

**SYNTHESIS AND CHARACTERIZATION OF
VAN DER WAALS HETEROSTRUCTURES,
AND NANOFABRICATION OF
ELECTRONIC DEVICES BASED ON
TWO-DIMENSIONAL MATERIALS**

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By
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Synthesis and Characterization of van der Waals heterostructures,
and Nanofabrication of Electronic Devices Based on Two-Dimensional
Materials

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November 2017

We certify that we have read this thesis and that in our opinion it is fully adequate,
in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

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Last two decades have seen a phenomenal shift of the dimensionality paradigm in materials processing, from zero-dimensional nanoparticles and quantum dots to one-dimensional nanowires and nanotubes, to two-dimensional materials. Each above-mentioned category of the nanomaterial can be manipulated exclusively, and mentored to drive special properties. However, for each of them, it may take time to discover their true potential and proper application in contemporary technology.

The emergence of graphene in 2004 triggered the scientific community to turn their vision toward investigation of two-dimensional materials. The impact of the discovery of graphene with its rare characteristics was such huge that no subject had been studied in the past as much as two-dimensional materials have. Nowadays, there are brand new two-dimensional materials with more intriguing properties which no one could imagine. However, our current technology had developed based on bulk material, and it is not ready yet to accept the use of nanomaterials. Recent advances in nanoscale characterization opened up new opportunities for nanomaterials to be investigated so delicately.

The other face of the discovery of nanomaterial is the need for ingenious fabrication method. Integration of electronic and optoelectronic circuits in confined space is one of the top paid objectives in research and development. The goal is providing a faster computational speed, lower energy consumption, and reducing the size of these systems. Although this is a long-term plan, it is not farfetched once we connect the dots and think outside the box.

Herein, we address synthesis, characterization, and manipulation of various two-dimensional materials. A thorough report on chemical vapor deposition of molybdenum disulfide and tungsten diselenide is provided in this study. Besides this two material we encountered some anomalies in the behavior of an unknown two-dimensional material which we synthesized it in our lab. The next step is to establish novel methods in order to fabricate electronic devices supporting atomically-thin structures. We could formulate a straightforward method to assemble atomically thin flake of material on transmission electron microscope grid, compatible for microscopy of thin materials and adjustable for various characterization method including Raman spectroscopy, and atomic force microscopy.

Last but not least, we introduced a novel method to induce mechanical strain on the two-dimensional flake. This method allows a dynamic scanning electron microscopy of the strained structure, which could be utilized for versatile applications. It worth to mention that, a fabrication process is mainly based on mentoring wet-transfer, focused ion beam, and electron beam lithography.

Keywords: Two-Dimensional Material, Chemical Vapor Deposition, Physical Vapor Deposition, Electron Beam Lithography, Focused Ion Beam, Wet-Transfer and Manipulation Methods, Uniaxial-Strain Gauge..

ÖZET

VAN DER WAALS HETEROYAPILARININ SENTEZİ, KARAKTERİZASYONU VE İKİ-BOYUTLU MALZEME TEMELLİ ELEKTRONİK AYGITLARIN ÜRETİMİ

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Geçtiğimiz yirmi yıl içerisinde bilim dünyası sıfır-boyutlu nanoparçacık ve kuantum noktalardan, tek-boyutlu nanotel ve nanotuplere, dahası iki-boyutlu malzemelere dayalı pek çok keşif ile olağanüstü bir paradigma kayması yaşamıştır. Yukarıda bahsi geçen malzemelerin her biri istenilen özellikleri göstermek üzere işlenebilmektedir. Ancak, bu malzemelerin gerçek potansiyellerinin tamamıyla anlaşılabilmesi ve günümüz teknolojisine yakışır bir biçimde uygulamaya geçirilebilmesi yakın gelecekte mümkün görülmemektedir.

2004 yılında gerçekleşen grafen malzemesinin keşfi, bilimsel toplulukların dikkatlerini iki-boyutlu malzemelere çevirmesine neden olmuştur. Oyle ki, grafen'in sıra dışı özellikleri dolayısıyla yarattığı etki, iki-boyutlu malzemeler konusu hakkında en çok araştırma yapılan alan haline gelmiştir. Günümüzde, insanın hayal dahi edemeyeceği derecede ilgi uyandırıcı özelliklere sahip yeni iki-boyutlu malzemeler keşfedilmiştir. Buna rağmen, sahip olduğumuz teknoloji yığinsal malzemeler üzerine kurulu olduğundan, nanomalzemelerin kullanıma geçebilmesine henüz hazır değildir. Nano-boyut mertebesinde yapılan karakterizasyon çalışmalarında yakın zamanda oluşan bulgular, nanomalzemelerin detaylıca incelenebilmesi için önemli fırsatlar ortaya çıkarmaktadır.

Nanomalzeme araştırmalarının bir diğer yuzu de üretim tekniklerini olabildiğince etkili hale getirme ihtiyacı olarak kendini göstermiştir. Gerçekleştirilen Ar-He çalışmalarında en yüksek ödeneğe sahip konuların başında elektronik ve optoelektronik yapıların kapalı ortamlarda entegre edilmeleri konusunun gelmesi bu nedendendir. Buradaki amaç daha yüksek bir işlem hızı sunarken, enerji tüketimini ve elektronik devre ebatlarını minimuma indirebilmektir. Bahse konu amaç

her ne kadar uzun vadede gerçekleşecek bir plan olarak görünse de, gerekli noktaları birleştirdiğimiz ve var olan düşünce sistemimizin dışına çıktığımızda bunun yakalanmasının çok da uzak olmadığını göreceğiz.

Bu çalışmada, çeşitli iki-boyutlu malzemelerin sentezi, karakterize edilmesi ve işlenmesi konularına değinilmiştir. Ayrıca molibden disulfid ve tungsten diselenit'in kimyasal buhar biriktirme yöntemiyle büyütülmeleri detaylı olarak sunulmuştur. Bu iki malzeme dışında ise, özellikleri hakkında türlü anomaliler gözlemlendiğimiz henüz tanımlanamayan bir iki-boyutlu malzemeye daha rastlanmıştır. Bir sonraki adımda ise atomik incelikteki yapıları destekleyen elektronik aygıtların üretilmesi için yeni metotların geliştirilmesi gerekmektedir. Uygulanabilirliği olan bir yöntem olarak, atomik incelikteki yapıların transmisyon elektron mikroskobu ızgarasında birleştirilmesi akla gelmektedir. Böylece hem ince malzemeler mikroskop altında gözlemlenebilmekte, hem de Raman spektroskopisi ve atomik kuvvet mikroskobu gibi çeşitli karakterizasyon tekniklerine uygun hale getirilmektedir.

Son olarak, yapılan bu çalışmada iki-boyutlu malzemeler üzerinde mekanik stres oluşturulmasını sağlayan yeni bir yöntem sunulmuştur. Bu sayede stres altındaki malzeme dinamik bir biçimde taramalı elektron mikroskobu altında incelenebilmekte, böylece çeşitli uygulamalara yeni yollar açılmaktadır. Bunlara ek olarak, kullanılan fabrikasyon teknikleri temel olarak malzeme transferi, odaklı iyon demeti ve elektron demeti litografi teknikleri üzerine kurulmuştur.

Anahtar sözcükler: İki boyutlu malzemeler, kimyasal buhar biriktirme, fiziksel buhar biriktirme, elektron demeti litografisi, odaklanmış iyon demeti, yaş transfer ve manipülasyon metodları, tek eksenli gerinim ölçer..

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Contents

1	Introduction	1
1.1	Materials in Two-Dimensional limit	2
1.2	Properties of Two-Dimensional Materials	5
1.3	Crystal Structure of Two-Dimensional Materials	5
1.4	Characterization of Two-Dimensional Materials	9
1.4.1	Scanning Probe Microscopy	9
1.4.2	X-ray Photoelectron Spectroscopy	10
1.4.3	Electron Microscopy	11
1.5	Growth and Synthesis Methods	11
1.5.1	Chemical Vapor Deposition	12
1.5.2	Physical Vapor Deposition	13
1.5.3	Exfoliation Techniques	14
2	Materials and Methods	15

2.1	Growth Process	15
2.1.1	Low-Pressure CVD Growth Process of Molybdenum Disulfide	16
2.1.2	Ambient-Pressure CVD Growth Process of Tungsten Diselenide	17
2.1.3	Free-Standing Heterostructure of Graphene and Tungsten Diselenide	19
2.1.4	Micromechanical Exfoliation of Layered Materials	22
2.2	Device Fabrication	23
2.2.1	Manipulation of Flakes and Transfer Methods	23
2.2.2	Strain Grip Fabrication and Assembly	25
2.2.3	Electron Beam Lithography	28
2.2.4	Thermal Evaporation	30
2.2.5	Lift-off Process	31
2.2.6	Wirebonding	32
2.3	Raman Spectroscopy	32
3	Results and Discussion	34
3.1	Tungsten Diselenide Growth and Characterization	34
3.1.1	Graphene/Tungsten Diselenide Heterustructure	44
3.2	Molybdenum Disulfide Device	46

3.2.1 Strain Dependent characterization	48
---	----

4 Conclusion and Future Outlook	51
--	-----------



List of Figures

1.1	Cartoons of different polymorphs in TMDCs from different crystallographic planes. Two lower insets reveals the intrinsic difference between two allotropes	6
1.2	Crystal structure of diverse layered structures. a) The orthorhombic structure which exists in phosphorene and bismuth. Bismuth also has rhombohedral structure. b) This structure is periodic buckled structure. Green and gray atoms can be designated as two different elements (such as group III chalcogenides) or can be identical (like in silicene). c) The well known graphene-like structure which happens in <i>hBN</i> , and silicene.	8
1.3	Representation of different steps in CVD process	13
1.4	Representation of different steps in PVD process	14
2.1	A SEM micrograph of hydrothermally synthesized <i>MoO₃</i> nanoribbons on copper substrate. This porous structure, with high active surface is so critical in large-area growth. The scale bar is 10 μm .	17
2.2	A Cartoon of the split CVD-furnace used in all experiments. The exhaust system could be paired with vacuum pump for low pressure process.	18

2.3	Optical microscopy image of graphene monolayer transferred on silicon substrate. Local wrinkling is obvious and torn part is obvious in the image. The scale bar is $600\ \mu m$	20
2.4	SEM image of graphene transferred on perforated TEM grid. some of the pores are covered with graphene monolayer. The scale bar is $30\ \mu m$	21
2.5	The main steps of the TEM sample preparation are shown here. a) A PC thin film is heated on the silicon substrate, and after cooling down it is cut to the pieces, considering the rough location of the flakes. b) Detaching the PC film at room temperature, and transferring it to the target using micro-manipulator. c) PC film is placed on TEM grid, considering the location of pores in a perforated membrane. d) A secondary melting step provides the adhesion of flakes to the surface. This polymer sacrificial layer will be dissolved in chloroform. The scale bar in a and b is $600\ \mu m$, and in c and d is $20\ \mu m$	24
2.6	A photograph of the as-fabricated silicon grips. These grips should be handles delicately since they are fragile due to the narrow silicon-joint which supports the whole structure. The scale bar is $1\ cm$	26
2.7	An Illustration of a transferred MoS_2 flake on a strain gauge. The scale bar is $20\ \mu m$	27
2.8	A photograph of a finalized strain gauge setup with all connections mounted on a SEM sample holder. The scale bar is $1\ cm$	28
2.9	An OM micrograph of a completed pattern after metallization and after lift-off process. The inset shows the higher magnification image, which indicated the fine structure of a hall bar, and attached connections to each leg. Scale bars are 300 and $20\ \mu m$ for the main frame and the inset, respectively.	31

- 3.1 a) The optical microscopy of as-grown WSe_2 crystals cover the silicon substrate. Inset is a higher magnification image, and it reveals the poly-crystalline nature of the flakes. Jagged and dentate edges reside to different crystal orientation in which they growth epitaxially and overlap. The scale bar is $600\ \mu m$ in the main frame, and $20\ \mu m$ in the inset. b) An ambient-temperature Raman spectrum of a WSe_2 flake, grown on silicon substrate. The laser excitation wavelength is $532\ nm$ 35
- 3.2 a) An optical microscopy image of the unknown crystal, distributed scarcely on silicon. The scale bar is $20\ \mu m$. b) A polarization dependent Raman spectra for a monolayer sample. Intensities are not normalized. c) Raman spectra acquired from different samples, namely monolayer flake, intermediate multi-layer, and clumps of bulk unknown material. Thickness was determined prior to the Raman spectroscopy either by contrast method using OM or by AFM. d) Photoluminescence measurements on a monolayer of unknown material, grown on the silicon substrate. The inset is the corresponding PL map of $1.56\ eV$ peak. The scale bar is $2\ \mu m$. . . 37
- 3.3 a) The SEM image of a transferred flake on TEM grid, after the annealing process. The flake is indicated by a triangle in the middle of the image. Those regions of the flake which are located on holes are going to be investigated via $HR-TEM$. The scale bar is $3\ \mu m$. b) The Raman scattering of a flake, accumulated regionally from the thinner part, the intermediate layer, and the thicker layer, respectively. The inset shows the exact location of the laser spot. The scale bar is $10\ \mu m$ 39

- 3.4 a) A bright-field *HR-TEM* micrograph of a free-standing monolayer of the unknown flake. The inset shows *FFT* of the *HR-TEM* image an scattering planes are indicated by indices. The image is locally blurred due to the polymer residue on the surface and rippling of the monolayer. The scale bar is 4 *nm*. b) The convolution image from the filtered *FFT* clearly shows the honeycomb lattice of the material. Two *X* and *Y* directions are indicated on the image arbitrarily. Intensity profiles along *X* and *Y* dashed lines are shown in the inset. The scale bar is 4 *nm*. c) A magnified *inverse-FFT* with depicted tungsten and selenium atoms overlaid, considering the structure belongs to *WSe₂*. The primitive cell is denoted with a dashed parallelogram. The scale bar is 0.5 *nm*. d) The topography map of the unknown material, obtained by AFM contact mode. The scale bar is 5 μm in the main panel, and 1 μm in the magnified scan. 41
- 3.5 The IV curve of the 2-terminal device constructed on unknown 2D material. The inset is the OM image of the same device. The crystal is located between the contact, however the halo beneath the crystal makes it hard to visual the crystal. The existence of triangular crystal is conformed by *SEM* measurement. The scale bar is 10 μm 44
- 3.6 A high magnification SEM image of custom-made *TEM* grid. This free standing structure ease the process for *TEM* measurements and eliminates excessive steps. Inset is a *HR-TEM* of heterostructure of *graphene/WSe₂*. Identification of *WSe₂* flakes is done by analyzing *FFT* data. The scale bar is 1 μm 46

- 3.7 a) A mechanically cleaved MoS_2 crystal, where the bluish color of the crystal is a sign of thinner layer. b) Raman spectra accumulated from different locations with various thicknesses on the sample shown in panel *c*). c) A magnified AFM height trace of monolayer and double-layer MoS_2 . Roughness on a silicon substrate is more than roughness on the crystals. The scale bar is 1 μm . d) OM image of CVD-grown MoS_2 continuous film, where there is no detectable grain boundary. Such film can elongate as few hundred microns and still remains monolayer. The scale bar in a) and d) is 20 μm 48
- 3.8 a) The strain-dependent Raman scattering of a few layer device, accumulated from the same location on the sample, at room temperature. b) A strained MoS_2 flake inside the *SEM* chamber, showing the dynamic microscopy of the device. The hexagonal flake is quite deformed and previously shown wrinkled part is flattened. The scale bar is 20 μm 49

List of Tables

2.1	Time evolution of the CVD furnace parameters	19
2.2	Time evolution of the CVD furnace parameters, for WSe_2 /Gr heterostructure.	22
3.1	Time evolution of the CVD furnace parameters, for the synthesis of the novel material.	36

Chapter 1

Introduction

Last two decades has seen a phenomenal shift of the dimensionality paradigm in materials processing, from zero-dimensional nanoparticles and quantum dots to one-dimensional nanowires and nanotubes, to two-dimensional material driven by the emergence of graphene. Recent advances in nanoscale characterization and device fabrication have opened up new opportunities for two-dimensional materials to be used in versatile application. Through this final thesis different families of 2D materials will be explained in a thorough review. Afterward, some architectures of chosen material will go through investigation.

1.1 Materials in Two-Dimensional limit

The definition of two-dimensional materials (2DMs) is still debatable since, during last years, some studied misinterpreted this concept [3]. However, planar domain of material, few atoms thick (typically less than 5 *nm*) with domain size larger than 100 nm could be designated as ultra-thin 2DMs. The first quantitative report of an atomically thin semiconductor is dated back to that work of P. Joensen, et al. which has been published in Mat. Res. Bulletin, at 1986. In this report *MoS₂* had been exfoliated via intercalation of lithium between the layers, resulted in single layer of *MoS₂* suspension in aqueous solution [4]. The empirical part was basically based on X-ray diffraction (XRD) pattern of suspension. Nevertheless, none of the experimental and theoretical works could successfully attract the attention of the scientific society, including the innovative chemical exfoliation of graphite, namely Hummers' method, which was reported at 1958 [5]. It was only A. Geim and K. Novoselov who could unravel the mystery of two dimensional materials after they could report a solid study concerning the discovery of graphene in 2004 [6]. A bulk of Graphite is stacks of graphene sheets held together by van der Waals interaction between the layers. The first report of isolation of graphene is by means of mechanical exfoliation (scotch tape method) [6]. This discovery attracted the copious amount of attention to this class of materials, and since then there are new reports of synthesis, properties, and application of novel 2D materials. In order to have a coherence discussion, atomically thin materials can be classified based on their electrical properties.

