgap remained direct.

### 2.3 Results and Discussion

The morphology of WO$_3$ NPs, which were hydrothermally synthesized, was investigated by SEM (Figure 2.1(a)). The thickness and lateral size of the NPs was estimated to be tens of nanometers and a few microns, respectively. WO$_3$ NPs were further characterized by Raman spectroscopy analysis. Raman spectra of WO$_3$ (Figure 2.1(b)) display three major Raman modes at 809 cm$^{-1}$ and 708 cm$^{-1}$ (O-W-O stretching modes) and 271 cm$^{-1}$ (O-W-O bending mode), consistent with previous studies. [20]
Figure 2.1 The morphology and Raman spectra of the WO$_3$ crystals. SEM image (a) and Raman spectra (b) of WO$_3$ NPs.

The low (Figure 2.2(a)) and mid-high (Figure 2.2(b)) magnification optical images of a typical sample show that our growth method produces primarily triangular and multi-point star shaped WS$_2$ domains which are several microns in size and have a clear contrast from SiO$_2$ substrate. We can hypothesize that the diffusion of S into WO$_3$ NPs results in WS$_2$ nuclei in conjunction with chemisorbed sulfur species. [21] The thinner WS$_2$ layers then expand from the edges of the nuclei upon further sulfurization with the supply of WO$_3$ vapor.

It is known that any compositional inhomogeneity on SiO$_2$/Si substrate surface can provide lower necessary activation energy for the formation of WS$_2$ nuclei. [19] Therefore, we employed WO$_3$ NPs as nucleation promoters for the growth of WS$_2$ crystals by bottom-up CVD process. We found that the distribution of WS$_2$ domains is not homogenous on the substrate (Figure 2.2(a)) due to the heterogeneous distribution of WO$_3$ NPs over the substrate. This is a current limitation of our experimental approach that can be resolved technically in the future. We also observed that the dense WO$_3$ seeds
promote a large number of WS$_2$ domains to form aggregates and continuous sheets (Figure 2.2(b)).

In the course of these experiments, we noticed that WO$_3$ crystals with different morphologies can form (Figure 2.2(c,d)). Although these observations were not common in our experiments, it clearly shows that the morphology of WO$_3$ dictates the size and shape of the grown WS$_2$ domains, consistent with previous studies. [13] Moreover, since the activation energy for the nucleation is substantially low due to the roughness and edges provided by WO$_3$ crystals, more layers are grown from the same origin, which creates thicker regions on the layers.
**Figure 2.2** The morphology of the WS$_2$ crystals. Low (a) and mid-high (b) magnification optical microscopy images of a typical WS$_2$ film grown on SiO$_2$/Si. Note that the alignment marks were made after the WS$_2$ growth for the device fabrication. SEM images (c, d) of WS$_2$ domains with different morphologies.

AFM is a powerful method to determine the thickness of 2D materials with a precision of 5 %. [22] The AFM topography image (**Figure 2.3**) of a bilayer WS$_2$ domain reveals the presence of the sharp edges forming a $60^\circ$ angle. Their edges are along a specific crystallographic direction, and only one edge termination is energetically favored. [23] Although our experiments cannot determine whether the preferred edge is the W-edge or S-edge, it is expected that the preferred edge is the W-edge in WS$_2$ domains owing to the sharp edges. [24] The thickness of the first layer was determined to
be 1.3 nm, which is higher than that of the second layer with a thickness of 0.7 nm (Figure 2.3). [16, 19] This discrepancy arises from differences in the interactions of the tip with the sample and substrate. [22] Therefore, the thickness of a monolayer WS$_2$ can be better determined by measuring the height of a second WS$_2$ layer on a first layer since the tip-layer interactions are constant.

![AFM thickness analysis of the WS$_2$ crystal.](image)

**Figure 2.3 AFM thickness analysis of the WS$_2$ crystal.** AFM image of a bilayer WS$_2$ crystal. The inset shows the height profile along the dashed line in the image.

Raman spectroscopy was used to confirm that the grown domains are indeed WS$_2$. The Raman spectrum (**Figure 2.4(a)**) of a monolayer WS$_2$ using a laser with a wavelength of 532 nm demonstrates the characteristic in-plane vibrational ($E_{1g}$) mode and the out-of-plane vibrational ($A_{1g}$) mode at 350.25 cm$^{-1}$ and 417.50 cm$^{-1}$, respectively.
The frequency difference between the $E_{12g}^{1}$ and $A_{1g}$ modes was determined to be to be 67.25 cm$^{-1}$, consistent with what was observed on the CVD-grown monolayer WS$_2$.

The PL study showed that WS$_2$ exhibits a transition from indirect band gap semiconductor in the form of bulk to direct band gap one in monolayers, similar to MoS$_2$. A strong and sharp PL peak at 1.94 eV was found in monolayer WS$_2$ (Figure 2.4(b)), which indicates an indirect to direct band gap transition in monolayer WS$_2$. The PL intensity was found to be extremely weak on bulk WS$_2$, consistent with an indirect band gap semiconductor in bulk form. To gain further insight, we computed the electronic band structures of monolayer and bulk WS$_2$ using ab-initio DFT. According to our calculations (Figure 2.4(c,d)), monolayer WS$_2$ has a direct band gap of 1.90 eV and bulk WS$_2$ has an indirect band gap of 1.48 eV, which is consistent with prior reported studies on the electronic structure of WS$_2$ and our PL data on monolayer WS$_2$. [28, 29]
Figure 2.4 Raman-PL spectra and DFT-calculated electronic band structure of the WS$_2$ crystals of different thickness. Raman spectra (a) of monolayer WS$_2$. PL spectra comparison (b) of monolayer and bulk WS$_2$. DFT-calculated electronic band structures of monolayer (c) and bulk (d) WS$_2$.

We also performed Raman mapping of the WS$_2$ domains with different morphologies by plotting the intensity ratio of E$_{12g}$ and A$_{1g}$ peaks. It is known that intensity ratio mapping provides a more accurate characterization and better resolution for 2D layers with different thicknesses. [30] The Raman mapping image (Figure 2.5(a)) of the WS$_2$ domain with perfect triangular shape revealed the presence of the second layer on the nucleation site, which is not visible in the optical microscopy image (Figure 2.5(b)). The second layer nucleates in the vicinity of the edges of the WO$_3$ nucleus where the first layer grows, and it follows the growth direction of the underlying layer. [13] It was also found that a large WS$_2$ domain can be formed by joining several layers from the same nucleus. Although the grain boundaries are not clear in the optical microscopy image
(Figure 2.5(d)) of the multi-point star WS$_2$ domain, the Raman mapping image (Figure 2.5(e)) clearly shows the boundaries between the triangular shaped flakes, proving the capability of Raman spectroscopy in characterization of atomically thin 2D TMDs.

![Raman imaging of WS$_2$ crystals of different morphologies](image.png)

**Figure 2.5 Raman imaging of the WS$_2$ crystals of different morphologies.** Raman mapping and optical images of the triangular (a, b) and multi-point star (c, d) shaped WS$_2$ domains, respectively.

We also synthesized MoS$_2$-WS$_2$ heterogeneous layers using WO$_3$ NPs as nucleation promoters in order to study the electronic and optical properties of the heterogeneous systems. The intensity ratio ($E_{1g}^{1}/A_{1g}$) mapping image (Figure 2.6(a)) and Raman spectra (Figure 2.6(b)) taken from different regions of a typical MoS$_2$-WS$_2$
domain confirm the coexistence of MoS$_2$, WS$_2$ and Mo$_{1-x}$W$_x$S$_2$ layers. [31, 32] The PL measurements (Figure 2.6(c)) revealed that Mo$_{1-x}$W$_x$S$_2$ has a relatively strong PL peak at 1.87 eV (663 nm), lying between those of MoS$_2$ (1.85 eV) and WS$_2$ (1.94 eV).

Figure 2.6 Raman-PL spectroscopy characterization and DFT-calculated band gap of the MoS$_2$-WS$_2$ heterogeneous crystals. Raman mapping image (a) and optical microscopy image (inset) of a MoS$_2$-WS$_2$ domain. The corresponding Raman (b) and PL (c) spectra comparison of the P1 (MoS$_2$), P2 (WS$_2$), and P3 (Mo$_{1-x}$W$_x$S$_2$) points in (a). The variation in band gap as a function of the composition of W atoms in the Mo$_{1-x}$W$_x$S$_2$ supercell by the DFT calculations (x=0 denotes a MoS$_2$ supercell while x=1 denotes a WS$_2$ supercell) (d).

To verify the modification of the PL peak in the Mo$_{1-x}$W$_x$S$_2$ system and understand the dependence of the band gap on Mo and W composition, we conducted the DFT calculations on a Mo$_{1-x}$W$_x$S$_2$ monolayer supercell and showed the variation in band
gap as a function of the composition of W atoms in monolayer Mo$_{1-x}$W$_x$S$_2$ supercell (Figure 2.6(d)). The calculation results are in close agreement with our experiment results and the previous reports. [31, 33]

2.4 Conclusion

In conclusion, we have demonstrated the synthesis of 2D semiconductor WS$_2$ layers on SiO$_2$/Si via CVD using hydrothermally synthesized WO$_3$ NPs as seeds. The DFT computational results show that an indirect-to-direct band gap transition occurs in WS$_2$ monolayers, in good agreement with PL spectroscopy measurements. AFM results confirm that this growth method produces atomically thin WS$_2$ layers with a monolayer thickness of 0.7 nm. We have also synthesized MoS$_2$-WS$_2$ heterogeneous layers by using this method, showing our capability to fabricate a variety of different 2D crystalline materials and their heterogeneous systems. We hope that the results reported herein create a basis for the systematic exploration of these materials in research and potential applications.

References


Chapter 3 Large-Area Synthesis and Anisotropic Etching of 2D WS$_2$

Abstract

Emergent properties of WS$_2$ at the quantum confinement limit hold promise for electronic and optoelectronic applications. Here we reported on the large-area synthesis of two-dimensional (2D) WS$_2$ with strong photoluminescence (PL) properties via sulfurization of the pre-deposited W films. Detailed characterization of the pre-deposited W films and WS$_2$ films were performed using various microscopy and spectroscopy methods. By directly heating WS$_2$ in air, we showed that the films tend to be etched into a series of triangular shaped pits with the same orientations, revealing the anisotropic etching behavior of WS$_2$ edges. Moreover, the dimensions of the triangular pits increase with the number of layers, suggesting a thickness dependent behavior of etching in WS$_2$. This method offers a promising new avenue for engineering the edge structures of WS$_2$.

