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Growth and Characterization of 2D layered Materials

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Growth and Characterization of 2D Layered Materials

by

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of the requirements for the degree of
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Dedication

This thesis is dedicated to my parents and my sister, for without their constant support I would not be able to complete it.

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I would like to personally thank everyone involved in helping me undertake this research project and write the following thesis. First and foremost, I would like to thank my research advisor, Dr. Humberto; not only did he allow me to join his lab, but without his constant guidance, patience, and understanding, I would not have been able to complete this project. I also would like to thank my wonderful lab team members including:

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They all helped me so much throughout this study and have become my second family.

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Abstract

2D layered materials are becoming an important area of research due to their exceptional electrical and optical properties. Specifically, 2D layered monochalcogenides are known for their high carrier motilities, whereas layered metal halides have been shown to have noteworthy photoresponsivity. Despite the assortment of 2D layered materials, the search for reliable and scalable synthesis methods is still a challenge in this family of materials. Often a certain growth technique will compromise a desirable trait needed for further fabrication, such as the quality of the crystal or its coverage on a substrate. In this study, two growth techniques that incorporate changeable parameters allowing for the controllable growth of 2D layered monochalcogenides and metal halides are explored. Following the growth of each material, characterization techniques are employed to confirm their identity, structure, and validate the success of each growth. By utilizing these growth techniques, it is expected to find superior ways at growing 2D layered materials that can potentially be used as next-generation devices.

Chapter 1: Introduction

In 2004 an experiment transpired that ushered new depth in the fields of materials science and condensed matter physics. The experiment that evoked this revolution was a simple procedure; two scientist, Andre Geim and Konstantin Novoselov, found that by sticking a piece of scotch tape on a piece of graphite they were able to separate the material into thin layer forms[1]. The resulting atomically thin layer forms was the long-theorized structure graphene and its discovery marked an era of a new class of materials known as two-dimensional (2D) materials. 2D materials, aptly named, are materials that have one dimension restricted, or confined, to the nanometer scale[2].

Because of their atomic scale thickness, 2D materials undergo novel physical phenomena not seen in their bulk counterparts. One of the interesting effects of the transition from bulk to 2D materials involves the modification of the electronic structure of the material. As the size of the material shrinks down past a certain point, the movement of the electrons are confined to move only in certain directions[3]. Conversely the excitons, quasiparticles generated when an electron-hole pair is created, increases in energy resulting in an increase of the bandgap of the material[4]. This widening of the bandgap is known as the quantum confinement effect.

Despite the outpour of discovery of other 2D materials, graphene remains the 2D theoretical model of choice for most active research groups[5]. Owing to its high crystal quality and exceptional electrical properties, it is not hard to see why graphene is still relevant in materials research. Indeed, most of the extraordinary properties of graphene can be attributed to

its flat honeycomb monolayer lattice. When the structure of graphene is examined in detail it is shown to be made up of three sp^2 orbitals and one p_z orbital [6]. In a sequence of graphene layers, the p_z orbitals form pairs of π and π^* bonds that act as the valence and conduction band of the material respectively[6]. When the layers separate to form a single layer of graphene, the π band electrons form a linear electronic dispersion leading to a zero-energy band gap[6,7]. To further illustrate this effect, figure 1.1 shows the zero energy band gap discussed above.

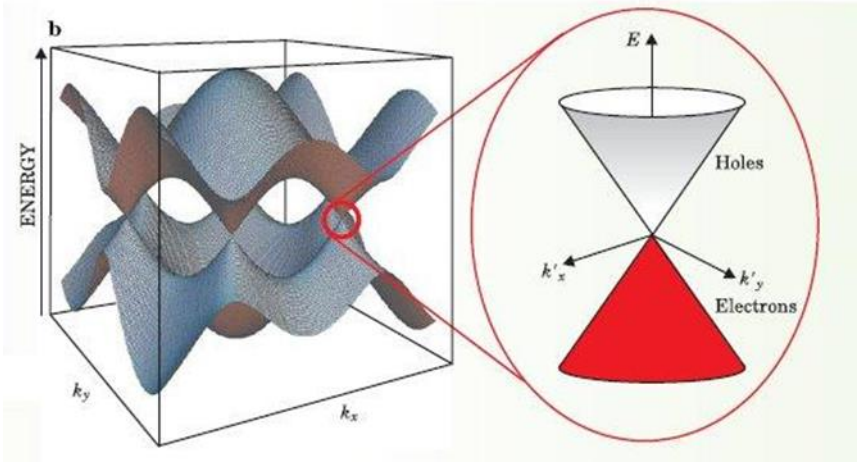


Figure 1.1: Energy-K diagram of graphene. Note. From "A bandgap semiconductor nanostructure made entirely from graphene", by Lavocat, J, 2012, graphene.com. CC-BY-NC 2012. Reprinted with permission

The result of graphene's unique structure allows it to have a variety of interesting properties. One of the more distinctive features is its electrical properties; it is reported of having a charge carrier concentration as high as 10^{13} cm^{-2}, with mobilities, at room temperature, expected to reach as high as 100,000 cm^2 $V^{-1}s^{-1}$ [5]. In addition, groups have utilized the optical properties of graphene and managed to make devices out of the material. Muller's group, for example, was able to construct a photodetector out of graphene flakes on top of Si/SiO_2 substrates [9]. They obtained a responsivity of 6.1 mA W^{-1} at an operating wavelength of 1.55 μm[9]. Even though graphene remains the model for two-dimensional materials, other material types have recently started gaining steam in the 2D

research community, with some showing properties that not only complement graphene but also rival its usage in potential devices.

1.1 Transition Metal Dichalcogenides

An important 2D layered group that resulted from the surge of researchers looking for alternatives to graphene is transition metal dichalcogenides (TMDs). Unlike graphene, 2D TMDs have a bandgap that allow for more possible applications in fields such as electronics and optics. Much like before, an examination of the crystal and electronic structure can give insight on the properties that TMDs have. To start, TMDs have a 3-atom thick monolayer; with a transition metal sandwiched between two chalcogenide atoms[10]. As shown in figure 1.2, the atoms within each layer are held together by strong covalent bonds forming a structure without dangling bonds; while the stacked layers are attracted to each other by weak van der waals interactions[10].

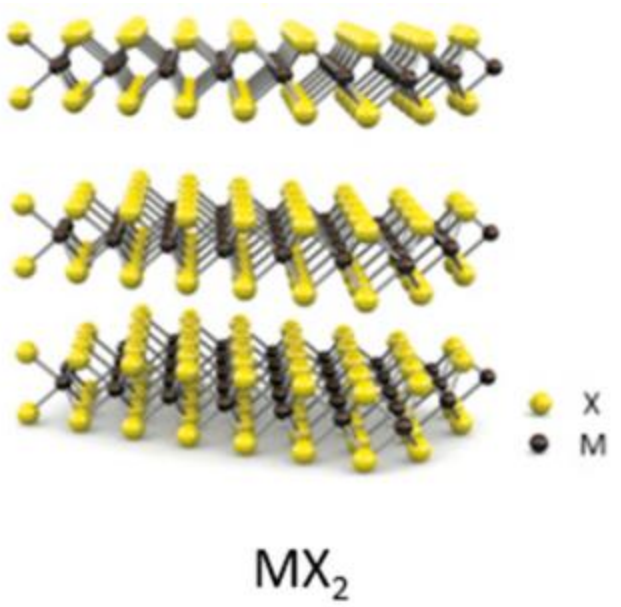


Figure 1.2: Crystal structure of a typical TMD. Where X= chalcogen atom (S, Se, Te), and M= transition metal (Mo, W, etc.). Note. From "Two-Dimensional Semiconductor Optoelectronics Based on van der Waals Heterostructures", by Lee, J, 2016, Nanomaterials. CC-BY-NC 2016, by MDPI. Reprinted with permission

Besides having a different crystal structure from graphene, the electronic structure of a typical TMD shows a tremendous difference with respect to the simple dirac cones that are generated from the zero-band gap of graphene. To illustrate the electronic structure of a TMD and how it changes from bulk to monolayer, the MoS_2 electronic structure is shown below.

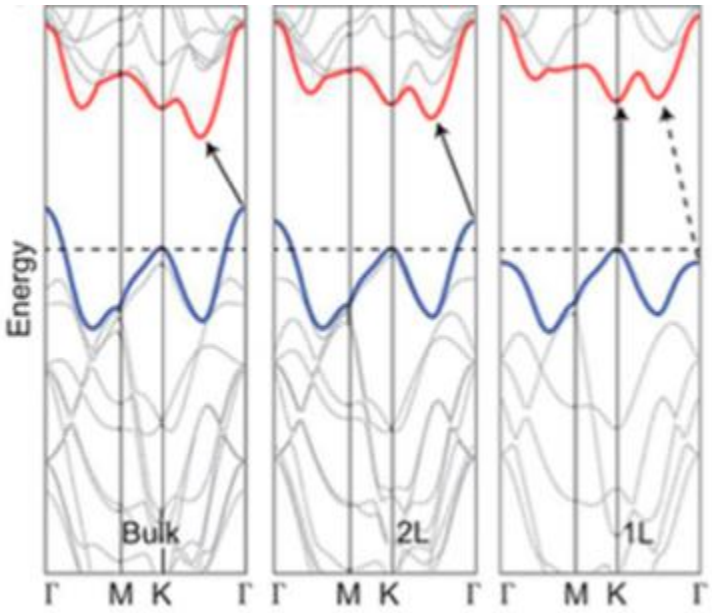


Figure 1.3: Transition of the electronic structure of MoS_2 from bulk to 1L. Note. From "Two-Dimensional Semiconductor Optoelectronics Based on van der Waals Heterostructures", by Lee, J, 2016, Nanomaterials. CC-BY-NC 2016, by MDPI. Reprinted with permission

As shown in the figure, the states at the Γ point are strongly affected by the number of layers. The reason for this phenomenon lies in the configuration of the molecular orbitals of the structure. It is known that the band structure of MoS_2 is effected by the molybdenum d and sulfur p orbitals[11]. These orbitals experience mixing as the number of layers increases leading to coupling interactions that effect the position and energy of the band gap[12]. Incidentally p orbitals interact more readily than d orbitals and primarily make up the states at the Γ point, explaining why states there are

influenced immensely by the number of layers[10,12]. Because of the influence the p orbitals has on the Γ point they acquire a greater change in energy as the layers decrease while states at the K point remain relatively the same[12]. The result is a shift in the valence band maximum (VBM), from the Γ point to the K point, and a transition from an indirect band gap of 1.29 eV to a direct band gap of 1.90 eV[13].

Due to the ability of TMDs to emit light strongly, they have found applications in various fields related to optics and optoelectronics. Sanchez's group was able to fabricate a MoS_2 monolayer photodetector with a responsivity of 880 AW^{-1}, a huge increase from the graphene-based photodetector mentioned earlier[14]. Even to this day more avenues are being explored where TMDs can be incorporated and eventually commercialized and mass produced.

1.2 Monochalcogenides

Although transition metal dichalcogenides provide an attractive alternative to graphene, there exists another group of layered material with properties that can exceed the TMDs. Group III-VI compounds, or metal monochalcogenides (M=Ga, In; X=Se, S, Te) are a group of 2D layered materials that have been gaining a great deal of attention due to their high carrier mobility, direct band gap electronic structure, high charge density, and other properties that help facilitate its application in an assorted number of fields[15]. The elements of this section will provide the necessary background information on one of the groups of material that is studied for this project. In order to gain an understanding of any material, a detailed look at how the structure, properties, and how it is synthesized are needed; what follows exemplifies this process.

1.2.1 Structure

Like graphene and TMDs, metal monochalcogenides (MX) arrange themselves in a hexagonal crystal structure, with metal atoms and chalcogen atoms alternatively bonded to one

another. However, differences in crystal structures arises when one considers how the material arranges itself in one layer. Unlike TMDs, which are made up of three atomic layers of X-M-X, monochalcogenides monolayers have a quaternary arrangement in which the two atomic planes composed of metal atoms are sandwiched between the chalcogen atoms (X-M-M-X)[15]. The figure below shows a side and a top view of an example monochalcogenide, InSe.

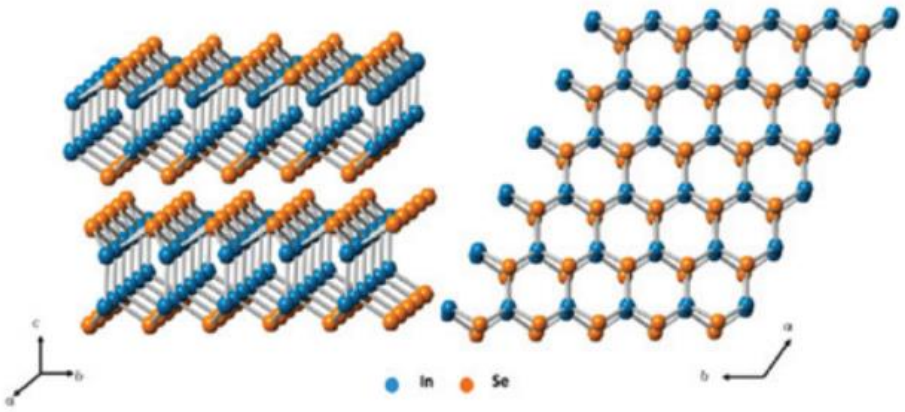


Figure 1.4: Crystal structure of InSe. The side (left) and top (right) views are both shown. Note. From "Synthesis, properties and applications of 2D layered MIIIXVI (M = Ga, In; X = S, Se, Te) materials. ", by Xu, K, 2016, Nanoscale. 2016, by American Chemical Society. Reprinted with permission

Incidentally different monolayer thicknesses have been reported for different monochalcogenides. For example, the thickness of monolayer GaSe was found to be 0.8 nm, while that of GaS was reported to be 0.75 nm[15].

One of the defining differences between the monochalcogenides and the transition metal dichalcogenides is that unlike TMDs, monochalcogenides experience a direct to indirect band gap transition from the bulk to monolayer. To illustrate the evolution of the change of the electronic structure, the results from the theoretical calculations performed on GaSe are shown in figure 1.5. In

1.5a as the number of layers of GaSe decreases the maximum of the valence band (VBM) starts to split symmetrically about the T point revealing the transition to an indirect band gap[16]. Furthermore, shown in 1.5c, as the number of layers decreases the energy of the band gap increases demonstrating the quantum confinement effect mentioned previously[16].

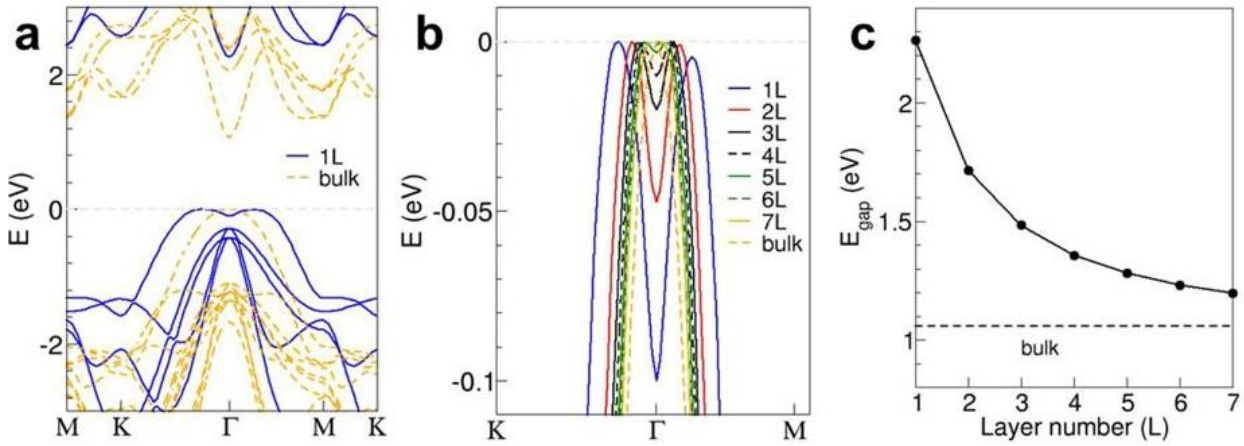


Figure 1.5: Bandgap of GaSe as a function of the number of layers. (a) shows the energy bands for bulk and monolayer GaSe. (b) shows the energy band near the VBM. (c) shows the band gap energy as a function of the number of layers. Note. From "Controlled Vapor Phase Growth of Single Crystalline, Two-Dimensional GaSe Crystals with High Photoresponse. ", by Li, X, 2014, Scientific Reports. CC-BY-NC 2014, by Springer Nature. Reprinted with permission

1.2.2 Electrical and Optical Properties

At the beginning of the section it was mentioned that metal monochalcogenides offer exceptional physical properties, even more so than TMDs. One of the properties that show enhancement in the monochalcogenide family was the high carrier mobility. It was reported that InSe can achieve low temperature mobilities of about 10^3 cm^2 V^{-1} s^{-1} while MoS_2 can only attain mobilities of about 0.1-200 cm^2 V^{-1} s^{-1} [15,17,18]. This can be traced back from the effective mass of the electron and its relationship with the mobilities of free charges. The following equation shows that relationship:[19]

$$\mu = \frac{e\tau}{m^*}$$

Where e is the charge of the electron, τ is the scattering relaxation time, and m* is the effective mass of the charge carrier (hole or electron). Owing to the inverse relationship between effective mass and carrier mobility it is expected that the lower the effective mass the higher the mobility; a fact confirmed when the effective mass of MoS_2, $0.45m_0$, is compared with that of InSe, $0.145\ m_0$[15,20,21].

Additionally, to exhibiting attractive electrical properties, monochalcogenides also display interesting optical properties. For instance, InSe can present PL emission in a broad range from visible to the infrared, an important area for next generation photodetectors [15,22]

1.2.3 Applications

Like other 2D layered materials, monochalcogenides are finding their way in a multifarious of different applications. One of the areas finding use of the adoption of these layered materials is the electronic device community, specifically field effect transistors (FETs). FETs are devices with three terminals: gate, source, and drain; that use the influence of an electric field to control the charge carrier's concentration in the channel and hence the amount of current that flows through the device. A simple schematic is posted below.

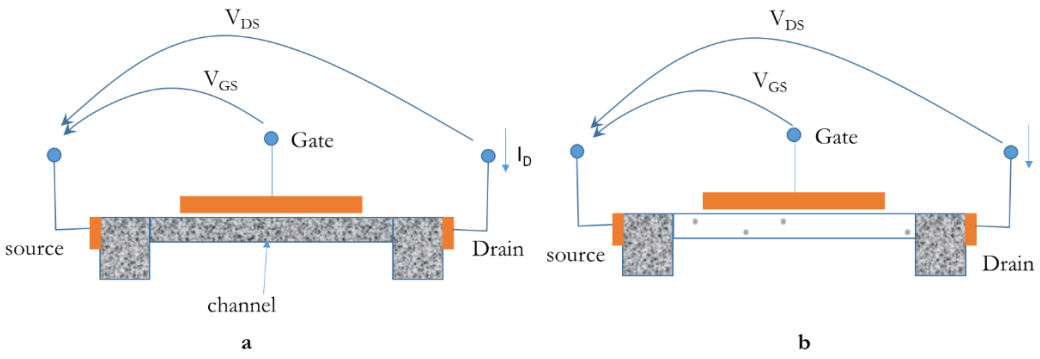


Figure 1.6: FET conduction states (on/off). (a) FET in the "on" state. (b) FET in the "off" state

In the figure it is illustrated that the device can be in two operational modes: "on" or "off". The device will always be "on" when the voltage between the drain and the source is greater than the voltage between the source and gate[24]. Incidentally, to turn off the current the voltage between the gate and source should be higher than the drain source voltage. An important component in these devices is the channel, a semiconducting material the current traverses through. Due to the ever shrinking down of the transistor, channel materials, such as silicon, start to experience problems that delay optimal performance of the device[23]. Related to the performance of the device is the channel material's mobility, and because silicon offers only mediocre mobilities its value as a next generation FET comes into question[23].

2D layered metal monochalcogenides provide attractive alternatives to the conventional materials used as FET channel materials. Efforts came into fruition in 2012 when Late's group fabricated the first single layer GaSe/GaS FETs[25]. Upon repeated measurements of varying gate voltage, with constant drain-source voltage, the researchers found consistent curves of current behavior, suggesting a stable transistor was made[25]. Remarkably GaS, an n-type semiconductor, experiences the same electrical behavior as GaSe, a p-type semiconductor[25].

The research mentioned highlights only a fraction on how 2D layered metal monochalcogenides can be applied to different areas of use. Even now researchers have extended their efforts into integrating these materials into optoelectronics, allowing for modified LEDs or photodetectors. With the continued efforts of these researchers, the research activity on monochalcogenides should see an increase in the following years.

1.3 Layered Metal Halides

The other materials that were studied for this project were layered metal halides. As diverse as the group is, this work focuses only on 2D layered lead iodide (PbI_2). Admittedly although PbI_2 is

capable of forming stable 2D forms, hardly any research is reported on its monolayer and few-layer growth [26]. Despite this, some interest remains in synthesizing these structures into single layer to multi-layer form. One of the motivations comes from the development of perovskite solar cells. PbI_2 is a precursor for lead halide perovskites, and the ability to grow 2D layered lead iodide would allow for 2D perovskites, enhancing the current capabilities of the solar cells of today[27].

1.3.1 PbI_2 Structure

Like TMDs, lead iodide has a hexagonal crystal structure where each layer is composed of a lead atom sandwiched between two iodide atoms[27]. The figure below shows the crystal structure as seen from the top view. Furthermore, the thickness of one layer of PbI_2 was reported to be approximately 0.76 nm[26].

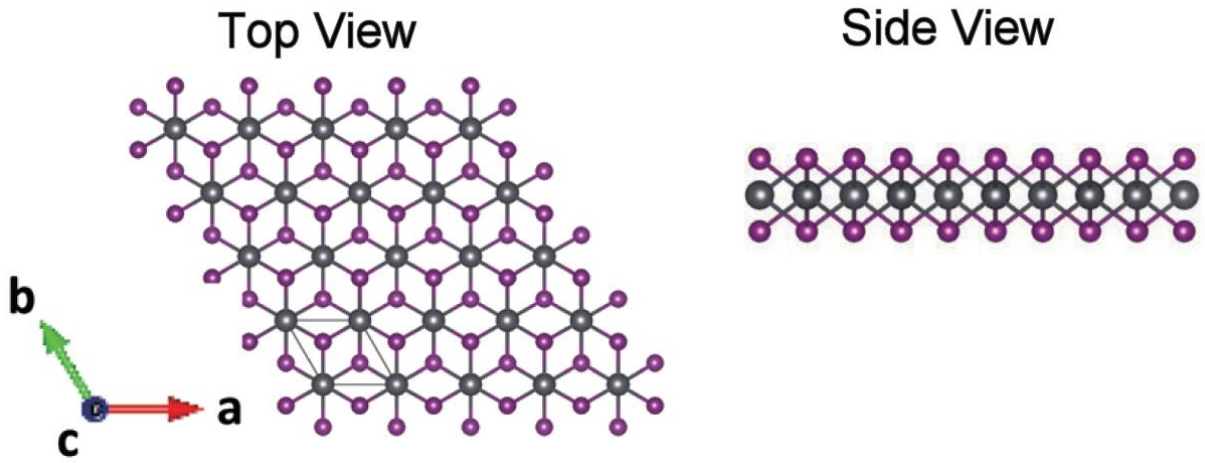


Figure 1.7: Top (left) & Side (right) view of PbI_2 crystal structure. Note. From "Band Structure Engineering of Interfacial Semiconductors Based on Atomically Thin Lead Iodide Crystals.", by Sun, Yi, 2019, Advanced Materials. Copyright 2019, by John Wiley and Sons. Reprinted with permission

Following the crystal structure, Zhou's group demonstrated that by using DFT an accurate representation of the band structure can be generated[28]. Figure 1.8 shows the different band

structures calculated using different functionals. Upon comparison with experimental data the Heyd-Scuseria-Ernzehof (HSE06) method combined with spin-orbit coupling effects gives the most accurate value of the monolayer band gap at 2.63 eV[28]. While each correction gives different approximation for the band gap, they all predict an indirect band gap transition, similar to the monochalcogenides[28].

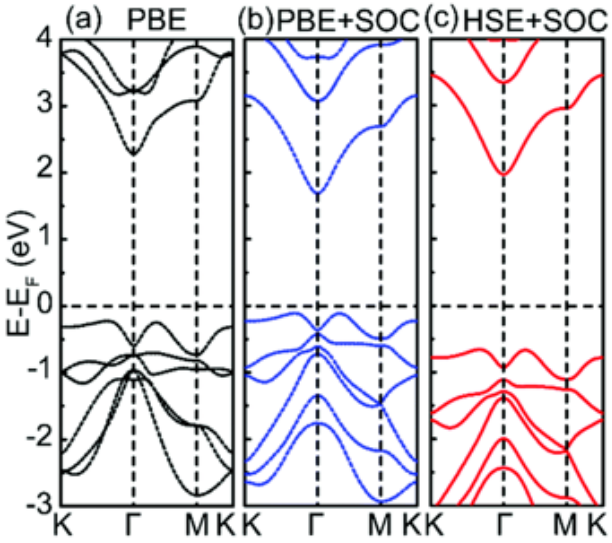


Figure 1.8: PbI_2 monolayer electronic structure. Calculated with (a) PBE functional without spin-orbit coupling. (b) PBE with spin-orbit coupling. (c) HSE06 functional with spin-orbit coupling Note. From "Single layer lead iodide: computational exploration of structural, electronic and optical properties, strain induced band modulation and the role of spin–orbital-coupling.", by Zhou, M, 2015, Nanoscale. Copyright 2015, by RCS Pub. Reprinted with permission

1.3.2 Layered Metal Halides Properties

Using a phonon scattering model, a group was able to predict a mobility of 122 $cm^2 V^{-1} s^{-1}$ for single layer lead iodide[28]. While not as high as the monochalcogenides, PbI_2 offers carrier mobility values comparable to monolayer TMDs, and its band gap allow for potential applications in transistors or other electronic devices[28].

Another set of properties that remains consistently dependent on the layers are the optical properties. The optical band gap of PbI_2 was reported to go from 2.41 eV for bulk to 2.47 eV for monolayer[26]. To further illustrate how the PL changes with the thickness, the figure below shows the PL transition from bulk to monolayer of PbI_2.

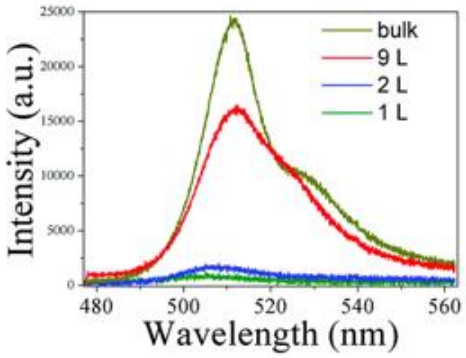


Figure 1.9: PL transition of bulk PbI_2 to 1L. Note. From "Large-scale 2D PbI2 monolayers: experimental realization and their indirect band-gap related properties", by Zhong, M, 2017, Nanoscale. Copyright 2017, by RCS Pub. Reprinted with permission

1.3.3 Layered Metal Halides Applications

As mentioned before, a lot of the motivation behind studying 2D layered metal halides, specifically PbI_2 comes from its direct involvement in lead halide perovskites. These materials are further fabricated into high performance photovoltaic cells and even light emitting diodes (LEDs). Despite the active interest in perovskite research, the layered metal halides also have potential applications in other areas. For example, Zhong's group fabricated monolayer based PbI_2 photodetectors to measure the optoelectronic response properties of single layer PbI_2[26]. Using a 450 nm laser the group was able to measure characteristic responses, which include: the photocurrent generated with varying light intensity, the response time, and the recovery time.

In addition, to having potential as photodetectors, the metal halides also show promise in van der waals heterostructure based devices. Generally, these devices enhance the capabilities of the separate materials and allow for control of the band structure across the interface[27]. Specific to these heterostructures are the type of heterojunctions that can form across the interface between the two structures: type I, type II, type III. In the type one heterojunction the band gap of one of the materials completely overlaps the band gap of the other material[29]. Ultimately this leads to charge carriers being transferred to one of the materials, allowing for enhancement of the band gap and consequently the PL. Next the type II band alignment is when the conduction band and the valence band of one material is lower than the corresponding bands of the other material[29]. As a result, the band gap of the higher conduction band tend to straddle the band gap of the lower band values and charge carriers separate into different materials. While the holes tend to go into the material with the lower band gap, the electrons go into the material with the higher band gap[29]. Finally the type III band alignment is when the band gaps do not overlap at all; in this sense it behaves as a more extreme type II[30].

