Synthesis and photo-response study on GaSe and InSe atomic layers

by

Sidong Lei

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE Master of Science

APPROVED, THESIS COMMITTEE

Pulickel M. Ajayan,
Professor, Department of Material Science and Nanoengineering, Chair

Jun Lou
Associate Professor, Department of Material Science and Nanoengineering, Associate Chair

Junichiro Kono
Professor, Department of Electrical and Computer Engineering, Department of Physics and Astronomy

HOUSTON, TEXAS
June 2013
ABSTRACT

Synthesis and Photo-Response Study on GaSe and InSe Atomic Layers

by

Sidong Lei

Insolation and characterization of atomic layers from layered crystal bonding by van der Waals interaction is a new-born and attractive realm in physics, chemistry and material science. It exhibits new domains of materials never explored before, referred as 2D materials. Two major tasks in this new born realm are to explore new materials with special properties and to develop reliable techniques for material synthesis and characterization.

Here, a review on 2D material research is presented, especially the opto-electronic properties. Then, a home-built opto-electronic characterization system specialized to 2D opto-electronic properties characterization is introduced in details, including the building principles, structures, measurement methods, etc., followed by an introduction to fundamental knowledge about 2D materials characterization.

With the home-built setup, layered GaSe and InSe atomic layers are studied; their band-structures and lattice interactions are explored and discussed in details. Both GaSe and InSe show good photo-response in this study, and they may serve as ultra-thin atomic layered photo-detectors.
Acknowledgments

First of all, I would like to appreciate my supervisor Dr. Ajayan. He gave me the great opportunity to work in this amazing group and area, to work with so many intelligent and friendly people. Dr. Ajayan is not only an outstanding professor that leads me to the frontier of science, but also a gentleman who gives me so much confidence and ambition to complete projects and realize dream.

Secondly, I would like to give my appreciation to Dr. Robert Vajtai. Robert is the one I always come to. I always knock his door and share my idea and feeling with him about anything, research, life, joke, etc. Every talking just makes me relaxed and refreshed.

Then, I want to thank my friends and labmates, Liehui Ge, Sina Najmaei, Antony George, Charudatta Galande, Yongji Gong, Lulu Ma. It is impossible for me complete my research without their suggestions and help. Also, these friends always help me overcome troubles, no matter what it is.

My wife, one of the most important parts of my life, always stands beside me to share my happiness and sadness, success and failure. She makes everything I am pursuing meaningful and enjoyable.

Last, but not least, I would like to thank my committee members, Dr. Lou and Dr. Kono. Unlike other committee members those may raise questions only during defense; they provide me valuable supports for my research, knowledge, instruments and instruction. I learned quite a lot from them.
# Contents

Acknowledgments ........................................................................................................ iii

Contents ..................................................................................................................... iv

List of Figures ............................................................................................................. vi

List of Tables ............................................................................................................... ix

Nomenclature ............................................................................................................. x

Start with Graphene ..................................................................................................... 1

1.1. Review on Graphene .......................................................................................... 3
    1.1.1. Graphene FET and Band Gap Open ......................................................... 3
    1.1.2. Graphene Photo-Detector ........................................................................ 8

1.2. 2D Materials beyond Graphene ........................................................................ 10
    1.2.1. Boron Nitride (BN) .................................................................................. 11
    1.2.2. Transition Metal Dichalcogenides (TMDC) ............................................. 13

III-VI Layered Semiconductors ................................................................................... 16

2.1. Crystal and Band Structures .............................................................................. 17

2.2. Growth Method for Bulk and Thin Films ......................................................... 20

2.3. Application of III-VI Semiconductors ............................................................... 22

Principles and Setups ................................................................................................. 24

3.1. Raman Scattering Spectra of III-VI Layered Semiconductors ......................... 25
    3.1.1. Raman Fundations .................................................................................... 26
    3.1.2. Virtual Level and Resonant Raman .......................................................... 28

3.2. Photoconductivity .............................................................................................. 30
    3.2.1. Basic Principle of Photoconductivity ....................................................... 30
    3.2.2. Important Parameters ............................................................................. 31
    3.2.3. Configuration of Photo-Detectors ......................................................... 33

3.3. Opto-Electronic Characterization System ........................................................ 40
    3.3.1. Probe-Station and Vacuum Build-Ups ..................................................... 41
    3.3.2. Photo-Conductivity Measurement ......................................................... 43
    3.3.3. Low Current Level Measurement- Connections for DC Measurement .... 45
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.4. Low Current Level Measurement- Lock-In Amplifier</td>
<td>48</td>
</tr>
<tr>
<td>3.3.5. Lock-In Amplifier V.S. Low Noise DC Amplifier</td>
<td>50</td>
</tr>
<tr>
<td>3.3.6. Laser Stabilization and Modulation</td>
<td>52</td>
</tr>
<tr>
<td>3.4. Device Fabrication</td>
<td>54</td>
</tr>
<tr>
<td>3.4.1. Photo Lithography</td>
<td>54</td>
</tr>
<tr>
<td>3.4.2. E-Beam Lithography</td>
<td>55</td>
</tr>
<tr>
<td><strong>Synthesis of Few-Layered GaSe and Photo-Conductivity Study</strong></td>
<td>57</td>
</tr>
<tr>
<td>4.1. Introduction</td>
<td>58</td>
</tr>
<tr>
<td>4.2. Material Synthesis</td>
<td>61</td>
</tr>
<tr>
<td>4.2.1. VPT Growth Reactor</td>
<td>61</td>
</tr>
<tr>
<td>4.2.2. GaSe Growth Principle</td>
<td>63</td>
</tr>
<tr>
<td>4.2.3. Precursor Preparation</td>
<td>65</td>
</tr>
<tr>
<td>4.2.4. Sample Growth and Characterization</td>
<td>68</td>
</tr>
<tr>
<td>4.3. Raman Study</td>
<td>74</td>
</tr>
<tr>
<td>4.4. Photo-Conductivity Study</td>
<td>76</td>
</tr>
<tr>
<td>4.5. Conclusion</td>
<td>80</td>
</tr>
<tr>
<td><strong>Atomically Layered InSe Isolation and Characterization</strong></td>
<td>81</td>
</tr>
<tr>
<td>5.1. Introduction</td>
<td>82</td>
</tr>
<tr>
<td>5.2. InSe Crystal Growth</td>
<td>85</td>
</tr>
<tr>
<td>5.3. Atomic Layer Isolation and Fundamental Characterization</td>
<td>87</td>
</tr>
<tr>
<td>5.4. Raman Study</td>
<td>90</td>
</tr>
<tr>
<td>5.5. Photo-Conductivity Study</td>
<td>96</td>
</tr>
<tr>
<td>5.6. Conclusion</td>
<td>100</td>
</tr>
<tr>
<td><strong>Conclusion</strong></td>
<td>101</td>
</tr>
<tr>
<td><strong>References</strong></td>
<td>103</td>
</tr>
<tr>
<td><strong>Appendix A</strong></td>
<td>112</td>
</tr>
</tbody>
</table>
List of Figures

Figure 1.1 – Graphene based back gating FET ........................................................... 4
Figure 1.2 – Graphene growing on SiC substrate ......................................................... 6
Figure 1.3 – ARPES intensity maps taken on single-layer graphene on 6H-SiC. 6
Figure 1.4 – Graphen band-gap open by bending ...................................................... 7
Figure 2.1 – A typical layered III-VI semiconductor lattice structure .................. 17
Figure 2.2 – van der Waals epitaxy mechanism ...................................................... 20
Figure 2.3 – Two kinds of interfaces for GaSe expitaxial film on Si (111) .......... 22
Figure 3.1 – Raman Scattering Process .................................................................. 28
Figure 3.2 – Photo-responsivity of typical silicon photo-detector ......................... 32
Figure 3.3 – Photo-current gain process in Ohmic MSM photodetector ............ 34
Figure 3.4 – Photo-current gain process in Schottky MSM photodetector .... 35
Figure 3.5 – pn junction photo-detector working in voltage mode..................... 37
Figure 3.6 – pn junction photo-detector working in current mode. ..................... 38
Figure 3.7 – PIN junction photo-detector principle ............................................. 39
Figure 3.8 – Home-built photo-electronic measurement setup.......................... 41
Figure 3.9 – The vacuum probe-station .................................................................. 42
Figure 3.10 – Transmission spectrum of fused silica view port ......................... 43
Figure 3.11 – Diagram of opto-electronic measurement system ....................... 44
Figure 3.12 – An example of triaxial cables ............................................................. 47
Figure 3.13 – Connections for triaxial cable ............................................................ 47
Figure 3.14 – Diagram of lock-in amplifier .............................................................. 50
Figure 3.15 – Laser power stablization and modulation loop................................................................. 53
Figure 3.16 – Digital markers on 285 nm thermal oxidized silicon.............................. 56
Figure 4.1 – Demonstration of crystal structure of GaSe layer.................................. 59
Figure 4.2 – VPT growth reactor........................................................................................................ 62
Figure 4.3 – Vacuum connectors for VPT reactor ................................................................. 62
Figure 4.4 – Fundamental process for GaSe VPT growth ...................................... 63
Figure 4.5 – Structure of an effusion cell ....................................................................................... 65
Figure 4.6 – Ga-Se system phase diagram............................................................................... 66
Figure 4.7 – SEM image of synthesized GaSe micro-crystal ......................................... 67
Figure 4.8 – EDX spectra of synthesized GaSe micro-crystal ........................................ 67
Figure 4.9 – Configuration of GaSe flake growth reactor .............................................. 68
Figure 4.10 – Optical, AFM and TEM imaging of GaSe flakes....................................... 70
Figure 4.11 – Optical, AFM and TEM imaging of GaSe flakes........................................ 71
Figure 4.12 – AFM imaging of a single GaSe flake ................................................................. 72
Figure 4.13 – TEM imaging of a single GaSe flake ................................................................. 73
Figure 4.14 – Raman spectra of GaSe with different thicknesses ................................ 75
Figure 4.15 – Dark and photoresponse I-V curve of GaSe flake ..................................... 76
Figure 4.16 – Photo-response spectrum and band-structure of GaSe flake ....... 78
Figure 5.1 – Lattice structure of InSe ....................................................................................... 83
Figure 5.2 – Absorption spectra of bulk InSe and GaSe ..................................................... 83
Figure 5.3 – In-Se system phas diagram ............................................................................... 86
Figure 5.4 – SEM image of InSe crystal grown from non-stoichiometric melt.... 86
Figure 5.5 – TEM image and electron diffraction pattern of InSe flake ............... 87
Figure 5.6 – AFM image of InSe flake .......................................................... 88

Figure 5.7 – Resonant Raman of non-resonant Raman of InSe flakes with different thicknesses ................................................................. 91

Figure 5.8 – Photo-Conductivity Spectra of InSe with different thicknesses .... 97

Figure 5.9 – Photo-Conductivity I-V curve of InSe ........................................ 99

Figure 5.10 – Time-resolved photo-current measurement on InSe .............. 100
List of Tables

Table 5.1 -Resonant Raman (different layers) and Non-resonant Raman modes observed in InSe flakes ................................................................. 93
Nomenclature

2D  Two Dimensional
FET  Field Effect Transistor
TMDC  Transition Metal Di-Chalcogenides
CVD  Chemical Vapor Deposition
PECVD  Plasma Enhanced Chemical Vapor Deposition
SHG  Second Harmonic Generation
FWHM  Full Width at Half Maximum
S/N  Signal to Noise Ratio
MSM  Metal-Semiconductor-Metal
SMU  Source Meter Unit
AMP  Amplifier
AOM  Acoustic Optical Modulator
DUT  Device Under Test
RF  Radio Frequency
VPT  Vapor Phase Transport
AFM  Atomic Force Microscope
TEM  Transmission Electron Microscope
P.D.  Photo Diode
EDX  Energy-Dispersive X-Ray Spectroscopy
Chapter 1

Start with Graphene

Carbon, one of the most abundant elements, exhibits the most amazing properties with its activities and stability, simplicity and complexity. Its combinations with itself and other elements establish uncountable forms of materials: graphite, diamond, carbon dioxide, polymers, proteins, DNA and life. Whether realized or not, most parts of the modern scientific research are relevant to carbon directly or indirectly, such as chemistry, physics, material science, biology. Although, the human being believe they have already studied the carbon for hundreds of years and know every detail of it, carbon still astonish people again and again, even as the simplest form-elemental carbon.

The discoveries of buckminsterfullerene\(^1\) and carbon nanotube\(^2\) lead people to a new era of material science. After that, tremendous effort has been devoted to the research and development of nano-science and nanotechnology. During the past decade, various nano-structures have been built artificially not only from carbon.
The materials exhibit special properties that bulk materials do not have, such as extremely large special surface area, surface quantum states, quantum states confinement, etc. All these effects strongly alter the properties of nano-structures and make them very different from bulky counterparts. At the same time, nanotechnology promotes the development of nano-fabrication techniques which are widely used in the various realms, such as electronics.

Traditionally, nano-structure was referred to zero-dimensional structures, such as quantum dots, one-dimensional structures, nano-wires, and more complicated composite three-dimensional structures. However, the isolation of graphene (single layered graphite) in 2003, added another space for nano-structure fabrication: two-dimensional. After that, another branch of materials started to thrive and draw the attention from physicist, chemists, and material scientists for decade. People now refer it to Two-Dimensional (2D) Materials.
1.1. Review on Graphene

It is believed that graphene has been discovered long time ago\textsuperscript{4,5}, however, the systemic study of graphene began at 2004, after Novoslov and co-workers successfully isolated single atomic layers of carbon atoms from bulk graphite single crystal and measured the electronic properties of it\textsuperscript{3}. Soon after the report on this successful isolation, extensive studies followed. Graphene, although just a building block of graphite, exhibits quite different properties from its bulk counterpart and provides a really good platform for fundamental and application research. In physics research, the interests on graphene mainly focus on the realms of electronic transportation\textsuperscript{6-9}, photo-electronics and photonics\textsuperscript{10-15}.

1.1.1. Graphene FET and Band Gap Open

The report on graphene by Novoslov and co-workers\textsuperscript{3} mainly focus on the material characterization and did not explore and discuss the physical properties in details. However, it touched one of the most important properties of graphene and opened the door to a totally new realm. In this report, the mobility of graphene is estimated to be in the order of thousand. In addition, graphene can be treated as an ideal two-dimensional electron-gas system, while, traditionally, people would use semiconductor hetero-junction to fabricate quasi two-dimensional electron-gas systems. These two facts make graphene a good candidate to study quantum Hall effect\textsuperscript{16-19}, Coulomb drag effect\textsuperscript{19} and other Fermion transport properties.
Besides these fundamental research, application orientated studies are also vigorously pursued and one major focus has been field effect transistor (FET)\textsuperscript{20-23}. Field effect has been widely used in modern semiconductor device industry. Figure 1.1 shows a typical graphene based FET. By changing the gate voltage, the Fermi level in graphene can be manipulated. As graphene does not have a band gap, the Fermi level shift from conduction band to valence band is continuous, i.e. by gating, graphene can behave like both an n-type or p-type semiconductor.

![Graphene based back gating FET](image)

**Figure 1.1 – Graphene based back gating FET**

However, graphene is zero-band gap semiconductor, i.e., there is no forbidden band between valence band and conduction band, and it behaves like metal more or less. It is very easy to generate charge carriers by thermal excitation, photo excitations, electrical fields and other effects. So in pure graphene, it is really hard to avoid any charge carriers. So it is very challenging to shut down a graphene
based FET totally and it always has large leakage current in OFF state. As a result, perfect graphene lattice cannot provide very high ON/OFF ratio, which is a very important parameter for modern FET fabrication and can seriously affect the reliability, stability and power consumption. A typical silicon based FET device always has an ON/OFF ratio in the order of $10^4$ to $10^7$\textsuperscript{24}, but graphene based FET can only show an ON/OFF ratio in order of 100 to 1000\textsuperscript{24}. Meanwhile, even at off state, graphene still allow a large amount of current pass through it, which will lead to large power consumption, especially in integrated structures. All these make graphene impossible for any commercial application.

To utilize the high mobility of graphene and avoid the disadvantage of zero band-gap, large amount of attempts have been reported to open a band gap without sacrificing the mobility.

It is predicted by theory that the graphene ribbons with zigzag edges or armchair edges will have bandgap and the width of the gap is reversely proportional to the width of the ribbon. Hongjie Dai and his research group\textsuperscript{25} developed a chemical method to fabricate graphene nanoribbons with a dimension range from less than 10 nm to tens of nanometer, which shows an ON/OFF ratio in the order of $10^7$.