3.1 Introduction

Graphene-like 2D semiconducting transition metal dichalcogenides (TMDs), especially WS$_2$, with sizeable band gaps have showed vast potential for electronics and optoelectronics due to exotic physical and electronic properties, recently. [1, 2] WS$_2$ is a layered semiconductor material with a direct band gap of $\sim$1.95 eV in monolayer form. [3] For electronics, the presence of a band gap allows field-effect transistors (FETs) to have high on/off ratios, and its ultrathin nature allows the channel length to be reduced relative to those fabricated with conventional semiconductors. [4, 5] For optoelectronics, the direct band gap produces high photoconductivity, and strong PL. [3, 6] To explore
new fundamental properties and to further develop their electronic and optoelectronic applications, synthesis of large-area atomically thin WS\(_2\) layers with uniform properties by a facile and scalable method is an essential requirement.

Recent top-down approaches including mechanical exfoliation and liquid exfoliation to obtain high crystalline WS\(_2\) flakes have attracted considerable attention.\(^7,\)\(^8\) However, lateral dimensions of the flakes synthesized by the exfoliation methods are limited to few microns, which limits their applications in large-scale electronics and optoelectronics.

In contrast, chemical vapor deposition (CVD) techniques have great potential in producing large-area WS\(_2\) over macroscopic sizes, which are ideal for integration with current CMOS platform. Typically, CVD growth of WS\(_2\) includes vapor phase reaction or deposition of gaseous metal and chalcogenide feed stocks, and sulfurization or decomposition of the pre-deposited films.\(^9\)-\(^12\)

Among the CVD techniques, sulfurization of the pre-deposited thin films is emerging as a quick and easy way to obtain large-area atomically thin WS\(_2\) films on insulating substrates. Recently, several studies have reported direct sulfurization of WO\(_3\) films deposited either by thermal evaporation or by atomic layer deposition (ALD).\(^11,\)\(^12\) However, to the best of our knowledge, large-area growth of atomically thin WS\(_2\) films on SiO\(_2\) substrates by sulfurization of W films deposited by e-beam deposition has not been reported yet.

In parallel with the recent advances in the synthesis of TMDs, numerous methods have been developed to enable their identification and characterization. PL spectroscopy
is a powerful method of probing the electronic structure of TMDs. [13] Recent studies report that MoS$_2$ shows laser-dependent PL spectra, where the PL intensity and position are affected by varying the duration and intensity of laser irradiation. [14] To the best of our knowledge, there is no systematic study concerning the effect of laser power on PL spectra of WS$_2$, which is essential to probing the PL characteristics of WS$_2$.

Recently, there has been an increasing interest in the nanoscale control of edge structures of TMDs. Nanoscale control of edge structures offers new pathways toward fine tuning the electronic, optical, chemical, magnetic, and catalytic properties of TMDs. [15-18] One way to engineer edge structures of TMDs is heating them in an O$_2$ environment. [19, 20] For example, high density triangular pits with the Mo or S terminated zigzag edges on the surface of MoS$_2$ sheets have been obtained upon annealing them in air, which might arise from the anisotropic etching of the active MoS$_2$ edge sites. [19] Such edge terminated MoS$_2$ structures find applications in diverse catalytic reactions. [21, 22] As mentioned above, most studies so far have focused on the oxidative etching of MoS$_2$. However, to the best of our knowledge, the etching behavior of WS$_2$ films has yet to be experimentally studied.

In this study, we demonstrate the large-area synthesis of atomically thin WS$_2$ films on SiO$_2$ substrates. Briefly, the W films are deposited on SiO$_2$ substrate by using e-beam deposition method. In the next step, the as-deposited W films are annealed at 500 °C and then sulfurized at 850 °C to obtain WS$_2$ films. The fundamental morphologic, electronic, optical and chemical properties of the pre-deposited W films and WS$_2$ films are investigated using optical microscopy, atomic force microscopy (AFM), scanning
electron microscopy (SEM), X-ray photoemission spectroscopy (XPS), Raman spectroscopy and PL spectroscopy. We also systematically investigate the dependence of PL spectra of WS$_2$ films on laser power. Furthermore, we introduce a simple method to etch WS$_2$ films with well-oriented triangular-shaped pits by heating them in air.

### 3.2 Experimental Section

#### 3.2.1 Materials Synthesis

WS$_2$ films were synthesized via three steps: i) deposition of the W films, ii) annealing of the W films, and iii) sulfurization of the annealed W films. First of all, the W films with a thickness of $\sim$15 nm were deposited on SiO$_2$ substrates (300 nm thick SiO$_2$ layer deposited thermally on Si wafer) by e-beam deposition method. The deposition of the films was carried out in a load-lock chamber at a base pressure of $\sim$10$^{-6}$ Torr and deposition pressure of $\sim$10$^{-5}$ Torr, with an average growth rate of 1 Å/s. Next, the as-deposited W films were annealed at 500 °C in open air for 60 min in order to oxidize the films in a single-zone vacuum tube furnace with 2-inch diameter quartz tube. The annealed W films were then put at the center of the heating zone, and 250 mg of S powder was put in a ceramic boat at the upstream where S starts evaporating when the temperature of the center of the tube is 525 °C. High-purity Ar gas with a constant flow of 100 sccm was used as the carrier gas. After that, the furnace was pumped down to remove the air, and the pressure was stabilized at 250 Torr. Further, the center of heating zone was heated to 850 °C with a heating rate of 5 °C/min, and it was kept at that temperature for 10 min. Finally, it was naturally cooled down to room temperature. The
etching of WS\textsubscript{2} films was performed in the same furnace by simply heating them in air at 500 °C for 45 min.

### 3.2.2 Materials Characterization

The morphology of WS\textsubscript{2} films was investigated using SEM. Raman and PL spectra were collected using a 532 nm laser (<2 mW excitation power, 100x objective lens) at RT. Surface chemical analysis was carried out by using a XPS system equipped with an Al K\textalpha{} monochromated X-ray source and a 165-mm mean radius electron energy hemispherical analyzer. The vacuum pressure was kept below $3 \times 10^{-9}$ torr, and the neutralizer was applied during the data acquisition. The thickness measurements were performed by AFM in tapping mode.

### 3.3 Results and Discussion

The morphology and thickness of the W films before and after annealing are determined by AFM analysis. The AFM height image (**Figure 3.1(a)**) of the as-deposited films reveals island type morphology with a height of about 15 nm. The simultaneously recorded AFM phase contrast image (**Figure 3.1(b)**) reveals an additional contrast on the surface of islands, which may be attributed to the ‘native oxide layer’.
Figure 3.1 AFM analysis of the as-deposited and annealed W films. AFM height and corresponding phase images for the as-deposited (a, b) and annealed (c, d) W films on SiO$_2$ substrates, respectively. The AFM height and phase contrast images are taken in an area of 2x2 μm$^2$. The insets in (a) and (c) show the height profiles for the island morphologies.

The as-deposited W films are annealed in open air for 60 min at 500 °C. Annealing is found to induce changes in the morphology and thickness of the films. The AFM height image (Figure 3.1(c)) of the annealed W films reveals roughly triangular island type morphologies with a height of about 6 nm. While the density of the islands increases, the thickness of the islands decreases upon annealing. This could be explained as follows: It is known that when Tammann temperature (~599 °C for WO$_3$) is achieved,
the evaporation of metal oxide thin films can be initiated even though the processing
temperature is lower than their melting point (~1473 °C for WO₃). [23] It is possible that
surface oxidation of the as-deposited W films may occur during deposition. Thus, the as-
deposited W films with the native oxide layer might become thinner possibly due to the
partial evaporation of the metal oxide layer upon annealing. The AFM phase contrast
image (Figure 3.1(d)) reveals layered-type island morphologies with one single phase
contrast, which can indicate a completed oxidation.

The as-deposited and annealed W films are investigated by XPS analysis. The
high-resolution XPS spectra (Figure 3.2(a)) of the as-deposited films reveal four major
peaks at 37.99 eV, 35.87 eV, 33.38 eV and 31.2 eV. The typical doublet W 4f peaks of W
are clearly visible in the spectra, which are at 33.38 eV and 31.2 eV. [9] The two upper
binding energy peaks at 37.99 eV, 35.87 eV can be attributed to WO₃, confirming the
existence of WO₃ in the as-deposited films. [24] It is also found that there is a shoulder at
upper energy side of each W peak, and the shoulders are related to WO₂ and WOₓ. [24]
We can conclude that W, WO₃ and sub-stoichiometry tungsten-oxides exist in the as-
deposited film. The high-resolution XPS spectra (Figure 3.2(b)) of the annealed films
reveal only two W 4f peaks at 37.97 eV and 35.87 eV, which are assigned to WO₃. After
annealing, the metallic W peaks and the shoulder peaks related to WO₂ or Wₓ completely
disappear. This evidence strongly supports the stoichiometry phase evolution of the as-
deposited films.
Figure 3.2 XPS analysis of the W and WS$_2$ films. High resolution XPS spectra of W 4f core levels of the as-deposited (a) and annealed (b) W films. High resolution XPS spectra of W 4f (c) and S 2p (d) core levels of WS$_2$ films.

The XPS data of WS$_2$ films are also captured to analyze surface composition of the WS$_2$ films. The two peaks of each core level appear due to spin orbital splitting of W 4f (Figure 3.2(c)) and S 2p (Figure 3.2(d)) core levels. The peaks at 38.89 eV, 35.40 eV, and 33.2 eV are ascribed to W 5p$_{3/2}$, W 4f$_{5/2}$, and W 4f$_{7/2}$ orbitals, respectively. The binding energies for the S 2p$_{1/2}$ and S 2p$_{3/2}$ are located at 164.0 eV and 162.82 eV, respectively. The binding energies of the W and S elements are consistent with the W (+4) and S (-2) oxidation states in WS$_2$, further confirming the formation of a pure WS$_2$ phase. [25]

To study the effect of annealing on the growth of WS$_2$ films, we have synthesized WS$_2$ films by sulfurizing the as-deposited and annealed W films. It is observed that
sulfurization of the as-deposited W films leads to thick WS$_2$ films with poor coverage (Figure 3.3(a,b)). However, thinner WS$_2$ films with high coverage are obtained by sulfurization of the annealed W films (Figure 3.3(c,d)). For clarification, monolayer, few-layer and thick regions of WS$_2$ films and the substrate are indicated by arrows on the high magnification SEM images (Figure 3.3(b,d)), as confirmed by Raman and PL spectroscopy. We can conclude that the WS$_2$ growth is substantially improved by annealing the as-deposited W films before sulfurization.