Incidentally, Sun's group was able to synthesize and characterize lead iodide and TMD (MoS_2, WS_2, WSe_2) heterojunctions, similar to the ones discussed above. The results show that PbI_2/MoS_2 heterostructures involving quenching of the PL, while PbI_2/WSe_2 and PbI_2/WS_2 enhance the PL of the TMD[27]. Hence, the band alignments for the former are type II, while the band alignments of the latter are type I. By forming these different heterojunctions, the materials can be used in different applications. For example, the type II band alignments are favored as light harvesting devices, while the type I materials are favored as light emitting devices[27].

The goal of this project was to synthesize and characterize large, continuous, single-layer to few-layer areas of 2D monochalcogenides and metal halides. In addition, an effort will be made to

study the optical properties of these materials in detail. By using the techniques discussed in chapter 2, a comprehensive study of 2D layered materials can be developed.

Chapter 2: Experimental Techniques

In growing 2D films, or films of any size, the nature of the growth plays an essential role on the structure and properties of the material[31]. The technique used to deposit a thin film on a substrate can influence whether a film is an insulating material or a film with high electrical and thermal conductivity. Even more important than the method used to grow the materials, are the multiple characterization techniques used to study its structure. By employing characterization methods, not only can features such as the composition and structure can be analyzed, but they also can serve as feedback that allow one to improve on the material's properties and progress toward more functional materials[32]. In this project chemical vapor deposition was used to grow 2D layered monochalcogenides, while a solution method was used to grow 2D metal halides. Following the growth of the materials the characterization techniques used were: Raman spectroscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and atomic force microscopy (AFM).

2.1 Material Growth

The following section provides the procedures used for the growth of both the monochalcogenides and the metal halides. The instruments that was used for chemical vapor deposition (CVD) was a 120 V Lindberg/Blue M Mini Mite tube furnace and a crucible boat. In addition, for the solution growth an isotemp hotplate, beaker, and model 30 lab oven was used.

2.1.1 CVD growth of Monochalcogenides

For this project 2D monochalcogenides were grown by chemical vapor deposition under atmospheric conditions. The figure below shows the apparatus used to conduct the experiment. As shown in the figure a quartz tube is used to house a powder source (M=Ga, In, X=Se, S), along with SiO_2/Si substrates situated downstream from the spot of thermal evaporation. The carrier gas used for each set of experiments is a H_2/Ar mixture.

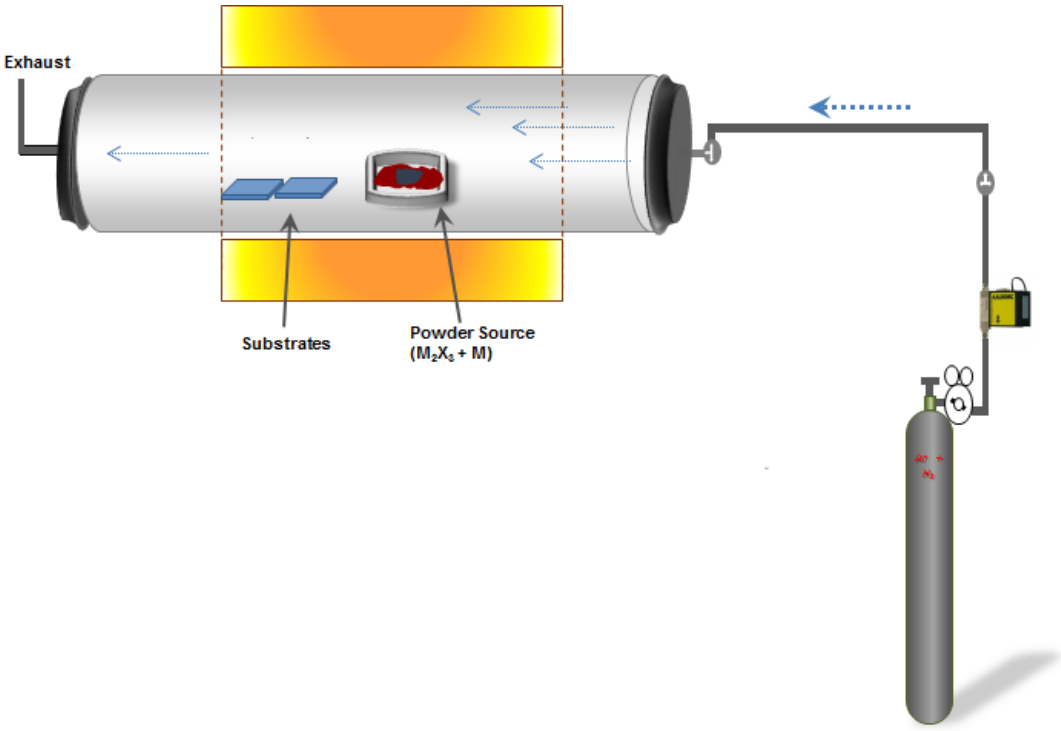


Figure 2.1 CVD setup

It should be emphasized that while the synthesis of certain monochalcogenides may differ slightly by growth conditions, each material followed the same principle of growth. First, before starting any experiment the phase diagrams and vapor pressure curves for each material was examined to get an estimate on what the growth parameters (temperature, time, flow rate) should be.

The phase diagrams and vapor pressure curves are listed in appendix A. After, the M_2X_3 and M powders are weighed and mixed in a molar ratio of 1:1, and subsequently placed in a boat for an experiment. The boat is then loaded in the quartz tube, alongside with substrates that are placed a distance downstream from the powder. Finally, the furnace is preheated to the desired temperature of growth, while a flow rate of carrier gas is introduced to the system. After the growth is completed the system is cooled down fast, and the experiment is concluded.

2.1.2 Metal Halide Growth

The metal halides in this study were grown by a solution-based method. Similar to the growth of monochalcogenides, the start of each experiment began with the weighing of powders of metal halides. Once the appropriate weight was gathered, 100 mL of distilled water was placed in a beaker and heated until boiling. The powder was then added to the water and stirred until an acceptable amount was dissolved. Next, a substrate was placed in a small petri dish, where a solution of the metal halide was then pipetted into. After a sufficient amount of solution was pipetted into the dish (enough to cover the substrate), a glass slide was used to cover the substrate. Finally, the petri dish was placed in an oven, allowing time for all the water to evaporate out of the dish. A schematic is provided below showing the details of the experimental set-up.

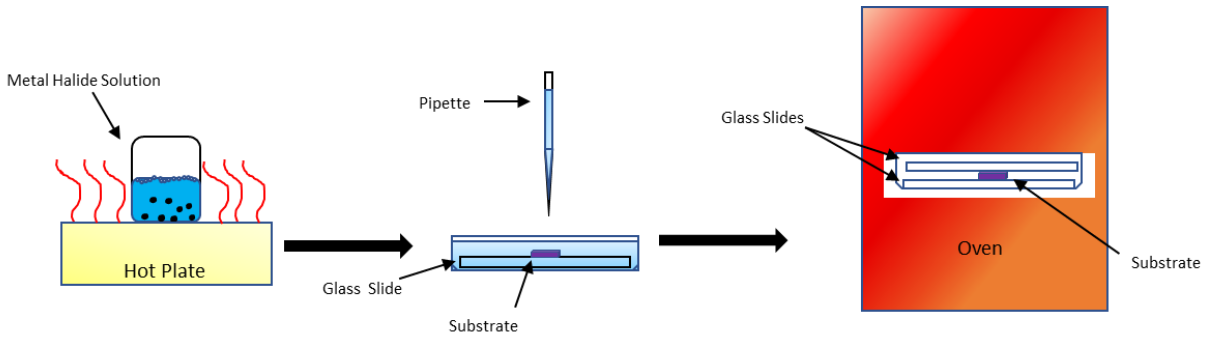


Figure 2.2: Solution-based setup

2.2 Raman Spectroscopy

In our experiments, Raman spectroscopy was frequently used as a routine characterization technique after the growth. The Raman spectrometer, or Raman microscope, is designed to measure the vibrational frequencies of atoms in the solid (phonons) based on their shift from an incident laser beam. Because each chemical bond has specific frequencies of vibration, Raman spectroscopy can act as a "fingerprint" to identify a material. Even more it can be used to identify the phase of the material, the residual strain, crystallographic orientation, and its composition[33]. Because of the importance of the Raman measurements, the following passages will be dedicated to explaining a brief overview of the theoretical framework and instrumentation of Raman spectroscopy.

2.2.1 Basic Principles

In reality, atomic nuclei are in a state of constant erratic motion. However, the complexity of the system is made simpler when the vibrational motion of the atoms is proposed to be made up of a linear combination of normal vibration modes, completely independent of one another[34]. For example, in the figure below the vibrational motion of the CO_2 molecule can be represented with 3 normal modes: two stretching vibrations (one symmetric and one antisymmetric), and one bending vibration[34]. The figure is a classical representation of what goes on in a chemical bonding system, with the bonds being represented as massless springs influenced by Hooke law forces.

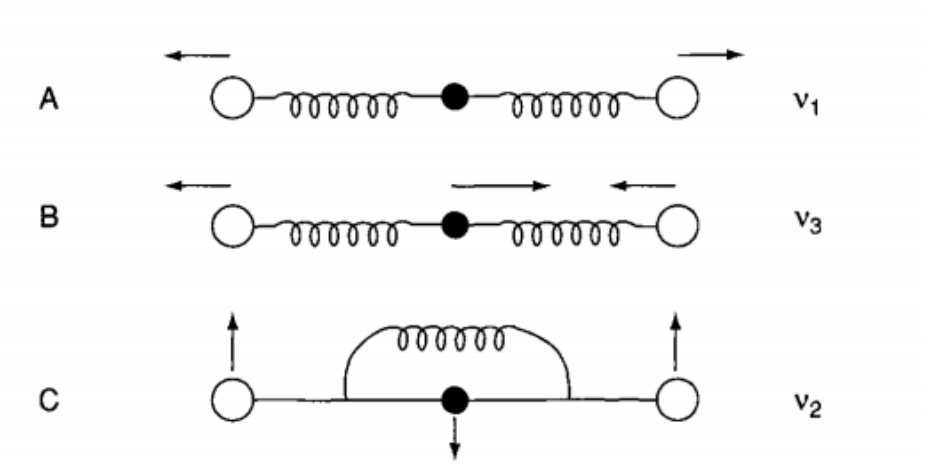


Figure 2.3: Independent Phonon modes of CO_2. (a) symmetric stretching. (b) antisymmetric stretching. (c) bending. Note. From "Introductory Raman Spectroscopy", by Ferraro, 1994. Copyright 1994, by Elsevier. Reprinted with permission

In order to calculate the number of independent modes of vibration, a degree of freedom analysis must be done on each atomic nuclei of the molecule. Using an N-atom molecule as an example, the degrees of freedom can be calculated the following way: first, motion in every coordinate direction is considered for each nuclei, yielding 3N total degrees of freedom. Next the translational motion of the whole molecule, in every direction, is subtracted from 3N so that the molecule's translational motion is restricted. The same is done for the rotational motion of the molecule. The final result, 3N-6 (3N-5 for linear molecules), gives the number of modes of vibration for an N-atom molecule[34].

Corresponding to the modes of vibrations are its energy levels. Using the classical representation above, where the bonds are interpreted as massless springs, the vibrational energy of molecules can be found quite easily. Taking a diatomic molecule as an example, the force between the two atoms is shown to have the form of:

$$F = -K\Delta r = -K(r - r_e)$$

Where K is the force constant, r is the displacement between the two atoms, and r_e is the equilibrium distance[33]. Incidentally the potential energy can be expressed as E_{vib}[33]:

$$E_{vib} = \frac{1}{2}K\Delta r^2 = \frac{1}{2}K(r - r_e)^2$$

Despite offering good approximations at low displacements, real molecular vibrational energy levels are described using quantum mechanics. The Schrodinger equation used to describe the same diatomic molecule is expressed as[34]:

$$\frac{d^2\psi}{dr^2} + \frac{8\pi^2\mu}{h^2}\left(E - \frac{1}{2}Kr^2\right)\psi = 0$$

Where μ is the reduced mass and all the information that is known about the system is now contained in the wave function, ψ. Following the solution, a set of eigenvalues, or discrete vibrational energies the system is allowed to have is given as[34]:

$$E_{vib} = h\nu_0\left(v + \frac{1}{2}\right) \quad \nu = 0, 1, 2, 3\ldots$$

$$\nu_0 = \frac{1}{2}\pi\sqrt{\frac{K}{\mu}}$$

Where ν is the vibrational quantum number that is used to describe different energy transitions (phonons). The schematic representation of the vibrational energy levels is shown in figure 2.4.

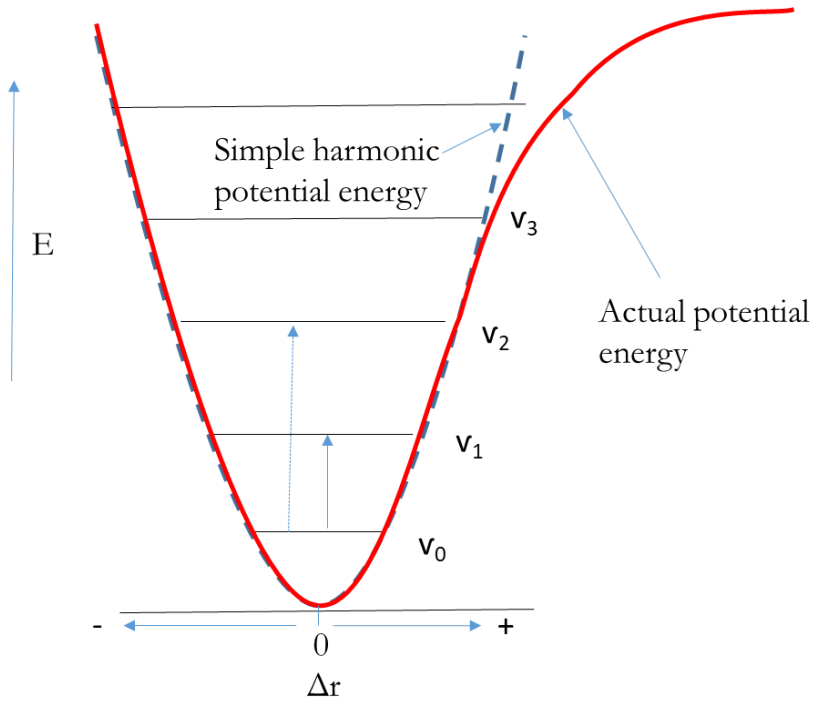


Figure 2.4: Vibrational energy levels of diatomic molecule

Using spectroscopic methods, such as IR and Raman spectroscopy, the modes of vibration that are experienced as different energy levels, can be analyzed and studied.

Although energies of the infrared region match accordingly with vibrational energies, vibrational spectra can also be generated when a molecule is irradiated by a laser in the UV-visible region[34]. As shown in the figure below, in the backscattering geometry, used in this study, signals are generated when the laser beam hits the sample and scatters in a direction 180 ° with respect to the incident beam. Different signals are generated from the diverse light-mater interaction processes including: photoluminescence, Rayleigh scattering, Raman scattering, etc. For simplicity we draw only the last two signals mentioned above.

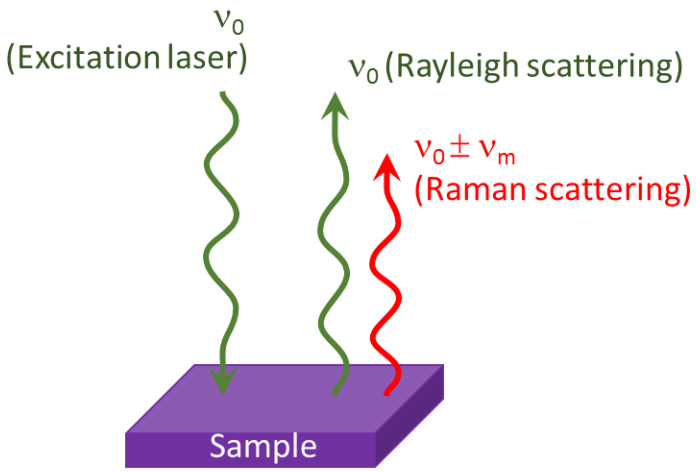


Figure 2.5: Mechanism of Raman scattering in backscattering geometry

In one scenario, a photon hits a molecule (or individual atom in a solid) and is scattered back with the same frequency as the incident beam. This is known as Rayleigh scattering and its information provides no insight on the structure of the material. The second phenomena that occurs is the light scattering by the lattice vibrations; this is a phenomenon that involves three quasi-particles (photons, electrons and phonons). The incoming photon excites an electron in the sample to a higher energy level, this electron is then scattered by the ionic cores where the electron adsorbs or release energy to the lattice in a quantized form (phonons), once the electron relaxes back to a lower energy level a second photon is emitted with a slightly different frequency compared to the initial incident photon. This interaction is recognized as Raman scattering, and its information provides a great deal concerning the collection of atoms.

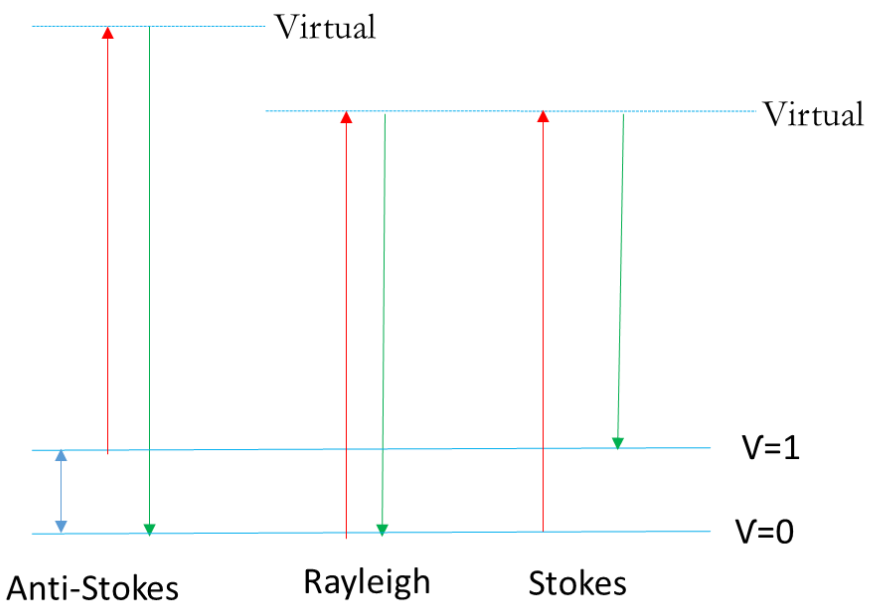


Figure 2.6: Rayleigh and Raman scattering

Following the above description of the Raman scattering, there are two types of Raman lines that are possible. The first is when the photon frequency increases compared to the incident beam ($\nu_0+\nu_m$) due to the absorption of a phonon; this situation produces anti-stokes lines. If otherwise the frequency is smaller than that of the incident photon ($\nu_0-\nu_m$), from the creation of a phonon, stokes lines are made[33]. In our experiments we monitor the Raman spectrum from the stokes region. Figure 2.6 summarizes the previous information.

2.2.2 Instrumentation

All of the Raman measurements in this project are taken with a Raman microscope, an instrument that allows the user to examine the microstructure of samples by focusing a laser down to the micrometer level[33].The Raman microscopes permits not only acquisition of spectroscopic data, but also imaging of the sample in magnitudes of micrometers. Every commercial Raman

microscope includes the following components: laser source; sample illumination & collection system; spectral analyzer; and detection & computer control & processing system[33]. A diagram of the general setup of a Raman microscope is provided below.

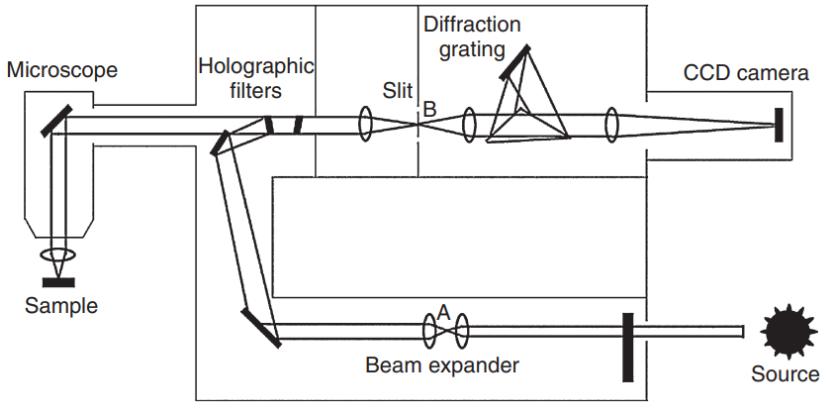


Figure 2.7: Raman microscope schematics. Note. From "Materials Characterization: Introduction to Microscopic and Spectroscopic Methods", by Leng Y 2008. Copyright 2008, by John Wiley and Sons. Reprinted with permission

At the start of any Raman microscope is the excitation source, frequently assigned to a specific laser. One of the common laser sources available are continuous-wave lasers; these lasers can generate power of up to 5 mW for sample excitation[33]. Some common examples include gas lasers: Ar^+, Kr^+, and He-Ne; however, the technology is quickly moving to solid state diode lasers (like those used in this project). Following the laser is the microscope system: an optical pathway that scatters and collects the light needed for analysis. Before the laser enters the microscope, it passes through a series of filter to allow the passage of one wavelength of light and remove any diffraction rings that would cause disturbance to the Raman signal[33]. Once the light enters the microscope it illuminates a microscopic region of the sample and the scattered light is focused by the objective lens into an array of prefilters[33]. The filters in this case block out any light that has the same frequency as the incident beam; without them the Raman signal would be hard to detect[33].

After filtering out any signal of Rayleigh scattered light, the resultant light proceeds to a diffraction grating (the key component of the spectral analyzer), where it disperses the Raman scattered light according to its wave number[33]. Finally the dispersed light is recorded by a detector, usually a charged-coupled device, CCD, and the now converted electric signal is recorded into a plot of Raman shift vs wave number by a computer processor[33].

The specific system that was used for these experiments was a Horiba LabRAM HR Evolution Raman system. For the monochalcogenides a 532 nm diode-laser was used but for the layered metal halides a 405 nm and 633 nm diode-laser were utilized as well. In addition, a 100 m^{-1} grating was used for fine resolution of spectral lines[35]. Finally, LabSpec software was used to analyze the results that were obtained by the processing system.

2.3 Scanning Electron Microscopy

In order to analyze the morphology of the films, and examine fine details not seen by the optical microscope, a scanning electron microscope was used. The scanning electron microscope (SEM) operates using a focused electron beam, or probe, to scan a microscopic area of a specimen, providing a magnified version of an image that can reach magnifications up to 100,000X[33]. In addition, the SEM is equipped with an X-ray spectrometer that allows chemical composition information to also be obtained. The SEM that was used for the series of experiments was a JEOL JSM-6390 LV, equipped with an INCAx-sight 7582M microanalyzer for Energy Dispersive Spectrometry measurements.

2.3.1 Principle Arrangement

Even though the exact operation of an SEM differs from many traditional microscopes it still stands that the internal mechanics of scanning mechanics are notably comparable to optical microscopes. For instance, in both microscopes, a source of illumination traverses through a series

of lenses where it then irrevocably strikes a specimen, on a stage, to provide magnified details of the microstructure of the particular specimen. But while compound light microscopes can only resolve the microstructure of a material down to 0.2μm, the SEM can reach resolving powers down to 15.0 nm[33].

The primary cause of this huge discrepancy comes from the source of illumination. In optical microscopes the image is produced by using visible light, while scanning electron microscopes, and other electron microscopes (TEM), use a beam of electrons. This is further illustrated by examining the equation for resolution in an optical microscope[33]:

$$R = \frac{d}{2} = \frac{0.61\lambda}{\mu sin\alpha}$$

In order to get higher resolving powers a shorter wavelength of illumination is needed; while the shortest wavelength of visible light is 400 nm, the wavelength of electrons in SEM are capable of reaching wavelengths 10,000 times shorter[33]. Another advantage of the SEM comes from its large depth of field. When viewing objects from an optical microscope a compromise must be made on which areas one wants to resolve in fine detail while leaving other areas unresolved. Because of the large depth of field of an SEM, which can reach to orders of micrometers, the whole image can be resolved in detail, yielding a 3-dimensional appearance[33].

To understand how an image in an SEM is exactly generated it is beneficial to look at the optical arrangement, mentioned earlier, in greater detail. First a stream of electrons is ejected from an electron gun. The standard electron gun consists of a cathode, wehnelt electrode, and an anode[33]. Next, the then formed electron beam, traverses through the column and passes through two sets of condenser lenses. As delineated in figure 2.8, the condenser beams act to reduce the crossover diameter of the electron beam, with the objective lens reducing the final diameter of the beam to a

nanometer scale[33]. Finally, using a beam deflected system, that is incorporated within the objective lenses, a line by line scanning of the specimen surface is done by the probe[33]. Electrons ejected from the surface are then collected by a detector to create an image that is displayed on a nearby screen.

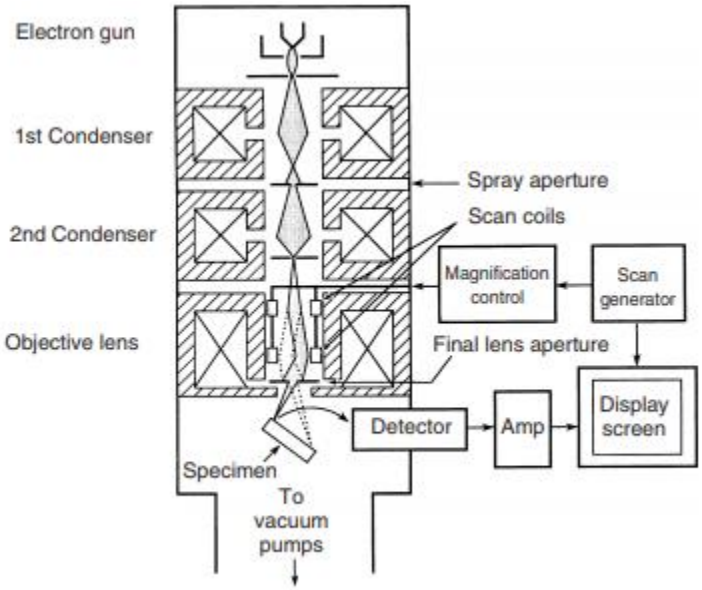


Figure 2.8: Schematic of an SEM arrangement. Note. From "Materials Characterization: Introduction to Microscopic and Spectroscopic Methods", by Leng Y 2008. Copyright 2008, by John Wiley and Sons. Reprinted with permission

2.3.2 Signal Electrons

When the electron beam interacts with a sample there are different types of electrons that can be ejected from the surface (figure 2.9). The ones that are used in SEM imaging are backscattered electrons (BSEs), and secondary electrons (SE). While both BSEs and SEs can provide SEM images from the sample, they both differ in the mechanism in which they are formed. As a result, different images can be formed from each signal electron. BSEs are continually formed when the electron beam collides elastically with the sample. These types of wide-angle collisions result in little energy loss, retaining 60- 80% of the energy of the incident electrons[33]. BSEs can be

used to generate an image based off the different sizes of atomic nuclei. On the other hand, SEs are signal electrons that come from the inelastic scattering from the incident beam and the sample. Contrary to BSEs scattering, for a SEs to be detected the incident beam has to collide and transfer most of its kinetic energy to an orbital electron of one of the sample's atom. Once the kinetic energy is enough, a SEs is ejected, at an energy considerably lower than the incident beam[33]. SEs are used to generate images based off topographical differences.