Breaking the sublattice symmetry can also lead to a band-gap open. A. Lanzara and his research group found that the interaction between graphene and its substrate can be strong enough to bring this kind of symmetry breaking to open the gap\textsuperscript{26}. The structure of graphene on SiC substrate is shown in Figure 1.2. The ARPES
data is shown in Figure 1.3, from which one can find the band gap does open even under a weak interaction that break the symmetry.

Bending the graphene can also open a band-gap\textsuperscript{27}. Graphene is grown epitaxially on SiC nano-trench, shown in Figure 1.4. Due to the bend, local strain and Coulomb potential appears in the graphene layer and leads to gap opening.

**Figure 1.2 – Graphene growing on SiC substrate**

**Figure 1.3 – ARPES intensity maps taken on single-layer graphene on 6H-SiC**
The epitaxial graphene on SiC is a good candidate for electronics fabrication. It is possible for people to grow large area of graphene and apply lithography techniques to fabricate demanded devices and even integrated circuit.

Another possibility for modification of the band structure of graphene is doping, just as conventional semiconductors. Boron nitride domain in graphene can lead to an open gap\textsuperscript{28,29}. Nitrogen doping can also provide an open gap\textsuperscript{30}.

To sum up, graphene, as a novel 2D material, has lots of amazing physical properties. However, there are still problems to make graphene devices commercially applicable. To open a band gap is one of the most important problems one has to overcome. Doping and applied proper substrate are two most important and promising methods to induce a bandgap in graphene lattice for FET device fabrication. However, it is still hard to get large area of graphene with stable quality and physics properties. So it is still a question whether graphene can replace silicon as the next generation of material for electronic application.
1.1.2. Graphene Photo-Detector

Besides efforts on FET, graphene also exhibits opto-electronic properties. The photo-response in graphene is different from traditional concept that photo-electrons generated by radiation contribute to the conductivity of material.

Instead, other effects contribute to graphene photo-response, as graphene has no band gap. Because of this fact, large bias or (and) gate has to be applied to graphene based device so that the electron-hole pair generated by radiation can be separate before recombination and reach electrode\textsuperscript{11}. While other researchers think the photo-response of graphene is a thermal process, because the radiation warms the material up and changes the charge carrier distribution\textsuperscript{13}.

Other possible mechanism is the graphene and metal contact properties. In Fengnian Xia’s work\textsuperscript{12}, the photo-response I-V curve is very different from typical photo-response I-V curve. The slope of the I-V curve does not change, instead the whole curve shifts. This feature indicates an additional bias applied to the device when a light is shine onto the sample, and it is possible because one electrode is warmer than the other one and a potential difference is generated. This is similar to the process of thermal couple.

To sum up, although graphene has some photo-response, this mechanism is still confusing. More important, in all these reports, the dark current is extremely large and optical ON/OFF ratio is extremely small. This means if one use graphene as photo detector, the device will waste most of the energy on dark current. As a
result, in the present form, graphene is impossible to be utilized as a photo-detection material.
1.2. 2D Materials beyond Graphene

Graphene is not only a 2D material, but also works as a catalyst for the birth of a new field. Scientists realized that other layer-structured crystal bonding by van der Waals interaction are also possible to be exfoliated into few and even single layer on top of special substrate. So soon after the discovery and research on graphene, people begin to explore other types of layered materials, such as boron nitride, molybdenum disulfide, etc. These materials exhibit different physical properties and expand the frontier of 2D material.

The most common layered van der Waals type crystals contains boron nitride (BN), IV-VI compounds (like Bi$_2$Se$_3$, Bi$_2$Te$_3$), transition metal dichalcogenides (TMDC like TiS$_2$, TaS$_2$, MoS$_2$, WSe$_2$, etc.), III-VI semiconductors (like GaSe, InSe, etc.). And every type of compounds has their own striking properties. For example, BN has a layered structure very similar to graphene, but with a very large band gap$^{31,32}$, as a result it is used to modulate the band structure of graphene by doping$^{33-35}$. Meanwhile, it can also form continuous hetero-structure with graphene to form super-lattice structures$^{36,37}$ for electronic and optical application.

IV-VI compound has interested scientists for quite a long time as they are a group of material so called topological insulator$^{38-41}$, which means as a bulk crystal, their surface can contribute some conductivity to the material, whereas the inner part of them are semiconductor or insulator. However, when going down to few or single layer, all the structure the material has is surface. Hence the topological
properties of this group of materials will seriously change and have potential research and application value.

TMDC is another type of layered materials those are widely and deeply studied nowadays besides graphene. Their band structures are more complicated than graphene and have more special electronic and photonic properties. They have detectable band-gap which make them have higher ON/OFF ratio\(^\text{42}\). As well, they response to radiation which makes them suitable for ultra-thin photo-detectors\(^\text{43}\). Valleytronics\(^\text{44, 45}\) is another interesting phenomenon observed in these structures. Besides, some TMDS’ are also strong correlated materials, exhibiting the properties like superconductivity, Mott insulator, etc.

Finally, III-VI semiconductor is another important group of layered materials and it is the focus of the discussion in the thesis. III-VI semiconductors are widely used as photo-detecting material\(^\text{46}\). As well, they are well-known THz generators due to their large non-linear coefficient\(^\text{47, 48}\). I will spend next chapter to discuss layered III-VI semiconductor. But first, I would like to have a quick review of the research on 2D materials beyond graphene.

1.2.1. Boron Nitride (BN)

The meaning of research on BN lies in two aspects. One is the research on pure BN, containing the BN CVD growth, BN physical property studies. The other side is BN/Graphene hybrid structures, or BCN system.
Pure BN has some special physical properties. It is an excellent insulator, as well, an excellent thermal conductor\textsuperscript{49}. Meanwhile, the lattice constant of BN is nearly the same to graphene\textsuperscript{37}. All these facts make BN a really good material working as a substrate for graphene based devices. This is because BN can serve as a buffer layer that will reduce the effect of substrate on graphene. As well, BN layer is very flat and the lattice constant is nearly the same to graphene, so the electron scattering in graphene can be mitigated by using BN as a substrate\textsuperscript{50}.

Right now people have figured out several ways to grow BN by CVD methods. Ajayan’s group used ammonia-borane to grow BN film\textsuperscript{37}.

However, as-grown BN film is not ideal, because the growth process is very different from graphene. For graphene, the copper or nickel foil will dissolve carbon atom at high temperature and release them rapidly when temperature dopes done, then crystal forms. So it is possible to form large area of continuous film. But for BN, the substrate plays a less important role. Take the growth process using ammonia-borane as an example. When ammonia-borane enters the high temperature zone of the reactor (typically a tube furnace), ammonia-borane will dehydrate into BN fragments. In other word, small pieces of BN have already formed before touching the substrates (such as copper or nickel foil) and they will deposit onto the substrate physically. Although the BN fragment will realign into larger lattice, there is still no crystallization process in any stage of growth. Meanwhile, the deposition is a random process, which cannot promise the uniformity. As a result the CVD BN always shows poor quality, i.e., not uniform, un-continuous, lots of defect, etc.
While, BCN is another branch drawing great attention. The phase diagram consisting of boron, nitrogen and carbon (BNC) is rich in the large number of layered (hexagonal) phase compositions. From pure graphene to hexagonal boron nitride (h-BN) there exist a large number of BNC phases (BCN, BC2N, BC4N, BC3, C3N4 etc.), with the electronic structures varying from pure conductor (graphene) to pure insulator (h-BN). It is important to synthesize and isolate individual atomic layers of h-BNC compositions to realize the full potential of graphene based materials.

Poorly grown h-BCN hybrid films have been obtained by methods such as thermal CVD and plasma enhanced CVD (PECVD) by thermally decomposing B, C, and N containing precursors. Unfortunately, these as-prepared h-BNC films show very poor crystallization, and lack the properties of ideal h-BNC films predicted by theory.

1.2.2. Transition Metal Dichalcogenides (TMDC)

Although graphene shows interesting phenomena, its shortcomings affect its applications. To overcome these shortcomings and expend the frontier of 2D material research, people have start to study other material with detectable band gap and one of the interesting groups of materials is so-called TMDC and the very first one researched among this group is MoS2.

Bulk MoS2 has long been used as solid state lubricant, because of its layered structure similar to graphite. In the past, people once confused among graphite,
MoS$\textsubscript{2}$, and PbS$\textsubscript{2}$, since the physical properties are so similar to each other. Bulk MoS$\textsubscript{2}$ is semiconductor with an indirect band-gap of 1.2 eV. The band gap will open up as the number of layers decreases and eventually ends up 1.8 eV in single layered MoS$\textsubscript{2}$, and becomes direct band-gap semiconductor$^{43, 51, 52}$.

Because of the existing of band gap, MoS$\textsubscript{2}$ shows strong photo-response. So people start to explore the possibility of MoS$\textsubscript{2}$ to serve as ultra-thin photo-detector. The earlier study shows that MoS$\textsubscript{2}$ can provide a photo-responsivity of 0.42 mA/W$^{52}$, corresponding to a quantum efficiency of $\sim$0.08%, which is not high enough. However, later research shows an extremely high photo-responsivity of 880 A/W$^{53}$, which is the highest photo-responsivity value reported on 2D materials. Although the responsivity is strongly dependent on the contact type and condition (will be discussed later), it at lease shows the great potential of this material.

Because of the band-gap, MoS$\textsubscript{2}$ FET also shows smaller leakage current and larger ON/OFF ratio. But the problem is that the charge current mobility in this material is much lower (in the order of 10 cm$^2$/Vs) than graphene. Although it is once reported that the mobility was in the order of hundreds cm$^2$/Vs$^{54}$, it was soon been pointed out this fault came from improper theoretical model applied for mobility calculation$^{55}$.

Besides all of these studies, another special property of these materials is that the band-gaps locate at K and K’ points, which is similar to the position of Dirac points in graphene. This makes this material an ideal platform for valleytronics
study which is hard to be realized in graphene system due to its high six-fold symmetry\textsuperscript{44,45}. 
III-VI Layered Semiconductors

III-VI layered semiconductors refer to GaS, GaSe, GaTe, InS and InSe. III-VI semiconductors are important photo-sensitive material that can be used as photodetector\textsuperscript{56-58} and photo-voltage devices\textsuperscript{59}, due to their large non-linear effects, they can also be used as second-harmonic generation and THz generation sources\textsuperscript{60,61}. This chapter will discuss the fundamental properties of III-VI semiconductors and mainly focuses on selenide compound, but this discussion can also be applied to other III-VI semiconductors. This chapter will provide important information on crystal and band structures, which are closely related to the photo-conductivity measurement in the following chapters. Meanwhile, the symmetry analysis and Raman theory will provide key points for understanding the Raman spectra discussions later.
2.1. Crystal and Band Structures

All these layered III-VI semiconductors have similar structure and are composed of C-M-M-C (M-metal, C-chalcogen) layer, with hexagonal structure, as show in Figure 2.1 (InSe crystal structure, representing typical structure for III-VI compounds). Due to different stacking, the III-VI compounds have several phases. But for single layered III-VI compounds, they always show $C_{3h}$ symmetry, i.e. three fold rotation symmetry with reflection plane in middle parallel to the lattice plane, which is similar to 2H phase MoS$_2$.\textsuperscript{62,63} It may be possible to transform III-VI compound into 1T phase, but there is no related reported yet.

![Figure 2.1 - A typical layered III-VI semiconductor lattice structure](image)

The lattice structure of layered III-VI semiconductors is very unique, and they are composed by $M_2C_2$ molecular unit. Take InSe for example, the fundamental molecular unit is In$_2$Se$_2$. In this structure both selenium and indium atoms are in the configuration of $sp^3$ hybrid, which gives a tetrahedron shape.
Each selenium atom has three bonds connected to the indium, and all these bonds are nearly in lattice (xy) plan, and the electron orbitals are named p$_{xy}$-like orbital. The other orbital of Selenium atom is perpendicular to the lattice plane is called p$_{z}$-like orbital and is occupied by paired electrons provided by selenium atom alone. This structure is very similar to the ammonia molecule: the nitrogen atom has three bonds with hydrogen atoms and the other orbit is fully occupied by paired electrons provided by nitrogen alone.

For each Indium atom, there are four bonds surrounding it. Three of these bonds are formed with selenium atoms and the rest one is indium-indium bond, which is perpendicular to the lattice plane. In two of the three In-Se bonds, indium will provide an electron to pair with the other electron from selenium to form bond, while, for the rest one, both of the electrons are provided by selenium atom alone, and this band is so-called coordination bonding, just similar to the bond between nitrogen and boron in ammonia boron molecule.

As the p$_{z}$-like orbital of selenium atoms is perpendicular to the lattice plane, the electron cloud in such orbital will expand along z-direction and extend out of the lattice plane, so the p$_{z}$-like orbital coming from neighboring layers will overlap and strongly coupled to each other. The p$_{z}$-like orbitals from different layers are degenerate quantum states having the same eigen energy value. However, due to the overlapping and splitting of degenerate quantum states, the p$_{z}$-like orbitals from different layers will split and form a continuous energy band when the number layer is high enough. On the contrary, if the number of layer decreases, the interaction will
be weaken and the continuous energy band will reduce back to isolated quantum states and eventually the band due to $p_\sigma$-like orbital will disappear. This phenomenon is observed in our research and will be discussed in the following chapters.
2.2. Growth Method for Bulk and Thin Films

The melting point of III-VI semiconductors is relatively low, and they are still stable in liquid phase. (some other layered material will decompose at high temperature before melt ), so it is easy to get large size of bulk crystal from traditional crystal growth methods.

However, people have used III-VI semiconductors to study so-called van der Waals epitaxial for a long time. For a typical epitaxial growth, the first requirement is the lattice matching. When the lattice mismatch is too large, film will not grow on top of substrate. However, for van der Waals epitaxial, the lattice matching is not very strict. The substrate will only serve as a template to induce the material growth, but has no chemical bonding to the material growing on top. Figure 2.2 shows the mechanism of van der Waals epitaxy growth.64

Figure 2.2 –van der Waals epitaxy mechanism
Layered III-VI semiconductors, especially GaSe, are widely explored in the area of van der Waals epitaxial growth. Because they are stable, easy to be evaporated at high vacuum and, more importantly, the lattice constant of GaSe is very similar to the atomic spacing on silicon (111) surface (although lattice constant mismatching is not important, it is still easier to form large continuous films on a substrate with matched lattice constant).

However, people still have different opinion about the growth process. All the studies show that in the evaporation process GaSe will decompose into Ga₂Se and Se₂.⁶⁵ For the following steps, people have different views. Some believe that it is Ga that form chemical bonding with silicon first, then Se will attach to the Ga atoms and a half layer of GaSe is formed as a transition layer, on top of which full GaSe begin to grow.⁶⁶ Others believe that there is no transition layer, and the silicon will catch the Se atom first to form a hexagonal structure, and Ga will form banding to the Se atoms to form a continuous layer. After the banding between Ga and Se forms, Se will be released from Si atoms. These two process is demonstrated in Figure 2.3.⁶⁷

No matter which mechanism is correct, the van der Waals epitaxy provides a possibility for large area III-VI semiconductor atomic layer growth.
2.3. Application of III-VI Semiconductors

III-VI semiconductors exhibit lots of interesting optical properties. Because of its non-invertible central symmetry, III-VI semiconductor has large 2nd order nonlinear factor. GaSe is widely used as a second-order generation (SHG) crystal. Meanwhile, due to its high order nonlinear effect, it is also applied as THz crystal. Besides, III-VI semiconductors show strong photo-conductivity response, which makes them good materials for photo-detector and photo-voltage devices.
Because of this, people have started to explore the properties of atomically layered III-VI semiconductors, especially, their photo-response. In most of these reports, the photo-responsivity can reach very a large value, and this may result from optimized electrode configuration.

GaS layers show a photo-responsivity of 19.2 A/W\textsuperscript{68}, however, the band-gap is large so that it can only serve as NUV or UV detector. Mechanically exfoliated GaSe shows smaller band gap and the reported photo-responsivity of 2.8A/W\textsuperscript{69}.