The family of elemental 2DMs (X-ene) consists of a periodic unit cell of single type of atom. For instance graphene, silicene (2D layers of silicon atoms), borophene (2D layers of boron atoms), and phosphorene (2D layers of phosphorus atoms) are designated as elemental 2D material. Their properties can vary from metallic and semi-metallic in borophene [7], and semiconductor in phosphorene (it is a buckled honeycomb structure, which is known as blue phosphorus) [8], to superconductivity in germanene [9]. Elemental 2DMs have a large window of bandgap, while the carrier mobility is highly dependent on topography and crystallographic structure.

The instability of elemental 2DMs under the ambient condition is a huge barrier toward real-life applications. Apart from graphene, elemental 2DMs are highly prone to oxidation and buckling in free-standing form. However, future efforts can partially address the stability of these materials to provide longer lifespan which is going to be discussed later on.

The second category of 2DMs has a chemical characteristic of MX_2 , where M is a transition metal atom (i.e. *Nb, T, or V*), and X is designated to chalcogen atoms (i.e. *Se, S, or Te*). Although transition metal dichalcogenides in bulk form have their cathedra in the industry as temperature-resistant lubricant, atomically thin transition metal dichalcogenides (TMDCs) such as MoS_2 , WSe_2 , and $TeSe_2$ seem to be rediscovered. Metal atom is sandwiched by a strong covalent bond between chalcogenide atoms. This group of 2DMs is so intriguing for fundamental research projects, due to facile production, a broad range of electronic band structure, and high-stability under ambient condition.

The third division of 2DMs could be identified by MX symbol, which is an illustration of two different types of atom embedded in the lattice structure. One of the subdivisions of this group is two-dimensional nitrides, carbides, and carbonitrides of transition metals, namely known as MXene (firstly reported by Y. Gogotsi in 2011) [10]. By means of control on synthesis parameters, the thickness of MXene sheets could be on the order of $1\ \mu m$, but this thinness might not be truly suitable for all sectors. Application of MXene is mainly in energy harvesting industry owing to its good conductivity, and high cycle-ability rate [10, 11]. This type of ceramics could be widely used in replacing of the electrodes in sodium ion batteries, lithium-ion batteries, and supercapacitor, since it can increase voltage window and therefore energy stored.

Another subdivision of MX is Group IV monochalcogenides, such as SnS, GeS, SnSe, GeSe. These layered materials are electronically identical to phosphorene, but they own orthorhombic crystal structure. Despite their indirect bandgap, their two-fold degeneracy in one axis of Brillouin zone brings spin-orbit splitting [12], and makes them a proper choice for valleytronics applications.

The other milestone of MX two-atom structures is hexagonal boron nitride (hBN), also known as white graphene. The honeycomb lattice of hBN consist of boron and nitrogen atoms, and it is analogous to graphene hexagonal rings. Atomically thin hBN possesses remarkable mechanical strength, large bandgap (6 eV), transparency over a wide range of wavelength, an inert structure, and low roughness [13]. Thus, this insulator has been utilized to cap variety of 2DMs for the sake of electrical, and ambient encapsulation of heterostructures. One of its outstanding features is that hBN does not modify electronic band structure of graphene near the Dirac point (it requires delicate misalignment of the crystallographic orientation in heterostructure) [14]. Since hBN is readily exfoliated down to few-layer, and there is almost no drastic change between few-layer and monolayer of it, exfoliation is a facile method to obtain large area flake for laboratory scale applications.

As it was defined here, 2DMs do not include atomically thin alkali films, thinned structures, transition metal films and surface reconstructions, which deserve a separate attention.

The instability of 2DMs in working environment can reduce time life of such devices. In order to expand the stability of 2DMs, there are two different approaches: Chemical modification, and encapsulation of the material. The chemical modification consists controlled reaction of hydrogen [15], chlorine [16] and oxygen [17] with unsatisfied covalent bonds in the lattice under ultra-high vacuum (UHV) conditions. Such process inevitably modifies the bandstructure in which the material cannot be recognized as its pristine form. Encapsulation method which prohibits interaction of reactant media with an unstable target. In this manner, an inert material such as polymeric film or hBN can provide a physical barrier or a cap. Although chemical modification is restricted to a few choice of material, encapsulation of volatile structures has been practiced for a variety of 2DMs. For instance, encapsulation of graphene with hBN prohibits plasmonic scattering in graphene, causing electron transport enhancement [18]. Besides, by a small modification one can create a tunnel junction of two layers of graphene separated by hBN [19]. Elimination of surface impurity, and providing an atomically smooth surface are other benefits of encapsulation method [20].

1.2 Properties of Two-Dimensional Materials

The family of 2D materials has been proven both experimentally and theoretically to possess outstanding mechanical properties, all in analogy to graphene. A defect-free structure with no grain boundary (single crystal) held by strong in-plane covalent bond can withstand high uniaxial stress, but vulnerable to shear stress. The confinement of wavefunction in two dimensions is the main reason that triggers outstanding characters in 2DMs, which are so different from their 3D counterparts. This confinement conceivably changes the density of the state (DOS) in Brillouin zone of the material, leading to drastic changes in macroscopic scale. Many 2D layers have excellent transparency in visible regime, while others show magnificent absorption (high absorption index) in a wide spectrum range. Besides, intense photoluminescence (*PL*, spectacular photocurrent, and ballistic conductivity are some instance which makes these materials ideal for fundamental study in quantum mechanics and solid state physics [21, 22]. The large lateral size in such material endows ultrahigh specific surface area. Unique K-diagram gives varieties of properties such as massless Dirac fermions, and high mobility of charge carriers. In the flip side, TMDCs nanosheets show large bandgaps with moderate carrier effective mass. To summarize the above mentioned, 2DMs own diverse properties, and one can devise a new method to observe the synergistic effect within the 2D world.

1.3 Crystal Structure of Two-Dimensional Materials

The arrangement of atoms in space depends on the combination of elements, and the thermodynamics of the system at a particular condition. Stability of a particular phase is highly related to different conditions including temperature, electromagnetic field, mechanical strain, and effect of the substrate on overlayer, which lead to either a stable or a metastable phase. Although in 2DMs atoms are spread in a few layers, but their arrangement could be quite diverse, so their

properties. The simplest structure one could imagine is the hexagonal arrangement of atoms having no buckling. This is the well-known honeycomb structure of graphene, therefore it is also named as graphene-like structure (figure 1.2c).

The crystallographic structure of TMDCs is correlated to the coordination spheres of the transition metal atoms. Different stacks of the transition metal atoms are sandwiched between two layers of the chalcogenide atoms. The most practical structures of TMDCs are either trigonal prismatic ($2H$) or octahedral ($1T$) coordination (Figure 1.1 in which atoms are bonded with strong covalent bond, and between layers, there are weak van der Waals forces. The $2H$ coordination in terms of stacks of atoms is an AB configuration in which chalcogenide atoms occupy the same position A , on top of each other in different layers. In contrast, $1T$ phase corresponds to ABC configuration where chalcogenide atoms (i.e. A and C in the figure 1.1 bottom-left panel) are not placed on top of each other. Figure 1.1 represent the structure of $1T$ and $2H$ phase in TMDCs. Considering that there are more than 28 theoretically-predicted TMDCs layered material, investigation of the structural phase and their effect on properties in each case is a cumbersome task.

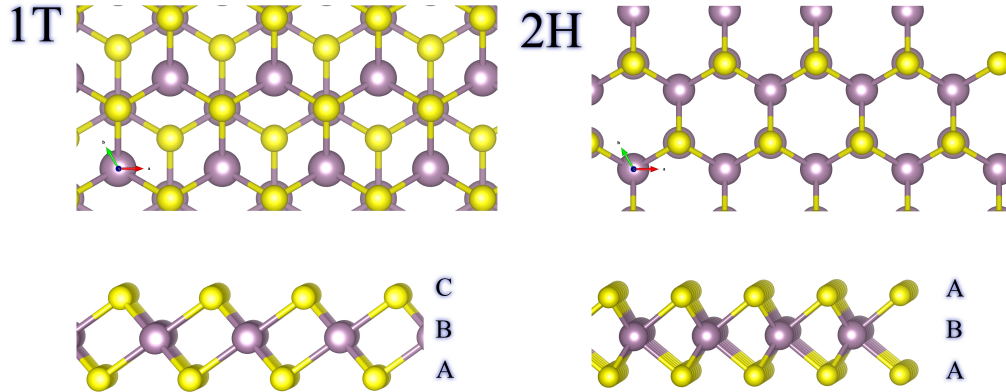


Figure 1.1: Cartoons of different polymorphs in TMDCs from different crystallographic planes. Two lower insets reveals the intrinsic difference between two allotropes

In contrast with aforementioned structures, there are other 2DMs with more elusive and ambiguous structure. For instance, silicene with more than 5 different

predicted polymorphs is the milestone [23]. This diversity arises from the non-planar bonds which hold substrate-supported silicene [24]. In other words, the interaction between the substrate and overlayer atom, and hybridization between Ag and Si orbitals cause such variance. The honeycomb structure of silicene shows complex buckling arrangements, which could be described by Wood's notation. The nomenclature $N \times N$ describe the periodicity of the overlayer silicene with respect to the substrate crystal structure. For instance, $\sqrt{3} \times \sqrt{3}$ has a unit cell which keeps repeating itself by $\sqrt{3}$ times of the lattice constant of the substrate. It worth to mention that atomic-resolution scanning tunneling microscopy (STM) is the one powerful tool that allows us to investigate the correlation between the substrate and overlayer atoms.

Two-dimensional phosphorus exhibit multiple polymorphs, in analogy to multiple allotropes of bulk phosphorus. Phosphorene could be readily get exfoliated from bulk form of black phosphorus which owns orthorhombic crystal structure of weakly bound layers. Apart from phosphorene, there are other allotropes which only could be grown on a substrate but not exfoliated. The semiconducting blue-phosphorus has a buckled honeycomb structure which could be grown via UHV molecular beam epitaxy (MBE) on metal substrate [25].

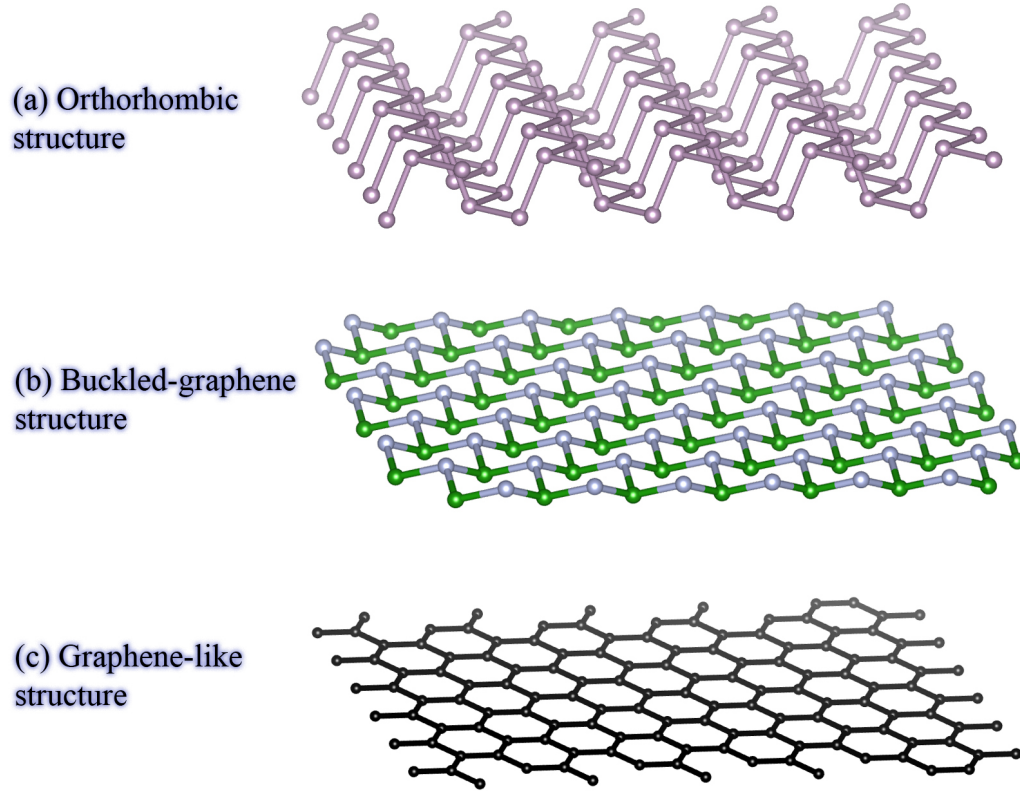


Figure 1.2: Crystal structure of diverse layered structures. a) The orthorhombic structure which exists in phosphorene and bismuth. Bismuth also has rhombohedral structure. b) This structure is periodic buckled structure. Green and gray atoms can be designated as two different elements (such as group III chalcogenides) or can be identical (like in silicene). c) The well known graphene-like structure which happens in hBN , and silicene.

1.4 Characterization of Two-Dimensional Materials

In company with the synthesis of novel 2DMs, innovation in characterization methods could unravel new features out. Occasionally, some of the oldest methods could be able to prove their virtue for an innovative characterizing method. Categorically, these methods focus on different aspects of material such as composition, crystal structure, defect and chemical state, and electronic and magnetic state. In this manner, reliability, speed of the whole process, specificity, and accuracy can be the main concerns. Appreciation of the physics behind each method plays a critical role in which it could facilitate the data analysis or it can cease further progress.

Certainly, visibility of ultrathin 2D nanomaterials under an ordinary optical microscope (OM) was a big assist for identification of layered materials since the discovery of graphene. This phenomenon arises from the reflection/absorption of light at interfaces of overlayer and substrate. Geim et al. illustrated that the maximum optical contrast of 2DMs flakes could be obtained by using SiO_2 (90, or 280 nm)/ Si substrates [26]. Yet, the role of dielectric SiO_2 layer, and the silicon beneath it, the perturbation of electromagnetic wave and optical path, and opacity of the flakes need further investigations. Rather than bright-field optical microscopy (BF-OM), there is not much of benefit in other OM techniques, including differential interference contrast (DIC), or dark field OM. Apart from optical microscopy, there are some advanced methods which provide subtle characterization of confined media, which are going to be discussed in the following sections.

1.4.1 Scanning Probe Microscopy

The gigantic family of scanning probe microscopes (SPM) share a mutual working principle with each other: formation of a topography image by using a physical

probe that scans the specimen. The atomic-resolution Scanning Tunneling Microscopy (STM) could reveal the crystallographic orientation of atoms, something that is so important in the study of 2D heterostructures. To interpret the importance of this technique, one could study the effect of metallic substrate, on the as-grown 2DMs overlayer. In other word, properties of layered heterostructures can be studied in a non-destructive method. Even the in-situ STM experiments are feasible after a few adjustment, to further prohibit sample degradation. However, Atomic Force Microscopy (AFM) by itself has enough potential to reveal topography map of 2DMs in a relatively straightforward way. It worth to mention that AFM collects the information from the magnitude of repulsive forces, while STM detects the information from the interaction between the atoms, and from highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO/LOMO) orbitals. Complication of the STM measurements vanishes in the AFM analysis, and comprehension of data is way easier in the latest case.

1.4.2 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (*XPS*) is one of the surface sensitive techniques which works based on excitation of photoelectron from the outer orbital shell of the specimen. This phenomenon could be explained completely as a quantum mechanic process, where the energy of the emitted electron is correlated to the band energy of the corresponding shell. The sensitivity of *XPS* is down to 1% *Wt* of compound saturation. This is while the surface sensitivity of this method is down to 10 *nm*, and by implementing a few adjustment, the data acquisition could happen in the first 1 *nm* of the surface. All above mentioned, plus easy sample preparation makes this non-destructive test a handy method for the study of 2D materials.

1.4.3 Electron Microscopy

Scanning Electron Microscopy (SEM) is a powerful tool to study morphology and particle size distribution of the specimen. There could be additional tools within the SEM such as energy dispersive spectroscopy (EDS) for elemental analysis, and immersion lens to identify grain boundaries and defects, et cetera. On the other hand, high-resolution transmission electron microscopy (HR-TEM) has more potential to unravel atomic structure, defect density, crystallographic orientation, the degree of rippling in structure, and elemental analysis. Aberration correction scanning transmission electron microscope (AC-STEM) is a powerful tool for spacing measurements. Due to high acceleration energy of electron beam in a conventional TEM setup, the fragile structure of 2D layers could be modified easily by knock-on displacement. This will cause an alteration in nano-scale and may generate an amorphous structure from the initial crystalline structure. In order to prohibit such defects, one can make use of AC-STEM to perform imaging at much lower acceleration energy (60 to 120 eV) [27] to obtain atomic resolution micrographs. Besides, STEM Dark Field (DF) mode has the potential to reveal small deviation in composition. Studies show that sensitivity of this method to lighter elements is higher in Bright Field (BF) and Annular Dark Field (ADF), while the High-Angle Annular Dark Field (HAADF) is sensitive to a variety of atoms with a different atomic number, hence less sensitive to lighter elements.

1.5 Growth and Synthesis Methods

Growth process has always been challenging in industry and laboratories, to satisfy reproducibility, cost, the scale of production, and reliability. Contamination within the bulk material is a concern, but in reduced dimensions, contamination needs another level of care, since a tiny change in the stoichiometry of the material would lead to a huge change in properties. In general, 2DMs are obtained by the assist of three different approaches which are going to be described in upcoming lines. What these three methods share is a gentle adjustment in order to

prohibit any stoichiometry disorder, interstitial vacancy, surface contamination and so forth.

1.5.1 Chemical Vapor Deposition

Chemical vapor deposition (CVD) technique has many divisions including metal organic CVD (MO-CVD), MBE, Low-pressure to high-pressure CVD, Laser Assisted CVD (L-CVD), and more importantly atomic layer deposition (ALD). The dissociation of precursors under controlled condition will lead the formation of atomically thin materials on the substrate. Subtle control on concentration of precursors, reactor temperature, pressure, and time of reaction are means to have sufficient monolayer, multilayer or bulk of grown materials.