**Figure 3.3 The morphology of the WS$_2$ films.** Low and high magnification SEM images of WS$_2$ films obtained by sulfurizing the as-deposited (a, b) and annealed (c, d) W films, respectively.

The growth mechanism of WS$_2$ films can be explained as follows. The reaction of S vapor with WO$_3$ islands result in WS$_2$ nuclei. This reaction includes a transition to WO$_{(3-x)}$ species along with the subsequent formation of oxisulfides. As the reaction proceeds, a complete conversion to WS$_2$ occurs, and thinner WS$_2$ layers expand from the edges of WS$_2$ nuclei, in a similar manner as in MoS$_2$. [26]
We have taken Raman and PL spectra from monolayer and few-layer regions of a WS$_2$ film as indicated by arrows on the optical microscopy image (Figure 3.4(a)) of the film. The Raman spectra (Figure 3.4(b)) of monolayer region of the WS$_2$ film demonstrate the characteristic in-plane vibrational ($E^{12g}$) mode and the out-of-plane vibrational ($A_{1g}$) mode at $\sim$350 cm$^{-1}$ and $\sim$416 cm$^{-1}$, respectively. [27, 28] The frequency difference between the two modes is found to be $\sim$66 cm$^{-1}$. These results are consistent with what has been reported for WS$_2$ in the previous studies. [29] The PL spectra (Figure 3.4(c)) of monolayer and few-layer regions of the WS$_2$ film are compared. For monolayer WS$_2$, the PL peak has a maximum at 1.96 eV, which falls in the range of the reported PL peak positions for monolayer WS$_2$. [7, 29] The PL peak of monolayer WS$_2$ is also higher and sharper than that of the few-layer WS$_2$, which indicates the presence of a direct band gap in monolayer WS$_2$. [30] For few-layer WS$_2$, the PL peak shifts toward lower photon energy ($\sim$1.93 eV), and its intensity decreases dramatically, revealing the thickness dependent PL characteristics of WS$_2$. 
Figure 3.4 Raman-PL spectroscopy characterization of the WS$_2$ films. Optical microscopy image (a) of a WS$_2$ film. Monolayer and few-layer regions of the WS$_2$ film and the substrate are indicated by arrows. Raman spectra (b) of monolayer region of the WS$_2$ film. PL spectra (c) of monolayer and few-layer regions of the WS$_2$ film. Laser power dependent PL spectra (d) of monolayer region of the WS$_2$ film.

We have also investigated the effect of laser power on PL spectra of monolayer region of the WS$_2$ film with increasing laser power ranging from 0.1 mW to 0.5 mW with a step of 0.05 mW, and from 0.5 mW to 5 mW with a step of 0.5 mW (Figure 3.4(d)). It is observed that the PL intensity increases with increasing laser power, consisted with the results reported for MoS$_2$. [14] Moreover, the PL peak shifts toward lower photon energy as laser power increases. The shift in the PL peak can be attributed to the defect related optical transition. [31] Thus, we conclude that laser power must be carefully controlled in
the applications of PL spectroscopy in order to draw reliable conclusions about the PL characteristics of TMDs.

Furthermore, by directly heating a WS$_2$ film in air at 500 °C, we show that the WS$_2$ film is tend to be etched with a series of the triangular-shaped pits with the same orientations (Figure 3.5). The triangular shape of the pits indicates that the WS$_2$ film is etched preferentially along a specific crystallographic direction that is parallel to the edges of the pits with a preferential edge termination (W-edge or S-edge). [19] The etching is likely to be initiated at the intrinsic structural defects in the WS$_2$ film. [19] We also show that the size of the pits is greatly affected by the WS$_2$ film thickness, where the sizes of the pits increases with the thickness. The sizes of the triangular pits on a multilayers region (with a thickness of about 10.2 nm) of the WS$_2$ film (Figure 3.5(a)) is found to be larger than these of the pits on a few-layer region (with a thickness of about 3.2 nm) of the film (Figure 3.5(b)). This suggests the thickness dependent behavior of the etching on the WS$_2$ film. [32] These results are similar to previous reports on the etching of MoS$_2$. [19, 32, 33]
Figure 3.5 AFM analysis of the triangular pits formed on the WS$_2$ films by air-annealing. AFM height images showing the formation of the triangular pits on multilayers (a) and few-layer (b) regions of a WS$_2$ film. The AFM images are taken in an area of 2x2 μm$^2$. The insets in (a) and (b) show the height profiles for the triangular pits.

3.4 Conclusion

In summary, we report a facile method for the large-scale synthesis of atomically thin WS$_2$ films with strong PL properties via sulfurization of the pre-deposited W films. Thermal annealing of the W films before sulfurization is found to substantially improve the quality of WS$_2$ films in terms of thickness and uniformity. We also find that WS$_2$ films show laser power dependent PL characteristics, where the PL peak shifts toward lower photon energy, and its intensity increases with laser power. Furthermore, we introduce a simple method to etch WS$_2$ films with well-oriented triangular pits with a preferential edge termination. The edge sizes of the pits increase with the thickness of WS$_2$ films. This etching method enables successful formation and modification of the edge structures of WS$_2$ films with potentially tunable electronic, optical and magnetic properties, which promise various applications ranging from catalysis to energy harvesting.
References


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Chapter 4 Phase Engineering of 2D Tin Sulfides

Abstract

Tin sulfides can exist in a variety of phases and polytypes due to the different oxidation states of Sn. A subset of these phases and polytypes take the form of layered Two-dimensional (2D) structures that give rise to a wide host of electronic and optical properties. Hence, achieving control over the phase, polytype, and thickness of tin sulfides is necessary to utilize this wide range of properties exhibited by the compound. This study reports on phase-selective growth of both hexagonal tin (IV) sulfide SnS$_2$ and orthorhombic tin (II) sulfide SnS crystals with diameters of over tens of microns on SiO$_2$ substrates through atmospheric pressure vapor-phase method in a conventional horizontal quartz tube furnace with SnO$_2$ and S powders as the source materials. Detailed characterization of each phase of tin sulfide crystals is performed using various microscopy and spectroscopy methods, and the results are corroborated by ab-initio density functional theory (DFT) calculations.

4.1 Introduction

2D tin sulfides belong to a broad class of van-der-Waal (vdW) materials that have been the subject of intense research. Their constituent elements Sn and S are inexpensive and abundant in nature. The atomically thin geometry combined with the ability to tune the electronic structure of 2D tin sulfides as a function of thickness makes them attractive candidates to be used in nanoelectronics and optoelectronic devices. [1] These sulfides can crystallize in a variety of crystal phases, such as SnS$_2$ and SnS, which possess distinct physical and electronic properties. [2] Therefore, identifying approaches for controlling
crystal phase is essential for tailoring the properties of these materials to specific applications.

Tin sulfides possess desirable properties for numerous electronic and optical applications. SnS$_2$ is an intrinsic n-type layered semiconductor with a bandgap of 2.18-2.44 eV. [3-6] Potential applications of SnS$_2$ include novel electronics devices, flexible electronics, optoelectronics, and energy storage. [7-10] The high electron affinity of SnS$_2$ makes it a suitable candidate to achieve broken-gap heterostructures which enable the design and operation of 2D tunnel field-effect transistor (TFETs). [7, 11] Moreover, SnS$_2$ crystals show high charge carrier mobility ($\sim$ 230 cm$^2$/Vs) combined with high on/off current ratios ($>10^6$) in field-effect transistors (FETs), fast photocurrent response time ($\sim$ 5 $\mu$s) in photodetectors, and high theoretical specific capacity ($\sim$ 920 mAh/g) in lithium-ion batteries (LIBs) as the anode material. [1, 9, 12] On the other hand, SnS is an intrinsically p-type layered semiconductor with an indirect and a direct bandgap at $\sim$ 1-1.1 eV and $\sim$ 1.3-1.5 eV, respectively. [3, 13-16] The desirable bandgap, high absorption coefficient ($>10^4$ cm$^{-1}$) and sensitivity of its properties to changes in dimensionality, and elemental composition make SnS a promising material for optoelectronic applications. [15, 17-21] Furthermore, combined SnS and SnS$_2$ heterostructures have been reported to show improved photocatalytic performance on photodegrading organic dyes, compared with that of as-synthesized pure phases of SnS and SnS$_2$. [4]

Selective pure phase synthesis of single crystalline tin sulfides is a challenging task due to the high sensitivity of the different phases to growth conditions. Tin sulfides have been previously synthesized mostly in the form of bulk single crystals or thin films.
The bulk single crystals have been grown by the Bridgman method and chemical vapor transport (CVT); the thin films have been synthesized using various deposition methods. [2, 5, 22-27] However, relatively few studies have reported the synthesis of 2D crystals of SnS$_2$ and SnS using vapor-phase methods. [3, 9, 28, 29]

In this study, we demonstrate phase-controlled synthesis of 2D SnS$_2$ and SnS crystals using an atmospheric pressure vapor-phase method. The fundamental structural and electronic properties of each crystal phase are comprehensively investigated using optical microscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), Raman spectroscopy, and ultraviolet photoelectron spectroscopy (UPS) and compared with results of ab-initio DFT calculations.

4.2 Experimental Section

4.2.1 Materials Synthesis

SnO$_2$ and S powders were used as source materials in a conventional single-zone horizontal quartz tube (1 in.) furnace. In a typical experiment, SnO$_2$ (~15 mg) powders in a quartz crucible were placed in the center of the tube furnace. Also, S (~350 mg) powders in a quartz crucible were placed 13 cm upstream from the center of the tube furnace. The degenerately boron-doped (0.001-0.005 Ω cm) Si substrates (~1x1 cm$^2$) with 285 nm SiO$_2$ capping layer were cleaned by sonication in acetone and isopropyl alcohol (IPA) baths, sequentially for ~1 min each, followed by drying with N$_2$ gas. The SiO$_2$ substrates were placed downstream to the center at a distance of about 9 (where the temperature was ~550 °C) and 11.5 cm (where the temperature was ~425 °C),
respectively, for the growth of SnS and SnS₂ crystals. The temperature of the substrates was determined by using a type K thermocouple. The tube furnace was pumped down to remove the air and then filled with a high-purity Ar gas (~ 100 sccm) to atmospheric pressure. The center of heating zone was heated to 705 °C within 35 min. When the center of heating zone reached 705 °C, the temperature of the S powders was measured to be ~ 350 °C by using the thermocouple. The tube furnace was kept at 705 °C for 40 min, and cooled down to RT.