Besides the photo-response, GaS and GaSe also show field effect\textsuperscript{70}. Exfoliated GaS is a n-type semiconductor having an ON/OFF ratio of 10\textsuperscript{4}, while GaSe is a p-type semiconductor with ON/OFF ratio of 10\textsuperscript{5}. However, as the band-gap is large, it needs large bias to control such FFT devices.
Chapter 3

Principles and Setups

In the chapter, the basic principles for experiment and data analysis are discussed, including the principle of Raman scattering spectra and symmetry analysis, the mechanism of photoconductivity and principle for device fabrication. As the photoconductivity measurements are performed on a home-built opto-electronic characterization system, the principles and designs of this system will also be discussed in details.
3.1. Raman Scattering Spectra of III-VI Layered Semiconductors

Raman is a very powerful method for 2D material characterization, since the coupling strength, scattering cross section are strongly determined by the number of layers. Raman scattering was first applied to graphene sample to study vibration modes of it and was also used as a quick thickness estimation method\(^{71-74}\). Meanwhile, the position of the peaks and the full width at half maximum (FWHM) can be used to estimate the defect in the sample\(^{75}\).

The other advantage of Raman scattering spectra lies in the fact that the Raman spectrum-meters are commonly integrated with microscopy system (Raman-microscope). The research on 2D materials are still in the early stage and people have not figured out a way for large area sample growth except graphene, so the layered flakes are always in the size of micrometers, on which one cannot use inferred spectra to study the lattice vibration, whereas, Raman spectra become very powerful in the research on 2D materials. The Raman-microscope can not only provide the Raman spectra but also can provide Raman-mapping\(^{71,73}\), which will give important space-resolved information, such as variation of thickness, boundary conditions, tension in samples\(^{76}\), interaction with substrate\(^{77,78}\), etc. Meanwhile, in many Raman setups, the double gratings design (to increase the spectral resolution, people will use two high density gratings in series in Raman spectrometer. Refer to double grating Raman spectrometer manufacture handbook for more information) will provide very large spectral region in the order of thousands of \(\text{cm}^{-1}\) without sacrificing resolution.
This type of Raman spectrometer can also be used as fluorphotometer to catch the fluorescence emission spectra from materials. Just as Raman mapping, people can also do fluorescence-mapping on 2D material to get information on band-gap and its distribution in space.\textsuperscript{79, 80} However, it is worth to notice that this kind of fluorescence spectrum can only serve as a reference when determine the band-gap, because it only provides the emission spectra. To analyze band-structure, electron transitions between levels and other related properties, one should analyze emission spectra, excitation spectra (the emission intensity as a function of excitation wavelength, it will provide more information about energy levels) and even absorption spectra simultaneously to get reliable conclusion. It is not convincing to state that the band-gap is larger (smaller) from the blue (red) shifting of the fluorescence emission spectra. This is a very common mistake in 2D realm and rarely noticed even nowadays!

\textbf{3.1.1. Raman Fundations}

To use Raman as a powerful method for 2D material study, one should be familiar with the fundamental principle of Raman scattering. Raman is a method to study the interaction between photons and lattice vibrations (in quantum point of view, the interaction between photons and phonons.). When the vibration in lattice changes the electric susceptibility of the material, it will induce Raman scattering. The classical physics describe the process in such a way.

The electric susceptibility can be described as following equation when considering the modulation due to lattice vibration,
\[ \chi = \chi_0 + a \sin(k \cdot \vec{r} + \omega t) \]

where \( \vec{k} \) is the wave vector and \( \omega \) is circular frequency of the vibration. Then the polarization can be expressed as

\[
P = \chi \varepsilon_0 E = E \varepsilon_0 \chi_0 + E \varepsilon_0 a \sin(k \cdot \vec{r} + \omega t) = E \varepsilon_0 \chi_0 + E \varepsilon_0 a [e^{i(k \pm \vec{p}) \cdot \vec{r} + (\omega_p \pm \omega)t}] \]

One can note that in the second term, the frequency of the incident light (\( \omega_p \)) will charge into \( \omega_p + \omega \) and \( \omega_p - \omega \). This means the modulation due to lattice vibration will shift the frequency of incident. By determine the frequency different from the Raman scattering, one can know the lattice vibration frequency. The term corresponding to \( \omega_p - \omega \) is called Stokes scattering and the other term is called anti-Stokes scattering.

Although the classic theory gives a very simple and clear picture, it is hard to explain more complicated Raman scattering process, such as resonant Raman. It is also hard to deduct the Raman selection rule from it. So it is important to introduce the quantum theory of it. Deduction of Raman scattering theory will not be discussed in the main-text of this thesis; one may refer to the appendix for it (The deduction is done by me (Sidong Lei), and the attitude may be different from majority text-books). However, some simple conclusion and equations can help to understand the quantum view-point about Raman scattering.

According to quantum theory, the Raman scattering strength can be expressed as approximately.
Here $|f>$ is the final quantum state, $|i>$ is the initial quantum state, and $|n>$ is some intermedia state, $E_p$ is the energy of excitation photon, $E_v$ is the energy of phonon corresponding to the Raman scattering process and $E_{nl}$ is the energy difference between intermedia state and initial state. The whole quantum transition process can be expressed as Figure 3-1. If the final state has one more phonon than initial state, the whole process is called Stokes scattering; if the final state has one less phonon, the whole process is called anti-Stokes scattering.

\[
p = \beta \sum_n \frac{<f|H|n><n|H|i>}{E_p - (E_{nl} \pm E_v)}
\]

**Figure 3.1 – Raman Scattering Process**

**3.1.2. Virtual Level and Resonant Raman**

One of the most important concept involving in the whole quantum picture is virtual state, which is illustrated with dashed line in Figure 3.1. Virtual state is an imaginary quantum state, and is not necessary to correspond to any actual quantum
state. From the above equation, one will find that the whole process is a summary of all possible routes, i.e. $\sum |n > < n|$. So virtual state is not a special quantum state, instead, a summary of all possible intermedia quantum states. One call also considers the virtual state in a more classic way. A string always has its eigen vibration states. However when the string is forced to vibrate at a certain frequency, which does not equal to any eigenvalue of the string, it will vibrate exactly at the frequency of the force. But this vibration mode is not any eigen-mode of the string. So one can call this vibration mode the virtual vibration state of the string.

One special situation is that when the energy of photon equal to energy gap between to actual energy levels. Then the dominator of the expression above will tend to infinity. At this time, only the transition between these two levels dominates and will give a very large transition possibility. If this happen the selection rules for Raman scattering will get loosen and the scattering intensity will be much stronger. This process is called resonant Raman. When still applying the analogy mentioned above, the string is forced to vibration at a frequency equaling exactly to the eigen-mode of it, then the amplitude of the vibration will be strongly enhanced; and classically, this process is called resonance.

Resonant Raman is an important process that is utilized to analyze the energy level structure information of 2D material and relevant experiment will be discussed in following chapters.
3.2. Photoconductivity

Photoconductivity is another important branch in 2D material research besides FET. The purpose of this research has two aspects. First of all, for 2D material it is hard to measure the absorption since the flakes are usually very small. The photo-conductivity measurement can partially replace absorption measurement to characterize the band-structure and excitation in 2D materials. Meanwhile, it is also important to fabricate 2D photo-sensitive materials into ultra-thin photo-detectors or solar cells. As a result the photoconductivity measurement can provide important data for both scientific research and application.

3.2.1. Basic Principle of Photoconductivity

In principle, any material having forbidden band should have the property of photoconductivity. Photoconductivity refers to the effect that when a piece of non-metallic material exposed to illumination of radiation with energy larger than the forbidden band-gap, the conductivity or resistivity of this material changes. This is because that in non-metallic materials, the conductivity are mainly contributed by the charge carriers. The charge carriers can be electrons or holes. The conductivity is proportional to the number of charge carriers. The more charge carriers the material has, the more conductive it will be.

When shining a light or radiation onto the surface of the material, electron will be excited into the conduction band leaving a hole in the valence band, if the energy of the photo is larger than the band-gap. In the way, the radiation will help to
generate electron and hole pairs, i.e. number of charge carriers increases and so does the conductivity of the material. However, in some rare case, the radiation will decrease the conductivity of the material and this effect is called negative photoconductivity\textsuperscript{81}.

Since the energy of the photo in photoconductivity measurement should be equal or higher than the excitation energies in materials, so the photoconductivity spectrum can be utilized to analyze the band structure and excitation in materials.

Meanwhile, the effect of photo-conductivity will continuous even after the radiation disappears if the electron and hole do not recombine to each other. So by measuring the time resolved photoconductivity, one can tell the life time of the electron-hole pairs and even tell the interaction between them\textsuperscript{52, 69}. Also, the life time of electron-hole pairs also affect the response speed of a photo-detector, so the life time or response time is a very important parameter to determine the performance of a photo-detector.

### 3.2.2. Important Parameters

To analyze the photoconductivity and characterize the performance of a photo-detector, there are several important parameters need to be concerned, spectral response, photo-responsivity, linear dynamic range, signal to noise ratio (S/N), response time, etc.

Spectral response refers to the response of photodetector as a function of wavelength or photon energy. This is mainly determined by the energy level
structures, such as band gap. Similar to absorption spectra, the photo-response will drop down when the energy of photon is smaller than the band gap of material. Figure 3.2 shows the typical spectral response of commercial silicon photo-detector. The spectrum edge corresponds to the band-gap of silicon which is at about 0.8 eV.

![Figure 3.2 - Photo-responsivity of typical silicon photo-detector](image)

One common phenomenon is that the response of the material, especially the bulk crystal, always shows stronger response near the edge, and drops down as the wavelength goes shorter. This is because the shorter the wavelength is, the sallower the light will penetrate\textsuperscript{82}. Then at shorter wavelength, the excitation is not as effective. However, for silicon, the response in whole spectral region is near a constant which makes silicon serve as a standard to calibrate other photo-detectors.
3.2.3. Configuration of Photo-Detectors

The generation of electron-hole pair is just the first step for photo-sensing process. The fabrication and configuration of photo-detectors strongly affect the transportation of the electron and hole, and consequently, affect the performance of photo-detectors. Here several commonly used photo-detector configurations are discussed.

*Metal-semiconductor-metal (MSM) photo-detectors*

MSM photo-detector is one of the simplest types of photo-detectors. It is just a piece of photo-sensitive semiconductor between two pieces of (same) metallic electrodes serving as anode and cathode.

For measurement purpose, people always want to choose metals with smaller work functions to promise the Fermi level of the metal is higher than the bottom of conduction band in the semiconductor so that the photo-excited electrons can be easily collected by the electrodes. Typically, people will use aluminum, sodium, potassium and even lithium. However, this configuration will lead to large dark current, (current passing through the material even there is no light shining onto the material) since the conduction band serve as a channel allowing electrons to be injected by the electrode and pass it. At the same time, this configuration may lead to external quantum efficiency larger than 100%. This is because once the electrons are excited into the conduction band, the material will serve as a conductive channel and electrons can pass through it for several times, demonstrated in Figure 3.3. This will not improve the sensitivity of the material.
(The recycling of electrons will not change the excitation process which determine the sensitivity of the photo-detector, as the quantum efficiency for photo-electron generation will not be improved.), but will help to increase the S/N.

![Diagram of Ohmic MSM photodetector](image)

**Figure 3.3 – Photo-current gain process in Ohmic MSM photodetector**

As a contrast, people prefer to use metal with a deeper work function to serve as electrodes. The ideal position for Fermi level should be in forbidden band. The matel will form Schottky contact to both p-type and n-type-semiconductors. This configuration leads to several benefits, as discussed below.

The following discussion is based on the assumption that the material is n-type, but it can also be applied to p-type semiconductors. The band-structure of Schottky MSM photo-detector is demonstrated in Figure 3.4. It is actually two Schottky diodes sitting back to back. When there is no light illuminating the
semiconductor and at low bias, electrons cannot pass through the semiconductor channel as they cannot pass the barriers. Even at higher bias, the dark current is still very limited, as there is always one-side has Schottky barrier which blocks the electrons.

![Diagram of Schottky MSM photodetector](image)

**Figure 3.4 – Photo-current gain process in Schottky MSM photodetector**

However, when a light is shined onto the semiconductor, the holes will be generated, and the Schottky barrier for electrons is not barrier for holes, so the holes can pass through it easily. With the help of bias, the cathode serves as hole collector and anode serves as electron collector and current generates. The electron and hole will recombine to each other at cathode.

Hence the Schottky MSM always show very limited dark current and high sensitivity, as the band bending due to Schottky contact can help to separate electron-hole pairs and inject them into collectors (electrodes). At the same time, it
is a good way to measure the quantum efficiency of the material. Because, unlike in
Ohmic contact case, the electrons can only pass through the semiconductor once
before they recombine to each other. If one wants to measure the quantum
efficiency and intrinsic photo-responsivity of the material, he should use Schottky
configuration instead of Ohmic one.

Here, it is necessary to give a brief discussion about the MoS$_2$ work published
on Nature Nanotechnology$^{53}$. In this paper, they stated that the photo-responsivity
of the material is 880 A/W, which is really huge, corresponding to a quantum
efficiency of 200,000%. One possible explanation is that the contact they used is
Ohmic, or even they had Schottky barriers, they were strongly eliminated by large
bias. So they were just recycling the electrons. This will not help to increase the
sensitivity of the material but maybe help to improve the ON/OFF ratio and S/N of
the device. However, to state “ultra-sensitive” is misleading!

**PN junction photodetectors**

As discussed in Schottky MSM photo-detector, electron-hole separation with
the help of band bending and external bias is very important to improve the speed
and sensitivity of photo-detector, because it can help separate the electron-hole pair
by build-in electrical field and prevent the recombination. One way to improve the
performance of photo-detector is to fabricate some structure with band bending on
purpose; and one of the most commonly used configurations is pn junction.

When a pn junction serves as photo-detector, two working modes are
commonly use. One is photo-voltage mode and the other is photo-current modes. In
photo-voltage mode, there is no bias applied onto the detector externally and the load of the external circuit tends to be infinity (so operational amplifier is always added to the circuit). When photo electron-hole pairs are generated, they will be separated with the help of electrical field in the depletion region, and hole goes to p region and electron goes to n region, as shown in Figure 3.5.

![Figure 3.5 - pn junction photo-detector working in voltage mode.](image)

This process will lower the barrier in the pn junction and increase the diffusion current to compensate the photo-current to maintain the whole system electrically neutral. The dropping of barrier is measured as a forward voltage across the devices.

In photo-current mode, a reversed bias is applied to the pn-junction to increase the height of barrier and the external field will superposition with the build-in field to increase the speed of electron-hole separation, as illustrated in Figure. 3.6. In this case, the depletion region is wider and the capacitance is smaller, meanwhile, the electrons and holes move faster due to larger electrical field, as a
result, the photo-current mode give the detector faster response speed. Higher bias will help this process, but it may also breakdown the device.

![Photo-excitation](image)

**Figure 3.6 – pn junction photo-detector working in current mode.**

*PIN junction photodetectors and Avalanche photodetector*

As the photo-generated electrons and holes are typically generated and separated in depletion region, it will help to increase the efficiency by increasing the depletion region width. However, the depletion region is determined by the material and not very controllable. To solve this problem, PIN junction photodetector are fabricated. In this device, there is an intrinsic layer between p-type and n-type semiconductor, and the band structure and working principle are shown in Figure 3.7. The intrinsic layer here has the same function of depletion region in pn junction and the photo-generated charge carriers will be generated and separated in this region. The benefit of this structure is that the intrinsic layer can be much thicker
than depletion region so that more photos can be absorbed and the quantum efficiency can be improved.

![PIN junction photo-detector principle](image)

**Figure 3.7 – PIN junction photo-detector principle**

The structure will also serve as so called avalanche photo-detector. When a large reverse bias is applied to the device, the electrons and holes generated by photos will be accelerate to a very high energy so that it will generate more electron-hole pairs during scattering. As a result, the photo-current will be amplified. The whole process is very similar to photo multiplier tube.

In this thesis, only Schottky MSM photo-detector configuration will be discussed.
3.3. Opto-Electronic Characterization System

2D material is a new realm to every physical, chemical and material scientist. It provides great opportunity to discover new phenomena and extend the frontier of science. However, it also brings challenge to researchers. One problem is how to characterize the properties of 2D material properly and correctly, especially the optical and opto-electronic properties. Most of the traditional opto-electronic devices are based on bulk materials, and even they are integrated into device with smaller size, the properties are still the same to bulk ones. So one can always study the optical and opto-electronic properties of them will large crystals and apply the data to device fabrication with smaller size.