Growth occurs when conditions are suitable for diffusion or sublimation processes, generating volatile compounds rich from the precursor elements. Further evolution of these compounds would complete synthesis process and final product forms on the substrate. For this reason, the choice for the substrate is limited to those that can dissolve precursor, or provide the diffusion of the precursor. In bottom-up synthesis, the role of the substrate is so critical in the properties of the overlayer and highly effects the compilation steps of transfer and fabrication. Generally speaking, the solubility of the overlayer in the substrate is not desirable, hence the formation of any compound on top of precursor will terminate the CVD process. After all these considerations, polished oxide and nitride of silicon, Sapphire, and even van der Waals heterostructure is a choice of substrate for the growth of TMDCs, and a metallic substrate such as Ag, Cu, and Au is used for growth of elemental 2DMs.

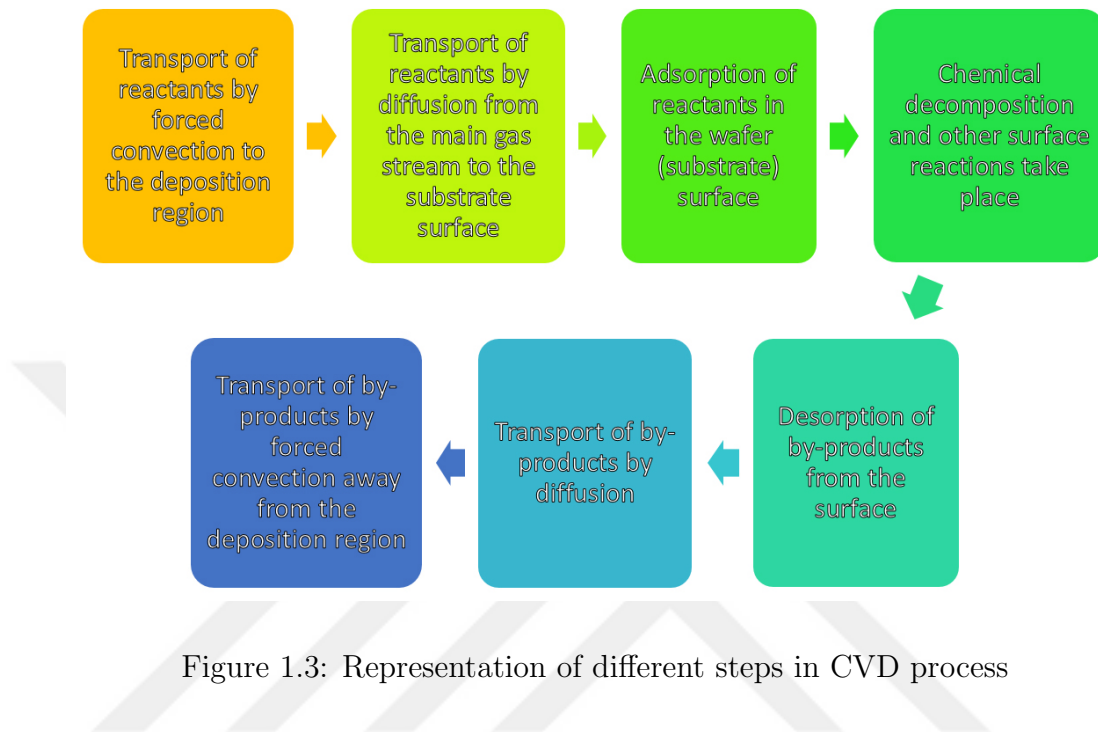


Figure 1.3: Representation of different steps in CVD process

1.5.2 Physical Vapor Deposition

The migration and deposition of desired material on top of a substrate, exclusive of any chemical reaction is known as physical vapor deposition (PVD). The deposition of elemental 2DMs on top of a metal substrate requires delicate adjustment of parameters, including UHV, and Ultra purified source and substrate [28]. Electron beam evaporation, thermal evaporation, pulsed laser deposition (PLD), and sputtering are the main methods to achieve atomically thin layered material.

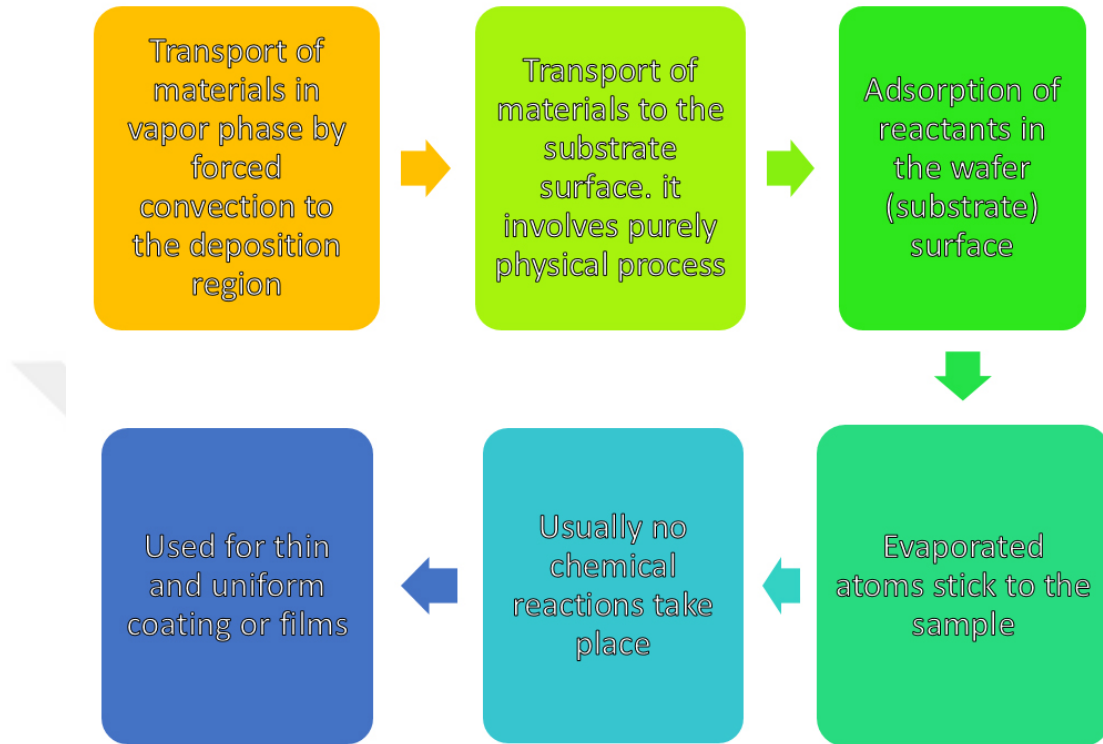


Figure 1.4: Representation of different steps in PVD process

1.5.3 Exfoliation Techniques

The exfoliation of a few-layer structure from a bulk layered material is known as micromechanical cleavage (so-called Scotch tape method). Basically, the first report of isolation of graphene is mentoring Scotch tape technique back in 2004 [6]. Although the micromechanical exfoliation is helpful for preliminary electronic devices, the small lateral size of exfoliated flakes and limited choice of exfoliative material is an obstacle which should be addressed. The chemical exfoliation and electro-chemical exfoliation provides larger flake size well dispersed in a solvent, but chemical modification of the flakes and surface defect makes the obtained crystals unsuitable for electronics [29]. For the sake of clarification, in this study, we have not utilized any chemical or electrochemical exfoliation, due to the low yield of this process.

Chapter 2

Materials and Methods

2.1 Growth Process

A delicate design of growth is a prerequisite of any experimental process. Further investigation of the growth mechanism and effect of variables seems so critical in the synthesis of 2DMs. In this master study, different approaches have taken towards the fabrication of van der Waals heterostructures. These methods are going to be explicitly described in this chapter.

2.1.1 Low-Pressure CVD Growth Process of Molybdenum Disulphide

Top-down synthesis of atomically thin crystals of MoS_2 gained copious attention during last decade. In order to obtain long-range uniformity in thickness, size and distribution of flakes the understanding of the growth mechanism is so crucial. One scalable technique is sulphurization of molybdenum-containing films [30,31]. No restriction in choice of substrate (e.i. Al_2O_3 , Cr , Au , and Au/Cr as a choice of the substrate) is the other advantage of this method. However, the carrier mobility of CVD-grown semiconductor is on the order of $0.004\text{-}0.04\text{ cm}^2V^{-1}s^{-1}$, where as-exfoliated samples own $0.1\text{-}10\text{ cm}^2V^{-1}s^{-1}$. A relatively recent study regarding to the solid sulphurization of molybdenum thin film reports large surface-area poly-crystalline or monolayer MoS_2 [32]. Sulphurization of molybdenum trioxide (MoO_3) is in fact the traditional approach to get highly crystalline, large domain size, uniform MoS_2 [33]. To the best of our knowledge, the formation of MoS_2 flakes is limited by the diffusion of MoO_{3-x} .

In this study, MoO_3 nanoribbons have been synthesized by a simple hydrothermal process. A 1.2 g Heptamolybdate tetrahydrate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ is dissolved in 40 ml of 2.2 M nitric acid and then poured in a Teflon container. The flask then is heated to 170 °C for 3 hours [34]. After ceasing the process by dilution with Deionized water (DI water), the obtained aqueous solution is vacuum filtered and centrifuged at 6000 rpm, until pH value becomes approximately 6. Large-area films are formed by drop-casting of this solution on silicon substrates and used as a precursor of molybdenum. Figure 2.1 represent the morphology of drop-cast nanoribbons on top of an arbitrary substrate. A few cleansed silicon substrates are placed adjacent to the MoO_3 covered wafer, in the hot zone of the CVD chamber. The sulfur source (0.8 - 1.2 g placed in alumina boat) is placed upside down above the MoO_3 source. Evaporation of sulfur starts when hot-zone of the furnace reaches to 600 °C (thus sulfur source is approximately at 200 °C). After reaching that point the temperature increases to 850 °C in a slower rate of 20 °C/min. After lingering at 850 for 10 min, the furnace will be quenched down to 100 °C. The carrier gas in this process is Ar, which is purged into the

furnace with a ceaseless rate of 200 *sccm*. The internal pressure of the furnace has been controlled by vacuum rotary pump and a pin valve, which provides sufficient situation for the growth process.

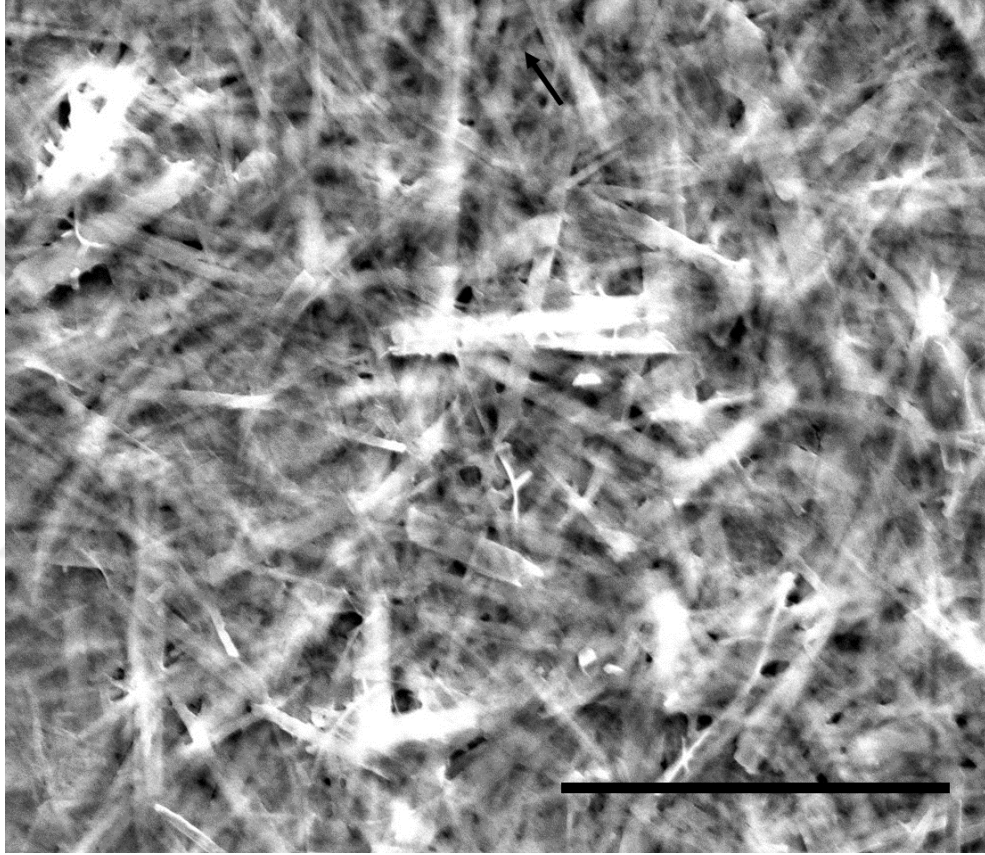


Figure 2.1: A SEM micrograph of hydrothermally synthesized MoO_3 nanoribbons on copper substrate. This pores structure, with high active surface is so critical in large-area growth. The scale bar is 10 μm

2.1.2 Ambient-Pressure CVD Growth Process of Tungsten Diselenide

Synthesis procedure of atomically thin WSe_2 is analogous to the process reported in the previous section. A 100 *mg* WO_3 powder is placed in the hot zone of the furnace, and 300 *mg* pristine selenium powder is placed at the neck of the furnace.

The placement of the Se boat is in a way that molten selenium provides reducing environment during the whole process. Figure 2.2 illustrate the configuration of the split CVD-furnace which is used for all growth process in this study and the placement specified for the WSe_2 growth. The distance between the substrate and the precursors is critical in a way that defies the density and distribution of the flakes.

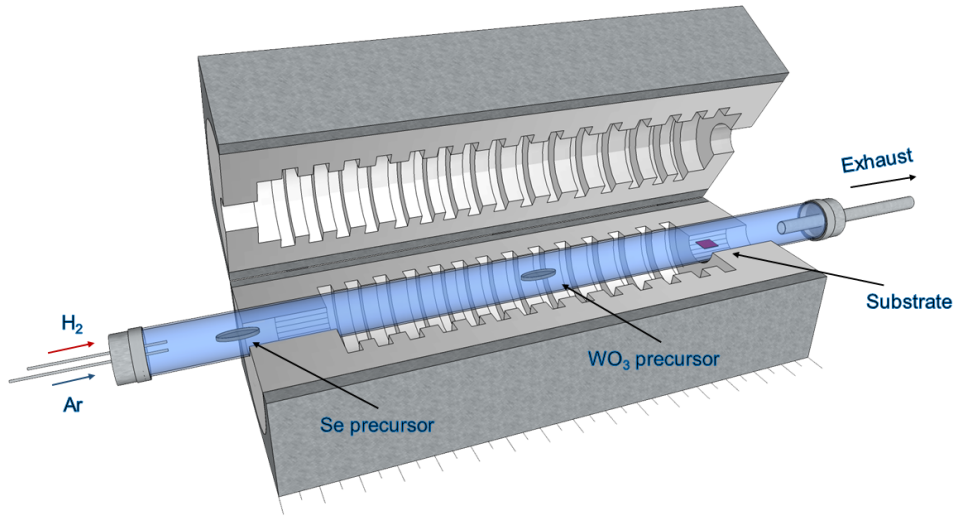


Figure 2.2: A Cartoon of the split CVD-furnace used in all experiments. The exhaust system could be paired with vacuum pump for low pressure process.

The table 2.1 provides the detail of this method. The first 10 *min* of this process is purge of huge amount of inert and reactive gas, in order to eliminate oxygen content inside the chamber. Although oxygen could not be completely eliminated from the chamber, samples should be exposed to the lowest dose of oxygen possible. The substrate is placed downstream, where the temperature reaches to 600 °C.

Time (<i>min</i>)	0	10	50	55	80
Temperature ($^{\circ}C$)	25	25	920	920	100
Gas flow (<i>Ar</i> (<i>sccm</i>))	500	500	10	80	10
Gas flow (<i>H₂</i> (<i>sccm</i>))	200	200	5	10	0

Table 2.1: Time evolution of the CVD furnace parameters

2.1.3 Free-Standing Heterostructure of Graphene and Tungsten Diselenide

There have been so many efforts to fabricate vertical stacking of 2DMs during last few years [35]. In this MS study, we could achieve direct growth of two-dimensional crystals of WSe_2 on top of graphene. The CVD grown Monolayer of graphene has been synthesized on ultra-pure copper foil, using acetylene gas as carbon source and hydrogen gas for purification [36]. After synthesis has been completed the metal substrate is dissolved by ammonium persulfate (APS 0.1 *M*) causing the graphene layer get released from the copper and floats on top of DI water. After rinsing so many times, the graphene layer could be transferred to any arbitrary substrate by fishing the floated graphene [37]. Figure 2.3 illustrates a CVD-grown graphene transferred on top of a silicon substrate.