4.2.2 Materials Characterization

To transfer the as-grown crystals from a SiO₂ substrate to a Cu TEM grid, an all-dry transfer method that employs a polydimethylsiloxane (PDMS) film was developed. Briefly, the PDMS film was placed on the as-grown crystals on the SiO₂ substrate and then peeled off. To ensure the transfer of the crystals from the SiO₂ substrate to the PDMS film, the film was slightly rubbed on by a q-tip. Next, the TEM grid was placed on the area of the film and then peeled off. FEI Titan G2 60-300 aberration-corrected STEM equipped with a CEOS DCOR probe corrector was used in this study. Annular dark-field scanning TEM (ADF-STEM) images (2048×2048 pixel²) were acquired with the STEM operated at 200 keV using a dwell time of 6 μs per image pixel at a camera length of 130 mm. The beam convergence angle, αobj, was measured to be 26 mrad. The ADF detector inner and outer angles of collection were measured to be 54 and 317 mrad, respectively. The measured probe size was ~ 0.8 Å.

UPS characterization was carried out by using a XPS system equipped with a He I of UV source. The aperture for UPS has a diameter of 110 μm. Vacuum pressure was
kept below $3\times10^{-9}$ Torr, and neutralizer was applied during the data acquisition. For UPS spectra comparison, commercial available bulk SnS$_2$ crystals were used.

Microstructural analyses were done by SEM. Raman spectra were collected using a 532 nm laser ($\leq$2 mW excitation power, 100x objective lens). For Raman spectra comparison purposes, commercial available bulk SnS$_2$ crystals were used. Thickness measurements were performed using AFM in tapping mode.

4.2.3 DFT Calculations

The calculations were based on the first-principles DFT and density functional perturbation theory using the projector augment wave method as implemented in the software package VASP. [42] For the electronic structure calculations, a Monkhorst-Pack scheme was adopted to integrate over the Brillouin zone with a k-mesh of $12 \times 12 \times 8$ ($8 \times 8 \times 1$) for the bulk (few-layer) structures. A plane-wave basis kinetic energy cutoff of 500 eV was used. vdW interactions in bulk and few-layer SnS$_2$ were accounted for using a semi-empirical correction to the Kohn Sham energies when optimizing each structure. [43] The optimized lattice constants for bulk SnS$_2$ and SnS were $a=3.70$ Å, $c=11.85$ Å and $a=4.35$ Å, $b=3.99$ Å and $c=11.21$ Å, respectively. This study used the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional to obtain accurate values for the bandgaps and ionization potentials for each phase. [44] The HSE calculations incorporated 25% short-range Hartree-Fock exchange and the screening parameter was set to 0.2 Å$^{-1}$. Calculations of the vibrational frequencies at $\Gamma$ point relied on density functional perturbation theory.
4.3 Results and Discussion

2D tin sulfide crystals with lateral sizes over tens of microns were synthesized by atmospheric pressure vapor-phase growth method in a horizontal quartz tube furnace (Figure 4.1(a)). In a typical synthesis, SnO$_2$ and S powder precursors were located at the center and upstream of the tube furnace, respectively. SiO$_2$ substrates were placed close to each other at downstream of the tube furnace. The 2D crystals were obtained on the SiO$_2$ substrates by heating the tube furnace to 705 °C and maintaining this temperature for 40 min before cooling down to room temperature (RT) (see ‘Experimental Section’ for the details).
Figure 4.1 The growth set-up, morphology and atomic structure of the SnS$_2$ and SnS crystals. The growth setup (a) for the growth of SnS$_2$ and SnS crystals. Optical microscopy images of SnS$_2$ (b) and SnS (c) crystals grown on SiO$_2$ substrates. Low magnification ADF-STEM images of SnS$_2$ (d) and SnS (e) crystals transferred to a TEM grid. Filtered atomic-resolution ADF-STEM image of SnS$_2$ (f) and SnS (g). Ball-and-stick models are overlapped to highlight atomic positions.

Optical images of the SiO$_2$ substrates show that SnS$_2$ crystals (Figure 4.1(b)) grow at a lower substrate temperature of $\sim$ 425 °C while SnS crystals (Figure 4.1(c)) form at a higher temperature of $\sim$ 550 °C. SnS$_2$ crystals show a trapezoidal shape, and SnS crystals have a rectangular shape.
Since SnS and SnS\(_2\) possess different crystal structures, atomic resolution STEM imaging can be used to directly verify the phases obtained from the growth. SnS\(_2\) and SnS crystals obtained by the previously described recipe were first transferred to separate TEM grids and imaged in a STEM (see ‘Experimental Section’ for the details). **Figure 4.1(d,e)** show low magnification ADF-STEM images of SnS\(_2\) and SnS crystals, respectively. **Figure 4.1(f,g)** show filtered high-resolution ADF-STEM images of both phases obtained along the [001] zone axis where the crystal structure of the two phases can be distinguished. The image filtering procedure followed that used by Wu et al. [30] SnS\(_2\), as seen in the ADF-STEM image, appears to crystallize in the 1T polymorph. This arrangement is similar to that observed for 1T-MoS\(_2\). [31, 32] On the other hand, the ADF-STEM image of SnS shows its orthorhombic arrangement, which can be clearly differentiated from the image of SnS\(_2\).

The growth of the 2D crystals can be explained by the reaction of SnO\(_2\) and S. When the temperature of the tube furnace is above the Tammann temperature of SnO\(_2\) (\(T_{\text{Tam}}\approx 400\) °C), SnO\(_2\) evaporation will be initiated, even though the applied temperature is lower than its melting point in powder form (\(T_{\text{melt}}\approx 1350\) °C). [33, 34] At the early stage of the growth (~ 400 °C), SnO\(_2\) vapor from solid SnO\(_2\) powders makes contact with the substrate and forms small SnO\(_2\) clusters which act as nucleation sites for tin sulfide crystals. [35] SnO\(_2\) vapor from solid SnO\(_2\) powders reacts with S vapor to initiate the formation of SnS\(_2\) according to the equation (1) [3]

\[
\text{SnO}_2 (s) + 1.5\text{S}_2 (g) \rightarrow \text{SnS}_2 (s) + \text{SO}_2 (g)
\]
As the reaction temperature increases, the growth of SnS$_2$ will eventually stop due to its phase instability on the high temperature. [2, 36, 37] At the same time, S source will be eventually depleted, which results in a reducing atmosphere in the tube. As a result, SnS growth will be favored according to the equation (2) [3]

$$\text{SnO}_2 (s) + \text{S}_2 (g) \rightarrow \text{SnS} (s) + \text{SO}_2 (g)$$  \hspace{1cm} (4.2)

To help further understand the underlying growth mechanisms of tin sulfide crystals, we performed a series of experiments by using three different growth recipes. Recipe I served as the control experiment where the furnace with the quartz tube was heated from RT to 705 °C and then kept at this temperature for 40 min, followed by cooling down to RT. In recipe II, the furnace with the quartz tube was heated from RT to 625 °C, and immediately cooled down to RT without further heating. For recipe III, the quartz tube was initially held outside the furnace. While the furnace was being heated to 705 °C, the quartz tube was immediately slid inside the furnace at 625 °C. Then, the furnace with the quartz tube was kept at 705 °C for 40 min, followed by cooling down to RT. Only one long rectangular SiO$_2$ substrate was used for each experiment, and the growth parameters such as heating rate, gas flow rate, pressure, precursors, and substrates were kept constant for all the experiments.

Recipe I yielded both SnS$_2$ and SnS crystals, but the two were spatially separated on the substrate (Figure 4.2(a)). SEM imaging (Figure 4.2(b,c)) and Raman spectroscopy (Figure 4.3(c,f,i)) confirmed that SnS was grown on the hotter side of the substrate compared to SnS$_2$. On the other hand, recipe II resulted in primarily SnS$_2$ crystals at the lower temperature side of the substrate while recipe III gave mainly SnS
crystals, which appears only in the hotter region. These results indicate that the growth of SnS₂ crystals is initiated mostly during the early stage of heating, while the formation of SnS crystals starts in the later stage of the heating. Hence, the formation of SnS occurs at higher temperatures compared to that of SnS₂, which is consistent with results of previous reports on the growth of SnS₂ and SnS crystals. [2, 36, 37]

We also studied the trace reaction products of SnO₂ (Figure 4.2(d)) and S found in the SnO₂ crucible. It was found that recipe II produced yellow transparent SnS₂ powders (Figure 4.2(e)), while recipes I and II yielded dark grey SnS powders (Figure 4.2(f)) as confirmed by Raman spectroscopy (Figure 4.3(c,f,i)). For recipe II, since the growth was performed at low temperature for a short period of time, SnO₂ powders was sulfurized to form solid SnS₂ as a result of the reaction according to the equation (1). For recipes I and III, as the reaction proceeds, solid SnS₂ dissociation occurs as a result of the incongruent sublimation, which is promoted by both high temperature and S depletion. [38] The dissociation of solid SnS₂ results in the phase transition from SnS₂ to SnS by the equation (3) [38]

\[
\text{SnS}_2 (s) \rightarrow \text{SnS} (s) + 0.5 \text{ S}_2 (g)
\]  \hspace{1cm} (4.3)

In this series of experiments, we also observed a growth of multi-stacked SnS₂ crystals (Figure 4.2(g-i)). The interlayer S vdW interactions between consecutive SnS₂ layers can result in misorientation of the layers during growth. 2D multistacked SnS₂ crystals with varying configurations may possess some novel electronic and optical properties. Controlling stacking is beyond our scope in this study, but we point out that
this simple method can be further optimized in order to achieve the control over the stacking.