However, for 2D material, everything changes. The properties of few-layered material are very different from the bulk one. One can never speculate the properties of few layers from the bulky measurement. Meanwhile, 2D material realm is very young and very far from fully-developed, even half-developed. For most layered materials, one can only get flakes with sizes of micro-meters. All these bring challenges to 2D material characterization. As mentioned above, it is hard to apply commercial absorption-meter, fluorophotometer to study the material directly. As a result, just as the beginning of every other scientific realm, one has to try to build his own system that specialized to his research.

The home-built opto-electronic system is shown in Figure. 3.8. It has functions of photo-conductivity and photo-voltage measurement, field-effect measurement, time-resolved measurement and temperature dependent
measurement (under construction). And the whole system consists the following modules, vacuum probe-station, low current level source-meter unit (SMU), lock-in amplifier, low-noise DC amplifier, monochromator, laser source, laser stabilization and modulation system, close cycle cryo-state. The principles and designs of the system will be described in detail below.

![Home-built photo-electronic measurement setup](image)

**Figure 3.8 – Home-built photo-electronic measurement setup**

### 3.3.1. Probe-Station and Vacuum Build-Ups

The vacuum probe-station is built with standard parts for vacuum instruments so that it is very easy to do any modification or upgrading to the system. The picture and design diagram of the probe-station is shown in Figure 3.9. The probe-station contains four tri-axial BNC feedthroughs connected with probes in chamber, and two of them are equipped with edge welded bellows and xyz stage
so that one can manipulate the sample and measure multi-samples without venting the chamber. The fixed ones are mainly used for gating.

**Figure 3.9 – The vacuum probe-station**

The top-cover of the chamber has an optical view port made of fused silica (Thorlabs UV Fused Silica High-Precision Window), whose transmission spectrum is shown in Figure. 3.10. It can meet the demand for most of the near-UV, visible and near-IR measurement. Meanwhile, another similar cover has a sapphire view port to satisfy the requirement of UV measurement.
The bottom of chamber is sealed with a KF 50 blank flange temporally and a close-cycle cryo-state will be attached to it for temperature dependent measurement.

### 3.3.2. Photo-Conductivity Measurement

To realize the photo-conductivity measurement, two major parts should be contained in the system. One is light source; the other is electrical measurement system. The basic configuration is demonstrated in Figure 3.11.

Followed by focusing, the light (either from monochromator or laser) will be shined onto the device. The light will be focused onto the flake with electrode on top it. The probes connected to the vacuum feedthrough will be loaded on to the small pads for electrical signal collection and amplification. Typically, the measurements performed on this setup contain response-spectrum measurement, light intensity dependent I-V curve measurement and time-resolved measurement.
When one wants to know the spectral response of the material, a continuously light source covering the whole spectral range is necessary. Here, we use Xenon lamp or Tungsten lamp as light source followed by a monochromator. The monochromatic light emerging from the outlet port will be focused onto the sample. Then the photo-conductivity change will be recorded by a SMU or oscilloscope.

**Figure 3.11 – Diagram of opto-electronic measurement system**
As the power of the monochromic light coming from the monochromator is commonly very weak, the electrical signal from the device is undetectable unless it is amplified. Two amplification methods are typically applied, lock-in amplifier and low-noise DC amplifier (They will be discussed later.). After amplification, the signal is send to SMU or oscilloscope for recording.

For light intensity dependent measurement, such as external quantum efficiency or responsivity, one needs to know and control the power of the light source precisely. In this case, monochromator is not ideal, as it is hard to control the output power of it. Instead, laser is a better option. The laser beam will pass through an acoustic-optical modulator (AOM) first, then will be focused and shined onto the sample. The AOM has two functions. (The principle of AOM will be discussed in the laser stabilization and modulation section.) One is to stabilize and control the power of the laser; the other is to modulate the laser for time-resolved measurement.

Generally, the power of laser is much stronger than the power output by monochromator so that the photo-response of the material is much stronger and no amplifier is necessary before measurement and data collection.

3.3.3. Low Current Level Measurement- Connections for DC Measurement

As mentioned in last section, sometimes, the signal coming from the device is very weak and need to be amplified before doing any measurement. However, it is not enough to just amplify a signal without care, as when one amplify a signal, he also amplify the noise accompanying signal, especially when he is using low-noise
DC amplifier. The “low-noise” here means the amplifier will not generate much noise itself, but it do not mean that it can filter the noise generate by the device and connection. (Lock-in amplifier is designed to filter the noise, so the requirement for measurement when using a lock-in amplifier is much more relaxed than DC amplifier.) One cannot get rid of the noise from the device, as it is an intrinsic property of it, but one can reduce the noise coming from environment and connections.

The chamber itself is a good shielding for measurement, because the whole probe-station chamber is made of stainless steel and properly grounded, and it is isolated from vibration by optical table. The only possible part may suffer from the radiation hazard is the view port.

The other major source of the noise is the BNC cables and connectors. By bending, twisting, vibrating the cable, one can generate a current of hundreds of pico-ampere. So one should always make sure all the cables are anchored steadily. However, even with careful treatment, the ordinary co-axial BNC cable is not suitable for the measurement with a current level lower than nano-ampere, as the leakage from central cord to outer shell is in the order of tens to hundreds of pico-ampere, especially when long cable is applied. In order to measure a current smaller than this value, one should use tri-axial cable and connectors instead of co-axial BNC cable and connectors\(^\text{84}\). (One can still use co-axial cable for lock-in amplifier.) As demonstrated in Figure 3.12, the only different between tri-axial and co-axial cable is that there is an additional cylindrical cord between the central cord
and outer shield, and this layer is called guarding, which prevent the leakage between central cord and outer shell.

![Diagram of triaxial cable components](image)

**Figure 3.12 – An example of triaxial cables**

When connected to the device under test (DUT), the guarding layered is always kept at the same voltage level to the central core so that there will be no leakage between the central cord and guarding layer. The leakage will only happen between guarding and outer shell, which will not be detected by the ammeter connected to the DUT via central cord, as demonstrated by Figure 3.13.

![Diagram of triaxial cable connections](image)

**Figure 3.13 – Connections for triaxial cable**

All the DC measurement performed on this setup is done with the help of triaxial cable. For lock-in amplifier measurement, a tri-axial to co-axial adapter is
provides. In this adaptor, the outer shells and central cord are connected together respectively, living the guarding layer unconnected.

### 3.3.4. Low Current Level Measurement - Lock-In Amplifier

The principle of lock-in amplifier is introduced in details nearly in every book talking about signal treatment and measurement. Here, a brief introduction and discussion will be proposed.

Typically, the signal coming from DUT always accompanies noise. Whether the signal can be distinguished from the noise depends on the ratio between the level of signal and the level of the noise (S/N). When the S/N is really lower, the measurement will become very noisy and un-interpretable.

However, the noisy signal is based on the view-point of time domain. If one does Fourier transformation to the noisy signal, he will find that the noise spectrum spears the entire frequency domain, and the signal is one Fourier peak in the entire spectrum. Although in time domain, the S/N of the modulated signal is small, in frequency domain, one can still distinguish the Fourier component peak from the noisy back ground. Meanwhile, the higher modulation frequency is, the more striking the signal Fourier component peak appears, because at the higher frequency region, the noise level will decrease significantly.

The question is how to get the high frequency signal and how to select the special peak due to the signal from the noise peaks. The solvent is to modulate the DUT. Typically, the signal coming from the DUT is the response to some physical
parameters. For example, in photo-detector, the electrical signal is a response to light intensity. So by modulating the injection light, the output electrical signal will also be modulated and give out a high frequency signal. If one wants to study the resistivity of a material, one can modulate the voltage across the DUT and the output current will follow the change of voltage and be modulated. To sum up, one should always modulate the input of the DUT and measure the modulated output. It is worth to mention that the output of the DUT is not necessarily modulated at the same frequency to the input modulation. One example is $3\omega$ method for thermal conductivity measurement.

The next job is to determine which Fourier component in the spectrum corresponds to the signal because not only the signal, but some other interference can also give a striking peak, such as the 60 Hz from the electrical lines and its double frequency, some radio broadcasting signals, mobile phone signals. This task is finish by an instrument called mixer, it will do the following calculation determine which Fourier component is the one corresponds to the signal.

\[
sin(\omega_0) \times \int A(\omega) \sin(\omega t) \, d\omega = A(\omega_0)\delta(\omega_0 - \omega) + \frac{1}{2} \int \cos(\omega_0 - \omega) + \sin(\omega - \omega_0) \, dx
\]

From the above equation, it can be seen that the mixer will multiply the output signal with a reference signal with modulation frequency, and the component with the same frequency to the reference will be shifted to zero frequency, i.e. a DC output. When using a mixer, one will send the DUT signal and a
reference signal to the mixer. The reference signal is generally just part of the modulation signal which is applied to the input of the DUT.

In an actual lock-in system, there are several parts: modulator, DC amplifier, mixer and filter. The diagram of the system is shown in Figure 3.13. The modulator will modulate the input of the DUT. The output from the DUT will be send to DC amplifier for amplification. In this stage, both signal and noise will be amplified. Then the amplified signal is send into the mixer followed by filtering. The mixer pick up the Fourier component corresponds to the output signal by shifting it to DC. Then the output is sent to filter to get rid of all other component with non-zero frequency and leave only the DC component, i.e. the signal origin from the DUT.

![Diagram of lock-in amplifier](image)

**Figure 3.14 – Diagram of lock-in amplifier**

### 3.3.5. Lock-In Amplifier V.S. Low Noise DC Amplifier

Lock-In amplifier is a very powerful instrument for weak-signal and low S/N signal measurement. But we still prefer to use low noise DC amplifier in some case. In our system, both methods are provided.
The drawback of lock-in amplifiers lies in such facts. One has to modulate the input of the DUT, so that all the outputs actually represent the AC response of the DUT. It is hard to get the DC response of the DUT by lock-in amplifier, especially when the response of the DUT is non-linear.

At the same time, for some DUT the response is too slow to be modulated, as a result, the lock-in amplifier cannot be used.

Meanwhile, the DUT always have some capacitance which will allow AC current to pass through the device. Although this current is not due to the response of the DUT, it always has the same modulation frequency and hard to get rid of.

More important it is impossible to use lock-in amplifier to do time-resolved measurement.

If the above issues become concerns of the experiment, one should choose low noise DC amplifier instead of lock-in amplifier. Two kind of DC amplifier are provided in this system. One is SRS (Stanford Research System) low noise current preamplifier and low noise voltage amplifier. This system will amplify the signal to a level that oscilloscope can detect and record. As they are pure analog instrument, they can operate at a very high speed. So we use them for time resolved measurement. Other system is Keithley 2634B SMU. This SMU can detect a current in order of fA, so no other preamplifier is needed before it. One can control the system with software to realize automatic instrument control, data acquisition and analysis. However, SMU is a digital instrument, the data acquisition, storage and transferring are controlled by the micro-processor inside it, and all these operations
will take one or more clock circles. So unlike pure analog instrument, the SMU will not work in a real time way.

3.3.6. Laser Stabilization and Modulation

As mentioned earlier, when power dependent measurement is performed on this setup, laser will be used and the power of the laser needs to be precisely controlled and stabilized. Meanwhile, when performing time-resolved measurement, one may also need to modulate the laser. To achieve all these purposes, AOM is applied to control the laser power.

AOM is made from a piece of crystal or glass with a radio frequency (RF) piezoelectricity transducer. The transducer will change the RF radiation into mechanical vibration and inject it into the crystal or glass. As the mechanical vibration wave propagates along the crystal or glass, some parts of the crystal or glass will be compressed, and some parts will be stretched, so that a structure similar to grating will be formed by the wave. The intensity of the first order diffraction is determined by the amplitude of the mechanical wave propagating in the crystal or glass, and the amplitude is determined by the power of the RF. So by changing the RF power, one can control the intensity of the first order diffraction. In practice, a laser will be focused onto the crystal or glass, and first order diffraction will be selected by an iris and all the other diffraction will be cut off.

To control and stabilize the laser power, a feed-back loop is constructed as demonstrated in Figure 3.15. A small amount of first order beam will be split off by a
piece of slide glass and injected into a photo-detector to monitor the intensity of the beam, and the rest of the beam will be sent to the DUT. The signal from the monitoring photo-detector will be sent to the feed-back circuit to compare with the set point. If the laser intensity is lower, the circuit will command the RF driver to increase the power, and vice versa.

![Diagram of laser power stabilization and modulation loop](image)

**Figure 3.15 – Laser power stabilization and modulation loop**

To modulate the light intensity for time-resolved measurement, one can just command the signal source to give out a demanded waveform instead a DC set-point.
3.4. Device Fabrication

At the end of this chapter, I would like to introduce the typical methods for device fabrication. Although one can always refer to textbook or technical website for more details about lithography, material deposition, it still necessary to describe the device fabrication process in this thesis. One the one hand, it is part of the entire work and nearly the most important part. One the other, it will provide important information if one want to follow this thesis and repeat the works. Based on these purposes, only the key parameters and steps will be listed in this chapter and no principles will be discussed.

3.4.1. Photo Lithography

Photo lithography is for fabrication of repeat and large areas of patterns. Here a strategy for fine pattern fabrication (~500 nm) will be discussed. Typically, 1813 photoresist will be applied in this process. The photoresist will be spin coated on the substrate with a speed of 4000 RPM, which will give photoresist layer with a thickness of 200 nm. This speed is for very fine pattern fabrication, since the 1813 do not support large height/width ratio, i.e. the width of a line should not smaller than its height, and otherwise, the whole structure will collapse. Meanwhile, no LOR (lift off resist) layer is applied, because fine structures are very easy to collapse with undercut structure.

The coated substrate will baked at 120 degree Celsius for more than 1 min. After that it will be exposed to UV light on masker aligner with a dose of 150
mJ/cm². Then dip the exposed substrate in FM 319 for 5-10 seconds followed by very gentle washing with DI water.

Following the steps described above, one can get a pattern as small as 500 nm.

However, the photo lithography process may contaminate the sample. As a result, in this thesis, photo lithography is typically applied for pattern fabrication, such as makers, gating electrodes, etc. When it is needed to put electrode on samples, e-beam lithography is a preferred method.

### 3.4.2. E-Beam Lithography

E-beam lithography can give very precise and fine patterns so it is utilized to fabricate device on exfoliated few-layered samples, since the size of the flakes are usually very small (several micro-meters).

The exfoliation is usually done on top of markers (SiO₂ substrate with numbers on it to help localize the sample), which is shown in Figure 3.16. Then a layer of PMMA A3 is coated on top with a spin speed of 2000 RPM for 1 minute and this process will leave a layer of 200 nm PMMA. After baked at 120 degree Celsius for 1 min, the substrate is ready for E-beam lithography.
Figure 3.16 – Digital markers on 285 nm thermal oxidized silicon

During lithography, 30 kV high voltage is applied and the current is chosen to be 40 pA. The explosion dose is 450 μC/ mm².
Chapter 4

Synthesis of Few-Layered GaSe and Photo-Conductivity Study

From this chapter, we will begin the discussion on the major parts of these works. Before beginning the following chapters, it is strongly recommended that reader should read at least Chapter Three, as it describes the experimental setups and methods in details. The following chapters will not repeat relevant context.
4.1. Introduction

As discussed in Chapter One, although graphene shows large electron and hole mobility with a value of $10^6 \text{ cm}^2/(\text{Vs})$, the absence of band gap limits the feasibility of graphene based field effect transistors, because of its poor on/off current ratio\textsuperscript{24}, and results challenges in building semiconductor logic circuits. Meanwhile, the zero band-gap structure in graphene also restricts the application of the material in the realm of opto-electronics.

To overcome the shortage of graphene, people begin to search for other similar van der Waals type of layered material for electronic and opto-electronic application. Gallium selenide (GaSe) is one layered crystal widely used in the field of opto-electronics\textsuperscript{86}, nonlinear optics and terahertz experiments\textsuperscript{48,87,88}, and its single and few atomic layers have begun to attract the scientific community.