Considering the specification of the flakes, and characterization methods a custom-made TEM grid has been design with specified structure. A Si/Si_3N_4 (100 *nm*) is patterned by optical lithography profoundly and then etched using potassium hydroxide (*KOH*) to dissolve the beneath silicon, and leave a large window of silicon nitride membrane (The yellow square in the center of the figure 2.5b). The as-prepared membrane then is ready for further modifications. Using focused ion beam (FIB) ion gun (FEI Nova NanoSEM600, equipped with Ar ion gun, and platinum deposition source), spherical pores are etched through the Si_3N_4 membrane. These pores should be big enough to provide enough lateral space for TEM-related measurements and should be narrow enough that can support the free-standing structure (Figure 2.4). A monolayer of graphene, could be also transferred on top of such TEM grid. This grid could be used for the characterization steps after direct growth of heterostructure on top of graphene. It is noteworthy to say that, a similar method has been exploited for the fabrication

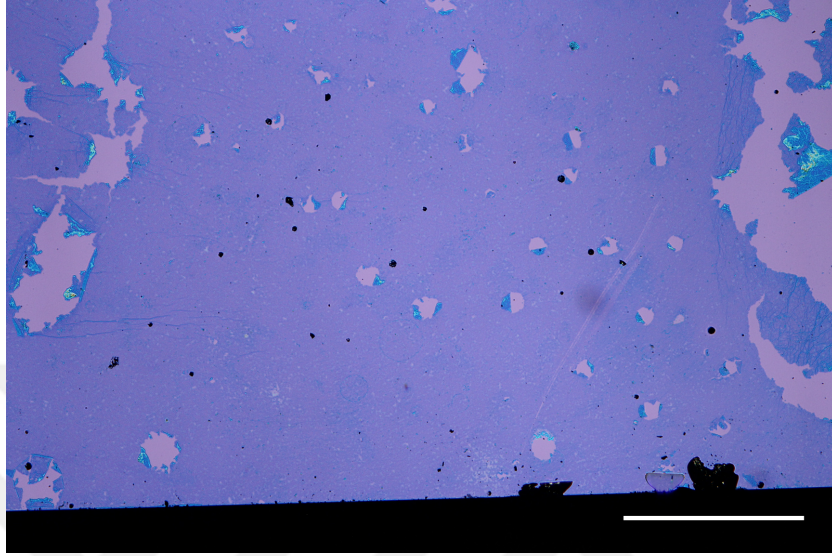


Figure 2.3: Optical microscopy image of graphene monolayer transferred on silicon substrate. Local wrinkling is obvious and torn part is obvious in the image. The scale bar is $600\ \mu\text{m}$.

of free-standing pristine WSe_2 flakes (Figure 2.5). These holey membranes are so suitable for TEM measurements, since there will be less background signal from the substrate, and the target itself is completely suspended. Therefore, selected area electron diffraction (SAED), High-Resolution TEM (HR-TEM), and DF microscopy is feasible on prepared atomically thin samples.

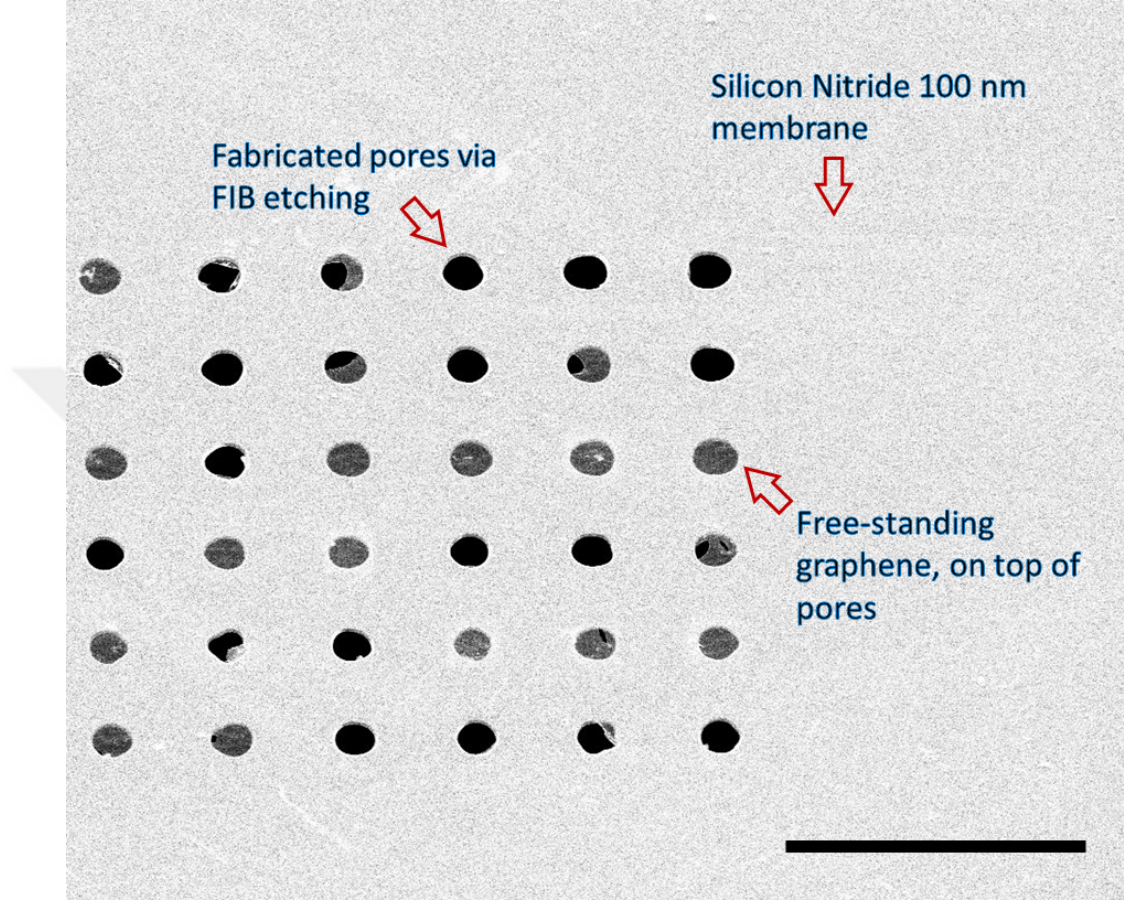


Figure 2.4: SEM image of graphene transferred on perforated TEM grid. some of the pores are covered with graphene monolayer. The scale bar is $30\ \mu\text{m}$.

The gist of this process is a modified version of the synthesis method of WSe_2 on a bare silicon substrate, but here the substrate is the as-prepared TEM grid with transferred graphene on top 2.4. A silicon oxide substrate provides a very smooth surface without any dangling bond, no defect sites, and with almost no topographical feature. In contrary, graphene surface is full of unsatisfied bonds, polymer residue, and wrinkling which thermodynamically are suitable nucleation sites. Consequently, amount of precursors and purged gas should decrease immensely to avoid the appearance of bulk structures instead of few-layer crystals. Table 2.2 represent the growth parameters. The substrate itself is located downstream where the maximum temperature rises to $400\ ^\circ\text{C}$. The type and the

amount of WO_3 and Se are equivalent as previously reported WSe_2 CVD procedure.

Time (<i>min</i>)	0	10	40	65
Temperature ($^{\circ}C$)	25	25	850	100
Gas flow (Ar (<i>sccm</i>))	500	500	10	60
Gas flow (H_2 (<i>sccm</i>))	200	200	10	20

Table 2.2: Time evolution of the CVD furnace parameters, for WSe_2 /Gr heterostructure.

The free-standing graphene could easily get oxidized at an elevated temperature in an ambient atmosphere. To prohibit any evolution of the graphene monolayer, excess hydrogen is purged to the furnace and temperature of the substrate does not exceed above $400\text{ }^{\circ}C$ through the whole process.

2.1.4 Micromechanical Exfoliation of Layered Materials

Since the CVD growth of different layered material is not always feasible, one detour towards a facile fabrication of few-layer materials could be attained by exfoliation methods. Here in this study, we employed the traditional mechanical exfoliation method to obtain atomically thin crystals.

In this manner, A highly oriented large domain size source is so crucial in order to maximize the lateral size of flakes. A controlled amount of bulk material is placed on top of a commercial scotch tape. Following former steps in a dust-free environment, repeated peeling of layered material would continue for a couple of rounds. Then, the mother tape will be stuck to a silicon substrate for further investigation. This process may lead to a few thin crystals with large lateral size. In the first place, optical microscopy would give a good sense of the thickness of the crystals, and further identification will be executed by AFM height-trace measurements. The AFM measurements have been conducted mentoring *Park Systems XE-100*. The isolation of an atomically thin material correlated to the van der Waals which attaches the layers together in the first place. The most

desirable condition is when in-plane bonding is stronger than out-of-plane interactions. Consequently, the interaction between layers and tape is strong enough to detach layers from each other.

2.2 Device Fabrication

Investigation of confined structures needs deliberate adjustment in the measurements setup. Dealing with micron-size targets requires ingenious methods of device fabrication. Through the following line, there will be the extended explanation of some original or inspired-by methods.

2.2.1 Manipulation of Flakes and Transfer Methods

Manipulation is defined as some versatile techniques to transfer flakes from an initial substrate, into a secondary substrate, without altering the properties of the flakes and without contaminating the sample. Wet-transfer, dry-transfer, and Pick-and-lift techniques are three most resourceful approaches in the assembly of 2DMs [38, 39]. Wet-transfer includes isolation of flakes in a solution and transferring it to a tertiary substrate by means of drop-casting, spinning or fishing. Dry-transfer, also known as viscoelastic stamping, as well as Pick-and-lift method, provide a polymer free surface and eliminates any source of contamination among the assembled layers. A self-cleansing mechanism is an intrinsic trait of Pick-and-lift technique, which pushes contamination away from the interface of the heterostructure [40].

However, in this study, we decided to use the wet-transfer method which is more feasible and more convenient. This technique is based on the transfer of a sacrificial layer accompanied with 2D crystals, aligning and placing it on another target, and then dissolving the sacrificial layer. In the early works, the sacrificial layer chosen to be Cellulose Acetate Butyrate (CAB). Based on further observations, Poly Carbonate (PC) shows superior to CAB, due to a lower content of

polymer residue.

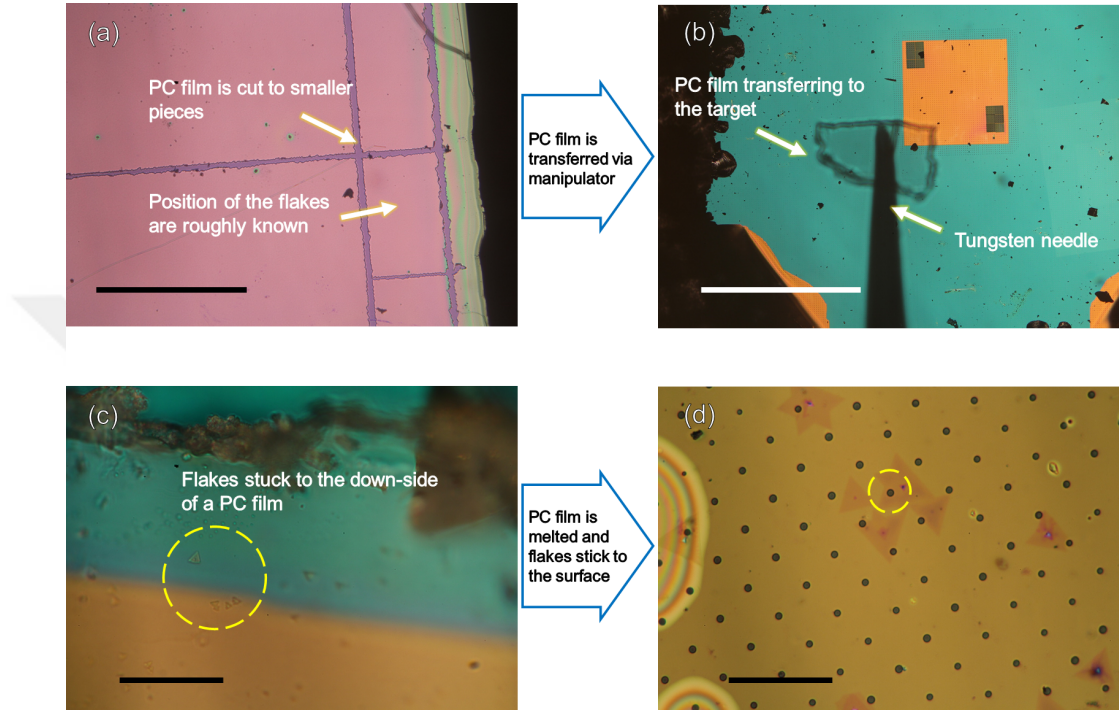


Figure 2.5: The main steps of the TEM sample preparation are shown here. a) A PC thin film is heated on the silicon substrate, and after cooling down it is cut to the pieces, considering the rough location of the flakes. b) Detaching the PC film at room temperature, and transferring it to the target using micro-manipulator. c) PC film is placed on TEM grid, considering the location of pores in a perforated membrane. d) A secondary melting step provides the adhesion of flakes to the surface. This polymer sacrificial layer will be dissolved in chloroform. The scale bar in a and b is $600\ \mu\text{m}$, and in c and d is $20\ \mu\text{m}$.

A 6% wt of PC granule dissolved in 100 ml chloroform is used to prepare thin films of PC by drop casting of the solution on a microscope slide. This film is transparent under visible light of the microscope, thus, it is possible to place a piece of this film on top of as-grown flakes (figure 2.5a). This film can adhere to flakes once it gets melted (above $150\ ^\circ\text{C}$) and by use of a micromanipulator (3 axes motorized Marzhauser Wetzlar) which is assembled on an optical microscope (figure 2.5c). A tungsten needle ($0.3\ \mu\text{m}$ diameter) attached to the micromanipulator provides delicate positioning of the PC film (figure 2.5b). Then, a secondary melting process makes the whole structure of polymer-flakes stick to the target. The polymeric film gets dissolved in chloroform for 2 h following by the annealing

step. The flake would attach to the structure if the van der Waals adhesion force overcome the repelling forces (figure 2.5d). Annealing process consists of heating the whole structure under Ar/H_2 atmosphere for 3 h is so effective in order to eliminate polymer residue from the surface [40]. Figure 2.5 illustrates the main steps of transfer process in TEM sample preparation.

2.2.2 Strain Grip Fabrication and Assembly

Investigation of mechanical properties of 2DMs has been a very intriguing topic since the discovery of graphene. However, applying proper uniform stress on nanometers-thick, and few micron wide layer has been a challenge. One clever approach is to apply uniaxial stress to thin film using a flexible substrate. The choice of substrate is limited to some polymers, such as polytetrafluoroethylene (PTFE), and PC in which it can bear bending test. Once a flake is clamped on polymeric beam, the sample will be flexed by an apparatus (either three-point or four-point bending). This bending in the substrate leads to a uniaxial-stress in the transferred flake. This method is limited to a certain amount of strain (i.e. below 3%), and beyond that limit defects in the substrate, and sliding of the flake cause failure. Further observations promise inventive flexible electronic devices supporting 2DMs as their active material [41].

The other method to convey study on mechanical properties of thin films and thin flakes is to employ nanoindentation technique. This study starts by transferring the flake on top of a perforated substrate. Interpretation of force-displacement behavior of the tip statically pushing on the free-standing flake reveals mechanical properties of the material. To the best of our knowledge, this method drives the most accurate result so close to the theoretical values. Nanoindentation can study materials behavior in linear and non-linear regime (elastic and plastic behavior) and can measure intrinsic strength of 2DMs [42,43].

We demonstrate an inventive method and try to implement an old idea and make it compatible with our setup. The idea is to apply strain to the thin film directly by means of a silicon grip. Fabrication process of this chip includes

multiple steps:

First, a $3\ \mu\text{m}$ of 5214 photoresist has been coated in both sides of a complete wafer to prohibit random etching. After a standard photo-lithography step, the structure has been etched by buffered oxide etch (BOE 7:1) to remove front side SiO_2 layer. Consequently, the silicon substrate is etched using a deep reactive ion etching (DRIE) process, including 800 cycles to remove $350\ \mu\text{m}$ of silicon. Using a mechanical dicer machine, the rest of silicon is cut through and a tiny gap is left in on side to act as a hinge. Later, these structures are cut to smaller chips using the mechanical dicer. The result is silicon grips, which are hinged by a narrow silicon joint in one side, and free to flex from other side. Later, the polymer resist will be dissolved in acetone. Figure 2.6 illustrates our custom-made strain grip. Depending on the precision of former steps, and etch duration the gap size can be set to be less than $10\ \mu\text{m}$ wide.

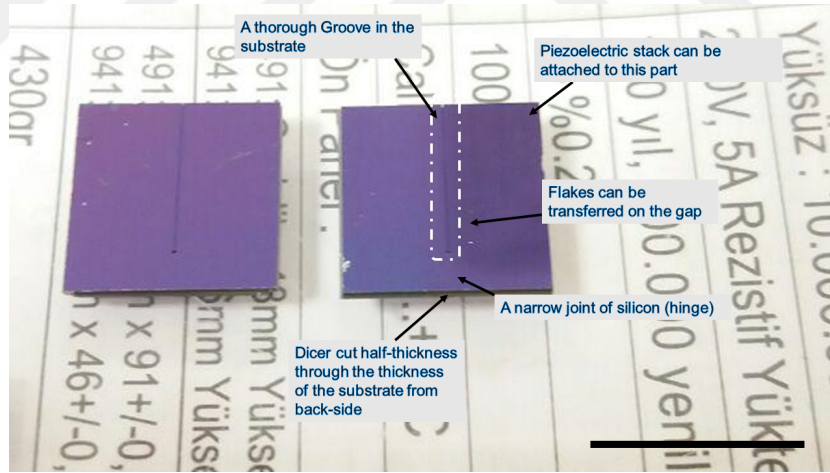


Figure 2.6: A photograph of the as-fabricated silicon grips. These grips should be handles delicately since they are fragile due to the narrow silicon-joint which supports the whole structure. The scale bar is $1\ \text{cm}$.

After preparation of the grips, crystal transfer method will be the complementary step. Approximately, a thin flake with at least $15\ \mu\text{m}$ lateral width is a proper choice for the transfer. In this work, we transferred few-layer MoS_2 flakes on top of these grids. This process needs careful attention, noticing that the grips are so fragile and brittle. Following the former steps, electrical contacts can be easily built upon by putting indium needles on the sample. Indium needles are produced by drawing out the tip of tungsten needle out of molten In source.