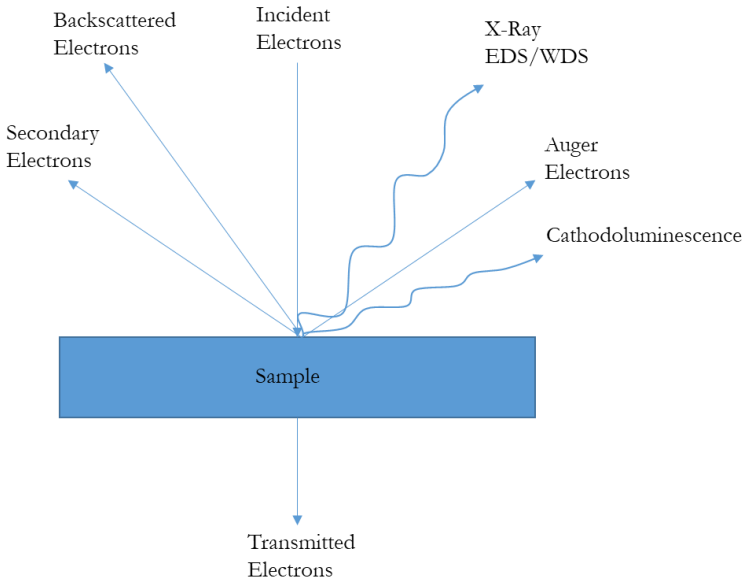


Figure 2.9: Types of signal electrons

2.3.3 Instrumentation

The JSM-6390 SEM microscope is composed primary of a tungsten filament electron gun; a 4-port specimen chamber; detectors for secondary electrons, backscattered electrons, and characteristic x-rays; a system of electromagnetic lens; and finally an OS that runs on Windows XP. Above all the features of the SEM, it is the existence of the detectors that allow us to see the images

that are produced from the ejected electrons. At the bottom of the objective lens, the JSM-6390 has a secondary- electron detector, backscattered-electron detector, and a photon detector. Because of the detectors the user can switch to two imagining modes, and collect x-ray spectroscopy information.

2.3.4 EDS

As stated previously, the SEM comes equipped with a photon detector to allow the analysis of characteristic x-rays that are emitted from the sample. By analyzing the signals that are produced from characteristic x-rays, information regarding the chemical composition can be obtained. This characteristic technique is known as X-ray spectroscopy. The X-rays from X-ray spectroscopy can be measured two ways: by their wavelength and by their energy. Energy dispersive spectroscopy (EDS), the technique employed for this SEM, is the measurement technique when the energies of X-rays are used to distinguish chemical elements from each other. First, the beam of electrons is focused on a microscopic area on the sample. Once the electrons penetrate a wide enough depth in the sample, characteristic x-rays are emanated and collected by the detector. The photon detector in this system is made up a Si(Li) diode, which converts X-ray photons into electron-hole pairs. After the electron-hole pairs are created they are picked up by the detector diode and are converted to electrical pulses[33].

2.3.5 Sample Preparation

Samples characterized by SEM/EDS were placed on a tungsten holder and held in place by double-sided carbon tape. In addition, because each sample was grown on a SiO2/Si substrate, a thin piece of copper tape was added to minimize surface charging and allow a place for excess electrons to travel. An example of a sample on the tungsten holder is shown below.

Figure 2.10: SEM holder with sample

2.4 Atomic Force Microscopy

Another characterization technique that was employed was atomic force microscopy (AFM). AFM, a subset of scanning probe microscopy, involves scanning the material surface with a fine tip probe resulting in topographical information of the sample. Unlike optical and electron microscopy, AFM utilizes near-field forces on the sample under consideration. Near field forces are the forces that arise from the interactions between the probe tip and the surface of the sample being scanned. As a result of these near field forces, a sample's surface can be mapped out through the careful detection of attractive and repulsive forces. To complete each measurement, each AFM is typically equipped with a probe, motion sensor, scanner, electronic controller, computer, and a vibration isolation system[33]. The following section will give a brief overview on how the AFM is operated and the basic instrumentation involved.

2.4.1 Principal Operation

An AFM can operate under two distinct modes: a static mode and dynamic mode[33]. When the AFM is operating under static mode, the tip that is attached at the end of the cantilever is

constantly touching the surface of the sample. It is only when the cantilever bends to a certain degree that the tip adjusts its vertical position with respect to the sample[33]. As a result, a typical scan consists of the probe dragging across the sample. Coincidentally this mode is also called contact mode. Unlike static mode, dynamic mode has the cantilever move at a preset oscillation value[33]. Once that value is disturbed a feedback loop will initiate to correct it back to the desired amplitude. Incidentally, in dynamic mode the AFM can be of contact and noncontact origin[33].

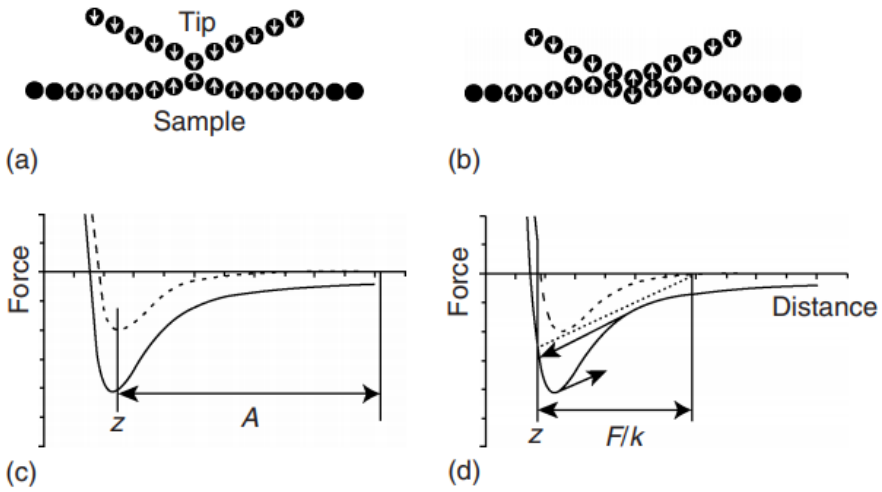


Figure 2.11: AFM tip-sample interactions. (a) noncontact mode. (b) contact mode (c) force-distance diagram with noncontact mode. (d) force-distance diagram with contact mode. Note. From "Materials Characterization: Introduction to Microscopic and Spectroscopic Methods", by Leng Y 2008. Copyright 2008, by John Wiley and Sons. Reprinted with permission

Because each tip operation of the AFM requires different contact with the surface of the sample, different near force interactions occur for each mode. To illustrate the different interactions, the figure below shows what happens the tip from each mode approaches the surface. As demonstrated in figure 2.11, when the tip is in dynamic noncontact mode all the forces between the tip and the sample are attractive[33]. Even the short-range forces, or the forces that are experienced between the outermost atom at the tip of the probe, and the surface atoms of the sample, experience an attractive force. This is further exhibited in figure 2.11c, where the force versus distance is

illustrated; the solid line represents the total force, while the dashed lines represent the short-range force; z represents the distance at which the tip comes closest to the surface. In contrast, figure 2.11b represents the static contact mode. As seen at the tip apex, the interaction that is experienced is short-range repulsion. The force diagram for static contact mode is shown in figure 2.11d. In this case, the contact position, z, is on the repulsion side of the force distance diagram[33].

2.4.2 Instrumentation

All the following measurements were taken using an AFM operating in dynamic noncontact mode. As stated before, in this mode the cantilever oscillates at a delineated frequency set by the operator. In order to monitor the tip-sample interactions a system of position-sensitive photodiodes is integrated as the force sensor component[33]. In a routine scan if the amplitude of the oscillation goes below or above the value the laser, reflecting off the cantilever, will shift its striking position on the photodiodes. The signals that are generated by the photodiodes indicate the amount of deflection, which can further be converted to the force that results on the tip (leng, 173)[33]. Finally, the computer system processes the frequency-shift signals and provides a three-dimensional atomic resolution of the surface[33].

The Horiba-AIST-NT NanoRaman was the specific AFM instrument used for characterization techniques in these experiments. In addition, the type of tips used were n^+ silicon with a resistivity of 0.01-0.02 cm. The resonance frequency of the probe operated at 204- 497 kHz and the tip height was approximately 10 μm.

Chapter 3: Layered Monochalcogenides Results and Discussion

In this chapter the results will be presented on the growth of 2D layered monochalcogenides. Following the results will be a discussion on how the experimental methodologies effected the growth of each material, by studying their Raman and photoluminescence. In addition, SEM and AFM techniques will be used to confirm the morphology and layer number of the materials grown.

3.1 Monochalcogenides

In order to grow group-III monochalcogenide films, we used the CVD setup described in chapter 2 (Figure. 2.1). A small modification was introduced to the system, where the one zone furnace is mounted on wheels and able to move over a long quartz tube (shown in figure 3.1). This modification leads not only to fast heating a sample, but also fast cooling after the growth. As a result of the fast cool down, the structure and morphology of the as-grown films are quenched. Unlike conventional slow cooling down, where the sample transits through different temperature regimes, any post-growth evolution of the film is minimized using this modified process. With the utilization of the CVD process, the 2D layered monochalcogenides were successfully grown on SiO_2/Si substrates. As it will be discussed in the next sections, we observed that the number of layers depends on the temperature of the furnace, amount of precursor used, gas flow rate, and the time of the synthesis.

Figure 3.1: One zone furnace used for growth of the monochalcogenides

3.1.1 GaSe Results

The first monochalcogenide to be discussed in this work is Gallium Selenide (GaSe). As mentioned in 2.1.1, a mixture of Ga_2Se_3 + Ga in a stoichiometric 1:1 ratio was used as solid powder source for the CVD growth of GaSe. Based off the Gallium-Selenium phase diagram (appendix A), multiple phases exist when Ga and Se are mixed; therefore, to ensure enough Ga_2Se_3 and Ga would vaporize to form a film with the right GaSe phase at the lower temperature zone, the temperature was kept below 1273ºC. Finally, by manipulating the parameters, discussed above, reasonable control for the synthesis of layered GaSe was obtained.

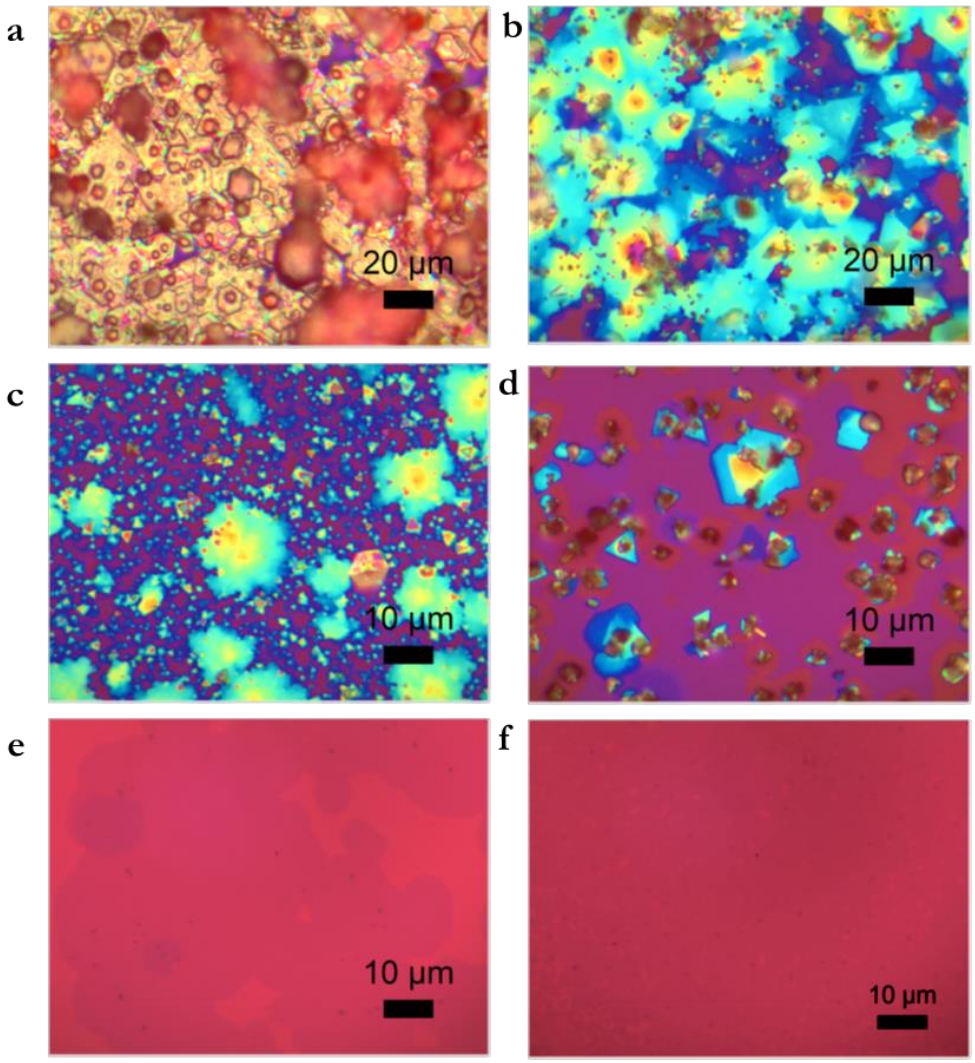


Figure 3.2: Optical images of GaSe samples grown in varying temperature conditions. T_b= temperature at which the boat is, and T_s= temperature at which the substrate is, with (a) T_b= 1030-1070˚C, T_s= 930-970˚C. (b) T_b= 930-970˚C, T_s= 850-890˚C. (c) T_b= 910-950˚C, T_s= 800-840˚C. (d) T_b= 860-900˚C, T_s= 760-800˚C. (e) T_b= 810-850 ˚C, T_s= 700-740˚C. (f) T_b= 760-800˚C, T_s= 650-690˚C

Using a constant flow rate (200 sccm), growth time (10 min), and precursor amount (50 mg) Ga_2Se_3, (8 mg) Ga, a series of experiments were conducted with the variation of the furnace temperature. Above (figure 3.2), are the optical images obtained from the temperature dependent

series. As described in the figure caption, we called T_b the temperature range at which the material is vaporized, and T_s the temperature ranges the substrate is at, in which the material deposits on.

Starting at high vaporization and substrate temperatures, it is shown that the substrate is almost entirely covered with material with mixed morphologies and thickness. For example, figure 3.2a exhibits bulk, circular chunks, as well as thick flakes of GaSe that stack on each other vertically in different directions. Nonetheless, when the temperature is dropped the density of bulky domains, deposited on the substrate, decreases and the samples consist primary of scattered multi-layered islands. Decreasing the T_b even more from 910˚C to approximately 860˚C; and T_s from 800 ˚C to 760˚C, causes the multi-layered islands to develop well-defined edges. This effect is demonstrated in figure 3.2 (c,d); when temperature decreased, the edges from the irregular shaped multi-layers (figure 3.2c) evolve into well truncated triangles (figure 3.2d). Finally, at the lowest temperature conditions complete coverage of single layer GaSe was obtained on the substrate (figure 3.2f).

To help further illustrate the structure of the grown GaSe flakes, figure 3.3 illustrates SEM images that were obtained from a chosen set of experiments. In figure 3.3a, the SEM is taken from when the sample was vaporized at 1030-1070˚C and deposited at 930-970 ˚C; in this image it is clear that triangular and hexagonal GaSe stack continuously on top of the substrate forming a multi-layer configuration of GaSe flakes. Conversely, figure 3.3c shows SEM image of single layer GaSe islands, obtained when the sample was vaporized at 760-800˚C and deposited at 650-690 ˚C. Because much of the substrate was covered with continuous single layer GaSe, the image was taken at the end of the substrate where the film starts to break down into scattered single layer islands. Noteworthy is the change in shape of the single layer flake with respect to the multi-layer flake. While the mulit-layer flakes have more of a defined, regular shape, the single layer flakes devolve into rounded, almost circular islands, with large lateral sizes. Finally, the AFM was used to confirm the film

thickness of single layer GaSe. Figure 3.4 shows a height of approximately 0.9 nm, which roughly agrees with reported data[16].

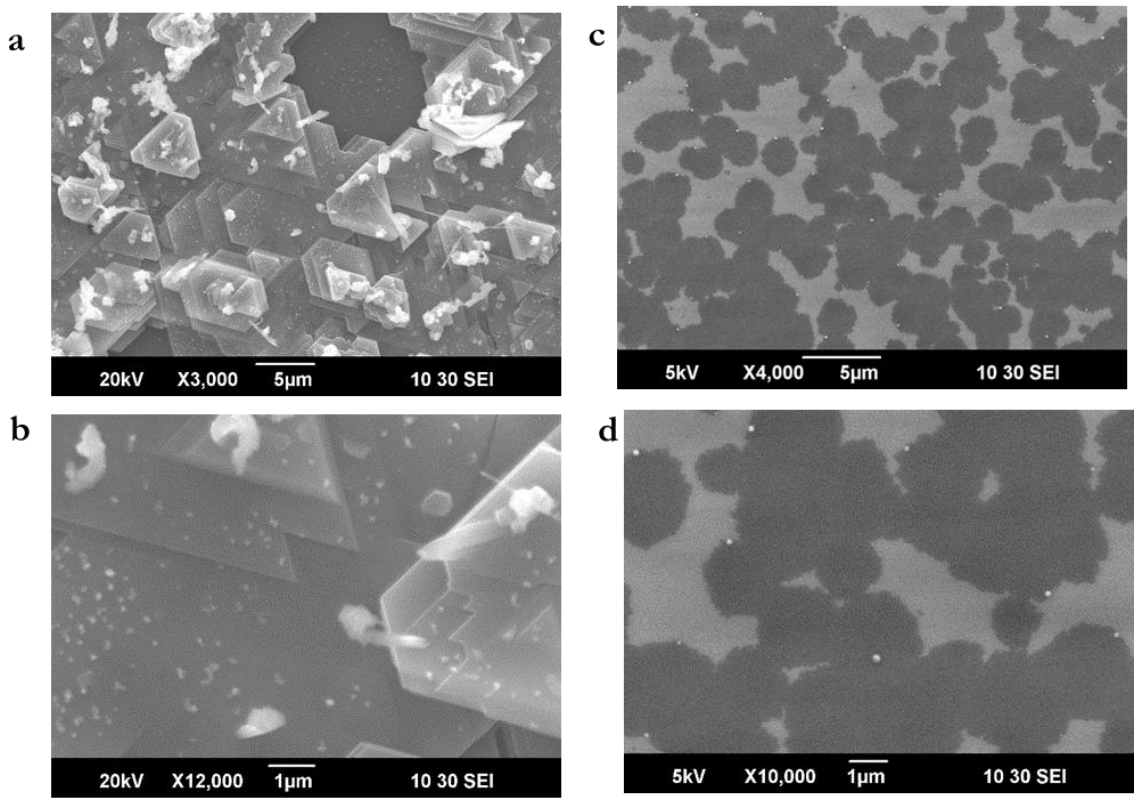


Figure 3.3: SEM images of GaSe. (a) multi-layered GaSe, 3000X. (b) multi-layered GaSe, 12,000X. (c) SL GaSe 4,000X. (d) SL GaSe 10,000X

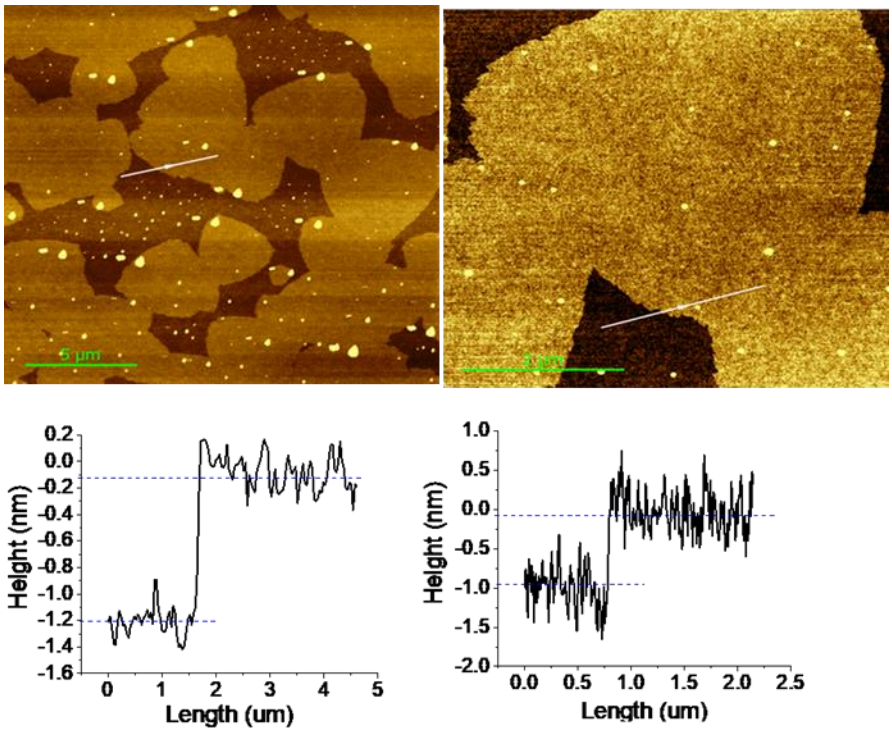


Figure 3.4: AFM measurements of SL GaSe

An important verification that GaSe was grown came from extensive collection of Raman spectra. Indeed, the layer dependency of the GaSe Raman also allows for a rough estimate on how thick particular flakes are on a sample. When the Raman spectra was collected from the multi-layered sample (3.2a), with bulk pieces aggregated on top, the Raman spectrum presents peaks at 133.94 cm^{-1}, 212.64 cm^{-1}, 251.99 cm^{-1}, and 307.87 cm^{-1} (Figure 3.5a). Corresponding to these peaks are the vibrational modes: A^1_{1g}, E^1_{2g}, E^2_{1g}, A^2_{2g}, respectively, where symbols A and E represent out of plane and in plane stretching[16]. The different phonon modes can further be elaborated in figure 3.6.

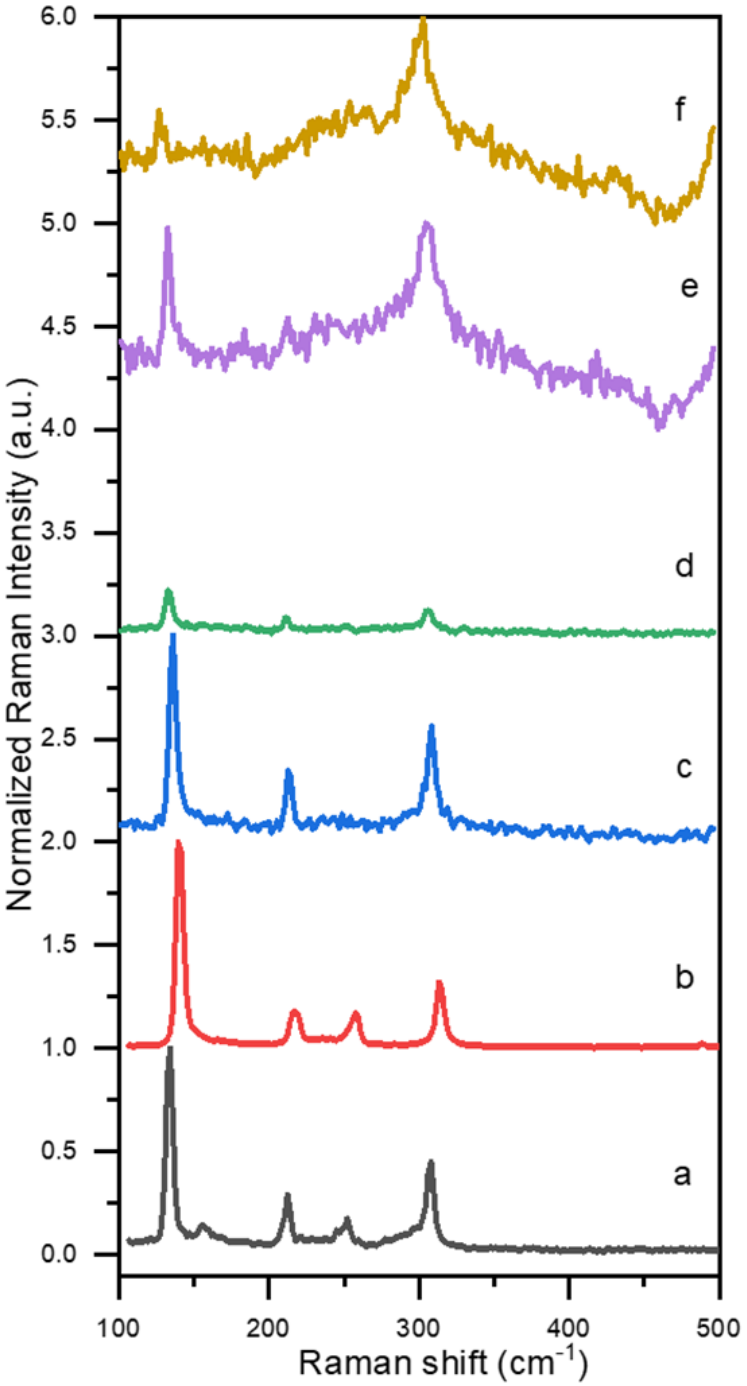


Figure 3.5: Raman spectra collected from the samples in figure 3.2 (a-f)

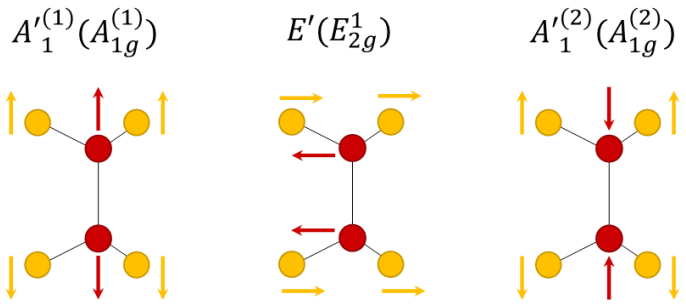


Figure 3.6: Phonon modes for GaSe. Notation within the parenthesis represents multi-layer GaSe; and notation outside parenthesis represents monolayer GaSe

Based on the results, as the number of layers decrease, not only do the relative intensities of the peaks decrease but the peak position shifts as well. For example, the A^1_{1g} peak shifts from 133.94 cm^{-1}, in multi-layer GaSe to 129.08 cm^{-1} in single-layer GaSe (Figure 3.5). Furthermore, the vibrational modes, E^1_{2g} and E^2_{1g} vanish completely as the layers reduces from multi-layer to single layer. The shift in peaks, as well as decrease in intensities has been speculated to be due to the decrease in inter-layer interaction[16].

Another finding that was linked to the structure was the photoluminescence. As shown in figure 3.7, the PL emitted from many layers is around 625 nm or 1.98 eV. This value agrees well with the direct bandgap of 2 eV reported for bulk GaSe[16]. As the layers decrease the PL intensity decreases and the electronic structure transitions to an indirect bandgap. Because the indirect bandgap is reported to be around 3.5 eV for monolayer GaSe the PL shift could not be detected with the 532 nm excitation laser used in these experiments[36].

Finally, EDS spectra were collected from the samples to confirm that GaSe have the right composition. Figure 3.8 shows that Ga and Se content is very close to a 1:1 atomic ratio, confirming GaSe was synthesized precisely.

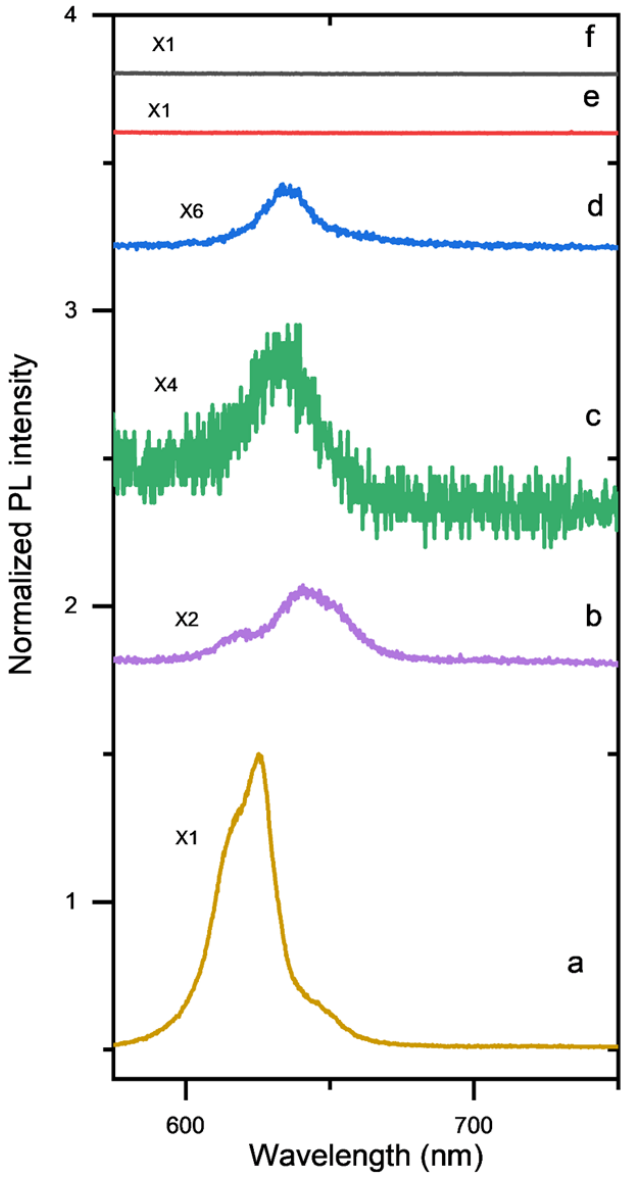


Figure 3.7: PL spectra collected from the samples in figure 3.2 (a-f)

Element	Weight%	Atomic%
Ga K	45.08	50.43
Se L	50.18	49.57
Totals	95.26	

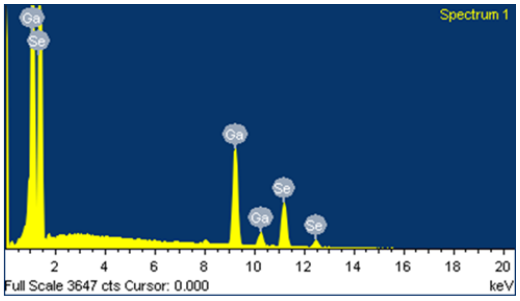


Figure 3.8: EDS spectra taken from multi-layered GaSe

Another parameter that considerably affects the material formed on the substrates was the amount of precursor used for each growth. To properly examine how the amount of precursor influenced the growth, the flow rate and time were kept constant at 200 sccm and 10 minutes, respectively. Then two sets of temperatures of the substrate and boat were investigated (T_b= 840-880 ˚C; 810-850 ˚C. T_s= 730-770 ˚C; 700-740 ˚C), in order to see if the temperature can promote pronounced changes when the precursor amount is also changed. By keeping the stoichiometric ratio of Ga and Se 1:1, successful experiments, as a function of precursors mass, were able to be produced.