Bulk GaSe has a band gap about 2.0 eV\textsuperscript{89,90}, and shows different crystal structures, such as $\beta$-GaSe, $\epsilon$-GaSe, $\gamma$-GaSe, etc\textsuperscript{91}. Although having varied stackings, they are all generated from the same fundamental layered building block, the GaSe layer, as shown in Fig. 3-1. Each GaSe layer has a Ga-Se-Se-Ga structure\textsuperscript{91}, with a $C_3h$ symmetry\textsuperscript{92} and a lattice constant of 3.74 nm\textsuperscript{93}. GaSe is usually a p-type semiconductors, due to the Se vacancy\textsuperscript{94}. This native defect in bulk crystal leads to large carrier density about $10^{15}$ to $10^{16}$ cm$^{-3}$ \textsuperscript{94,95} and a hole mobility in tens of cm$^2/(\text{Vs})$ range for bulk materials. Recently, there have been some reports on properties and applications of exfoliated GaSe. These exfoliated samples shows good photo-response, and on/off ratio\textsuperscript{69,70}. 
However, more complicated device fabrications needs large area of single crystals, which cannot be met by exfoliation from bulk materials. At the same time, the electron transportation may strongly depend on the orientation of the crystal. But it is hard to study the anisotropy of the material unless one can determine the orientation precisely.
Hence, the technique for single crystal growth of layered materials is an important step for 2D material preparation and pursue of their application. So far, CVD graphene\textsuperscript{96}, h-BN\textsuperscript{97}, MoS\textsubscript{2}\textsuperscript{43} have been realized. Van de Waals epitaxial growth of GaSe is one of the most important techniques developed for preparation of its few-layered samples. As the lattice constant along a-axis of GaSe is very close to the atomic spacing on Si (111) surface, which also comprises of a hexagonal order, GaSe can grow on Si (111) surface epitaxially. Extensive researches on understanding this growth mechanism have been done. However, the epitaxial material is hard to be removed from the substrate, and this entail difficulties in material characterization and application. So it is important to develop a method to grow GaSe on insulating substrate.
4.2. Material Synthesis

The growth method discussed in this thesis is vapor phase transport (VPT). It is a process of vaporization, transport and recrystallization. The whole material synthesis processes contains GaSe crystal preparation, VPT growth seed preparation and VPT growth.

Before describing the growth process, it is necessary to describe the growth setup first.

4.2.1. VPT Growth Reactor

The design of the VPT growth Reactor is shown in Figure 4.2. The reactor should sustain high temperature under high temperature, so fused quartz tube is utilized. One end the tube is closed, the other end is attached to a quartz tube to CF 1.33” stainless steel flange adaptor. After loading the sample, the CF flange is connected to a below vacuum valve with other CF flange by a copper gasket, shown in Figure 4.3. The leakage from the copper gasket can be ignored. The below valve (Swagelok SS-BNFR4-P) can help to hold the high vacuum (leaking rate 4×10⁻⁹ cm³/s). The other end of the below valve is connected to a KF25 flange which can be connected to pump directly and quickly for pumping down.
After loading the samples and seal CF flanges, one should open the valve and connect the KF flange to pump. Then one should pump the tube down and flush it with high purity argon and repump it down. After repeating this process several times, one can close the valve after the vacuum reaches the desired level, turn off the pump and disconnect the KF flanges from the pump. After all these steps, the tube is ready for warming up.
The other important feature is the contraction on quartz tube near the closed end (15 cm away for the close end), and the function of it will be introduced in following section.

4.2.2. GaSe Growth Principle

Figure 4.4 demonstrates the fundamental process for the growth. The VPT tube is placed in a two zone furnace, in the high temperature zone, GaSe will decompose into Ga$_2$Se and Se$_2$, and both of these species are in vapor phase. Under high vacuum, these two kinds of molecules will move nearly freely from the surface of GaSe to low temperature zone and begin to grow on a substrate with seeds for crystal growth on top.

![Figure 4.4 – Fundamental process for GaSe VPT growth](image)

Figure 4.4 – Fundamental process for GaSe VPT growth
On the high temperature end, the evaporation rate is determined by lots of factors, such as GaSe surface condition, the way putting GaSe source, temperature fluctuation, etc. Under the influence of so many factors, it is hard to control the evaporation rate. One way to solve this problem is to fabricate an effusion cell, demonstrated in Figure 4.5, and this is the purpose of the contraction on the quartz tube. In an effusion cell, large amount of molecules will be trapped in a vessel with a small opening, from where the molecules will escape. As the open is so small comparing with the volume of the vessel that the escaping of molecules will not change the thermal distribution of the molecules in the vessel. In other word, in the vessel, the molecular gas is in thermal equilibrium and the thermal state of gas is only determined by temperature and has nothing to do with other factors. In this case, the velocities of the escaping molecules are determined by the equilibrium distribution and are only determined by temperature. To sum up, the function of the effusion cell (the contraction in our case) is to provide a more controllable evaporation rate which is determined by temperature only.
On the low temperature end, the Ga$_2$Se and Se$_2$ will recombine into GaSe and the crystal will begin to grow under some special conditions, such as the existence of crystalline site (growth seed) or template (silicon (111) surface is one typical template, as explained in Chapter Two.). In this research, it is necessary to get GaSe on top of insulator substrate, so silicon wafer with 285 nm thermal oxidized SiO$_2$ surface is chosen, on top of which small GaSe particles are dispersed to serve as seed for crystal growth and GaSe few-layered flakes can grow around it.

4.2.3. Precursor Preparation

As mentioned above, both evaporation source and growth seed are made of GaSe crystals, so crystal synthesis is the first step for precursor preparation.

GaSe crystal is prepared with Ga$_2$Se$_3$ (99.99%, Alfa Aesar Company) and gallium (>99.99%, Sigma Adrich Company). Ga$_2$Se$_3$ is grounded into powder and mixed with gallium with a molar ratio of 1:1, then sealed in a quartz tube under vacuum (<10$^{-5}$ torr). Guided by the phase diagram of Ga-Se system$^{98}$, shown in Figure 4.5, the mixture was heated up to 950 $^\circ$C in 2 hours and kept at 950 $^\circ$C for 1 hour. Then the system was cooled down to 850 $^\circ$C in 2 hours followed by natural cooling down.
The aim of this growth method is to provide small size crystals for next steps, as both evaporation source and growth seeds need GaSe powders instead of bulk crystal with large volume. We cannot use gallium and selenium mixture because the will give bulk crystal will large size.

Figure 4.5 shows the SEM image of as-grown crystal. The acquired samples have a diverse morphology, but most of them have triangular or hexagonal structures and have cracks between van de Waals molecular gaps showing a mica-like shape obviously, which is an evidence of layered structures. For further elemental analysis of the crystals, the energy dispersive X-ray spectroscopy was applied to different positions of the crystals and all of them and revealed an atomic
ratio around 1:1, suggesting a successful synthesis of GaSe in this process, as shown in Fig. 3-8.

Figure 4.7 – SEM image of synthesized GaSe micro-crystal

Figure 4.8 – EDX spectra of synthesized GaSe micro-crystal
The crystals then are separated into two parts for precursor preparation. One part is grounded into finer powder mechanically to serve as evaporation source, while the rest is dispersed in isopropanol by sonication to form small pieces with a size of micro-meter or nano-meter. Then the isopropanol dispersed with GaSe flakes is further diluted and dropped to cleaned silicon wafer with 285 nm thermal oxidized layer to serve as growth seeds.

The powder will be sent to the close end with a thin tubing, and the treated silicon wafer will be dropped into the VPT tube and get stuck by the narrower part in front of the contraction. After all these treatments, the VPT tube will be pumped down to vacuum.

4.2.4. Sample Growth and Characterization

The treated wafer and GaSe source were sealed in the quartz tube with two vessels under vacuum (<10⁻³ torr), shown in Fig. 3-9.

![Figure 4.9 – Configuration of GaSe flake growth reactor](image)
The vacuum environment can protect the precursor from oxidization and provide a mean free path large enough for mass transfer. The source vessel and substrate vessel were heated up to 750 °C and 720 °C respectively. Held for 20 min, the tube was rapidly cooled down to room temperature.

The optical images of GaSe single crystal grown by VPT are shown in Fig. 3-10. These samples commonly grow from a nucleation cite in center. The crystal orientation of the nucleus is very important for the crystal growth. Generally, the exfoliated GaSe flakes serving as nucleation sites should have the c-axial normal to the surface of the silicon. However, sometime small bulk crystals also exist in the exfoliated GaSe solution used for substrate treatment. As a result, the crystal will grow in an arbitrary direction, and one can observe clusters of very thin flakes growing in random directions.

Figure 4.10 shows the optical GaSe flakes With the increasing of the distance from the source to the substrate, the shape of the flakes transform from triangle to truncated triangle and finally lose the geometric symmetry. Generally, the shape of the crystals will experience a transform from triangles (A) to truncated triangles (B) as the distance from nucleation cites to the source increases. The flake seldom grows into perfect hexagonal shape, although it does appear some times (C). One can get large triangular flake when putting the wafer nearer to the source, but it becomes very hard to control as the crystal grows very fast and thick. On the contrary, the truncated ones can become much larger, and the positions of them are further from the source. When the nucleation cites are further away from the
evaporation source, the crystals will loss the geometric symmetry (D). The reason can be explained as follow.

![Image]

**Figure 4.10** – Optical, AFM and TEM imaging of GaSe flakes

In the VPT process, GaSe crystal will decompose into Se$_2$ and Ga$_2$Se$_6$ and diffuse to the substrate freely. At lower temperature zones and with the existence of nucleation centers, these two species will be reconstructed into GaSe. These two kinds of molecules will have different velocities and mean free paths when moving in the similar temperature and vacuum conditions. As a result, the ratio of the two species at the far end of the substrate will deviate from 1:2. The lack of one species will impede the growth of the crystal, and it cannot develop fully into a complete triangular domain and will lose the geographic symmetry, as shown in B,C,D in Figure 4.10. This process is demonstrated in Figure 4.11.
This phenomenon is also observed in the growth of MoS$_2$ atomic layers$^{43}$. As the concentration of sulfur decreases, the MoS$_2$ flakes will transform from triangles to hexagons.

Figure 4.11 – Optical, AFM and TEM imaging of GaSe flakes

Atomic force microscopy (AFM) is applied to determine the thickness of the flakes (Figure 4.12). The AFM image shows a complete piece of thin triangular flake with a nucleus in center. The measured thickness of the sample is measured along the cross section labeled with the black dashed line in the picture, which shows a thickness about 1.5 nm. The lattice constant of GaSe along c-axis is about 1.6 nm, indicating that the flakes grown in our experiments predominantly consist of one or two layers of molecules. Meanwhile, the surface of the sample is very flat. This is an advantage of direct growth of the material on SiO$_2$ substrate. This allows us for device fabrication on these samples without any material transfer which can compromise the material's quality.
Transmission electronic microscopy (TEM) was performed to characterize the crystal structure of the samples as shown in Figure 4.13. The atomic image and diffraction shows a good crystal quality. The lattice spacing of [100] plain is measured along <100> and shows a value of 0.36 nm, while the reported value is 0.374 nm. The insert on the right lower corner is the diffraction pattern of GaSe flake with electron beam shine along <001> direction. The insert on the right upper corner shows high resolution image.
Figure 4.13 - TEM imaging of a single GaSe flake
4.3. Raman Study

Raman spectroscopy was utilized to examine the vibration modes of these atomic layers, as shown in Figure 4.14. Single-layered GaSe has a $C_{3h}$ symmetry, as a result it will have six vibrational modes: four in-plane modes ($E'$ and $E''$), and two out of plane mode ($A_1'$ and $A_2''$). Except $A_2''$ mode, all the others are Raman active and significantly thickness dependent.

In our Raman study, three peaks appear in all spectra, one $E_{1g}^1$ at 59 cm$^{-1}$ ($E''$ mode for single layer) and two strong $A_{1g}$ ($A_1'$) modes at 132 cm$^{-1}$ and 306 cm$^{-1}$, respectively. As number of layers decreases from bulk to single layer, the relative intensity of the $E_{1g}^1$ peaks decreases. This is a result of the reduction in the scattering centers for $E_{1g}$ mode become less, i.e. the Raman scattering for this mode becomes less effective. One $A_{1g}$ mode appears at 132 cm$^{-1}$ in all samples, but as the number of layers decreases, the relative intensity decreases as well, even tend to vanish for one or two layered samples. This is in agreement with the observation on mechanically exfoliated samples. The other $A_{1g}$ mode shows a little red-shifting when the number of layers is reduced. It shifts from 306 cm$^{-1}$ in bulk material to 302 cm$^{-1}$ in single or double layered samples, which represents softening of the force constant in the atomic layer as the sample comes thinner. This phenomenon is also same to the observation on mechanical exfoliated samples. We do not observe any peak around 208 cm$^{-1}$ $E_{2g}$ mode in thin samples. However, a 230 cm$^{-1}$ peak shows up in single or bi-layered samples, which shifted to 227 cm$^{-1}$ in few layered samples. There are two possible explanation for this peak. It is possible origin from another
weak $E''_{1g}$ mode in bulk material, or it is shifted from $E_{2g}$ locating at 208 cm$^{-1}$ in bulk sample. But previous study shows the $E''_{1g}$ mode becomes more intense as the number of layers decreases, so it possibly comes from this mode and experiences a red shift due to the interaction to the substrate. Generally, the relationship between Raman Scattering and the number of layers agrees very well to that shown in exfoliated samples.

Figure 4.14 – Raman spectra of GaSe with different thicknesses
4.4. Photo-Conductivity Study

GaSe is an important material for photo detector and nonlinear optics. So it is important to test the photo response of the material. To characterize the photo-response and band gap of the material, dark current and photo-current of a flake with 6-8 layers is measured with Ti/Au electrodes, shown in Figure 4.15. The photocurrent is measured under a 0.5 mW/mm² 405 nm laser. Unlike previous studies in photo-response of the mechanical exfoliated layered samples, the dark current of the sample is extremely low, and in the order of pA, shown in the insert part of Figure 4.15. The native Se defects in bulk crystal leads to large charge carrier density, ~ $10^{15}$ to $10^{16}$ cm$^{-3}$. So GaSe has large dark current, although the hole mobility is small, or even smaller for layered sheet.

Figure 4.15 – Dark and photoresponse I-V curve of GaSe flake
However, in VPT material the dark current is very limited, which makes this material more suitable for photo detector and sensor, because low dark current helps reduce the noise of such devices. On the other hand, it also indicates that the VMT sample might have lower carrier density, i.e. lower defects density. Silver is also selected to study the effect of electrode material, since Ag electrode tends to form higher Schottky barrier with GaSe and change the I-V feature. Meanwhile, GaSe has no dangling bond that can change the surface states unpredictably, and it will not react with silver\textsuperscript{100}. But the I-V curves of dark current and photo-current with Au and Ag as electrode materials are nearly the same to each other, which also indicates that VPT GaSe has fewer carriers unless excited by light. But this needs to be confirmed by other measurement such as Hall effect.

The spectra of photocurrent are also measured to detect the band-structure with lock-in amplifier modulated at 177 Hz, as shown in Figure 4.16, part . The black curve corresponds to thick samples, (This sample is a cluster of GaSe flakes with thickest parts more than ten layers, and the thick parts a connected by thin layers. Refer to supplemental materials). The spectrum has a sharp peak locating at 370 nm with a shoulder at 380 nm, which corresponds to 3.35 and 3.26 eV. Besides the peak, a tail extends to 700 nm which is contributed by the thicker part. There is a weak peak at 620 nm, and this comes from the band edge excitation of bulk material. For bulk crystal, one can only find a peak at this position\textsuperscript{90}. This peak at 380 nm comes from the thinner part in the cluster. This result matches the theoretical result\textsuperscript{93}. The red curve is from a thinner sample. It can be seen that the tail decreases, and one can hardly find the weak peak at 620 nm. This tail may come from the seed of the
crystal which is always very thick comparing to the edge of the flake. As a result, it is hard to get rid of this feature by VPT method.