We performed Raman spectroscopy on the SnS$_2$ and SnS crystals obtained by the discussed growth recipes. The Raman spectra of an 8L SnS$_2$ crystal (~5.08 nm as measured in AFM with monolayer thickness of 0.6 nm [1]) show a strong Raman peak at 314.9 cm$^{-1}$, corresponding to the A$_{1g}$ phonon mode of SnS$_2$ (Figure 4.3(a-c)). [39] In addition to the A$_{1g}$ mode, an intra-layer E$_g$ mode with peak at ~206.2 cm$^{-1}$ is observed in multilayer (ML) SnS$_2$ crystal with a thickness of ~17.94 nm (30L) (Figure 4.3(d-f)). [39] The absence of the E$_g$ mode in the 8L SnS$_2$ is presumably due to the undetectably weak rejection of the Rayleigh scattered radiation. [8] The Raman spectra from a ML SnS crystal (Figure 4.3(g)) was also measured. The thickness of the SnS crystal was estimated to approximately 30L (determined by cross-sectional STEM image in Figure 4.3(h)). The Raman spectra of the SnS crystal show a very different Raman pattern (Figure 4.3(i)) with the peaks centered within the range of 50-250 cm$^{-1}$. The peaks at 95.6 cm$^{-1}$, 192.0 cm$^{-1}$, and 218.3 cm$^{-1}$ can be assigned to the A$_g$ mode, and the peak at 163.9 cm$^{-1}$ corresponds to the B$_{3g}$ phonon mode of SnS. [3, 40]
Figure 4.2 The photo, SEM and optical images of the crystals obtained by various recipes. Photo image (a) of a long SiO$_2$ substrate after the growth. A stark boundary on the substrate surface of 2D SnS crystals in the high temperature region of the tube furnace to 2D SnS$_2$ crystals in the cooler region can be seen. SEM images of an SnS$_2$ crystal (b) and an SnS crystal (b) obtained from the surface of the SiO$_2$ substrate in (a). Photo images of SnO$_2$ powders (d), SnS$_2$ powders (e) obtained by recipe II, and SnS powders (f) obtained by recipes I and III. Optical images (g-i) of multi-stacked SnS$_2$ crystals.

To support results of the experimental Raman spectroscopy, we calculated the zone-center vibrational modes of bulk SnS$_2$ and SnS using ab-initio DFT (see ‘Experimental Section’ for the details). The vibrational modes at Γ point gave us insight
into the allowed Raman active modes for each phase. For bulk SnS$_2$, we calculated the vibrational modes that correspond to the out-of-plane $A_{1g}$ and in-plane $E_g$ Raman active modes. The calculated values of 313 cm$^{-1}$ and 204 cm$^{-1}$ obtained for the $A_{1g}$ and $E_g$ modes, respectively, are in good agreement with the Raman spectrum we obtained for the 2D SnS$_2$ crystal (Table 1).

**Table 4.1.** Comparison of experimentally measured and ab-initio DFT calculated Raman spectra peak positions in SnS$_2$ and SnS in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Phases</th>
<th>SnS$_2$</th>
<th>SnS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_{1g}$</td>
<td>$E_g$</td>
</tr>
<tr>
<td><strong>Experimental</strong></td>
<td>314.9</td>
<td>206.2</td>
</tr>
<tr>
<td><strong>Calculated</strong></td>
<td>313</td>
<td>204</td>
</tr>
</tbody>
</table>

For bulk SnS, we also calculated vibrational modes that correspond to the $A_g$ and $B_{3g}$ Raman active modes of the bulk orthorhombic structure of SnS. Based on the displacements of these modes, we determined $A_g$ modes at 95 cm$^{-1}$, 196 cm$^{-1}$, and 216 cm$^{-1}$ and the $B_{3g}$ mode at 163 cm$^{-1}$. These values are also in good agreement with our assignment of the Raman modes using the measured Raman spectra (Table 1) and prior Raman scattering studies on SnS. [40] The agreement between our theoretical calculations of the Raman modes for each phase of tin sulfides and our experimental Raman spectra is further demonstration of the controlled growth we have over each phase. Moreover, we do not observe Raman peaks at 474 cm$^{-1}$, 632 cm$^{-1}$, or 774 cm$^{-1}$.
associated with SnO₂. [41] This implies negligible chemical reaction between the crystals and substrate. [35]

**Figure 4.3 Raman spectroscopy characterization of the SnS₂ and SnS crystals.**
Optical image, AFM image and Raman spectra of an 8L SnS₂ crystal (a-c) and a 30L SnS₂ crystal (d-f). Optical image, cross-sectional ADF-STEM image and Raman spectra of a ~ 30L SnS crystal (g-i).

The ionization potential for each tin sulfide phase can be determined by UPS. Using the He source at photon energies of 21.22 eV, we determined the ionization potential, φ, by subtracting the width of the UPS spectra from 21.22 eV. We determined the ionization potential of our as grown SnS₂ and SnS crystals and compared them to the measurements on commercial SnS₂ crystals. The ionization potential of our as-grown SnS₂ was found to be 7.51 eV (Figure 4.4(a)), close to that of commercial SnS₂ crystal.
(7.7 eV) (Figure 4.4(b)). The ionization potential of SnS was determined to be 5.78 eV (Figure 4.4(c)).

![Figure 4.4](image)

**Figure 4.4 The ionization potentials for the SnS<sub>2</sub> and SnS crystals.** UPS spectra acquired for our as-grown SnS<sub>2</sub> crystal (a), commercial SnS<sub>2</sub> crystal (b), and our as-grown SnS crystal (c).

Using DFT we evaluated the ionization potentials for SnS and SnS<sub>2</sub> using an explicit slab model. 8L slabs of (001) SnS<sub>2</sub> and (100) SnS were predicted to have bandgaps of 2.31 eV and 1.07 eV, respectively, which are close to the bandgap values for
the respective bulk structures. Calculations of each 8L structure were then used to obtain the difference between the average of the electrostatic potential in the bulk and the eigenenergies with respect to the vacuum potential. This provided an ionization potential of 7.51 eV and 4.9 eV for SnS$_2$ and SnS, respectively, which is in good agreement with the ionization potential of 7.51 eV and 5.78 eV we obtain for SnS$_2$ and SnS, respectively.

4.4 Conclusion

Highly crystalline 2D SnS$_2$ and SnS crystals with lateral sizes over tens of microns have been directly synthesized on SiO$_2$ substrates using a simple atmospheric pressure vapor-phase method. High-resolution ADF-STEM imaging reveals the phases of 2D hexagonal SnS$_2$ (1T) and orthorhombic SnS crystals. The phase purity of SnS$_2$ and SnS crystals is confirmed by the analysis of the Raman and UPS spectra, and the results are corroborated by ab-initio DFT calculations. A series of growth experiments are performed to determine the growth process of the 2D crystals. It is found that temperature determines the phase of each crystal. SnS$_2$ crystals grow at lower temperatures compare to the case of SnS crystals. Moreover, we have showed that the hexagonal SnS$_2$ phase can be transformed into orthorhombic SnS phase upon high temperature treatment during growth. This temperature controlled process is advantageous for the purpose of avoiding highly toxic byproducts such as H$_2$S in H$_2$ reduction. Overall, these results are useful for future studies of the structural, electronic, and optical properties of 2D hexagonal SnS$_2$ and orthorhombic SnS and may offer important guidance for realizing SnS$_2$- and SnS-based electronic and optoelectronic devices.
References


Chapter 5 Facile Synthesis of 2D SnS$_2$ Nanowalls

Abstract

Two-dimensional (2D) layered metal chalcogenides (LMCs), especially tin sulfides, have recently received great interest due to their enticing physical and chemical properties and hold promise for various applications. We reported on synthesis of phase-pure 2D SnS$_2$ nanowalls (NWs) by a facile vapor-phase synthesis method on insulator substrates such as SiO$_2$ and MgO using SnO$_2$ and S powders as precursors. The synthesized SnS$_2$ NWs were characterized to study their fundamental properties by using various techniques such as scanning electron microscopy (SEM), x-ray diffraction (XRD), Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron spectroscopy (UPS). The synthesized films have an open network structure constituted of very uniform interconnected NWs with high crystallinity.

5.1. Introduction

Recently, 2D layered LMCs have been the subject of intense research due to their exotic physical and chemical properties. [1, 2] Tin sulfides are particularly interesting members of the family of LMCs. Their constituent elements, Sn and S, are inexpensive, environmentally friendly, and abundant in nature. Sn sulfides can exist in diverse crystal phases, such as orthorhombic SnS and hexagonal SnS$_2$, owing to the oxidation characteristics of the elements Sn and S. [3]

SnS$_2$ is a layered compound semiconductor with CdI$_2$-type crystal structure. It is composed of layers of Sn atoms sandwiched between two closed-packed layers of S atoms. SnS$_2$ has been reported to be an intrinsic n-type semiconductor. [3] SnS$_2$ can exist
in various polytypes which differ in the stacking sequence of the sandwich layers. [4] The three common polytypes of SnS₂ are 2H, 1T, and 4H. The distinctions between polytypes of SnS₂ are mostly revealed in physical and electronic properties of the crystals. [5]

**Figure 5.1 The growth set-up, thermal process and growth process for the SnS₂ NWs.** Illustration of experimental setup (a), thermal process (b), and synthesis process (c).

Along with their interesting properties, nanostructured SnS₂ crystals with different morphologies hold great promise for various applications ranging from energy storage to photocatalytic degradation. The high electrical conductivity and theoretical capacity of SnS₂ NWs make them a promising material for anodes of lithium (Li)-ion batteries (LIBs). [6] The open spaces between neighboring SnS₂ NWs can accommodate volume changes associated with insertion and extraction of Li ions and allow easy diffusion of electrolyte solution in LIBs. SnS₂ nanostructures can be annealed to form tin dioxide
(SnO₂), which opens avenues for applications such as gas sensing of chemicals such as ethanol and n-butanol. [7] It has also been shown that SnS₂ nanosheets can be used as counterelectrode material for dye-sensitized solar cells owing to their excellent catalytic activity for triiodide reduction. [8]

To date, synthesis of SnS₂ nanocrystals with various morphologies, such as nanoparticles, nanoplates, nanosheets, nanotubes, and nanoflowers, has mainly been based on reactions in liquid media or chalcogenization of thin films, and scale-up of current processes has been limited due to expensive or corrosive precursors. [9-13] To the best of our knowledge, large-area growth of SnS₂ NWs on insulator substrates from powder precursors has not been reported yet.

