

**EXPERIMENTAL AND THEORETICAL INVESTIGATION OF 2D
MATERIALS**

Ayberk ÖZDEN

PhD THESIS

Programme in Materials Science and Engineering

Supervisor: Assoc. Prof. Dr. Feridun AY

2nd Advisor: Assoc. Prof. Dr. Cem SEVİK

Eskişehir

Eskişehir Technical University

Institute of Graduate Programs

May, 2019

FINAL APPROVAL FOR THESIS

This thesis titled “Experimental and Theoretical Investigation of 2D Materials” has been prepared and submitted by Ayberk ÖZDEN in partial fulfillment of the requirements in “Eskişehir Technical University Directive on Graduate Education and Examination” for the Degree of Doctor of Philosophy (PhD) in Material Science and Engineering Department has been examined and approved on 28/05/2019.

Committee Members	<u>Title Name Surname</u>	<u>Signature</u>
Member (Supervisor)	: Assoc. Prof. Dr. Feridun AY	
Member	: Assoc. Prof. Dr. Nihan K. PERKGÖZ	
Member	: Prof. Dr. Servet TURAN	
Member	: Prof. Dr. İdris AKYÜZ	
Member	: Assist. Prof. Dr. Faruk DİRİSAĞLIK	

.....
Director of Graduate School of Sciences

ABSTRACT

EXPERIMENTAL AND THEORETICAL INVESTIGATION OF 2D MATERIALS

Ayberk ÖZDEN

Department of Materials Science and Engineering
Eskisehir Technical University, Graduate School of Sciences

Supervisor: Assoc. Prof. Dr. Feridun AY

In this thesis, a comprehensive study of monolayer MoS₂ growth by Chemical Vapor Deposition (CVD) has been carried out and investigated by Raman, Photoluminescence and Fluorescence lifetime spectroscopy. Several aspects of CVD growth parameters have been investigated: growth zone geometry, precursors ratio, H₂ utilization, and effect of different substrates. Moreover, structural integrity of the flakes grown in these experiments has been studied. It has been found that local changes of the S to Mo vapor ratio in the growth zone is a key factor for the change of shape, size and uniformity of the resulting MoS₂ formations. Therefore, in order to obtain continuous monolayer films, the S to Mo vapor ratio is needed to be kept within a specific range throughout the substrate. Large area homogeneous growth of MoS₂ film (3 cm x 4 cm) and flakes is achieved by using glass substrates with minimal stress contribution. Moreover, observations on the flakes revealed that growth zone geometry and hence residual stress accumulation has a profound effect on the fracture behavior of the flakes and their stability with time. Another 2D material family has been investigated using Density Functional Theory (DFT) calculations to find new electrene materials, which are 2D counterparts of electriles. Therefore, dynamically stable exfoliatable electrene family has been extended beyond Ca₂N to Ba₂As, Ba₂P, Ba₂Sb, Sr₂P and Sr₂N. Adsorption energies of Na, Ca, and K on these new electrines have been found to be extremely low with very low diffusion energy barriers making these electrines excellent candidates for ultrafast charging battery anode applications.

Keywords: MoS₂, Monolayer, 2D, CVD, Electrene, DFT, micro-Raman Spectroscopy

ÖZET

İKİ BOYUTLU MALZEMELERİN DENEYSEL VE TEORİK İNCELENMESİ

Ayberk ÖZDEN

Malzeme Bilimi ve Mühendisliği Bölümü

Eskişehir Teknik Üniversitesi, Fen Bilimleri Enstitüsü

Danışman: Doç. Dr. Feridun AY

Bu tez çalışmasında, tek katmana sahip MoS_2 ' in Kimyasal Buhar Biriktirme (KBB) yöntemi ile üretilmesi üzerine kapsamlı bir çalışma yürütülmüş ve Raman, Foto ışıma ve Işıma Ömrü spektroskopisi kullanılarak üretilen yaprak ve filmler incelenmiştir. Büyütme bölgesi geometrisi, öncül oranları, gaz akış kompozisyonu ve çeşitli alttaşların büyütme üzerine etkisi incelenmiştir. Buna ek olarak, üretilen yaprakların zamana bağlı yapısal değişimleri gözlenmiştir. Yapılan çalışmalar sonucunda Mo ve S konsantrasyonunun alttaş yüzeyindeki değişiminin, MoS_2 yapılarının şekil, büyüklük ve homojenliğini belirleyen anahtar parametre olduğu tespit edilmiştir. Homojen bir büyütme için Mo ve S oranının yüzey üzerindeki dağılımının belirli bir oranda tutulması önerilmiştir. Geniş alanda homojen büyütme (3 cm x 4 cm) cam alttaşlar üzerinde, Si/SiO₂ alttaşına göre MoS_2 yapraklarında daha az stres içerecek şekilde gerçekleştirilmiştir. Zamana bağlı yaprak yapısındaki gözlemler, yaprakların çatlama davranışı ile büyütme bölgesi geometrisi ve stres birikimi arasında bir ilişki olduğunu göstermiştir. Tezin teorik kısmında ise, Yoğunluk Fonksiyonel Teorisi (YFT) hesaplamaları kullanılarak yeni “electrene” sistemleri araştırılmıştır. Yapılan çalışmalar sonucunda, dinamik olarak kararlı ve yapraklarına ayrılabilir Ba₂As, Ba₂P, Ba₂Sb, Sr₂P and Sr₂N sistemleri “electrene” ailesine eklenmiştir. Na, Ca ve K’ un bu sistemler üzerindeki adsorpsiyon enerjisi ve enerji bariyerleri oldukça düşük çıkmıştır. Dolayısıyla bu sistemlerin pil uygulamalarında mükemmel bir anot malzemesi adayı olduğu gösterilmiştir.

Anahtar Kelimeler: MoS_2 , Tek Katman, 2D, CVD, Electrene, YFT, Raman

ACKNOWLEDGEMENTS

Foremost, as a member and now an alumni member of Micro Nano Systems and Devices Research Group (MIDAS), I would like to express my sincere gratitude to my advisors: Assoc. Prof. Dr. Feridun AY, Assoc. Prof. Dr. Cem SEVİK and Assoc. Prof. Dr. Nihan KOSKU PERKGÖZ for providing one of the best possible working environment available in Turkey. During this almost 7 years of Ph.D. work, I witnessed and learned that research (or life) is not a straight line. Without your support, endless efforts to establish the laboratory, guidance, patience, constant motivation and the freedom you provide, this work wouldn't be possible.

I would like to also express my gratitude to my thesis committee members (Prof. Dr. Servet Turan, Prof. Dr. İdris AKYÜZ and Asst. Prof. Dr. Faruk DİRİSAĞLIK) for their critical reading and valuable comments.

I would like to thank my friends and colleagues in MIDAS research group (Hüseyin ŞAR, Mustafa DEMİRTAŞ, Büşra YORULMAZ, Uğur YORULMAZ, Cem ODACI, Ezgi ŞAHİN, Merve ÖPER, Mehmet BAY, and Tuğbey KOCABAŞ) for their direct contribution to this work. Growing a 2D material is not easy and it feels so magical. Thank you for sharing with me the same enthusiasm and hard work during long days and sleepless nights (and of course weekends!). We did it together. I would like to also thank the rest of the MIDAS research group and my friends in Materials Science and Engineering Department (MatSe family) especially for Mr. Alper ÇINAR and Ali KANDEMİR for their friendship and great fun.

I would like to specially thank Prof. Dr. Ender SUVACI. You are a role model for me starting from my B.Sc. studies. I feel so lucky to observe you and learn your research philosophy that guided me through M.Sc. and Ph.D work.

I acknowledge the support of The Scientific and Technological Research Council of Turkey with Grant No: 113F096 and 116F080 and Scientific Research Project Units of Anadolu and Eskişehir Technical Universities with Grants:1407F335 and BAP1605F424.

I would like to also express my deepest gratitude to my beloved friend Dr. Merve GEÇGİN for all her love, encouragement and support. We survived together.

And finally, I offer my biggest thanks to my family Bülent ÖZDEN and Sedef ÖZDEN for their love, financial and motivational support during this Ph.D. work. You taught me the meaning of family. I dedicate this thesis to my family.

Ayberk ÖZDEN

28.05.2019

STATEMENT OF COMPLIANCE WITH ETHICAL PRINCIPLES AND RULES

I hereby truthfully declare that this thesis is an original work prepared by me; that I have behaved in accordance with the scientific ethical principles and rules throughout the stages of preparation, data collection, analysis and presentation of my work; that I have cited the sources of all the data and information that could be obtained within the scope of this study, and included these sources in the references section; and that this study has been scanned for plagiarism with “scientific plagiarism detection program” used by Anadolu University, and that “it does not have any plagiarism” whatsoever. I also declare that, if a case contrary to my declaration is detected in my work at any time, I hereby express my consent to all the ethical and legal consequences that are involved



Ayberk ÖZDEN

TABLE OF CONTENTS

TITLE PAGE	i
FINAL APPROVAL FOR THESIS	ii
ABSTRACT.....	iii
ÖZET	iv
ACKNOWLEDGEMENTS	v
STATEMENT OF COMPLIANCE WITH ETHICAL PRINCIPLES AND RULES	vi
LIST OF TABLES	x
LIST OF FIGURES	xi
INDEX OF ABBREVIATIONS AND SYMBOLS	xvii
1. INTRODUCTION.....	1
1.1. Brief Overview of 2D Materials: From Instability to Dreamscape	1
1.2. Motivation of the Work	4
2. MATERIALS AND METHODS	6
2.1. Crystal Structure of MoS ₂	6
2.2. Indirect to Direct Band-Gap Transition in MoS ₂	10
2.2.1. Electronic structure and electronic transport properties.....	10
2.2.2. Photoluminescence and absorption of MoS ₂	14
2.3. CVD Growth of Monolayer MoS ₂	17
2.3.1. Thermal vapor sulfurization	18
2.3.2. Thermal vapor deposition	19
2.3.2.1. Strategies to grow MoS ₂ monolayers.....	21
2.3.2.2. Growth mechanism and flake size	22
2.4. Characterization Techniques	22
2.4.1. μ -Raman, photoluminescence and FLIM imaging.....	23
2.4.1.1. Raman spectroscopy of monolayer MoS ₂	23

2.4.1.2. Raman and PL imaging of monolayer MoS ₂	25
3. EXPERIMENTAL INVESTIGATION OF 2D MATERIALS: MONOLAYER MoS₂ GROWTH	28
3.1. Growth Zone Configurations.....	28
3.1.1. Horizontal growth: set-1.....	29
3.1.1.1. Assessment of the growth area for horizontal configuration	32
3.1.2. Face-down growth configuration.....	33
3.1.2.1. Face-down: set-2 growth configuration	34
3.1.2.2. Face-down: set 3 growth configuration.....	36
3.1.3. Conclusion and assessment of growth zone configurations.....	40
3.2. Fluorescence Lifetime Measurements	41
3.2.1. Region of interest.....	41
3.2.1.1. Film area	42
3.2.1.2. Analysis of separate flakes	45
3.2.2. Conclusion of FLIM measurements	48
3.3. Time Related Observations on the Grown Flakes	49
3.3.1. Structural changes of the MoS ₂ flakes with respect to time.....	49
3.3.1.1. Transfer process of the flakes	52
3.3.2. Raman and FLIM analysis of the flakes for stress evaluation.....	54
3.3.3. Conclusion.....	56
3.4. H ₂ Inclusion to Carrier Gas	57
3.4.1. Experimental parameters	57
3.4.2. Results	58
3.4.3. Conclusion for H ₂ inclusion.....	59
3.5. CVD Growth of MoS ₂ Using Glass Substrate	59
3.5.1. Materials and methods	60

3.5.2. Growth patterns of the glass substrates	62
3.5.3. Raman and photoluminescence analysis of flakes.....	65
3.6. Conclusion.....	68
4. THEORETICAL INVESTIGATION 2D MATERIALS: ELECTRENES	70
4.1. Electrene Systems and Their Battery Performance.....	70
4.2. Frame of the Theoretical Work	72
4.3. Computational Details	73
4.4. Determination Stable Electrene Systems	74
4.5. Anode Performance Assessment of Stable Electrenes	82
4.6. Conclusion.....	86
5. CONCLUSIONS	88
6. FUTURE WORK	89
REFERENCES.....	90
APPENDIX-1	
APPENDIX-2	
APPENDIX-3	
APPENDIX-4	
RESUME	

LIST OF TABLES

Table 3.1. Amounts of the precursor and obtained morphology with maximum flake size	38
Table 3.2. EDX analysis of the utilized glass substrates.....	62
Table 3.3. Raman analysis of the three selected points from flakes grown on glass	65
Table 4.1. Structural information on dynamically stable systems. a_m and a_b are the lattice constants of monolayer and bilayer structures, respectively. c_b indicates the distance between layers for bilayer structure. c_b/a_b is the ratio of the distance between the layers and the lattice constant of the bilayer system	80
Table 4.2. Exfoliation energy of dynamically stable electrene systems	81
Table 4.3. Adsorption energies (in eV/atom) of K and Na atoms on electrene systems	86

LIST OF FIGURES

- Figure 1.1.** Some of the parent 3D layered bulk crystals and their respective monolayers obtained by early methods: mechanical and liquid exfoliation techniques ... 3
- Figure 2.1.** A schematic periodic table demonstrating transition metals (M) that can form MX_2 type layered TMDs compounds with all of the chalcogenide atoms ($X = S, Se \text{ and } Te$). Blue highlighted elements such as Co, Rh and Ir and Ni don't form lamellar structures with all of the chalcogen atoms. For example, NiS_2 is not a layered compound like MoS_2 but $NiTe_2$ resembles MoS_2 phase. Adopted and reorganized from [26] 7
- Figure 2.2.** a) Transition metal coordination types: Trigonal prismatic and octahedral that is building blocks for b) 3 different unit cells for TMDs that is 1T, 2H and 3R. Adopted from x and y 9
- Figure 2.3.** a) Layer dependent band-structure of 2H- MoS_2 (redrawn from [50]) b) d orbital schemes of Mo atom in trigonal prism coordination symmetry, where red center depicts Mo atom surrounded with 6 S atoms (yellow) (redrawn from [53]). c) Redrawn and zoomed band-gap region of bulk MoS_2 indicating important symmetry points as VBM(1), CBM (2), K(3) and K(4) together with contribution of Mo and S orbitals to these points (from [50]) 12
- Figure 2.4.** Layer number and band-gap and emission wavelength of TMDs calculated by Yun et al.[52] 13
- Figure 2.5.** Schematic depiction a) generation of electron-hole pair, b) illustration of Wannier-Mott excton and c) illustration of Frenkel exciton 16
- Figure 2.6.** Thermal Vapor Sulfurization (TVS) method, a) Deposition of the thin film material. Although not limited, materials and deposition methods are given with references on the figure. Note that spin coating and dip coating may not require sulfur atmosphere due to thermolysis of the sulfur containing precursor, b) Sulfurization process or annealing under the sulfur rich atmosphere as a second step. TVS method generally results in low crystallinity, small grain size films but with a possible advantage of large area deposition..... 18
- Figure 2.7.** Some of the challenges during growth of MoS_2 or in general TMDs materials in CVD systems, a) TEM image indicating multilayer structure, b) flakes having different shapes, c) flakes having broad size distribution, d) vertical

	growth morphologies or vertically aligned flakes (nanowalls). Note that scale bar of a is 5 nm, scale bar of b and d is 10 μm and scale bar of c is 2 μm ..	20
Figure 2.8.	a) Confocal image of the flakes, b) DIC image of the flakes, c) Δn Raman map of the flakes, and d) spectrums taken from points P1 and P2 in image c	25
Figure 2.9.	a) Integrated and normalized total PL intensity, b) single spectrum of a random point taken from the flake and the fitted curves, c) B exciton peak center map, d) A exciton peak center map, e) Trion peak center map	26
Figure 2.10.	Intensity ratio of map of A exciton to trion.....	27
Figure 3.1.	Schematic illustration of different growth configurations a) horizontal growth (set-1), b) face down growth (set-2) using a cylindrical boat and c) face-down growth (set-3) with a larger quartz boat with respect to set-2	29
Figure 3.2.	SEM images of the samples with nano-wall formations from 2.5 cm to 3.5 cm (a) and SEM (b) and confocal image (c) of thick pyramidal film formations from 3.5 cm to 4.5.. Confocal images of the same MoS ₂ triangular formations at 5.5 cm (d), 7.5 cm (e) and 9.5 cm (f).....	30
Figure 3.3.	Raman finger prints of the samples	30
Figure 3.4.	PL spectra taken from the same Raman points given in Figure 3.3.....	31
Figure 3.5.	Monolayer flake growth region from 0 (edge) to 1500 μm and corresponding flake size distributions.....	32
Figure 3.6.	SEM micrograph of the center of the horizontal growth configuration.....	33
Figure 3.7.	SEM images and Raman spectra characterization of set-2, (a) schematic representation of the growth zones on the substrate, (b) 100X SEM image for growth duration of 5 min (no baking), (c) 5000X SEM image demonstrating MoS ₂ flakes, (d) number of layer characterization obtained by Raman spectra from the center of the substrate (#1) to the outer rim of the sample (baking duration of 10 min., growth duration of 5 min.), horizontal lines indicate number of layers, (e) 100X SEM image of the sample with 10 min. bake demonstrating one part of the ring structure, and (f) 5000X SEM image of the flakes of the ring structure	34
Figure 3.8.	Shape and size evolution of films and flakes from the inner to the outer part of the ring-like structure: (a) general view, (b)-(d) size evolution from the left to the right of the marked rectangle in (a)	35

Figure 3.9. Typical growth pattern for the set-3 growth configuration along the flow direction. Left corner schematic image depicts the two-lane growth formation. Optical images are taken from the numbered boxes as indicated on the illustration (left upper corner)	37
Figure 3.10. MoS ₂ flake and film characteristics as a function of S/MoO ₃ precursor ratio	39
Figure 3.11. Optical images of (a) the flakes with sizes of 10 – 20 μm when the ratio of S to MoO ₃ [R] = 20, (b) flakes with sizes of 80 – 90 μm when [R] = 66 (c) MoS ₂ film when [R] = 66, (d) circular film like shapes with a thick central region when [R] = 300. In the insets, Raman scattering, and PL spectra are shown. For (c) and (d) both the points chosen from the film area and the center of the circular shapes are shown	40
Figure 3.12. Figure depicts MoS ₂ growth area and dashed zones indicate two region of interest: standalone flakes and film area	42
Figure 3.13. a) Confocal image of the film zone. Colored cross marks are the points where single point Raman measurement is performed. b) Raman spectrum of point 1 (P1, red cross mark) to point 8 (yellow cross-mark). c) A _{1g} and E _{2g} peak center differences and corresponding layer number of the cross marked points. Horizontal dashed lines indicate specific values corresponding to number of layers in literature [13-14]	43
Figure 3.14. a) Total PL intensity map, b) Fluorescence lifetime map, c) Single point photoluminescence measurements. See Figure 2 for the positions of the points	45
Figure 3.15. AFM measurement a) AFM image, and b) Profile heights	46
Figure 3.16. a) PL mapping, and b) FLIM mapping of the separate flakes. c) Map of difference between peak centers of E ¹ _{2g} and A _{1g}	47
Figure 3.17. Comparison of the PL spectra of edge and interior points at a) 3 mW CW laser power with 10 meV PL shift, and b) 9 mW CW laser power with 19 meV PL shift.....	48
Figure 3.18. Schematic view of CVD growth of face-down and horizontal positions. Arrow 1 and 2 indicate the surface where the MoS ₂ flake grow. S and N ₂ indicate the Sulphur and Nitrogen gaseous, respectively	50

Figure 3.19. SEM images of freshly grown a) FD flakes and b) H flakes. Insets demonstrate 1.83 eV PL bandgap indicating monolayer MoS ₂	50
Figure 3.20. a) FD flakes grown 18 months ago, b) Bright field image of FD grown flakes at the present time, c) Dark field image of the flakes at the present. Note that all scale bars are 10 μ m. Dashed red circles points similar contrast with the substrate for both bright and dark field images.....	51
Figure 3.21. Line scan analysis on the FD flake, a) Position of line scan 1 (L1), b) Maximum intensity of Si and E mode of MoS ₂ through the L1, c) Single Raman spectrum of points taken from P1 and P2, d) Position of line scan 2 (L2), e) Maximum intensity of Si and E mode of MoS ₂ , f) Labelling of single spectrum points (P1 and P2) and structural features as crack line and void/pore on Confocal image of the flake	52
Figure 3.22. Schematic procedure of the transfer technique using PMMA and water as transfer medium	53
Figure 3.23. Left column: Sample before the transfer, middle column: remaining flakes on the old substrate after the transfer, right column: transferred sample on a new substrate. Dark field image (right column, image of second line) shows wrinkles and fully intact flakes	54
Figure 3.24. a) Confocal image of the transferred sample, b) Raman spectra of before transfer and after the transfer, c) PL measurement of the flake interior and edge of the transferred flake, d) homogeneous lifetime map of the transferred flake.....	55
Figure 3.25. a) Cracked FD flakes, b) dark field image of cracked flakes, c) confocal optical image of transferred FD flakes, d) Raman signatures of the cracked FD, transferred, freshly grown FD and H flakes. Arrow indicates a blue shift of the Raman modes of face-down sample	56
Figure 3.26. a) Schematic demonstration of the growth zones on the substrate for samples grown by H ₂ inclusion between 1 sccm to 3. 75 sccm (S1), and 5 sccm to 20 sccm (S2), b) Raman spectra of sample S2, c) Normalized PL spectra of sample S2, d) SEM image of zone 1 of sample S1, e) SEM image of sample S1 from point T, and f) SEM image of sample S1 from zone 2	58
Figure 3.27. Schematic depiction of glass growth configuration	60

- Figure 3.28.** Representative EDX analysis of the glasses. a) and b) belong to Glass-1 measurement area and spectrum, respectively, c) and d) indicate EDX area and representative spectrum, respectively 61
- Figure 3.29.** Depiction of growth schemes for a) glass substrates, b) Si/SiO₂ substrates for horizontal growth approach. Orange color indicate flakes and flake growth regions 62
- Figure 3.30.** Growth wafer 1 (Si/SiO₂) a) MoS₂ formation around the sacrificial wafer holder, b) MoS₂ flake formations at the downstream direction of the flow 63
- Figure 3.31.** Growth morphology on the glass substrates along the glass substrate (2) 64
- Figure 3.32.** a) Confocal optical image of flakes grown on the glass substrates and selected points (P1, P2 and P3), b) Raman spectrum of selected points, and c) PL spectrum of selected points 66
- Figure 3.33.** a) and b) Optical image of the transferred flakes, c) PL curves with integrated total intensity images 67
- Figure 3.34.** FETs fabricated from MoS₂ grown on Si/SiO₂ and by using glass substrates by Şar et al.[65] 68
- Figure 4.1.** a) Bulk anti-CdCl₂ structure, where M represents the metal layers, X represents the non-metal layers. A, B and C indicate the stacking order of the sheets. b) and c) demonstrate the monolayer and A-B stacked bilayer structures, respectively. Green dashed line indicate distance between inplane M and X atoms. Blue dashed line indicates interlayer distance between M atoms. Red line indicate distance between interlayer M and X atoms. d) Demonstration of the elements to construct M₂X electrene systems..... 73
- Figure 4.2.** Phonon dispersion curves for all the studied structures along high symmetry K points. Red: Not stable systems, Green: Stable electrines, Blue: Stable structures demonstrating no electrene character 75
- Figure 4.3.** a) Table of considered M₂X systems and their corresponding dynamical stabilities. b) PED isosurface plot of K₂N. c) PED isosurface plot of Ca₂N. Large spheres in b and c are cations and the smaller ones are the non-metal elements..... 77
- Figure 4.4.** Electronic band structure representation of the bilayer electrene systems along the high symmetry points. Fermi energy level is set at zero. PED isosurfaces around the Fermi level is drawn below each band structure for the

bilayer systems. Red lines indicate the band that is used to calculate the PED

78

Figure 4.5. Adsorption energies of Na, K, Li and Ca on Site 1 of the dynamically stable electrene crystals 83

Figure 4.6. Diffusion energy barriers of K and Na on the dynamically stable systems for depicted migration paths. Inset shows diffusion energy profile example of K on Ba_2Sb 84



INDEX OF ABBREVIATIONS AND SYMBOLS

2D	: Two Dimensional
PL	: Photoluminescence
TMD	: Transition Metal Dichalcogenide
FLIM	: Fluorescence Lifetime Imaging
CVD	: Chemical Vapor Deposition
VBM	: Valance Band Maximum
CBM	: Conduction Band Minimum
σ	: Electrical Conductivity
μ	: Charge Carrier Mobility
n	: Charge Carrier Density
e	: Electrical Charge
$E_{b,exc}(n)$	: Exciton Binding Energy
$E_{exc}(n)$	: n^{th} Transition of Exciton Energy Level
μ_e	: Effective mass of electron
μ_h	: Effective mass of hole
ϵ_{eff}	: Effective Dielectric Constant
E_g	: Electronic Band Gap
G-1	: Glass 1
G-2	: Glass 2
TEM	: Transmission Electron Microscope
SEM	: Scanning Electron Microscope
AFM	: Atomic Force Microscope
DFT	: Density Functional Theory

1. INTRODUCTION

In this dissertation, we investigate the growth of monolayer MoS₂ flakes in a custom-made Chemical Vapor Deposition (CVD) system and use Density Functional Theory (DFT) as a tool to find out application promising new 2D materials belonging to electrene family. Introduction part of this dissertation aims to provide a brief background to understand the problems that this dissertation intends to provide a solution to and explains motivation of the work.

1.1. Brief Overview of 2D Materials: From Instability to Dreamscape

While we have a large family of 2D materials today, it is surprising to know that early theoretical studies on the atomically thin materials predict them thermodynamically unstable [1, 2]. This argument is based on two ideas. First idea was that the level of the thermal fluctuations in 2D crystals results in atomic displacements larger than that of the interatomic distances or bond lengths. Second idea was that the relation between melting temperature and film thickness decrease as the thickness of the film gets thinner, leading to decomposition or segregation of the film into clusters [3, 4]. Therefore, as the surface science progressed, monolayers of materials were only considered (or grown) on epitaxial single crystals but not explored without such an epitaxial 3D base substrate. Surprisingly, the idea of thermodynamic instability of the 2D crystals was completely abandoned in 2004, thanks to the seminal work of Andre Geim, Kostya Novoselov and their colleagues [5]. They have demonstrated that it's possible to mechanically exfoliate graphite layers into one atom thick carbon sheets (or so-called graphene) which are observed to be stable at room temperature (R.T) on oxidized silicon substrates (a non-epitaxial dielectric substrate for graphene) [5]. In addition to the thermodynamic stability of the graphene layers at R.T., they have also experimentally confirmed that the electrons behave like massless Dirac fermions as a result of linear $E(k)$ dispersion around the K point of the Brillouin zone [6, 7]. Linear dispersion provides a ballistic electronic transport in this 2D system and more importantly allows observation of quantum phenomena up to RT [5, 8, 9]. After only 6 years of the discovery and experimental verification of the theoretical predictions of the graphene sheet, Kostya Novoselov and Andre Geim were awarded with the Nobel prize in 2010 “for groundbreaking experiments regarding the two-dimensional material graphene”. And now within a relatively short time, we have many 2D materials systems and much more is emerging.

The expansion of 2D materials family after the Novoselov's and Geim's work is based on several factors. The exfoliation technique that they use was simple and revolutionary, cost effective, and replicable by the other researchers easily. Monolayers obtained by the exfoliation techniques can be detected by using an optical microscope due to phase contrast between 2D material and commonly employed oxidized silicon substrate [7, 10]. Moreover, presence of abundant number of bulk layered crystals having different electronic structures (dielectrics, semiconductors and metals) bonded with weak van der Waals forces, and of course expected novel physical properties from those materials together with their potential applications could be listed as a reason of that huge interest towards 2D materials. Figure 1.1. demonstrates some of these 3D layered parent crystals and exfoliated 2D materials from them.

After the graphene, graphite like parent crystals having weak van der Waals bonds (a common point for these crystals) have been subjected to a rapid exploration to investigate the room temperature stability of the single sheets and their electronic and optical properties. Weak van der Waals bonds ensures the success of the exfoliation procedure down to monolayer synthesis. Indeed, the exfoliation energy of the graphite and some early 2D materials is often used as a metric to indicate exfoliability of a newly synthesized layered material (e.g. not limited to: electrides [11], Zintl [12] or Zintl-Klemm phases [13]). Before the rush of searching layered materials having van der Waals forces, some of the early 2D materials are instantly exfoliated after the graphene's success. These can be listed as boron nitride (BN, a dielectric material), MoS₂ (an n-type semiconductor), NbSe₂ (a semimetal like graphene) and Bi₂Sr₂CaCu₂O_x (a complex superconductor oxide) that have been successfully exfoliated in 2005 again by Geim and Novoselov [10]. In addition, predicted novel physical phenomena by the first principle calculations and expected applications also contributes to this expansion. Some of the novel physical phenomena reported for 2D materials can be named as unusual quantum hall effects in monolayer and bilayer graphene (or in silicene and germanene[14]), Berry's phase [15], very large spin-orbit coupling in TMDCs [16], accessible valley degree of freedom or valley polarization (in graphene and TMDCs) [17], or thickness dependent band-gap, *etc* [18].

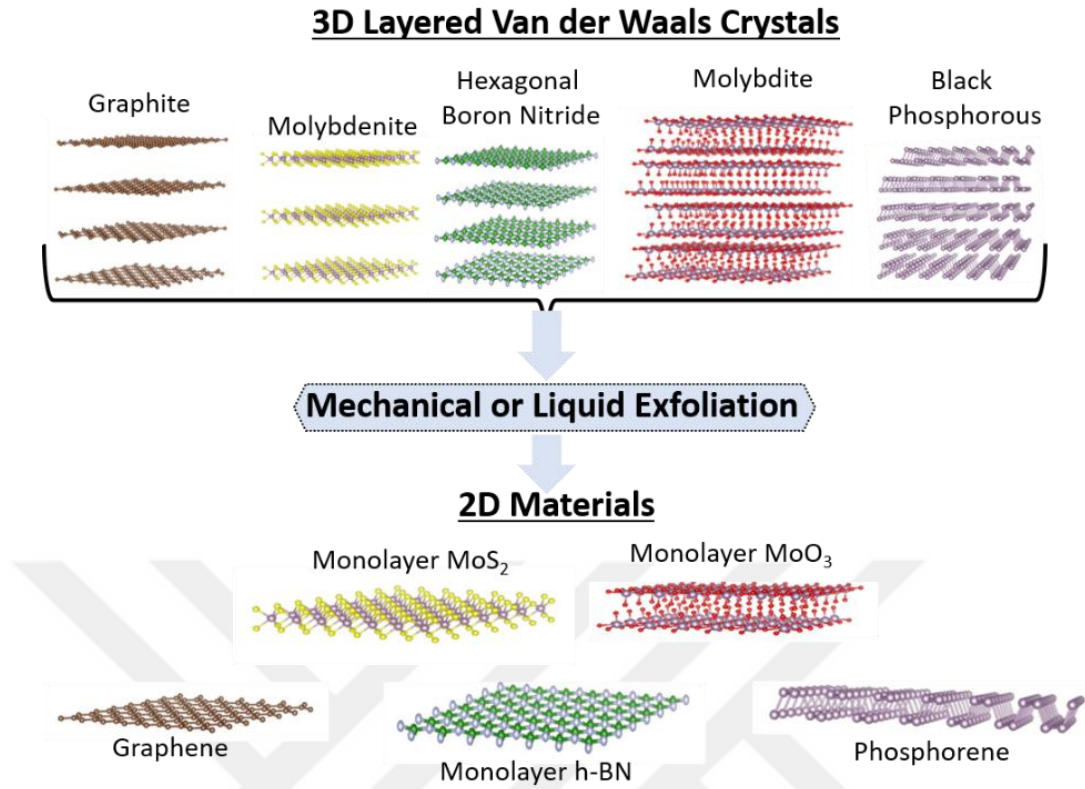


Figure 1.1. Some of the parent 3D layered bulk crystals and their respective monolayers obtained by early methods: mechanical and liquid exfoliation techniques

What makes 2D materials appealing is not only their exotic properties or production procedures that will be discussed in the next chapters, but their ability to form vertical and lateral heterostructures. In principle, analogous to Lego blocks, any number of 2D materials can be brought together to synthesize a heterostructure that can be used as an active material of a device to perform a specific task or to demonstrate a specific property. As described by Geim et al. the philosophy of designing and implementing such a structure by using atomically thin building units for specific needs forms a “dreamscape” and reflects the current trend in 2D materials [19]. However, reaching this goal requires first the prediction of the properties of the heterostructure, where DFT and related techniques are utilized. And then large area synthesis of the individual layers should be performed which is one of the main goals of this dissertation. Development of the transfer techniques of the layers onto each other or epitaxial growth techniques of the multilayered structures are required to form heterostructures. Characterization of the grown or transferred structures to understand interactions between the layers, realization of the devices and protection of the layers from ambient conditions can be listed as next steps.