In bulk crystal, 620nm corresponds to a band gap of 2.0 eV. Generally, in layered semiconductor, the band gap increases as the number of layers approaching atomic dimension. For example, the band gap of MoS2 changes from 1.2 eV in bulk to 1.8 eV in single layer\textsuperscript{43}. In GaSe, the band gap changes more dramatically which is predicted by theoretical calculation, and supported by experiments\textsuperscript{91} that the mechanism for this dramatic change in band gap is the existence of three dimensional electronic interactions in GaSe in addition to van de Waals interaction in other types of layered materials such as graphene. In GaSe, the top of the valence band is mainly formed by a pz-like orbit from the Se atoms. Deeper in the valence

\textbf{Figure 4.16 – Photo-response spectrum and band-structure of GaSe flake}

In bulk crystal, 620nm corresponds to a band gap of 2.0 eV. Generally, in layered semiconductor, the band gap increases as the number of layers approaching atomic dimension. For example, the band gap of MoS2 changes from 1.2 eV in bulk to 1.8 eV in single layer\textsuperscript{43}. In GaSe, the band gap changes more dramatically which is predicted by theoretical calculation, and supported by experiments\textsuperscript{91} that the mechanism for this dramatic change in band gap is the existence of three dimensional electronic interactions in GaSe in addition to van de Waals interaction in other types of layered materials such as graphene. In GaSe, the top of the valence band is mainly formed by a pz-like orbit from the Se atoms. Deeper in the valence
band, there are px and py-like orbits which contribute to an inter-band transition with an energy around 3.2 eV, shown in Figure 4.16. The overlap of pz orbit of Se atoms\textsuperscript{93} leads to a more intense inter-layer interaction and energy level splitting, significantly narrowing the band gap in bulk GaSe. When the number of layer is reduced, this coupling becomes weaker and effective density of state is reduced so that the absorption in the range from 400 to 620 nm is strongly weakened. Instead, px and py-like orbits are in-plane electronic states which are not effected by nearby layers significantly, so the reduction of number of layers does not change the 3.26 eV transition.
4.5. Conclusion

we demonstrated here a vapor phase mass transport method for large area few-layered GaSe crystal growth directly on insulating substrates. The AFM and TEM data confirm that few layer high quality GaSe single crystal as large as tens of micrometers have been synthesized. Raman study reveals the relationship between number of layers and Raman peaks and shows similar results to the mechanically exfoliated samples, indicating good crystal quality of the grown layers. The 2D GaSe crystal is good material for application in photo-detectors with a low dark current. The photo-current spectra show an intense blue shift of the excitation edge and expanded band gap due to a weaker p_z-like orbit interaction as the number of layer decreases. This provides clues to modulate the electronic orbital structure of the few layered GaSe material for opto-electronics and optical application.
Chapter 5

 Atomically Layered InSe
 Isolation and Characterization

In this chapter, we will begin a discussion on InSe, which is very similar to GaSe, not only the lattice structure, but also band-structure and other physical properties. As InSe has narrower band-gap, it gives better photo-response as a photo-detection material.
5.1. Introduction

In Chapter 4, GaSe synthesis method is discussed in details, as well, the photo-response properties of GaSe are also discussed. GaSe shows good photo-responsivity and large on/off ratio, meanwhile, a very limited dark current. All of these factors make GaSe a good candidate for atomically layered photo-detectors. However, few-layered GaSe shows larger band-gap (3.2 eV) as discussed in last chapter, due to the disappearance of inter-layer $p_z$-like orbital interactions. As a result, the photo-response cannot cover the whole visible spectrum, which will limit the use of GaSe as visible light photo-detection.

InSe is a layered material, the physical properties of which are very similar to GaSe. The lattice structure is shown in Figure 5.1. The lattice constant along $a$ and $b$ directions are both 0.40 nm, and the spacing between layers is 0.84 nm. The energy band structure is very similar to that of GaSe. Figure 5.2 shows the absorption spectra of both materials$^{47}$, from which one can find that each peak observed in InSe can also be observed in GaSe, and the only different is that there is an energy shifting in InSe about 0.8 eV. And this change is mainly origin from change in $p$-orbital of cation, which contributes most to the formation of the bottom of conduction band.
Figure 5.1 – Lattice structure of InSe

Figure 5.2 – Absorption spectra of bulk InSe and GaSe
As discussed in chapter 4, the band gap in few layered GaSe is mainly determined by \(p_x p_y\)-like orbital to conduction band transition, and the band structure of InSe is similar to GaSe except a red shifting about 0.8 eV. So it is reasonable to speculate that few layered InSe will have a narrower band-gap and then stronger absorption in visible light region.

In this chapter, an extensive study on (a) synthesis and isolation (b) optical and electrical properties, and (c) thin film photodetector application of few-layered InSe are presented. Direct correlation between resonance Raman spectra and the photoconductivity reveals a systematic evolution of the 2D band structure from bulk to few layered InSe. Detailed analyses of photoconductivity spectra show that few-layered InSe has an indirect band-gap of 1.4 eV. Furthermore, we demonstrate that few layered InSe is an excellent candidate for thin film photodetector application with a photo-responsivity of 34.7 mA/W and a response time of 488 μs, which are an order of magnitude larger than previous measurements on other layered 2D semiconductors, including the extensively studied single to few layered MoS\(_2\)^{52}.

The discussions in this chapter are based on mechanical exfoliated samples. So it is necessary to discuss the bulk crystal preparation first.
5.2. InSe Crystal Growth

For InSe study, we have to grow the InSe crystal first, as high purity crystals are not commercially available. To grow the InSe crystal, we referred to early study on crystal growth with non-stoichiometric melt\textsuperscript{101}.

The synthesis of bulk InSe crystal was performed by using a non-stoichiometric melt of Indium (>99.99%, Alfa Aesar Co.) and Selenium (>99.99%, Sigma-Aldrich Co.). Indium and Selenium were mixed with a molar ratio of 52:48\textsuperscript{101} and sealed in a quartz tube under vacuum ($10^{-3}$ Torr). The precursor was then heated to 685 $^\circ$C, and the temperature was maintained for 3 hours to ensure a full reaction between Indium and Selenium. Further, in accordance to the phase diagram of In-Se system\textsuperscript{98}, as in Figure 5.3, the temperature was increased to 700 $^\circ$C and maintained for 3 hours to form a uniform InSe melt. The melt was then cooled down to 500 $^\circ$C at a ramp rate of 10$^\circ$C per hour, followed by natural cooling to room temperature in 6 hours to achieve InSe crystals with high quality.

The InSe crystal got from the method have a black crust outside, the crust has no layered structure and relative hard. But the ratio between In and Se is not 1 :1, so this crust must contain some material other than InSe. However, the inside part has very obvious layered structure, which is confirmed by the SEM, shown in Figure 5.4. The interesting phenomenon is that if one mix In and Se according to the molar ration of InSe, one cannot get InSe crystal, instead, by deviating from this ratio, one will get good crystal.
Figure 5.3 – In-Se system phas diagram

Figure 5.4 – SEM image of InSe crystal grown from non-stoichiometric melt
5.3. Atomic Layer Isolation and Fundamental Characterization

After crystal synthesis, the hard crust will be removed and a piece of InSe flake will be peeled from the inner part by fine tip tweezers and load on top of Scotch tape. Then by following the same method for graphene exfoliation, one can get some few layered InSe flakes on top of silicon dioxide wafer. The exfoliated samples show very good crystal quality and the TEM study shows that the lattice structure determined by electron diffraction and high resolution image (Figure 5.5) agrees to the reports exactly.

![TEM image and electron diffraction pattern of InSe flake](image)

**Figure 5.5 – TEM image and electron diffraction pattern of InSe flake**

TEM image of InSe shows perfect hexagonal lattice structure of the synthesized material. The lattice constant measured along (100) direction gives a value of 0.40 nm, which is in agreement with the reported lattice constant of InSe$^{101}$. The selected area electron diffraction pattern is shown in figure 1d and presents a six-fold symmetry, which is an indicator of the overall crystalline quality, thus
confirming that the synthesized InSe has a good crystal structure and justifies its use as the starting material for the investigation of the optical and electrical properties of few layered InSe.

The atomic force microscope (AFM) was used to measure the thickness and roughness of the exfoliated InSe flake on top of SiO2. Figure 5.6 shows the AFM topography images and the corresponding optical images of typical samples studied here. The thickness of the exfoliated samples typically varied from 4 nm to 10 nm, which corresponds to four to eleven atomic layers. The exfoliated top surface was extremely flat along the cleavage plane of InSe crystal, suggesting weak van der Waals coupling between the layers.

Figure 5.6 – AFM image of InSe flake

Figure 5.6 b shows a flake with several cleaved edges, and each of them shows sharp thickness variation. However, in our exfoliated samples the changes of thickness always have a step size of 2 nm or more, which indicates a stacking of two
layers. Meanwhile, these two-layer-unit flakes can extend to relatively large size spans. On the contrary, single-layered steps seldom appear in our exfoliated samples. Although structure does appear occasionally; it spans very limited area (only hundreds of nano-meter as shown in the profile curve). This phenomenon may be relevant to the way the sample got exfoliated. As the layers get peeled by tapes, it is unavoidable that some shear strain appears. The single layered InSe may be broken into smaller pieces during exfoliation, while double layered InSe is stronger.
5.4. Raman Study

For layered materials, Raman spectroscopy is a very powerful tool to characterize the lattice vibration mode and structure changing. Generally, Raman spectrum is very sensitive to the number of layers and the quality of samples, so Raman scattering become a very useful method for 2D material characterization and quality control. Hence, Raman scattering was applied to study the structure, corresponding vibrational modes and its thickness dependencies in InSe samples to provide important data for further study. More important, in InSe, the inter-band E1′ transition (pₓ,pᵧ-like orbitals to conduction band transition) has an energy of roughly 2.4eV\textsuperscript{47,102}.This gap corresponds to a wave length of 514 nm. So the 514 nm emission from Argon ion laser can be utilized to study the resonant Raman scattering of exfoliated InSe flakes. As discussed in Chapter 3, resonant Raman will not only provide more lattice vibration information, but can also give an insight into electron energy level structures, as resonant Raman is an electron-phonon coupling process.

The observed modes are illustrated in Figure. 5.7a, and the details of the label for each mode will be discussed later. The resonant Raman spectra for samples with different thickness is shown in Figure 5.7b. For comparison, the corresponding non-resonant Raman spectra with 633 nm laser excitation are collected and shown in Figure 5.7c.
As resonant Raman will show more complicated pattern (because some weak peak may be magnified and even some Raman forbidden mode may appear) and provide more information about the phonon behavior in the lattice, it is worth to first discuss the vibration modes and the origin of each peak in detail. The following discussion is based on the assumption that the sample is ε-InSe or (and) γ-InSe enriched, as the Raman spectra agree well with previous studies in these structures\(^\text{103}\). The Mulliken symbols are used to label the corresponding ε-InSe vibration modes (ε-InSe has the same point group symmetry to single InSe layer, so all the discussion about ε-InSe can also be applied to single InSe layer) and the Σ

---

**Figure 5.7 – Resonant Raman of non-resonant Raman of InSe flakes with different thicknesses**
symbols is used for γ-InSe as a reference for comparing with previous works. In each unit cell of ε-InSe, there are two layers of Se-In-In-Se atomic unit, i.e. 8 atoms in each unit cell; as a result it has 24 vibration modes. Because of the $D_{3h}$ symmetry, it has four $A_2$" modes, four $A_1"$ modes, four two-dimensional $E'$ modes and four two-dimensional $E''$ modes. In γ-InSe, each unit cell has 12 atoms and, consequently, 36 vibration modes. In $C_{3v}$ symmetry, they are divided into twelve $\Gamma_1$ modes and twelve two-dimensional $\Gamma_3$ modes. The demonstration and correlation of the observed modes in our study are shown in Figure 5.7a.

In resonant Raman, we observed seven modes (two modes in Figure 5.7a, will split into longitudinal and transverse optical modes, so seven modes in total) in our measurement, as listed in Table 5-1. Considering three modes with frequencies out of our detection range, it is only possible for us to observe ten modes. The reason comes from two factors. Firstly, most of the vibration modes are degenerated or near degenerated, because the inter-layer interaction is mainly van der Waals force and the vibration in each layer is nearly independent. So if the difference among different vibrational modes is only relative phase changes between layers, they will have the same or similar eigen-energy. Secondly, lots of polar optical modes do split into transverse optical mode (TO) and longitudinal optical mode (LO). Typically, a polar optical mode will split into TO and LO modes due to different coupling mechanism between mechanical vibration and electro-magnetic field generated by dipole momentum$^{104}$. Predicted by group theory, nine modes in ε-InSe are polar modes and all the non-acoustic modes in γ-InSe polar optical modes. So all of them should split into TO and LO modes. But only $A2"$ ($\Gamma^11$) mode and one
E’ (Γ₃¹) do split. The IR spectra observations may explain this phenomenon, because if a polar mode does split due to existence of dipole momentum, it is also IR active. According to the reported IR observation¹⁰⁴,¹⁰⁵, only one A₂'' (Γ₁¹) mode and one E’ (Γ₃¹) are observable and split TO and LO respectively, which indicates although all the other optical phonon modes are allowed by symmetry analysis, they do not generate actual dipole momentum, so they will not be observed by IR spectra and will not split into TO and LO modes as well, i.e. they are degenerated and only Raman active.

Table 5.1 –Resonant Raman (different layers) and Non-resonant Raman modes observed in InSe flakes

<table>
<thead>
<tr>
<th>Mode</th>
<th>A₁'(Γ₁²)</th>
<th>E'(Γ₃¹)-TO &amp; E''(Γ₂²)</th>
<th>A₂''(Γ₁¹)-TO</th>
<th>A₂''(Γ₁¹)-LO</th>
<th>E'(Γ₃¹)-LO</th>
<th>A₁'(Γ₃²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resonant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk</td>
<td>117</td>
<td>179</td>
<td>---</td>
<td>201</td>
<td>---</td>
<td>227</td>
</tr>
<tr>
<td>~20 L</td>
<td>117</td>
<td>179</td>
<td>---</td>
<td>199</td>
<td>---</td>
<td>228</td>
</tr>
<tr>
<td>~10 L</td>
<td>117</td>
<td>179</td>
<td>187</td>
<td>201</td>
<td>212</td>
<td>227</td>
</tr>
<tr>
<td>7.8 L</td>
<td>115</td>
<td>179</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-resonant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

On the contrary, the non-resonant Raman only shows A₁' (Γ₁²) mode at 117 cm⁻¹, E'(Γ₃¹) -TO and E''(Γ₃³) modes at 179 cm⁻¹, and A₁'(Γ₁³) mode at 227 cm⁻¹, because other modes are either Raman-forbidden or relatively weak. Meanwhile, one can observe Rayleigh tail in the resonant Raman pattern, which results from the fluorescence accompanying the resonant process. This phenomenon will not happen in non-resonant Raman pattern.
In resonant Raman patterns, as the number of layers decreases, the peak positions do not change significantly, but the relative peak intensity changes. In bulk sample, the resonant $A_2''(\Gamma_1^1)$-LO peak at 201 cm$^{-1}$ is relative weak, at the same time, $A_2''(\Gamma_1^1)$-TO and LO branch of $E'(\Gamma_3^1)$-LO mode are unobservable. As the number of layers decreases, the intensities of $A_2''(\Gamma_1^1)$ modes do not decrease as much as other peaks. So the relative peak intensity of $A_2''(\Gamma_1^1)$-LO increases and can be used as a reference to estimate the number of InSe layers. Figure 5.7d and Figure 5.7e show the optical imaging of one InSe flake with variant thickness, and the corresponding Raman mapping which shows the relative peak intensity of $A_2''(\Gamma_1^1)$-LO peak (Ratio between $A_2''(\Gamma_1^1)$-LO and $E'(\Gamma_3^1)$-TO is applied as a reference, because both of them propagate along c axes and will be thickness sensitive). It is obvious that the thicker parts give lower intensity, while the thinner part show stronger $A_2''(\Gamma_1^1)$-LO mode. Because of resonance, all the Raman peaks are still observable till 7 layers. But with 633 nm excitation, only $A_1'$ mode at 227 cm$^{-1}$ is still detectable for few-layered sample.

However, as the number of layers decreases to 3-5 layers, all the Raman peaks (resonant and non-resonant) disappear leaving behind a broad envelope indicated by the blue curve in figure 4b. The observation of the resonance Raman peaks up to ~ 7 layers suggests the energy gap between px,py-like orbitals and the bottom of the conduction band does not change appreciably for up to ~ 7 layers. However as the number of layers becomes less than ~7 layers, both pz orbital the px,y-like orbitals should strongly be affected by the suppressed inter-layer coupling
and result in observable changes in the electronic band structure that lead to the
disappearance of the resonance Raman peaks.