Herein, we report a scalable facile vapor-phase synthesis method for growth of well-aligned SnS₂ NWs on insulator substrates including silicon dioxide (SiO₂) and MgO using SnO₂ and S as vapor sources. The vapor-phase synthesis of SnS₂ is based on the reaction of SnO₂ vapor with S vapor at elevated temperature. The advantage of this method lies in its use of precursors that do not require conversion of a reactant solid phase to product. The fundamental properties of the SnS₂ NWs have been studied by using various techniques. The results suggest that the grown films are indeed highly crystalline SnS₂ with an open network structure constituted of interconnected NWs.

5.2 Experimental Section

5.2.1 Materials Synthesis

A facile vapor-phase synthesis method was used to synthesize SnS₂ NWs on insulator substrates such as SiO₂ (300-nm-thick SiO₂ layer deposited thermally on Si
wafer) and MgO. S powder (99.5%, Alfa Aesar) and SnO$_2$ powder (99.9%, Alfa Aesar) were selected as precursors. The reaction took place in a single-zone vacuum tube furnace with a 1-inch quartz tube (MTI OTF-1200X-S50-2F) (Figure 5.1(a)). High-purity Ar gas at constant flow of 60 sccm was used as carrier gas. In a typical growth process, 25 mg SnO$_2$ powder was put in a polished quartz boat at the center of the heating zone, and 250 mg S powder was put in another polished quartz boat at the upstream. The substrates (~ 1x1 cm$^2$) were cleaned by sonication in acetone and isopropyl alcohol (IPA) baths, sequentially for 1 min each. Immediately following the cleaning procedure, the substrate was placed at the downstream of the furnace. The furnace was pumped down to remove air, and the pressure was stabilized at ~ 0.1 Torr. Next, the center of the heating zone was heated to 710 °C within 30 min. The furnace was kept at 71 °C for 10 min, then naturally cooled down to room temperature (Figure 5.1(b)).

5.2.2 Materials Characterization

The morphology of the NWs was investigated using scanning electron microscopy (SEM, FIB NNS450). X-ray diffraction (XRD) studies were carried out using a Philips X’Pert diffractometer with Cu Ka radiation in Bragg-Brentano geometry. Raman spectra were collected using a Horiba system with a 532-nm laser (<2 mW excitation power, x100 objective lens). All Raman spectra were calibrated using the 520.5 cm$^{-1}$ line of a Si wafer. For Raman spectra comparison purposes, commercially available bulk SnS$_2$ crystals (2D Semiconductors Inc.) were used. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) characterization were carried out using a Kratos AXIS ULTRADLD XPS system equipped with an Al Ka
monochromated x-ray source, He I ultraviolet (UV) source (21.22 eV), and a 165-mm mean radius electron energy hemispherical analyzer. The slot size for XPS was 300 µm x 700 µm, and the aperture for UPS had a diameter of 110 µm. The vacuum pressure was kept below 3 \times 10^{-9} \text{ torr}, and the neutralizer was applied during data acquisition. The C 1s peak at 284.8 eV was used for binding energy calibration.

5.3 Results and Discussion

The formation of SnS$_2$ NWs includes the following three major steps (Fig. 1c):

The first step involves sublimation and reaction of S and SnO$_2$ to produce gaseous SnS$_2$ species. As the temperature is about 425 °C, which is the Tammann temperature of SnO$_2$, evaporation of SnO$_2$ will be initiated, even though the applied temperature is lower than its melting point. S also starts evaporating when the temperature at the center of the tube is 425 °C. As a result, SnO$_2$ vapor will react with S vapor to form SnS$_2$ species. In the experiments, we used excess amount of S (mass ratio of S to SnO$_2$ of about 10) to ensure far more vapor of S than of SnO$_2$. As a result, we can reasonably assume that the reaction of SnO$_2$ is complete. Next, SnS$_2$ species will be transferred to the downstream by Ar gas. The final step includes diffusion of SnS$_2$ species from the gas phase onto the receiving substrates and finally precipitation.
**Figure 5.2 The morphology of the SnS$_2$ NWs.** Low- and high-magnification SEM images of SnS$_2$ NWs/SiO$_2$ (a, b) and SnS$_2$ NWs/MgO (c, d).

Low-magnification (**Figure 5.2(a)**) and high-magnification (**Figure 5.2(b)**) SEM images of synthesized SnS$_2$ NWs on SiO$_2$ substrates (SnS$_2$ NWs/SiO$_2$) reveal that the SnS$_2$ films have an open network structure constituted of interconnected, well-ordered NWs. The thickness of the NWs and the film is estimated to be several tens of nanometers and a few microns, respectively, from the high-magnification SEM image of the NWs (**Figure 5.2(b)**). To further examine the role of the interaction with the substrate, we studied growth on different receiving substrates such as SiO$_2$ and MgO. We grew SnS$_2$ films on these substrates under identical experimental conditions. The morphology of SnS$_2$ NWs grown on MgO substrates (SnS$_2$ NWs/MgO) (**Figure 5.2(c)**)
was found to be similar to that of SnS$_2$ NWs/SiO$_2$ (Figure 5.2(a)). However, the size of the SnS$_2$ NWs/MgO was noticeably smaller (Figure 5.2(d)).

![Figure 5.3 XRD and Raman spectroscopy analysis of the SnS$_2$ NWs.](image)

**Figure 5.3 XRD and Raman spectroscopy analysis of the SnS$_2$ NWs.** XRD pattern of SnS$_2$ NWs/SiO$_2$ (a). Reference data are also shown. Raman spectra of SnS$_2$ NWs/SiO$_2$ (b), SnS$_2$ NWs/MgO (c), and commercially available SnS$_2$ crystals (d). The left insets in (c, d) show the magnified E$_g$ peaks.

The crystallographic structure of SnS$_2$ NWs/SiO$_2$ was determined by XRD analysis. In the XRD pattern (Fig. 3a), the (001) (100), (101), (102), (003), (110), (111), (103), (201), and (202) diffraction peaks of SnS$_2$ NWs are observed at 2θ angles of 15.029°, 28.200°, 32.125°, 41.887°, 46.122°, 49.961°, 52.452°, 54.962°, 60.621°, and 67.154°, respectively. All the diffraction peaks can be indexed to hexagonal SnS$_2$ [Joint Committee on Powder Diffraction Standards (JCPDS) card file no. 23-677], indicating synthesis of pure SnS$_2$. [15] The strong and sharp peak at 2θ = 15.029° indicates preferred growth orientation along the (001) plane of hexagonal SnS$_2$. Such observation of preferred growth orientation of the SnS$_2$ crystals along the (001) plane can be
explained by considering the surface energies of SnS$_2$ crystal planes. [16] Surface energy theory suggests that the equilibrium form should be such that the crystal has minimum surface energy per unit volume. As reported in literature, the (001) plane of SnS$_2$ may possess the lowest surface energy and thus adsorb more SnS$_2$ species than the other planes of SnS$_2$ during growth. [17]

Raman spectroscopy has proven to be a versatile tool for studying various 2D materials. [1] We performed Raman spectroscopy characterization on SnS$_2$ NWs/SiO$_2$, SnS$_2$ NWs/MgO, and commercially available SnS$_2$ crystals (for comparison purposes). The two typical Raman-active modes of SnS$_2$ NWs/SiO$_2$ appear in the spectrum (Figure 5.3(b)), namely a strong $A_{1g}$ Raman mode at 313.3 cm$^{-1}$ and a weak $E_g$ Raman mode at 204.4 cm$^{-1}$, confirming that the synthesized NWs are indeed SnS$_2$. [18] The intensity of the $E_g$ peak is much lower than that of the $A_{1g}$ peak, presumably due to the reduction in the scattering centers for in-plane scattering. [3,19] Similar to SnS$_2$ NWs/SiO$_2$, the Raman spectra (Figure 5.3(c)) of SnS$_2$ NWs/MgO show the $A_{1g}$ peak at 313.8 cm$^{-1}$ and the $E_g$ peak at 204.8 cm$^{-1}$, indicating a negligible effect of the substrate on the Raman features of the SnS$_2$ NWs. We also performed Raman spectroscopy on commercially available SnS$_2$ crystals for comparison purposes. The Raman spectra (Figure 5.3(d)) of SnS$_2$ crystals show the $A_{1g}$ peak at 313.8 cm$^{-1}$ and the $E_g$ peak at 204.9 cm$^{-1}$, being very similar to those of SnS$_2$ NWs/SiO$_2$ and SnS$_2$ NWs/MgO. Thus, we can conclude that the synthesized SnS$_2$ NWs are similar in quality to SnS$_2$ crystals.
Figure 5.4 XPS and UPS analysis of the SnS\textsubscript{2} NWs. Survey XPS (a) and high-resolution XPS spectra for Sn 3d (b) and S 2p (c) binding energies of SnS\textsubscript{2} NWs. (d) He-I UPS spectra of SnS\textsubscript{2} NWs.

XPS was used to investigate the chemical surface composition of the NW samples. The survey XPS spectrum (Figure 5.4(a)) of the samples revealed two strong peaks indicating presence of Sn and S. Oxygen, whose O 1s peak is located at ~ 532 eV (Figure 5.4(a)), was only present in negligible amounts. The high-resolution spectra of the samples were used to determine the oxidation states of the elements. Two peaks appear for each core level due to spin-orbit splitting of Sn 3d (Figure 5.4(b)) and S 2p (Figure 5.4(c)) core levels. The binding energies for Sn 3d\textsubscript{3/2} and Sn 3d\textsubscript{5/2} are 495.7 eV and 487.3 eV, respectively, with energy separation of 8.4 eV, being near the value reported for S\textsuperscript{IV} in SnS\textsubscript{2}. [20] The S 2p binding energies of the SnS\textsubscript{2} NWs are 163.6 eV.
and 162.4 eV, for S 2p\textsubscript{1/2} and S 2p\textsubscript{3/2}, respectively. The results demonstrate that no elemental sulfur (164.05 eV) is present in the product. [20] We also used UPS to determine the ionization potential of the SnS\textsubscript{2} NWs. The ionization potential was measured to be 6.66 eV, which is close to the ionization potential value of SnS\textsubscript{2} crystals reported by Schroeder et al. [21] This result further confirms that the crystals are indeed SnS\textsubscript{2}.

### 5.4 Conclusion

We demonstrated facile, large-scale synthesis of highly oriented SnS\textsubscript{2} NW films on insulator substrates by reaction between SnO\textsubscript{2} and S vapors. The SnS\textsubscript{2} NWs exhibited high crystallinity with preferred growth orientation along (001) plane and an open network structure constituted of interconnected NWs. Such highly crystalline SnS\textsubscript{2} NWs may find applications in energy storage, solar cells, sensors, and catalytic applications where specific surface area plays an important role in overall productivity.