In this regard, we witness a steady development of 2D materials and their heterostructures. This can be deduced from the published extensive reviews on 2D materials emerged about 10 years after of Geim and Novoselov's work [5] each covering small steps of the solution such as growth of 2D materials [20], device characteristics (FETs [21-23] [24]), heterostructures [25], light-matter interactions (e.g. exciton physics in 2D materials [26, 27]), defect formations in 2D materials [28] or their utilization in some other specific applications such as electrochemical devices, photocatalysts for hydrogen evolution or oxygen reduction reactions [29-31].

1.2. Motivation of the Work

2D semiconducting analogues of graphene are highly demanded by the scientific and industrial community. Graphene was the first and one of the most studied 2D materials highlighted due to its many intriguing properties such as high transparency (97.7% transmittance in the visible spectrum), high Young's modulus (1.1 TPa) and high electrical conductivity ($\sim 10^4 \Omega^{-1} \text{ cm}^{-1}$). It is expected that graphene would provide a small size, light-weight, flexible and transparent optoelectronic devices. But these expectations are hindered by the one of the most widely accepted drawbacks of the graphene: its zero-bandgap due to its symmetrical conduction and valence band around the Dirac point. Therefore, 2D materials with semiconducting nature are highly demanded to fulfil switching and optoelectronic functionalities.

While there are many successful efforts to open band-gap in graphene by contacting it with for example h-BN monolayers, there exists an important number of intrinsically semiconducting 2D materials [32]. For example, monolayer molybdenum disulfide or MoS_2 is one of them. Monolayer 2H- MoS_2 is an n-type semiconductor having a 1.8 eV band-gap. According to the extensive research on either mechanical or liquid exfoliation or CVD grown MoS_2 monolayers, it has been demonstrated that 2D MoS_2 has an excellent, optical, electrical, mechanical, electrochemical and thermal properties with high chemical stability. Thus, 2D MoS_2 has attracted a significant amount of interest in the application areas where a 2D semiconductor is needed especially when light-matter interactions are important such as photodetectors, solar cells, light emitting diodes or photocatalysts [28, 33].

Regarding the general perspective given above, this dissertation contributes to homogeneous growth of the individual monolayers on Si/SiO₂ and glass substrates and

their characterization by microscopic and spectroscopic techniques. In addition to that, the dissertation aims to find out new potential 2D materials by predicting their dynamical stability. To achieve the growth goal, MoS_2 , which is a member of TMDs family is chosen as a prototype 2D material and CVD is also selected as a cost-effective growth technique. DFT is chosen as a theoretical tool to investigate new 2D families such as recently emerged electrene systems. In the next subsections, we will briefly introduce why MoS_2 is chosen as an important prototypical material and why Chemical Vapor Deposition is a suitable technique for the homogenous growth of 2D materials (and for heterostructures).



2. MATERIALS AND METHODS

In the sections of this chapter, the material of interest, MoS₂ will be introduced in more detail. The most important property that makes monolayer MoS₂ a future optoelectronic material is its indirect to direct band-gap transition. Therefore, understanding of that property is essential. Therefore, the crystal structure of MoS₂ is addressed first. After that, indirect to direct band gap transition of the monolayer MoS₂ is explained. Electronic transport properties of the MoS₂ are also briefly summarized.

Most widely utilized techniques used in this dissertation, which are Confocal Raman, Photoluminescence and Fluorescence Lifetime spectroscopies are detailed in this chapter. Moreover, a literature survey on CVD growth of monolayer MoS₂ is presented.

2.1. Crystal Structure of MoS₂

Most of the interesting properties of the MoS₂ come from the atomic (d and p) orbitals, unit cell (trigonal prismatic or octahedral coordination) and nano level (monolayer or multilayer) type of structure-property relationship. Therefore, some of the basics are addressed in this chapter.

MoS₂ is an important and widely studied member of TMDs family which exist together with other 39 TMDs compounds (excluding alloy systems). Most of the TMDs compounds adopt a layered structure resembling graphite like crystal structure that gives rise to anisotropic features for their electrical, chemical, mechanical and thermal properties [34, 35]. TMDs have a formula of MX₂, where M is a transition metal having an oxidation state of +4 and X is a chalcogenide atom (S, Se or Te) with an oxidation state of -2 [34]. Transition metal elements have 6 coordination number with the chalcogenide atoms forming trigonal prismatic or octahedral building blocks a very important feature to distinguish especially electronic properties of MoS₂ and other TMDs. Elements forming TMDs compounds are demonstrated in a representative periodic table shown in Figure 2.1. 40 different TMDs can be synthesized by using the elements shown in that periodic table. MoS₂ is a group 6 semiconductor member of that family. It is important to note that not all the TMDs compounds are semiconductors and not all the compounds form the layered crystal structure desired for the monolayer synthesis. For example, Group 4–7 TMDs (M = Ti, Zr, Hf, V, Nb, Ta, Mo, W, Tc and Re) together with metals Pd and Pt (Group 10) can form layered structures with all the chalcogenide atoms (S, Se and Te), whereas this is not true for the group 8–10 TMDs (M= Co, Rh, Ir, Ni).

For example, while NiS₂ is not adopting a layered structure, NiTe₂ can form a layered crystal [34]. MoS₂ crystallizes readily in the form a layered crystal structure available in the nature, forming mechanically and chemically robust monolayers a key reason for its exclusively wide usage in electronic device research despite the existence of other semiconducting TMDs FETs such as WS₂ [36], WSe₂ [36, 37] and others [22].

Typically, metal atoms (M) in MoS₂ or TMDs form a hexagonally packed layer that is sandwiched between two layers of chalcogen atoms (X) resembling a sequence of X-M-X [23]. The thickness of such a layer (or monolayer) is between 6~7 Å. The 2H structure of MoS₂ adopts a space group of P6₃/mmc. The lattice parameters of bulk 2H-MoS₂ are a = 3.15 and c = 12.3 Å [34, 38, 39].

MX ₂ M = Transition metal X = Chalcogen						
4	5	6	7	9	10	
Ti	V			Co	Ni	S
Zr	Nb	Mo	Tc	Rh	Pd	Se
Hf	Ta	W	Re	Ir	Pt	Te

Figure 2.1 A schematic periodic table demonstrating transition metals (M) that can form MX₂ type layered TMDs compounds with all of the chalcogenide atoms (X = S, Se and Te). Blue highlighted elements such as Co, Rh and Ir and Ni don't form lamellar structures with all of the chalcogen atoms. For example, NiS₂ is not a layered compound like MoS₂ but NiTe₂ resembles MoS₂ phase. Adopted and reorganized from [34]

Intralayer bonds of 2H MoS₂ is primarily covalent and there exist a weak van der Waals bonding between the layers allowing perfect cleavage of the crystal either by mechanical or liquid exfoliation techniques [40] [34]. Covalent bonding arises due to the interaction of the d orbitals of metal with the p orbitals of chalcogen within the MX₂ monolayer, which is given in detail in the electronic properties chapter [41]. Mechanical and chemical robustness of the monolayer surface is directly affected by the fact that orbitals of M and X at the cleavage surface (0001) are only involved in the interlayer

bonding, leaving only the high-energy antibonding orbitals for intralayer or external bonding [41, 42]. This leads to the widely mentioned argument of absence of dangling bonds on the monolayer surface, which has also important implications in the case of FET and catalysis applications separately discussed below.

There are two different coordination types for the transition metals with the chalcogenide atoms, namely trigonal prismatic (D_{3h}) and octahedral (D_{3d}) acting as building blocks for three different unit cells or phases of TMDs and MoS_2 . These coordination types are demonstrated in Figure 2.2.a. The trigonal prismatic building units form 2 different unit cells: 2H and 3R. Octahedral building blocks form 1T phase. As the name of 2H implies, this phase contains two layers (2) per unit cell that is stacked in the hexagonal symmetry (H) with trigonal prismatic coordination. Single layer of 2H phase might be termed as 1H phase in the literature. In the case of single layer, stacking order of atomic layers in trigonal prismatic coordination is AbA, where A is a chalcogen and b is a metal. And likewise, 3R phase contains three layers (3) per unit cell that is stacked in the rhombohedral (R) symmetry with again trigonal prismatic coordination (again with AbA stacking order) shown in panel b of the Figure 2.2. While 2H phase is dominant in nature and more stable than that of 3R phase, 1T phase which contains octahedral coordination symmetry can only be synthesized in Li assisted liquid exfoliation or oxidation of potassium thiomolybdate [43, 44]. Therefore, 1T phase is not found in nature. It is experimentally realized and identified by electron diffraction [45] and powder x-ray pattern [44] in 1992 way before the 2D rush has begun. As noted in the literature, the crystal structure of 1T MoS_2 has never been added in the Inorganic Crystal Structure Database (ICSD) due to the lack of a strict structural refinement [46]. It is metastable and transforms into 2H phase either by aging or heating (for example at 300 °C) [47, 48]. Moreover, it has been reported that 1T phase always coexist together with 2H phase forming a hybrid structure [46]. It should be noted that stacking order of atoms in 1T phase is AbC, where A and C are chalcogenide atoms and b is the metal. Therefore, in the case of octahedral symmetry, one chalcogenide layer is shifted with respect to the other chalcogenide layer.

When 2H phase transforms into 1T, electronic structure of the MoS_2 changes from semiconducting to metallic state. For example, conductivity of 1T MoS_2 phase is known as 10^7 times higher than that of the semiconducting 2H phase. Phase transformation is best explained by change in Density of States (DOS) or with ligand field theory (or d

electron counting) indicating difference between trigonal prismatic coordination and octahedral coordination [44].

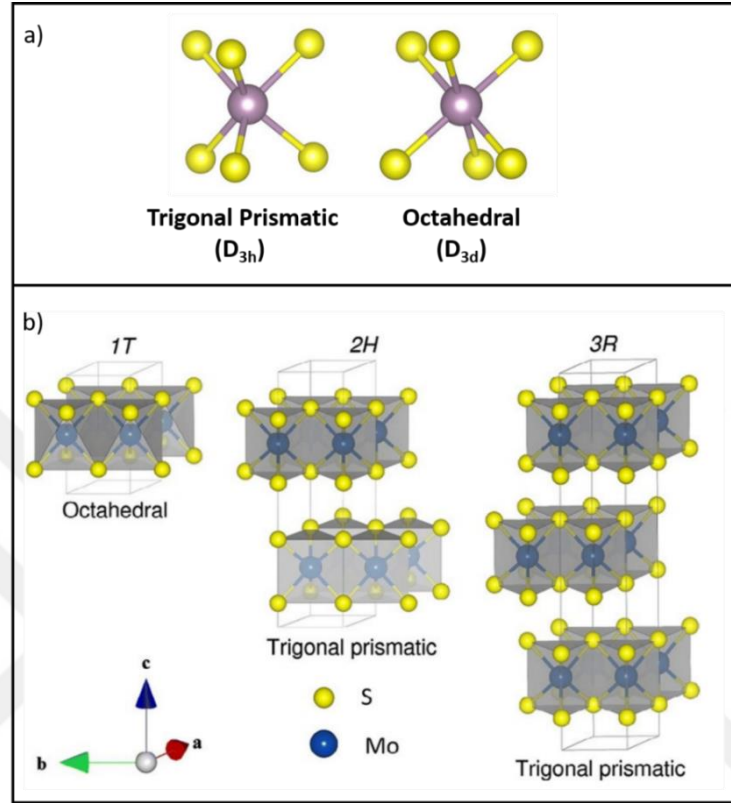


Figure 2.2. a) Transition metal coordination types: Trigonal prismatic and octahedral that is building blocks for b) 3 different unit cells for TMDs that is 1T, 2H and 3R. Adopted from [38] (a) and [49] (b)

Another issue related with the crystal structure is the dangling bonds that explains some of the superior physical properties (such as FET performance). In the case of pristine TMDs no dangling bonds are expected to form on the surface as explained earlier due to the chalcogen termination, having lone-pair electrons [34, 50]. Therefore, surfaces of the TMDs layers are expected to be stable against reaction with environmental species. But absence of dangling bonds means also a lower basal plane activity for some certain applications such catalysis. Therefore, there are many research efforts that focus on the activity of edge sites of the MoS_2 layers [51, 52].

In the case of device applications, absence of dangling bonds is expected to provide better FET performance than that of 3D bulk ultrathin semiconductors (such as ultrathin Si), where those dangling bonds act as a source for electron traps in 3D case [22]. Therefore, advantage and disadvantage of that dangling bond issue should be considered

for each specific application. Moreover, in reality there is no pristine surface in nature and all surfaces contain structural defects due to the equilibrium and the kinetics of processing [28]. In fact, surface defects are very crucial in the case of defect engineering and functionalization of TMDs materials especially for widely studied MoS₂ layers. Moreover, as explained in the section 2.2.1, effect of defects in TMD based FETs are tried to get lowered by employing high K dielectrics and encapsulation. Therefore, dangling bond free surface just reflects the ideal pristine nature (or ultrahigh quality material).

2.2. Indirect to Direct Band-Gap Transition in MoS₂

Atomic level (trigonal prismatic or octahedral) and nano level (layer number), structural changes control the electronic and optical properties of the MoS₂ profoundly. Such a control over these structural levels evolve the use of the material from the field of lubrication [53] to a future candidate for nanoelectronics and optoelectronics [54]. Therefore, in the case of electronic structure, some concepts have prime importance. These can be listed as layer number dependent electronic properties originating due to quantum confinement, coulomb screening effect on the mobility and n-type character of MoS₂ (unintentional doping). Since optical properties are directly related with the band-gap structure of the MoS₂, addressing the above concepts are expected to provide a background for the optical properties as well. In the case of optical properties, adsorption and photoluminescence properties will be addressed, which are governed by generation and recombination of excitons. Moreover, photoluminescence measurements and Raman measurements are one of the most studied characterization tools in this dissertation. Therefore, a brief background will be provided.

2.2.1. Electronic structure and electronic transport properties

Despite the progress of 2D semiconductor electronics toward the ultra-low power consumption FETs, it is surprising to know that n-type origin of MoS₂ is still not very well known. Without any doping, it is expected that MoS₂ should be an intrinsic semiconductor. However, it has a n-type semiconducting character which directly contributes to the formation of negative trions as will be discussed in section 2.2.2. Controlled tunneling and spectroscopy techniques reveal a ~ 1.3 eV bandgap for bulk MoS₂ with a ~ 0.35 eV fermi level (E_F) position of below the conduction band confirms

n-type character [55]. Moreover, sulfur defects in bulk MoS₂ is found as a major contributor to this intrinsic n-type character. In addition to the bulk MoS₂, monolayer MoS₂ deposited on SiO₂/Si wafers demonstrate higher level of n-type doping [55, 56]. This is attributed to the higher number of sulfur vacancies and effect of the substrate which leads to charge traps at the substrate-film interface [55, 57]. The latter effect is known as unintentional doping and has an important impact first on electronic and indirectly on optical properties of MoS₂ [58, 59].

A well-known feature of 2H-MoS₂ is its layer dependent electronic structure, where the properties such as transparency and high quantum yield arises from. According to the experiments and DFT studies in the literature, bandgap and effective hole (m_h) - electron masses (m_e) demonstrate strong dependence on layer number as a result of strong interlayer coupling and quantum confinement effects [60]. In the case of monolayer limit, the so-called quantum confinement changes the hybridization between the p_z orbitals of S atoms and d orbitals of Mo atoms (shown in Figure 2.3.a) that dominate conduction and valence bands [18, 61, 62]. An explanation why monolayer MoS₂ has layer dependence or has direct band-gap in single layer form was given by Galli et al. backed by other DFT studies. DFT studies indicate indirect band-gap nature of MoS₂ where valence band maximum (VBM) exist at the Γ -point and a conduction band minimum (CBM) exists at a midpoint along the Γ -K symmetry lines [62, 63]. It should be noted that up to four layers from the bulk, the indirect gap remains between the Γ -point of VBM and the midpoint of CBM with enhancing the gap energy. As evidenced from Figure 2.3.a the energies near the Γ point decrease as the number of layers decrease down to monolayer. Sulfur's p_z electrons and molybdenum's d_z^2 electrons contributes to these states which have an antibonding nature. Therefore, when the layer number decreases, interaction between layers are weakened. Thus, energy due to antibonding states (around Γ point) are lowered. On the other hand, both the top of the VBM residing at K point and the CBM near the K-point are primarily composed of orbitals localized in the xy plane, and these states around K point basically are unaffected by a change of distance along z. Moreover, these states subject to minimal interlayer coupling since Mo atoms are in the middle of the S-Mo-S unit cell.

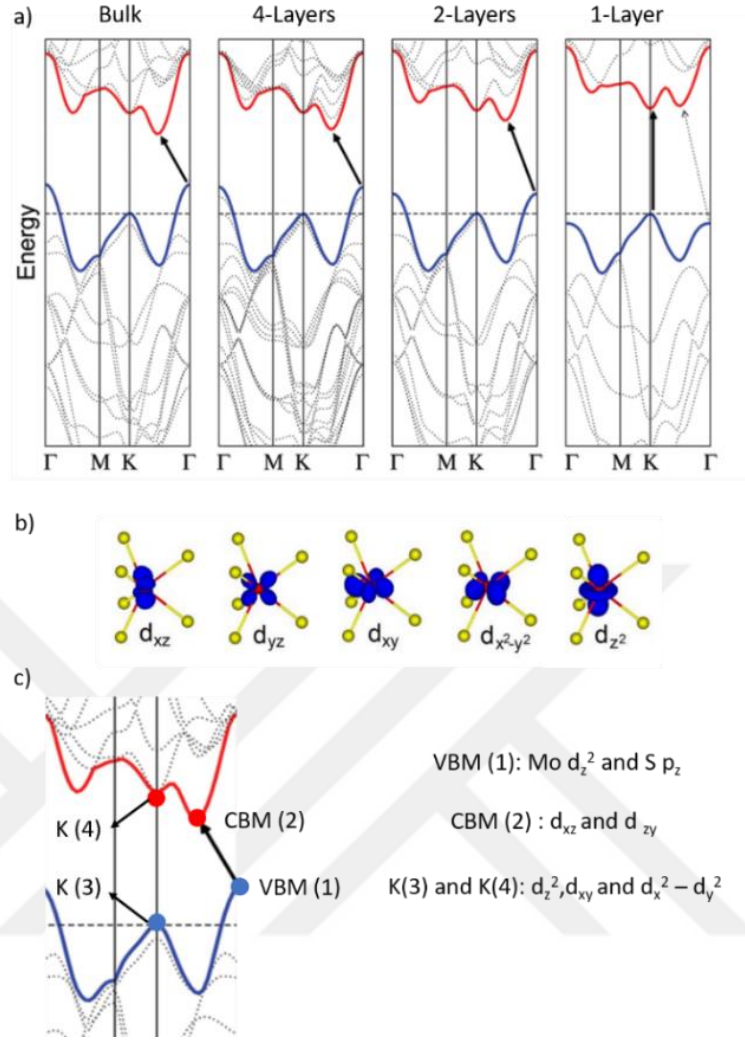


Figure 2.3 a) Layer dependent band-structure of 2H-MoS₂ (redrawn from [61]) b) d orbital schemes of Mo atom in trigonal prism coordination symmetry, where red center depicts Mo atom surrounded with 6 S atoms (yellow) (redrawn from [64]). c) Redrawn and zoomed band-gap region of bulk MoS₂ indicating important symmetry points as VBM(1), CBM(2), K(3) and K(4) together with contribution of Mo and S orbitals to these points (from [61])

CBM states between Γ -K symmetry lines are also formed by dz^2 , xz and yz orbitals which are again prone to interlayer distance. These states (CBM point 2 in Figure 2.3.a and Figure 2.3.c) get lower with respect to layer number. This indirect to direct band-gap transition in the monolayer limit and hence high quantum yield is a general property of group 6 TMDs (2H-MX₂; M = Mo, W; X = S, Se, Te) as also reported by very early studies for example for WS₂ [65, 66] in 2001-2002 and for WSe₂ (1999) [67]. Band-gaps of TMDs therefore cover some of the visible spectrum (≈ 600 nm) to infrared (≈ 2060 nm) that explains significant interest on these materials for opto-electronics. More interestingly, while this indirect to direct transition occur in these materials, E_g significantly gets larger than that of their bulk counterparts as seen in Figure 2.4.

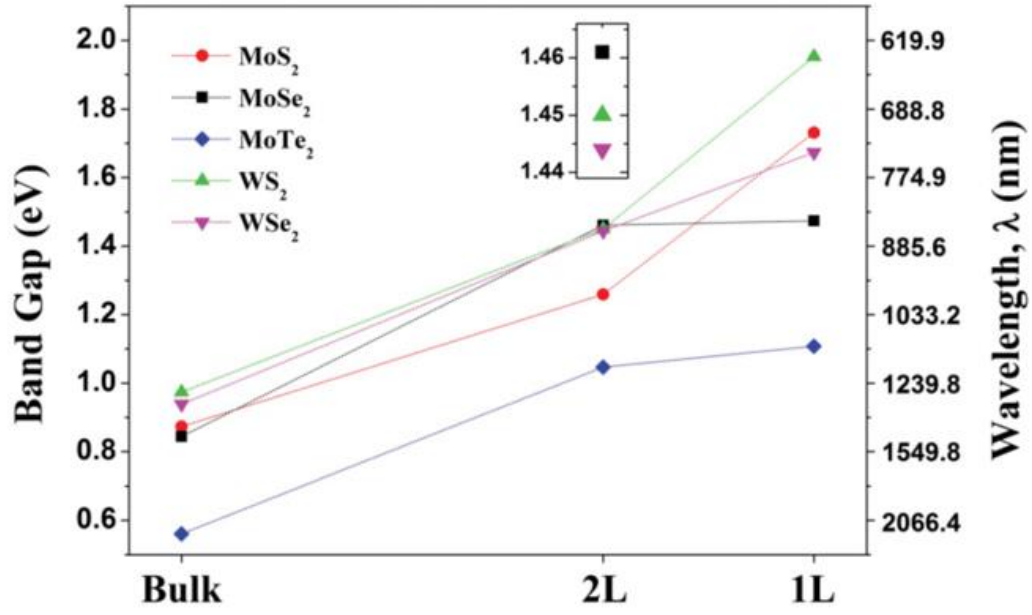


Figure 2.4. Layer number and band-gap and emission wavelength of TMDs calculated by Yun et al.[63]

In the case of transport properties, effective mass, charge carrier mobility (μ), and carrier density (n) are important as these are also the parameters for the conductivity together with electric charge (e) in a well-known general form as shown in equation 1.1:

$$\sigma = ne\mu \quad (2.1)$$

Not just for TMDs but for the other newly emerging 2D materials, properties are always compared with the graphene. In this regard, it is known that graphene has exceptionally high charge carrier mobility, which is in principle limited to an extremely high value as $2 \times 10^5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (exceeds best known material InSb - $7.7 \times 10^4 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) due to electron acoustic phonon scattering. However, it is potentially limited to $4 \times 10^4 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ due to surface phonon scattering when Si/SiO₂ substrates are considered [68, 69]. Experimentally realized values are $5 \times 10^4 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at room temperature using CVD grown graphene [70] and $2 \times 10^5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ limit for the suspended graphene [71]. In addition to the high mobility, readily tunable charge carrier density (n) around the Dirac point demonstrates ambipolar nature of graphene, which all together indicates high electrical conductivity (σ) [4, 5, 8, 41]. In the case of semiconducting TMDs, neither mobility nor charge density increase when going from bulk to monolayer. However, it's very important to obtain high mobility for single layer flakes due to the proposed ultralow stand-by power dissipation and lower electrical consumption than that of Si based

conventional transistors [72]. There are many factors effecting the charge carrier mobility of semiconducting 2D materials. Most of the research is related to eliminating those negative effects, some of which are summarized by Velicky et al. as follows: charge carrier polarity, number of layers, substrate, charged impurities, localized states, defects, device geometry, and contacts [41]. In addition to those, synthesis method (i.e. exfoliation or CVD) of the material itself directly relates with the material quality (defect density) and changes the mobility and charge carrier density through sulfur vacancies or other defects. Depending on the above factors, reported mobility values for the MoS₂ range within very broad values. For example, 0.03 cm²V⁻¹s⁻¹ for mechanically exfoliated MoS₂ on Si/SiO₂/Si, fabricated with traditional photolithography, larger than 100 cm²V⁻¹s⁻¹ for again mechanically exfoliated MoS₂ on ALD grown Al₂O₃ (50 nm) to prevent coulomb scattering [73] and ≈ 200 cm²V⁻¹s⁻¹ with a room temperature current on/off ratio of 10⁸ for when HfO₂ dielectrics are used [72], and 34×10^3 cm²V⁻¹s⁻¹ Hall mobility at room temperature for 6 layers of MoS₂ encapsulated within BN sheets to prevent intrinsic and extrinsic scattering due to Sulphur vacancies and charged impurities and remote optical phonons from oxide dielectrics [74].

Like mobility, the charge carrier density depends on the intrinsic and extrinsic doping levels, electric field, and recombination centers. The typical values of $\sim 10^{12}$ cm⁻² increase significantly to 10^{13} – 10^{14} cm⁻² through top-gate engineering of the FET device such as by employing electrochemical top-gating using polymers or ionic liquids, or organic solvents [41, 75].

2.2.2. Photoluminescence and absorption of MoS₂

Optical phenomena in 2D semiconductor materials are based on the generation and recombination of excitons. Excitons are quasiparticles that are formed by interaction between negatively charged electrons and positively charged holes which are generated by absorption of electromagnetic energy in semiconductors or insulators. The process of absorption and generation of e-h pair is shown in Figure 2.5. This electron-hole pair has its own energy states resembling an atomic hydrogen. These energy states and exciton binding energy ($E_{b,exc}$) can be approximated by Hydrogenic Rydberg Model which is also used to evaluate optical measurements in 2D materials. Hydrogenic Rydberg Model is given in Equation 1.2:

$$E_{b,exc}(n) = \frac{\mu e^4}{2\hbar^2 \mathcal{E}_{eff}^2 (n - \frac{1}{2})^2} = E_g - E_{exc}(n) \quad (2.2)$$

where $\mu = 1/(\mu_e^{-1} + \mu_h^{-1})$ is the effective reduced mass of electron and hole, $\mathcal{E}_{eff}$ is the effective dielectric constant, E_g is the electronic band gap and $E_{exc}(n)$ is the n^{th} transition of exciton energy level. Regarding Eq. 2.2, there are two prime parameters determining binding energy of the exciton: effective reduced mass and dielectric constant. Depending on these parameters, some significant differences emerge between bulk and 2D semiconductors. First, the binding energy, which is given in equation 1.2 between electron and hole pair is rather small for the excitons generated in bulk semiconductors (1 to 10 meV) resulting a negligible effect due to thermal fluctuations at room temperature [27, 76]. Low binding energy in bulk semiconductors is a result of small electron and hole effective masses and high dielectric constant of the typical semiconductors indicating a strong screening effect. It means that electrons surrounding the exciton pair directly reduce the Coulomb force between hole and electron. As a result of lower effective mass, higher dielectric constant and strong screening effect, the binding energy is thus low and hence the distance between e-h pair is on the order of several unit cell (depicted schematically in Figure 2.5.a) in bulk semiconductors. Such excitons are classified as Wannier-Mott exciton (Figure 2.5.b). Moreover, when electron screening is low (low dielectric constant) such as in organic or metal halide compounds, excitons have much more localized character. That means distance between excitons are close to the unit cell (depicted in Figure 2.5.c). This type of excitons are classified as Frenkel excitons. As expected, the binding energy (0.1 to 1 eV) is much higher than that of Wannier – Mott excitons [77].

Binding energy varies in the range of 300 to 500 meV in the case of 2D Group VI TMDs [27, 77]. Therefore, excitons survive at room temperature and recombine with a high quantum yield (even with 100 % quantum yield) that generate photoluminescence with an approximately 100 ps lifetime before the recombination [78]. Such a high binding energy of excitons are reported as a result of large electron and hole effective masses, reduced dielectric screening and strong Coulomb interaction as can be also deduced from the equation 2.1[27]. Moreover, it has been found that electronic valleys of 2D materials hosts the excitons which results the emerge of valleytronics field that is expected to benefit from additional valley degree of freedom besides the charge of electrons for quantum computation and excitonic circuits [79, 80]. Moreover, some “more traditional”

applications like Light Emitting Diodes (LEDs) [81] and Lasers are expected to shift to 2D realm due to the tunability or external stimuli of excitons by various methods.

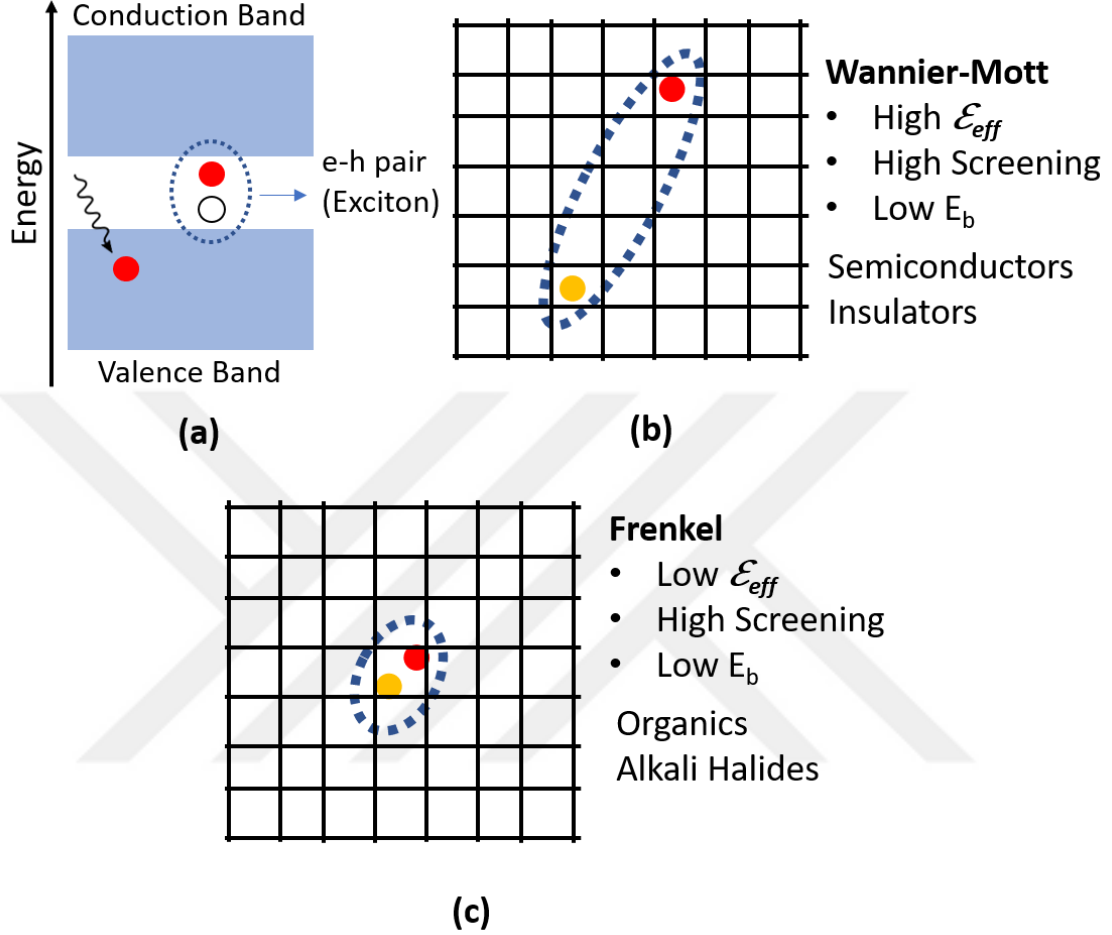


Figure 2.5. Schematic depiction a) generation of electron-hole pair, b) illustration of Wannier-Mott exciton and c) illustration of Frenkel exciton

As a result of previously explained strong excitonic effects in 2D TMDs, a MoS₂ monolayer can absorb as much as 10% of the normal incidence light at its excitonic peaks (615 and 660 nm) fivefold higher than that of graphene, which is 2% [82, 83].