All these phenomena indicate that the energy level gap between the bottom
of the conduction band and the px,py-like orbitals do not change significantly with
the variation of layer numbers when it is larger than 7, and only the position of the
valence band top may change, i.e. pz-like orbitals. But when the number of layers
decrease further, the energy gap between px,y-like orbital to conduction band will
also change. However, one will not know whether the changing is a blue shifting or
red shifting, and photo-conductivity measurement is necessary.
5.5. **Photo-Conductivity Study**

To directly probe the changes in the electronic band structure and to understand the disappearance of Raman modes with the decreasing number of layers of InSe, we performed photoconductivity experiments, which are illustrated in Figure 5.8. InSe metal-semiconductor-metal (MSM) photo-detector devices were fabricated on layered InSe flakes with different thicknesses, with Ti/Au (10 nm / 30 nm) electrodes. Figure 5.8 a captures the changes in the photocurrent spectra as a function of the number of layers of InSe. The red dashed line separates the spectra into two parts. The left part (400 nm to 550 nm, corresponds to the electronic transition from px,y-like orbital (referred to as xy-band in the following discussion) to the bottom of conduction band, and the right part (550 nm to 800 nm, refer to z-band in the following discussion) corresponds to electronic transition from pz-like orbitals to the bottom of conduction band. As the number of layers goes down below ~7 layers, the photocurrent response in z-band decreases sharply. This is because the interaction between pz-like orbitals (which is perpendicular to the layer plane) in neighboring layers is strongly suppressed. This is consistent with measurements on GaSe that has the same crystal structure. In addition, we also observe that the E1’ peak in xy-band arising from px,y-like orbital to conduction band experiences a strong blue shift of ~ 150-200 meV shifting the E1’ transition energy from 2.41 eV ($\lambda \sim 514$ nm) to ~2.6 eV (480 nm). This blue shift in the E1’ transition with decreasing number of layers is consistent with the disappearance of the Raman modes. Resonance Raman modes can no longer be excited with a 514 nm laser line.
and leads to the disruption of the resonance Raman process and subsequent vanishing of the Raman peaks for few-layered.

![Photo-Conductivity Spectra of InSe with different thicknesses](image)

**Figure 5.8 – Photo-Conductivity Spectra of InSe with different thicknesses**

We also extract the band-gap of a multilayered InSe from the shape of the measured photocurrent spectra for a 10 layered device (see black curve in figure. 5.8). It was difficult to extract band-gaps for thinner layers (7-8 and 3-4) due to the lack of a clear band-edge in the photocurrent spectra (the distribution of the density of electron states in thinner samples will be discussed later in the manuscript). We observe that the photocurrent spectra decays gradually with increasing wavelength, suggesting that the few layered InSe has an indirect band-gap. This is in sharp contrast to a direct band-gap semiconductor where the photocurrent is expected to turn off sharply below the band-gap of the material. By assuming that the internal quantum efficiency of photo-current ($I_{ph}$) is a constant in the 700 nm to 800 nm, the
photocurrent is proportional to the absorption in this wavelength range, i.e.
\[ I_{ph} = \alpha \times d \times \eta, \]
where \( \alpha \) is the absorption, \( d \) is the thickness of the InSe flake \( \eta \)
(quantum efficiency) is a constant. For indirect band gap semiconductors the
following equation applies:

\[ \alpha \propto (E - E_g)^{1/2}, \text{therefore} \]
\[ I_{ph} \propto (E - E_g)^{1/2} \]

(Here, we assume that the absorption rate \( 1 - e^{-\alpha d} \) can be expressed as \( \alpha d \)
for thin films). By fitting the spectrum edge, as shown in inset of figure 5a, we
extract a band-gap of around 1.4 eV. This phenomenon is similar to few-layered
GaSe[27] but strength of the inter-layer interaction is not as strong as GaSe, where,
as the number of layers decreases, the coupling due to the pz-like orbitals vanishes,
leading to an effective band-gap of 3.26 eV. Thus correlation between resonance
Raman spectroscopy and photoconductivity measurements allows us to track the
changes in the electronic band structure of InSe with decreasing number of layers.

We also measured the photo-detector response and critical figures of merit
for a few layered InSe in the visible region and the results are illustrated in figure
5.9. These were collected from the device (number of layers \( \sim 10 \)) shown in the
inset of figure 5.9. Figure 5.9 shows the current-voltage curve of the device with an
effective exposure area of 23 \( \mu \text{m}^2 \) measured in the dark and with a 532 nm laser
with an intensity of 2.5 mW/mm\(^2\). The dark current (\( I_{dk} \)) is in the order of 10 pA,
which is at the detection limit of the current amplifier used for our measurements.
The photocurrent is 2 nA with a 3 V bias, corresponding to an on/off ratio of 200, a photo-responsivity \( (I_{\text{ph}} - I_{\text{dk}}) / \text{light intensity} \) of 34.7 mA/W, and an external quantum efficiency of 8.1 %. The measured photo-responsivity is two orders of magnitude larger than that reported for MoS2 based photodetector (responsivity of 0.42 mA/W)\(^2\). We also measured a response time of 488 µs (Figure 5.10), which is an order of magnitude faster than that measured on MoS2.

Figure 5.9 – Photo-Conductivity I-V curve of InSe
5.6. Conclusion

In summary, we provide a comprehensive study of synthesis, characterization and optoelectronic application of atomic layered InSe. Direct correlation between resonance Raman spectroscopy and photoconductivity measurements allows us to systematically track the evolution of the 2D electronic band structure of InSe as we approach few layers. We demonstrate that few layered InSe has an extremely strong photo-response and is an excellent 2D material for its incorporation as an ultra-thin photodetector with a high photo-responsivity of 34.7 mA/W and fast response time of 488 μs.
Chapter 6

Conclusion

To sum up, GaSe and InSe, atomically layered materials, are systematically studied in this research. GaSe flakes are successfully synthesized with VPT method. TEM, SEM and EDX showed good crystal quality. Raman could provide a useful way for quick thickness estimation. Photo-conductivity measurement revealed a band gap of 3.26 eV for few layered GaSe flakes.

InSe atomic layers were successfully isolated from bulk crystal. TEM and SEM data showed an excellent crystal quality. Resonant Raman spectrum, together with photo-conductivity measurement, revealed the evolution of band structure as the number of layers decreased. Due to the elimination of p\textsubscript{\textit{z}}-like orbital interaction, the top of valence band shifted to more positive (deeper) position leading to a larger band gap. Few layered InSe has an indirect band gap of 1.4 eV.
Both GaSe and InSe show good photo-response and they are candidates for ultra-thin photo-detector materials.

Meanwhile, to characterize the photo-conductivity of layered materials, a home-built photo-electronic characterization system was successfully built up with the abilities of photo-conductivity measurement, time-resolved measurement, temperature dependent measurement, FET measurement, etc. The system is equipped with lock-in amplifier, low-level current measurement SMU, high precision DC-amplifier, laser modulation and stabilization, and low vacuum ability.

All the photo-conductivity measurements on GaSe and InSe were performed on this setup and it will serve as a very powerful platform for 2D material opto-electronics property characterization.
References


48. Shi, W.; Ding, Y. J.; Fernelius, N.; Vodopyanov, K. Efficient, tunable, and coherent 0.18–5.27-THz source based on GaSe crystal. *Optics letters* 2002, 27, 1454.


Appendix A

Raman Scattering Strength Model with Density Matrix Method

\[
H = \frac{p_e^2}{2m_e} + \frac{p_l^2}{2m_l} + V_{e-L} + V_{L-L} + H_p
\]

\[
= \frac{p_e^2}{2m_e} + \frac{p_l^2}{2m_l} + V_{e-L}(X_0 - x_l) + \frac{\partial V_{e-L}}{\partial X} \cdot X + V_{L-L} + H_p
\]

\[
= \frac{p_e^2}{2m_e} + V_{e-L}(X_0 - x_l) + \frac{p_l^2}{2m_l} + V_{L-L} + \frac{\partial V_{e-L}}{\partial X} \cdot X + H_p
\]

\[
= \frac{p_e^2}{2m_e} + V_{e-L}(X_0 - x_l) + \frac{p_l^2}{2m_l} + V_{L-L} + \frac{\hbar}{2m_l \omega_l} \cdot \frac{1}{2} \left( a \cdot e^{-i\omega_1 t} + a^* \cdot e^{i\omega_1 t} \right) + H_p
\]

\[
= H_{e0} + H_{L0} + \Delta \cdot H_Y + H_p
\]

The quantum state could be described as \( |m, \alpha\rangle \), and \( m \) stands for electron state, and \( \alpha \) stands for photon state.

\[
\rho_{\alpha\alpha, \beta\beta}^{(1)} = -i \omega_{\alpha\alpha, \beta\beta} \rho_{\alpha\alpha, \beta\beta}^{(0)} - \frac{i}{\hbar} \langle m, \alpha | H_p + H_Y | n, \beta \rangle \cdot (\rho_{n\beta, n\beta}^{(0)} - \rho_{m\alpha, m\alpha}^{(0)})
\]

\[
= -i \omega_{\alpha\alpha, \beta\beta} \rho_{\alpha\alpha, \beta\beta}^{(0)} - \frac{i}{\hbar} (\rho_{n\beta, n\beta}^{(0)} - \rho_{m\alpha, m\alpha}^{(0)}) \times \langle m, \alpha | \Delta \cdot a \cdot | n, \beta \rangle e^{-i\omega t} + \langle m, \alpha | \Delta \cdot a^* | n, \beta \rangle e^{i\omega t} + \langle m, \alpha | E \cdot r | n, \beta \rangle (e^{-i\omega t} + e^{i\omega t})
\]

Suppose that \( \rho_{\alpha\alpha, \beta\beta}^{(1)} = S_{\alpha\alpha, \beta\beta}^{(1)} \times e^{-i\omega_{\alpha\alpha, \beta\beta} t} \) (3).

Substitute equation (3) into equation (2), it could be obtained equation (4) as follow.

\[
\dot{\rho}_{\alpha\alpha, \beta\beta} e^{-i\omega_{\alpha\alpha, \beta\beta} t} = -\frac{i}{\hbar} (\rho_{n\beta, n\beta}^{(0)} - \rho_{m\alpha, m\alpha}^{(0)}) \times \langle m, \alpha | \Delta \cdot a \cdot | n, \beta \rangle e^{-i\omega t} + \langle m, \alpha | \Delta \cdot a^* | n, \beta \rangle e^{i\omega t} + \langle m, \alpha | E \cdot r | n, \beta \rangle (e^{-i\omega t} + e^{i\omega t})
\]

Solve the equation via following process.
\[ S_{mn,\alpha\beta}(t) = -\frac{i}{\hbar} (\rho_{\alpha\beta,\alpha\beta}^{(0)} - \rho_{\text{max,\alpha\beta}}^{(0)}) \times \int_{-\infty}^{t} dt' \ e^{i\omega_{\text{max,\alpha\beta}}t'} \times \\
\{ \langle m, \alpha | \Delta \cdot a | n, \beta \rangle e^{-i\omega_{\alpha\beta}t'} + \langle m, \alpha | \Delta a^+ | n, \beta \rangle e^{i\omega_{\alpha\beta}t'} + \langle m, \alpha | \vec{E} \cdot \vec{r} | n, \beta \rangle (e^{-i\omega_{\alpha\beta}t'} + e^{i\omega_{\alpha\beta}t'}) \} \]
\[ = -\frac{i}{\hbar} (\rho_{\alpha\beta,\alpha\beta}^{(0)} - \rho_{\text{max,\alpha\beta}}^{(0)}) \times \\
\{ \Delta \frac{\langle m, \alpha | a | n, \beta \rangle e^{i(\omega_{\text{max,\alpha\beta}} - \omega_\gamma)t}}{i(\omega_{\text{max,\alpha\beta}} - \omega_\gamma)} + \Delta \frac{\langle m, \alpha | a^+ | n, \beta \rangle e^{i(\omega_{\text{max,\alpha\beta}} + \omega_\gamma)t}}{i(\omega_{\text{max,\alpha\beta}} + \omega_\gamma)} + \\
+ \frac{\langle m, \alpha | \vec{E} \cdot \vec{r} | n, \beta \rangle e^{i(\omega_{\text{max,\alpha\beta}} + \omega_\gamma)t}}{i(\omega_{\text{max,\alpha\beta}} + \omega_\gamma)} \} \] (5)

Then
\[ \rho_{\text{max,\alpha\beta}}^{(1)} = -\frac{i}{\hbar} (\rho_{\alpha\beta,\alpha\beta}^{(0)} - \rho_{\text{max,\alpha\beta}}^{(0)}) \times \\
\{ \Delta \frac{\langle m, \alpha | a | n, \beta \rangle e^{-i\omega_\gamma t}}{i(\omega_{\text{max,\alpha\beta}} - \omega_\gamma)} + \Delta \frac{\langle m, \alpha | a^+ | n, \beta \rangle e^{i\omega_\gamma t}}{i(\omega_{\text{max,\alpha\beta}} + \omega_\gamma)} + \\
+ \frac{\langle m, \alpha | \vec{E} \cdot \vec{r} | n, \beta \rangle e^{i\omega_\gamma t}}{i(\omega_{\text{max,\alpha\beta}} + \omega_\gamma)} \} \] (6)

\[ \dot{\rho}_{\text{max,\alpha\beta}}^{(2)} = -\omega_{\text{max,\alpha\beta}} \rho_{\text{max,\alpha\beta}}^{(2)} - \frac{i}{\hbar} [H_V, \rho^{(1)}]_{\text{max,\alpha\beta}} - \frac{i}{\hbar} [H_P, \rho^{(1)}]_{\text{max,\alpha\beta}} \] (7)

Now, calculate the item \([H_V, \rho^{(1)}]_{\text{max,\alpha\beta}}\). (Two phonon process is neglected.)
\[
[H_V, \rho^{(1)}]_{\text{max, n\beta}} = \sum_{l, \gamma} \langle m, \alpha | a^{\dagger} e^{-i\omega_p t} | l, \gamma \rangle \rho_{l, \gamma, n\beta}^{(1)} + \langle m, \alpha | a e^{i\omega_p t} | l, \gamma \rangle \rho_{l, \gamma, n\beta}^{(1)} - \rho_{\text{max, l} \gamma}^{(1)} \langle l, \gamma | a^{\dagger} e^{-i\omega_p t} | n, \beta \rangle - \rho_{\text{max, l} \gamma}^{(1)} \langle l, \gamma | a e^{i\omega_p t} | n, \beta \rangle
\]
\[
= -\frac{1}{\hbar} \Delta x \sum_{l, \gamma} \left[ (\rho_{n\beta, n\beta}^{(0)} - \rho_{l, \gamma, n\beta}^{(0)}) \langle m, \alpha | a | l, \gamma \rangle \frac{\langle l, \gamma | \vec{E} \cdot \vec{r} | n, \beta \rangle}{(\omega_{l, n\beta} + \omega_p)} e^{i(\omega_p - \omega_p) t} + \rho_{n\beta, n\beta}^{(0)} - \rho_{l, \gamma, n\beta}^{(0)} \right] \langle m, \alpha | a^{\dagger} | l, \gamma \rangle \frac{\langle l, \gamma | \vec{E} \cdot \vec{r} | n, \beta \rangle}{(\omega_{l, n\beta} + \omega_p)} e^{i(\omega_p + \omega_p) t} + \rho_{n\beta, n\beta}^{(0)} - \rho_{l, \gamma, n\beta}^{(0)} \langle m, \alpha | a^{\dagger} | l, \gamma \rangle \frac{\langle l, \gamma | \vec{E} \cdot \vec{r} | n, \beta \rangle}{(\omega_{l, n\beta} - \omega_p)} e^{i(\omega_p - \omega_p) t} + \rho_{l, \gamma, n\beta}^{(0)} - \rho_{\text{max, max, l} \gamma}^{(0)} \frac{\langle m, \alpha | \vec{E} \cdot \vec{r} | l, \gamma \rangle}{(\omega_{\text{max, l} \gamma} + \omega_p)} \langle l, \gamma | a | n, \beta \rangle e^{i(\omega_p - \omega_p) t} + \rho_{l, \gamma, n\beta}^{(0)} - \rho_{\text{max, max, l} \gamma}^{(0)} \frac{\langle m, \alpha | \vec{E} \cdot \vec{r} | l, \gamma \rangle}{(\omega_{\text{max, l} \gamma} - \omega_p)} \langle l, \gamma | a^{\dagger} | n, \beta \rangle e^{i(\omega_p + \omega_p) t} + \rho_{l, \gamma, n\beta}^{(0)} - \rho_{\text{max, max, l} \gamma}^{(0)} \frac{\langle m, \alpha | \vec{E} \cdot \vec{r} | l, \gamma \rangle}{(\omega_{\text{max, l} \gamma} + \omega_p)} \langle l, \gamma | a^{\dagger} | n, \beta \rangle e^{i(\omega_p + \omega_p) t} + \rho_{l, \gamma, n\beta}^{(0)} - \rho_{\text{max, max, l} \gamma}^{(0)} \frac{\langle m, \alpha | \vec{E} \cdot \vec{r} | l, \gamma \rangle}{(\omega_{\text{max, l} \gamma} - \omega_p)} \langle l, \gamma | a^{\dagger} | n, \beta \rangle e^{i(\omega_p - \omega_p) t}\right]
\]
\[\tag{8}\]
Now, calculate the item $[H_V, \rho^{(1)}]_{\text{mat,} \alpha' \beta}$: (Two photon process is neglected.)