The speed of tungsten needle is inversely proportional to the diameter of the In needle. This type of needle can then be placed precisely on the specimen (by means of the same micromanipulator) and it usually provides good physical and electrical contact with the target crystal. The desired specimen is also heated to the melting point of the In ($156.6\text{ }^{\circ}\text{C}$), and the needle wets the surface, and daubs onto the target once it touches the surface. An exemplar of transferred thin crystal, which is wrinkled in the middle (it is due to thermal expansion of the substrate during the heat-up process) is shown in figure 2.7.

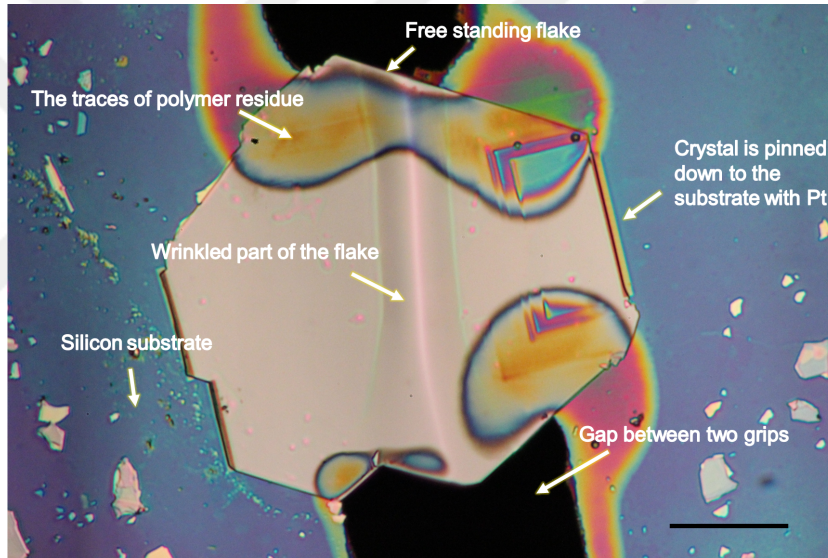


Figure 2.7: An Illustration of a transferred MoS_2 flake on a strain gauge. The scale bar is $20\text{ }\mu\text{m}$.

The nomenclature of strain grip rises from the fact that mechanical strain occurs due to physical displacement of two sides of the grip (the opening and closing mechanism of the grip). For this purpose, A DC piezoelectric stack (Thor Labs, AE0203D08F) has been utilized to induce strain in the substrate. This type of actuators consist of many ceramic stacks that are laminated in series mechanically, and in parallel electrically. This stack gets attached to the top surface of the substrate. By connecting the terminals to a piezoelectric-controller, and applying positive bias voltage (up to 150 V), the stack goes under expansion, and apply uniaxial force to the grip and the transferred crystal. Since silicon substrate owns a polished surface, and the flake is placed on top, the shear stress and torsion will be eliminated automatically.

This strain grip setup is so practical in the case that it could mount to an optical microscope, a confocal Raman microscope, scanning photocurrent microscopy (SPCM), and even inside the SEM chamber. Complementary results will be provided in the results and discussions chapter. In order to perform in-situ scanning electron microscopy on a strained thin crystal, the piezoelectric-controller get connected to the interior of SEM chamber via special ducks embedded on the machine frame and provides connection to the interior of the chamber. All connections are done by special Bayonet Neill–Concelman coaxial cables (BNC), and it is attached to the sample stage and placed in a very narrow gap between the electron-gun, and SEM stage.

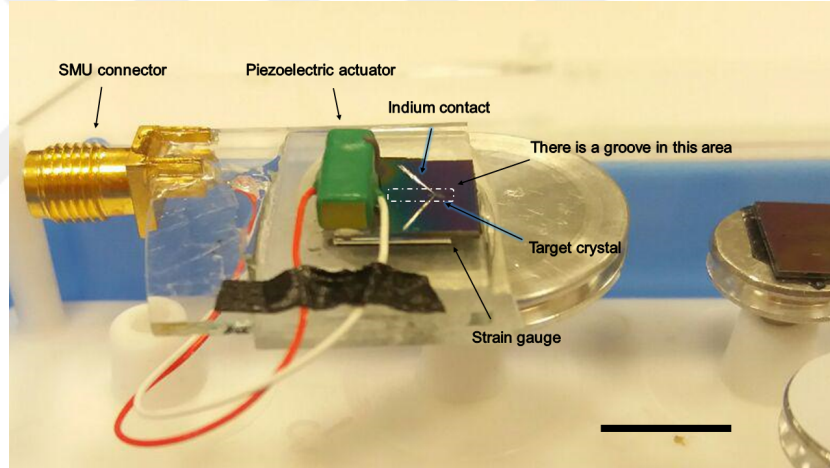


Figure 2.8: A photograph of a finalized strain gauge setup with all connections mounted on a SEM sample holder. The scale bar is 1 *cm*.

2.2.3 Electron Beam Lithography

The highly precise maskless lithography method can ease the fabrication process effectively. The precision of electron beam lithography (EBL) is not limited by the diffraction of the incident light. Therefore, by considering a few adjustment in sample preparation, and careful design such as lowering the density of features or distribution of pattern one can achieve sub 100 *nm* features. Through different part of this study, electron beam lithography is been utilized to fabricate fine

structure for electrical measurements. The EBL used here is not a standalone EBL, but it is a common SEM (FEI Nova NanoSEM-600) which has been modified by third-party components (RAITH pattern generator module, and magnetic coils and beam blanker) and it can manipulate the exposure of electron beam.

Surface of the sample should be free from solid particles, contamination and any roughness. To increase the quality of resist, the sample is washed and rinsed with acetone, IPA, and DI water respectively. This step is followed by dehydration of the sample by baking at $120\text{ }^{\circ}\text{C}$ on the hotplate for 10 min . Then, a double-layer photoresist is coated on the sample to obtain a total of 100 nm thick poly-(methyl methacrylate) PMMA. More specifically, in the bilayer PMMA coating, first a layer of PMMA 495K A2 is spun on the substrate, followed by a layer of PMMA 950K A4. Because PMMA 495K is composed of smaller chains, bottom-layer is more sensitive to the electron exposure compared to 950K formula. when the photoresist is exposed to the electron beam, the bottom layer will be more undercut than the top layer. This a finer structure in top-layer of 950K, since the higher the molecular weight, the better the contrast will be, which results in an improved lift-off process. The 950K and the 495K refers to the molecular weight (i.e. the length of the PMMA chains 950 kDa and 495 kDa respectively), A stands for the solvent anisole, which is better for the environment than the chlorobenzene solvent (grade C), and the 2 indicates that the solvent contains 2% PMMA by weight percent. Solvents should be transferred using a glass pipet, and after each step of spin coating the specimen is baked for 10 min at $180\text{ }^{\circ}\text{C}$.

In order to facilitate the lithography step, multiple mapping using optical microscopy, and SEM is compulsory, and it is done before applying any photoresist. Exposure of a photoresist layer to the visible light or electron beam leads to the development of the layer. Besides, it is not possible to observe an atomically thin flake buried under photoresist, using SEM due to intense charging in a resistive polymer. Thus, reference points should be carved on photoresist manually using a sharp tool such as the tungsten needle attached to our manipulator setup. These marks are used to pattern exterior features, accompanied with fine and well-defined position marks. After the first round of EBL (FEI Nova NanoSEM600), the structure is agitated in methyl isobutyl ketone and IPA (MIBK:IPA 1:3) for

60 s, then Agitated in IPA for 15 s, rinse with DI water, followed by drying by blowing nitrogen gas on the sample, in a process called developing process. In our case, there is a secondary step of patterning, which designated for putting internal features and precise patterning. The internal pattern is connected to exterior pattern using extension arms.

2.2.4 Thermal Evaporation

One of the subsets of PVD is thermal evaporation technique, which provides a smooth thin layer of material on the substrate. The precursors get melted exploiting the DC electrical current passing through the conducting boats. These crucibles are high temperature resistant, but mechanically brittle. Thus, a careful handling is essential, and during the mounting process, there should be gentle assembly. These boats should withstand high current (around 100 A), and high temperature, and shall not react with the precursor. There are two commercial choices for it, tungsten boats for high melting point materials (such as Cr), and molybdenum boats which are more mechanically durable for moderate melting point materials (such as Au). Evaporator chamber is maintained under UHV ($10^{-9}bar$) in order to decrease collision of evaporated atoms with air molecule. A series of a rotary pump and turbo molecular pump grant this vacuum level. The thickness of deposited material is traced using a quartz crystal micro-balance. Atoms deposited on quartz crystal and add to its effective mass, thus the resonance frequency of the quartz crystal will change accordingly, and it gives an accurate sense from the mass of deposited layer. In order to drive a well-defined scale of the amount of material that strikes the substrate, an empirical calibration has to be done. Two factors of precursor temperature and time elaborately determine the film thickness. In favor of upcoming steps, a 5 nm thick Cr is deposited on silicon substrate with the rate of $0.1 \text{ \AA}/s$. This layer acts as adhesive seed layer for deposition of 100 nm of Au. This structure guarantees a proper lift-off process and a proper foundation for wire bonding. To minimize the famous defect of step-coverage, the substrate should be rotated during the process, and to prohibit cracks and deformity in the pattern, the substrate should rest about

15min before breaking the vacuum.

2.2.5 Lift-off Process

After lithography and metallization, there is a complementary step to strip away undesirable parts of the deposited metal layer. The metalized sample is soaked in acetone bath overnight to ensure a complete lift-off. Acetone dissolves underlying PMMA layer and leaves clean features with no polymer residue or contamination. There are two considerations to accomplish proper lift-off step; first, the thickness of the deposited layer should be 1/3 of photoresist thickness. Second, acetone should wet and dissolve buried photoresist through all notches and cervices. Later, the structure can be completely get isolated by using a mild bath sonication. Any existence of step-deposition leads to shortcut between pattern and undeveloped part. These bridge (step-deposition) fragment the liftoff process, and further effort is futile once acetone gets evaporated from the surface.

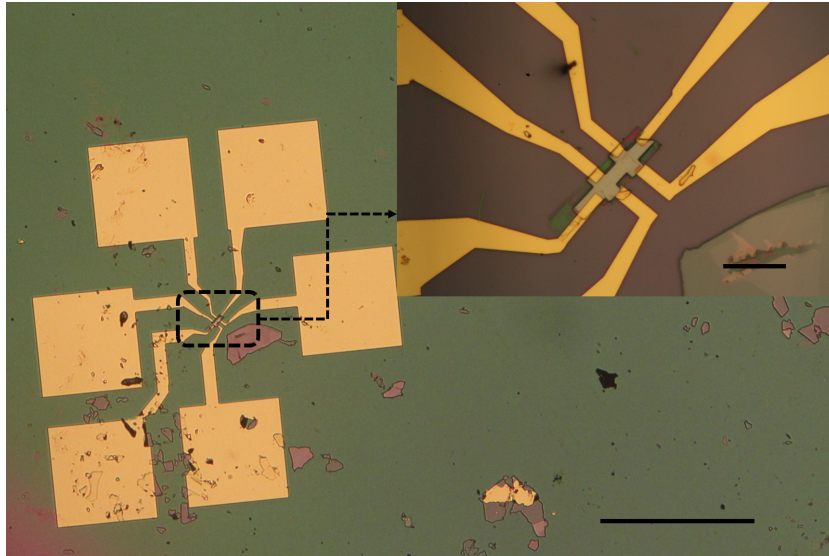


Figure 2.9: An OM micrograph of a completed pattern after metallization and after lift-off process. The inset shows the higher magnification image, which indicated the fine structure of a hall bar, and attached connections to each leg. Scale bars are 300 and 20 μm for the main frame and the inset, respectively.

2.2.6 Wirebonding

In order to remotely conduct measurements from electrical device there should be a way to safely connect measurement system to these delicately designed devices. One possible way is to physically attach conductive needle of the analyzer setup to the circuit pads. This is a facile way for DC measurements, whilst you can conduct experiment without exposing your sample to excess heat which may degrade the structure. Such measurements can be conducted using a source measurement unit (SMU, Keithley SCS parameter analyzer). This device benefits from micromanipulator in which can attach electrical connection to the circuit board directly. The main drawback of using micromanipulator to attach probes is this risk of any glitch in the connection nod, beside the fact that not all equipment has such adjustable probes. Thus, wirebonding endorses high quality connection among microscopic device and macroscopic system. Gold wires can be stitched to the gold pads either by ball or wedge bonding. In ball bonding an electrical spark cause local melting of the gold wire, produces a ball at the tip of the wire. This ball is then attached to the metallic pads by applying pressure via ceramic tip. In the later method, the wire itself has to be squeezed against the pads. An erroneous move in wire bonding process can destroy the interior material since the structure is so compact.

2.3 Raman Spectroscopy

Micro-Raman Spectroscopy is a non-destructive test in which it provides information about molecular symmetry. The interaction of visible light with phonon vibration which causes scattering of a portion of the incident light and partial absorption. If the symmetric molecule exists in the structure (centrosymmetric), the rule of mutual exclusion could be helpful to identify each Raman-active vibrational mode. The intensity of inelastically scattered light (Raman active scattering) as a function of its energy difference from incident radiation is called Raman shift curve. By means of Micro-Raman spectroscopy the structure and

chemical composition, the degree of degradation, the residual mechanical stress in the structure, and optical band-gap are extractable. Confinement of the laser spot on a small area of the sample allows regional data acquisition and Raman scattering map along with Photoluminescent map. In some cases, the Raman spectra can diagnose monolayer of 2DMs from multi-layer or the bulk counterpart of the studied material [44, 45].

Here in this MS study, we used a confocal Raman microscope (Witec Alpha-300 S), coupled with a green laser source (532 *nm* wavelength), and a motorized stage. This spectacular setup is basically a scanning near-field optical microscope (SNOM) which provide imaging beyond the diffraction limit of the light source. Albeit, manipulation of SNOM mode needs an extra expertise. Conducting a Raman scattering map, or a *PL* map the selected area on should be designated manually using optical image. Then, by assigning the desired scan density, dwell time, laser intensity and mode of imaging the setup can conduct the experiment remotely. Scan density is a similar concept which can be defined as dot per inch (DOI) in the photography field, it is the number of accumulation according to the dimension of the selected area.

In order to study the nature of the vibrational modes in 2DMs, we performed polarization-dependent Raman spectroscopy. Due to linearly polarized incident laser beam in the setup, and the circular polarizer after incident light, the non-polarized Raman spectra gives us the same result as $-Z(XX)Z$ gives. In the aforementioned Porto notation, XX means there are two linear polarizers which are parallel to X – *axis*, one before the incident of the beam to the sample, and one after it. Here the z -axis is normal to the substrate surface and y is the in-plane axes. A vertical polarization $-Z(XY)Z$ take place when the analyzer is rotated 90 °. E phonon symmetry modes (i.e. in-plane vibrations) are polarization independent, but the A phonon symmetry modes which are known as out-of-plane vibrations only can appear in parallel polarization.

Chapter 3

Results and Discussion

This section includes the result of various projects that I conducted during my master study. Although some of these works might seem inconclusive, the approach is so novel in which each of them could be mentored in form of a separate project.

3.1 Tungsten Diselenide Growth and Characterization

Here we report a successful CVD growth of WSe_2 crystal, accompanied by the characterization of it, and finally WSe_2 -base electronic device. A bright-field optical microscope image of exemplary crystals grown on a silicon wafer is presented in Figure ??a), which shows a high surface coverage. The Morphology and thickness of the flakes are correlated with the carrier gas flow, temperature of the chamber, and the growth time. Figure 3.1b represents a typical characteristic Raman spectrum obtained from a pristine flake with the focus on peaks between 200 and 400 cm^{-1} . The resonance mode at 248 cm^{-1} is designated to the out-of-plane A_{1g} , while the shoulder adjacent to it at around 256 cm^{-1} belongs to $2LMA$ mode. The later mode is an indicator of crystallinity of the flakes

which is not observed in some of the samples [46]. However, it still indicates a high degree of crystallinity through the monolayer and multi-layer CVD-grown flakes. It worth to mention that, there is a dim peak at 393 cm^{-1} which had been previously reported in lattice-vibration studies [47]. The absence of the peak at around 310 cm^{-1} could be a valid sign of the monolayer sample, in which it does not show this out-of-plane phonon vibration. During the growth process, tertiary layers can form epitaxially on top of the first layer.

Increasing the domain size of crystals, while maintaining in monolayer regime has always been a challenge. One approach is to introduce more nucleation site, and have monolayers of that material acquiring smaller domain size [48]. On the other hand, domain size can still increase by introducing a lower amount of volatile material to the chamber whilst increasing the growth time. In either case, the interface of crystals should be engineered wisely, otherwise, it will have a drastic effect on the properties.

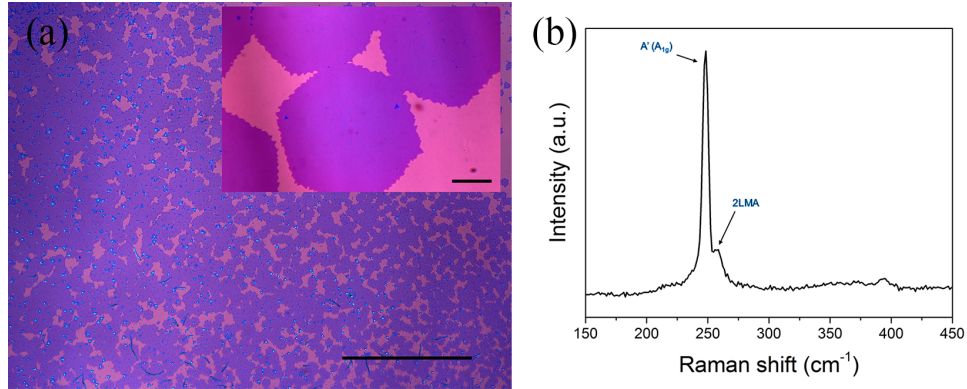


Figure 3.1: a) The optical microscopy of as-grown WSe_2 crystals cover the silicon substrate. Inset is a higher magnification image, and it reveals the poly-crystalline nature of the flakes. Jagged and dentate edges reside to different crystal orientation in which they growth epitaxially and overlap. The scale bar is $600\text{ }\mu\text{m}$ in the main frame, and $20\text{ }\mu\text{m}$ in the inset. b) An ambient-temperature Raman spectrum of a WSe_2 flake, grown on silicon substrate. The laser excitation wavelength is 532 nm .