Monolayer MoS₂ shows appreciable photoluminescence intensity due to direct band-gap transitions. Large spin-orbit interaction induces splitting of VBM around 160 meV at K point resulting two radiative band edge transitions observed as A⁰ exciton (at 1.92 eV) and B exciton (at 2.08 eV), respectively. Interesting optical properties are not limited to the band gap transition and spin-orbit coupling effects, but also include a wealth of exciton physics arising due to strong quantum confinement of excitons because of the larger Bohr radius of excitons (0.9 nm) compared to the thickness of the MoS₂ monolayer (0.7 nm). In addition, low quantum yield due to defective structure of CVD MoS₂ can be

increased from 0.6 % to near unity (95%) by chemical surface treatment [27]. For example, Amani et al. treats the mechanically exfoliated monolayer MoS₂ with bis(trifluoromethane) sulfonimide (TSFI-a superacid solution that has strong protonating property). Amani reports that minor carrier recombination lifetime increase from 0.3 ns to 10.6 ns. Although exact mechanism is not clear, superacid treatment is believed to result in a decrease in defect mediated nonradiative recombination. In another words, TSFI passivates the defects [78].

MoS₂ is an n-type semiconductor with a nearly 10^{13} cm^{-2} electron density due to the crystal defects (e.g. sulfur vacancies) and unintentional doping effects such as substrate – MoS₂ interaction or chemisorption on defect sites from environment [84]. Therefore, excess electrons in MoS₂ combine with neutral exciton (A^0 , one-electron and one-hole pair) and form a two-electrons and one-hole quasiparticle called negative trion (A^-). Strong Coulomb interaction and lower dielectric screening is responsible for extremely high trion binding energy that decrease the dissociation possibility of the trions even at room temperature in MoS₂ monolayers. Therefore, trions spectral weight [$I_{A^-} / (I_{A^-} + I_{A^0})$] where I_{A^-} and I_{A^0} are trion and neutral exciton intensities, respectively, can be used as a relative metric to compare the synergetic effect of defect density and unintentional doping levels of flakes grown with different process parameters [85-87].

2.3. CVD Growth of Monolayer MoS₂

In this section, a literature survey on the gas phase synthesis of 2-D MoS₂ layers are introduced. Scope of the gas phase growth is limited with the Thermal Vapor Sulfurization (TVS), Thermal Vapor Deposition (TVD) and some innovative additions to these techniques to obtain large area growth and larger flake size. These two techniques are named under the Chemical Vapor Deposition in the literature. Literature is examined in order to understand the effect of process parameters on the quality and size of the grown layers. Recently published articles on the growth mechanism is also summarized. These articles attempt to provide a quantitative explanation of the nucleation, size and the shape of flakes rather than just proposal of possible growth mechanisms. Moreover, morphology, quality and some of the physical properties of the deposited materials are discussed.

2.3.1. Thermal vapor sulfurization

Thermal vapor sulfurization is a two-step technique that consist of deposition of precursor/source material on to the substrate and annealing of that material under sulfur rich atmosphere to transform it into the MoS₂ layers. The term “Sulphur rich” atmosphere may not be required for sulfur containing source materials and the term can be extended to other chalcogenide atoms (Se, Te) to have large variety of TMDCs and their alloys. Film specs such as uniformity, impurity, grain size, film density depends on the growth method of source material. Therefore, the method used in the first step directly affects the quality and subsequent device and application performance.

There are various methods to deposit source material on to the wafer for the next sulfurization step. Almost all the thin film growth methods from very complex (expensive) to very simple (low cost) can be to grow source material growth. Some of them is given in schematic description of the TVS method in Figure 2.6: Spin and Dip Coating of (NH₄)₂MoS₂ [88, 89] [90], Electron Beam Evaporation of Molybdenum [91], Thermal Evaporation of MoO₃ [92], Atomic Layer Deposition of MoO₃ [93], Thermal Evaporation of MoO₂ [94] , can be listed as examples.

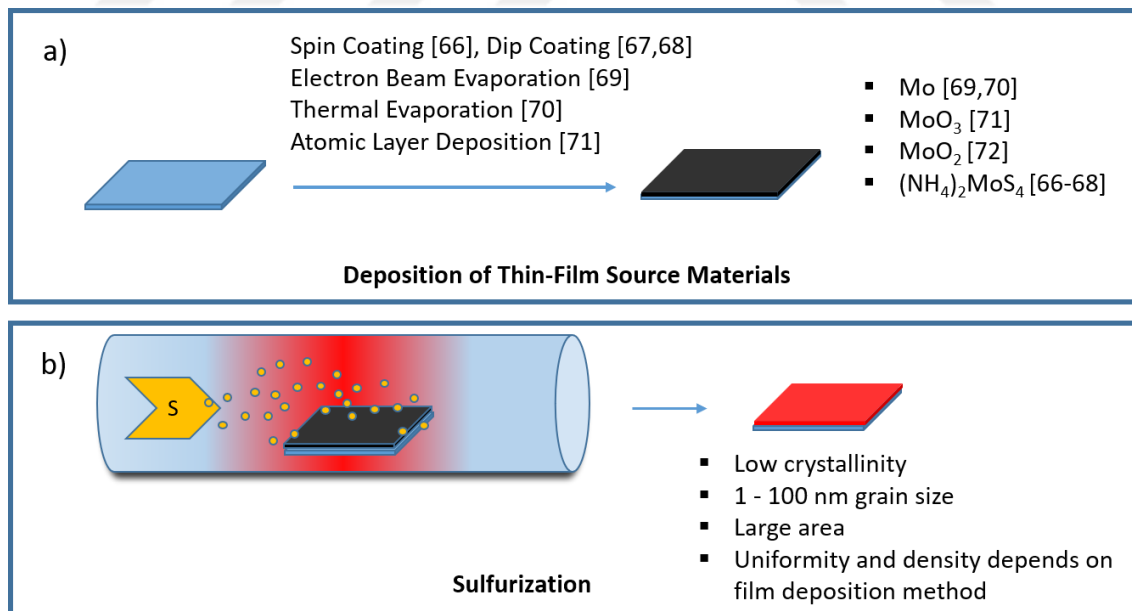


Figure 2.6. Thermal Vapor Sulfurization (TVS) method, a) Deposition of the thin film material. Although not limited, materials and deposition methods are given with references on the figure. Note that spin coating and dip coating may not require sulfur atmosphere due to thermolysis of the sulfur containing precursor, b) Sulfurization process or annealing under the sulfur rich atmosphere as a second step. TVS method generally results in low crystallinity, small grain size films but with a possible advantage of large area deposition

As noted in the Figure 2.6, there are advantages and disadvantages of the TVS method. Sulfurized area depends on the area of the deposited source material. Based on the deposition techniques mentioned above, there is no limitation for the coated area. On the other hand, low crystallinity and small grain size are the two important disadvantages of the method. Applying heat treatment to have a better crystallinity and to obtain larger grainsize by sintering (largest 100 nm) [95] is a possible solution. But still the film will be polycrystalline and subsequent physical properties such as FET mobility will be adversely affected. To understand this, mechanically exfoliated flakes (where there is no grain boundary present between the contact areas) can be considered. FET device research on the mechanically exfoliated flakes provide an optimum thickness for the highest mobility. Optimum thickness is a necessity of two competing mechanisms. First one is related with the number of van der Waals gaps that increases the contact resistance as the number of layers are increased that makes a negative impact. Second mechanism makes a positive impact on the mobility and it is the reduced screening effect of the substrate when the numbers of layers are decreased. Therefore, there is an optimum number of layers and it's within the range of 10-20 layers. The best mobility is reported for 10 nm MoS₂ thickness as 184 cm²Vs⁻¹ and using high -k dielectrics boosts the mobility up to 700 cm²Vs⁻¹ [96]. Low mobility of the TVS MoS₂ with respect to exfoliated one is related with the small lateral size and hence increased intensity of grain boundaries.

2.3.2. Thermal vapor deposition

Thermal vapor deposition includes the sublimation of the source materials, transport of the source materials and reaction of the source materials at the surface of the substrate. It has a bottom up technique where targeted structures are formed atom by atom. This gives enough flexibility to control film formation required for specific applications such as only flakes for FET or vertical structures for catalysis applications. However, the control of that flexibility is quite difficult. During this work, observed challenges are summarized in Figure 2.7 when S and MoO₃ are used as precursors in CVD system. These are;

- Absence of self-limiting growth mechanism makes it challenging to control number of layers. TEM image in Figure 2.7.a demonstrates a thick MoS₂ layer. Therefore, thicker layers coexist together with monolayer flakes frequently.

- Shape of the flakes depends on the local concentration of the precursor. It is extremely difficult to control concentration of the precursors homogenous through the substrate,
- It is hard to control size distribution of the flakes,
- Vertically aligned flakes usually coexist with monolayer flakes

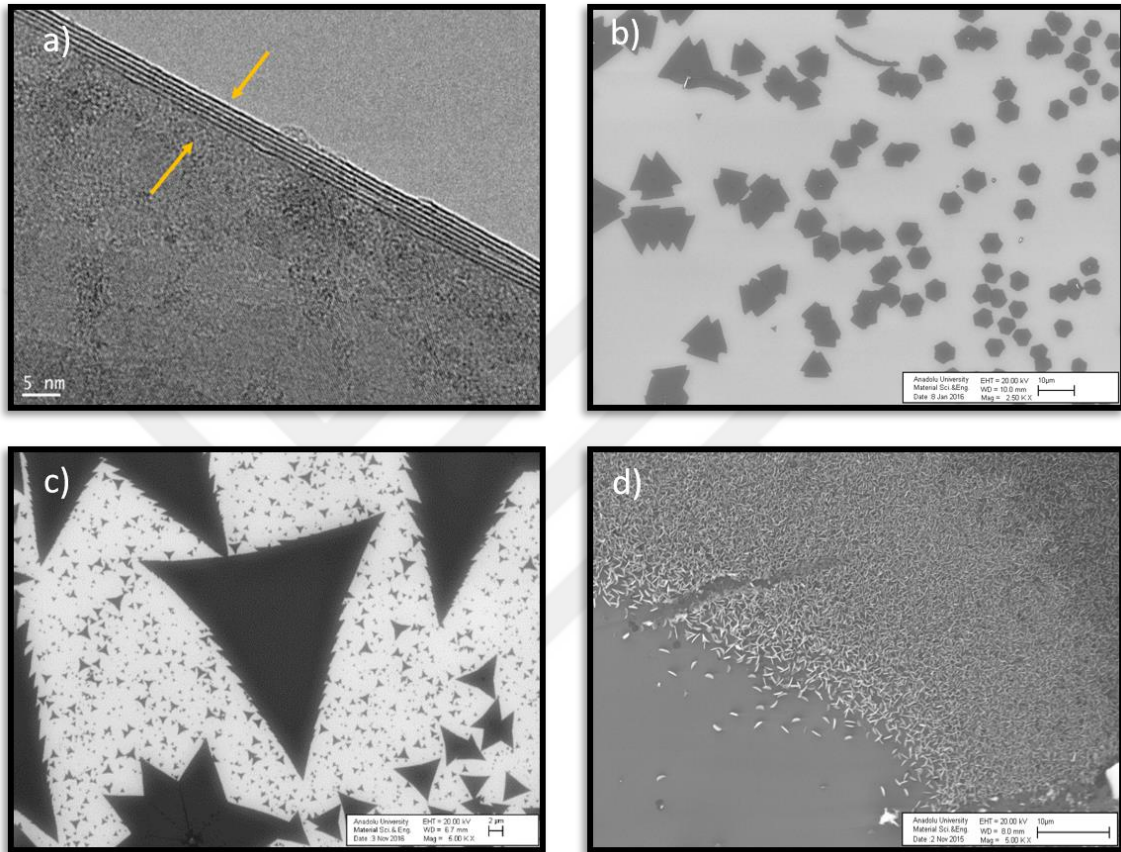


Figure 2.7. Some of the challenges during growth of MoS_2 or in general TMDs materials in CVD systems, a) TEM image indicating multilayer structure, b) flakes having different shapes, c) flakes having broad size distribution, d) vertical growth morphologies or vertically aligned flakes (nanowalls). Note that scale bar of a is 5 nm, scale bar of b and d is 10 μm and scale bar of c is 2 μm

Therefore, current MoS_2 growth literature is basically focused on to provide solutions above mentioned problems. Some of these can be found in excellent reviews that summarize the current literature with different source materials, their amounts, flow rates, their positions and process pressure including physical properties [95] [47, 97-100]. This literature survey focuses on strategies that use MoO_3 and S targeting specific morphologies including large area film growth and bigger domain (or flake) although several different Mo precursors exist to use in a CVD system such as Mo precursors such as MoO_3 , MoCl_5 , and Mo(CO)_6 [89, 100-107].

2.3.2.1. Strategies to grow MoS₂ monolayers

A careful inspection of the literature provides useful strategies that allows large area and bigger flakes. Interestingly, most of the time the two can't be achieved simultaneously. These strategies include using seeding molecules (aromatic molecules), using crystalline substrates, using plasma treated substrates, using O₂, using H₂ and if nothing present optimization of precursor amounts and position of the substrate with respect to sublimating source materials.

Idea of usage of the seeding molecules rely on the presence of amorphous substrate (SiO₂) that it doesn't provide an epitaxial growth. Molecules with hexagonal structure (such as PTAS) are used as nucleation promoters [108]. Hexagonal structure of the molecule provides an epitaxial growth of MoS₂, and since promoters are distributed evenly over the substrate, growth can proceed homogeneously. Films grown with seeding promoter provides a sharp PL around 1.83 and a Raman delta of 21 cm⁻¹. This basically tells that promoter molecule has no effect or interaction with the MoS₂ layer. A list of other seeding promoters rather than PTAS can be found in reference [100]. With this method largest flake size is reported as 60 μm (at the edge of the film) and a large area growth is possible.

Usage of the crystalline substrates such as c-Al₂O₃ (c-plane sapphire) and mica aims to provide an epitaxial environment similar to usage of seeding promoters [109] [110]. Beside the promotion of the large area growth, the term epitaxial critically used for the non-resistive grain boundary formation especially for c- Al₂O₃ for FET applications. It means that flakes are merged together epitaxially without any angle or twin boundary, where it's possible to obtain a single flake performance out of polycrystalline material [109] and high optical quality [110].

Plasma treatment of the substrate is also presented to have large coating area and it is claimed to control the number of layers (1 to 3) when different plasma treatment times are applied (90 seconds to 300 seconds). It is reported that the plasma treatment changes the bond structure of the surface and increases the surface energy [103].

In addition to above methods, using small amount of H₂ and O₂ in carrier gas directly aims to enlarge the flake size. With H₂ size of the flakes can be controlled with flow rate of H₂. Optimum H₂ value gives around 40 μm flake size [89]. On the other hand, optimum O₂ gives 350 μm flake with a mobility 90 cm²Vs⁻¹[102].

2.3.2.2. Growth mechanism and flake size

Despite the recent advances regarding the growth of different 2D films and flakes using CVD, we are still only at the verge of understanding the growth mechanisms in terms of seed formation, nucleation and thermodynamics aspects. For example, an oxichalcogenide nanoparticle encased by fullerene TMDC shell (MoS_2 or MoSe_2) is the first entity formed during the growth and act as a nucleation center suggesting a step-by-step growth of the monolayer flakes[111]. Moreover, thermodynamics calculations reveal that growth is controlled by the slowest diffusing precursor which is Mo rather than S in MoS_2 growth and predicted phase diagram provide a specific window that comprise a sulfur rich atmosphere (a larger sulfur mole fraction than 0.67) between 734 to 2004 K at 1 atm[112]. Furthermore, commonly observed shape evolution of flakes throughout a single substrate is attributed to the S to Mo ratio, which is not constant along the reaction chamber (in general, a quartz tube) and this experimental data is modeled successfully to determine size and shape of the 2D flakes[113, 114]. Another issue, vertically standing flakes, which are reported in different articles, are investigated by transmission electron microscope (TEM) and the underlying mechanism is suggested to be related with the compression and extrusion between the MoS_2 islands [100, 115-117].

Experimental studies on the flake size demonstrate that flake size depends on the concentration gradient of the precursors on the substrate surface or along the growth chamber which directly affect the number of formed nuclei on the surface [118], [119], [113]. Higher concentration ensures high nucleation density decreasing the distance between growth centers and lowering the flake size and even triggering film formations with overlapping multilayer grain-boundaries. Increasing precursor to substrate distance lowers nucleation density and flakes found space to grow. Further increase of the substrate distance or a lower local concentration zone on the substrate suppress the nucleation density too much and flakes cannot find enough “fuel” to grow laterally. Kinetic Monte Carlo simulations benefiting from experimental observations based on concentration gradient explanation also predicts accurate shape and size of the grown crystals [114].

2.4. Characterization Techniques

In this dissertation, Raman and Photoluminescence microscopy is utilized together with Fluorescence lifetime imaging (FLIM). All these three techniques are integrated in

a single commercial confocal microscope (Witec Alpha 300 R). Moreover, optical microscopy (Nikon Eclipse LV100NDA) together with differential imaging contrast (DIC) lenses is also used. Morphological features of grown flakes are also characterized by SEM and inlens-SEM techniques. Moreover, AFM (eZAFM nanomagnetics) is also used to validate the thickness of the flakes.

Since Raman provides the core characterization technique in terms of characterizing the monolayer nature of the flakes, it will be briefly introduced.

2.4.1. μ -Raman, photoluminescence and FLIM imaging

There are excellent sources to learn more details and theoretical background about Raman microscopy in the literature [120, 121]. Therefore, instead of giving a rigorous theoretical background, a practical perspective will be followed to explain how these techniques (Raman, Photoluminescence, FLIM and DF) are utilized in a correlative manner by investigating a CVD grown flake. Therefore, fitting procedures and relevant fitting functions together with important measurement parameters will be mentioned. Furthermore, I will briefly give why Raman is utilized mostly for 2D MoS₂ and what can we learn from this measurement.

2.4.1.1. Raman spectroscopy of monolayer MoS₂

In the case of Raman spectroscopy, a laser beam having a defined power intensity interacts with a sample. Sample may be in the form of solid, liquid or gas. Interaction of the laser beam with the material cause elastic (Rayleigh) or may cause inelastic scattering events (Raman) if the electric field component of the beam result polarization difference within the unit cell or molecule. Probability of this event is very low (1 photon in 10⁷ photons) occurs in femtosecond range (10⁻¹⁵ s) that makes hard to collect the signal .

Elastic scattering may red shift (Stokes) or blue shift (anti-Stokes) of the wavelength of the laser beam. Since anti-Stokes shifts are much weaker than that of Stokes, almost all Raman microscopes adopts Stokes shifts. Boltzmann distribution ratio of the two shifts could be used to reveal the low intensity of Anti-Stokes shift. While Stokes/Anti-Stokes ratio is 0.62 at 100 cm⁻¹ this drops to 0.008 at 1000 cm⁻¹ [122].

To have the Raman spectra scattered light must be collected and dispersed on to a CCD detector. Dispersion is performed by using gratings having different resolutions (300 g/mm, 600 g/mm, 1200 g/mm), where g/mm stands for grooves per millimeters. In

this dissertation all the Raman spectra are collected with 1200 mm/g (highest spectral resolution – 1cm^{-1}), if otherwise not stated. Before diffraction by the gratings, Rayleigh scattering must be blocked or filtered. Therefore, an edge filter is necessary in the optical path at least before the gratings. Although not necessary, the laser beam may be focused on the sample by an objective, and this objective is then helping to collect signal back efficiently. Besides increasing the intensity of the signal, numerical aperture (N.A.) and the wavelength of the laser (λ) determines the spot size of the beam. Therefore, spatial resolution is proportional with the λ/NA . In this thesis, 100x objective with 0.9 N.A. is utilized with the 532 nm laser (green) for the PL and Raman measurements in the confocal microscope configuration. 485 nm laser with 80 MHz repetition rate is utilized for the FLIM measurements. These values give roughly 400 nm to 500 nm spatial resolution. Depth resolution is proportional to λ/NA^2 which roughly makes a 1 μm depth resolution. Therefore, since MoS_2 growths are performed on the 300 nm thick SiO_2 oxide on the Si wafers, we always observe Si peak intensity at 521 cm^{-1} , which is beneficial for checking the calibration of the measurements.

Two distinct Raman modes of MoS_2 (E_{2g}^1 and A_{1g}) that arise due to in plane (E_{2g}^1) and out of plane vibration of S atoms (A_{1g}) is used to evaluate monolayer materials properties. Other Raman modes of the MoS_2 can be found in literature. Followings can be learned from these two Raman modes and can be correlated with other (PL and FLIM) measurements:

- **Layer number:** When moving from single layer to multilayer the frequency of E_{2g}^1 mode increases, whereas in the case of A_{1g} mode it moves towards lower frequencies [123-126]. Therefore, number of layers can be determined from the peak center differences (Δn). While Δn is generally reported as 18 to 19 cm^{-1} for exfoliated flakes, its in the range of 20-22 cm^{-1} for the CVD grown samples.
- **Coulombic interactions:** It has been shown that E_{2g}^1 mode is controlled by the long-range interlayer Coulomb interaction between molybdenum atoms. On the other hand, A_{1g} mode is less affected by interlayer interactions [127]. Therefore, Raman spectra can be used to investigate the interaction between MoS_2 surface and surrounding medium.
- **Electron doping and Adsorbates:** According to literature, A_{1g} mode is more sensitive to electron doping and adsorbed species [128, 129]. Especially in the case of electron doping, softening and broadening of the A_{1g} phonon is very likely,

whereas the other Raman-active E_{2g}^1 mode remains essentially inert. In the case of Raman measurement taken from MoS₂ transistors under operation, A_{1g} significantly broadens due to the electron doping.

2.4.1.2. Raman and PL imaging of monolayer MoS₂

Raman imaging of 2D materials is a very powerful tool to analyze the monolayer nature and relevant stress-strain effects in these materials together with the photoluminescence maps. Such an analysis is performed by first determination of the region of interest (ROI) by using either confocal image (Figure 2.8.a) or by using a dark field image Figure 2.8.b. Raman imaging is performed by first collecting Raman data from determined region with pre-determined number of spots. For example, ROI in Figure 2.8.a is 40 μm x 40 μm . Since the spot size is close to 300 nm, 120 x 120 points per image is applied with an integration time of 1 seconds. Therefore, such a measurement takes 14400 seconds (4 hours). That means that a piezo scanner below the sample moves in x and y direction with 300 nm steps. Raman data is collected for each point (or pixel) and processed. Such collected spectrum can be seen in Figure 2.8.d. In this case, Witec Project 4 software is utilized for the construction of the Raman image (Figure 2.8.c). E and A Raman mode of the MoS₂ is fitted with a Gaussian function to find the spectral positions of the curves.

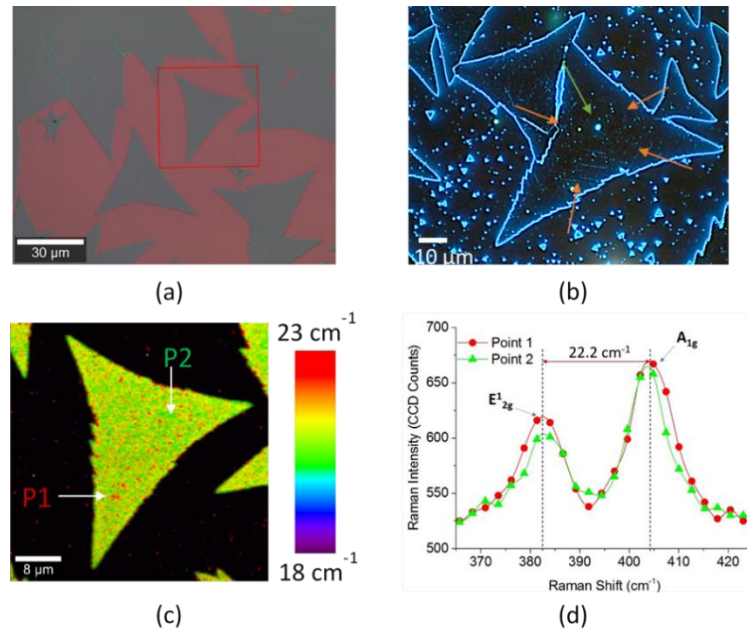


Figure 2.8. a) Confocal image of the flakes, b) DIC image of the flakes, c) Δn Raman map of the flakes, and d) spectrums taken from points P1 and P2 in image c

Therefore, two new datasets are created, one comprising peak position of A and its spatial coordinates and the other is peak position of E with its spatial coordinates. Subtracting these two datasets provide a new dataset. This dataset spatially resolved peak difference, which gives insight about the monolayer nature of the flakes. In this example, majority of the flake is monolayer having difference below 22 cm^{-1} .

Photoluminescence maps can also be performed for the same area and can be correlated with Raman images. As indicated in the optical properties section, by processing of the collected spectra, spatially resolved distribution of the different excitonic contributions' peak centers, peak intensities, and exciton integrated area ratios can be provided. For example, Figure 2.9 demonstrates an example of spatially resolved PL maps. As always, a fitting procedure for each pixel is required. And then image can be formed separately from each dataset.

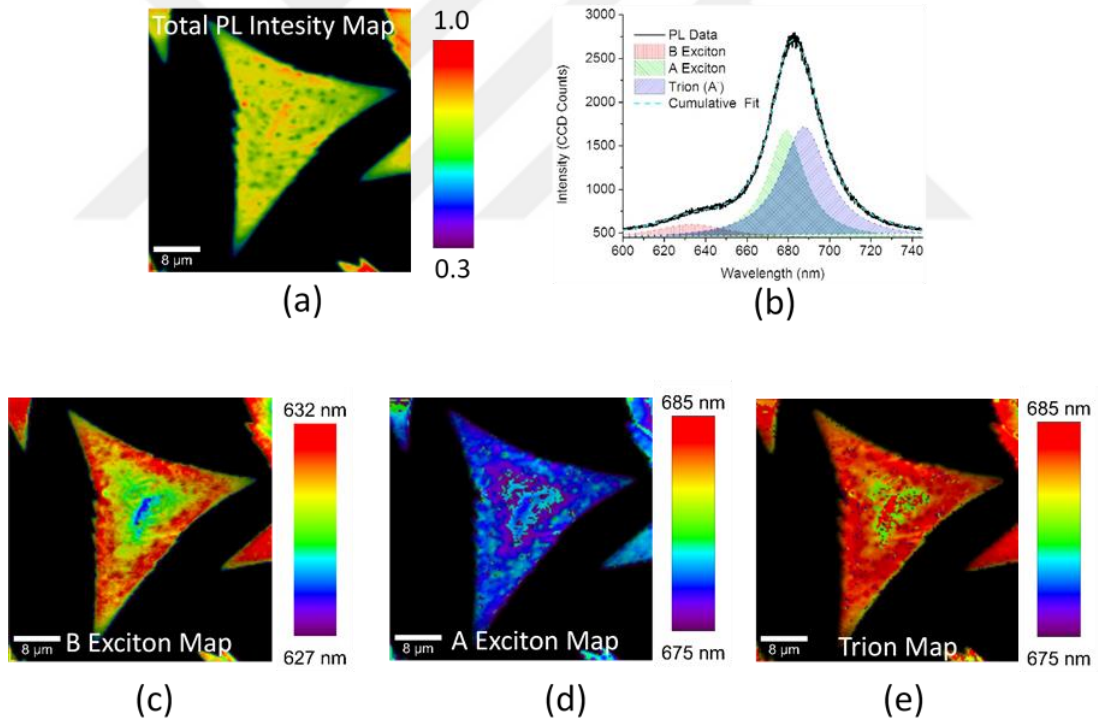


Figure 2.9. a) Integrated and normalized total PL intensity, b) single spectrum of a random point taken from the flake and the fitted curves, c) B exciton peak center map, d) A exciton peak center map, e) Trion peak center map

PL spectrum of the MoS_2 that is demonstrated in Figure 2.9.b can be deconvoluted to the three Lorentzian peaks [86, 87, 130]. These deconvoluted peaks can be further be used to study the PL phenomena in these materials. Physical interpretation of those are

related with the exciton and trion generation and recombination. They are B exciton, ranging between 627 nm to 632 nm (Figure 2.9.c), A exciton ranging between 675 nm to 678 nm (Figure 2.9.d), and trion (A^-) peak between 680 nm to 685 nm (Figure 2.9.d). Different energy levels of A and B peaks are attributed to the valance band splitting at K point due to the strong spin-orbit coupling inherent to the TMDC materials as explained in previous section. It is interesting to note that the PL peak center of the A, B and A^- shifts according to flake position, which accompanies the intensity variation. By using the intensity data of the A and A^- from the fitted curves, we may map the major photoluminescence mechanism. To do that intensity ratio of the A and A^- is calculated and the resulting map image is demonstrated in Figure 2.10.

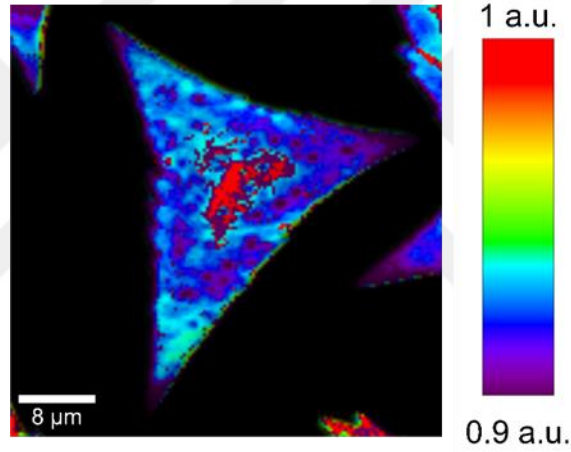


Figure 2.10. *Intensity ratio map of A exciton to trion*

Figure 2.10 depicts that the majority of the edges are slightly dominated by the trion PL mechanism (A/A^- is just below 1). A small fraction at the center zone (where possibly the seed resides) dominated by the A exciton.

3. EXPERIMENTAL INVESTIGATION OF 2D MATERIALS: MONOLAYER MoS₂ GROWTH

In this chapter, result and discussion of the MoS₂ growth experiments by using CVD system is provided. The work demonstrated here is basically the optimization procedure of the growth zone configuration applied to Si/SiO₂ substrates. In addition to growth zone configurations, CVD growth experiments on the glass substrates have been also performed and compared with the Si/SiO₂ substrates.

Under the concept of growth zone configuration, precursors to substrate distance, precursor ratios and gas flow composition (H₂ and N₂) is also studied. Moreover, although pressure is kept 1 atm in most of the experiments, the pressure is regulated by two approaches. In the first approach, no pressure controller is used but pressure is constantly monitored to be sure that the working pressure is in the vicinity of atmospheric pressure by an external vacuum gauge. In the second approach, a pressure regulator is used.

Optimization procedures deliver some useful insight about the growth mechanism and resulting size and shape of the deposited MoS₂ flakes. They also help us to determine the best configurations for photolithographic fabrication of devices suitable for fundamental device research (transistors, photodetectors, etc.). Moreover, comparison of the growth methods especially different growth zone configurations leads us to understand aging behavior of the flakes and provides a relation between how growth zone configuration effects the aging related properties of the flakes.

The grown flakes are analyzed by using Raman, Photoluminescence and Fluorescence Lifetime imaging techniques. Essence of these techniques has been explained in previous chapter. In addition to mentioned techniques, SEM, AFM and TEM techniques are also used. Especially FLIM technique and Raman measurements that applied to as grown and transferred flakes help us to identify the stress state of the grown flakes qualitatively.

3.1. Growth Zone Configurations

In this part of the thesis, two different approaches regarding the position of the substrates with respect to the precursors in our CVD furnace: horizontal and face-down as illustrated in Fig. 3.1 is followed. These approaches are employed under identical growth conditions in order to compare flake size, composition and growth pattern as illustrated in Figure 3.1. Furthermore, we study the effect of substrate holder boat

geometry (as shown in Fig. 3.1) and S-to-MoO₃ ratio, effect of H₂ inclusion and the type of the pressure regulation on the resulting growth patterns.

3.1.1. Horizontal growth: set-1

1 cm x 1 cm (Si/SiO₂) substrates is put side by side next to the precursors. We call this approach horizontal. Horizontal approach is labeled as SET-1 in that chapter. The horizontal growth scheme is also illustrated in Figure 3.1.a. All the experiments were performed by using 1 mg of MoO₃ and 200 mg of S at 700 °C. Heating rate of the furnace is 10 °C/min. Growth time is set to 10 minutes, when the temperature is reached 700 °C.