The optical images, in figure 3.9, show the results of the experiments where the precursor amount is changed. In both sets of experiments, the substrate is covered primarily with single layer GaSe; nonetheless by examining the lateral sizes of the additional layers (bi-layer, triple layer, etc.) formed on top of the monolayer, a trend was observed for each series. Using the series with T_b=840-880˚C as an example, when the precursor amount is increased from 50 mg to 75 mg the average lateral size of the bi-layer islands doubles in size. Additionally, the bi-layer for 50 mg lacks sharply defined facets, but when 75 mg is used, the bi-layer starts to form well-defined triangular shapes.

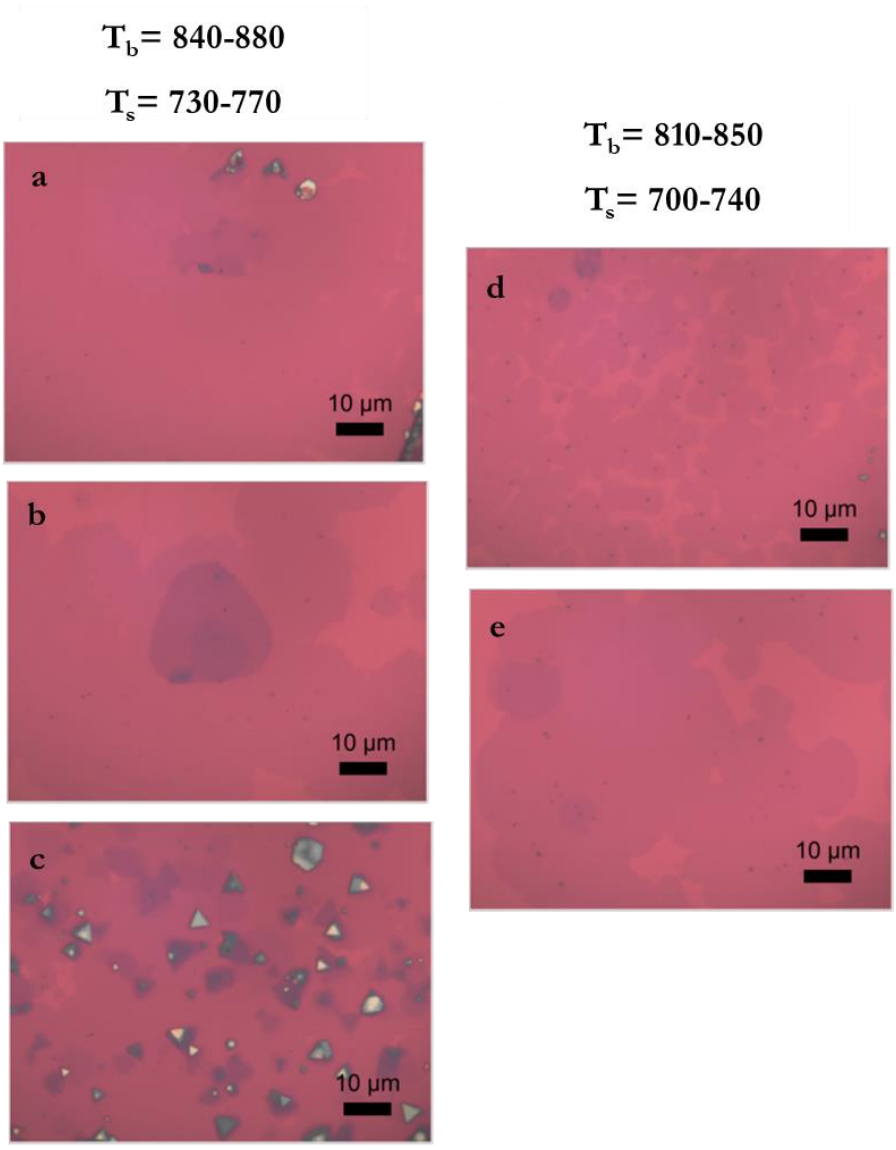


Figure 3.9: Optical images of GaSe samples grown in varying precursor amount. (a) 50 mg Ga_2Se_3. (b) 75 mg Ga_2Se_3. (c) 100 mg Ga_2Se_3. (d) 50 mg Ga_2Se_3. (e) 100 mg Ga_2Se_3.

However, when the amount is increased to 100 mg, the multi-layers islands decrease in lateral size but increase in thickness and density. This last observation is consistent with the fact that higher amount of powder precursors will result in higher concentration of gas species. A higher incoming flux of gas precursors usually reduces the mobility of atoms on the surface of the substrate and promotes 3D growth instead of 2D lateral growth. The same trend of increasing lateral size, is

observed at a lower temperature (3.9d, e), but the lateral size of the bi-layer islands are smaller in comparison to the higher temperature series. Another difference between the two temperature series, is that when T_b is around 840°C and the precursor amount is 75 mg, sizeable tri-layer islands begin to form; however no tri-layer islands can be seen with any precursor amount variation when the T_b is about 810°C.

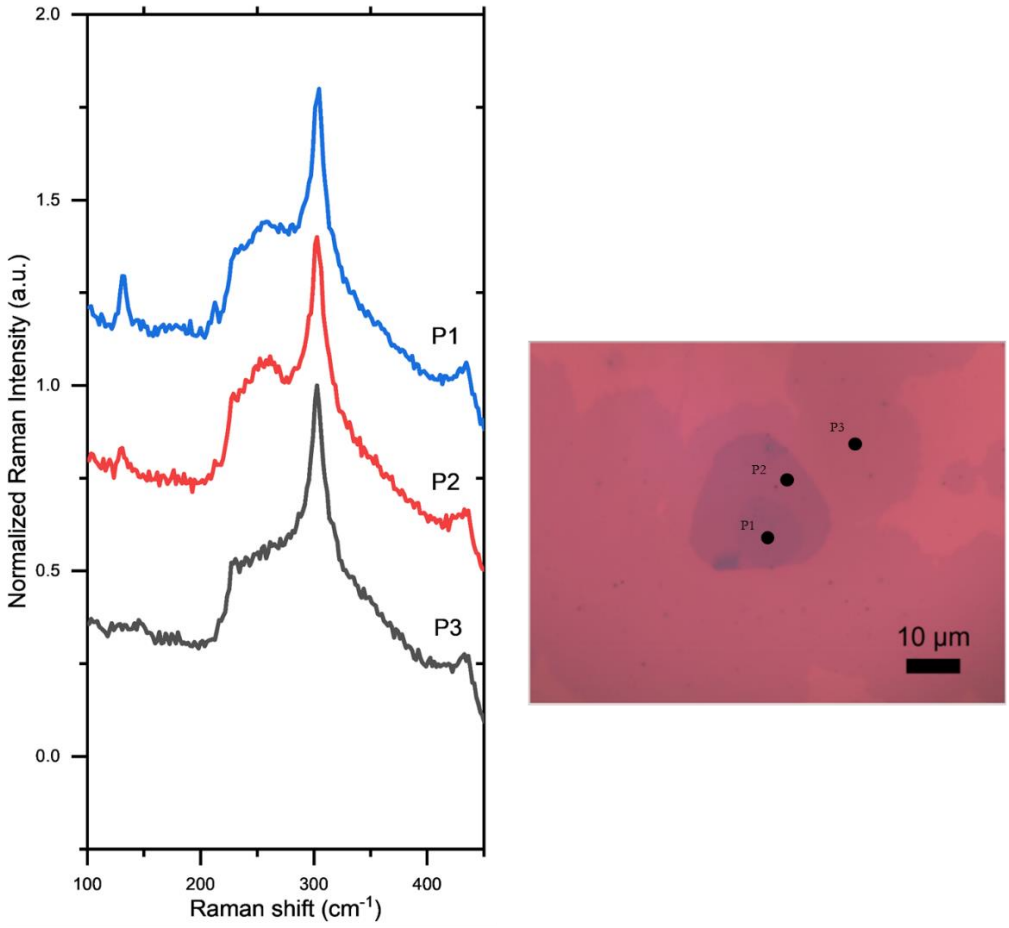


Figure 3.10: Raman point scans on Tri-layer GaSe (P1), Bi-layer GaSe (P2), SL GaSe (P3)

In order to investigate how the Raman signal of GaSe changes from single layer to tri-layer, a sequence of point spectra was acquired on sample whose morphologies show clear distinction between each layer (Figure 3.10). Because the A^2_{2g} peak of GaSe is very close to the Raman mode

from the Si substrate at ~303.3 cm^{-1}, all subsequent analysis was done with consideration of the A^1_{1g} peak at ~129.08 cm^{-1} [16].

Based on the results in the tri-layer island, the A^1_{1g} mode is a well-defined peak with a position around 130 cm^{-1}. In the Bi-layer island the peak remains in the same position but it has less intensity. Finally, the point scan at the single layer spot results in loss of the peak altogether. The low or no intensity of this peak for monolayers, when the Raman spectrum is collected under ambient conditions from a single spot, has been a constant limitation in the literature. This is a direct consequence of the quick deterioration of the monolayer, as a result of the oxidation process that is accelerated under the influence of the laser.

In addition to the temperature and precursor amount, a series of experiment was also pursued regarding the growth time. Using a constant set of parameters of: T_b=760-800 °C, T_s= 650-690 °C, H_2/Ar flowrate of 200 sccm, and precursor amount 50 mg, a substantial set of experiments was able to be conducted. The subsequent data summarizes what was found when the growth time was allowed to change.

Figure 3.11 illustrates the results of the series of experiment with the growth time allowed to vary. As expected, increasing the growth time of the experiment results in an increased coverage of 1L GaSe on the corresponding substrate. For example, at 90 minutes the substrate is nearly completely covered with monolayer GaSe (Figure 3.11a), while at 40 minutes, the substrate shows fragments of tiny 1L islands (Figure 3.11c). However, increasing the growth time by 20 minutes causes the area of the monolayer to increase drastically (Figure 3.11b), until finally continuous coverage is formed.

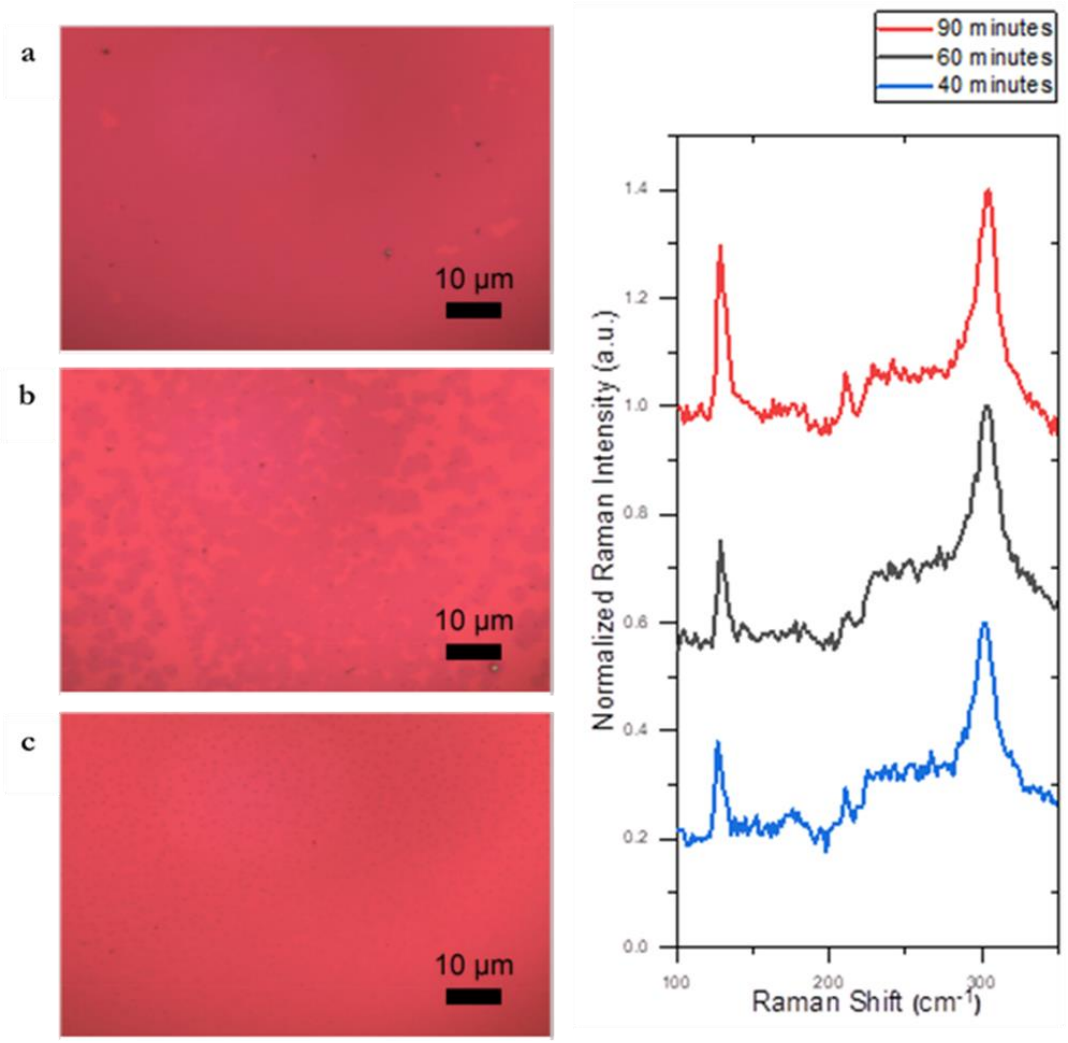


Figure 3.11: Optical images and Raman of GaSe samples grown with different growth times. (a) 90 minutes. (b) 60 minutes. (c) 40 minutes

In order to reduce the effect of oxidation due to prolonged exposure to the laser beam in a single spot, we collected the Raman spectrum from monolayers by continuously scanning the laser in a 20x20 microns large area. The thickness homogeneity in these samples guarantee that the observed spectrum is actually from monolayers and not an average of different thicknesses domains. The Raman from samples with different growth times showed agreement with the respective optical

images. The A_{1g} mode was shown to increase in intensity with growth time, which is consistent with increasing coverage and hence scattering volume.

3.1.2 GaS Results

Building on the successful growth of continuous single layer GaSe, as well as feasible control of few-layer to multi-layer deposition, we used the CVD method described above to also grow single layer GaS. Using similar conditions that gave optimal single-layer GaSe, a set of experiments were devised to optimize monolayer GaS. The following results show that by adjusting the temperature, while keeping the carrier gas composition, flow rate, and growth time constant (H_2/Ar= 200 sccm; t=10 min), monolayer GaS can be synthesized.

Figure 3.12 shows the optical images of GaS grown on a substrate by changing the temperature of the boat and substrate. Much like GaSe, at relatively high growth temperatures, GaS experiences an assortment of chunks and flakes deposited on the substrate (Figure 3.12b). The mulit-layer flakes form in scattered areas, while bulk pieces of the material cover the substrate throughout. As the temperature is reduced to a T_b range of 860-890 °C and a T_s range of 760-800 °C, the lateral size of the multi-layer flakes decreases exceedingly, where average sizes are around 1 μm. Finally, a single layer film that covers almost the entire substrate, was successfully obtained with a temperature range of 700-740 ºC.

Accompanying the optical images are the Raman spectra that was taken for the designated experiments. When the Raman for the multi-layer to bulk pieces are examined the signals found were: 187.33 cm^{-1}, 291.63 cm^{-1}, and 358.17 cm^{-1}, corresponding to the A^1_{1g}, E^1_{2g}, A^1_{2g} modes respectively (figure 3.12)[37]. As the layers decrease the relative intensity of the peaks go down also, as well as the spatial resolution. For monolayer GaS, the Raman modes that shift are: E^1_{2g} (306.04 cm^{-1}),

and A^1_{2g} (360.2 cm^{-1}). Coincidentally, both the E^1_{2g} mode of GaS, and the A^2_{2g} mode of GaSe, coincide with the Raman mode for the silicon substrate.

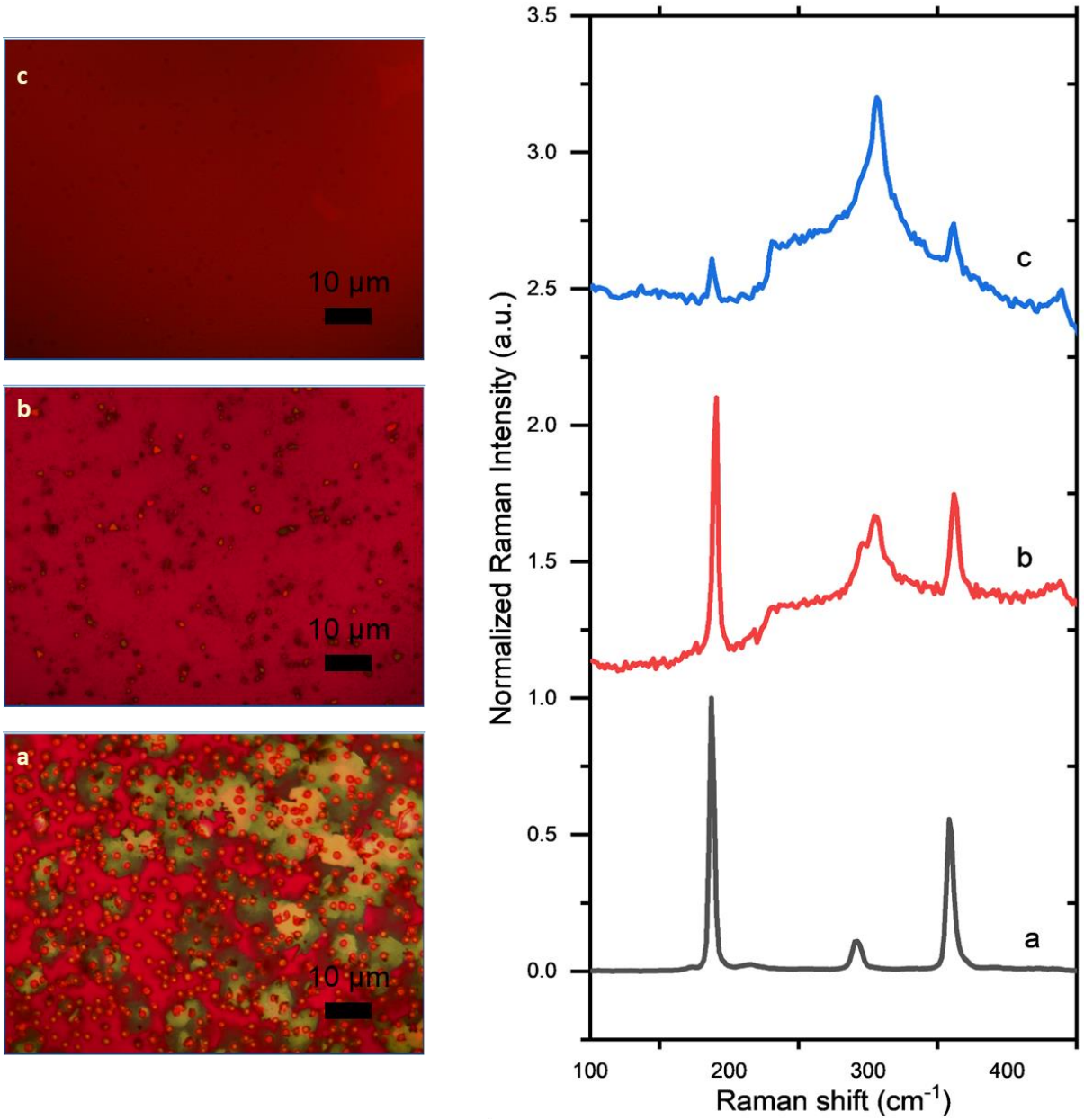


Figure 3.12: Optical images and Raman spectra GaS grown at different temperatures. (a) T_b ~ 930-970 ° C. T_s ~ 850-890 ° C. (b) T_b ~ 860-900 ° C. T_s ~ 760-800 ° C. (c) T_b ~ 810-850 ° C. T_s ~ 700-740 ° C.

To examine the morphology in detail, of monolayer GaS, SEM and AFM measurements were taken (Figure 3.13). The SEM measurements were taken at the side of the substrate farther from the source, where the film is slightly more discontinuous, confirming that large coverage of monolayer material was attained.

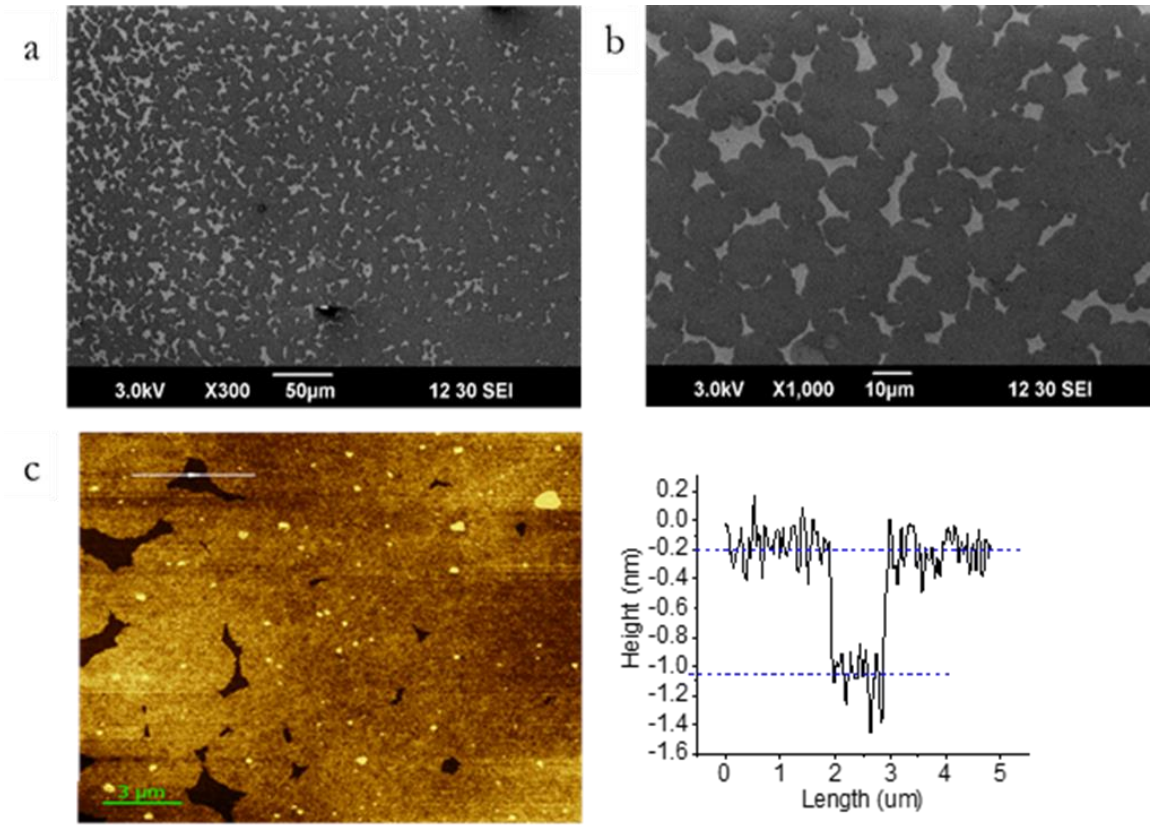


Figure 3.13: Morphology of SL GaS. (a) SEM image at 300x. (b). SEM image at 1,000X. (c) AFM image and measurement

In addition, Figure 3.13b shows higher magnification SEM images of the single layer islands structure, demonstrating that each monolayer island grows laterally quasi-isotropic with rounded edges, instead of the straight sharp edges (facet-like) of the multi-layer islands. Finally, the AFM measurement shows an approximate layer thickness of 0.8 nm (Figure 3.13c,d), which agrees with previously reported values for monolayer GaS[37].

3.1.3 InSe Results

The last monochalcogenides results to be reported is the attempted growth of layered InSe. Unlike GaS and GaSe, difficulties were encountered in growing InSe in 2D flakes, even when using the same growth technique that resulted in multi-layer and monolayer forms for the GaSe and GaS. While numerous growth parameters were tested (flow rate, growth time, precursor amount, etc.) here only a small series of experiments for different temperatures will be discussed.

Figure 3.14 displays the results of the sequence of experiments conducted when the temperature is changed. Instead of thin layers, the material was only able to be synthesized in bulk, circular chunks. Furthermore, the chunks range in size and spatial arrangement for different growth temperatures. For example, when T_b was around 1030-1070 °C and T_s approximately 930-970 °C the chunks clustered together and lateral sizes reached values of up to 10 μm. However, when T_b was around 860-900 °C and T_s about 760-800 °C, the growth on the substrate reverted to segregated chunks with lateral sizes that are as small as 1 μm. Following the same trend, at lower temperatures the bulk InSe decreases in size until finally it grows into a diminutive, powder form (Figure 3.14 c).

Together with optical images, Raman spectra was also collected from the samples. From figure 3.14b, the bulk pieces show Raman peaks at: 115.6 cm^{-1}, 176.52 cm^{-1}, 198.06 cm^{-1}, 208.95 cm^{-1}, and 225.61 cm^{-1}, these values are close to those reported for the A^1_{1g}, E^1_{2g}, A''_2-LO, E'-LO, A^2_{1g},

vibrational modes, respectively.[38,39] For smaller pieces the A"$_2$-LO and E'-LO (3.14b,c) modes are absent from the spectrum, while the other modes decreased in intensity.