### References


Chapter 6 Synthesis of MoSe\textsubscript{2} via Rapid Thermal Processing and Laser Annealing

Abstract

Few-layers MoSe\textsubscript{2} granular films were prepared using rapid thermal processing (RTP) of stacked elemental layers (SELs) deposited using electron beam evaporation in the sequence of Mo/Se/Mo. RTP was carried out at various temperatures ranging from 550 to 750 °C, and durations ranging from 90 to 150 s. Morphology and microstructure of granular thin films were characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Compositional and electronic structure analysis of the films were done by X-ray photoelectron (XPS), photoluminescence (PL) and Raman spectroscopy. The results confirmed the formation of four-layer MoSe\textsubscript{2} granular thin films at 750 °C for 90 s. Density functional theory (DFT) calculations showed that the direct gap at K is near degenerate with the calculated indirect band gap in the 4L structure. In addition to RTP, Raman laser annealing (RLA) was performed on SELs with various laser powers. Raman spectroscopy results revealed the local formation of MoSe\textsubscript{2} with increasing laser energy.

6.1 Introduction

Semiconducting phases of transition metal dichalcogenides (TMDs) have attracted great attention recently because of their fascinating physical properties. \[1\] MoSe\textsubscript{2} is a semiconductor phase of TMDs and crystallizes in a strongly covalent bound Se-M-Se sandwich structure (Figure 6.1(a)) Consecutive Se-Mo-Se layers are weakly bound by van-der-Waal (vdW) interaction. MoSe\textsubscript{2}, with an indirect band gap of 1.1 eV in
the bulk form and a direct band gap of 1.55 eV in the monolayer (ML) form, exhibits tunable electronic properties, allowing for the realization of its potential in optoelectronics and spintronics. [2-4] The potential applications of MoSe₂ have motivated the development of large scale synthesis of atomically thin MoSe₂ films.

Figure 6.1 The ball-and-stick model and synthesis process for MoSe₂. The ball-and-stick model (a) of MoSe₂. The schematic (b) of SELs deposited on SiO₂/Si substrate. The schematic view (c) of RTP system working principles. The illustration (d) of the thermal process performed for MoSe₂ growth.

Recent top-down approaches such as mechanical and liquid exfoliation to obtain large area MoSe₂ thin films have received considerable attention. [5, 6] Nevertheless, the lack of uniformity in thickness and size undermines the viability of such approaches. Selenization of molybdenum trioxide (MoO₃), which is a conventional bottom-up approach for synthesis of MoSe₂, has been recently performed to grow MoSe₂ films in a
chemical vapor deposition (CVD) system. Making use of the elemental Se and MoO$_3$ powders' low melting and evaporation temperatures, Shaw et al. and Lu et al. have demonstrated that elemental Se and MoO$_3$ are suitable precursors for CVD of MoSe$_2$ thin films. [7, 8] Although CVD methods are promising techniques for future efficient production of MoSe$_2$, current production status of MoSe$_2$ by the aforementioned methods is still in a nascent stage. Alternative MoSe$_2$ synthesis techniques have focused on the direct selenization of Mo-containing films. Pouzet and Bernede have synthesized MoSe$_2$ films by solid phase selenization of Mo thin films in a CVD furnace. [9] However, each of these growth techniques is hampered by the formation of thick films, including perpendicularly grown three-dimensional (3D) structures, with small grain sizes and poor crystallinity. Alternatively, Lee et al. have reported on the synthesis of thick MoSe$_2$ films during rapid thermal processing (RTP) of Mo-coated glass under Se pressure. [10] We extend this study by reporting on the formation of few-layers (FL) MoSe$_2$ granular films following RTP of stacked Mo/Se/Mo layers.

Raman spectroscopy is widely used as a very efficient and non-destructive method to study two-dimensional (2D) materials such as graphene and TMDs. [11-13] Recently, laser annealing using Raman spectroscopy has been performed for thinning of 2D materials. Gomez et al. have reported on the laser-thinning of multilayer MoS$_2$ down to a ML 2D crystal using Raman spectroscopy. [14] An optical microscope-focused laser beam system has been used to construct reduced multilayer graphene oxide sheets. [15] Laser direct writing of graphene patterns on SiO$_2$ has been shown by Fan et al. [16]
However, the formation of MoSe$_2$ from stacked elemental layers (SELs) using Raman laser annealing (RLA) has not been reported.

In this study, we have successfully synthesized FL MoSe$_2$ granular films using RTP of SELs in the sequence of Mo/Se/Mo on SiO$_2$/Si. The morphology of the films has been characterized by optical microscopy, AFM and SEM. The phase composition of the films has been studied by XPS. PL and Raman spectroscopy have been performed to investigate the optical and electronic properties of the films. Our PL data has been compared to the results of electronic band structures of ML and four layer (4L) MoSe$_2$ using first-principles DFT calculations. Moreover, we have also investigated the formation of MoSe$_2$ from SELs by RLA using Raman spectroscopy.

6.2 Experimental Section

6.2.1 Materials Synthesis

Films subjected to RTP were prepared using e-beam evaporation of 0.5 nm Mo, 34 nm Se, and 0.5 nm Mo films (Figure 6.1(b)) on p-type (100) oriented Si wafers ($\sim$1 cm$^2$) with 300 nm thermal SiO$_2$, which was previously cleaned by sequential sonication in toluene, acetone and isopropyl alcohol (IPA) for 30 min, respectively. The purpose of the Se layer between two Mo layers was to prevent the loss of Se during the thermal step. The deposition was carried out in a load-lock chamber at a base pressure of $\sim$10$^{-7}$ Torr and deposition pressure of $\sim$10$^{-6}$ Torr, with an average growth rate of 0.1 Å/s. Before deposition, the vacuum chamber was completely covered with aluminum foil to prevent Se contamination on the walls of the chamber. After deposition, the foil was coated by a thicker nickel layer, and properly disposed of.
RTP of deposited films was then performed in a RTP system at various temperatures (550 to 750 °C) and durations (90 to 150 s). The temperature of the system was controlled by a pyrometer, exposed to the back of the sample holder (a 4” Si wafer), and calibrated by means of a thermocouple in contact with it (Figure 6.1(c)). The RTP system was ramped to 550-750 °C with a heating rate of ~100 °C/s, and the temperature was maintained for 90-150 s. Annealing was followed by a rapid cooling step down to ~200 °C with a cooling rate of ~100 °C/s, and then to room temperature (RT) by a slow cooling rate of 20 °C/s. The purpose of the rapid heating and cooling steps was to prevent loss of Se and induce the recrystallization process. The thermal cycle is illustrated in Figure 6.1(d) for clarity. The MoSe₂ flakes were mechanically exfoliated from the bulk MoSe₂ crystals by a conventional scotch tape method. [2]

6.2.2 Materials Characterization

AFM imaging and thickness measurements were done in tapping mode. Microstructural analysis was performed by SEM. The compositional analysis of the films was done by a XPS system equipped with an Al Kα monochromated X-ray source and a 165-mm electron energy hemispherical analyzer. The vacuum pressure was kept below 3 × 10⁻⁹ Torr and a neutralizer was applied during the data acquisition. Raman and PL spectra of the MoSe₂ film and MoSe₂ flake were collected using a 532 nm laser (100x objective lens) at RT. The laser beam, with a laser power of ~0.06 mW, was focused on a 0.8 µm diameter spot. The effect of laser power on RLA process of SELs was also investigated by varying the laser power from 0.0065 mW to 32.5 mW. All measurements were performed at RT and in air.
6.2.3 DFT calculations

Our calculations were based on first-principles DFT using the projector augmented wave method as implemented in the software package VASP. Standard approximations of DFT at the LDA or GGA level of theory are known to underestimate the band gaps in the TMD family of materials. To account for this, the screened Heyd–Scuseria–Ernzerhof (HSE) hybrid functional was employed for this study. A Monkhorst-Pack scheme was adopted to integrate over the Brillouin zone with a k-mesh 9x9 x1 for the ML and FL structures. A plane-wave basis kinetic energy cutoff of 280 eV was used. Spin orbit coupling was included self-consistently. The lattice constants for the FL MoSe₂ structures were obtained from a volume optimized bulk 2H-MoSe₂ structure. The atomic coordinates for the thin film structures were optimized at this fixed lattice constant. Spin-orbit coupling (SOC) was included self-consistently within the band structure calculations. For the HSE calculations, 25% short-range exact Hartree–Fock exchange was used with the Perdew-Burke-Ernzerhof (PBE) correlation. The HSE screening parameter, μ, was empirically set to 0.3 (1/Å).

6.3 Results and Discussion

AFM was used to characterize the surface morphology and thickness of MoSe₂ granular thin films. Figure 6.2(a-d) show the AFM images of MoSe₂ films on SiO₂/Si after annealing at 550 °C for 90 s (referred to as sample A), 750 °C for 90 s (referred to as sample B), 750 °C for 120 s (referred to as sample C) and 750 °C for 150 s (referred to as sample D). The surface of all the samples appears to be granular.
Figure 6.2 The AFM height images of the MoSe$_2$ films at 550 °C for 90 s (a), 750 °C for 90 s (b), 750 °C for 120 s (c) and 750 °C for 150 s (d).

Figure 6.3 show the histogram of the heights of the MoSe$_2$ islands measured from the AFM images (Figure 6.2(a-d)). The heights of MoSe$_2$ islands from the substrate are 2.75-3.25 nm, 3-4 nm, 6.25-8 nm, and 15.5-20 nm for sample A, B, C, and D, respectively. The height of the MoSe$_2$ islands increases as the annealing temperature is raised. For the annealing step at 750 °C, the density of the number of islands decreases and the height of the islands increases with increased annealing time, possibly due to particle agglomeration. [18]
Figure 6.3 The histograms of the particle size distribution of the MoSe$_2$ films. AFM height histograms of MoSe$_2$ films at 550 °C for 90 s (a), 750 °C for 90 s (b), 750 °C for 120 s (c), and 750 °C for 150 s (d).