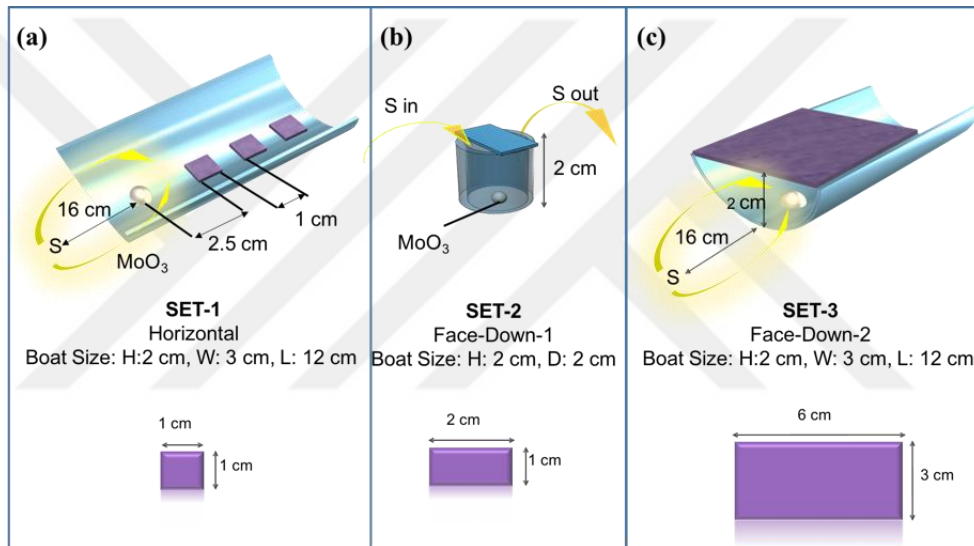


Figure 3.1. Schematic illustration of different growth configurations a) horizontal growth (set-1), b) face down growth (set-2) using a cylindrical boat and c) face-down growth (set-3) with a larger quartz boat with respect to set-2

Morphological and compositional changes were tracked with respect to the substrate distance by using SEM, confocal microscopy and Raman spectroscopy, respectively. Morphological differences can be divided into two categories. In the first category, vertical MoS₂ formations and thick MoS₂ pyramid like structures dominates the growth (Figure 3.2 a-c). These formations were observed up to 5.5 cm. Above 5.5 cm we observed the triangular flake formations (Figure 3.2 d-f.) where their concentration and sizes changes with respect to distance. In general, when the substrates are close to the MoO₃ source, we observe vertical nano-wall growth and thick MoS₂ formations (Figure 3.2. a - c). As the substrate distance increase triangular flake formations appears and with the further increase of the substrate distance, the size of the flake formations decreases.

Composition of the deposited material is analyzed by using Raman spectroscopy. To clarify the results, Raman finger-prints of the α -MoO₃ (precursor used in this study) and intentionally grown monoclinic MoO₂ (m-MoO₂) are used as reference spectra to determine the presence of mo-oxide in the samples. These two spectra are labeled as “ α ” and “m” as shown in Figure 3.3.a and vibrational assignments of these peaks can be found in elsewhere[106, 131, 132].

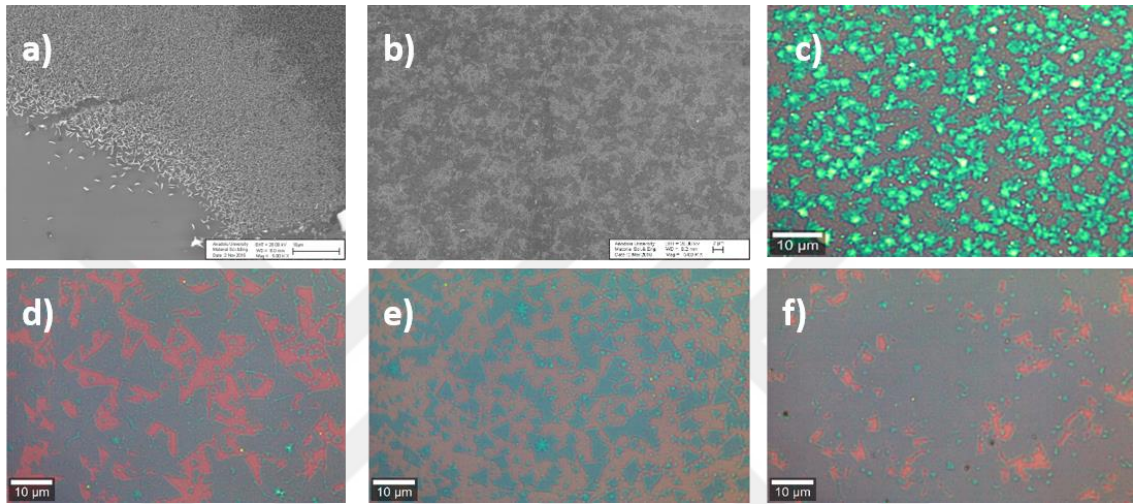


Figure 3.2. SEM images of the samples with nano-wall formations from 2.5 cm to 3.5 cm (a) and SEM (b) and confocal image (c) of thick pyramidal film formations from 3.5 cm to 4.5 cm. Confocal images of the same MoS₂ triangular formations at 5.5 cm (d), 7.5 cm (e) and 9.5 cm (f)

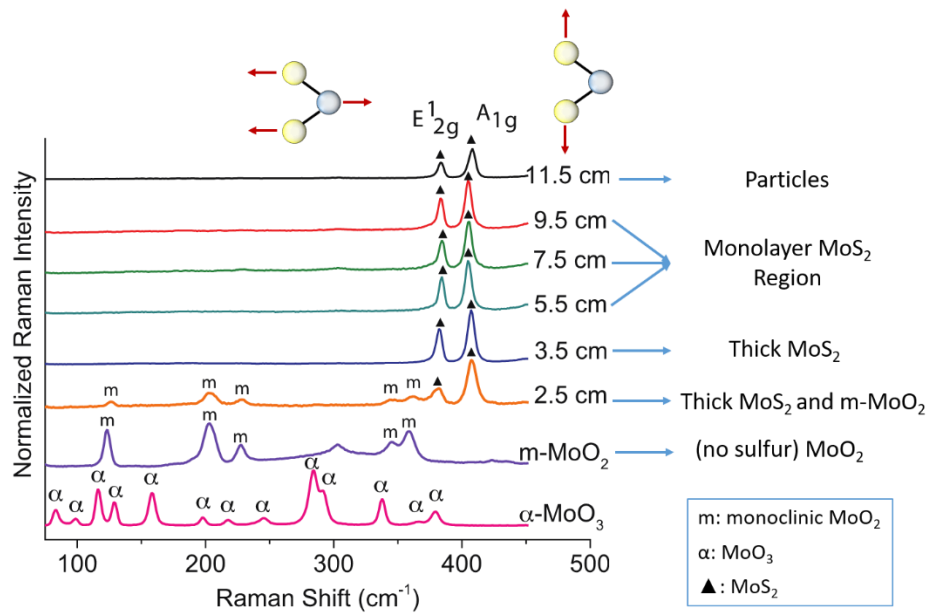


Figure 3.3. Raman finger prints of the samples

From 2.5 to 11.5 cm, we observe Raman finger-prints of MoS₂ (E_{2g}¹ and A_{1g}). However, only in the spectrum of the first sample (2.5 – 3.5 cm away from the precursor) m-MoO₂ is observed besides the MoS₂ phase. Presence of m-MoO₂ disappears or decrease below the detection limit of the Raman when the distance between substrates and precursor is increased above 3.5 cm. Raman peak difference of the E_{2g}¹ and A_{1g} peaks (26 cm⁻¹) of the first and second samples indicate multilayer MoS₂ while this difference decreases to 20 cm⁻¹ for the substrates between 5.5 and 9.5 cm indicating formation of monolayer MoS₂. As a conclusion of Raman analysis, it can be deduced that presence of Mo-oxide and thick MoS₂ between 0 – 4.5 cm indicates a high Mo concentration gradient. Moreover, emerging monolayer MoS₂ layers beyond 4.5 cm, indicates a specific concentration window for the growth of monolayer flakes.

Photoluminescence spectra of the samples from the same Raman measurement points are also used to validate to support the specific concentration window hypothesis. PL spectra are demonstrated in Figure 3.4. PL response measured from the samples demonstrates the highest PL intensity for the samples grown at the distances of 5.5, 7.5, and 9.5 cm (Figure 3.4). Together with the supporting Raman measurements (Figure 3.3) 5.5 to 9.5 cm region is therefore determined as the monolayer growth region.

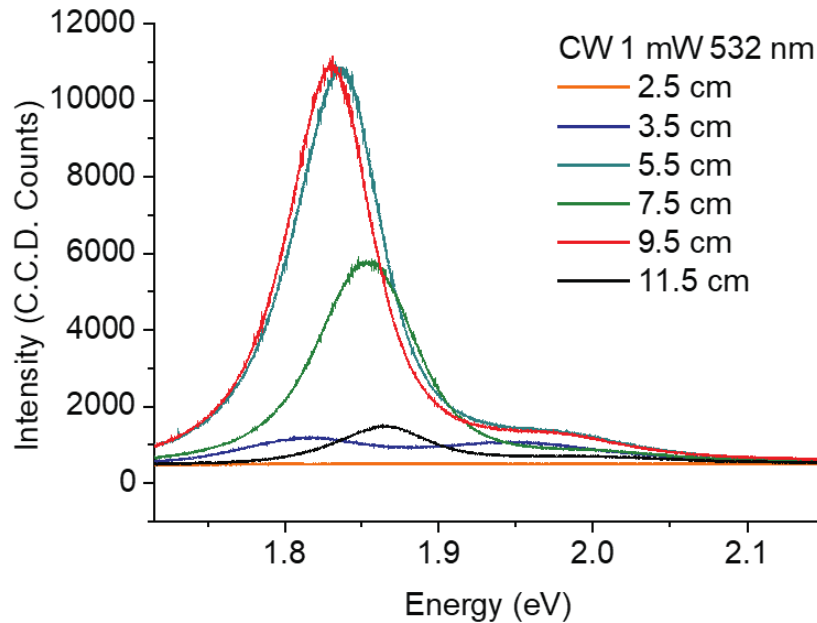


Figure 3.4. PL spectra taken from the same Raman points given in Figure 3.3

3.1.1.1. Assessment of the growth area for horizontal configuration

While it is possible to obtain monolayer flakes with this method, the coverage of the monolayer flake zone is very low. The width of the growth area is approximately 1500 μm from the edge along the flow direction as shown in Figure 3.5).

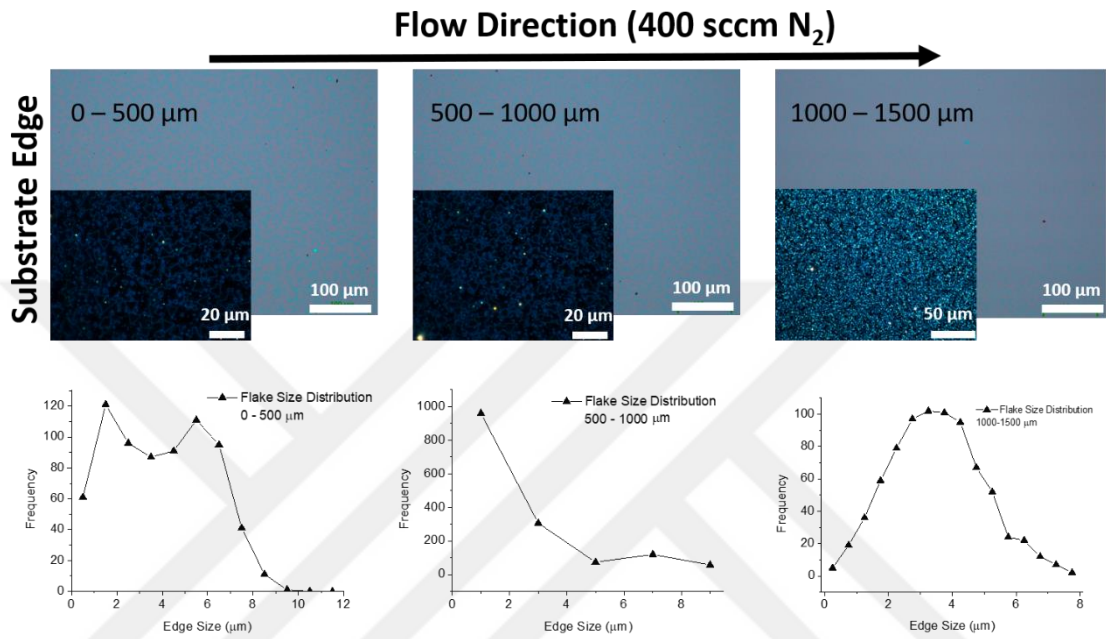


Figure 3.5. Monolayer flake growth region from 0 (edge) to 1500 μm and corresponding flake size distributions

As can be seen from the Figure 3.5, the monolayer flakes deposit at the edge of the substrates either at the edges perpendicular or parallel to the edges and flake size decreases with respect to distance from the edge. Edge deposition of the flakes occurs possibly due to the geometry of the used substrate holder (quartz boat). On the other hand, edges are energetically higher sites that could promote a higher nucleation. For example, Najmei *et al.* observed and reported that MoS₂ prefers to grow at the edges, around dust particles, rough surfaces and scratches [133]. The reason of this behavior is proposed as edge based catalytic behavior that reduce the energy barrier of the nucleation [133]. This proposal of the Najmei *et al.* depends on the preferential growth of the graphene around scratches of Cu film supported by energy calculations [134, 135]. Edges of the diced wafer could potentially have higher roughness than center of the substrate, which might support the proposal. However, large area epitaxial growth of the MoS₂ requires atomically flat lattice matched substrates such as sapphire as demonstrated by Dumcenco

et al [109]. Therefore, this contrary result to the proposed mechanism might indicate other factors governing the preferential edge growth. Besides, we have also investigated the center of the substrates as demonstrated in Figure 3.6. And very small (below 200 nm) flake deposits have been observed.

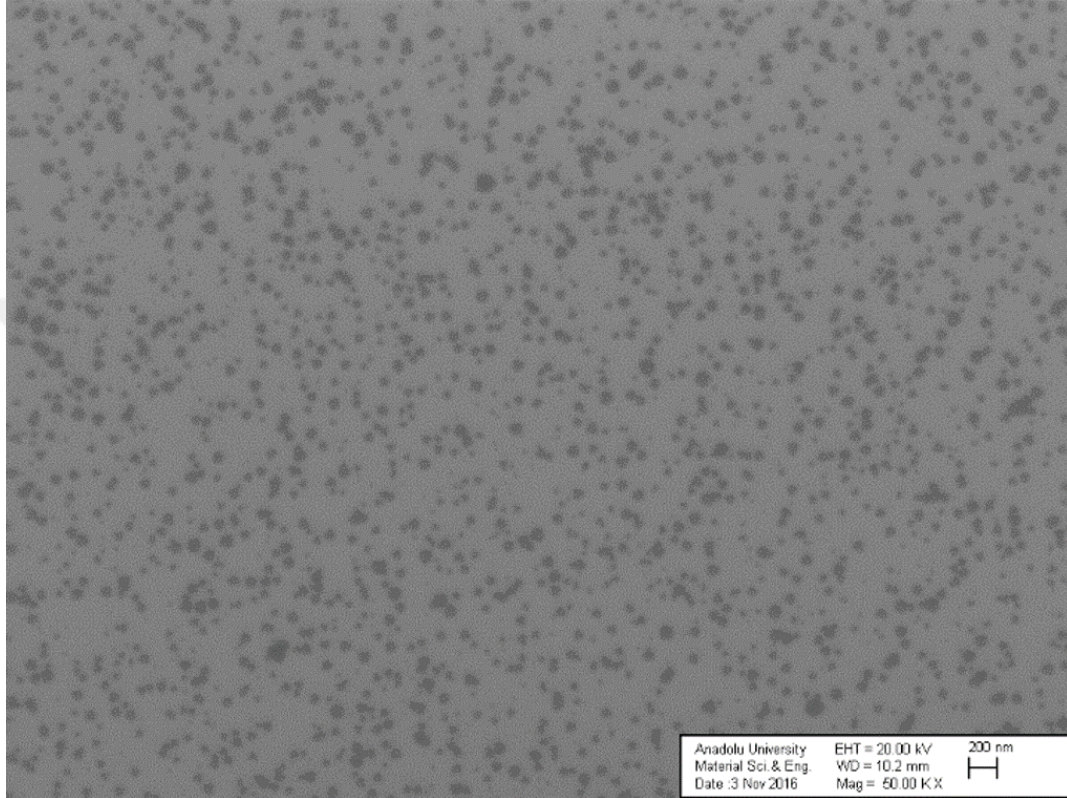


Figure 3.6. SEM micrograph of the center of the horizontal growth configuration

Observation of the small crystallites at the center and large flakes deposited at substrate edges either parallel or perpendicular to the flow direction indicate that utilized boat geometry profoundly alters the growth area. Therefore, other growth zone configurations are investigated to have large flakes and growth areas suitable for device fabrication.

3.1.2. Face-down growth configuration

In this part, we applied face-down growth configuration as illustrated in Figure 3.1. a and b. In Figure 3.1.a we have used a cylindrical boat geometry having 2 cm of diameter. Experiments performed by using this geometry labeled as set-2 and experiments performed by using a larger quartz boat in face-down configuration (Figure 3.1.c) labeled

as set-3. All the growth conditions are kept identical to compare with the horizontal growth.

3.1.2.1. Face-down: set-2 growth configuration

In the second experimental configuration (set-2), MoO_3 powder is placed in a quartz cylinder that has a height and a diameter of 2 cm. The substrate is placed on this cylinder and MoS_2 is formed on the downward facet of the substrate (see Figure 3.1.b). Precursor amounts are kept the same with set-1 to be able to understand the effect of the growth geometry.

As shown in Figure 3.1, there is a 2 cm vertical difference between the position of the precursor and the substrate. Substrate touches the quartz boat as shown in Figure 3.7.a. With this configuration, obtained flakes are radially distributed over the substrate as shown in Figure 3.7.a- Figure 3.7.c. Center of the substrate contains small flakes and these flakes gets larger when we get closer to the edges of the substrate.

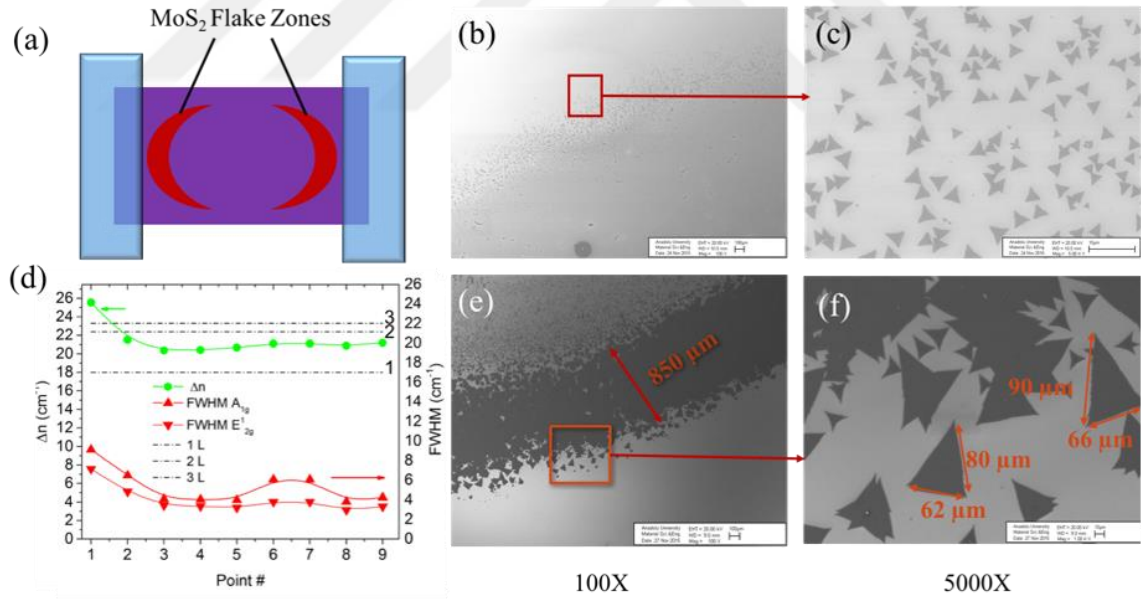


Figure 3.7. SEM images and Raman spectra characterization of set-2, (a) schematic representation of the growth zones on the substrate, (b) 100X SEM image for growth duration of 5 min (no baking), (c) 5000X SEM image demonstrating MoS_2 flakes, (d) number of layer characterization obtained by Raman spectra from the center of the substrate (#1) to the outer rim of the sample (baking duration of 10 min., growth duration of 5 min.), horizontal lines indicate number of layers, (e) 100X SEM image of the sample with 10 min. bake demonstrating one part of the ring structure, and (f) 5000X SEM image of the flakes of the ring structure

As mentioned before, we shift furnace to the left side (onto the Sulphur) when the growth zone reaches 700 °C. If we do not move the furnace to the left at growth temperature and we wait at this temperature for 10 minutes, and then shift the furnace onto the Sulphur, we get much larger flakes up to 90 μm (Figure 3.7.c) and a ring like film formation with a width of 850 μm is obtained as shown in Figure 3.7.e. It is known that the film formation occurs in TMDCs by the growth of individual flakes and their coalescence or merging[133, 136]. Therefore, 10 minutes extra growth time initiate a slower growth process (little S vapor can reach the substrate) and the flakes grow larger till they merge to form a continuous monolayer film. Raman investigation of the samples from this configuration only gives multilayers of MoS₂ at the center of the substrate and the rest of the flakes and film are monolayer MoS₂ (Figure 3.7.d).

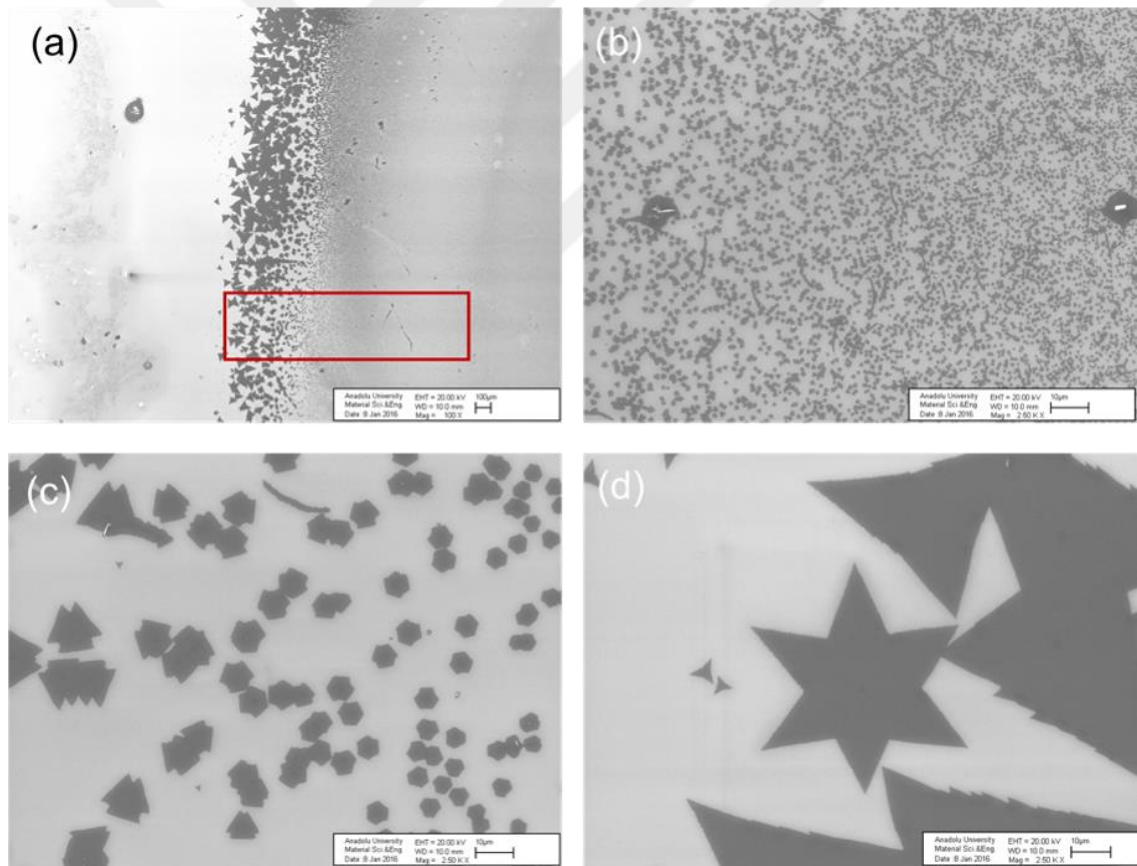


Figure 3.8. Shape and size evolution of films and flakes from the inner to the outer part of the ring-like structure: (a) general view, (b)-(d) size evolution from the left to the right of the marked rectangle in (a)

A radial shape evolution can be tracked around the ring like film as demonstrated in Figure 3.8.a to Figure 3.8.d. SEM images given in Figure 3.8.a – Figure 3.8.d are taken

from left to right of the red box illustrated in Figure 3.8.a, respectively. As mentioned before, the shape evolution is an indication of different Mo to S ratios locally distributed over the surface of the substrate[113, 133]. In these experimental conditions (set-2), we may assume a constant Sulphur concentration due to the large distance between sulphur source to substrate (16 cm) as proposed by Wang *et al.*[113]. Moreover, diameter of the quartz holder is 2 cm, which decreases the possibility of Sulphur concentration difference between points of Sulphur-in and Sulphur-out (see Figure 3.1). Therefore, the varying concentration precursor through the substrate can be suggested as Mo. To understand the deposition uniformity and film formation, it is necessary to review the basic evaporation theory discussing about a surface source and its evaporation sphere [137]. In this model, the substrate is assumed to be positioned above the source. Our growth geometry is in accordance with the model. According to the kinetic theory driven from the surface source model, center of the substrate subjects to the highest Mo concentration, and the Mo concentration decrease radially from center to the edge of the substrate. Therefore, at specific growth zones demonstrated in Figure 3.7.e and Figure 3.7.a, this configuration provides an appropriate Mo concentration regime, which allows the seeds to grow laterally. This explains the reason behind the thicker center Figure 3.7.d, shape evolution and more critically why there is a ring shape monolayer film and flakes around this region. However, the model does not answer the origin of size evolution or nucleation density variation from center to the edge. These can be attributed to the neglected factors such as a dynamic gas flow environment and Sulphur poisoning of the precursor. Especially, Sulphur gas reacts with the solid MoO_3 powder and turning it into the MoS_2 powder during the growth that may decrease the evaporation of Mo from the precursor dynamically during the growth.

Finally, by using this configuration, larger flakes and larger growth area is obtained with respect to set-1 or horizontal growth zone, which provides a better morphology for device fabrication. To further, increase this area, we adopted face-down set-2 approach to a larger boat which leads to set-3 experiments.

3.1.2.2. Face-down: set 3 growth configuration

In this growth scheme (Figure 3.1.c) face-down approach is utilized with a larger boat and with a larger substrate aiming to have larger growth zones. When the same parameters used with set-1 and set-2 (1 – 1.5 mg MoO_3 and 150 mg Sulphur), we observe

a two-lane symmetric growth pattern along the flow direction providing a larger growth area growth with respect to set-1 and set-2. One half lane of the pattern is shown in Figure 3.9. In this growth pattern, from left to right (along the flow direction), flakes start to emerge gets larger and overlaps to form a film as observed in set-2.

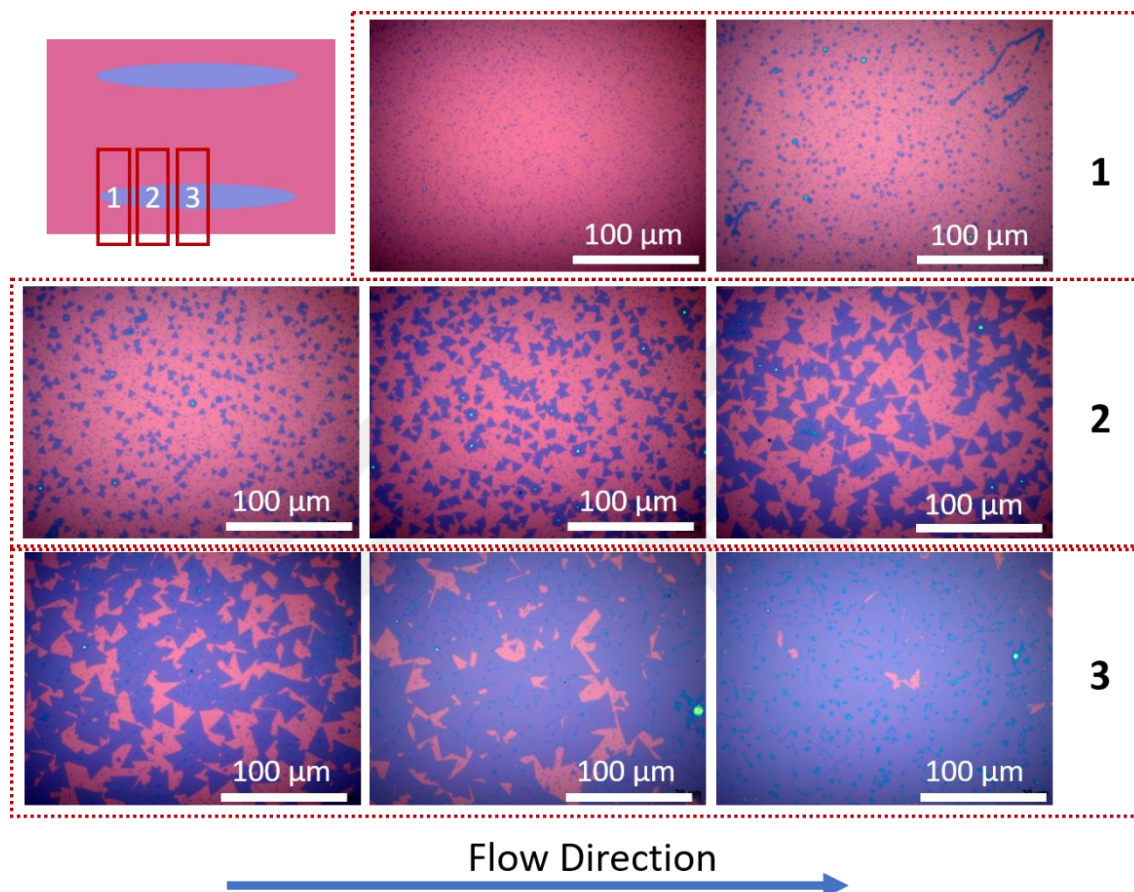


Figure 3.9. Typical growth pattern for the set-3 growth configuration along the flow direction. Left corner schematic image depicts the two-lane growth formation. Optical images are taken from the numbered boxes as indicated on the illustration (left upper corner)

Besides changing the growth geometry only, we change S to MoO₃ ratio and find that it is also a critical factor determining the quality in terms of having only one phase and size of the 2D MoS₂ formations. Experimental parameters have been demonstrated in Table 3.1. Results of the Table 3.1 have been summarized schematically in Figure 3.10, showing the change in growth composition (from the Raman scattering spectra analysis), morphology, and flake sizes (from confocal microscopy and SEM images) as a function of S/MoO₃ ratio. It should be noted that, in all growth experiments, circular flake formations are observed comprising different growth zones as well. Therefore, circular

flake formations are not related with growth configuration or precursors ratio. It is believed that circular growth formations are due to the defects (such as a pin hole) on the SiO₂ layer of the substrate. Such defects changes flow conditions and increase the local concentration of the precursors around these defects. In fact some growth strategies in the literature utilize engineered substrates, which means lithographically patterned substrates to manipulate flow pattern and flake formation around these patterned areas [138].

Table 3.1. Amounts of the precursor and obtained morphology with maximum flake size

Sample	MoO ₃ (mg)	S (mg)	S/MoO ₃	Furnace Cleaning	Result	Max. Flake
L1	1	300	300	C.	Few Circular	-
L2	1.5	300	200	C.	Few Circular	-
L3	2.5	300	120	Not C.	Flakes + Film	-
L4	2.5	600	240	Not C.	Circular	-
L5	2.5	375	150	Not C.	Flakes	50- 100 μm
L6	2.5	375	150	C.	Flakes + Film	70- 80 μm
L7	5	750	150	Not C.	Flakes + Film	150- 200 μm
L8	2	300	150	Not C.	Irregular	-
L9	1	150	150	C.	Circular	-
L10 (L5)	2.5	375	150	Not C.	Circular	-
L11	15	1000	66	Not C.	Flakes + Film	150- 200 μm
L12*	15	1000	66	Not C.	Flakes + Film	80- 90 μm
L13*	50	1000	20	Not C.	Flake + Film + MoO ₃	150- 200 μm

As depicted in Figure 3.10, when a low S/MoO₃ ratio is used, we start to observe Raman signatures from oxide phases, which degrades the film quality. This is also in alignment with the current literature [133, 139]. On the other hand, when this ratio exceeds 150, the triangular flakes become invisible and circular flakes appear or remains. Similarly, the morphology and the maximum flake sizes also change depending on the precursor's ratio.