After a successful series of WSe_2 growth, we attempted to grow a novel material using the same furnace. The internal compartment such as inner quartz tube has been changed or cleaned properly, but the piping and exhaustion system remains in the previous condition. We replaced the WO_3 source with a VO_2 source, and altered a few parameters consequently. The procedure was designed based on our contemporary knowledge about *CVD* (table 3.1). The prolonged growth time leads to consumption of 200 *mg* selenium at each attempt, but there was no evident change in VO_2 source, apart from the darkening of the powder. This growth process had been repeated more than 150 times during this MS study considering the low yield of 10 % we had few successful sample to conduct the experiments on them. Although we could not achieve our goals to synthesis VSe_2 , would like to share our findings. Figure 3.2a shows an optical microscopy image of the obtained crystals, which reveals uniform triangular flakes (which resembles TMDCs morphology) with small domain size on the order of 10 μm .

Time (<i>min</i>)	0	10	50	90	110
Temperature ($^{\circ}C$)	25	25	920	700	100
Gas flow (<i>Ar</i> (<i>sccm</i>))	500	500	10	80	10
Gas flow (H_2 (<i>sccm</i>))	200	200	5	20	0

Table 3.1: Time evolution of the CVD furnace parameters, for the synthesis of the novel material.

Raman spectroscopy on these flakes reveals the vibrational mode of this material which resembles WSe_2 characteristic spectrum (figure 3.2c). The resonance peak at 248 cm^{-1} is the characteristic phonon vibrational mode of Se-Se atoms in WSe_2 . The position of the adjacent shoulder at around 257 cm^{-1} is totally independent on the number of layers indicating that the degree of crystallinity does not change from thicker crystals to monolayer regime [46]. In multi-layer samples, the evolution of a 310 cm^{-1} peak (figure 3.2c) could be explained due to the thinning of the materials [49], and it vanishes in monolayer flakes because it does not own this out-of-plane scattering.

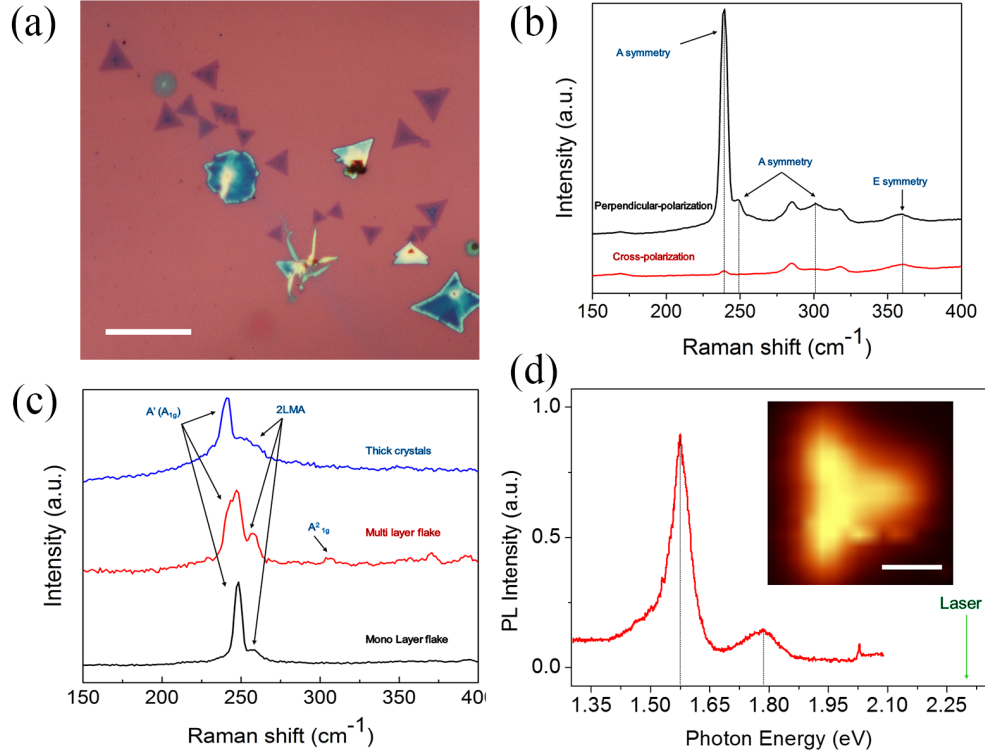


Figure 3.2: a) An optical microscopy image of the unknown crystal, distributed scarcely on silicon. The scale bar is $20\ \mu\text{m}$. b) A polarization dependent Raman spectra for a monolayer sample. Intensities are not normalized. c) Raman spectra acquired from different samples, namely monolayer flake, intermediate multi-layer, and clumps of bulk unknown material. Thickness was determined prior to the Raman spectroscopy either by contrast method using OM or by AFM. d) Photoluminescence measurements on a monolayer of unknown material, grown on the silicon substrate. The inset is the corresponding *PL* map of 1.56 eV peak. The scale bar is $2\ \mu\text{m}$.

If only we consider these flakes as WSe_2 , polarization dependent Raman spectroscopy confirms the origin of vibrational modes, formerly designated by theoretical works. Figure 3.2b reveals the modes at $239\ \text{cm}^{-1}$, and the shoulder next to it at $250\ \text{cm}^{-1}$ can be identified as *A* phonon symmetric vibrational mode with respect to C_n . That is because of they only can appear in perpendicular-polarization ($-Z(XX)Z$), but they vanish completely in cross-polarization ($-Z(XY)Z$). The rest

of the modes which are not polarization dependent could be considered as E symmetry which means 2 fold degenerate with respect to C_n .

Although these results are found through most of the samples, we could not certainly confirm the identity of these flakes. Specifically, in one sample, the vibrational mode accumulated from the center of the flake has a shift from the edge of the sample (figure 3.3b). This diversity includes a softening of the 248 cm^{-1} peak, and smearing of the 393 cm^{-1} peak. Such off modes do not show up only in Raman Spectra, but in PL spectroscopy there is a 0.07 eV blue shift in respect to the optical band gap of the monolayer WSe_2 (figure 3.2d). The intensity and dispersion of the one PL peak cannot be explained by the thickening of the flakes. In the case of multi-layer WSe_2 there are two excitons which emit at lower energies, however, the PL obtained in our study does not show more than one peak [50]. PL is the optical phonon vibration of the lattice, which is accumulated at room temperature using the same setup mentored for the Raman spectroscopy. Based on the PL map (Figure 3.2d-inset), the signal is evenly generated from the whole surface indicating no degradation in the surface. The smoothness of the PL map also demonstrates that there is no evident stress applied to the crystal since any residual strain could alter the PL peak position [51–53].

In order to explore the source of such anomalies in the result, we conducted TEM measurements. To investigate crystal structure of these flakes, $HR-TEM$ proved to be such a powerful tool. Yet, to achieve atomic resolution in thin flakes there is a need for a free-standing flake with the least amount of residual contamination. As it was described in the previous chapters, a custom-made silicon nitride perforated membrane has been used for this measurement. The challenge is to transfer crystals with the lateral size of about $4\text{ }\mu\text{m}$ on top of the perforated membrane. After the transfer step, these tiny flakes are not visible under the optical microscope. Thus, a set of SEM imaging is indeed necessary to provide the exact map of the TEM grid in which location of each free-standing flake is delicately confirmed. Figure 3.3a shows a transferred thin flake of unknown material on the TEM grid. The transparency of the flakes is an indication of its thinness, and wrinkles are evident in the SEM immersion mode.

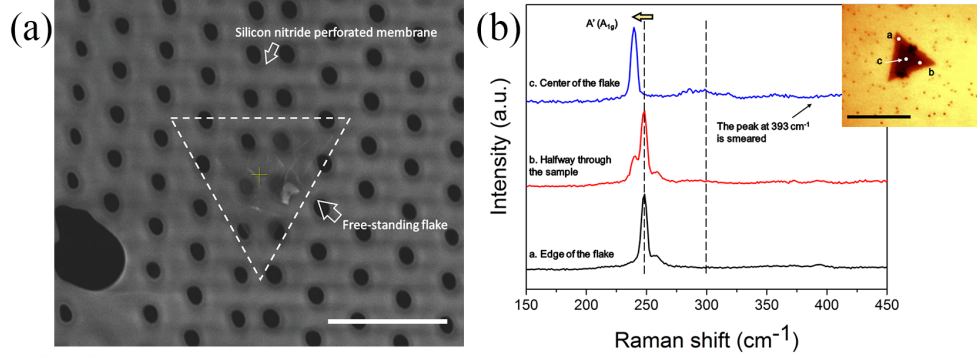


Figure 3.3: a) The SEM image of a transferred flake on *TEM* grid, after the annealing process. The flake is indicated by a triangle in the middle of the image. Those regions of the flake which are located on holes are going to be investigated via *HR-TEM*. The scale bar is $3\ \mu\text{m}$. b) The Raman scattering of a flake, accumulated regionally from the thinner part, the intermediate layer, and the thicker layer, respectively. The inset shows the exact location of the laser spot. The scale bar is $10\ \mu\text{m}$.

Figure 3.4a is a BF *HR-TEM* micrograph of the CVD-grown monolayer, which reveals a six-fold symmetric structure. A filtered image gives a better perspective of the two-dimensional structure. To generate such an image, first, a fast Fourier transform (*FFT*) of the original image should be acquired. Then diffraction planes (a diffraction plane appears as a spot in reciprocal space) will be selected manually, and by operating an inverse Fourier transform a high clarity image will be obtained (figure 3.4b). Figure 3.4b-inset is the intensity profiles taken through the center of the hexagons along *X* and *Y* directions (indicated on the main panel). These graphs show a uniform grey value which corresponds to the atomic distance in the structure. The in-plane lattice constant of this structure is $3.2\ \text{\AA}$ which is equivalent to the lattice constant of WSe_2 [47]. This technique achieves an atomic resolution microscopy on two-dimensional flakes, hence, it cannot study the phase of flakes. This is due to the fact that *HR-TEM* working distance is about $100\ \text{nm}$ deep, while for instance in *DF-STEM* the working distance is confined to sub-nanometer in *Z*-axis. Unfortunately, because of copious technical limitations, we could not perform *AC-STEM* on the sample, so we have no information about the exact phase of CVD-grown flakes.

The height trace scan over a triangular crystal is represented in figure 3.4d, which shows a 0.75 nm thick flake with a smooth surface. This thickness is also close to the Thickness of a monolayer WSe_2 . It worth to mention that the shiny spot on the crystal is the nucleation spot in which the growth commences.



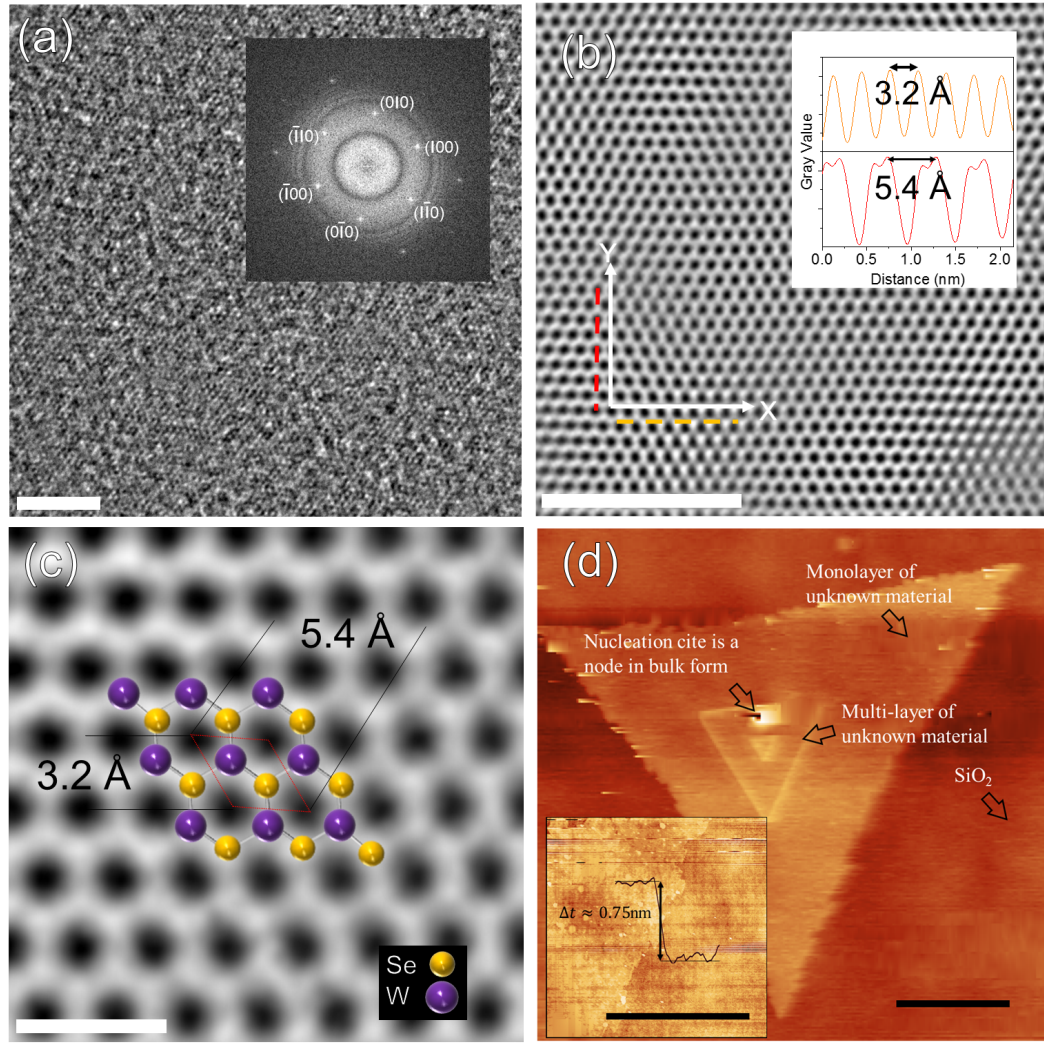


Figure 3.4: a) A bright-field *HR-TEM* micrograph of a free-standing monolayer of the unknown flake. The inset shows *FFT* of the *HR-TEM* image an scattering planes are indicated by indices. The image is locally blurred due to the polymer residue on the surface and rippling of the monolayer. The scale bar is 4 nm. b) The convolution image from the filtered *FFT* clearly shows the honeycomb lattice of the material. Two *X* and *Y* directions are indicated on the image arbitrarily. Intensity profiles along *X* and *Y* dashed lines are shown in the inset. The scale bar is 4 nm. c) A magnified *inverse-FFT* with depicted tungsten and selenium atoms overlaid, considering the structure belongs to WSe_2 . The primitive cell is denoted with a dashed parallelogram. The scale bar is 0.5 nm. d) The topography map of the unknown material, obtained by AFM contact mode. The scale bar is 5 μm in the main panel, and 1 μm in the magnified scan.

Considering all aforementioned clues, the existence of VO_2 precursor in the furnace does not lead to a drastic change in the synthesis since there is no trace of vanadium in any sample. Although there have been Multiple *XPS* surveys carried on different samples, there is no evident trace of neither vanadium nor tungsten. This could be due to the low surface coverage, and the scarcity of the flakes on the silicon wafer. Beside *XPS*, *EDS* measurements have been performed on the free-standing sample. Although *EDS* is not truly a surface sensitive method, one can deduct the signals originated from the substrate by reducing the electron beam spot size. Although we tried to delicately accumulate the data, there is almost no trace of tungsten, or vanadium, or any other metal through the samples. Presence of selenium in samples cannot be a solid indication of any structure by itself. Despite the anomalies in PL and some of Raman spectra, TEM and AFM measurements imply that CVD-grown crystals are indeed WSe_2 .

Here we would like to discuss three problems: First, how it is possible to obtain WSe_2 without having tungsten precursor in the furnace. Second, why VO_2 does not show up in the final product? Third, why there is a modulation in Raman and PL measurements?

To address the first question, we have to pay attention to the configuration of the furnace. As we mentioned before, we mentored an ambient-pressure CVD in which the byproducts cannot be flushed properly. Therefore, there is always sublimation of tungsten content right in the outfall of the furnace. Once the temperature rises, these compartments get hot and they may act as the source of tungsten. This is a mere hypothesis which seems true to us if we consider the long growth time at high-temperature which can heat up these parts.

We would like to note that, hydrogen gas at elevated temperature basically reduce all oxides including VO_2 . Since we purge a considerable amount of hydrogen gas through the whole process, the reduced product would be vanadium metal, which has 1910 °C and cannot take part in any reaction at working temperature of 900 °C.

Modulation in phonon vibrational mode and PL might rise from the deficiency

of tungsten atoms in the structure. We propose a tungsten-poor structure in WSe_2 structure, so that cause the shift in Raman and PL peaks. Although we tried to investigate this variation, we could not meticulously address these problems, and all we claim is in the level of a hypothesis. There is a need for more calculations in order to identify the origin of this behavior. Perhaps, density functional theory (*DFT*) and density functional perturbation theory (*DFPT*) calculations are strong tools to in this manner. Based on characterization data, we could successfully synthesis monolayer and few-layer of tungsten diselenide with a high degree of crystallinity, and low defect sites in the lattice. We also synthesized another material unintentionally, which resembles WSe_2 to an extent. A tad difference in Raman and *PL* measurements is diagnosed which can be explained by lack of content of tungsten in the structure. This fact might be a reason to explain why there is no signal of *W* atom in *XPS* and *EDS* surveys.