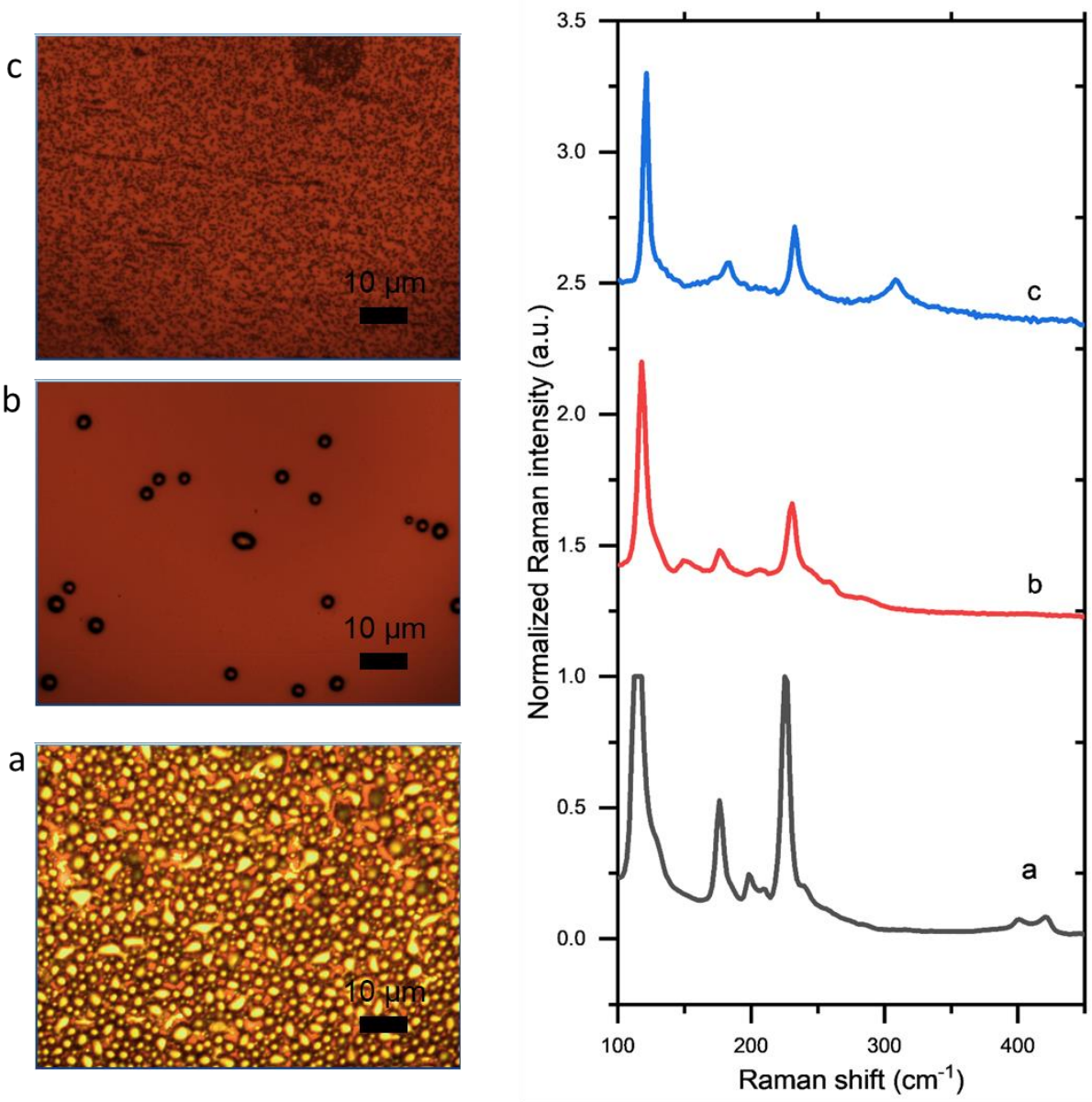


Figure 3.14: Optical images and Raman spectra InSe grown at different temperatures : (a) T_b~1030-1070 °C. T_s~930-970 °C (b) T_b~860-900 °C. T_s~760-800 °C. (c) T_b~760-800 °C. T_s~650-690 °C.

In order to pursue InSe flake structures, a slight variation of the CVD procedure described above, was attempted. For this procedure, a large substrate was placed on top of the boat, leaving a small gap for the inflow gas to enter. The results from the experiments, with the substrate partially covering the boat are summarized in figure 3.15.

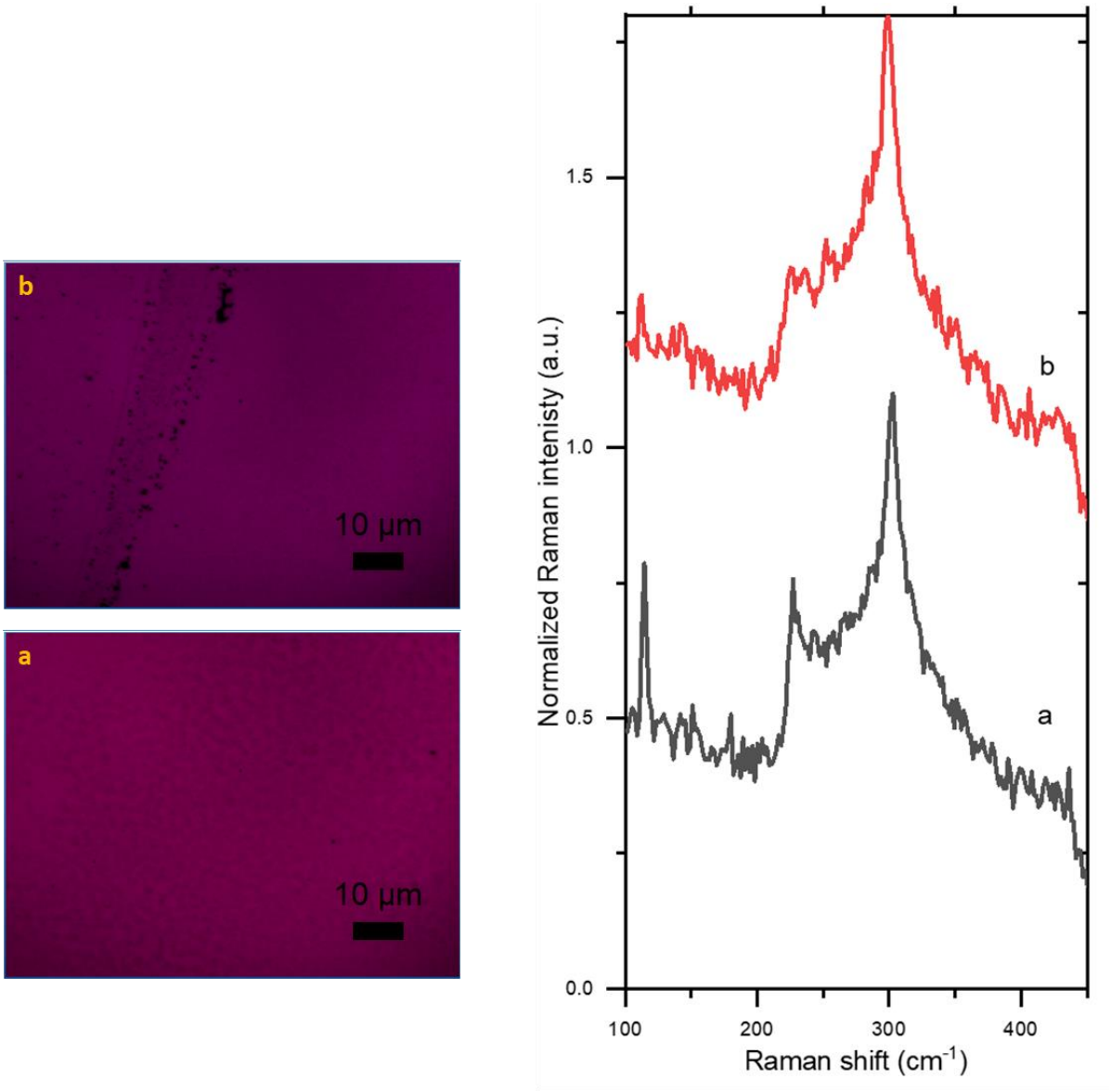


Figure 3.15: Optical image and Raman spectra taken at InSe cover experiments. With T_s~ 690-730 and H_2/Ar flowrate at (a) 60 sccm. (b) 80 sccm

By using a lower H_2/Ar flowrate (60/80 sccm), and a longer growth time, we were able to obtain a different morphology of the as-grown InSe. In both experiments the appearance of scattered film appears on the substrate with small chunks of material distributed throughout. However, when the flowrate is 60 sccm, the film appears to show more regularity (Figure 3.15 a).

Numerous Raman scans were collected in order to verify the composition of the InSe scattered film on the substrate. From the Raman spectrum only peaks at 110.43 cm^{-1} (A^1_{1g}) and 223.16 cm^{-1} (A^2_{1g}) are present. Additionally, these modes show a lower intensity (as compared to bulk samples) and shift from their bulk positions, which agrees with the literature[38.39].

3.1.4 GaSe-GaS Heterogeneous films

One of the final sets of experiments in the project was an attempt to grow GaSe-GaS heterostructures. Before starting the experiment, a substrate containing continuous coverage of monolayer GaSe (Figure 3.16), was examined under the Raman microscope. A black square is outlined on the figure to display the etched hole that was created after scanning the laser over that region to acquire the Raman spectrum. Subsequently, the GaSe sample was loaded at a zone in the tube furnace where the T_s would be around 650-690 ºC. After preparing the precursor powder (Ga_2S_3, Ga), the growth proceeded under normal conditions (T_b~ 760-800 ºC, H_2/Ar- 200 sccm, t- 10 min). After the growth, the sample was collected and studied under the Raman microscope. The morphology of the as-grown sample (Figure 3.16), displays a dusty scattered film formed on top of the SL GaSe. After taking a duoscan in the area, both GaSe (Figure 3.16 a) and GaS (Figure 3.16 c) peaks were observed in the spectra (figure 3.16 b), confirming that scattered GaS islands grew on top of the SL GaSe.

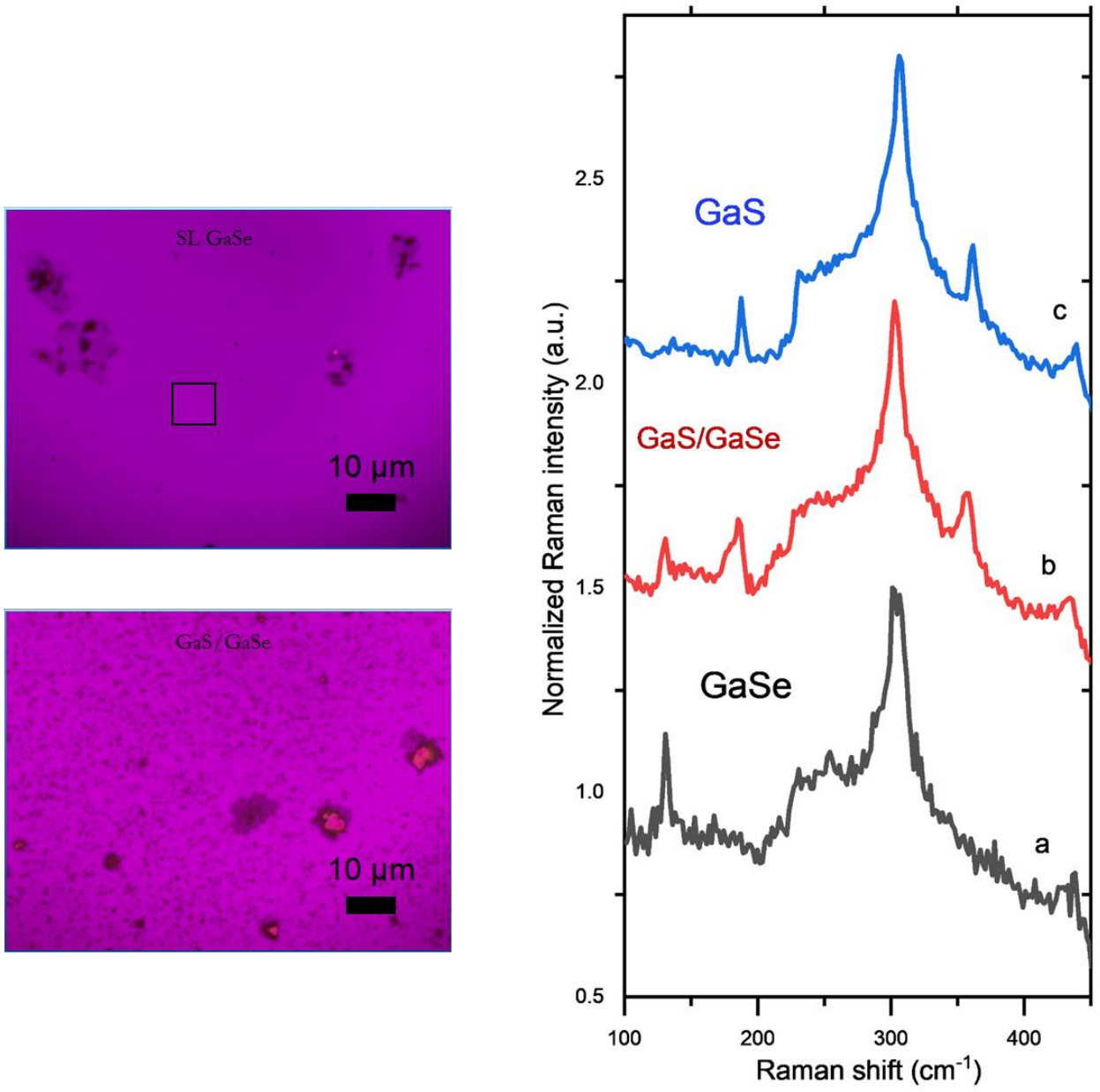


Figure 3.16: Optical images and Raman of heterogeneous GaSe-GaS. (a) Raman of SL GaSe. (b) Raman of hetrostructure of GaSe-GaS. (c) Raman of SL GaS

3.1.5 Monochalcogenides Discussion

The main goal of this chapter was to synthesize and characterize 2D layered monochalcogenides using an atmospheric CVD system with a post-growth fast cooling down step. By changing different parameters (temperature, time, precursor amount), the growth conditions for large area monolayer coverage was optimized. In addition, it was also demonstrated that using a combination of Ga_2Se_3 + Ga as evaporation sources, the growth of monochalcogenides can be significantly simplified; since there is no need of pre-synthesizing GaSe powder source as it has been reported in previous literature. The samples were extensively characterized by Raman spectroscopy, SEM, and AFM, as a function of the growth conditions. Incidentally, for the first time, under ambient conditions, the Raman spectra for monolayer monochalcogenides, with a reasonable signal-to-noise ratio, was able to be collected.

Due to the study of the Raman spectrum, collected from sets of experiments, a further understanding on the morphology of the material and layer dependent properties became possible. For example, each monochalcogenide displayed a decrease in intensity of the Raman signals as the number of layers were reduced from bulk to monolayer. This effect is particularly noticeable in figure 3.5 where the A^1_{1g} peak decreases in signal-to-noise ratio. The decrease in Raman intensity has been shown to be due to the decrease in sample thickness and thus Raman scattering volume[40]. Another trend in the Raman came from the shifting of specific modes when certain layers were present. Regarding the A^1_{1g} peak for GaSe again, a decrease in layers yielded a shift of the peak from 133.94 cm^{-1} in multi-layer GaSe, to 129.08 cm^{-1} in single-layer. In other literature a comparable trend can be seen with the same peak; described as a red shift of the peak[16]. While the intensity of the peaks is intimately related to how much material is present, the shifting of peaks is shown to be associated with the interlayer coupling that exists among layered materials[16]. As a result of some

modes having out-of-plane vibrations and others in-plane vibrations, the number of layers can greatly influence which mode is present, or which gets shifted[16,41]. Because of the out-of-plane nature of the A^1_{1g} peak, its frequency shift is most likely attributed to the decrease in inter-layer coupling[16].

Another layer dependent property that was examined was the PL emission. In figure 3.7, the general trend of the PL spectra, which was seen throughout the course of the experiments can be observed. With decreasing layers of thickness, the intensity of the PL diminishes to zero emission, associated to the transition from direct band gap in multilayers to indirect band gap electronic structure in few- and single-layer films.

Finally, an inspection of the high magnification images from SEM and AFM gave information how the film deposited on the substrate. Using both GaSe and GaS as an example, the single layer of both materials show that it almost completely covers the substrate with a nearly self-limited thickness growth for certain range of conditions. Indeed, even under the optical microscope the contrast is clear between the substrate and the monolayer. The SEM, however, clearly depicts the formation of continuous film growing on the substrate. Furthermore, when the scattered, single layer islands are shown at the end of the substrate (figure 3.3c,d; figure 3.13b), they present rounded edges instead of the straight edges as observed in the multi-layer islands. This also was observed when the material is grown in an evacuated tube[16].

Regardless of the difference in experiment methodologies, both techniques yielded the rounded shapes at relatively low growth temperatures. An explanation of this result can be derived from the formation energy of GaSe monolayer islands. It is predicted that the preferred, minimum energy shape of a GaSe island is a triangle[16]. However, at low growth temperatures, when a GaSe molecule, adsorbed on the substrate surface, is captured by a nucleation site, it doesn't have enough

kinetic energy to desorb or to move to a preferred low energy site, thus the growth is isotropic in all directions leading to the formation of rounded flakes[16].

In addition to using the shape of the edges of islands to study how the growth mechanism of the layered monochalcogenides, the lateral sizes of islands also gave information on possible explanations how the material deposited on the substrate. For the regime in which the 2D layer lateral growth is predominant, it was shown that the first layer spreads continuously throughout the substrate, but layers succeeding decrease greatly in terms of lateral size. For example, even when the monolayer growth of GaSe is optimized, the maximum size that was attainable for the bi layer was only 20 microns. Interestingly, GaSe is proposed to grow as a 'layer-plus-island' mode, in which after the formation of a continuous single layer, thermodynamically, small islands are favored[16,42].

Chapter 4: Layered Metal Halides Results and Discussion

By employing the solution-based technique that was delineated in chapter 2, it was found that metal halides (PbI_2) were able to be synthesized in layered structures containing few-layers in thickness. this new method offers an alternative way to grow thin film structures and its straightforward approach assures its potential for growing other layered materials through a solubility-controlled mechanism. The following chapter provides insight on the growth of PbI_2, as well as its optical properties.

4.1 PbI_2 Results

The initial experiments were done with the substrates surface directly exposed to the PbI_2-H_2O solution, e.g. immersed substrate without any type of coverage. Subsequently, the water in the solution is slowly evaporated in a convection oven. As the water evaporated, the solution saturates and start forming the PbI_2 solid phase. As a result of this setup a large amount of PbI_2 is deposited on the substrate surface. Once all the water had evaporated the substrate was collected and analyzed using similar characterization techniques (AFMA, SEM and Raman) that were used in chapter 3.

Figure 4.1 shows experiment described above. Under the optical image large irregular shapes cover the full substrate. Furthermore, the platelets stack on top of each other in random orientations with bulk pieces scattered throughout the substrate. In addition to the optical image, Raman spectroscopy was also utilized to characterize the samples. As shown in figure 4.1, when the sample is excited with a 532 nm laser, the spectrum is mainly composed of five peaks: 77.08 cm^{-1}, 96.29 cm^{-1}, 111.69 cm^{-1}, 166.72 cm^{-1}, and 218.91 cm^{-1}; which have been reported to respond to the E_g, A_{1g}, A_{2u}, $2E_g$, and 2LO(M) vibrational modes respectively[26,27,28,43].

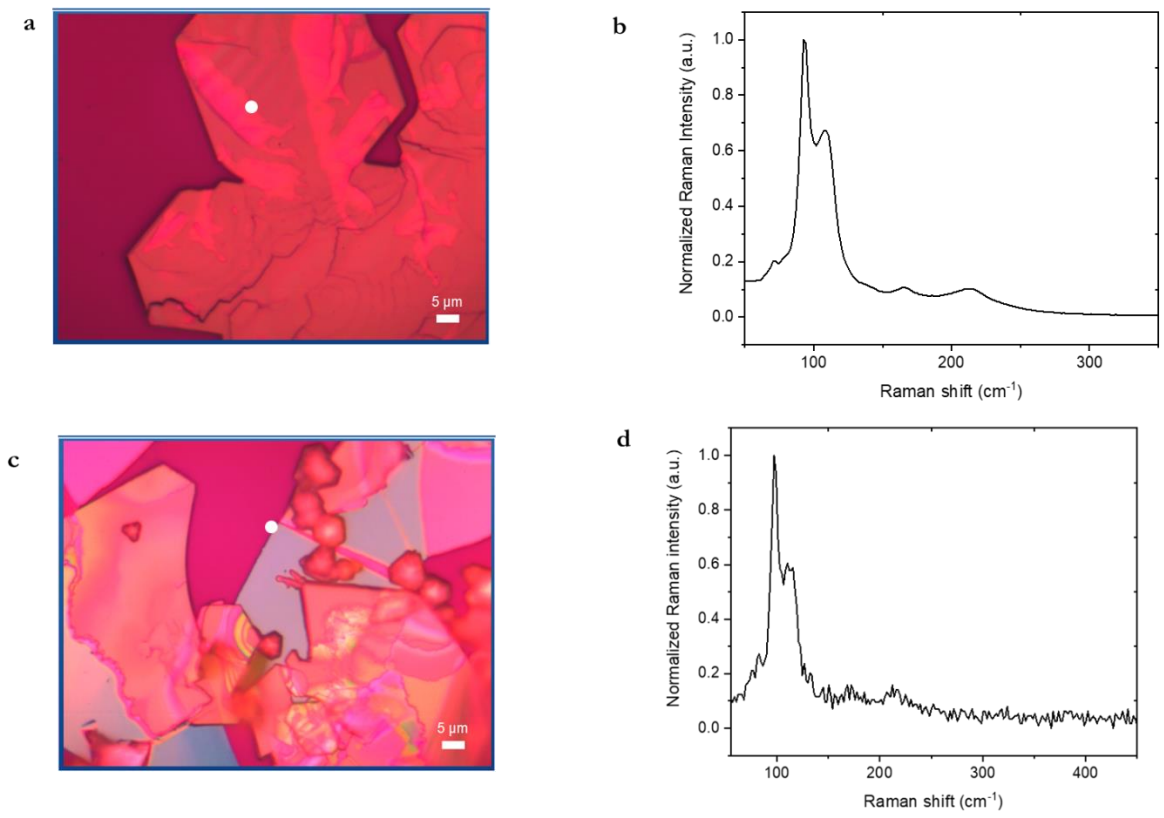


Figure 4.1: Optical Image and Raman of PbI_2 platelets using 532 nm laser. (a) point scan area of PbI_2 flake. (b) Raman spectra of (a). (c) second point scan area of PbI_2 flake. (d) Raman spectra of (c)

In an effort to control the size and distribution of the PbI_2 platelets another set of experiments was conducted that employed two glass slides, to sandwich the substrate contained in the PbI_2-H_2O solution. The results (Figure 4.2) are smaller PbI_2 platelets with a hexagonal morphology. As before, Raman spectroscopy was used to study the nature of the material. In addition to the 532 nm laser, a 633 nm laser was used as excitation source to see Raman shifts in the grown platelets. Upon investigation, when the outlined platelet was excited with the 633 nm laser the same vibrational modes (E_g, A_{1g}, A_{2u}, $2E_g$) observed with the 532 nm laser also appear (Figure 4.2a). However, there was a considerable shift in the E_g mode (73.73 cm^{-1}), and the 2Eg mode (164.08 cm^{-1}). In addition, the 2LO(M) mode was not observed using the 633 nm excitation laser.

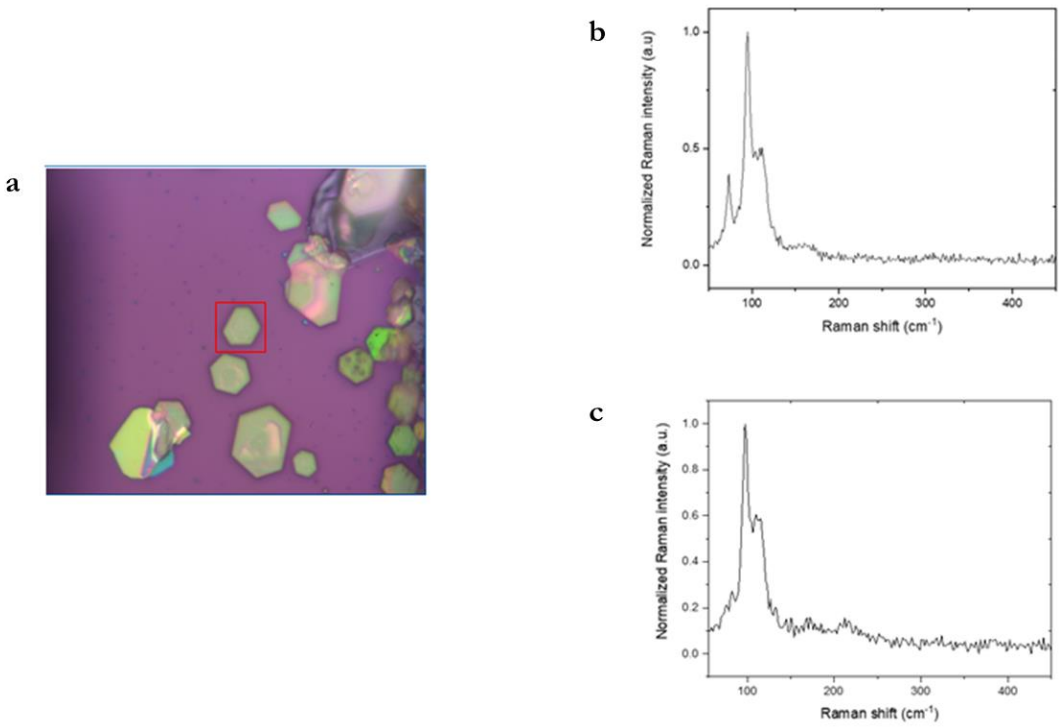


Figure 4.2: Optical Image (a) and Raman of PbI_2 using (b) 633 nm laser. (c) 532 nm lasers.

Another analysis that was performed on the sample was a series of Raman maps independently acquired with both the 633 nm and 532 nm lasers. The results from the Raman mapping can be seen in figure 4.3. The first map (Figure 4.3a) shows the intensity distribution of the Raman peak at 73.73 cm^{-1}. The distribution of color shows that the intensity of the 73.73 cm^{-1} peak is moderately uneven in the platelet: the edges and fractions of the center have a relatively high intense count, while the area directly above the bottom edge shows extremely low intensity counts. Incidentally, when the map includes the range 83-103.23 cm^{-1} it results in an enhanced Raman signal around the edges (Figure 4.3b). When the spectrum is examined it is shown that the enhancement comes from the 95.55 cm^{-1} peak. The intensity distribution map for the 112.28 cm^{-1} peak (Figure 4.3c) is like that in figure 4.3a, for the mode at lower wave number. Finally, the Raman spectra,

generated from a line scan across the middle of the platelet (see figure 4.3d), provided additional evidence that supported the enhancement of the Raman signal around the edges (figure 4.3e).

When the bottom of the graph is examined an intense Raman signal is shown (esp. from the 95.55 cm^{-1} peak), but once the scan traverses away from the edges the intensity of the signal decreases exceedingly and remains low until it reaches the top edge of the platelet.

Using the same island, a set of Raman intensity distribution maps was produced by the 532 nm laser (Figure 4.4). Because of the difference in the Raman shift from the laser sources (Figure 4.1, 4.2b), the resulting maps produced from the 532 nm laser gave slightly different results. In particular, the E_g mode is shown to be not as dominant when excited with the 532 nm laser. Consequently, the map for this mode (Figure 4.4a) results in a random intensity distribution due to the low signal-to-noise ratio, with intensities within the island matching those of the surrounding background.

Furthermore, the mapping corresponding to only the 96.20 cm^{-1} peak (Figure 4.4b), also showed differences, albeit slight. While both blue maps of the 633 nm and 532 nm laser show higher intensity at the edges, the enhancement from the A_{1g} mode, excited by the 633 nm laser, is more pronounced than it is when the island is excited with the 532 nm laser. In addition, the blue map from the 532 nm laser demonstrates characteristics like the green and red maps of figure 4.3. Indeed, each of these maps has areas in the center of the platelet where the intensity of the mode resembles that of the intensity of the edges. Likewise, the red map (Figure 4.4c) of the platelet, corresponding to the intensity distribution of the A_{2u} mode, produces color distribution identical to the blue map (Figure 4.4b). Lastly, the line spectrum provides further confirmation of edge enhancement from the Raman from the 96.20 cm^{-1} and 111.69 cm^{-1}peak, whereas the 77.08 cm^{-1} peak is very weak.