The optical microscopy images showing these morphologies are presented in Figure 3.11.a – Figure 3.11.d. Each confocal optical image includes μ-Raman and

photoluminescence spectra in the insets indicating monolayer growth of MoS₂. In Figure 3.11.a, at some parts, we observe dot like bright features, which are suggested to be nucleation centers (seeds) from which monolayer MoS₂ grows [111]. However, at some parts, there are no bright spots on the flake. This can be understood regarding the TEM studies performed by Cain et. al.

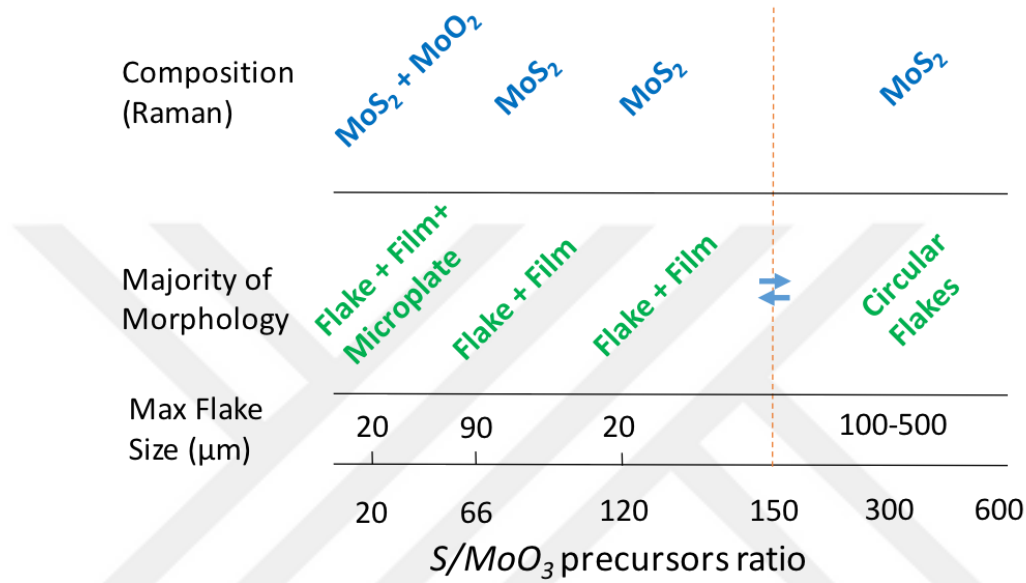


Figure 3.10. MoS₂ flake and film characteristics as a function of S/MoO₃ precursor ratio

TEM studies demonstrate that MoS₂ or in general TMDC 2D materials grow first from a spherical seed. Elemental analysis of the seeds demonstrates a core-shell system. Core of the seed (first entity formed during the growth) is an oxide rich Mo-O-S phase. This seed is then gradually sulfurized to form fullerene like layers around it (MoS₂ layers) [111]. Fullerene layers are then spread (or grow) laterally to form flakes suggesting a classical nucleation and growth scheme for the CVD growth. The size of the fullerene like seeds studied by the Cain et al. is around 5 to 10 nm. Such small seeds would not be visible in the confocal image. However, it is interesting to note that some seeds are large enough to be visible in the confocal microscope. This could be explained by the suggestion that some seeds could be formed during an early stage of the growth and enlarge as seeds until the furnace condition is matured for a lateral growth.

The flakes in Figure 3.11.b are in a triangular shape where the flakes do not overlap and do not cause grain boundaries. However, when the density of flakes increases, this leads to flakes to overlap, which results in formation of few-layer MoS₂ due to merging

of monolayer flakes. Figure 3.11.d exhibits the case of excessive S to MoO₃ ratio where we lose separate triangular shapes and realize merged flakes in a circular shape. 21 cm⁻¹ difference between Raman fingerprints of MoS₂ (E_{2g}¹ and A_{1g}) and high intensity PL spectra around 1.83 eV indicate that triangular flakes are single-layer MoS₂ (Figure 3.11.a and Figure 3.11.b). 24 cm⁻¹ and 26 cm⁻¹ difference between Raman fingerprints of MoS₂ taken from grain-boundaries and center of circular flakes, and low intensity of PL spectra of these points indicate the presence of few layer MoS₂ parts (Figure 3.11.c and 3.11.d) while the rest of the film or the circular flake is monolayer.

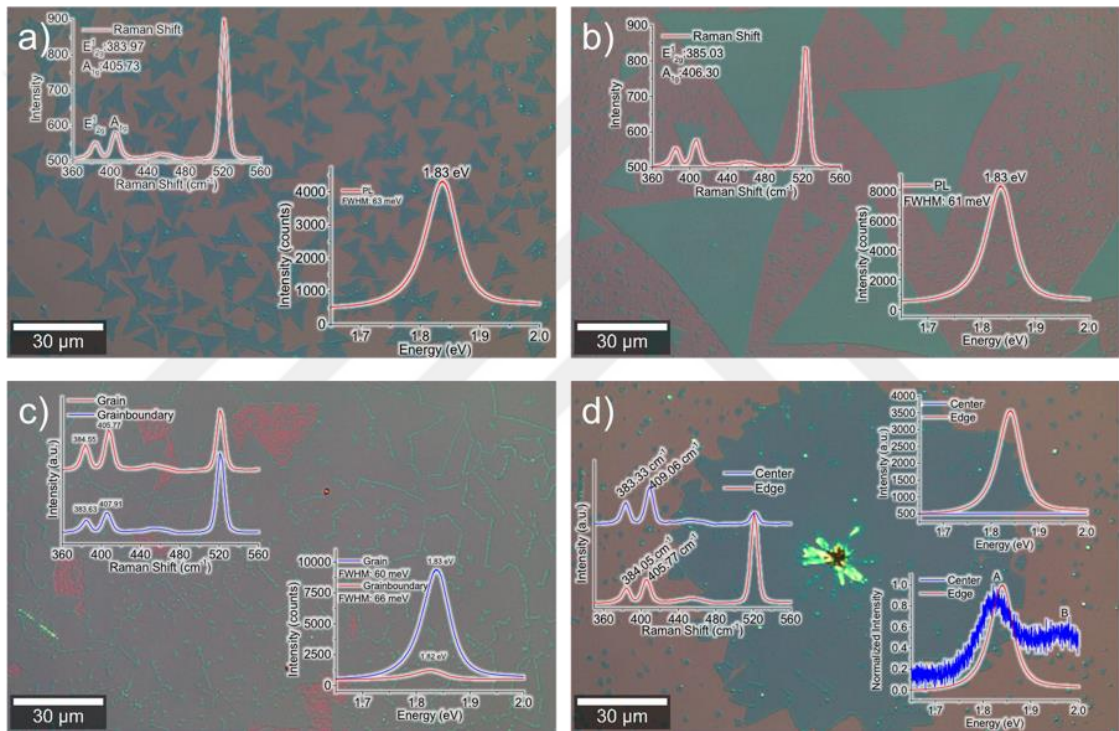


Figure 3.11. Optical images of (a) the flakes with sizes of 10 – 20 μm when the ratio of S to MoO₃ [R] = 20, (b) flakes with sizes of 80 – 90 μm when [R] = 66 (c) MoS₂ film when [R] = 66, (d) circular film like shapes with a thick central region when [R] = 300. In the insets, Raman scattering, and PL spectra are shown. For (c) and (d) both the points chosen from the film area and the center of the circular shapes are shown

3.1.3. Conclusion and assessment of growth zone configurations

In this section, widely-used two growth approaches: horizontal growth and face-down growth with identical growth conditions including S (150 mg) to MoO₃ (1 mg) precursor ratio, substrate temperature (700 °C), atmospheric pressure, and 400 sccm of N₂ carrier gas were performed and compared. In the case of face-down approach, we also changed substrate holder types to control the S to Mo vapor ratio, hence the interaction

between these vapors and the substrates. According to our results, face-down approach (set-3) is found to be more favorable to obtain larger flakes presumably because of higher Mo confinement in the growth zone. In the horizontal growth, it is observed that although all the surface is covered with monolayer MoS₂ formations, either these formations are too small (<200 nm) at the central area of the substrate or they are found at the edges (~10 μm). On the other hand, face-down approach gives much larger flakes (~90 μm) and larger continuous films (850 μm x 1 cm). In this research work using face-down approach, we could control size and shape of the flakes by changing S/MoO₃ ratio, where it is found to be between 66 to 150 to obtain larger and uniform monolayers. In short, we find that the local S and Mo vapor concentrations in the growth zone are of critical importance to control the shape, size and uniformity of the resulting MoS₂ flakes and films. Moreover, according to presented research, face-down approach (set-3) yields larger flakes and obtained deposition formation is more suitable for device fabrication (expected to provide higher working device number with respect to horizontal after lithography processes).

3.2. Fluorescence Lifetime Measurements

In this section, fluorescence life-time imaging and accompanying photoluminescence properties of a CVD grown MoS₂ by set-3 growth configuration is reported from flakes and from film area where flakes merges. Our investigation on individual monolayer flakes reveals a clear increase of the fluorescence lifetime from 0.3 ns to 0.45 ns at the edges with respect to interior region. On the other hand, investigation of the film layer reveals quenching of PL intensity and lifetime at the grain boundaries. These results could be important for applications where the activity of edges is important such as in photocatalytic water splitting. Finally, it has been demonstrated that PL mapping and FLIM are viable techniques for the investigation of the grain-boundaries in 2D materials.

3.2.1. Region of interest

In this part, face-down approach described in 3.1.2 is used. 1 g elemental S and 10 mg of MoO₃ are used as precursors (R = 100) and realized reaction at 700 °C and at atmospheric pressure to grow MoS₂ monolayers on the SiO₂/Si substrate with a 285 nm thick amorphous SiO₂ layer. The distance between S and MoO₃ is fixed at 18 cm. Split furnace is used to have a mobile heater body to control the growth process carefully. When the growth temperature is reached, the furnace is shifted to the S precursor region

to achieve enough flux of gaseous Sulphur to prevent formation of molybdenum oxides. When all the Sulphur evaporates, the upper furnace is lifted for fast cooling to prevent secondary nucleation. Figure 3.12 shows resulting film formations containing up to 80 μm 2-D triangular few layer flakes that merge to form around 1 cm^2 few layer MoS_2 film. FLIM investigations are performed from two region of interest area as also demonstrated on the Figure 3.12. First one is the film area and the second one is the region where flakes resides.

The method of FLIM analysis has been explained in Appendix 1.

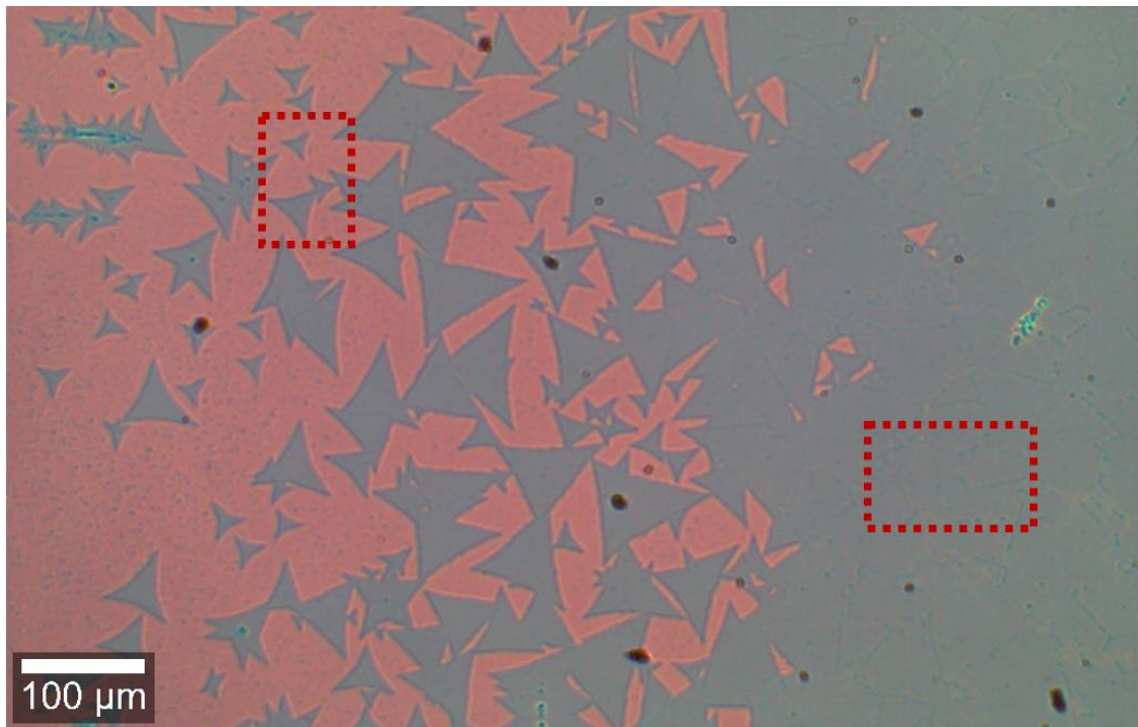


Figure 3.12. Figure depicts MoS_2 growth area and dashed zones indicate two region of interest: standalone flakes and film area

3.2.1.1. Film area

In the first part of these measurements, a structural characterization is performed from the film area. Confocal optical image of this zone is given in Figure 3.13.a. Image also shows the two regions of interest where Inspection of the confocal image provides additional layers and crack like boundaries (white lines) on a smooth surface. Splitting the furnace when the Sulphur is completely finished might result in an additional stress on the film due to the thermal expansion mismatch between MoS_2 and SiO_2 under layer. The stress issue will be discussed in the next chapter. In addition to cracks (or wrinkles),

thicker boundaries (greener contrast in the Figure 3.13.a) are observed as an extension of the cracks. Therefore, this selected region provides all the interesting points for PL and lifetime inspection: layer properties, structural defects (cracks), secondary nucleation on these boundaries and regions demonstrating no defect in the Confocal Image.

Point μ -Raman analysis of these zones is given in Figure 3.13.b. E_{2g} and A_{1g} Raman peaks demonstrates existence of MoS_2 layers with changing layer number with respect to structure on the film. Raman inspection except for obvious thicker points (1, 4, 5 and 6) indicates few layered MoS_2 . Number of layers of the selected points can be seen in Figure 3.13.c. In fact, our PL measurements reveal that these flakes are mostly in the form of few layers because we observe PL peak centers between 1.82 – 1.86 eV, which is consistent with monolayer and few layer PL measurements of MoS_2 [23,24].

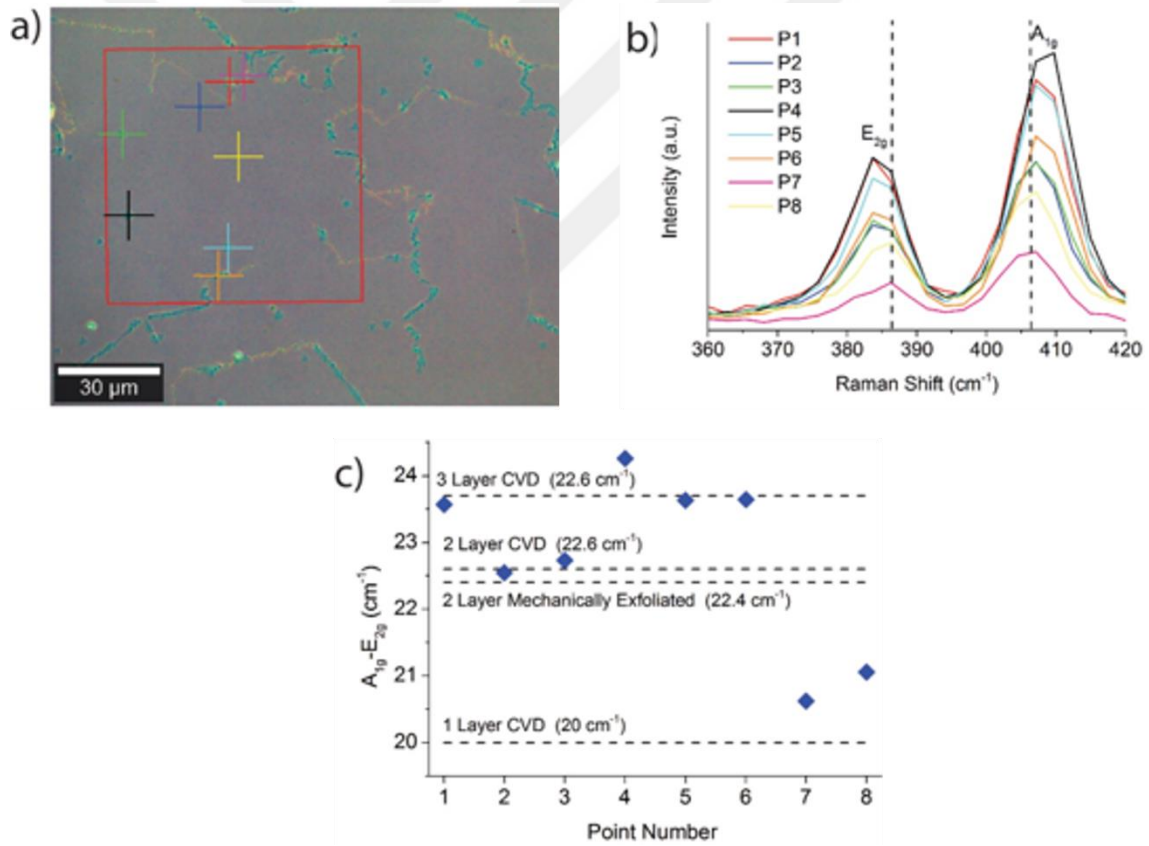


Figure 3.13. a) Confocal image of the film zone. Colored cross marks are the points where single point Raman measurement is performed. b) Raman spectrum of point 1 (P1, red cross mark) to point 8 (yellow cross-mark). c) A_{1g} and E_{2g} peak center differences and corresponding layer number of the cross marked points. Horizontal dashed lines indicate specific values corresponding to number of layers in literature [13-14]

Figure 3.14.a demonstrates the total photoluminescence intensity map and Figure 3.14.b demonstrates the FLIM image of the same region introduced in Figure 3.13. Figure 3.14.c is the single point photoluminescence measurement of the points (coloured cross marks) given in Figure 3. 13.a together with number of layers indicated at the legend of Figure 3.13.c. First, PL map reveals black lines (non-luminescent area) that we already mentioned as cracks (or wrinkles) in the confocal image (Figure 3.13.a). On the other hand, PL map also reveals secondary, very thin black lines, that separate hexagonal like grains which were not visible by confocal imaging. Total photoluminescence intensity map also reveals quenching of PL intensity at the boundaries (grain-boundaries or cracks). Lifetime imaging is in line with the photoluminescence map that demonstrates a higher lifetime in single layer regions (red zones) of the image (Figure 3. 14.b) with respect to the defective sites (secondary layers and grain-boundaries). Still, the measured fluorescence lifetime is within the range of reported room temperature theoretical value of bright A exciton of monolayer MoS₂, that is 0.27 ns [7]. PL peak centre of single point measurements shifts from 1.82 eV to 1.86 eV. As mentioned earlier, cracks are the indication of possible stress. Profound local stress effect on the narrowing of the band gap (up to 90 meV with 2.5% tensile strain) is reported. [15] Therefore, in addition to thickness and composition, stress isn't a negligible effect when considering PL shifts. Moreover, it has been demonstrated that CVD grown flakes possess also a compositional variance across the flakes possibly due to substrate position and concentration gradient along the quartz tube as explained in the previous section [11]. Variation of the PL intensities with respect to number of layers is also visible in Figure 3. 14.a and c, suggesting different quantum yields in multi-layered structures as explained in Chapter 2 and as already expected.

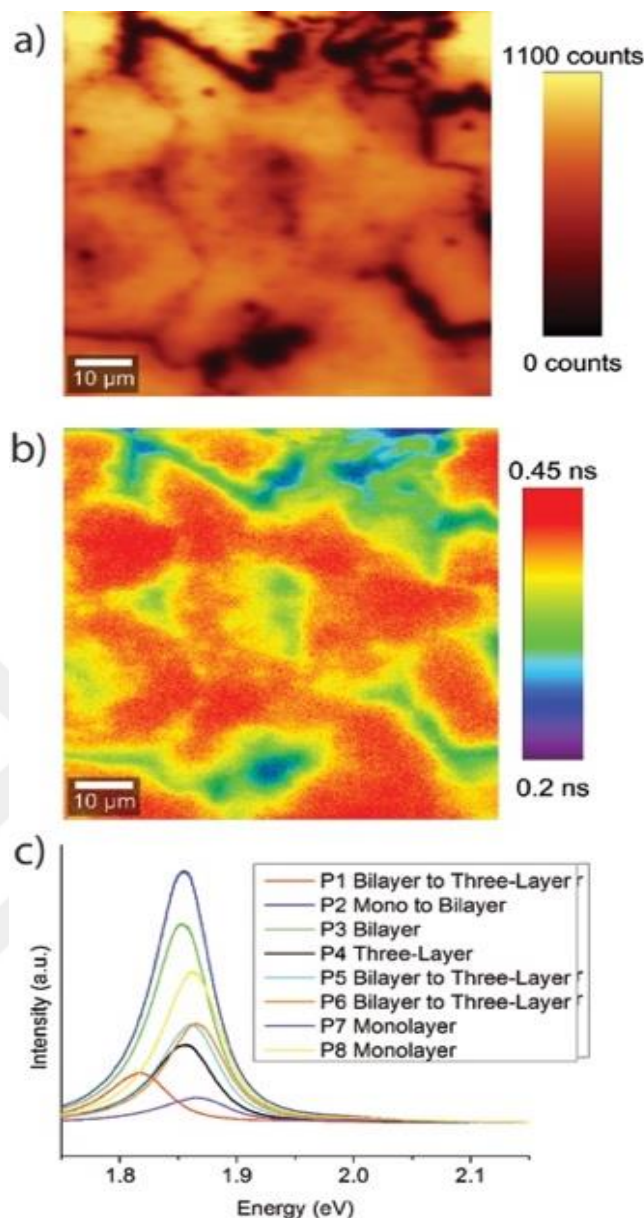


Figure 3.14. a) Total PL intensity map, b) Fluorescence lifetime map, c) Single point photoluminescence measurements. See Figure 2 for the positions of the points

3.2.1.2. Analysis of separate flakes

Herein, lifetime of the separate flakes, which do not exhibit grain boundaries and other structural defects, such as stress related cracks are demonstrated. To be completely be sure about the monolayer (or few layer) and defect free nature of the investigated separate flakes AFM analysis also performed as given in Figure 3.15. The height difference of the two points were taken as indication of the thickness. These are the crossing points of the vertical lines (Figure 3.15.b) with the profile lines. Height difference gives 1 nm for Profile 1, 1.2 nm for Profile 2, 1.2 nm for Profile 3, and 1.7 nm

for Profile 4, indicating 1 to 3 layers of MoS₂. Result indicates the few layer nature of the CVD grown MoS₂ in this work.

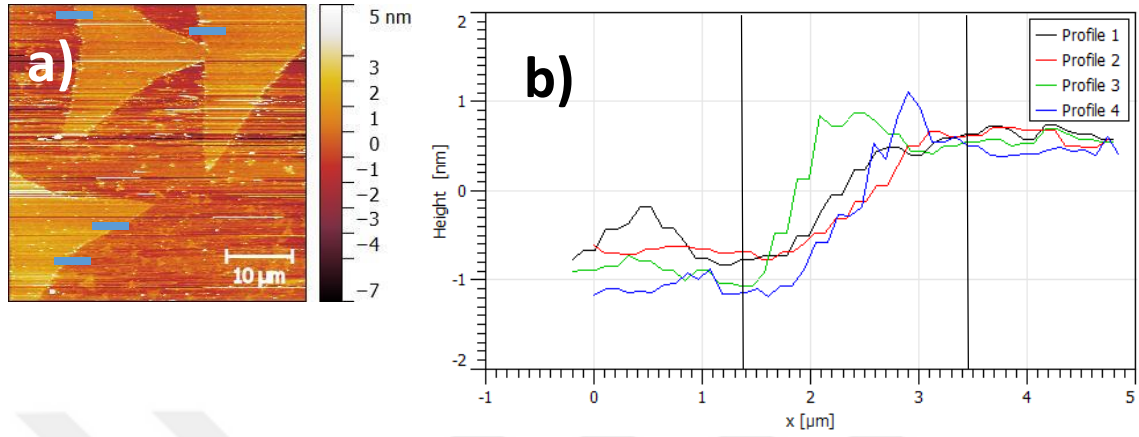


Figure 3.15. AFM measurement a) AFM image, and b) Profile heights

Figure 3.16.a and Figure 3.16.b show the PL map and corresponding lifetime imaging of the same region, respectively. Figure 3.16.c (inset of Figure 3.16.a) is the map of Raman shift difference between E_{2g} and A_{1g} peak centers of a selected flake. Delta values between 18 to 22 in Figure 3.16.c indicate a homogeneous monolayer flake. Absence of such a grain-boundary interaction and a better pristine structure (no PL visible cracks or wrinkles) lets us visualize the effect of the edges more clearly with respect to the interior part of the flake. Total PL intensity and lifetime of the edges are higher with respect to the interior or central regions (0.3 ns at interior and 0.45 ns at edges).

As demonstrated in Figure 3.14.b, interaction of grains via a grain boundary quenches lifetime and decrease PL intensity, possibly by increasing the non-radiative decay channels. As noted above, MoS₂ flakes exhibit brighter PL and longer lifetimes at the edges of the flakes when compared to the interior parts of the standalone flakes (Figure 3.16). In general, these results are attributed to the numerous factors such as charge carrier density, defect density, strain, screening, band-bending, crystallinity and grain boundaries [16-20]. The possible reasons for the brighter PL with the longer decay lifetimes at the edges and lower PL with the shorter decay lifetimes at the interior points can be listed as the higher defect density, change in crystallinity and higher charge carrier density.

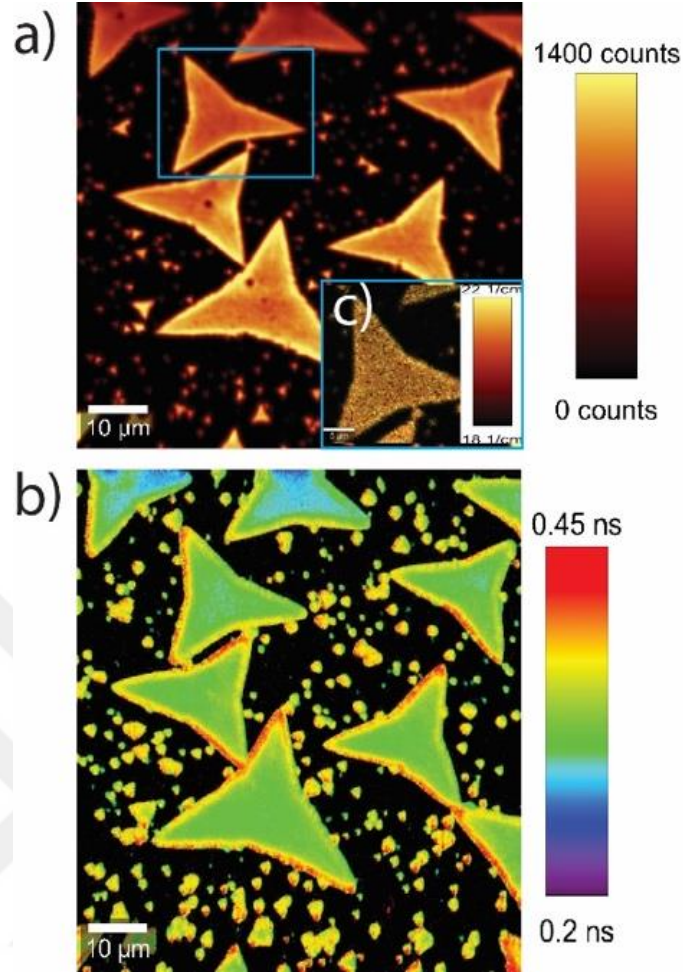


Figure 3.16. a) PL mapping, and b) FLIM mapping of the separate flakes. c) Map of difference between peak centers of E'_{2g} and A_{1g}

For the further investigation of these findings, we performed PL measurements by using 532 nm CW laser and at various laser powers, and we obtained steady-state PL spectra from the interior region and the edges of the standalone flakes. As given in Figure 3.17, we observed a significant red-shift in the PL spectra as the measurement point is moved from the lower PL point (interior region) to the higher PL point (edge region). Furthermore, this shift is significantly increasing with the increase in excitation power from 3 mW (10 meV) to 9 mW (19 meV). These observations made under relatively high excitation powers indicate that one possible reason for the weaker PL and shorter lifetimes at the interior regions of the flakes could be a favored formation of trions and excitons together leading to exciton-exciton annihilation or charge screening [21,22]. Furthermore, in addition to exciton and trions, the formation of other species of excitons such as biexcitons and/or bound excitons could lead to increased contribution of radiative component at the edges.

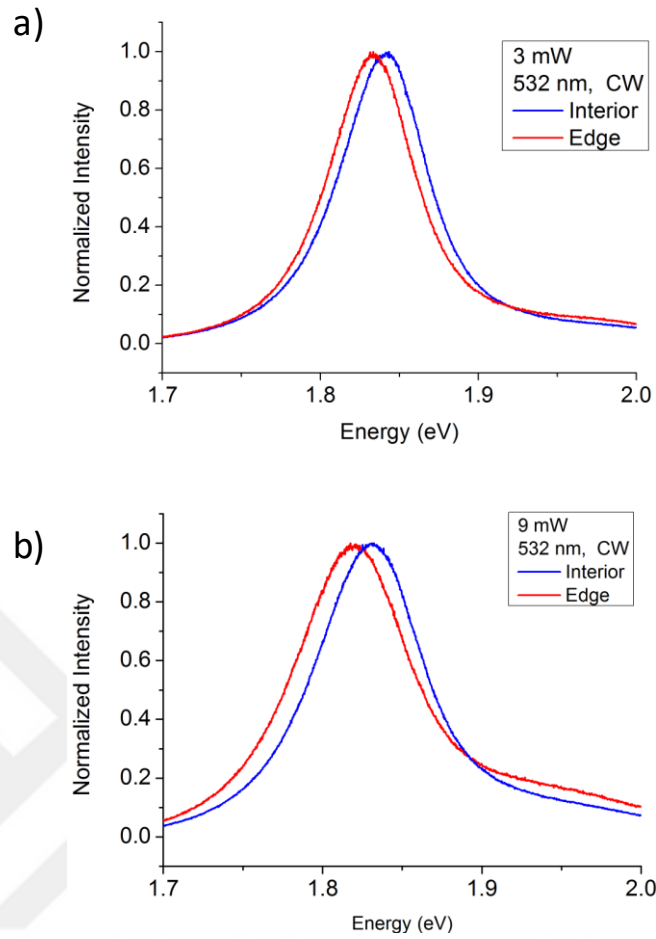


Figure 3.17. Comparison of the PL spectra of edge and interior points at a) 3 mW CW laser power with 10 meV PL shift, and b) 9 mW CW laser power with 19 meV PL shift

3.2.2. Conclusion of FLIM measurements

As a conclusion, the effect of structural defects, multiple layers, grain boundaries and edges on the optical properties of CVD grown MoS₂ layers are demonstrated. The structural defects and additional layers change the optical properties. It is observed that existence of grain boundaries both decrease the photoluminescence intensity and quench fluorescence lifetime, leaving defect free monolayers (inner of grains) with higher PL intensity and life-time. Separate flakes on the other hand, exhibit an opposite behaviour, where edges have higher life time and photoluminescence intensity. This could be important for applications where edges play a key role, e.g. hydrogen evolution catalysts. Our results further demonstrate that even for perfect monolayer flakes or films there exists an optical heterogeneity, possibly due to stress or local compositional change in flakes. Finally, usage of three imaging techniques (lifetime, Raman and PL) are demonstrated as a set of powerful tools to evaluate optical properties of a 2-D material.