Figure 6.2(b) shows that there are some flat MoSe$_2$ regions with a length of ~300 nm on the surface of sample B. The height of the flat regions is determined to be ~3.5 nm for sample B. This corresponds to a thickness of four monolayers (4L) assuming each monolayer is approximately 9 Å. [2] The surface roughness values, $R_a$ and $R_{rms}$, are determined to be 1.2 and 1.48 nm, respectively, for sample B. The surface roughness is relatively higher than expected since defects and contamination are possibly introduced during the rapid heating and cooling process.
The AFM phase images (Figure 6.4) of the samples reveal that the surface of the SiO₂/Si substrate is not completely covered by MoSe₂ possibly due to the loss of Se and Mo and agglomeration during the rapid heating and annealing. [19] It has been reported that annealing temperatures higher than 700 °C lead to enhanced layer growth of MoSe₂. [18]

**Figure 6.4** AFM phase images of the MoSe₂ films at 550 °C for 90 s (a), 750 °C for 90 s (b), 750 °C for 120 s (c) and 750 °C for 150 s (d).

**Figure 6.5** shows the optical microscopy images of sample B with a scratch before and after RTP. Since the color contrast of MoSe₂ on SiO₂/Si strongly depends on the oxide thickness of the substrate, lens magnification, and thickness of the film, surface
sensitive spectroscopy techniques are essential to characterize the quality of the synthesized films.

![Image of optical images of Mo/Se/Mo and MoSe\(_2\) films.](image)

**Figure 6.5 The optical images of the Mo/Se/Mo and MoSe\(_2\) films.**

It is well-known that XPS is a very useful method for the determination of chemical compositions and chemical states of material surfaces. The chemical composition of sample B was further investigated by XPS analysis (Figure 6.6). Mo 3d\(_{5/2}\) and Mo 3d\(_{3/2}\) peaks are found at 229.2 and 232.3 eV, confirming that Mo is in its Mo (IV) state; and the 3d peak of Se element is split into the well-defined 3d\(_{5/2}\) and 3d\(_{3/2}\) peaks at 54.8 and 55.7 eV, respectively (Figure 6.6(a,b)). [20, 21] The stoichiometric ratio (Se/Mo) estimated from the respective integrated peak area of the XPS spectra is approximately 2. This result further confirms the formation of MoSe\(_2\). More detailed analysis results reveal some contributions from MoO\(_3\), exhibiting two characteristic peaks at 236.2 and 233.4 eV, attributed to the 3d\(_{3/2}\) and 3d\(_{5/2}\) binding energies for the Mo (VI) state. [22]

High-resolution XPS with peak deconvolutions of the O 1s binding energy and Si 2p binding energy spectrum of sample B are given in Figure 6.6(c,d). The small peak at
531.1 eV is associated with MoO₃. [22] MoO₃ formed during the growth process may be due to the presence of trace amounts of O₂ in the system.

Figure 6.6 XPS analysis of the MoSe₂ films. High-resolution XPS with peak deconvolutions of the Mo 3d binding energy (a), Se 3d binding energy (b), O 1s binding energy (c), Si 2p binding energy (d) spectrum of the MoSe₂ film synthesized at 750 °C for 90 s.

Raman spectroscopy, a powerful and non-destructive tool for characterizing TMDs, was employed to study the lattice dynamics of sample B. [23-25] In Figure 6.7(a), we compare the Raman spectra of the as-deposited, post-RTP and exfoliated MoSe₂ flakes. The Raman spectra reveal that the MoSe₂ film has two characteristic A₁g (out-of-plane) and inline image (in-plane) Raman modes, confirming the formation of MoSe₂. [26] The A₁g and the inline image modes are identified at ~243.0 and 283.7 cm⁻¹, respectively, which is consistent with prior studies. [13] Moreover, the wavelengths and intensity ratios of the A₁g and the inline image peaks are similar in both the resultant
MoSe$_2$ and exfoliated MoSe$_2$ flake, showing that optical properties of the grown samples are comparable to those of the exfoliated single crystal MoSe$_2$ flakes. The details on MoSe$_2$ flakes are given in Figure 6.7(c,d).

Figure 6.7 Raman-PL spectroscopy characterization of the MoSe$_2$ film. Raman (a) and PL (b) spectra comparison of the as-deposited MoSe$_2$, post-RTP MoSe$_2$ film (sample B) and exfoliated MoSe$_2$ flake. The optical image (c) and corresponding AFM height image (d) of the exfoliated MoSe$_2$ flake.

PL spectroscopy was used to measure the quality and the thickness of sample B [4, 13]. Figure 6.7(b) illustrates the PL spectra comparison of the as-deposited, post-RTP, and exfoliated MoSe$_2$ flakes. It has already been reported that ML MoSe$_2$ has a very sharp and intense PL peak at 1.55 eV, corresponding to a direct band gap. [2, 7] We
have also observed a peak at ∼1.55 eV. However, the intensity of the peak is low and broadened, which is an indication of an indirect band gap in the resultant MoSe$_2$. [7]

The PL intensities and energies are close in both sample B (1.55 eV) and exfoliated MoSe$_2$ flakes (1.57 eV), showing the PL properties of the grown samples are comparable to those of exfoliated single crystal MoSe$_2$ flakes. Although the 4L has an indirect band gap the presence of a PL peak at 1.50-1.60 eV in the few-layers MoSe$_2$ is quite interesting, and can be explained by the DFT calculations. [13]

To gain further insight, we compute the band structure of 1L and 4L MoSe$_2$ using ab-initio DFT as shown Figure 6.8. Our prior studies on the electronic structure and lattice parameters of bulk MoSe$_2$ are good in agreement with prior experimental and theoretical studies. [27] The lattice parameters from this study are used for our simulations on 1L and 4L MoSe$_2$. Our calculations show monolayer MoSe$_2$ is a direct gap semiconductor at the K symmetry point with a band gap of 1.624 eV. For the 4L structure, the band gap becomes indirect with the valence band maxima shifted to Γ with a band gap of 1.600 eV. In the 4L structure, the direct gap at K is near degenerate with the calculated indirect gap, with a band gap of 1.605 eV.

![Figure 6.8 DFT-calculated electronic band structures of MoSe$_2$. DFT calculations of the 1L (red) and 4L (blue-broken) MoSe$_2$.](image)

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The effect of laser-induced heating on various materials such as carbon nanotubes, graphene, and silicon has been studied in the past two decades. [28, 29] Herein, we have studied the formation of MoSe$_2$ from SELs by RLA using a Raman spectroscopy system (Figure 6.9(a)). The Raman spectra variation of SELs has been examined when the laser power is tuned to 0.0065 mW (P1), 0.065 mW (P2), 0.65 mW (P3), 6.5 mW (P4), 16.25 mW (P5), and 32.5 mW (P6). Figure 6.9(b) shows the Raman spectra comparison of the films with various laser powers. For annealing with P1 and P2, no Raman peaks of MoSe$_2$ are observed. As the laser power is increased, the Raman features of the MoSe$_2$ and substrate become clear. For annealing with a laser power of P6, the $A_{1g}$ and the inline image peaks are clearly observed, confirming the formation of MoSe$_2$. The $A_{1g}$ and the inline image peaks are very similar to those of exfoliated MoSe$_2$ flakes. [2] However, we did not observe any PL possibly due to high thickness and poor crystallinity which is expect to be improved by tuning the thickness of the SELs and laser parameters. The intensity of the Si peak is also increased by the increased laser power, which is an indication of the heating and thinning effect of the laser beam. [14] Beyond P6, the MoSe$_2$ layer is completely removed from the substrate.
Figure 6.9 The RLA setup and laser-power dependent Raman spectra. The schematic diagram of RLA setup (a). Raman spectra of the films annealed at different laser powers (b).

Raman mapping has also been performed to form MoSe$_2$ from SELs with certain patterns on SiO$_2$/Si wafers as illustrated in Figure 6.10. The results reveal the potential of the laser at wavelength of 532 nm in forming of MoSe$_2$ patterns from the stacked layers when the laser power is adjusted. Our goal is to develop a laser technology that allows for precise formation and structuring of atomically thin MoSe$_2$ films on SiO$_2$/Si wafers.
Figure 6.10 The formation of MoSe₂ from SELs with certain patterns on SiO₂/Si. Optical microscopy image (a) of a Mo/Se/Mo film deposited on SiO₂/Si without heat treatment. Optical microscopy image (b) of a film after scanning a laser with incident laser power of 32.5 mW in the area marked by a dashed square (10x10 points). MoSe₂ and Mo/Se/Mo regions are marked with 2 in the blue-circle and 1 in the black-circle, respectively. Optical microscopy image (c) of a film after scanning a laser with incident laser power of 32.5 mW in the area marked by a dashed square (30x30 points). MoSe₂ and Mo/Se/Mo regions are indicated with blue and black arrows, respectively. The scale bar in all images is 5 µm. Raman spectra (d) of a MoSe₂ region on the film marked by a blue arrow in (c).

6.4 Conclusion

In summary, we have developed a procedure to fabricate few-layers MoSe₂ granular films. From their Raman and photoluminescence spectroscopy analyses, we
conclude that the semiconducting properties of rapid thermal processed few-layers granular films of MoSe$_2$ resemble that of single crystal MoSe$_2$ flakes. This method could now be implemented for the synthesis of other dichalcogenides materials. Moreover, we have shown that RLA can be employed to produce MoSe$_2$ in arbitrary shapes and patterns on SELs. Following the optimization of the thickness of SELs and laser parameters such as wavelength, power and exposure time, the quality of the laser processed MoSe$_2$ can be improved.

References


Conclusion

Herein, we have demonstrated various novel growth strategies for the production of several 2D materials, including growth of group VI transition metal dichalcogenides (TMDs) by chalcogenization of pre-deposited metal-containing precursors, and phase-engineered growth of group IV LMCs by vapor-phase reaction of metal oxide and chalcogen powders are demonstrated. Detailed characterization of each phase of tin sulfide crystals was performed using various microscopy and spectroscopy methods, and the results were corroborated by ab-initio density functional theory calculations. The significant results of this dissertation as following:

1. The large-scale production of 2D crystals can be obtained via by chalcogenization of pre-deposited metal-containing precursors.
2. Vapor-phase reaction of metal oxide and chalcogen powders with the help of the patterned seeds can provide ultrathin thin films with controlled thickness and morphology.
3. Crystal phase engineering of the crystals can be achieved by fine tuning of the reaction temperature.
4. Air annealing can be utilized to open active edges with well-defined shapes on the 2D crystals.
5. Laser annealing can be used to make nanopatterns of 2D metal chalcogenides on SiO₂/Si chips.