In order to study electrical properties of this material, a 2-terminal device is fabricated utilizing electron beam lithography. This process consists of a two-step EBL in order to increase the precision of the patterning. After lithography, metallization is done using thermal evaporator to form Au:Cr (100:5 *nm*) layer following an over night soaking in acetone for the sake of lift-off process. Then, the sample is wirebonded to a stage to insure a faithful measurement. Figure 3.5 illustrates the current vs. bias voltage (*IV* curve) under 0 *V* gating. Considering the fact that this material has an optical band gap of 1.56 *eV*, in analogy to WSe_2 a fundamental band gap of 1.25 *eV* is considerable for this material [54]. We anticipate a Schottky barrier at metal/semiconductor junctions with an energy barrier of 0.40 *eV* at both junctions [55]. This configuration acts like two back-to-back diodes in blocking direction. This assumption can be highly acceptable since a rectifying behavior is observed in *IV* curve accumulated from this material (figure 3.5). Beside, the amount of current passing through the device near zero voltage is almost zero, indicating a ideal Schottky barrier.

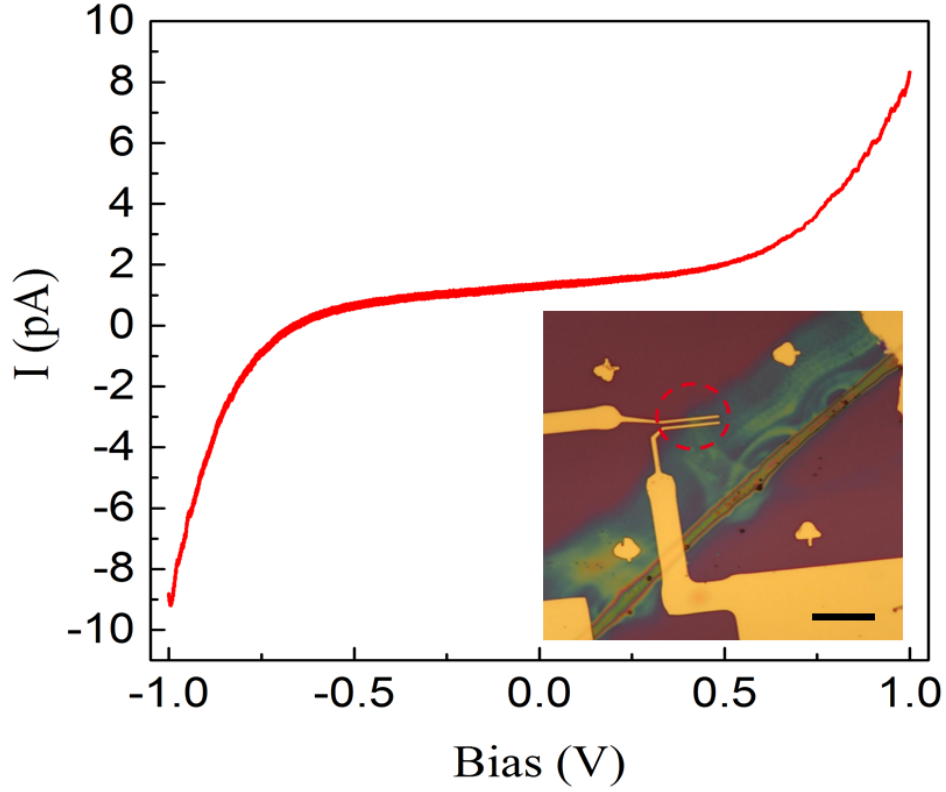


Figure 3.5: The IV curve of the 2-terminal device constructed on unknown 2D material. The inset is the OM image of the same device. The crystal is located between the contact, however the halo beneath the crystal makes it hard to visual the crystal. The existence of triangular crystal is conformed by *SEM* measurement. The scale bar is $10\ \mu m$

3.1.1 Graphene/Tungsten Diselenide Heterustructure

Assembly of van der Waals heterostructure could hardly be scaled up to please industrial counterparts. However, direct growth methods seem to be so promising, either by sequential CVD growth of two-dimensional crystals, or state-of-the-art epitaxial growth. In this study, heterostructure of $WSe_2/graphene$ is fabricated by replacing a free-standing graphene (graphene is assembled on a *TEM* grid, figure 2.4) as the growth substrate. Quality of the transferred graphene sheet enables a proper epitaxial growth. Figure 3.6 shows the substrate that has been used in this study, and also *HR-TEM* of $graphene/WSe_2$ van der Waals heterostructure. Although we could achieve a few large domain $WSe_2/graphene$

heterostructures, observing them under *TEM* did not happen. Nevertheless, depicted *HR-TEM* image shows a 10 *nm* wide crystal, which cannot really be useful for electronic applications, but for photonics.

The trigonal structure of WSe_2 has a lattice constant of 3.2 Å, and hexagonal structure of graphene has a lattice constant of 2.4 Å. Consequently, a van der Waals heterostructure of *graphene*/ WSe_2 has an intrinsic lattice mismatch of 33%. This value cannot be compensated by stretching in one of the layers, since both materials own high mechanical strength. The lattice mismatch hinders crystals to grow laterally and it leads to a limited lateral size of WSe_2 grain. Despite lattice mismatch, this epitaxial growth is a result of weak van der Waals interactions and absence of dangling bonds on graphene substrate [56, 57]. The fact that *W* atoms are superimposed periodically on *C* atoms results in an interesting electronic band structure, and a unique *moiré* pattern. However, the growth of large domain size heterostructure is crucial for further investigation.

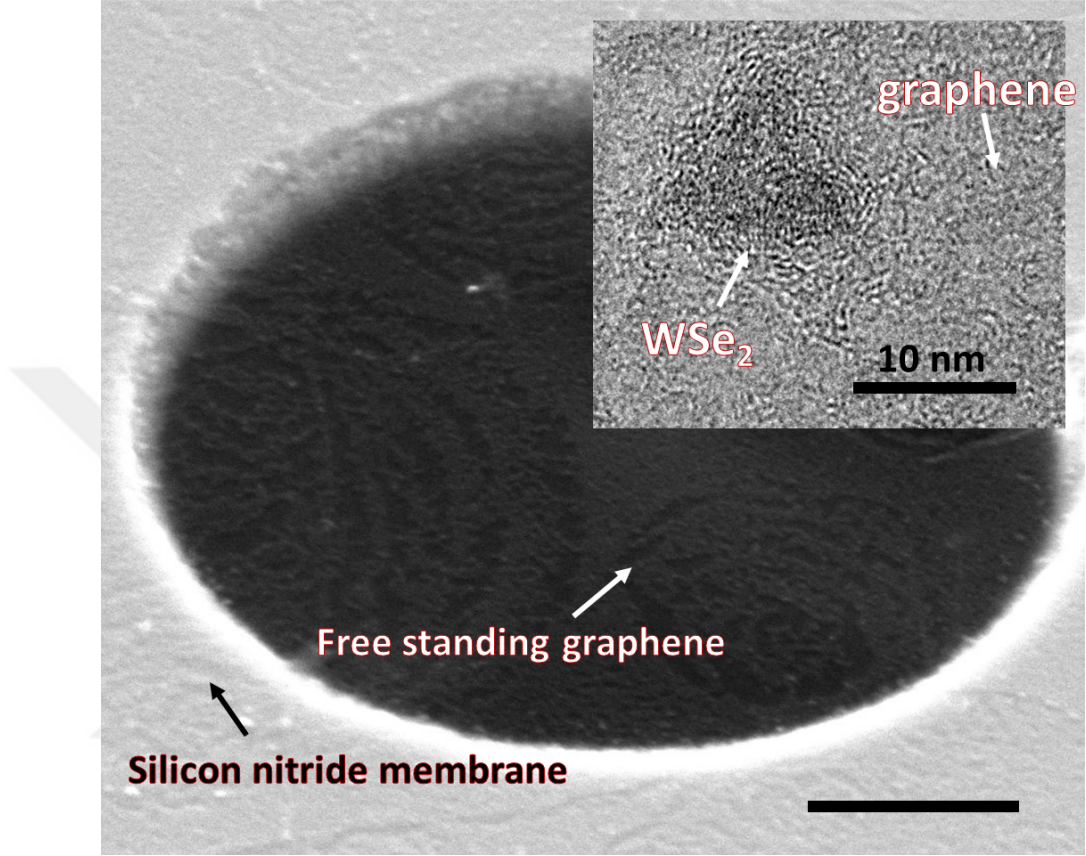


Figure 3.6: A high magnification SEM image of custom-made *TEM* grid. This free standing structure ease the process for *TEM* measurements and eliminates excessive steps. Inset is a *HR-TEM* of heterostructure of *graphene/WSe₂*. Identification of *WSe₂* flakes is done by analyzing *FFT* data. The scale bar is 1 μm .

3.2 Molybdenum Disulfide Device

Molybdenum disulfide has been synthesized mentoring micro-mechanical exfoliation of a highly oriented *MoS₂* bulk, also by LP-CVD technique. Due to weak van der Waals force between Se-Se layers, this material is effortlessly exfoliated down to monolayer regime. The contrast of the flakes on a silicon substrate in OM image can provide a good scale of the thickness of crystals [58], however,

AFM measurements or Raman spectroscopy is decisive for the sake of verification. Figure 3.2a shows an exemplar of MoS_2 flakes exfoliated on top of the silicon substrate. It worth to mention that, exfoliation process can be done on almost all surfaces including PC film or other polymeric surfaces, sapphire, and on top of other van der Waals heterostructures. The direct exfoliation on the desired substrate eliminates polymer residue, and deduct fabrication steps.

The CVD growth is an efficient method to obtain large area film of MoS_2 monolayer crystals 3.2. This continuous structure owns a high degree of crystallinity, with low defect sites, and no dangling bond which boosts the intensity of the acquired PL peak. This poly-crystalline film can either be directly used for further steps in device fabrication or be readily released from the silicon substrate and transferred to arbitrary targets. Some samples do not own a perfect surface coverage, but they show single-layer of isolated triangles, multi-layer crystals and at some point bulk crystals or desolated area.

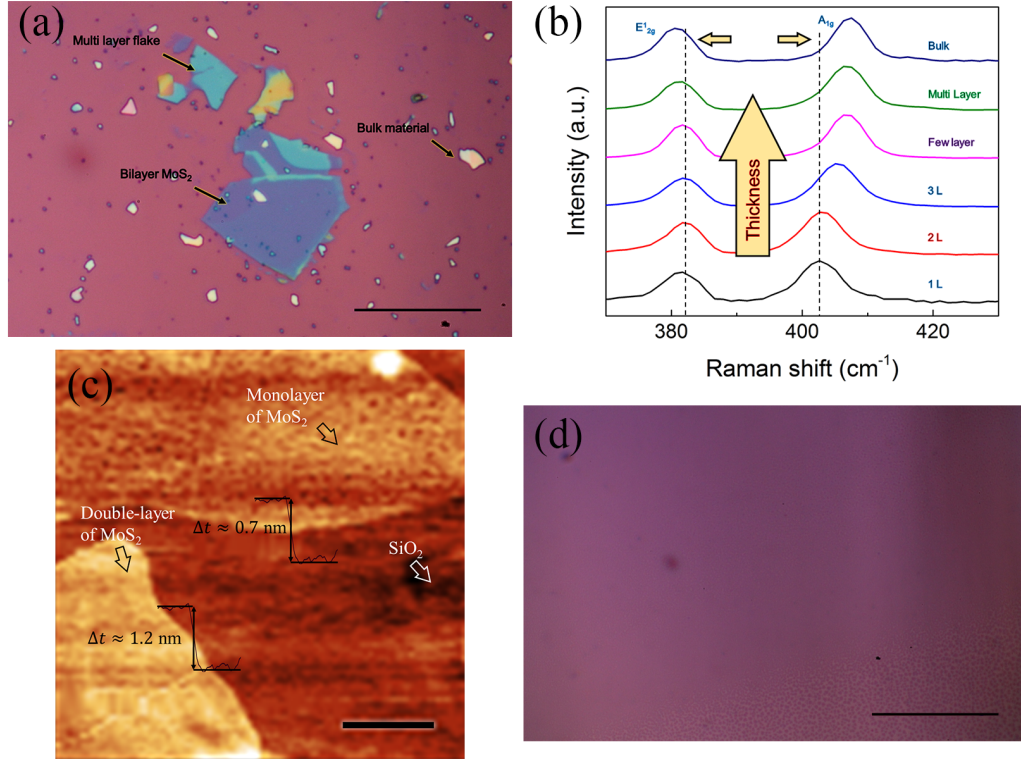


Figure 3.7: a) A mechanically cleaved MoS_2 crystal, where the bluish color of the crystal is a sign of thinner layer. b) Raman spectra accumulated from different locations with various thicknesses on the sample shown in panel c). c) A magnified AFM height trace of monolayer and double-layer MoS_2 . Roughness on a silicon substrate is more than roughness on the crystals. The scale bar is $1\ \mu m$. d) OM image of CVD-grown MoS_2 continuous film, where there is no detectable grain boundary. Such film can elongate as few hundred microns and still remains monolayer. The scale bar in a) and d) is $20\ \mu m$.

3.2.1 Strain Dependent characterization

The evolution of the Raman spectra of a multi-layer MoS_2 flake versus mechanical strain is illustrated in figure 3.8a. As it was reported previously, any mechanical strain cause change in the Raman scattering peak position. The out-of-plane A'_{1g} occurs at $406\ cm^{-1}$, and shows no evident shift in the peak position through

strained and strain-free conditions. On the contrary, by increasing the amount of strain, the in-plane E mode shows softening and a slight red shift. Although the quantity of this change is so modest, it is inconsistent with the previous report where this mode supposed to split into two subpeaks of E'^{-} and E'^{+} since the crystal symmetry is now distorted by the strain [53]. The intensity of out-of-plane modes remains steady, but the intensity of in-plane mode depletes and get spread between two sub-peaks. Since this split becomes visible above certain threshold [53], the amount of applied strain in this study supposed to be lower than 0.4%. These changes can be identified easier in monolayer sample, and it is harder to be tracked in a multi-layer sample which has been used in this study. Although phonon softening is detected in this study, data does not show a meaningful modification in the optical band-gap energy (i.e. PL peak position). This is again due to the fact that an efficient device should be benefited from a monolayer van der Waals structure.

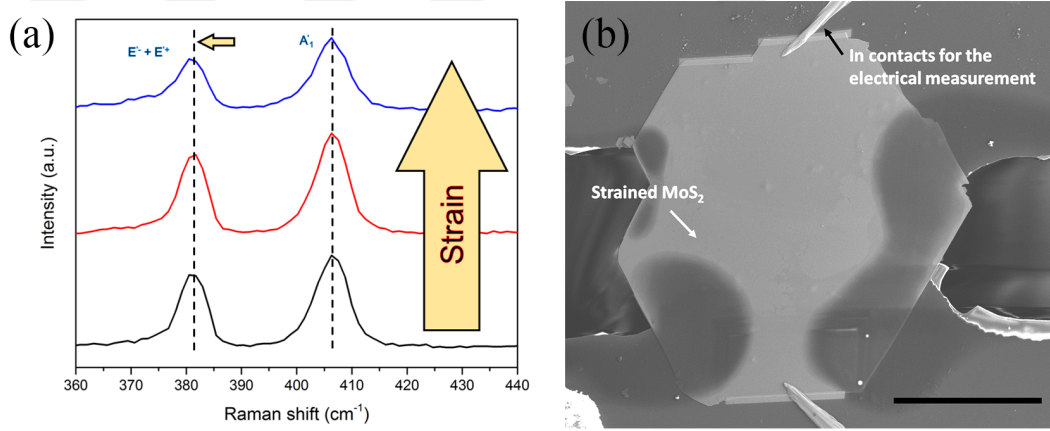


Figure 3.8: a) The strain-dependent Raman scattering of a few layer device, accumulated from the same location on the sample, at room temperature. b) A strained MoS_2 flake inside the SEM chamber, showing the dynamic microscopy of the device. The hexagonal flake is quite deformed and previously shown wrinkled part is flattened. The scale bar is $20\ \mu m$.

The importance of this section is that all thin films could be easily studied dynamically under variant strain. These methods can be spectroscopic techniques

such as scanning photoelectron microscopy (*SPCM*, *XPS*, and Raman-*PL* spectroscopy, or can be imaging methods such as *SEM* or *OM*. Breaking the symmetry in the crystal has always been at the center of attention to obtain novel bandgap structure. One of the most promising parts is to study heterostructure of distinct layered material, to tune the DOS using mechanical strain.



Chapter 4

Conclusion and Future Outlook

This MS study has been inspired by the worldwide attempts toward the investigation of two-dimensional materials. We could not imagine a solid aim alike gigantic laboratories who are working on such material and they are still not sure about certain cost-effective applications of two-dimensional materials. Thus, rather than presenting quantitative results, we could develop various experimental methods in which one can mentor them to conduct inventive experiments. We utilized so many methods, including bottom-up growth, manipulation, fabrication, and characterization of nanomaterials, and yet all of them could successfully be done at Bilkent University.