3.3. Time Related Observations on the Grown Flakes

In this section, the relationship between the formation of long-term fractures in monolayer MoS₂ flakes and the chosen CVD growth approach is demonstrated. The CVD method comprises either face-down (FD) or horizontal (H) growth approaches where the FD method is frequently used due to the possibility of growing rather larger flakes as demonstrated in previous chapters. However, time dependent observation of these flakes suggests that the flakes grown by FD method is spontaneously fractured. On the other hand, flakes grown by H approach remains intact and crack-free (for this research, this duration is limited by a period of 18 months). Spontaneous cracking of the FD grown flakes is attributed to the stress accumulation during the presumably faster CVD growth. In plane Raman mode shifts of the cracked and transferred flakes supports the stress accumulation during FD CVD growth together with the PL shifts and FLIM measurements demonstrated in previous chapters. These results are critical to understand and predict about the crack-free growth of 2-D materials for their devices to become commercialized in the future.

Several reports underline a cracking and aging problem of these structures, which is attributed to the residual thermal strain effect [140-146], still the reliability of such monolayers in terms of long term mechanical integrity is not thoroughly studied yet [144-146]. Thus, understanding and solving this problem is currently one of the utmost important issues. Therefore, in this work, time dependent fracture (or aging) comparison of the MoS₂ flakes grown by face-down and horizontal approach is demonstrated. CVD growth conditions such as growth time, precursor amounts, and temperature are kept constant. More importantly heating and cooling rates are kept identical for both configurations. A clear difference is found on the mechanical stability of the flakes grown by face-down and horizontal approaches, where the face-down flakes spontaneously crack but horizontal flakes are kept as grown even it exceeds 18 months after their growth.

3.3.1. Structural changes of the MoS₂ flakes with respect to time

In the first two reports, detailed analysis of the CVD grown MoS₂ flakes had been performed and results had been published in PSS-RRL and JJAP, respectively [1,2]. When the flakes grown in the past two periods of the research was re-examined, structural changes on the flakes had been observed depending on the substrate position with respect to the MoO₃ precursor. These positions can be seen in Figure 3.18, which is given as a reminder for the growth procedure.

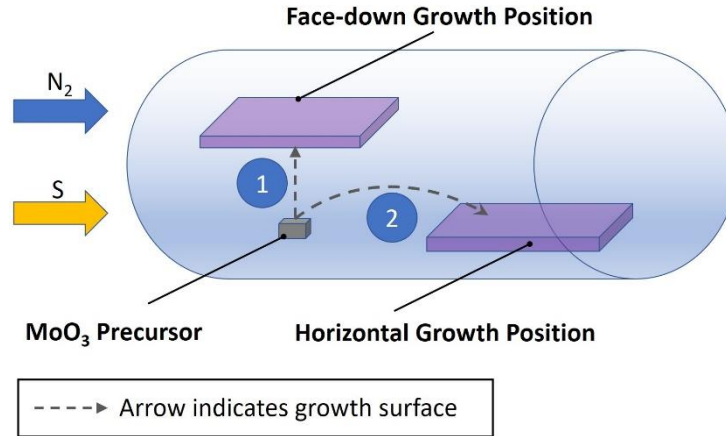


Figure 3.18. Schematic view of CVD growth of face-down and horizontal positions. Arrow 1 and 2 indicate the surface where the MoS_2 flake grow. S and N_2 indicate the Sulphur and Nitrogen gaseous, respectively

In summary, Si/SiO_2 substrates are positioned on top of the MoO_3 precursor in face-down (FD) growth and substrates are positioned next to the precursor in horizontal growth (H). 1 mg MoO_3 and 150 mg Sulphur are reacted for 10 minutes at 700°C to form MoS_2 flakes in a quartz tube at an atmospheric pressure. 400 sccm N_2 is used for both oxidation protection and as carrier gas. Much more details can be found in previous sections.

Figure 3.19 represents the freshly grown flakes by using the two approaches. PL peaks are centered at 1.8 eV for both of the samples. As noted before, the flakes of the face-down sample (Figure 3.19.a) are larger than the horizontally grown ones (Figure 3.19.b). Considering the 10-minute identical growth time, growth rate of the FD flakes is much higher than the H flakes.

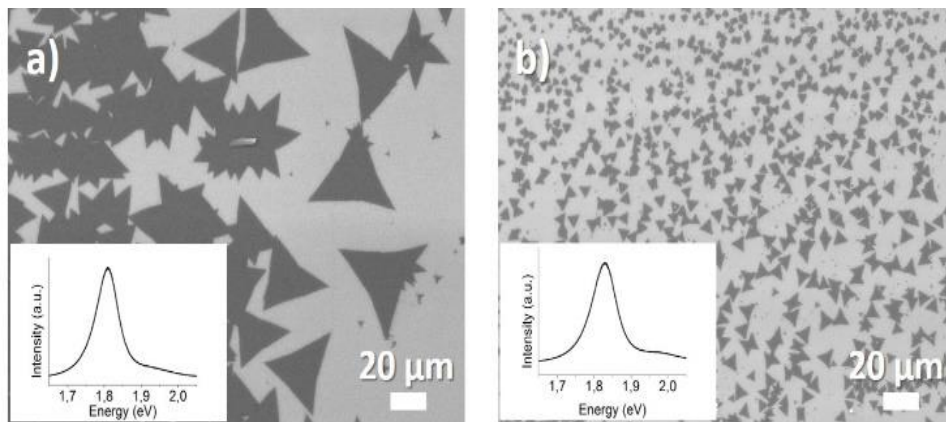


Figure 3.19. SEM images of freshly grown a) FD flakes and b) H flakes. Insets demonstrate 1.83 eV PL bandgap indicating monolayer MoS_2

Reexamination of the flakes after 18 months yield a structural difference with respect to their initial structure (Figure 3.19.a and Figure 3.20.a). This difference is observed only for the FD flakes even though H grown flakes are older than the FD ones. Figure 3.20 demonstrate the optical image (bright and dark field) of the flakes obtained after the CVD growth (Figure 3.20.a) and after 18 months later (Figure 3.20.b-c).

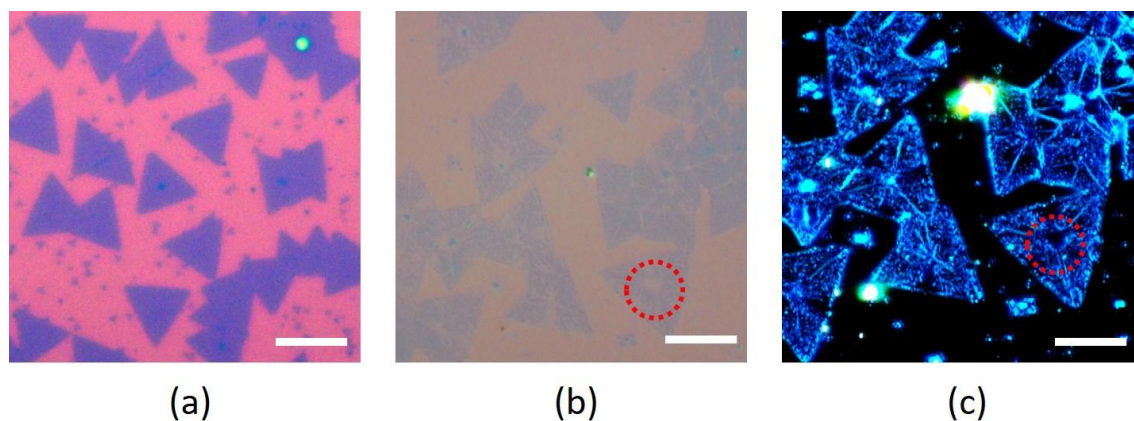


Figure 3.20. a) FD flakes grown 18 months ago, b) Bright field image of FD grown flakes at the present time, c) Dark field image of the flakes at the present. Note that all scale bars are 10 μm . Dashed red circles points similar contrast with the substrate for both bright and dark field images

According to Figure 3.20.b and Figure 3.20.c, a similar contrast is visible in most of the flakes. Dashed red circles on the selected figures in Figure 3.20.b-c show large void like structures at the flake center. This might indicate that flakes are fractured (or cracked) over time. To confirm whether the flakes are cracked Raman line scan is performed on the flakes. Figure 3.21 demonstrates the line scan results. Raman line scans reveal that at regions where the contrast are similar with the substrate, maximum intensity of MoS_2 E mode peak decreases (Figure 3.21.b and Figure 3.21.e). Moreover, at these points' Si Raman peak increase slightly. Furthermore, single point Raman spectrum (Figure 3.21.c and its inset figure) taken from these regions, for example from P1 and P2 points support the absence of MoS_2 forming structural features. These structural features are shown in Figure 3.21.f as crack lines and pores.

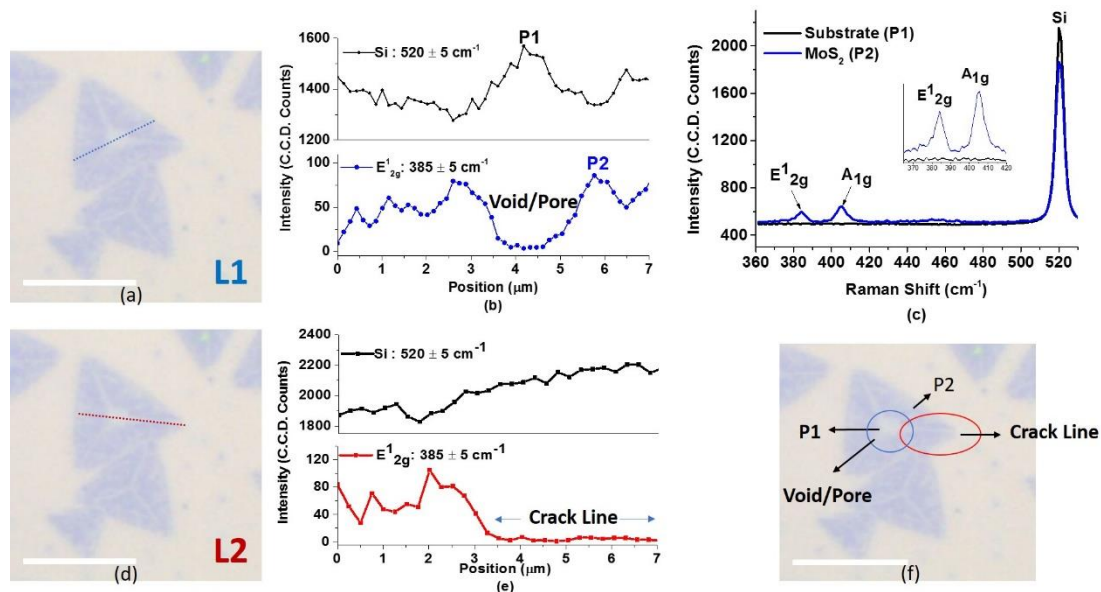


Figure 3.21. Line scan analysis on the FD flake, a) Position of line scan 1 (L1), b) Maximum intensity of Si and E mode of MoS₂ through the L1, c) Single Raman spectrum of points taken from P1 and P2, d) Position of line scan 2 (L2), e) Maximum intensity of Si and E mode of MoS₂, f) Labelling of single spectrum points (P1 and P2) and structural features as crack line and void/pore on Confocal image of the flake

After the confirmation of structural degradation of the flakes, origin of this effect is investigated. To do that, Raman shift of the several types of samples are investigated. These are H flakes, FD flakes, FD transferred flakes, and cracked flakes. To do that FD flakes are transferred to new substrates and Raman investigation is performed. Transfer procedures of the flakes are explained below as a separate section.

3.3.1.1. Transfer process of the flakes

In this transfer technique, PMMA-anisole solvent is used as a transfer medium for the 2D flakes. That means that PMMA-anisole is spin coat on the MoS₂/Substrate. It is dried to some extent (anisole is removed) leaving a rigid PMMA sheet on the MoS₂/substrate. Therefore, PMMA sticks to the flakes. Trimming the edges of the PMMA exposes PMMA and Si/SiO₂ interface to the air. Immersing the PMMA/substrate couple into the water leads slow penetration of water between PMMA and substrate layers. When water completely penetrates under the PMMA layer, PMMA layer starts to float at the surface. Flakes adhering to the PMMA layer easily removed from the surface due to the van der Waals bonding between flakes and substrates. Schematic of the procedure is given in Figure. 3.22. The floating PMMA/MoS₂ layer is then transferred to a new substrate and then PMMA is dissolved via hot acetone at 60 °C.

Although the scope of this dissertation is not the optimization of the transfer procedure, it might be beneficial to mention about the critical steps during this procedure. First of all, PMMA must stick uniformly to the new substrate or to a new surface for a successful transfer. If bubble presents between PMMA and surface, and if there are flakes around this region, this would cause lost of the flakes into the acetone during the removal of PMMA. Therefore, transfer & bake step on new surface is critical and it must be optimized for better results.

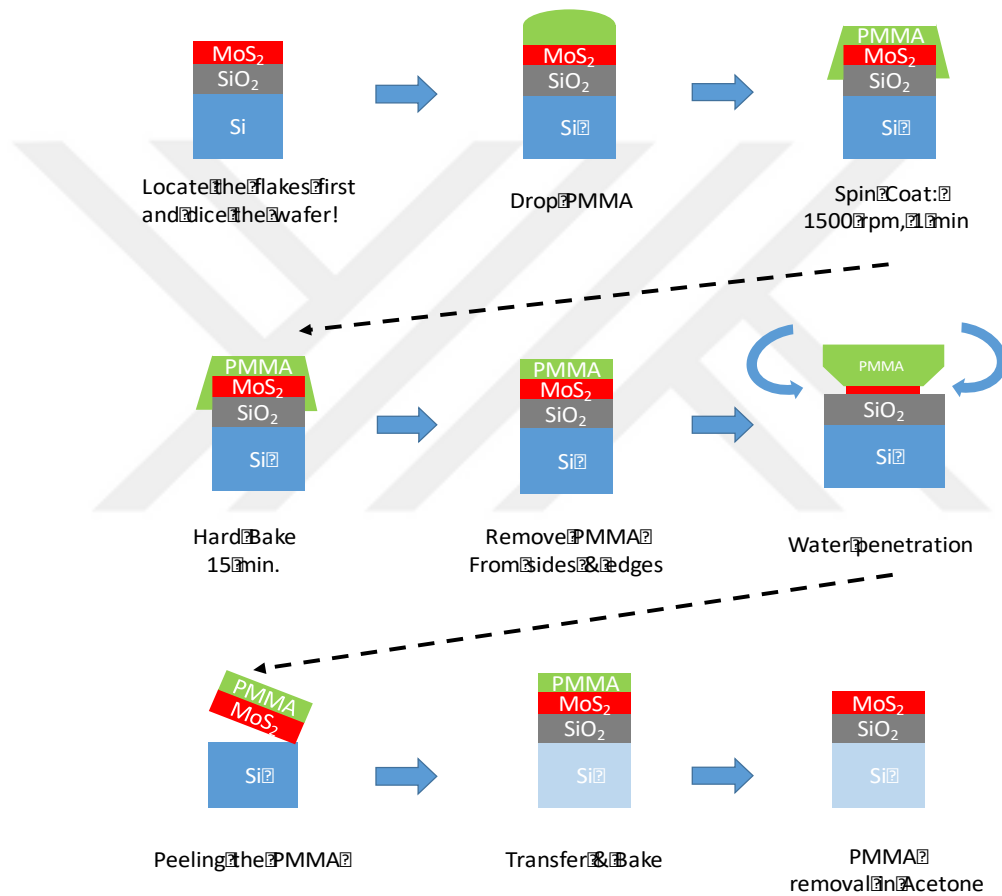


Figure 3.22. Schematic procedure of the transfer technique using PMMA and water as transfer medium

As mentioned previously, bubble formation during transfer might cause loss of some flake regions. These problems are also evident in the Figure 3.23. Not all the flakes are attached to the PMMA. Therefore, yield is low. However, as can be seen from the Figure 3.23. (DIC image of the transferred flakes) many intact flakes can be found and used to provide useful information to make an assessment on the stress levels of the flakes.

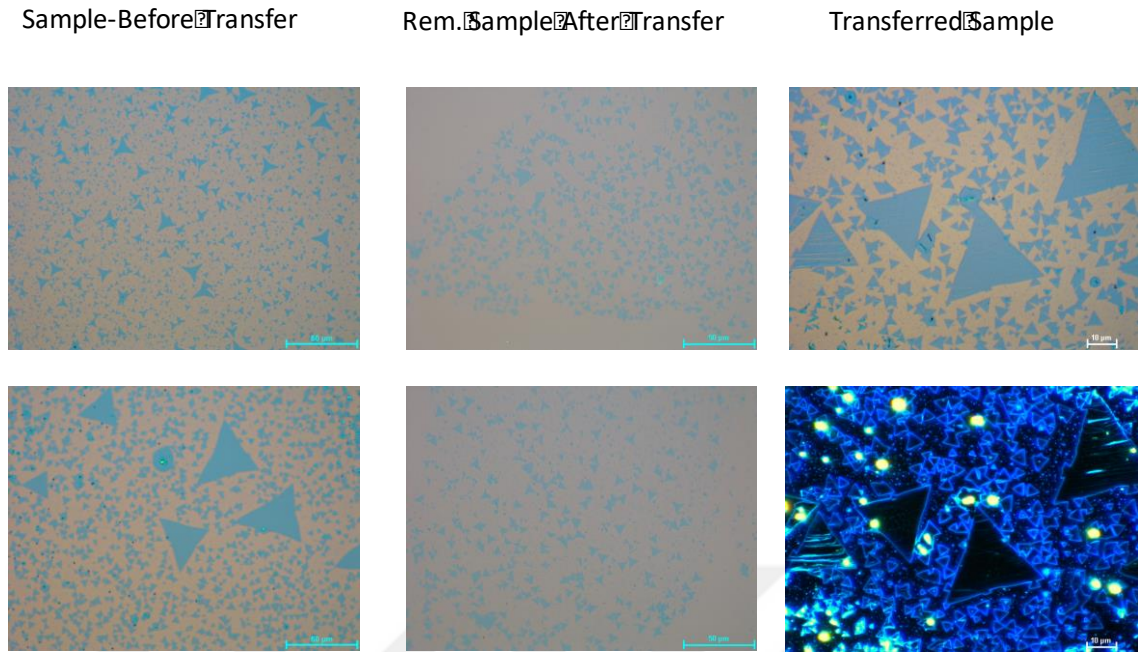


Figure 3.23. Left column: Sample before the transfer, middle column: remaining flakes on the old substrate after the transfer, right column: transferred sample on a new substrate. Dark field image (right column, image of second line) shows wrinkles and fully intact flakes

3.3.2. Raman and FLIM analysis of the flakes for stress evaluation

Raman, photoluminescence and lifetime measurements are performed to transferred flakes and results are compared with the as-grown MoS₂ structures. Confocal image of the transferred flakes (Figure 2.24.a) with clean transferred flake (marked with red rectangle), Raman measurement before and after (Figure 3.24.b) and PL measurement of the flake edge and interior (Figure 3.24.c) and Fluorescence lifetime mapping (Figure 3.24.d) are demonstrated. Following conclusions can be made:

- Raman measurement on the flakes demonstrate lower E and A Raman peak differences indicating stress relief after the transfer,
- PL measurements on transferred flakes show no edge and interior difference, indicating a homogeneous PL response, indicating existence of stress in as grown structures
- Lifetime map demonstrate sharp values (0.28 ns) through the flake surface, which was reported between 0.25 ns to 0.45 ns for as-grown flakes in previous chapter, supporting

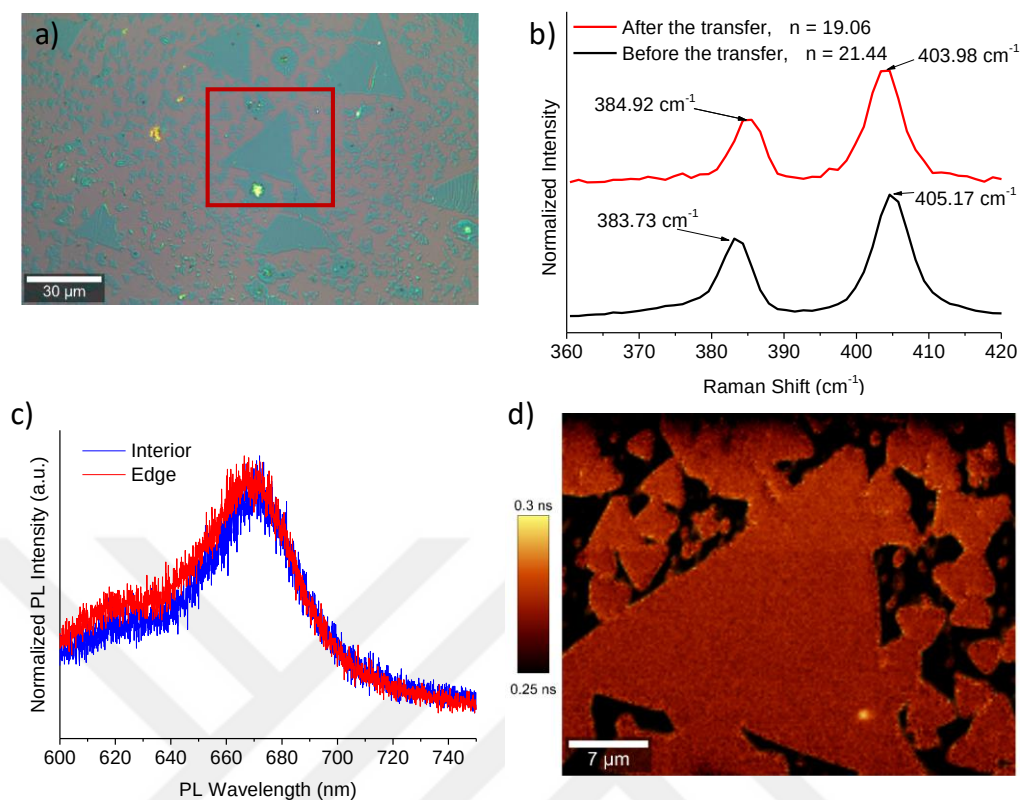


Figure 3.24. a) Confocal image of the transferred sample, b) Raman spectra of before transfer and after the transfer, c) PL measurement of the flake interior and edge of the transferred flake, d) homogeneous lifetime map of the transferred flake

Furthermore, Raman finger-prints of cracked, horizontal, facedown and transferred flakes are also demonstrated in Figure 3.25. Figure 3.25.a represents the confocal optical image of FD cracked sample, where centers of the flakes are fractured. Figure 3.25.b is the dark field optical image of the same flakes indicating new edges created after the fracture of the flake. Figure 3.25.c shows confocal image of a transferred FD flake on a new substrate. Figure 3.25.d demonstrates E_{2g}^1 and A_{1g} Raman signatures of the flakes.

Uniaxial strain studies on MoS_2 have clearly demonstrated that in-plane E_{2g}^1 vibrational mode blue shifts when tensile stress is applied [8]. In Fig.3.d, it is clear that Raman modes of the face-down sample blue-shifts with respect to H grown samples indicating a tensile stress inside the FD flakes. When these flakes are transferred on a new surface, this stress relaxes and Raman modes red shifts to their relaxed positions and overlaps with Raman modes of the horizontal case. Interestingly, when the Raman modes of the cracked face-down flakes are investigated, the same red shift is observed with the transferred flakes. This result indicates that the stress is relieved with the fracturing of the

flakes. Also, it is observed that the face-down approach provides a tensile stress inside the flakes comparatively higher than the horizontal growth. In other words, stress remained in samples grown by horizontal approach does not cause any cracking effect.

There is a striking thermal expansion difference between monolayer MoS₂ (10-5/°C) and the SiO₂ (5.6x10-8/°C) [7]. It is suggested that the high growth rate together with this high thermal expansion difference in FD growth cause rather a high stress in the films and/or flakes. This rather higher growth rate in FD configuration is asserted not only due to the larger flake size but also, due to the much higher amount of vapor phase radicals (Mo and S). In the case of horizontal growth, considerable number of radicals are lost by diffusion in the chamber.

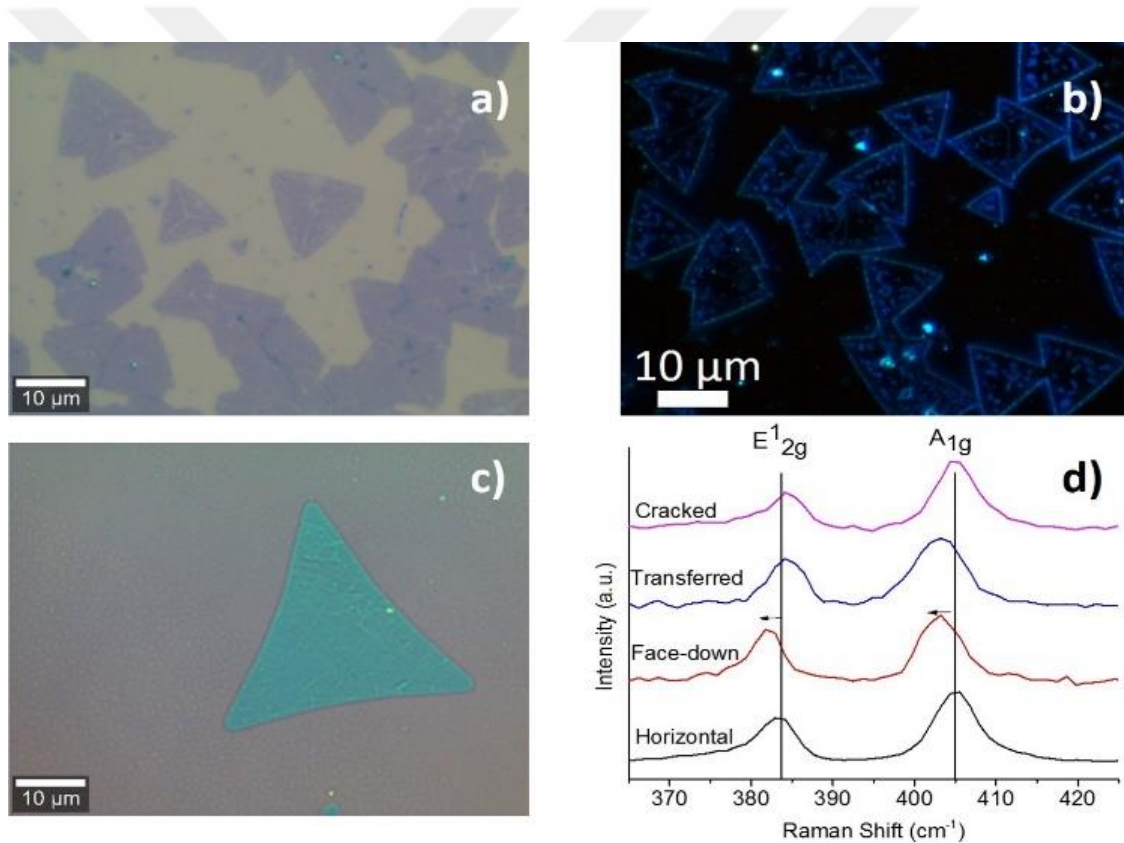


Figure 3.25. a) Cracked FD flakes, b) dark field image of cracked flakes, c) confocal optical image of transferred FD flakes, d) Raman signatures of the cracked FD, transferred, freshly grown FD and H flakes. Arrow indicates a blue shift of the Raman modes of face-down sample

3.3.3. Conclusion

In conclusion, two different growth approaches are compared by observing the change in their flake structures in time (for 18 months). It is demonstrated that face-down

growth approach yields larger flakes with a significant stress accumulation that leads to spontaneous cracking of the FD flakes. On the other hand, horizontal growth approach yields smaller but mechanically stable flakes that is at least stable for more than one and half year. It is observed that flakes grown by face-down approach can be transferred to fresh substrates after the growth to reveal the stress effect which cause long term cracking problem of the flakes.

3.4. H₂ Inclusion to Carrier Gas

In this section, experimental results of the H₂ inclusion to the carrier gas will be briefly demonstrated. Motivation of the H₂ inclusion is as follows. 2-D flakes, nanowalls and MoS₂ thin films are active materials for various applications ranging from sensors to catalysts. Therefore, controlled and selective growth of these structures are of utmost importance. When assisted with H₂, demonstrated CVD growth scheme in previous chapters (face-down) yields nanostructures such as 2D micro and nano-flakes, nanowalls and thin films at specific H₂ flow rates. In this part, critical H₂ inclusion range is determined as between 3.75 sccm to 5 sccm that provide the transition from thin film growth formation to 2-D growth in nanowall and lateral MoS₂ formations that comprise 1.87 eV direct band-gap. These formations are analyzed with Raman and photoluminescence spectroscopy, scanning electron microscopy and transmission electron microscopy techniques.

3.4.1. Experimental parameters

In this section, effect of including H₂ gas in addition to N₂ on the resulting MoS₂ formations are investigated. Hence, H₂ flow rate regimes, providing either nanowall and 2D flakes or thin film growth at identical process parameters (including temperature, pressure, precursor amounts, growth time and total flow rate) are demonstrated. In all the experiments, 15 mg MoO₃ and 1000 mg S are used. MoS₂ is deposited on Si/SiO₂ substrates at 700 °C with a 400 sccm total flow rate (H₂ + N₂) and 10 minutes growth time. H₂ inclusion into carrier gas is utilized as 1 sccm, 2.5 sccm, 3.75 sccm, 5 sccm, 10 sccm and 20 sccm.

3.4.2. Results

Figure 3.26.a schematically summarizes the effect of H_2 inclusion into the carrier gas. H_2 inclusion between 1 sccm to 3.75 sccm yield nanowalls (S1-zone 1 – Figure 3.26.d), nanowall to flake transition zone (S1-T, Figure 3.26.e) and 2-D Flakes (S1-zone 2, Figure 3.26.f) on the same substrate. However, flow rates above 5 sccm yield a film growth (S2 in Figure 3.26.a). Raman (Figure 3.26.b) and PL spectra (Figure 3.26.c) taken from zone-1 to zone-4 of thin films indicate a multilayer to monolayer transition, respectively. Multilayer zone of S2 still gives A and B exciton PL peaks that require further detailed analysis of that zone. This is performed by Transmission Electron Microscopy (JEOL JEM 2100F field emission TEM).

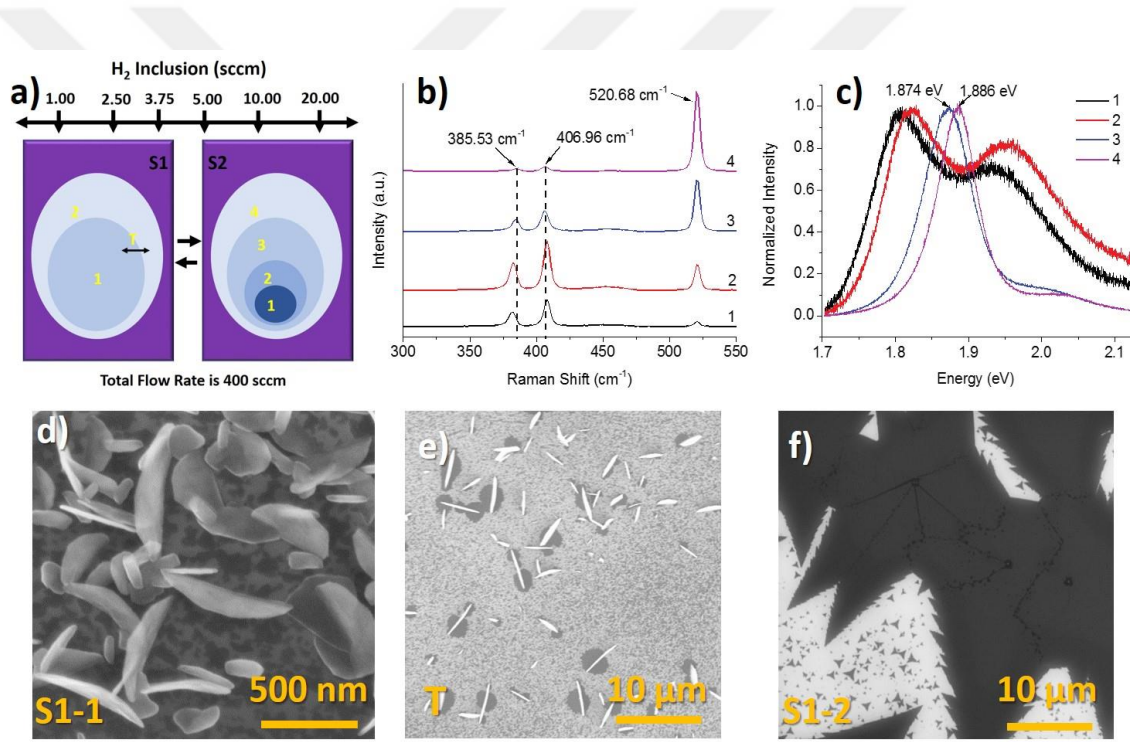


Figure 3.26. a) Schematic demonstration of the growth zones on the substrate for samples grown by H_2 inclusion between 1 sccm to 3.75 sccm (S1), and 5 sccm to 20 sccm (S2), b) Raman spectra of sample S2, c) Normalized PL spectra of sample S2, d) SEM image of zone 1 of sample S1, e) SEM image of sample S1 from point T, and f) SEM image of sample S1 from zone 2

STEM analysis of the multilayer zone (Figure 3.26.a) depicts grains where some of them have hexagonal and triangular morphology. In order to characterize the crystallinity of those grains, selected area electron diffraction (SAED) method is utilized. According to the SAED patterns, these complex structures are found to be polycrystalline as shown in Figure 3.26.b and all the rings belong to MoS_2 planes. Dark field (DF) TEM

technique is also used to visualize different grains at specific orientations. In Figure 3.26.d, DF-TEM image is taken by placing the objective aperture to the (010) ring. According to the DF-TEM images, polycrystalline nature of the film is supported with a grain size range between 25 nm to 150 nm.