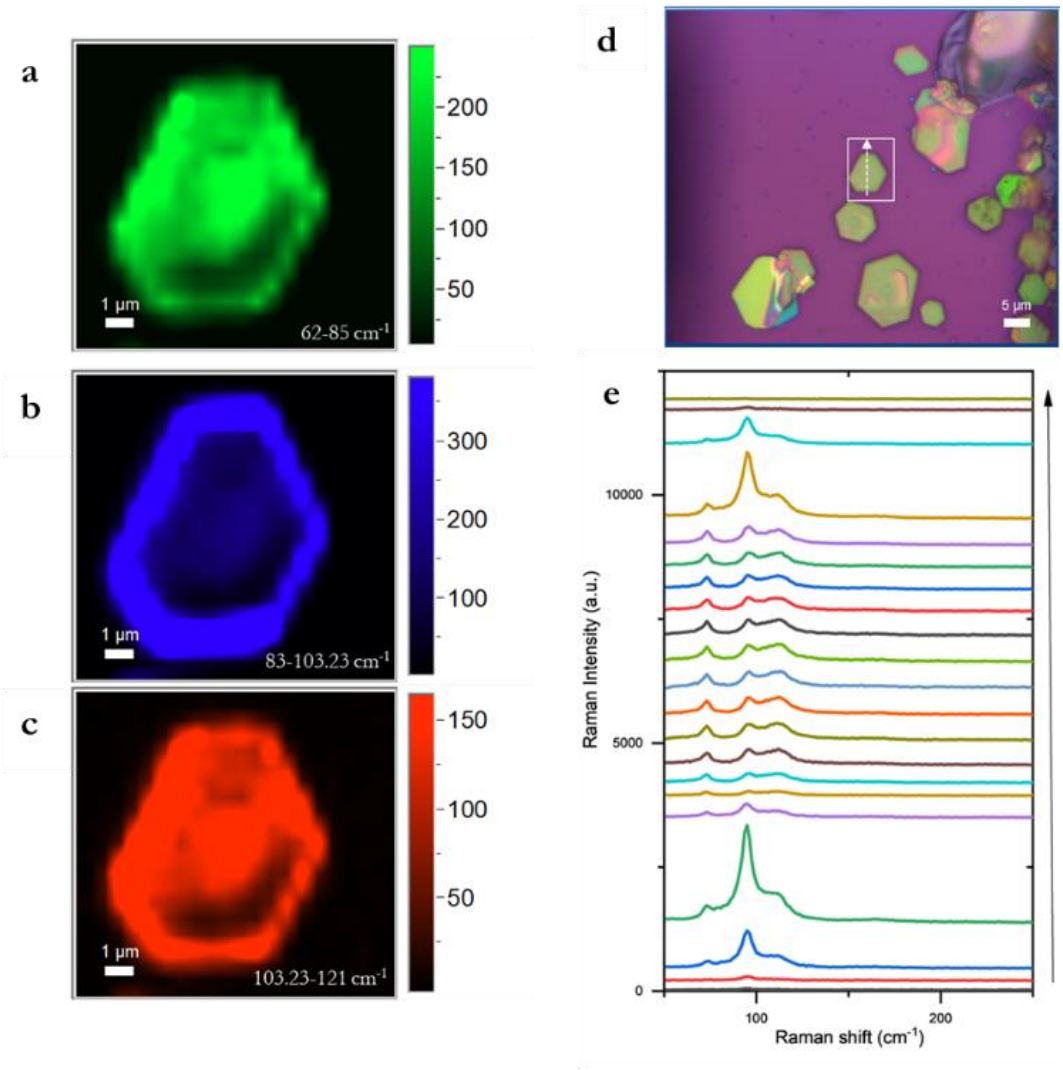


Figure 4.3: Raman Intensity maps at different wavenumbers (excited with 633 nm laser). (a) 62-85 cm^{-1}. (b) 83-103.23 cm^{-1}. (c) 103.23-121 cm^{-1}. (d) Optical image of mapping area. (e) Raman line spectra

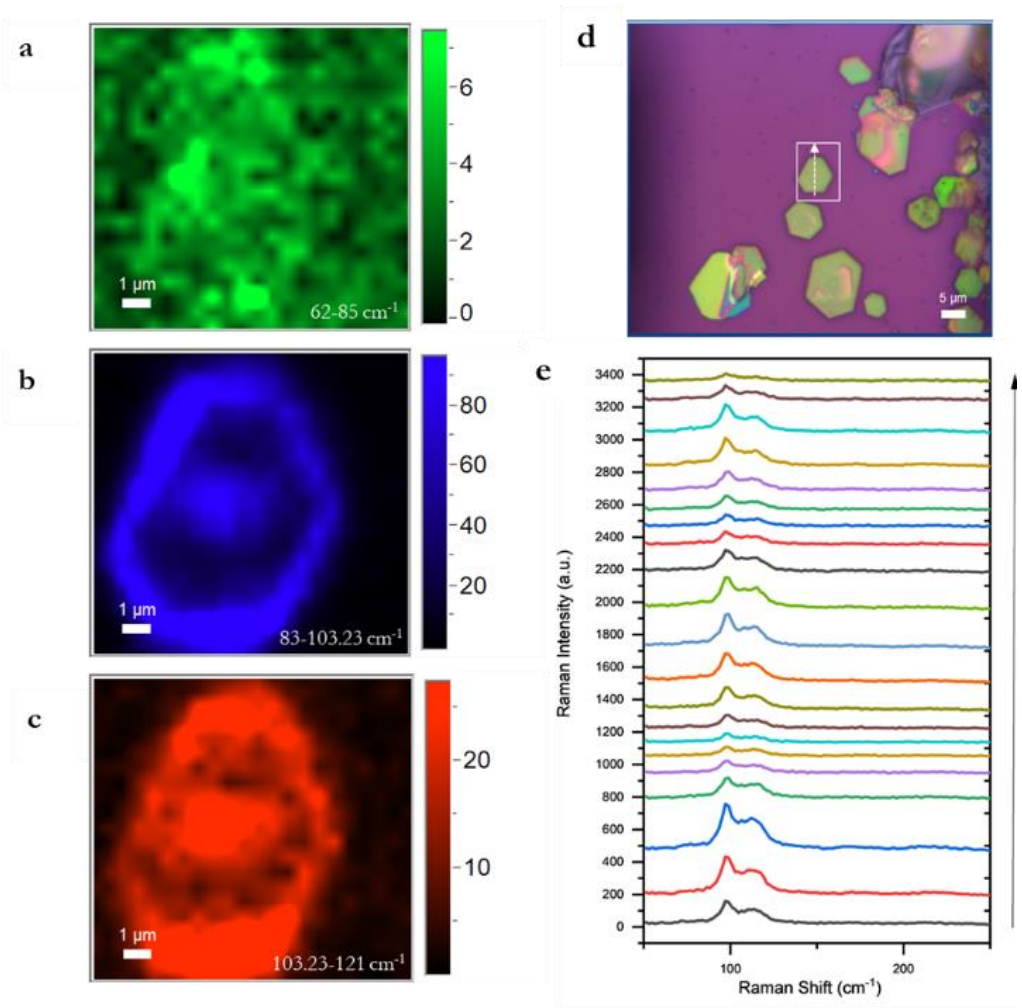


Figure 4.4: Raman Intensity maps at different wave numbers (excited with 532 nm laser). (a) 62-85 cm^{-1}. (b) 83-103.23 cm^{-1}. (c) 103.23-121 cm^{-1}. (d) Optical image of mapping area. (e) Raman line spectra

For the purpose of seeing if the edge-enhanced Raman intensity were size dependent additional Raman maps were conducted on PbI_2 hexagons with different edge lengths. Because the edge enhancement was more pronounce when exciting with the 633 nm laser, all subsequent analysis and studies were done with this excitation source. Using hexagons with lateral sizes ranging from 3 μm to 10 μm the Raman measurements were performed. The results for an island with approximately 10

μm in lateral size, is summarized in figure 4.5. As demonstrated, even when the edge lengths of the platelets changes, the Raman enhancement is still observed.

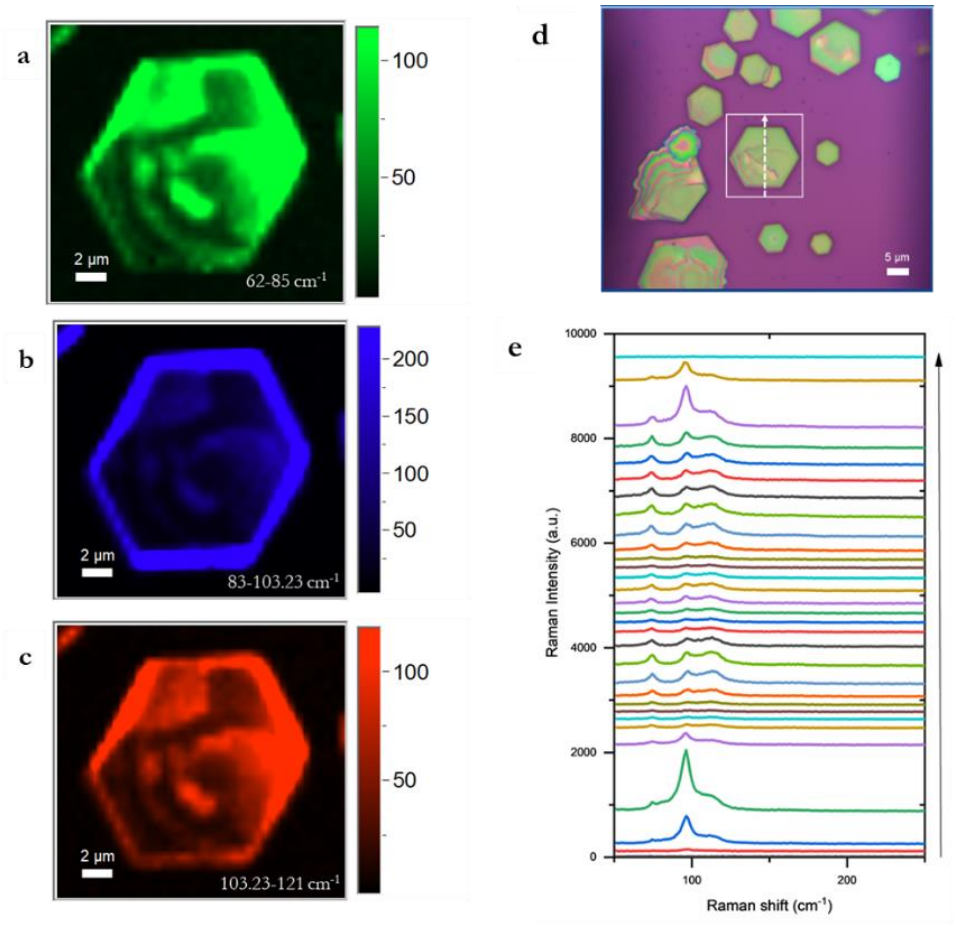


Figure 4.5: Raman Intensity maps at different wave numbers (excited with 633 nm laser). (a) 62-85 cm^{-1}. (b) 83-103.23 cm^{-1}. (c) 103.23- 121 cm^{-1}. (d) Optical image of mapping area. (e) Raman line spectra

Once maps were collected for a sizeable distribution of PbI_2 hexagons, the Raman from a single point at the edge of each island was used for comparison. This comparison is shown in figure 4.6; all Raman spectra was collected at the points highlighted in the optical images of each platelet at the right of the figure 4.6. Using the Raman peak at 111.69 cm^{1}, the intensity was plotted as a function of the edge length of the platelet. From the investigation, as the length of the edges of the hexagon increases, the intensity of the Raman signals decreases.

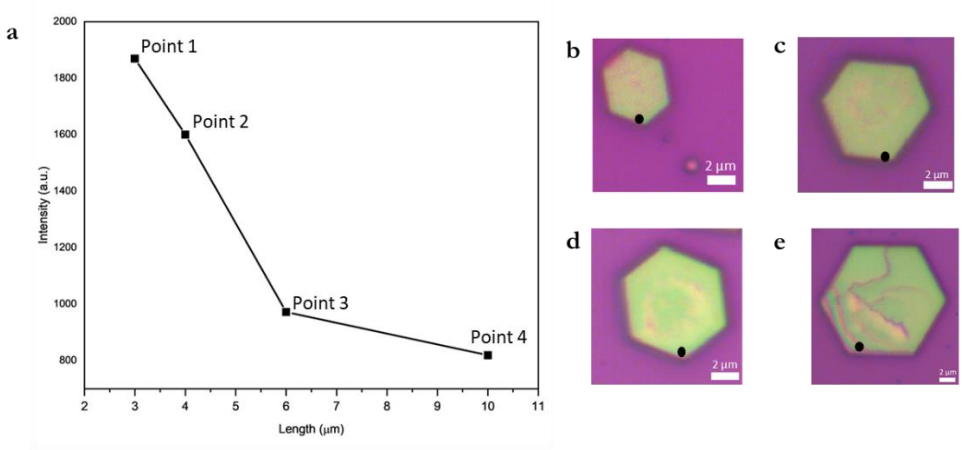


Figure 4.6: Raman intensity of 111.69 cm^{-1} peak at different edge lengths. (a) Line graph. (b) point 1. (c) point 2. (d) point 3. (e) point 4

In addition to the Raman measurements, a sequence of PL intensity maps was taken to investigate how the photoluminescence changes throughout an island that experiences Raman enhancement at the edges. In this case, the PL was acquired by using a 405 nm excitation laser which provides an energy larger than the bandgap in order to excite the inter-band electronic transition. As revealed in figure 4.7, the PL spectrum shows a peak approximately at 515.96 nm, as well as additional peaks around 600 nm and 750 nm. The peak around 515.96 nm is close to the values previously reported in the literature, and corresponds to the optical bandgap which in this case is around 2.40 eV [30,31]. The peaks between 600-750 nm can be due to light emission associated with electronic transition to states within the bandgap originated by crystalline defects. Because of the presence of these different peaks, three maps were generated: one that encloses all the peaks, another that just contains the 519.96 nm peak, and finally a map that just consists of the 600 nm and 750 nm peaks. The full spectrum map and the 519.96 nm map show an opposite trend of what is observed in the Raman intensity maps; inside the PbI_2 hexagon the PL intensity is relatively constant while at the edges it is slightly lower. The lower intensity at the edges can be just a consequence of the laser intensity profile (Gaussian profile) that, at the edges is partially exciting the material. There

is a region inside the island showing slightly lower PL intensity (green horizontal strip), the origin of this lower intensity could be associate with a higher density of defects in that region. This assumption is supported by the fact that the PL map which ranges from 575-800 nm (defect related emissions) (Figure 4.7c) displays the opposite trend to those maps in Figures 4.7a and 4.7b. Additionally, this last map also shows lower intensity on the borders due to the partial excitation of the material by the Gaussian laser profile.

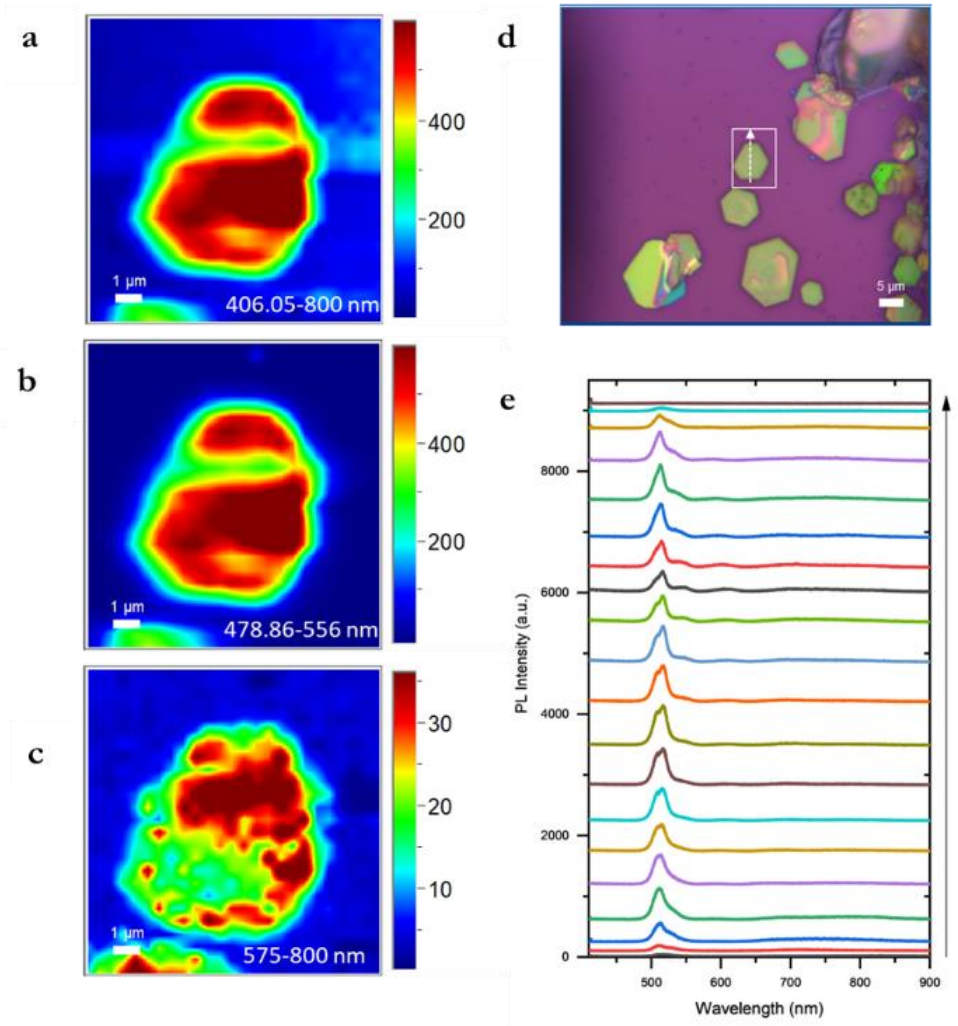


Figure 4.7: PL intensity maps at different wave numbers (excited with 405 nm laser). (a) 406.05-800 nm. (b) 478.86-556 nm. (c) 575-800 nm. (d) optical image of mapping area. (e) PL line spectra

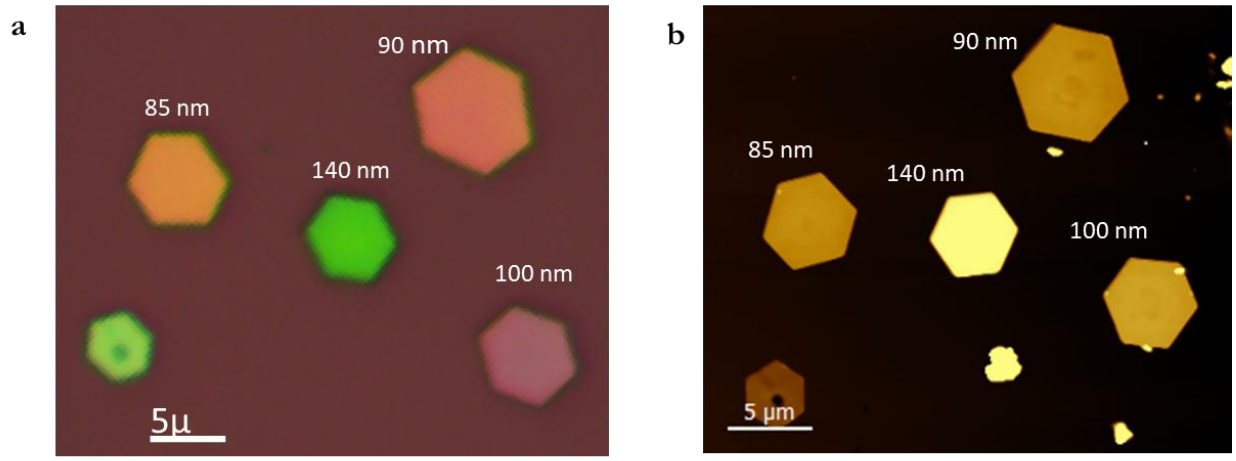


Figure 4.8: Optical Image (a) and AFM Image (b) of Area of Consideration

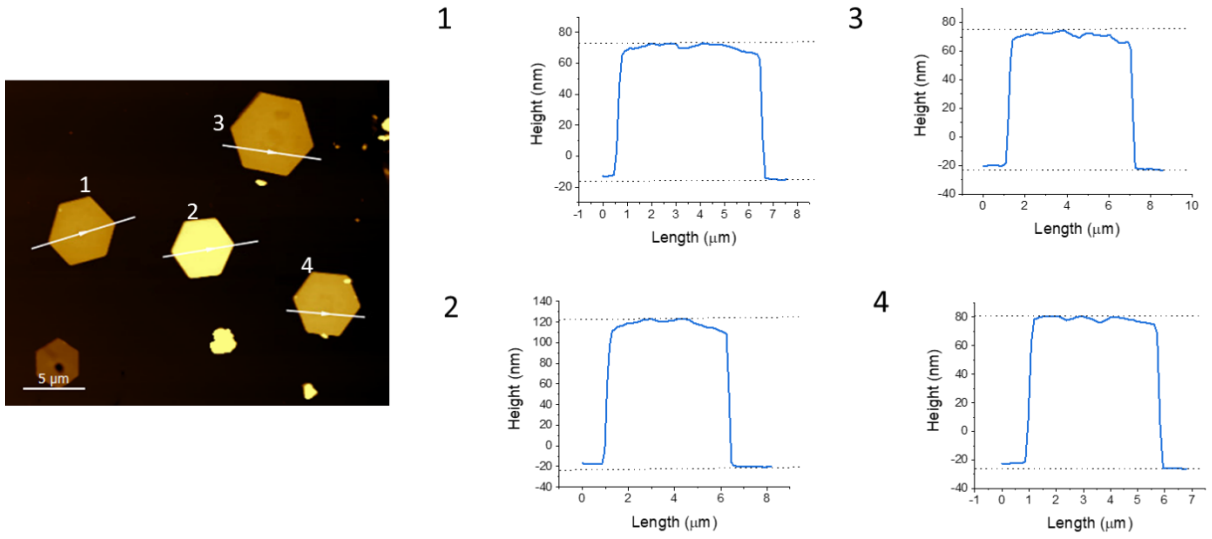


Figure 4.9: Height profiles of platelets

To further investigate the enhancement in the Raman signals on the edges of the hexagons, another experiment was performed that produced PbI_2 platelets with different thicknesses. Hexagons with different thicknesses appear with different colors in the optical images due to different constructive interference conditions in thin films (Figure 4.8a). The optical image in Figure

4.8 shows an area with hexagons that have edges of similar (or very close) length, but an assortment of colors (different thicknesses). Correlating the colors in the optical image and AFM data (Figure 4.8b), a color guide was constructed: coral pink corresponds to a thickness of around 90 nm; orange to a thickness of approximately 85 nm; purple to a thickness of 100 nm; and green correlates to thicknesses between 140-180 nm. Figure 4.9 shows the AFM height profiles that correspond to the AFM image in Figure 4.8.

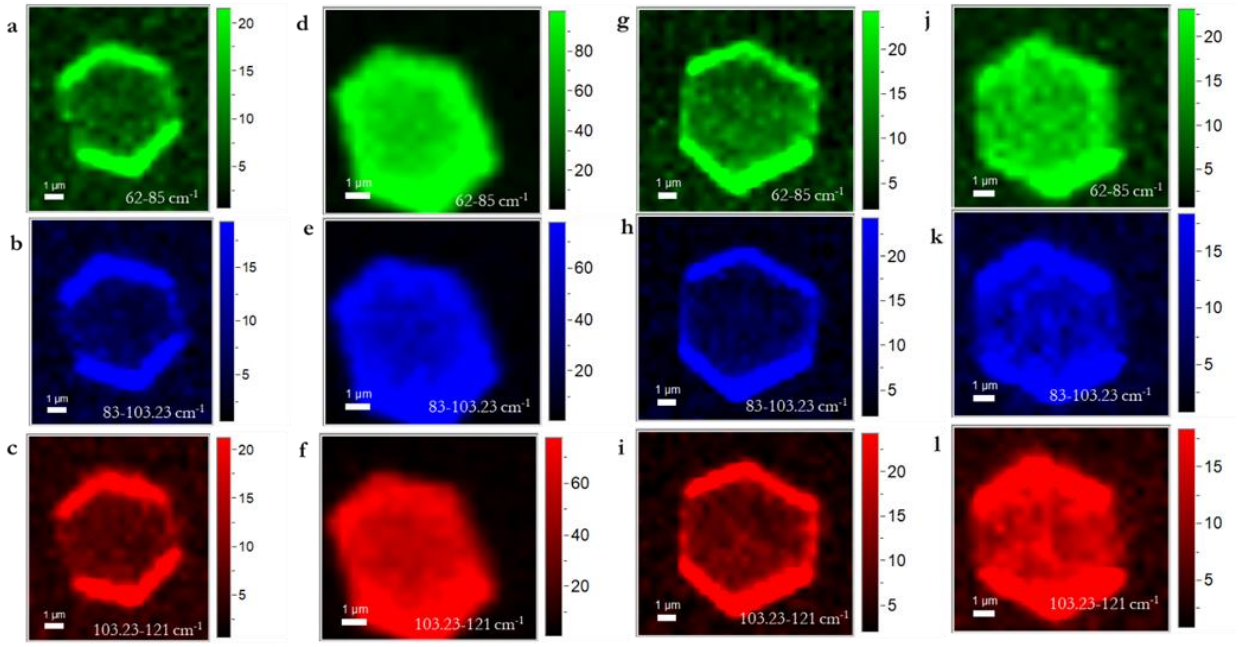


Figure 4.10: Raman Intensity maps performed at different thicknesses. (a-c)— 85 nm. (d-f)— 140 nm. (g-i)—90 nm. (j-l)—100 nm

Like before, Raman mapping was done on each hexagon to study the effect thickness had on the Raman enhanced edges. A summary of the Raman intensity maps is outlined in figure 4.10. The correspondence between the individual hexagons in the area of consideration (Figure 4.8) and the set of Raman maps is shown with: figure 4.10a-c representing the orange hexagon; figure 4.10d-f the green hexagon; figure 4.10g-i the coral pink hexagon; and figure 4.10j-l as the images that come from the purple hexagon. From examining this collection of Raman maps, it can be observed that not all the platelet thicknesses will guarantee the enhancement around the edges. Notably, the enhancement

around the edges is more prominent for thinner platelets (i.e. figure 4.10a-c, g-l); while for thicker platelets the distribution of the Raman intensity is more homogenous.

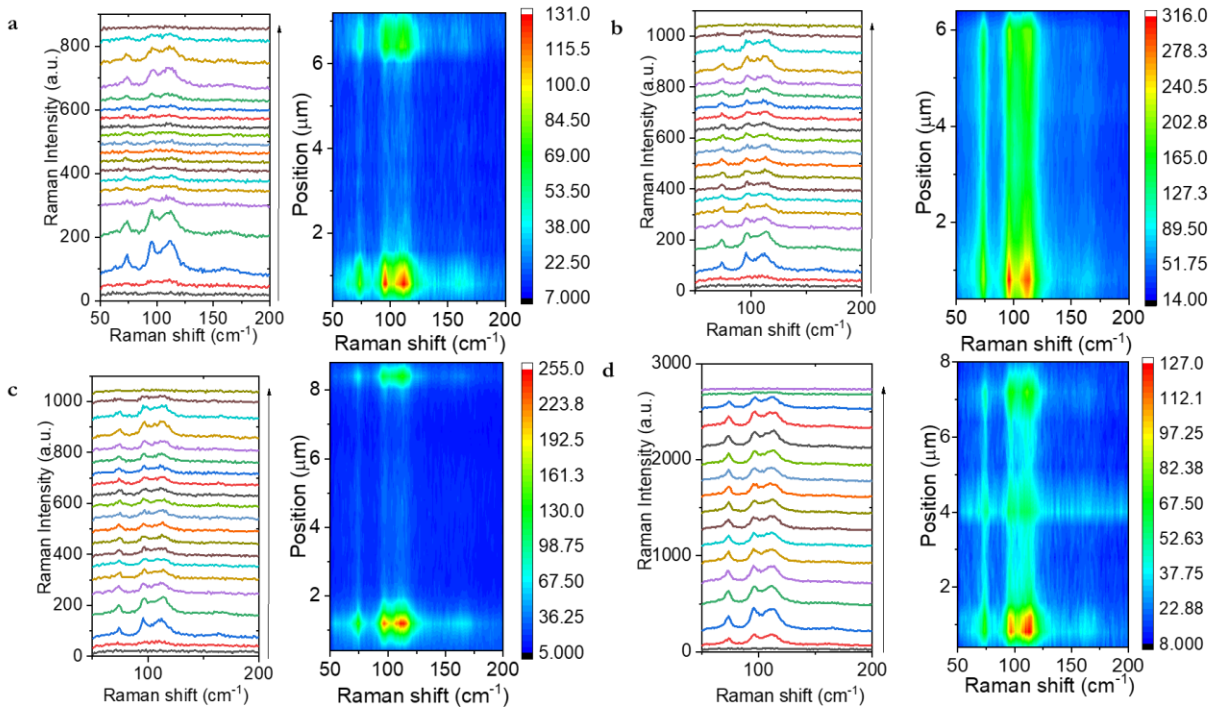


Figure 4.11: Line Raman spectra and contour maps of PbI_2 platelets at different thicknesses. (a) 85 nm. (b) 140 nm. (c) 90 nm. (d) 100 nm.