$$
[H_V, \rho^{(1)}]_{\text{mat,} \alpha' \beta} = \sum_{l, \gamma} \left( \langle m, \alpha | \bar{E} \cdot \vec{r} | l, \gamma \rangle e^{-i \omega_{\gamma} t} \rho_{l, \gamma, \alpha' \beta}^{(1)} + \langle m, \alpha | \bar{E} \cdot \vec{r} | l, \gamma \rangle e^{i \omega_{\gamma} t} \rho_{l, \gamma, \alpha' \beta}^{(1)} \right)
$$

$$- \rho_{\text{mat,} \gamma, \alpha' \beta}^{(1)} \langle l, \gamma | \bar{E} \cdot \vec{r} | n, \beta \rangle e^{-i \omega_{\beta} t} - \rho_{\text{mat,} \gamma, \alpha' \beta}^{(1)} \langle l, \gamma | \bar{E} \cdot \vec{r} | n, \beta \rangle e^{i \omega_{\beta} t} \right]
$$

$$= -\frac{1}{\hbar} \Delta \times$$

$$\sum_{l, \gamma} \left( (\rho_{n, \alpha' \beta}^{(0)} - \rho_{l, \gamma, \alpha' \beta}^{(0)}) \cdot \langle m, \alpha | \bar{E} \cdot \vec{r} | l, \gamma \rangle \frac{\langle l, \gamma | a^{\dagger} | n, \beta \rangle}{(\omega_{l, \gamma, n} - \omega_{\gamma})} e^{i(\omega_{\gamma} - \omega_{\beta}) t} + \right.$$
Suppose $\rho_{ma,\beta}^{(2)} = S_{ma,\beta}^{(2)} e^{-i\omega_{ma,\beta}t}$, then

\[
S_{ma,\beta}^{(2)}(t) = -\frac{i}{\hbar} \int_{-\infty}^{t} e^{i\omega_{ma,\beta}t'} \left( [H_V, \rho^{(1)}]_{ma,\beta} + [H_\beta, \rho^{(1)}]_{ma,\beta} \right) dt'
\]

\[
= \frac{1}{\hbar} \Delta \times \sum_{l,\gamma} \left( \rho_{l,\gamma}^{(0)} - \rho_{l,\gamma}^{(0)} \right) \frac{\langle m, \alpha | l, \gamma \rangle \langle l, \gamma | \tilde{E} \cdot \tilde{r} | n, \beta \rangle}{(\omega_p - \omega_L + \omega_{ma,\beta})(\omega_{l,\gamma} + \omega_{ma,\beta})} e^{i(\omega_p - \omega_L + \omega_{ma,\beta})t'} + \]

\[
(\rho_{l,\gamma}^{(0)} - \rho_{l,\gamma}^{(0)}) \frac{\langle m, \alpha | l, \gamma \rangle \langle l, \gamma | \tilde{E} \cdot \tilde{r} | n, \beta \rangle}{(\omega_p - \omega_L + \omega_{ma,\beta})(\omega_{l,\gamma} + \omega_{ma,\beta})} e^{i(\omega_p - \omega_L + \omega_{ma,\beta})t'} + \]

\[
(\rho_{l,\gamma}^{(0)} - \rho_{l,\gamma}^{(0)}) \frac{\langle m, \alpha | l, \gamma \rangle \langle l, \gamma | \tilde{E} \cdot \tilde{r} | n, \beta \rangle}{(\omega_p + \omega_L + \omega_{ma,\beta})(\omega_{l,\gamma} + \omega_{ma,\beta})} e^{i(\omega_p + \omega_L + \omega_{ma,\beta})t'} + \]

\[
(\rho_{l,\gamma}^{(0)} - \rho_{l,\gamma}^{(0)}) \frac{\langle m, \alpha | l, \gamma \rangle \langle l, \gamma | \tilde{E} \cdot \tilde{r} | n, \beta \rangle}{(\omega_{l,\gamma} + \omega_{ma,\beta})(\omega_p - \omega_L + \omega_{ma,\beta})} e^{i(\omega_p - \omega_L + \omega_{ma,\beta})t'} + \]

\[
(\rho_{l,\gamma}^{(0)} - \rho_{l,\gamma}^{(0)}) \frac{\langle m, \alpha | l, \gamma \rangle \langle l, \gamma | \tilde{E} \cdot \tilde{r} | n, \beta \rangle}{(\omega_{l,\gamma} + \omega_{ma,\beta})(\omega_p + \omega_L + \omega_{ma,\beta})} e^{i(\omega_p + \omega_L + \omega_{ma,\beta})t'} + \]

\[
\]

(10)
\[
\rho_{\mu,\alpha,\beta}^{(2)} = -\frac{i}{\hbar} \int d\tau' e^{i\omega_{\alpha,\beta}\tau'} \left\{ [H_{\alpha}, \rho_{\mu,\alpha,\beta}^{(1)}]_{\alpha,\beta} + [H_{\beta}, \rho_{\mu,\alpha,\beta}^{(1)}]_{\alpha,\beta} \right\} \\
= \frac{1}{\hbar^2} \Delta \times \sum_{l, l'} \left[ (\rho_{\mu,\alpha,\beta}^{(0)} - \rho_{l, l'}^{(0)}) \right] \\
= \frac{1}{\hbar^2} \Delta \times \sum_{l, l'} \left[ \left( \frac{\langle m, \alpha | l, \gamma \rangle \langle l, \gamma | \hat{E} \cdot \mathbf{r} | n, \beta \rangle}{\omega_p - \omega_b + \alpha_{\mu,\alpha,\beta}} \right) \left( \omega_{l, l'} + \alpha_{\mu,\alpha,\beta} \right) + \right]
\]

(10)
\[ P^{(2)} = \text{tr}(\rho^{(2)}) e \cdot \rho = e \sum_{n, n'} \rho_{n, n'}(\alpha, \beta) \langle n, \beta | r | m, \alpha \rangle \]

\[
\sum_{n, n'} \sum_{l, m} \sum_{j, j'} (\rho_{j, j'}^{(0)} - \rho_{j, j'}^{(0)}) - \rho_{j, j'}^{(0)} = \frac{e\Delta}{\hbar} \cdot \sum_{n, n'} \sum_{l, m} \sum_{j, j'} (\rho_{j, j'}^{(0)} - \rho_{j, j'}^{(0)})
\]

\[
\langle l, \gamma | E \cdot r | n, \beta \rangle \left( \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} + \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} \right) + \langle l, \gamma | E \cdot r | n, \beta \rangle \left( \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} + \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} \right)
\]

\[
\langle l, \gamma | a | n, \beta \rangle \left( \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} + \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} \right) + \langle l, \gamma | a | n, \beta \rangle \left( \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} + \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} \right)
\]

\[
\langle l, \gamma | a | n, \beta \rangle \left( \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} + \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} \right) + \langle l, \gamma | a | n, \beta \rangle \left( \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} + \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} \right)
\]

\[
\langle l, \gamma | a | n, \beta \rangle \left( \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} + \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} \right) + \langle l, \gamma | a | n, \beta \rangle \left( \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} + \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} \right)
\]

\[
\langle l, \gamma | a | n, \beta \rangle \left( \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} + \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} \right) + \langle l, \gamma | a | n, \beta \rangle \left( \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} + \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} \right)
\]

\[
\langle l, \gamma | a | n, \beta \rangle \left( \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} + \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} \right) + \langle l, \gamma | a | n, \beta \rangle \left( \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} + \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} \right)
\]

\[
\langle l, \gamma | a | n, \beta \rangle \left( \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} + \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} \right) + \langle l, \gamma | a | n, \beta \rangle \left( \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} + \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} \right)
\]

\[
\langle l, \gamma | a | n, \beta \rangle \left( \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} + \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} \right) + \langle l, \gamma | a | n, \beta \rangle \left( \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} + \langle n, \beta | r | m, \alpha \rangle e^{i(\alpha \gamma - \alpha \gamma)} \right)
\]
Consider the function of $a^+$ and $a$, and the orthogonality between different states.

$$P^{(2)} = tr(\rho^{(2)} e \cdot r) = e \sum \sum \rho^{(2)}_{\alpha \beta \nu \mu} \langle n, \beta | r | m, \alpha \rangle$$

$$= \frac{e \Delta}{\hbar^2} \times$$

$$\sum_{\alpha \beta \nu \mu} \sum_{\alpha' \beta' \nu' \mu'} E \left[ (\rho^{(2)}_{\alpha \beta \nu \mu} - \rho^{(2)}_{\alpha' \beta' \nu' \mu'}) \cdot \sqrt{\alpha + 1} \left( \frac{m, \alpha+1 | r | n, \beta}{\omega_p - \omega_\alpha + \omega_{m,n,\beta}} \right) \left( \frac{n, \beta | r | m, \alpha}{\omega_p + \omega_\beta + \omega_{m,n,\beta}} \right) e^{i(\omega_\alpha - \omega_\beta) \cdot r} + \right]$$

(12)
Consider the conjugate symmetry, only half of the equation (12) need be considered.

\[
P^{(2)}(\omega_p) = \frac{e \Delta}{\hbar^2} \sum_{maz} \sum_{nfl} \tilde{E} \cdot \left\{ (\rho_{maz,1,1}^{(0)} - \rho_{mfz,1,1}^{(0)}) \cdot \sqrt{\alpha + 1} \frac{\langle m, \alpha | r | n, \beta \rangle \langle n, \beta | r | m, \alpha \rangle}{(\omega_p - \omega_{\alpha} + \omega_{mfz,1f}) (\omega_{mfz,1f} + \omega_p)} e^{i(\omega_p - \omega_{\alpha}) \eta} + \\
(\rho_{mfz,1f} - \rho_{maz,1f}^{(0)}) \cdot \sqrt{\alpha + 1} \frac{\langle m, \alpha - 1 | r | n, \beta \rangle \langle n, \beta | r | m, \alpha \rangle}{(\omega_p + \omega_{\alpha} + \omega_{mfz,1f}) (\omega_{mfz,1f} + \omega_p)} e^{i(\omega_p + \omega_{\alpha}) \eta} + \\
(\rho_{mfz,1f}^{(0)} - \rho_{maz,1f}^{(0)}) \cdot \sqrt{\alpha + 1} \frac{\langle m, \alpha | r | n, \beta - 1 \rangle \langle n, \beta - 1 | r | m, \alpha \rangle}{(\omega_{maz,1f} + \omega_p) (\omega_p + \omega_{\alpha})} e^{i(\omega_p + \omega_{\alpha}) \eta} + \\
(\rho_{mfz,1f}^{(0)} - \rho_{maz,1f}^{(0)}) \cdot \sqrt{\alpha + 1} \frac{\langle m, \alpha | r | n, \beta + 1 \rangle \langle n, \beta + 1 | r | m, \alpha \rangle}{(\omega_{maz,1f} + \omega_p) (\omega_p + \omega_{\alpha})} e^{i(\omega_p - \omega_{\alpha}) \eta} + \\
(\rho_{mfz,1f}^{(0)} - \rho_{maz,1f}^{(0)}) \cdot \sqrt{\alpha + 1} \frac{\langle m, \alpha - 1 | r | n, \beta \rangle \langle n, \beta | r | m, \alpha \rangle}{(\omega_{maz,1f} - \omega_p) (\omega_p + \omega_{\alpha})} e^{i(\omega_p + \omega_{\alpha}) \eta} + \\
(\rho_{mfz,1f}^{(0)} - \rho_{maz,1f}^{(0)}) \cdot \sqrt{\alpha + 1} \frac{\langle m, \alpha | r | n, \beta - 1 \rangle \langle n, \beta - 1 | r | m, \alpha \rangle}{(\omega_{maz,1f} + \omega_p) (\omega_p + \omega_{\alpha})} e^{i(\omega_p - \omega_{\alpha}) \eta} + \\
(\rho_{mfz,1f}^{(0)} - \rho_{maz,1f}^{(0)}) \cdot \sqrt{\alpha + 1} \frac{\langle m, \alpha | r | n, \beta + 1 \rangle \langle n, \beta + 1 | r | m, \alpha \rangle}{(\omega_{maz,1f} - \omega_p) (\omega_p + \omega_{\alpha})} e^{i(\omega_p + \omega_{\alpha}) \eta} + \\
(\rho_{mfz,1f}^{(0)} - \rho_{maz,1f}^{(0)}) \cdot \sqrt{\alpha + 1} \frac{\langle m, \alpha | r | n, \beta \rangle \langle n, \beta | r | m, \alpha \rangle}{(\omega_{maz,1f} + \omega_p) (\omega_p + \omega_{\alpha})} e^{i(\omega_p + \omega_{\alpha}) \eta} \right\}
\]

Then,
\[ P_{\text{anti-Stokes}} = \frac{e\Delta}{\hbar^2} \times \hat{E} \times e^{i(\omega_p + \omega_v) \tau} \sum_{\text{na}} \sum_{\text{nf}} \]

\[ \left[ (\rho_{\text{na}1,\text{na}1}^{(0)} - \rho_{\text{m}1,\text{ma}1}^{(0)}) \cdot \sqrt{\alpha} \frac{\langle m, \alpha - 1 | \bar{r} | n, \beta \rangle \langle n, \beta | \bar{r} | m, \alpha \rangle}{(\omega_p + \omega_v + \omega_{\text{ma}1,\text{nf}} + \omega_{\text{ma}1,\text{na}1})} + \right. \]

\[ \left. (\rho_{\text{na}1,\text{nf}1}^{(0)} - \rho_{\text{ma}1,\text{nf}1}^{(0)}) \cdot \sqrt{\alpha} \frac{\langle m, \alpha | \bar{r} | n, \beta + 1 \rangle \langle n, \beta | \bar{r} | m, \alpha \rangle}{(\omega_{\text{ma}1,\text{nf}1} + \omega_p + \omega_v + \omega_{\text{ma}1,\text{nf}1})} + \right. \]

\[ \left. (\rho_{\text{na}1,\text{na}1}^{(0)} - \rho_{\text{ma}1,\text{ma}1}^{(0)}) \cdot \sqrt{\alpha} \frac{\langle m, \alpha + 1 | \bar{r} | n, \beta \rangle \langle n, \beta | \bar{r} | m, \alpha \rangle}{(\omega_{\text{ma}1,\text{ma}1} + \omega_p + \omega_v + \omega_{\text{ma}1,\text{na}1})} \right] \]

\[ P_{\text{anti-Stokes}} = \frac{e\Delta}{\hbar^2} \times \hat{E} \times e^{i(\omega_p + \omega_v) \tau} \sum_{\text{na}} \sum_{\text{nf}} \]

\[ \left[ (\rho_{\text{nf}1,\text{na}1}^{(0)} - \rho_{\text{ma}1,\text{ma}1}^{(0)}) \cdot \sqrt{\alpha} \frac{\langle m, \alpha - 1 | \bar{r} | n, \beta \rangle \langle n, \beta | \bar{r} | m, \alpha \rangle}{(\omega_p + \omega_v + \omega_{\text{ma}1,\text{nf}} + \omega_{\text{ma}1,\text{na}1})} + \right. \]

\[ \left. (\rho_{\text{na}1,\text{nf}1}^{(0)} - \rho_{\text{ma}1,\text{nf}1}^{(0)}) \cdot \sqrt{\alpha} \frac{\langle m, \alpha | \bar{r} | n, \beta + 1 \rangle \langle n, \beta | \bar{r} | m, \alpha \rangle}{(\omega_p + \omega_v + \omega_{\text{ma}1,\text{nf}1})} + \right. \]

\[ \left. (\rho_{\text{na}1,\text{na}1}^{(0)} - \rho_{\text{ma}1,\text{ma}1}^{(0)}) \cdot \sqrt{\alpha} \frac{\langle m, \alpha + 1 | \bar{r} | n, \beta \rangle \langle n, \beta | \bar{r} | m, \alpha \rangle}{(\omega_{\text{ma}1,\text{ma}1} + \omega_p + \omega_v + \omega_{\text{ma}1,\text{na}1})} \right] \]