3.4.3. Conclusion for H₂ inclusion

In conclusion, H₂ inclusion effectively changes the resulting MoS₂ formations, where low flow rates below 5 sccm promote flakes and nanowalls and flow rates above 5 sccm yields polycrystalline multilayer MoS₂ films surprisingly still giving rise to 1.86 eV PL response with a very low intensity due to thick nature.

3.5. CVD Growth of MoS₂ Using Glass Substrate

Recently, large scale MoS₂ and MoSe₂ has been made possible by the usage of glass substrates [147, 148]. Yang *et al.*, achieved 6 cm² monolayer coverage with 400 μm domains or grain size by using a CVD setup similar to CVD system described in this thesis. Method uses Na lime glass and Mo foil. In this method Mo foil is first oxidized by using O₂ supply (6 sccm) in CVD system. Glass and Mo foil (or MoO₃/Mo after oxidation) positioned face to face (Mo foil on top). There exists space between Mo foil and glass for the diffusion of sulfur and formation of MoS₂ film or flakes. Film characteristics such as domain sizes are controlled by this Mo to glass distance. Controlled oxidation of the Mo foil during the growth and subsequent sulfurization allow the growth of uniform large-scale films on the glass substrates. On the other hand, usage of MoO₃ powder as precursor yield very large flakes (400 μm). In the case of work of Yang *et al.*, MoO₃ precursor present next to the glass substrates like horizontal growth as demonstrated in section 3.1.1. Quality of the flakes depends on the distance between glass and powder precursor. In the case of Chen *et al.* (MoSe₂ growth on molten glass substrates) they place MoO₃ precursor underneath the glass substrate without any distance and flakes grow on top of the glass substrates and yields extremely large flakes having edge sizes around 2000 μm [148]. According to DFT and experimental studies performed by Yang *et al.* Na is the main reason of the fast and uniform growth rate. Therefore, when Na containing glasses are melt, homogeneous distribution of the Na inside the molten glass acts as a catalyst to promote homogeneous MoS₂ growth. In addition to that, molten glass surface also provides a defect free flat surface that Si/SiO₂ surface have not.

Absence of such defects improve the lateral distribution homogeneity of the flakes on the surface. Therefore, to get rid of lateral heterogeneity that is observed for Si/SiO₂ substrates, we adopted glass substrates and same recipe for the horizontal approach with minor configuration differences as shown in experimental section below.

3.5.1. Materials and methods

Growth zone configuration used for the MoS₂ growth on the glass substrate is depicted in Figure 3.27. Instead of using quartz boats, quartz plates are used as substrate holders. In this configuration, 1 mg MoO₃ precursor is placed on top of a small (0.5 cm x 0.5 cm) Si/SiO₂ substrate and this precursor couple is placed on top of another large (2 cm x 2 cm) Si/SiO₂ substrate. That substrate is labeled as “Growth Wafer 1” as shown in Figure 2.27. The distance between 1 mg MoO₃ and 150 mg of Sulphur is 16 cm. All experiments are conducted at 750 °C and at 1 atm.

Glass sticks to the quartz plate after the growth and makes quartz plate useless and contaminates with time. To protect the quartz plate sacrificial glass holders are used. Therefore, glass wafer (depicted as growth wafer 2 in Figure 3.27) is placed on top of 3 different glass holders. First one is Si/SiO₂ where glass interacts with the SiO₂ face. Glass cracks as expected during the solidification process when Si/SiO₂ substrates are used. To overcome that problem Mo foils and graphite are also examined. It has been decided that graphite is the best glass substrate holder in terms of cracking and multiple usage. Although glass doesn't stick to the Mo foil and doesn't crack, Mo foils are much expensive than graphite and more importantly Mo foil is prone to oxidation. Therefore, it's hard to control the precursor concentration especially when it's used multiple times.

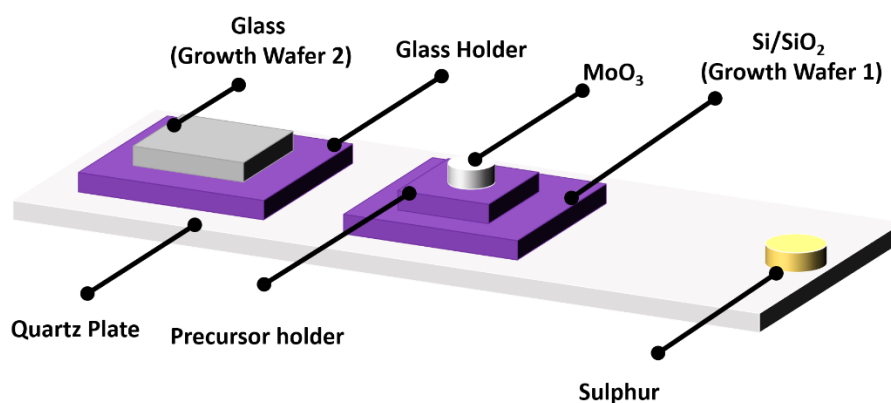


Figure 3.27. Schematic depiction of glass growth configuration

Underneath the MoO₃ substrate holder, an additional wafer is used for two reasons. First reason is to prevent minimization of contamination of the quartz plate by the precursor. Second reason is to track the growth of MoS₂ flake formations. Since growth is observed on the wafer this wafer is labeled as growth wafer 1 in Figure 3.27.

Two different glass is used to grow MoS₂ flakes. First glass has a thickness of 125 μm and dimensions as 2 cm x 2 cm. The second glass is a regular optical microscope lamella having dimensions around 3 cm x 7.5 cm with a thickness of larger than 500 μm . The second glass is used to demonstrate the large-scale growth ability of the glass substrates which is the main aim of the thesis. Representative EDX measurements from relatively large areas are shown in Figure 3.28. Figure 3.28.a and b indicate Glass – 1 EDX measurement area and representative spectrum, respectively. Likewise Figure 3.28.c and Figure 3.28.d indicate Glass – 2 EDX measurements. Average EDX compositions of the used glasses from three different locations are performed and are given in the Table 3.2 with corresponding standard deviation.

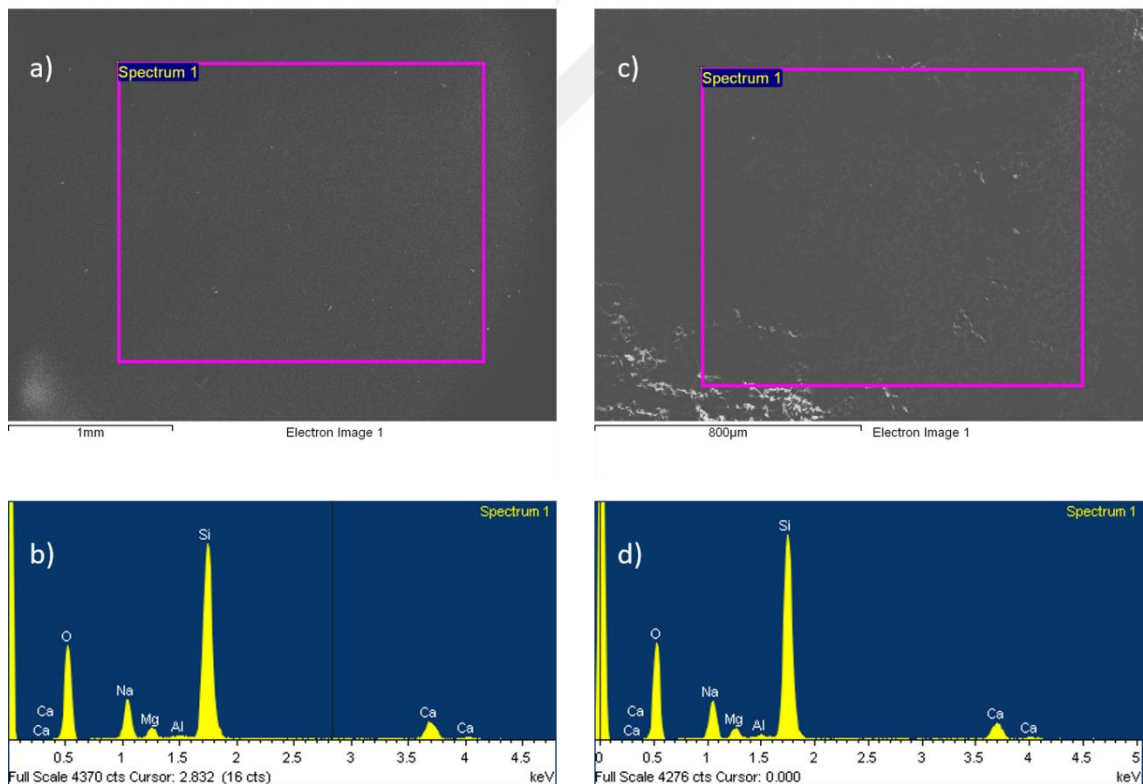


Figure 3.28. Representative EDX analysis of the glasses. a) and b) belong to Glass-1 measurement area and spectrum, respectively, c) and d) indicate EDX area and representative spectrum, respectively

Table 3.2. EDX analysis of the utilized glass substrates

Element	Weight % (G1)	Atomic % (G1)	Weight % (G2)	Atomic % (G2)
O K	51,30 ± 0,39	64,44 ± 0,31	53,00 ± 0,39	65,74 ± 1,25
Na K	9,5 ± 0,04	8,31 ± 0,03	9,63 ± 0,45	8,33 ± 0,33
Mg K	2,08 ± 0,08	1,72 ± 0,06	2,19 ± 0,12	1,80 ± 0,11
Al K	0,37 ± 0,05	0,28 ± 0,04	0,59 ± 0,19	0,44 ± 0,14
Si K	31,84 ± 0,21	22,79 ± 0,21	30,60 ± 1,61	21,66 ± 1,33
Ca K	4,91 ± 0,26	2,46 ± 0,14	3,94 ± 0,48	1,96 ± 0,25

According to Table 3.2 Total Na or even total alkali metal content (Na, Ca and Mg) are almost same for both glasses. Therefore, similar degree of catalysis effect can be expected from these two different glass substrates.

All growths are performed at 750 °C and at slightly overpressure conditions 750 Torr by using 1 mg of MoO₃ and 200 mg of S, which is similar to horizontal growth conditions (Section 3.2)

3.5.2. Growth patterns of the glass substrates

Unlike Si/SiO₂ substrates, glass substrates provide a homogeneous flake coverage all around the substrate that means no edge growth is observed. This difference is schematically depicted in Figure 3.29. Glass growth experiments may help us to provide more insight into why Si/SiO₂ allows edge growth.

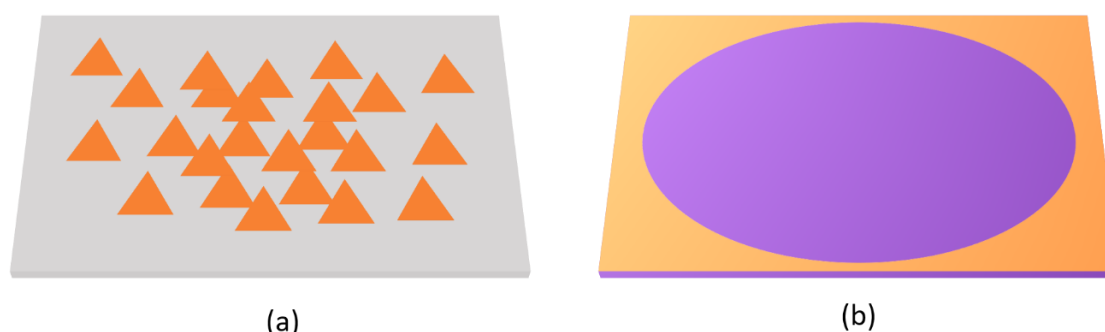


Figure 3.29. Depiction of growth schemes for a) glass substrates, b) Si/SiO₂ substrates for horizontal growth approach. Orange color indicate flakes and flake growth regions

First, as Yang et al. explains and as salt assisted growth experiments provide, alkali metals behave like a catalyst [147-149]. Moreover, Zhan et al. reports that the addition of

NaCl to the growth chamber (or mixing NaCl with MoO₃ or spreading NaCl on the substrate) lowers the growth temperatures. NaCl reacts first to form Na-containing intermediate compounds that reduce the energy of the reaction. Therefore, when compared with the Si/SiO₂ surfaces, it can be deduced that SiO₂ surface itself doesn't favor lateral MoS₂ growth. The reaction energy barrier between MoO₃ and S is high when bare SiO₂ surface is used for deposition of the MoS₂ growth compared to glass substrates. Since we observe flake growth at the edges and very small flake growth at the center (see for example SEM image of the center of the horizontal growth result in Figure 3.6) energy barrier should be lower with respect to center of the substrates. This can be attributed to the imperfect cleavage of the Si/SiO₂ substrates which cause either macroscopic or microscopic defects like cracks that alters both flow around these points or provide more dangling bonds that energetically favor the growth at the edges.

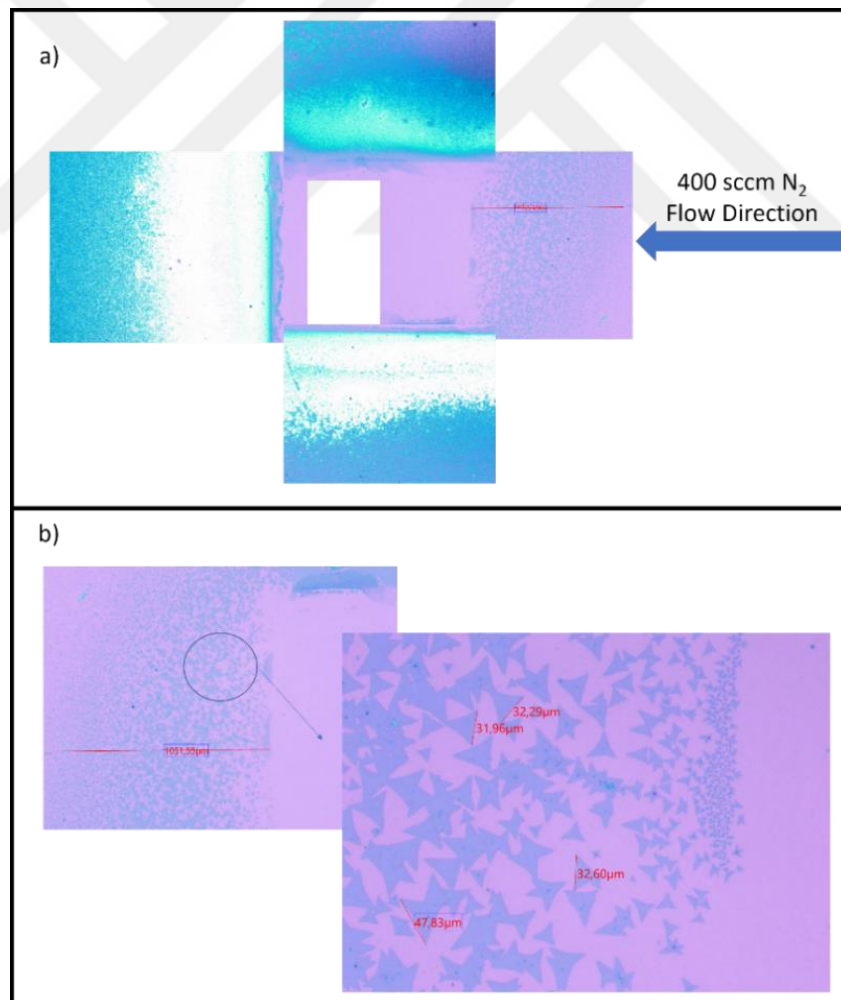


Figure 3.30. Growth wafer 1 (Si/SiO₂) a) MoS₂ formation around the sacrificial wafer holder, b) MoS₂ flake formations at the downstream direction of the flow

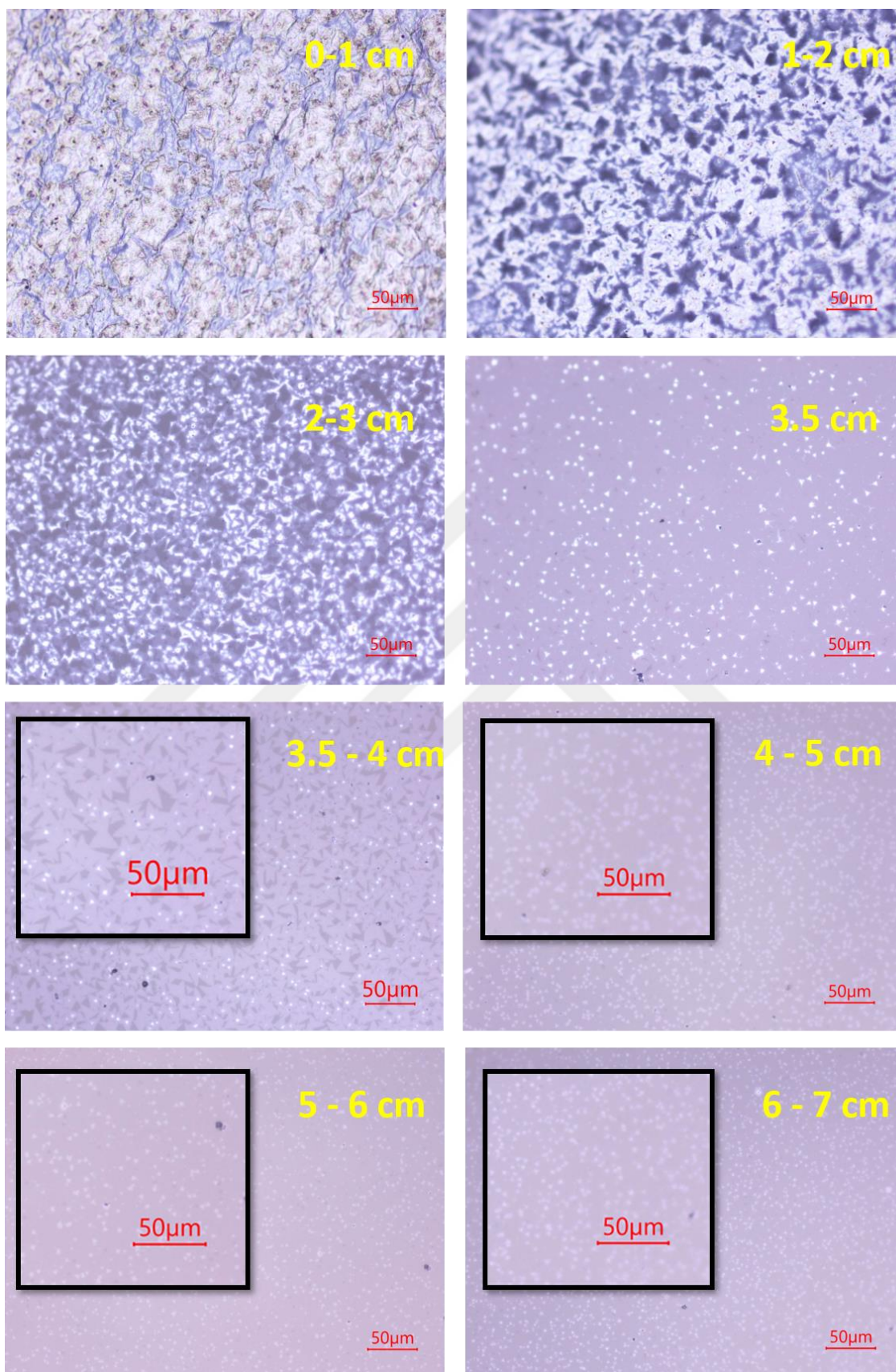


Figure 3.31. Growth morphology on the glass substrates along the glass substrate (2)

On the other hand, Figure 3.30 demonstrates the growth morphology on the growth wafer 1 (Si/SiO₂). Figure 3.30.a consists of 4 optical images demonstrating the growth pattern when the MoO₃ wafer holder is removed from the growth wafer (white region at the center). As can be seen from the Figure 3.30.a within the vicinity of the MoO₃ powder or within the vicinity of the precursor wafer, thick MoS₂ growth formations exist along and perpendicular to the flow direction. However, it is interesting to note that at the downstream direction, flake formations (Figure 3.30.b) present and unlike horizontal growth, these flakes grow not at the edge of the substrate but at a relatively central point of the substrate. Higher precursors concentration can be expected for the forward and perpendicular directions of the flow and that explains the growth of thicker MoS₂ formations. MoS₂ flakes at the downstream condition provides another aspect of the growth, which is the necessity of the suitable S and Mo-precursor concentrations regardless of the substrate conditions. Therefore, this experiment partially supports that growth observed at the edges in the section 3.2 comes from the local accumulation of the precursor concentration at the edges either because of the boat geometry or defects at the edges.

Figure 3.31 demonstrates the growth formations on the 3 cm x 7.5 cm glass. Distance dependent growth pattern is also in line with the observations with the horizontal growth scheme. A thick film formation (0-3 cm) is slowly turns into monolayer film region (3.5 cm), areal density of the film decreases (3.5 cm – 4 cm) and separate flakes emerges (> 4 cm). Size of the flakes gradually decrease along the flow direction.

3.5.3. Raman and photoluminescence analysis of flakes

In this section, a Raman and PL analysis of the flakes grown on the glass substrates and then transferred to the Si/SiO₂ substrates will be investigated.

Table 3.3. Raman analysis of the three selected points from flakes grown on glass

Point	E _{2g} ¹ (cm ⁻¹)	A _{1g} (cm ⁻¹)	FWHM E _{2g} ¹	FWHM A _{1g}	Δn
Point 1	385,64	405,12	5,69	5,97	19,48
Point 2	385,60	405,27	4,61	5,46	19,67
Point 3	386,09	405,19	5,54	5,51	19,10

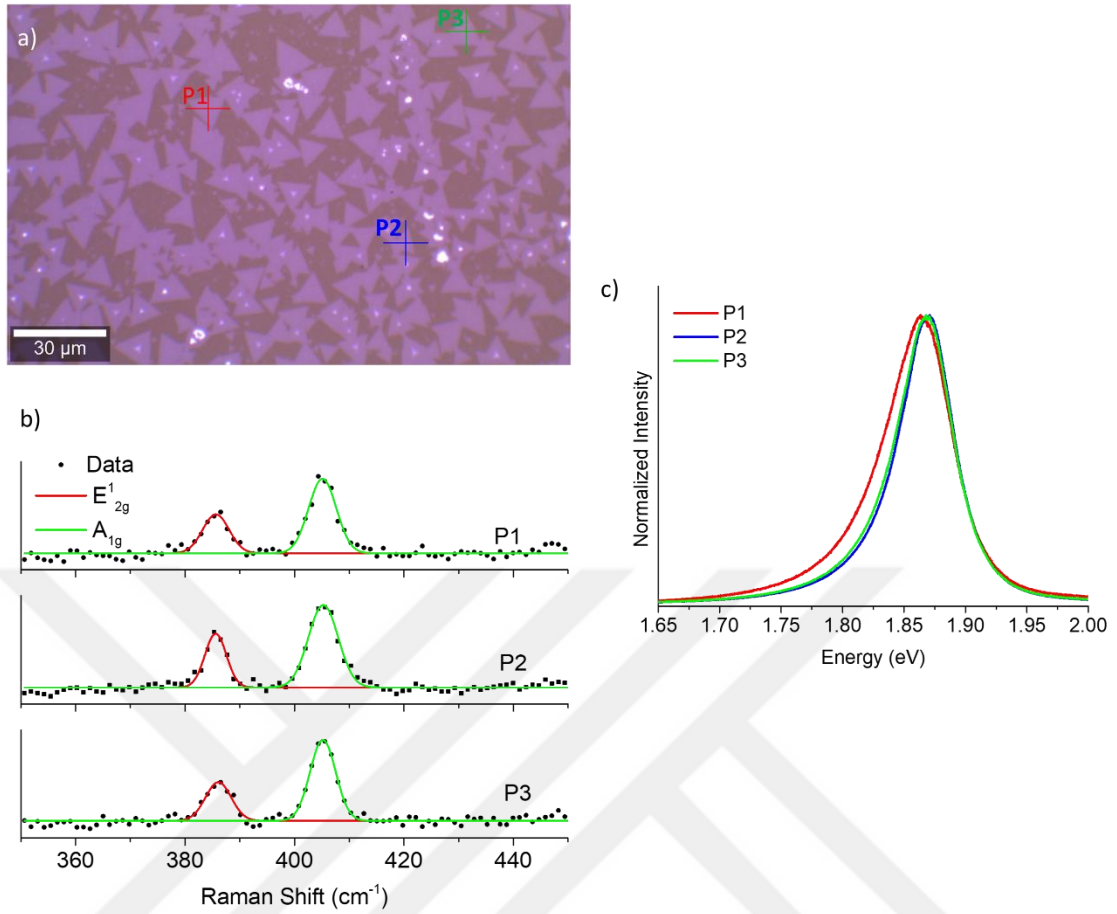


Figure 3.32. a) Confocal optical image of flakes grown on the glass substrates and selected points (P1, P2 and P3), b) Ramana spectrum of selected points, and c) PL spectrum of selected points

Figure 3.32.a provides typical growth pattern on the glass substrates taken from the separate flake region of the substrate though some flakes tend to merge. Figure 3.32.b demonstrates the Raman spectrums of the selected points (from flakes) together with Gaussian fit function curves. Table 3.3 provides the result of the Gaussian function fittings. All points give rise to Δn values smaller than 20 cm^{-1} indicating monolayer nature of the flakes. We know from section 3.2 that Δn values of flakes grown on the Si/SiO₂ are within the range of $21\text{-}22 \text{ cm}^{-1}$ (3.13.b). It is a good opportunity to remind that when freshly grown flakes are transferred to new substrates Δn values decrease below to 20 cm^{-1} indicating a stress effect (3.24.b). FWHM of the flakes grown on the glass and measured on the glass has a similar range with the Si/SiO₂ flakes which indicate a similar crystallinity of the flakes. On the other hand, PL measurements from these points (Figure 3.32.c) indicate a much narrow PL variation with respect to Si/SiO₂ flakes (Figure 3.4 or 3.14.c) which typically varies between 1.83 to 1.86. However, in the glass growth this variation is between 1.85 eV to 1.86 eV with a narrow PL FWHM.

Flakes grown on the glass substrates were transferred onto the Si/SiO₂ substrates without assistance of any PMMA layer. Glass/MoS₂ substrate is put in a water filled petri dish. MoS₂ flakes layers instantly detaches from the glass surface and floats at the top of the water layer. By using a fresh Si/SiO₂ substrate, layers can easily be scooped on the new surface.

Figure 3.33.a and b demonstrates the transferred region by using 10x and 100x objectives, respectively. Figure 3.33.c indicates averaged PL response of the three different flakes. Integrated intensity images of the same flakes are also shown as insets.

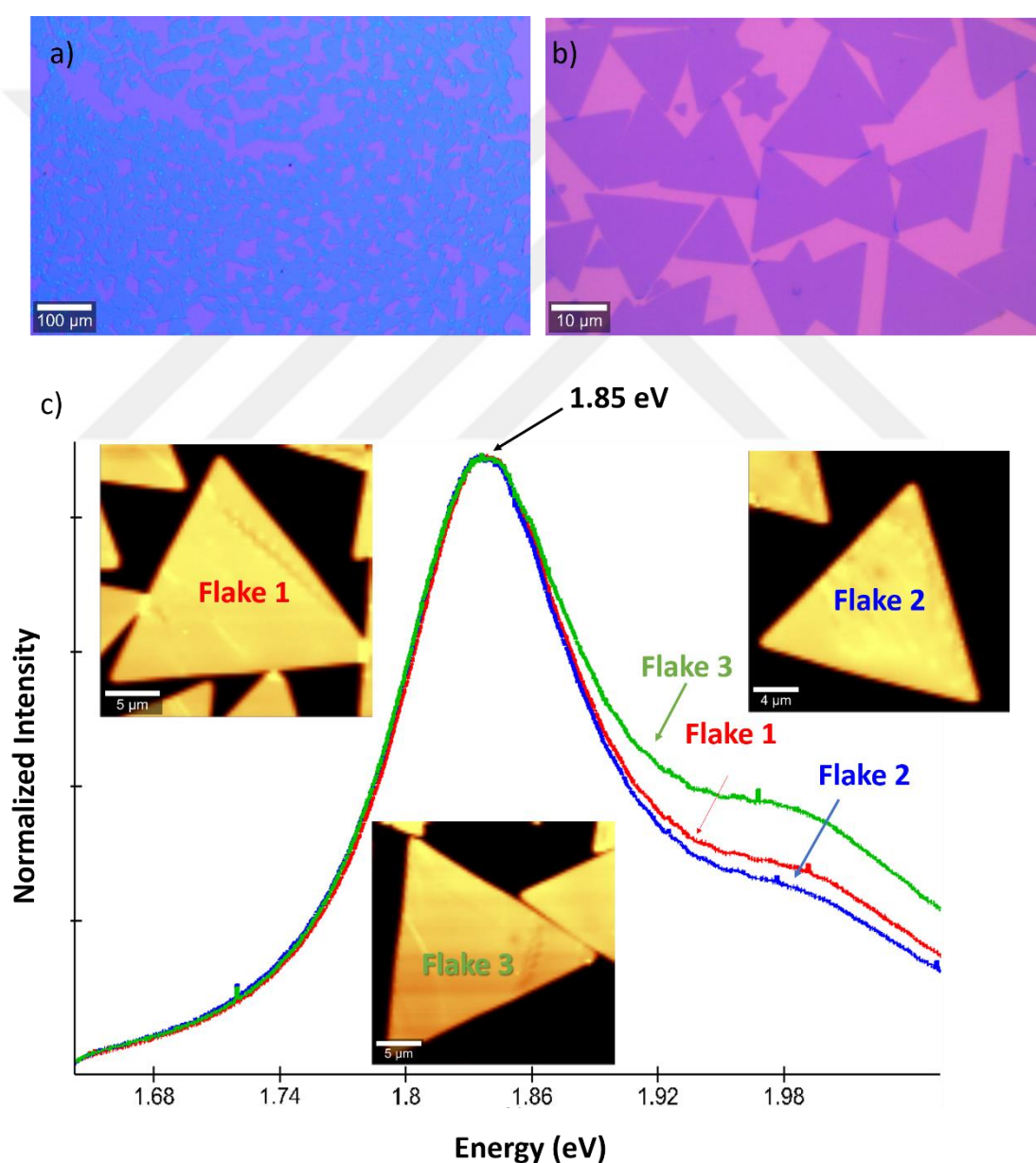


Figure 3.33. a) and b) Optical image of the transferred flakes, c) PL curves with integrated total intensity images

As also shown in Si/SiO₂ growths, initial small PL variation in glass grown flakes are also removed and uniform flake intensity all over the flakes are observed.

3.6. Conclusion

The aim of the experimental effort for the MoS₂ growth was to grow homogenous layers over the substrate for specially to assist device research. This is achieved by utilizing glass substrates. The heterogenous monolayer growth scheme in terms of growth zone, flake intensity and peak centers are controlled by using glass substrates. Therefore, the possibility of obtaining higher number of working devices is increased. This can be revealed in Figure 3.34, where devices (gold paths) fabricated on face-down grown flakes and flakes grown by glass substrates are compared.