To better visualize the differences in the Raman enhancement around the hexagon edges as a function of the thickness of the platelets, graphs of Raman line scans and equivalent contour color plots are shown in Figure 4.11. In these figures the entire spectrum is show for different positions on the platelets as the laser is scanned along a line crossing the platelet. The line maps convey comparable behavior to that of that Raman maps in figure 4.10. For example, in figure 4.11a (orange hexagon) the intensity of the Raman peaks at the edge is considerably less than the intensity at the edges for the green hexagon (Figure 4.11b). Incidentally, the difference in peak intensity between the edges (bottom and top of the graph) and middle of the orange hexagon (center of the graphs in Figure 4.11) are more prominent than that of the green hexagon; showing more evidence that lower

thickness platelets have a higher enhancement around the edges than the platelets with higher thicknesses.

SEM and EDS were used to further characterize the platelets that were grown from the experiment. Figure 4.12 shows a magnified version of a typical area with several PbI_2 hexagons. The regularity of the hexagons is clearly seen, with the average edge length of each hexagon around 5 microns.

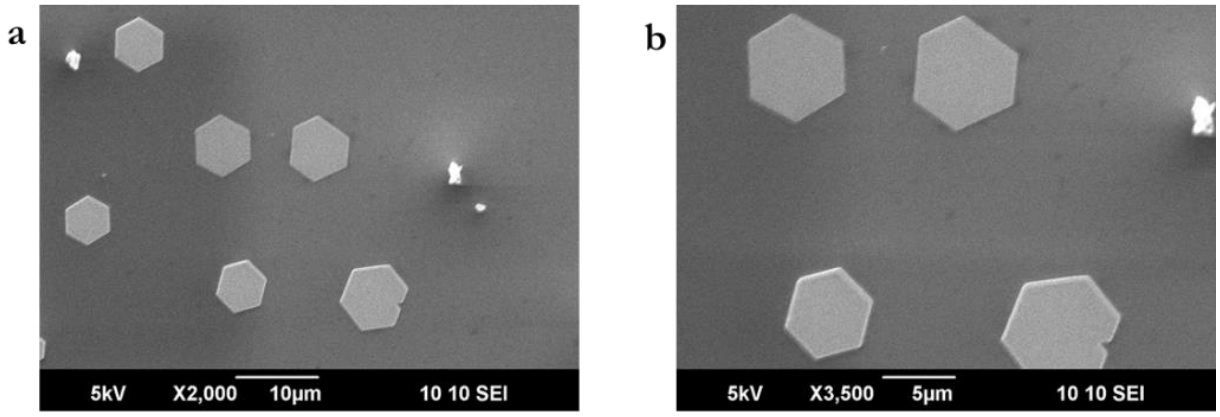
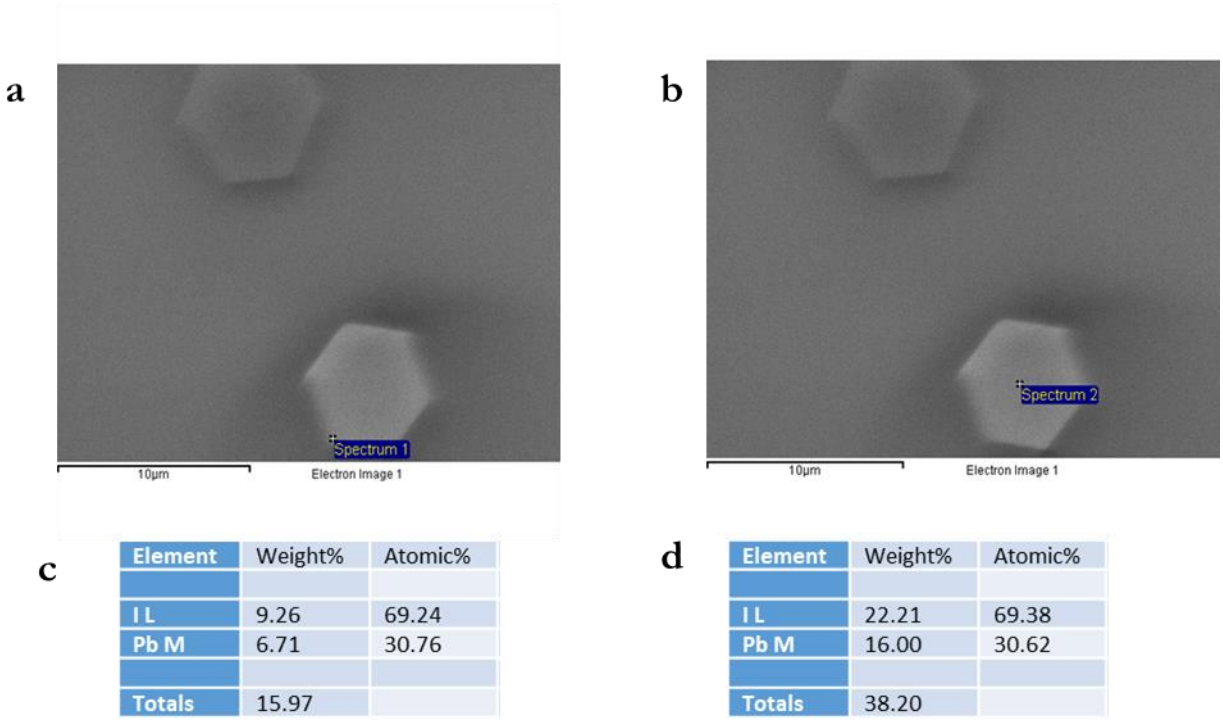


Figure 4.12: SEM of PbI_2 Platelets under different magnifications

Energy Dispersive Spectroscopy (EDS) was performed in order to determine if there was any composition (stoichiometry) difference between the edge and center of the hexagons that presented Raman enhancement (Figure 4.13). From the EDS, no significant difference in atomic percentage of Pb and I between the edge and center was found. Consequently, the Raman enhancement observed for certain islands cannot be attributed to stoichiometry variations along the hexagonal platelets. In the next section (4.2) we retake this discussion to propose a tentative explanation for the Raman enhancement at the edges.



Element	Weight%	Atomic%
I L	9.26	69.24
Pb M	6.71	30.76
Totals	15.97	

Element	Weight%	Atomic%
I L	22.21	69.38
Pb M	16.00	30.62
Totals	38.20	

Figure 4.13: EDS scan of different regions of PbI2 platelet. (a) edge of platelet. (b) center of platelet. (c) spectra of edge of platelet. (d) spectra of center of platelet

4.2 Layered Metal Halides Discussion

Ultimately, the solution-based technique provided a pertinent approach for the growth of 2D layered metal halides. Even more, it was discovered that by keeping the solution within a confined space during the evaporative crystallization, the size and amount of crystals could be controlled. Using the conventional characterization techniques (Raman, PL, SEM and AFM) the identity and structure of the materials were validated. Furthermore, using Raman spectral mapping, Raman-enhanced edges were identified on the PbI_2 platelets.

As stated before, one of the main objectives in this endeavor was to study the feasibility of using a solution-based method in growing layered metal halides. The approach consisted in

producing a supersaturated solution of metal halide by evaporating the excess water, this continuous evaporation and supersaturation initially results in segregation of small solid crystals that further growth laterally to form a large layered crystal of PbI_2. Interestingly, without anything on top of the glass dish (open space evaporation), large bulky crystals were produced. To circumvent this, the substrate was placed in between two glass slides, limiting the space and amount that could precipitate, in order to yield small and regular hexagons of PbI_2 with the platelets ranging from 80 nm to 150 nm in thickness.

An explanation on why the addition of glass slides allowed for manageable growth lies in the fundamental nucleation step. It is stated that when nucleation proceeds at a rapid pace, a considerable amount of small crystals grow on the specific medium[40]. By distributing the growth container with the glass slides, it is likely nucleation was allowed to proceed too fast, and the amount of precursor in solution was also limited, yielding small crystals. As evidence, when the same growth was done without glass slides, hardly any crystal was shown to be of a small scale (Figure 4.1).

Even though the Raman and PL were irrelevant in detecting the number of layers the metal halides had (due to significant number of layers), reliable structural information was still obtained when using these characterization techniques. For example, one of the interesting things found is using different excitation lasers leads to the shifting and intensity increasing of certain modes. A prominent mode, E_g, was hardly discernable when exciting a PbI_2 platelet with a 532 nm laser. However, the intensity of that same mode increased notably using the 633 nm laser. Results from the PL also gave insight on the crystal structure of the PbI_2 platelets. Namely, two additional peaks, around 600 and 750 nm, were found when an island was excited with a 405 nm laser; the same peaks were previously reported as results of defects from the crystal structure[41].

The most interesting finding, using Raman spectroscopy, was the enhancement of the Raman signal around the edges for certain types of platelets. Using Raman spectral mapping a few trends were observed. First, it was found that when the edge length of a hexagon of certain thickness is decreased, the intensity of the Raman enhancement increases (Figure 4.6). The fact that these results held consistent with all the Raman modes under consideration (E_g, A_{1g}, A_{2u}) indicates that the edge length of platelets could be related to enhancement. Another link between the structure of the platelets and the enhancement came from the thickness of the material. As demonstrated in figure 4.10, islands with thickness around 80-90 nm had a pronounced enhancement around the edges, but as the number of layers increased the enhancement starts to fade. The spatial distribution of the Raman intensity around the edges holds a remarkable similarity with the whispering gallery modes and the distribution of the electric field, recently reported by Liu, for this material (see Figure 4.14)[43].

Whispering gallery modes are electromagnetic waves that circulate within the cavities of dielectric structutes[42]. There propagation within these structures are supported by total internal reflections. The structures themselves have been around well over a hundred years; with historical contributions from the sound waves that circulate around the dome of the St Paul's Cathedral[42]. However, recently they have gained attention in fields such as optics and quantum electrodynamics for their ability to confine light in small volumes[42]. Indeed, one of the most prevalent usage is as a semiconductor micro-laser.

Although there are no current reports of whispering gallery modes, from the Raman modes of PbI_2, it has been reported for the PL at low temperature. Liu's group used a pulsed laser, under cryogenic conditions (77K-210K), to excite a PL emission~ 500 nm that circulated around the PbI_2 hexagonal cavity[42]. Using a finite-difference time-domain (FDTD), they were able to confirm the

whispering gallery mode lasing. Their results are summarized in figure 4.14. From figure 4.14, an optical image of the PbI_2 (thickness~150 nm) is provided, as well as the image of the PL emission without the fluence of the excitation laser. It is important to note that the emission spectra collect at the corners of the hexagon; this confirms the confinement of light that is characteristic of whispering gallery modes. The results of the simulation, that show the optical field distribution, show that both transverse magnetic, and transverse electric waves have a field that confines itself in the cavity. Ultimately, the group was able to attest that the whispering gallery modes were the result of the radiative recombination of biexcition peak XX, with the highest energy confinement from 45-300 nm[42].

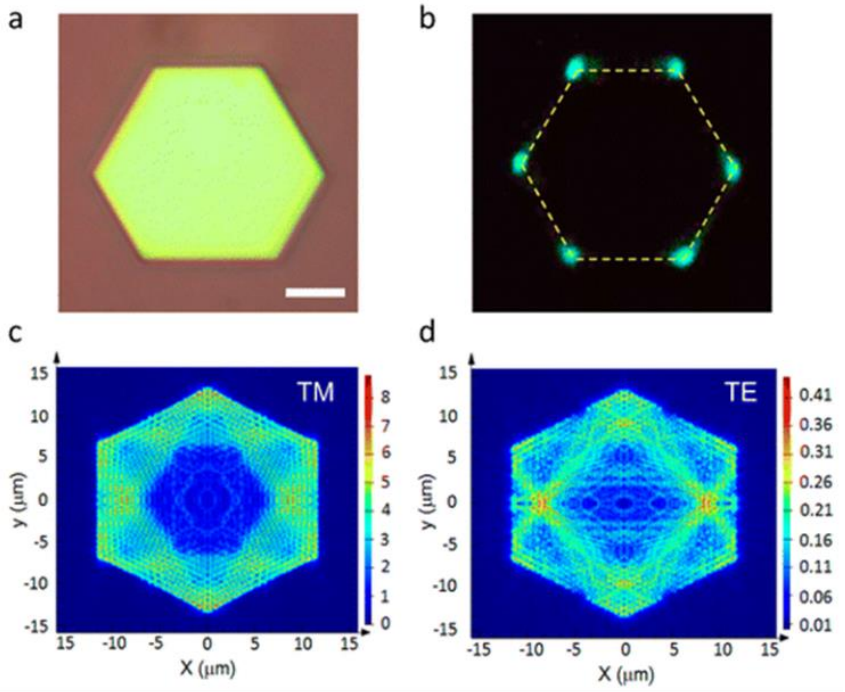


Figure 4.14: Results from Liu's FDTD simulation for hexagonal PbI_2 platelet. (a) optical image of platelet. (b) PL emission image after filtering pump laser line. (c) field distribution using TM mode. (d) field distribution using TE mode. Note. From "Whispering Gallery Mode Lasing from Hexagonal Shaped Layered Lead Iodide Crystals", by Liu, X 2015, ACS Nano. Copyright 2015, by American Chemical Society. Reprinted with permission

It is reasonable to believe that strong electric fields close to the edges (due to whispering gallery modes) can locally enhance the Raman signal when compared to the center of the platelet (resonant cavity). Raman spectra were collected from the edges and at the center of the PbI_2 platelets as a function of the laser power, (Figures 4.15 and 4.16). The excitation laser used in these experiments was 633 nm. Each spot on the hexagon showed that the intensity of the 112.2 cm^{-1} mode increased linearly with the power, with the bottom and top edge displaying the highest slopes in the curves. Although it is possible to associate the Raman enhancement with locally distributed whispering gallery modes; due to the linearity exhibited for each line it cannot be concluded that the Raman signal displays lasing activity. Lastly, it is important to emphasize that while the report by Liu and co-workers were done under cryogenic conditions, the PbI_2 experiments conducted for this study were all performed at room temperature.

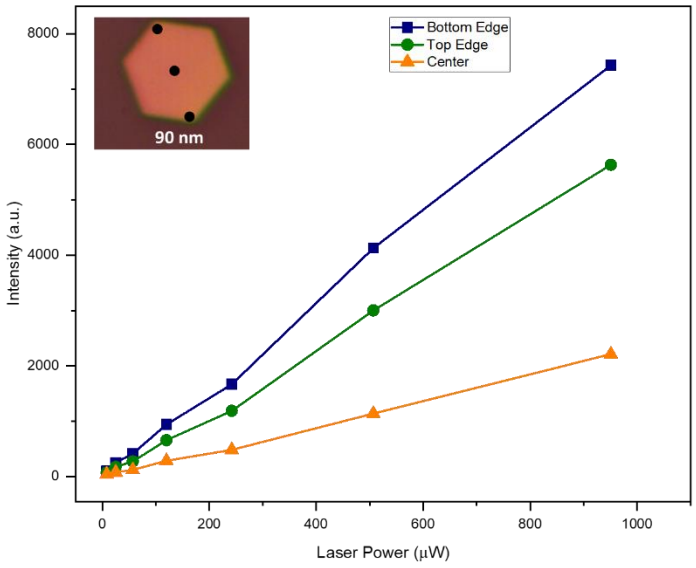


Figure 4.15: Laser power dependence of the Raman intensity. For the 112.2 cm^{-1} peak at the edges and center of PbI_2 platelet (thickness~90 nm). The inset shows the PbI_2 platelet

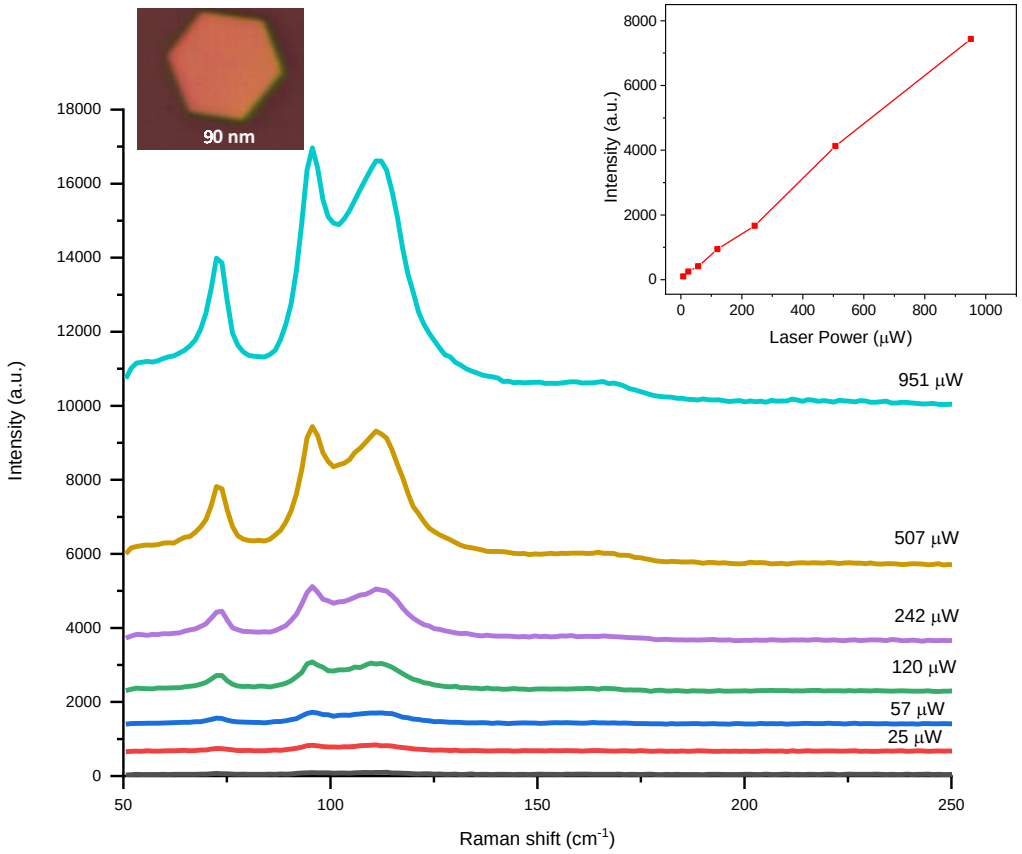


Figure 4.16: Raman emission spectra with increasing laser power. The insets shows the Laser Power v. Intensity of 112.2 cm^{-1} peak at the edge and the PbI_2 platelet

Chapter 5: Conclusion

The goals of the project were to synthesize and characterize 2D layered group-III monochalcogenides (GaSe, GaS, InSe) and metal halides (PbI_2,). Based on the characterization techniques used, the aims of the project were met. In general, there are several different ways that can be used to grow 2D crystals, or even thin films. Even more, each technique has its own challenges and benefits; a trade-off is usually required when choosing a growth method. However, using only chemical vapor deposition, it was found that the growth conditions for single layer to multi-layer monochalcogenides could be optimized by changing only the parameters (temperature, growth time, flow rate, etc.) for each experiment. In addition, while the synthesis of 2D layered PbI_2 remains relatively unexplored (compared to their 2D counterparts), their growth can also be attained using a low-cost solution-based technique.

On the other hand, the discovery of edge-enhanced Raman modes in PbI_2 platelets, has not been reported before. The possible connection between this effect and the existence of whispering gallery modes in these structures is not only interesting from the fundamental point of view, but also open new avenues to use these materials in novel optical devices. Further optimization of the crystalline structure could lead to Raman lasing devices, naturally formed from the growth without the needs of complex microfabrication procedures.

Finally, due to the time constraints, some areas of the research will be the topic of future studies. For example, while single layer coverage of GaSe and GaS was successfully achieved, InSe, InS and heterostructures of GaSe-GaS proved to be more challenging and require further optimization of the growth parameters.

References

1. Graphene Experiments Garner Nobel Prize. (2010, November). Retrieved September 28, 2019, from https://www.aps.org/publications/apsnews/201011/graphene.cfm.

2. Mas-Ballesté, R. (2011). 2D materials: to graphene and beyond. *Nanoscale*, (1), 20–30. Retrieved from https://pubs.rsc.org/en/content/articlepdf/2011/nr/c0nr00323a

3. Kumar, D. S., & Kumar, B. J. (2018). Quantum Nanostructures (QDs): An Overview. In Synthesis of Inorganic Nanomaterials Advances and Key Technologies (pp. 59–88). Cambridge, MA: Woodhead Publishing. doi: https://doi.org/10.1016/B978-0-08-101975-7.00003-8

4. Neikov , O. D., & Stepanovich , N. S. (2018). Nanopowders. In Handbook of Non-Ferrous Metal Powders: Technologies and Applications (2nd ed., pp. 98–98). Elsevier.

5. Geim, A. K. (2007). The rise of graphene. Nature Materials, 6, 183–191. Retrieved from https://www.nature.com/articles/nmat1849

6. Kotov, V. (2010). Electron-Electron Interactions in Graphene: Current Status and Perspectives. Physical Review B, 82(8), Retrieved from https://arxiv.org/pdf/1012.3484.pdf

7. Jorio, A. (2008). Carbon Nanotubes Advanced Topics in the Synthesis, Structure, Properties and Applications. Springer-Verlag Berlin Heidelberg. doi: https://doi.org/10.1007/978-3-540-72865-8

8. Lavocat, J.-C. (2012, December 6). A bandgap semiconductor nanostructure made entirely from graphene. Retrieved September 28, 2019, from https://www.graphenea.com/blogs/graphene-news/6969324-a-bandgap-semiconductor-nanostructure-made-entirely-from-graphene.

9. Mueller, T. (2010). Graphene photodetectors for high-speed optical communications. Nature Photonics , 4, 297–301. doi: 10.1038/nphoton.2010.40 · Source: arXiv

10. Lee, J. (2016). Two-Dimensional Semiconductor Optoelectronics Based on van der Waals Heterostructures. Nanomaterials, 6(11). doi: 10.3390/nano6110193

11. Shahriari, M. (2018). Band structure and orbital character of monolayer MoS2witheleven-band tight-binding model. Superlattices and Microstructures, 114, 169–182. doi: https://doi.org/10.1016/j.spmi.2017.12.030

12. Yang, W. (2018). Interlayer interactions in 2D WS2/MoS2 heterostructures monolithically grown by in situ physical vapor deposition. Nanoscale, 48(10), 22927–22936. doi: 10.1039/c8nr07498

13. Mak, K. F. (2010). Atomically Thin MoS2: A New Direct-Gap Semiconductor. PHYSICAL REVIEW LETTERS, 105(13). doi: 10.1103/PhysRevLett.105.136805

14. Lopez-Sanchez, O. (2013). Ultrasensitive photodetectors based on monolayer MoS2. Nature Nanotechnology, 8, 497–501. doi: 10.1038/NNANO.2013.100

15. Xu, K. (2016). Synthesis, properties and applications of 2D layered MIIIXVI (M = Ga, In; X = S, Se, Te) materials. Nanoscale, 8(38), 16802–16818. doi: 10.1039/c6nr05976g

16. Li, X. (2014). Controlled Vapor Phase Growth of Single Crystalline, Two-Dimensional GaSe Crystals with High Photoresponse. Scientific Reports, 4. doi: 10.1038/srep05497

17. Yin, Z. (2012). Single-Layer MoS2 Phototransistors. ACS Nano, 6, 74–80. doi: https://doi-org.ezproxy.lib.usf.edu/10.1021/nn2024557

18. Sucharitakul, S. (2015). Intrinsic Electron Mobility Exceeding 103 cm2/(V s) in Multilayer InSe FETs. Nano Letters, 15(6), 3815–3819. doi: : 10.1021/acs.nanolett.5b00493 Nano Lett. 2015, 15, 3815−3819

19. Yu, P. Y. and Cardona, M. (2010). Fundamentals of Semiconductors: Physics and Materials Properties. Fourth Edition. Springer Heidelberg Dordrecht London New York.

20. Yoon, Y. (2011). How Good Can Monolayer MoS2 Transistors Be? Nano Letters, 11(9), 3768–3773. doi: dx.doi.org/10.1021/nl2018178 dx.doi.org/10.1021/nl2018178

21. Feng, W. (2014). Back Gated Multilayer InSe Transistors with Enhanced Carrier Mobilities via the Suppression of Carrier Scattering from a Dielectric Interface. Advanced Materials, 26(38), 6587–6593. doi: 0.1002/adma.201402427

22. Mudd, G. W. (2013). Tuning the Bandgap of Exfoliated InSe Nanosheets by Quantum Confi nement . Advanced Materials, 25(40), 5714–5718. doi: 10.1002/adma.201302616

23. Schwierz, F. (2015). Two-dimensional materials and their prospects in transistor electronics. Nanoscale, 7(18), 8261–8283. doi: 10.1039/c5nr01052g

24. rolinychupetin. (2013, March 30). Retrieved September 28, 2019, from https://www.youtube.com/watch?v=SjeK1nkiFvI.

25. Late, D. J. (2012). GaS and GaSe Ultrathin Layer Transistors. Advanced Materials, 24(26), 3549–3554. doi: 10.1002/adma.201201361

26. Zhong, M. (2017). Large-scale 2D PbI2 monolayers: experimental realization and their indirect band-gap related properties. Nanoscale, 9(11), 3736–3741. doi: 10.1039/C6NR07924E

27. Sun, Y. (2019). Band Structure Engineering of Interfacial Semiconductors Based on Atomically Thin Lead Iodide Crystals. Advanced Materials, 31(17). doi: https://doi.org/10.1002/adma.201806562

28. Zhou, M. (2015). Single layer lead iodide: computational exploration of structural, electronic and optical properties, strain induced band modulation and the role of spin–orbital-coupling. Nanoscale, 7(83). doi: 10.1039/C5NR04431F

29. Nag, B. R. (2000). Band Offset. In Physics of Quantum Well Devices (pp. 22–35). doi: 10.1007/0-306-47127-2_3.pdf

30. Heterojunctions. (n.d.). Retrieved September 28, 2019, from https://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_5/backbone/r5_3_1.html.

31. Rossnagel, S. M. (2003). Thin film deposition with physical vapor deposition and related technologies. Journal of Vacuum Science & Technology A, 21(74), 74–87. doi: https://doi.org/10.1116/1.1600450

32. McCauley, J. W. (1986). Materials Characterization for Systems Performance and Reliability. Plenum Press.

33. Leng, Y. Materials Characterization: Introduction to Microscopic and Spectroscopic Methods. 2008.

34. Ferraro, J. R. (1994).Introductory Raman spectroscopy

35. Afaneh, T. (2018). Laser-Assisted Chemical Modification of Monolayer Transition Metal Dichalcogenides. Advanced Functional Materials, 28(37). doi: 10.1002/adfm.201802949

36. Rodriguez, R. D. (2014). Selective Raman modes and strong photoluminescence of gallium selenide flakes on sp2 carbon. American Vacuum Society, 32. doi: http://dx.doi.org/10.1116/1.4881995

37. Luxa, J. (2016). Layered Post-Transition-Metal Dichalcogenides (X@M@M@X) and Their Properties. Chemistry—A European Journal, 22(52). doi: https://doi.org/10.1002/chem.201604168

38. Venables, J. A. (1984). Nucleation and growth of thin films. Reports on Progress in Physics, 47(4), 399–459

39. Wang, Y. (2017). Achieving highly uniform two-dimensional PbI2 flakes for photodetectors via space confined physical vapor deposition. Science Bulletin, 62(24). doi: https://doi.org/10.1016/j.scib.2017.11.011

40. Vekilov, Peter G. "Nucleation." Crystal Growth & Design, vol. 10, 22 Oct. 2010, pp. 5007–5019., doi: 10.1021/cg1011633.

41. Baibarac, M. "Exciton-Phonon Interaction in PbI2 Revealed by Raman and Photoluminescence Studies Using Excitation Light Overlapping the Fundamental Absorption Edge." Materials Research Bulletin, vol. 70, 4 June 2015, pp. 762–772., doi:https://doi.org/10.1016/j.materresbull.2015.06.012.

42. Righini, G. C. "Whispering Gallery Mode Microresonators: Fundamentals and Applications." Nuovo Cimento, vol. 34, no. 7, 30 Mar. 2011, pp. 435–488., doi:10.1393/ncr/i2011-10067-2.

43. Liu, Xinfeng, et al. "Whispering Gallery Mode Lasing from Hexagonal Shaped Layered Lead Iodide Crystals." ACS Nano, vol. 9, no. 1, 2015, pp. 687–695., doi:10.1021/nn5061207.