During the course of this study, two distinct layered material has been at the center of attention. Therefore, each material has been investigating by certain objectives which is more correlated to the intrinsic potential of that material. Within chapter 2 accurate CVD procedures for the growth of two-dimensional MoS_2 and WSe_2 has been established. These methods require no preliminary steps in the preparation of the furnace, precursors contains elements of the final product, carrier gases is nitrogen and hydrogen gas to build a reducing medium, and all steps could be done modestly in a typical CVD furnace. These materials are grown on top of silicon substrates, hence, a thorough report regarding the transfer, and manipulation of such atomically-thin crystals is reported. Beside

the synthesis of conventional 2DMs, We attempt to synthesis of a novel material. Although we could not achieve our objective, we synthesis thin flake of a material, which mimics WSe_2 in some characters, and it shows distinct properties different than any known material. During the course of this project, some devices seem to require custom-designed equipment, and we could succeed to make them technically feasible. These techniques lead to the direct synthesis of WSe_2 on graphene which can open vast opportunity toward photonic application. Direct growth of heterostructure, on top of other heterostructures, is going to a self-centered objective where the band structure of the final cut product is totally different compared to those individual materials, and one can observe the synergistic effect.

In case of fabrication of electronic devices, we reached to the intrinsic limit of electron beam lithography, although we could not successfully perform any measurements on these devices due to technical faults in the measurement setup. These works include forgery of TEM grids through a multi-step process. These templates have been carved out of silicon/silicon nitride substrate, leading to a membrane of silicon nitride. An optical lithography step, and then chemical etching using KOH are two important step which should provide a mechanically stable membrane. This membrane gets perforated by FIB according to the specifications and criteria. A variety of atomically-thin material had been transferred on top of these TEM grids for different purposes.

We could adapt a traditional macro-scale uniaxial tension test and adjust it to for a sub-scale strain gauge. This method has been found effective to apply strain below 4%, but in order to increase this amount, there should be the use of new transfer method to cease overheating of the substrate and ultimately prohibit the thermal expansion of the gauge. Despite the fact that we could not observe any alteration in the optical band gap, there is an evident change in Raman scattering of the strained MoS_2 sample. The setup is so practical in the way that it can be implemented in different measurement setup. So that we could reveal a dynamic observation of the effect of uniaxial stress on the geometry of a thin flake of MoS_2 via scanning electron microscopy. Here, the most conceivable objective could be the performing of energy dispersive spectroscopy on the strained sample. Another

promising study is the observation of photocurrent on strained heterostructures in order to tune the intensity and distribution of photogeneration via tuning the band structure. A heterostructure of graphene/ WSe_2 is going to be a feasible case of study, especially there is an elaborated report of direct growth of such a structure here in this report. Nevertheless, these projects are far from their finale, they all need to be pursued wisely within the academia.



Bibliography

- [1] D. Nečas and P. Klapetek, “Gwyddion: an open-source software for SPM data analysis,” *Central European Journal of Physics*, vol. 10, pp. 181–188, 2012.
- [2] K. Momma and F. Izumi, “Vesta 3 for three-dimensional visualization of crystal, volumetric and morphology data,” *Journal of Applied Crystallography*, vol. 44, no. 6, pp. 1272–1276, 2011.
- [3] A. J. Mannix, B. Kiraly, M. C. Hersam, and N. P. Guisinger, “Synthesis and chemistry of elemental 2d materials,” *Nature Reviews Chemistry*, vol. 1, p. 0014, 2017.
- [4] P. Joensen, R. Frindt, and S. R. Morrison, “Single-layer mos2,” *Materials research bulletin*, vol. 21, no. 4, pp. 457–461, 1986.
- [5] W. S. Hummers Jr and R. E. Offeman, “Preparation of graphitic oxide,” *Journal of the American Chemical Society*, vol. 80, no. 6, pp. 1339–1339, 1958.
- [6] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, “Electric field effect in atomically thin carbon films,” *science*, vol. 306, no. 5696, pp. 666–669, 2004.
- [7] S. Cahangirov, M. Topsakal, E. Aktürk, H. Şahin, and S. Ciraci, “Two-and one-dimensional honeycomb structures of silicon and germanium,” *Physical review letters*, vol. 102, no. 23, p. 236804, 2009.

- [8] Z. Zhu and D. Tománek, “Semiconducting layered blue phosphorus: a computational study,” *Physical review letters*, vol. 112, no. 17, p. 176802, 2014.
- [9] M. Dávila, L. Xian, S. Cahangirov, A. Rubio, and G. Le Lay, “Germanene: a novel two-dimensional germanium allotrope akin to graphene and silicene,” *New Journal of Physics*, vol. 16, no. 9, p. 095002, 2014.
- [10] M. R. Lukatskaya, O. Mashtalir, C. E. Ren, Y. Dall’Agnese, P. Rozier, P. L. Taberna, M. Naguib, P. Simon, M. W. Barsoum, and Y. Gogotsi, “Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide,” *Science*, vol. 341, no. 6153, pp. 1502–1505, 2013.
- [11] B. Anasori, M. R. Lukatskaya, and Y. Gogotsi, “2d metal carbides and nitrides (mxenes) for energy storage,” *Nature Reviews Materials*, vol. 2, p. 16098, 2017.
- [12] L. C. Gomes and A. Carvalho, “Phosphorene analogues: Isoelectronic two-dimensional group-iv monochalcogenides with orthorhombic structure,” *Physical Review B*, vol. 92, no. 8, p. 085406, 2015.
- [13] L. Song, L. Ci, H. Lu, P. B. Sorokin, C. Jin, J. Ni, A. G. Kvashnin, D. G. Kvashnin, J. Lou, B. I. Yakobson, *et al.*, “Large scale growth and characterization of atomic hexagonal boron nitride layers,” *Nano letters*, vol. 10, no. 8, pp. 3209–3215, 2010.
- [14] C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard, *et al.*, “Boron nitride substrates for high-quality graphene electronics,” *Nature nanotechnology*, vol. 5, no. 10, pp. 722–726, 2010.
- [15] J. Qiu, H. Fu, Y. Xu, Q. Zhou, S. Meng, H. Li, L. Chen, and K. Wu, “From silicene to half-silicane by hydrogenation,” *ACS nano*, vol. 9, no. 11, pp. 11192–11199, 2015.
- [16] W. Li, S. Sheng, J. Chen, P. Cheng, L. Chen, and K. Wu, “Ordered chlorinated monolayer silicene structures,” *Physical Review B*, vol. 93, no. 15, p. 155410, 2016.

- [17] Y. Du, J. Zhuang, H. Liu, X. Xu, S. Eilers, K. Wu, P. Cheng, J. Zhao, X. Pi, K. W. See, *et al.*, “Tuning the band gap in silicene by oxidation,” *ACS nano*, vol. 8, no. 10, pp. 10019–10025, 2014.
- [18] A. Woessner, M. B. Lundeborg, Y. Gao, A. Principi, P. Alonso-González, M. Carrega, K. Watanabe, T. Taniguchi, G. Vignale, M. Polini, *et al.*, “Highly confined low-loss plasmons in graphene-boron nitride heterostructures,” *arXiv preprint arXiv:1409.5674*, 2014.
- [19] G.-H. Lee, Y.-J. Yu, C. Lee, C. Dean, K. L. Shepard, P. Kim, and J. Hone, “Electron tunneling through atomically flat and ultrathin hexagonal boron nitride,” *Applied physics letters*, vol. 99, no. 24, p. 243114, 2011.
- [20] K. Novoselov, A. Mishchenko, A. Carvalho, and A. C. Neto, “2d materials and van der waals heterostructures,” *Science*, vol. 353, no. 6298, p. aac9439, 2016.
- [21] A. K. Geim and K. S. Novoselov, “The rise of graphene,” *Nature materials*, vol. 6, no. 3, pp. 183–191, 2007.
- [22] M. Katsnelson, K. Novoselov, and A. Geim, “Chiral tunneling and the klein paradox in graphene,” *arXiv preprint cond-mat/0604323*, 2006.
- [23] D. Solonenko, O. D. Gordan, G. Le Lay, H. Şahin, S. Cahangirov, D. R. Zahn, and P. Vogt, “2d vibrational properties of epitaxial silicene on ag (111),” *2D Materials*, vol. 4, no. 1, p. 015008, 2016.
- [24] H. Enriquez, S. Vizzini, A. Kara, B. Lalmi, and H. Oughaddou, “Silicene structures on silver surfaces,” *Journal of Physics: Condensed Matter*, vol. 24, no. 31, p. 314211, 2012.
- [25] J. L. Zhang, S. Zhao, C. Han, Z. Wang, S. Zhong, S. Sun, R. Guo, X. Zhou, C. D. Gu, K. D. Yuan, *et al.*, “Epitaxial growth of single layer blue phosphorus: a new phase of two-dimensional phosphorus,” *Nano letters*, vol. 16, no. 8, pp. 4903–4908, 2016.

- [26] P. Blake, E. Hill, A. Castro Neto, K. Novoselov, D. Jiang, R. Yang, T. Booth, and A. Geim, "Making graphene visible," *Applied Physics Letters*, vol. 91, no. 6, p. 063124, 2007.
- [27] L. Karlsson, *Transmission Electron Microscopy of 2D Materials: Structure and Surface Properties*. PhD thesis, Linköping University Electronic Press, 2016.
- [28] A. Rockett, "Physical vapor deposition," *The Materials Science of Semiconductors*, pp. 505–572, 2008.
- [29] J. Peng, J. Wu, X. Li, Y. Zhou, Z. Yu, Y. Guo, J. Wu, Y. Lin, Z. Li, X. Wu, *et al.*, "Very large-sized transition metal dichalcogenides monolayers from fast exfoliation by manual shaking," *Journal of the American Chemical Society*, 2017.
- [30] Y.-C. Lin, W. Zhang, J.-K. Huang, K.-K. Liu, Y.-H. Lee, C.-T. Liang, C.-W. Chu, and L.-J. Li, "Wafer-scale mos 2 thin layers prepared by moo 3 sulfurization," *Nanoscale*, vol. 4, no. 20, pp. 6637–6641, 2012.
- [31] K.-K. Liu, W. Zhang, Y.-H. Lee, Y.-C. Lin, M.-T. Chang, C.-Y. Su, C.-S. Chang, H. Li, Y. Shi, H. Zhang, *et al.*, "Growth of large-area and highly crystalline mos2 thin layers on insulating substrates," *Nano Lett*, vol. 12, no. 3, pp. 1538–1544, 2012.
- [32] Y. Zhan, Z. Liu, S. Najmaei, P. M. Ajayan, and J. Lou, "Large-area vapor-phase growth and characterization of mos2 atomic layers on a sio2 substrate," *Small*, vol. 8, no. 7, pp. 966–971, 2012.
- [33] S. Najmaei, Z. Liu, W. Zhou, X. Zou, G. Shi, S. Lei, B. I. Yakobson, J.-C. Idrobo, P. M. Ajayan, and J. Lou, "Vapor phase growth and grain boundary structure of molybdenum disulfide atomic layers," *arXiv preprint arXiv:1301.2812*, 2013.
- [34] X. W. Lou and H. C. Zeng, "Hydrothermal synthesis of α -moo3 nanorods via acidification of ammonium heptamolybdate tetrahydrate," *Chemistry of materials*, vol. 14, no. 11, pp. 4781–4789, 2002.

- [35] A. Azizi, S. Eichfeld, G. Geschwind, K. Zhang, B. Jiang, D. Mukherjee, L. Hossain, A. F. Piasecki, B. Kabius, J. A. Robinson, *et al.*, “Freestanding van der waals heterostructures of graphene and transition metal dichalcogenides,” *ACS nano*, vol. 9, no. 5, pp. 4882–4890, 2015.
- [36] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, *et al.*, “Large-area synthesis of high-quality and uniform graphene films on copper foils,” *Science*, vol. 324, no. 5932, pp. 1312–1314, 2009.
- [37] J. W. Suk, A. Kitt, C. W. Magnuson, Y. Hao, S. Ahmed, J. An, A. K. Swan, B. B. Goldberg, and R. S. Ruoff, “Transfer of cvd-grown monolayer graphene onto arbitrary substrates,” *ACS nano*, vol. 5, no. 9, pp. 6916–6924, 2011.
- [38] L. Wang, I. Meric, P. Huang, Q. Gao, Y. Gao, H. Tran, T. Taniguchi, K. Watanabe, L. Campos, D. Muller, *et al.*, “One-dimensional electrical contact to a two-dimensional material,” *Science*, vol. 342, no. 6158, pp. 614–617, 2013.
- [39] C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard, *et al.*, “Boron nitride substrates for high-quality graphene electronics,” *Nature nanotechnology*, vol. 5, no. 10, pp. 722–726, 2010.
- [40] S. Haigh, A. Gholinia, R. Jalil, S. Romani, L. Britnell, D. Elias, K. Novoselov, L. Ponomarenko, A. Geim, and R. Gorbachev, “Cross-sectional imaging of individual layers and buried interfaces of graphene-based heterostructures and superlattices,” *arXiv preprint arXiv:1206.6698*, 2012.
- [41] H.-Y. Chang, S. Yang, J. Lee, L. Tao, W.-S. Hwang, D. Jena, N. Lu, and D. Akinwande, “High-performance, highly bendable mos2 transistors with high-k dielectrics for flexible low-power systems,” *ACS nano*, vol. 7, no. 6, pp. 5446–5452, 2013.
- [42] C. Lee, X. Wei, J. W. Kysar, and J. Hone, “Measurement of the elastic properties and intrinsic strength of monolayer graphene,” *science*, vol. 321, no. 5887, pp. 385–388, 2008.

- [43] I. Frank, D. M. Tanenbaum, A. M. van der Zande, and P. L. McEuen, “Mechanical properties of suspended graphene sheets,” *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena*, vol. 25, no. 6, pp. 2558–2561, 2007.
- [44] A. C. Ferrari, J. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. Novoselov, S. Roth, *et al.*, “Raman spectrum of graphene and graphene layers,” *Physical review letters*, vol. 97, no. 18, p. 187401, 2006.
- [45] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, “Emerging photoluminescence in monolayer mos₂,” *Nano letters*, vol. 10, no. 4, pp. 1271–1275, 2010.
- [46] N. Pradhan, D. Rhodes, S. Memaran, J. Poumirol, D. Smirnov, S. Talapatra, S. Feng, N. Perea-Lopez, A. Elias, M. Terrones, *et al.*, “Hall and field-effect mobilities in few layered p-wse₂ field-effect transistors,” *Scientific reports*, vol. 5, 2015.
- [47] W. Zhao, Z. Ghorannevis, K. K. Amara, J. R. Pang, M. Toh, X. Zhang, C. Kloc, P. H. Tan, and G. Eda, “Lattice dynamics in mono-and few-layer sheets of ws₂ and wse₂,” *Nanoscale*, vol. 5, no. 20, pp. 9677–9683, 2013.
- [48] B. Li, S. Yang, N. Huo, Y. Li, J. Yang, R. Li, C. Fan, and F. Lu, “Growth of large area few-layer or monolayer mos₂ from controllable moo₃ nanowire nuclei,” *RSC Advances*, vol. 4, no. 50, pp. 26407–26412, 2014.
- [49] H. Terrones, E. Del Corro, S. Feng, J. Poumirol, D. Rhodes, D. Smirnov, N. Pradhan, Z. Lin, M. Nguyen, A. Elias, *et al.*, “New first order raman-active modes in few layered transition metal dichalcogenides,” *Scientific reports*, vol. 4, 2014.
- [50] S. Mouri, Y. Miyauchi, M. Toh, W. Zhao, G. Eda, and K. Matsuda, “Nonlinear photoluminescence in atomically thin layered wse₂ arising from diffusion-assisted exciton-exciton annihilation,” *Physical Review B*, vol. 90, no. 15, p. 155449, 2014.

- [51] H. Shi, H. Pan, Y.-W. Zhang, and B. I. Yakobson, “Quasiparticle band structures and optical properties of strained monolayer mos 2 and ws 2,” *Physical Review B*, vol. 87, no. 15, p. 155304, 2013.
- [52] J. Feng, X. Qian, C.-W. Huang, and J. Li, “Strain-engineered artificial atom as a broad-spectrum solar energy funnel,” *Nature Photonics*, vol. 6, no. 12, pp. 866–872, 2012.
- [53] H. J. Conley, B. Wang, J. I. Ziegler, R. F. Haglund Jr, S. T. Pantelides, and K. I. Bolotin, “Bandgap engineering of strained monolayer and bilayer mos2,” *Nano letters*, vol. 13, no. 8, pp. 3626–3630, 2013.
- [54] H. Sahin, S. Tongay, S. Horzum, W. Fan, J. Zhou, J. Li, J. Wu, and F. Peeters, “Anomalous raman spectra and thickness-dependent electronic properties of wse 2,” *Physical Review B*, vol. 87, no. 16, p. 165409, 2013.
- [55] C. M. Smyth, R. Addou, S. McDonnell, C. L. Hinkle, and R. M. Wallace, “Wse2-contact metal interface chemistry and band alignment under high vacuum and ultra high vacuum deposition conditions,” *2D Materials*, vol. 4, no. 2, p. 025084, 2017.
- [56] A. Koma, “Van der waals epitaxy—a new epitaxial growth method for a highly lattice-mismatched system,” *Thin Solid Films*, vol. 216, no. 1, pp. 72–76, 1992.
- [57] A. Azizi, S. Eichfeld, G. Geschwind, K. Zhang, B. Jiang, D. Mukherjee, L. Hossain, A. F. Piasecki, B. Kabius, J. A. Robinson, *et al.*, “Freestanding van der waals heterostructures of graphene and transition metal dichalcogenides,” *ACS nano*, vol. 9, no. 5, pp. 4882–4890, 2015.
- [58] H. Li, Q. Zhang, C. C. R. Yap, B. K. Tay, T. H. T. Edwin, A. Olivier, and D. Baillargeat, “From bulk to monolayer mos2: evolution of raman scattering,” *Advanced Functional Materials*, vol. 22, no. 7, pp. 1385–1390, 2012.