44. Okamoto, H. Ga-Se (Gallium-Selenium). J. Phase Equilib. Diffus. 30, 658 (2009). https://doi.org/10.1007/s11669-009-9601-3

45. Zavrazhnov, A., Berezin, S., Kosykov, A. et al. The phase diagram of the Ga–S system in the concentration range of 48.0–60.7 mol% S. J Therm Anal Calorim 134, 483–492 (2018). https://doi.org/10.1007/s10973-018-7124-z

46. Okamoto, H. In-Se (indium-selenium). JPE 19, 400 (1998). https://doi.org/10.1361/105497198770342175

47. "Vapor Pressures of the Chemical Elements." Vapor Pressures of the Chemical Elements, Vapor Pressure of Metals and Halogens from -150 Degrees C to 3500 Degrees C Including Lead, Aluminum, Zinc, Iodine, Copper, Indium, Iodine, Magnesium, Selenium, Lithium, Iron, Sodium and Gallium, www.powerstream.com/vapor-pressure.htm.

Appendix A: Additional Figures

The following figures were used to assist in the start of the growth of the monochalcogenides[44,45,46,47]

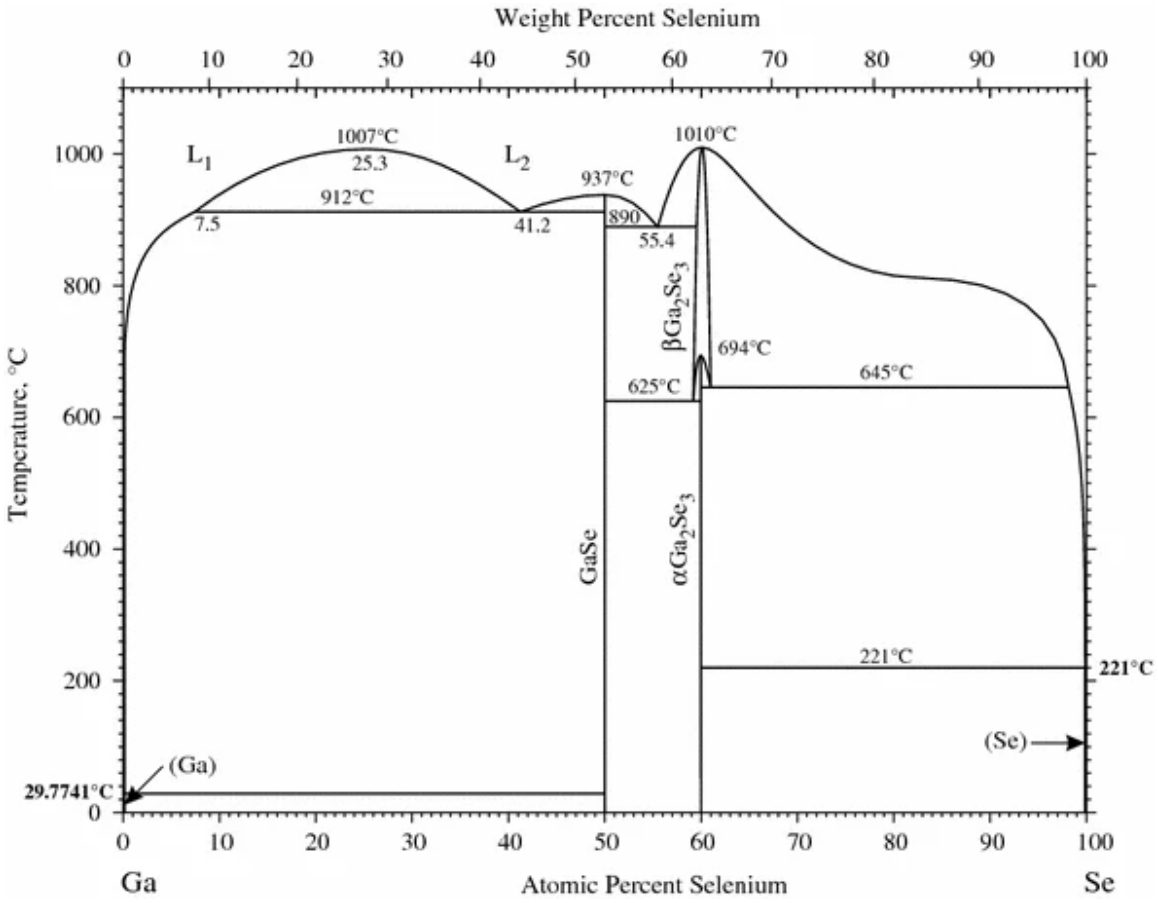
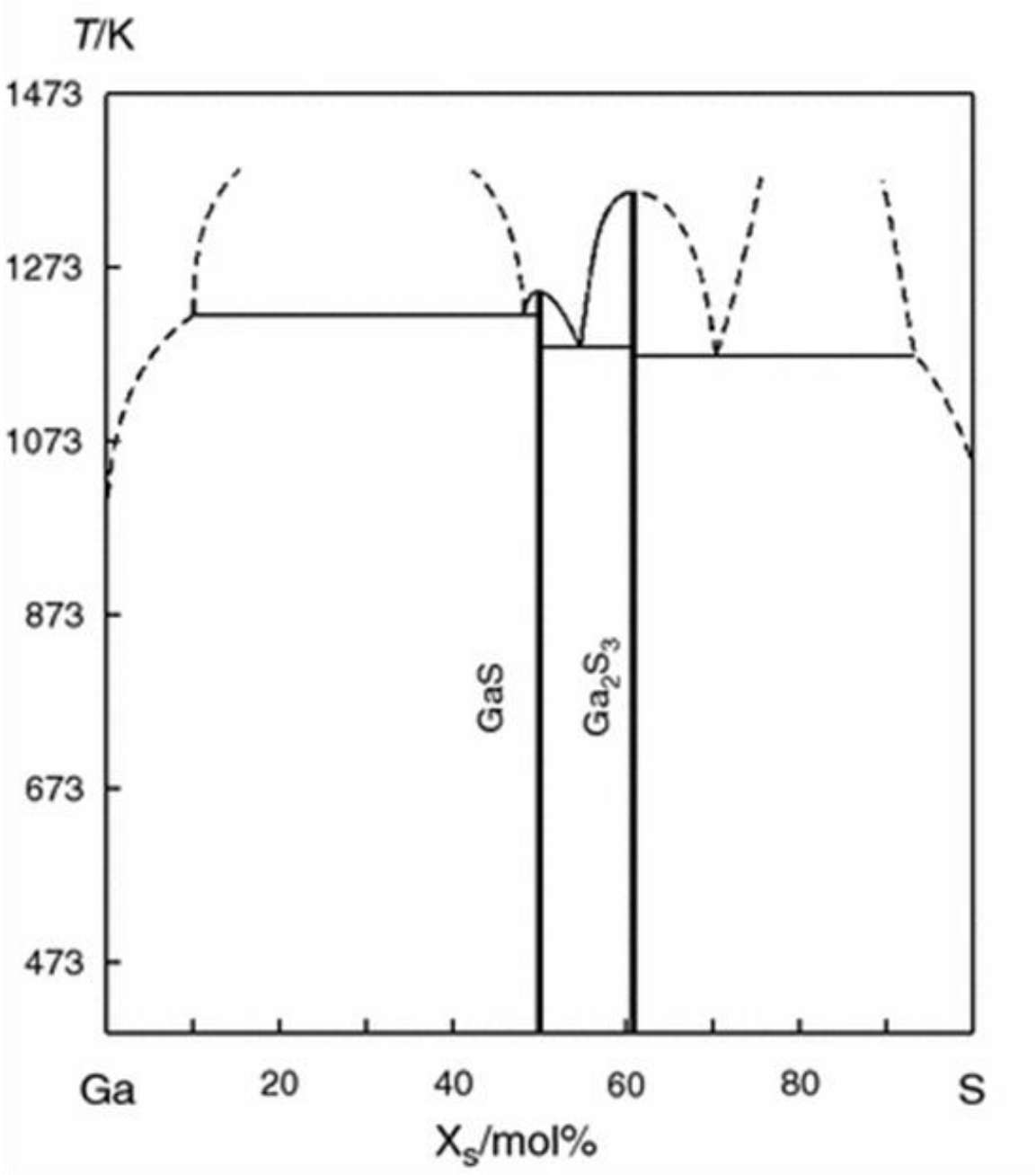


Figure a1: Ga-Se (Gallium Selenium) phase diagram. Note. From "Ga-Se (Gallium-Selenium), by Okamoto, H, J. Phase Equilib. Diffus. 2009. Copyright 2009, by Springer Nature. Reprinted with permission



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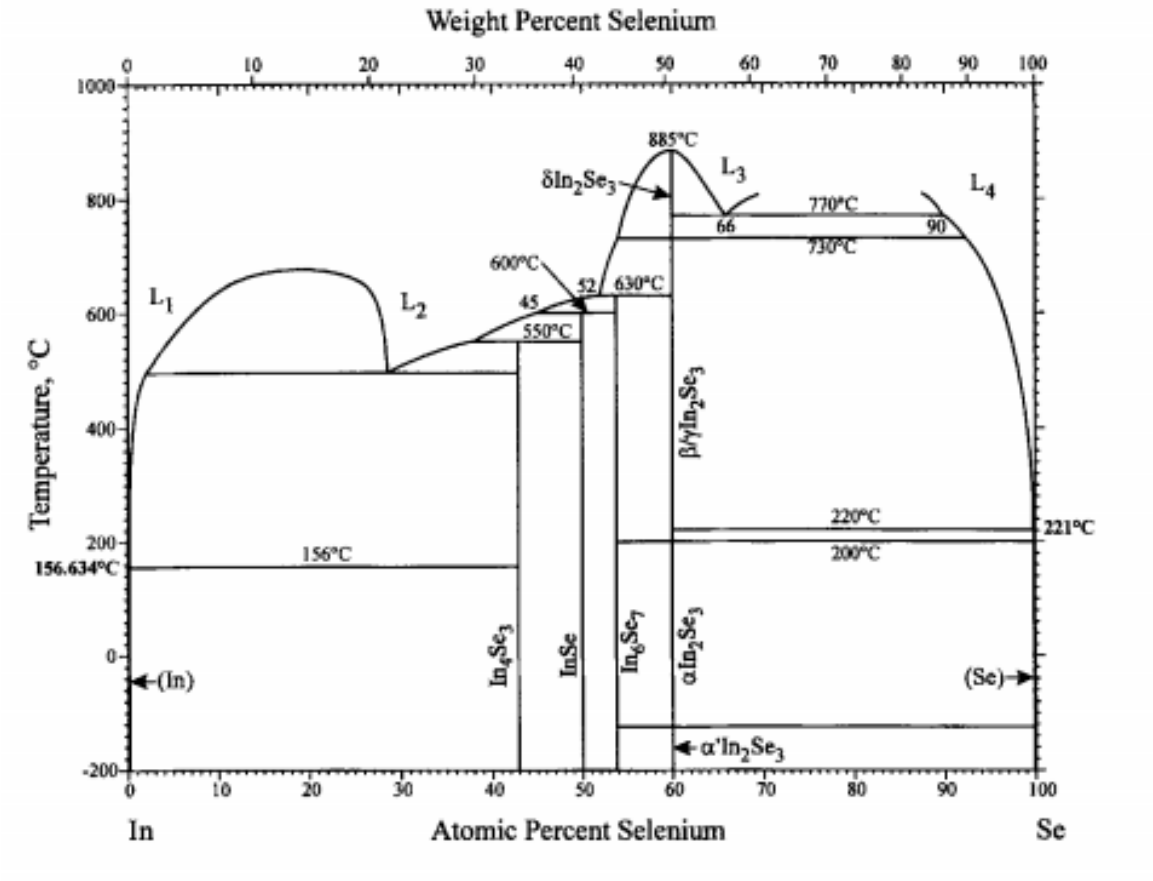

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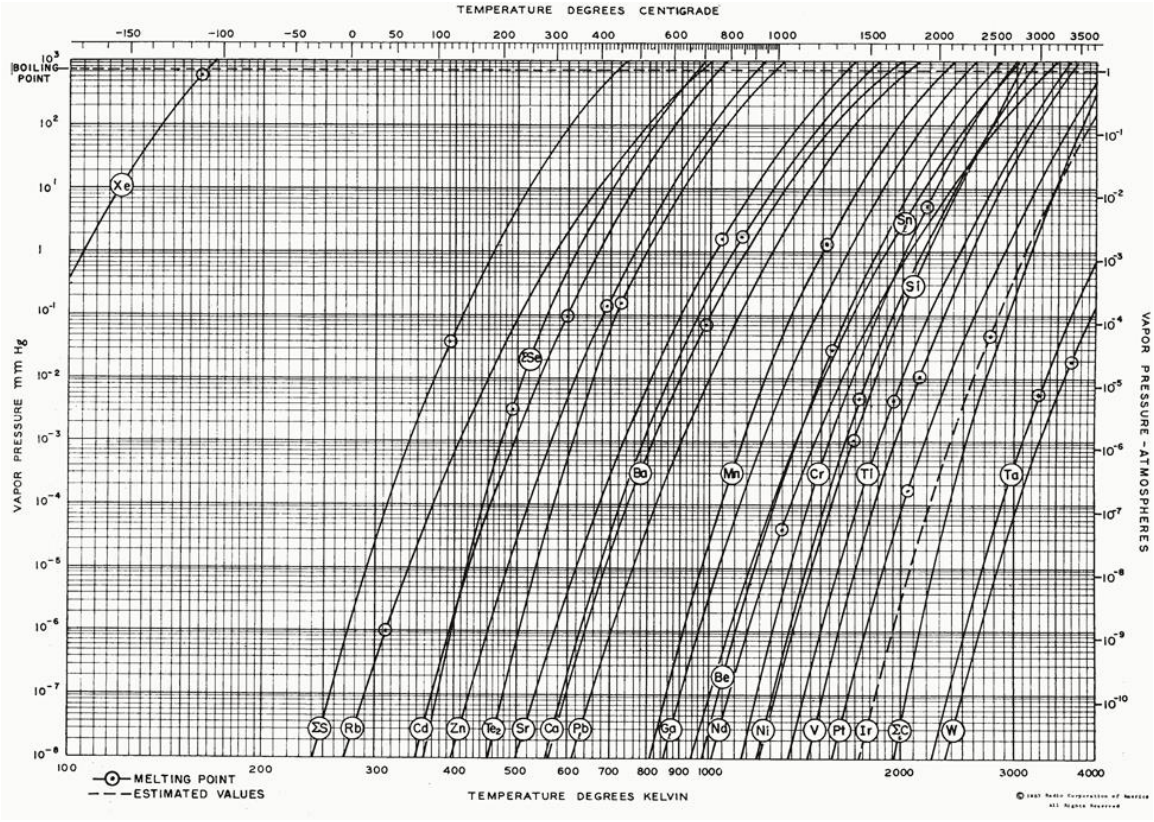

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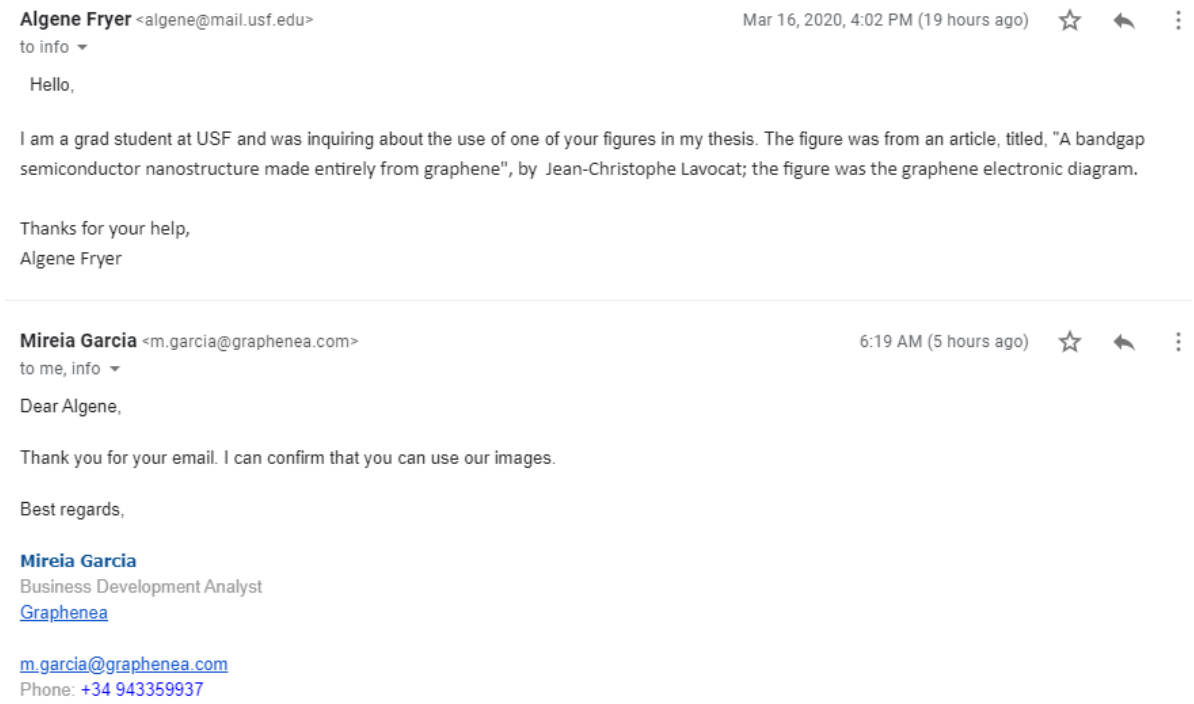

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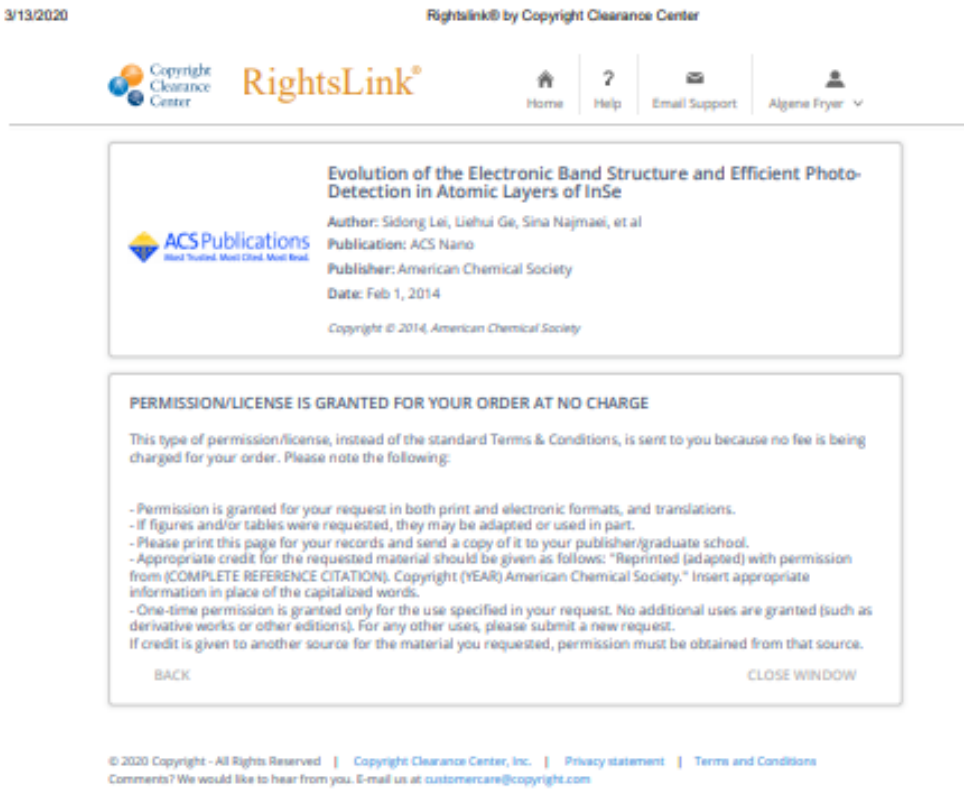

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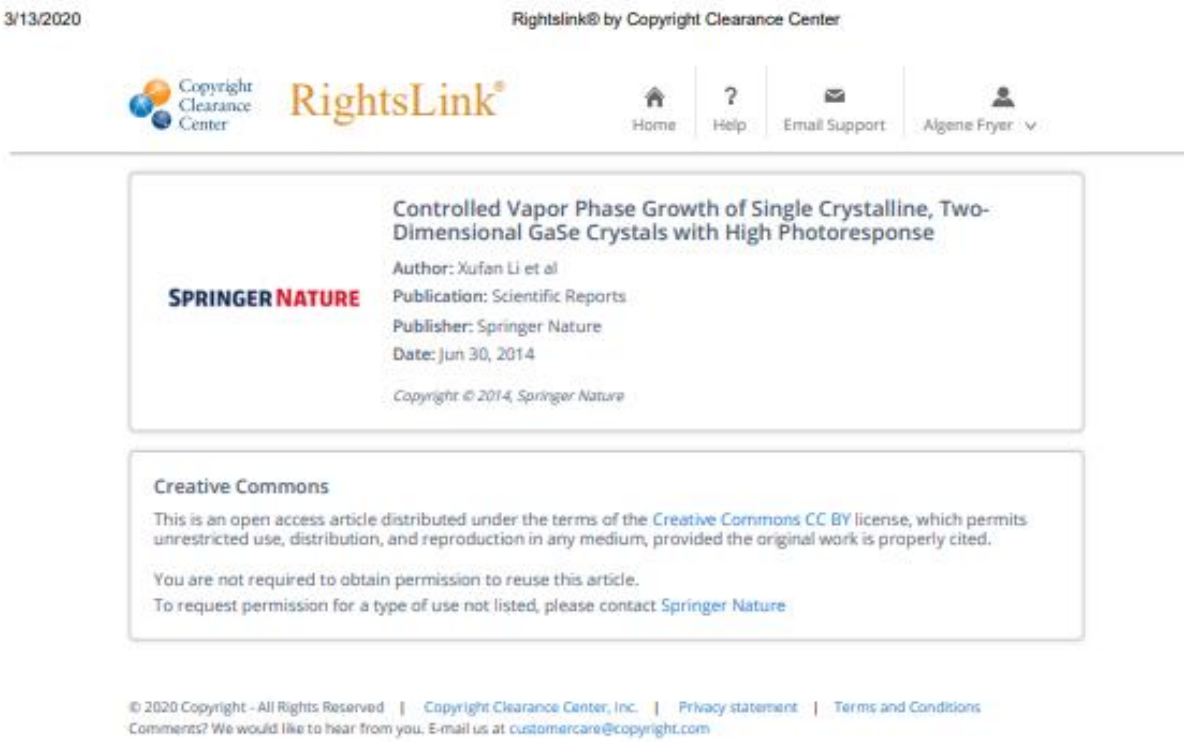

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Publication: Scientific Reports

Publisher: Springer Nature

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Volume of serial or monograph	N/A	Author of portion(s)	National Center for Nanoscience and Technology.; Royal Society of Chemistry (Great Britain)
Page or page range of portion	3738-3739		
		Issue, if republishing an article from a serial	N/A
		Publication date of portion	2009-01-01

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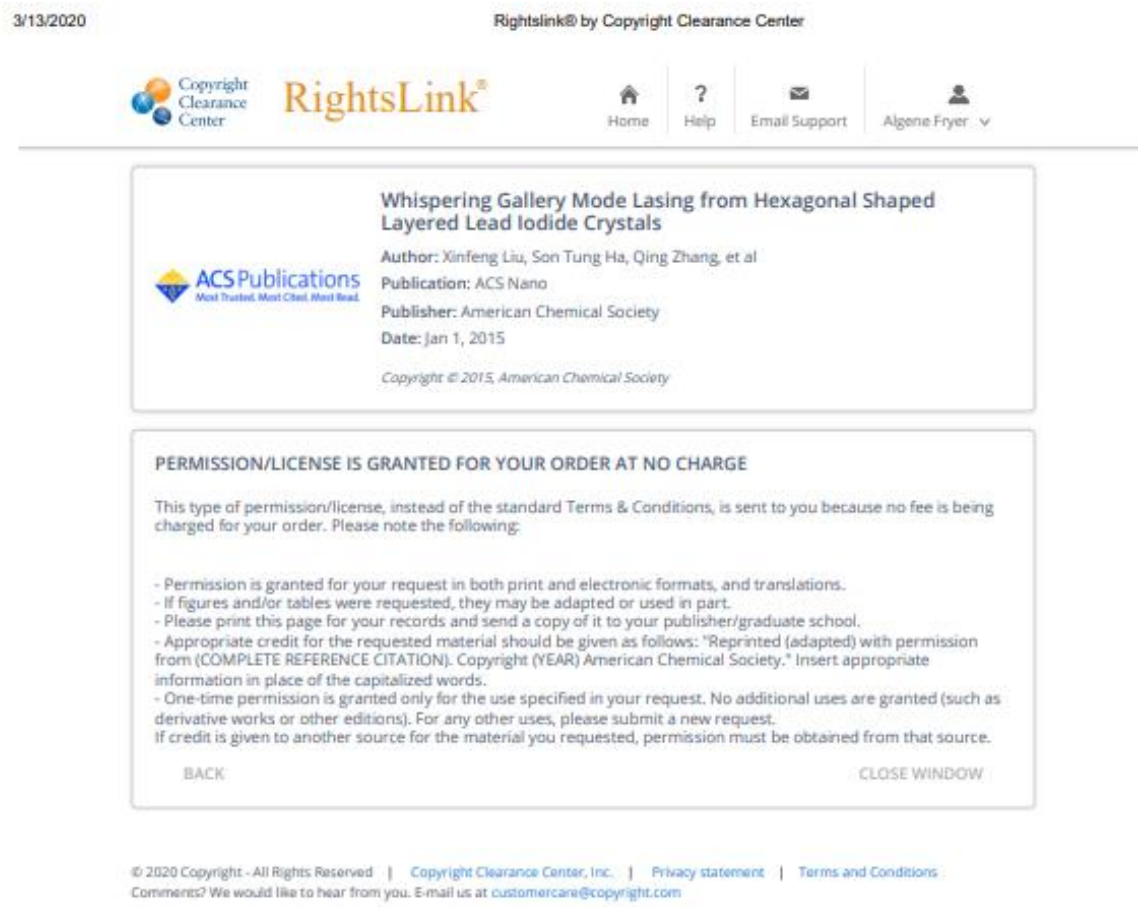

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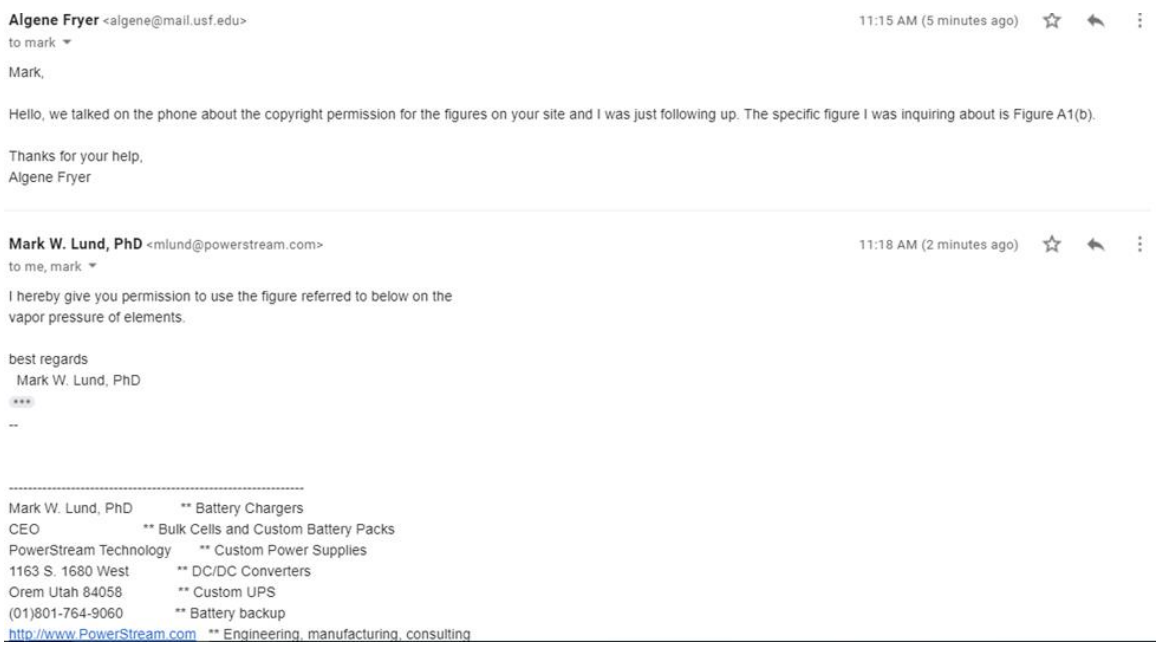

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