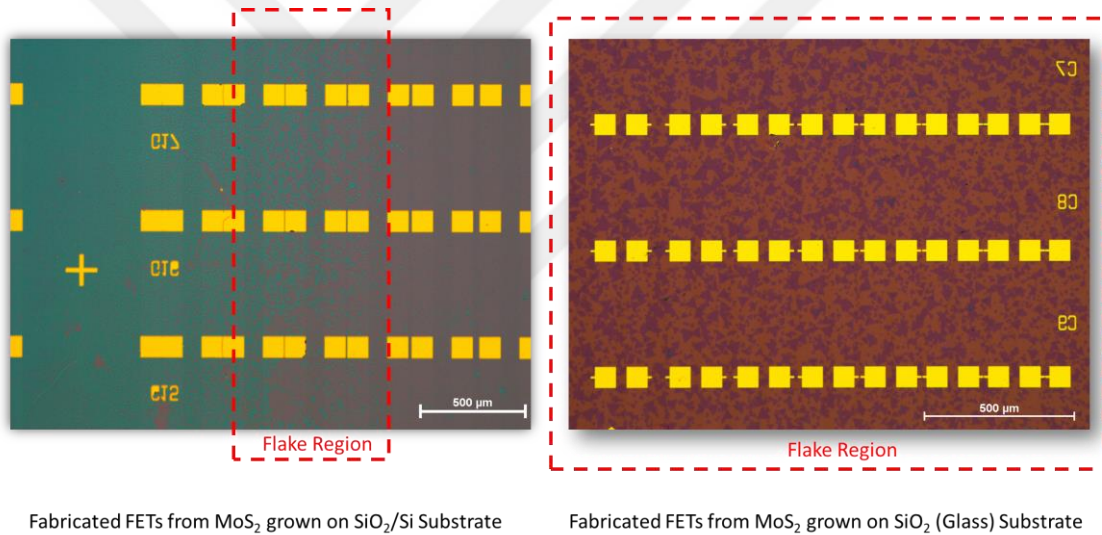


Figure 3.34. FETs fabricated from MoS₂ grown on Si/SiO₂ and by using glass substrates by Şar et al. [85]

On the other hand, flakes obtained by using horizontal and face-down growth methods are utilized in several fundamental research areas. For example, inherent cracking behavior of the flakes are investigated and published by Özden and Şar et al. [150]. Moreover, modifications of the demonstrated growth methods especially face-down approach allowed the investigation of the growth of WS₂ flakes by Yorulmaz et al. [151]. Moreover, growth of WS₂ flakes lead to FET and photodetector performance comparison study of MoS₂ and WS₂, which is performed by Şar et al. [85]. Moreover, flakes grown by face-down approach are provided and utilized by Taghipour et al. to investigate FRET mechanism between monolayer MoS₂ and colloidal quantum dots. Near

unity energy transfer efficiency together with extraordinarily long Förster radius (33 nm) are reported by Taghipour et al. [152]. Finally, small addition of Se and utilization of the growth scheme obtained from the glass growth experiments allowed to control of flake composition (S-Se ratio) which is reported by Bay et al. [153].



4. THEORETICAL INVESTIGATION 2D MATERIALS: ELECTRENES

In this chapter, results of DFT calculations (electronic band structure calculations, phonon calculations) on a new class of 2D material called “electrenes” will be given. In this effort, vibrationally stable electrene systems are first determined by using their phonon dispersion curves. Since this material have huge potential due to their low absorption energy for the alkali metals, their anode potential has also investigated.

4.1. Electrene Systems and Their Battery Performance

Research on layered solids play a fundamental role for the realization of new 2D materials that is expected to have novel physical phenomena and superior performance. This scientific effort leads to several 2D systems having different compositions and properties such as Transition Metal Dichalcogenides (TMDs), MXenes, perovskites and many others after the rise of the graphene. A new 2D material, flakes of Ca_2N , has been isolated from bulk and layered Ca_2N powder by using a liquid exfoliation technique [11]. Ca_2N crystal belongs to a large and unique material family called “electrides”. Electrides have nearly free electrons reside (or localize) at the cavities of an organic molecule or an inorganic crystal. After the isolation of the 2D flakes, the material is labeled as “electrene” and electrenes add several new research aspects, opportunities and application potentials to the already very large 2D materials family [154].

Nature of the bulk electride systems can be considered to reveal importance of the electrenes systems. Electride systems intrinsically acquire an electron charge density inside crystal voids that normally expected to be occupied by anions [155, 156]. To observe these *anionic electrons*, a heterointerface of ultrathin films is not necessary, such as a 2D electron gas in GaAs/AlGaAs [157] and $\text{LaAlO}_3/\text{SrTiO}_3$ [158]. Furthermore, the crystal structure determines the dimensionality of the charge density of the electrides and therefore their prefixes might change from 0D to 2D. For example, 0D charge densities are observed in cage like structures like alkali bound organic complexants [159] that form 0D electrides. It is possible to find the inorganic counterparts of the 0D electrides. For instance, Cs-doped silica zeolites [160] and Hosono’s $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}:4\text{e}^-$ [161] has been realized as 0D inorganic electrides. Moreover, 1D electrides, such as 1D $[\text{La}_8\text{Sr}_2(\text{SiO}_4)_6]^{4+}:4\text{e}^-$ [162] and recently synthesized Sr_5P_3 [163] have been theoretically and experimentally verified as 1D electride. These 0D and 1D electrides form the first examples of the electride systems. Since 0D organic electrides are not stable at ambient

conditions, researchers search new and stable inorganic electrides. Therefore, two new compounds inorganic electrides, one alkaline earth compound, $[\text{Ca}_2\text{N}]^{+}\text{e}^{-}$, and one rare-earth carbide, $[\text{Y}_2\text{C}]^{+1.8}\cdot 1.8\text{e}^{-}$ have been added to the inorganic electride family. Experimental and theoretical efforts verified that these electride compounds have layered crystal structure both adopts anti- CdCl_2 crystal structure [164-167]. In these systems, electron density is formed like a sheet between the positively charged basal planes of the crystal, giving rise to 2D electrides.

Electrenes can be used in many applications. The reasons for that are the significant research interest on the 2D materials as explained in the introduction part of the thesis, presence of excess electrons in a 2D system, and their reported ultra-small work functions (2.6 – 3.5 eV for Ca_2N) [154]. Therefore, these materials are investigated in a wide application range and are predicted to be useful as a transparent conductor [168], electron field emitter [169], catalyst [170], superconductor [171, 172] and anode material for battery applications [173-175]. Specifically for the non-Lithium based rechargeable batteries (sodium ion rechargeable batteries, SIB), previous investigations show that electrenes are promising anode materials. Ab initio calculations performed by Hu et al. predicted a very high theoretical capacity (1138 mAh/g for Ca_2N and 233 mAh/g for Sr_2N) and low migration energy barrier for Na ions (0.084 eV for Ca_2N and 0.025 eV Sr_2N) which are important properties for the progress of Na-ion rechargeable batteries [173]. Moreover, Y_2C is also predicted as a promising SIB anode material with a 564 mAh/g capacity and 0.01 eV Na migration energy [175]. Indeed, this potential of electrenes is verified by experimentally very recently. Guanghai et al. [174] demonstrated that the electrodes made of Ca_2N exhibit an initial discharge capacity of 1110.5 mAh/g and a reversible discharge capacity of 320 mAh/g.

Screening of the dynamically stable electrenes are very important when their promising application areas are considered. Bulk 2D electrides are explored by Inoshita [176], Zhang [177], Tada [178] and Ming [179] et al. by employing available materials database screening, global structure search with electron localization function, high-throughput ab-initio screening and global structure optimization method, respectively. In these theoretical works layered compounds are screened and the presence of 2D charge density are inspected between the basal planes of these multilayer (or bulk) crystals. Among them, a very few crystals are determined as electrides. However, phonon dispersion and dynamical stability of these bulk systems are not treated rigorously.

Regarding the M_2X type hexagonal (R-3m) 2D bulk electrides, where M is an alkali-metal and X is a non-metal, following bulk structures are reported as dynamically stable: Ca_2N , Sr_2N , Ba_2N , Sr_2P , Ba_2P , and Ba_2As [179]. However, Sr_2P has been demonstrated as thermodynamically metastable validated by the reaction enthalpy calculations and solid state reaction experiments by Wang et al [163]. Dynamical stability of the monolayer and bilayer counterparts (electrene systems) of these compounds are not discussed yet. Furthermore, reported high capacities makes the rest of the stable electrene systems ideal candidates for energy storage materials. Regarding concerns over the cost and sustainability of lithium sources [180, 181], electrines may provide high performance sodium, potassium and calcium batteries.

4.2. Frame of the Theoretical Work

Inspired by the recent trends in 2D materials and their indispensable role in the energy storage technologies [180], this study is planned as follows: Initially, dynamical stability of the M_2X type electrines are inspected where M is selected from I A and II A groups and the non-metal X is chosen from the C, N, P, As, and Sb. Partial electron density (PED) isosurfaces are then investigated by using bilayer structures to ensure that the considered systems confine excess electrons between their basal planes. After performing these analyses, the FAT band electronic structures of the predetermined vibrationally intact electrines (no negative phonon frequencies) are studied. After that, adsorption energies and the diffusion energy barriers for the most favorable migration paths of Na, Ca, Li and K on the dynamically stable electrines are evaluated to predict the promising electrines for battery applications.

In this work, M_2X type (R-3m) electrene structures are explored. Monolayer and bilayer electrene structures are modelled by using bulk anti- $CdCl_2$ crystal system as demonstrated in Figure 4.1.a This crystal system belongs to R-3m, 166 space group. It consists of 3-layer sheets that have A-B-C stacking as illustrated in the Figure 4.1.a. The anionic electrons reside at the space between those sheets. Each layer has hexagonal unit cell, where non-metal layer (X) is sandwiched between two metal layers (M). Figure 4.1.b and Figure 4.1.c demonstrate the monolayer and A-B stacked bilayer electrene, respectively. It should be noted that the symmetry groups of the monolayer and the bilayer structures are reduced to 164 P-3m as observed in other similar material systems due to the lack of inversion symmetry. During our calculations, a minimum vacuum spacing of

at least 10 Å is preserved by using 15 Å and 24 Å lattice vectors in z-direction for single and bilayer electrenes, respectively, to prevent any interaction between the periodic images. The M layers are constructed from I-A and II-A groups and non-metals are chosen from IV-A and V-A groups as shown in Figure 4.1.d. Therefore, we investigate dynamical, electronic and adsorption properties of 50 potential electrone materials.

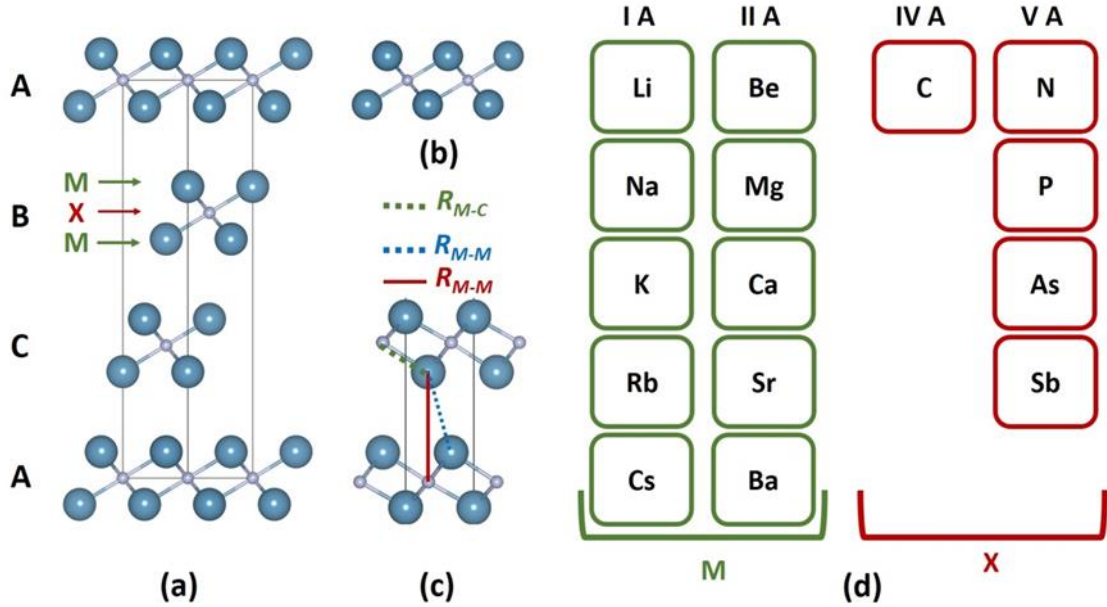


Figure 4.1. a) Bulk anti-CdCl₂ structure, where M represents the metal layers, X represents the non-metal layers. A, B and C indicate the stacking order of the sheets. b) and c) demonstrate the monolayer and A-B stacked bilayer structures, respectively. Green dashed line indicate distance between inplane M and X atoms. Blue dashed line indicates interlayer distance between M atoms. Red line indicate distance between interlayer M and X atoms. d) Demonstration of the elements to construct M₂X electrone systems

4.3. Computational Details

Computational method used in this work is based on Density functional theory as implemented in the VASP code [182] with generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) [183] formulation. The interaction between valence electrons and ionic cores is described by the projector augmented wave (PAW) method [184, 185] 450 eV plane wave energy cutoff and $16 \times 16 \times 1$ k-points sampling grid within the Gamma-centered scheme is used for relaxation and electronic calculations. The convergence criterion for electronic and ionic relaxations are set as 10^{-6} eV and 10^{-2} eV/Å. To obtain dynamical matrix which is required for calculation of phonon dispersion curves, Phonopy code [186] is used with $6 \times 6 \times 1$ supercell and with a $4 \times 4 \times 1$ k-points sampling. Moreover, $2 \times 2 \times 1$ supercells of dynamically stable systems are utilized to

determine the favorable sites and adsorption energies of Na, Li, Ca and K on the selected sites of the monolayer electrenes. Furthermore, favorable migration paths and migration energy barriers are calculated by using nudged elastic band (NEB) method [187] for $4 \times 4 \times 1$ supercells.

$|E-E_F| < 0.05$ eV energy range is utilized to calculate the partial electron density (PED) isosurfaces [188]. In Addition, for selected structures band decomposed electron density surfaces are calculated with a value between $0.002/\text{Bohr}^3$ and $0.003/\text{Bohr}^3$. The latter analysis is important in many ways. For example, monolayer case of some systems is dynamically stable, but bilayer counterparts of these systems strongly interact with each other where the interlayer spacing distance between the layers approaches to M-X bond length instead of a van der Waals gap. Furthermore, such strongly interacting layers are not expected to be exfoliated easily. Therefore, these systems are not labeled as electrenes in the present work.

4.4. Determination Stable Electrene Systems

In the beginning of this study, the dynamical properties of these structures through accurate density functional perturbation theory [189] calculations with the aim to evaluate their dynamical stabilities are systematically explored. Phonon dispersion spectra of all structures can be found in Figure 4.2. The investigated systems are determined as dynamically stable or unstable regarding the possession of imaginary vibrational frequency, and shown in Figure 4.3.a, accordingly.

Subsequent to the stability analysis, electrene character of the considered 2D compounds are studied through accurate electronic structure calculations. Figure 4.3.b exemplifies partial electron density (PED) iso-surface of one of the stable systems, Ca_2N , where electron density is clearly visible on the surface and between the layers of this crystal. The structures leading a similar charge density distribution are shown with green boxes in Figure 4.3.a, along with the ones, not supporting a 2D charge density between the layers, as represented with blue boxes. PED iso-surface plot of such a free electron lacking structure, (K_2N) is depicted as an illustration in Figure 4.3.c. Therefore, PED distribution of all the investigated systems are methodically inspected to recognize true electrene systems.

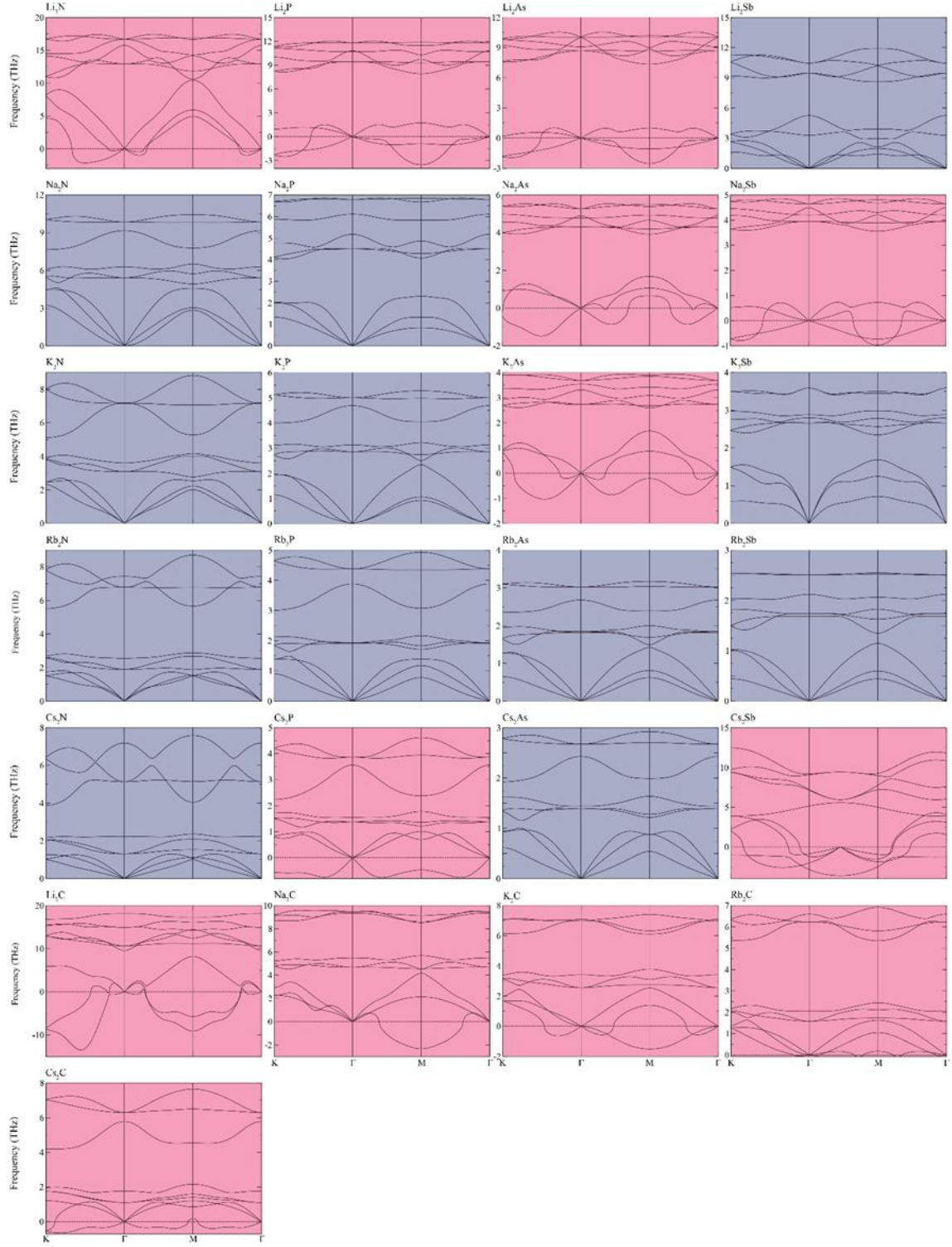


Figure 4.2. Phonon dispersion curves for all the studied structures along high symmetry K points. Red: Not stable systems, Green: Stable electrenes, Blue: Stable structures demonstrating no electrene character

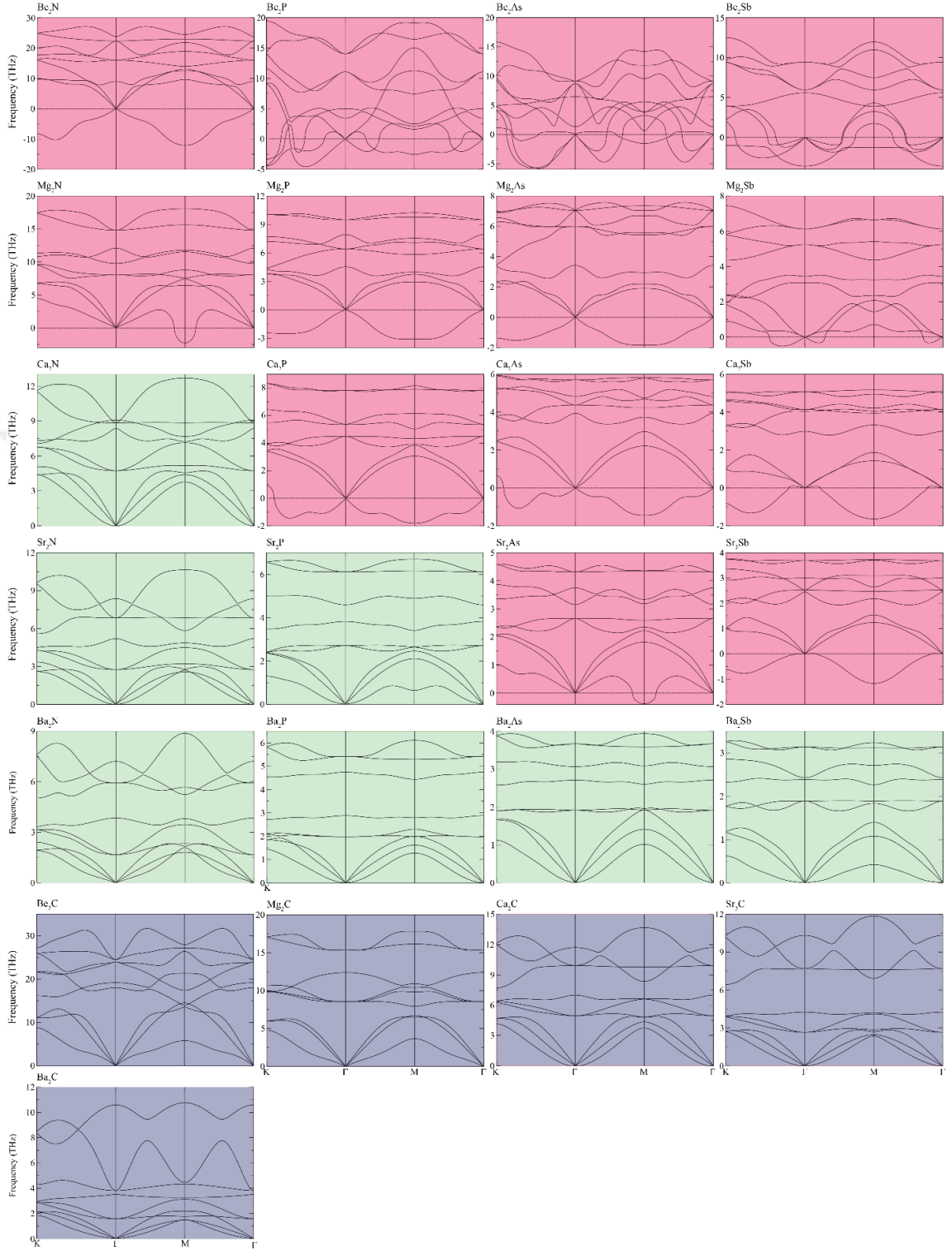


Figure 4.2. (Continued) Phonon dispersion curves for all the studied structures along high symmetry K points. Red: Not stable systems, Green: Stable electrines, Blue: Stable structures demonstrating no electrene character

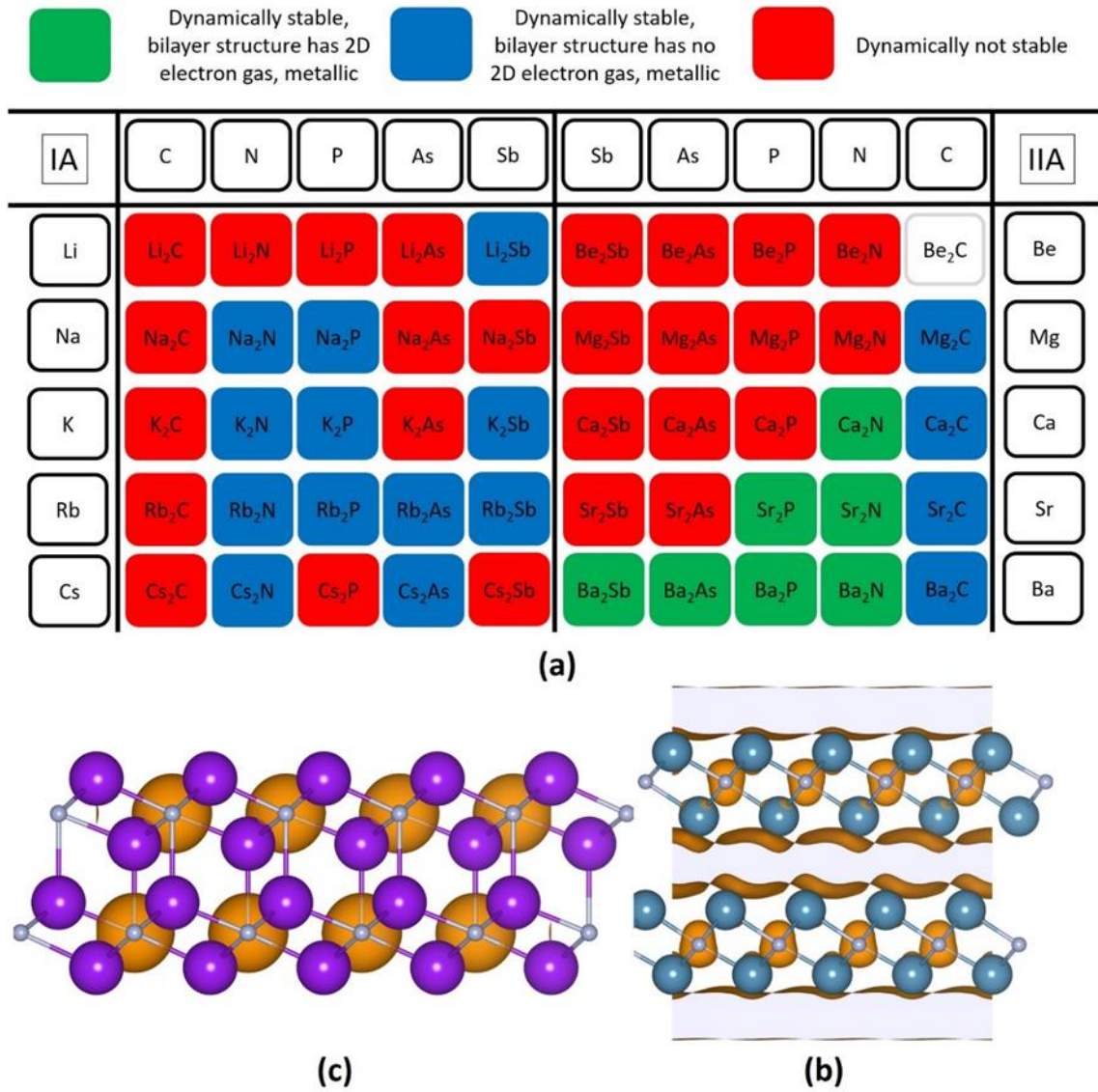


Figure 4.3. a) Table of considered M_2X systems and their corresponding dynamical stabilities. b) PED isosurface plot of K_2N . c) PED isosurface plot of Ca_2N . Large spheres in b and c are cations and the smaller ones are the non-metal elements

Figure 4.4 shows electronic band calculations results of the bilayer systems and corresponding partial electron density (PED) isosurfaces. All the structures have metallic character because of having partially filled dispersive energy bands. Guan *et al.* reported that bands crossing fermi level splits as the number of layers increases [188]. For bilayer systems, the band which splits into two from the monolayer counterpart is depicted by green lines in Figure 4.4. The electron density observed on the surface of monolayer and bilayer systems on PED isosurfaces exist because of these splitted bands. 2D free electron gas that confined between the layers of bilayer systems emerge from the band indicated by the red lines in Figure 4.4. Therefore, this band is selected for band decomposed charge

density calculations to demonstrate the existence of 2D electron gas in these systems. The band structures are very similar for electrene materials but different than carbides. In the case of electrene systems, the band corresponding to 2D electron gas is almost below fermi level and has significant contribution from *d* orbitals of group II-A metals and hence localized between the layers. However, in carbides, the corresponding band is almost above fermi level and therefore these systems do not have an occupied band between their layers. The main contribution below fermi level comes from the localized electron density around carbon atoms as seen in Figure 4.4.

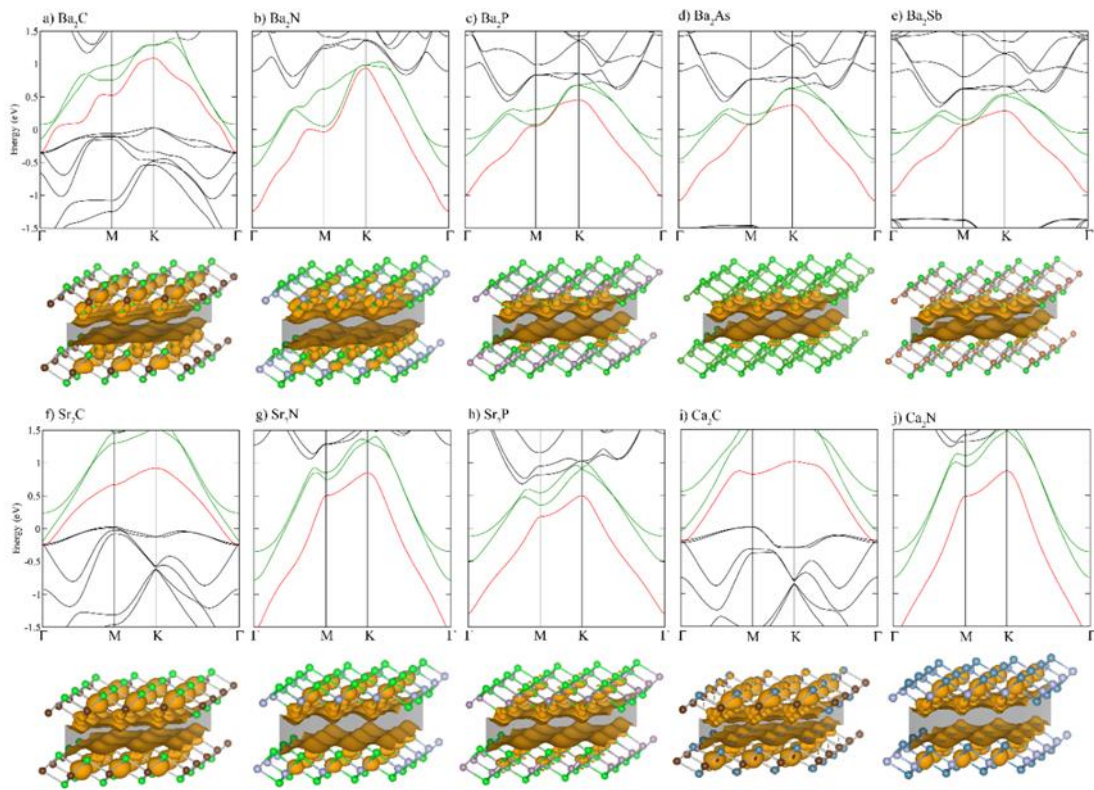


Figure 4.4. Electronic band structure representation of the bilayer electrene systems along the high symmetry points. Fermi energy level is set at zero. PED isosurfaces around the Fermi level is drawn below each band structure for the bilayer systems. Red lines indicate the band that is used to calculate the PED

It should be also noted that the carbides, Sr_2C and Ba_2C have been demonstrated as unstable in a previous work [177]. Moreover, Yan-Ling *et al.* shown that the Ca_2C is thermodynamically stable above 15 GPa and it adopts to the orthorhombic Pnma structure but not $\text{R}\bar{3}\text{m}$ [190]. The compound has been also synthesized experimentally at 24 GPa and 2000 K by the Yan-Ling *et al.*, proving Pnma adoption. Considering the cited literature, we also calculated the formation energies of carbide structures, Ca_2C , Sr_2C and

Ba₂C, with space group $R\bar{3}m$. On the contrary to their dynamically stable vibrational character, the predicted positive values (1.33, 1.87 and 2.06 eV, respectively) clearly indicate that the experimental realization of these structures are unlikely. Consequently, these carbide systems excluded from the possible electrene systems.

In order to find a distinctive trend for electrene systems, the ratio between the interlayer spacing distance of the bilayer structures (c_b) and corresponding lattice constants (a_b) are systematically investigated. We predicted that the stable electrene structures are clustered at a specific area due to two notable trends as seen in Table 4.1. First, lattice constants of the monolayer and bilayer systems increase as the atomic number of the cation increase. The second and more important trend is that the c_b/a_b ratio ranges between 0.83 to 1.04 for electrines, where this ratio is almost half of the electrines for stable but not electrene systems.

Although having 2D structure, the electrene systems reported here fulfils the three criteria necessary to observe anionic electrons in bulk layered electrines reported by Lee *et al.*[164]. The first criterion is that the system should have a cationic slab. The second criterion states the necessity of a high enough interlayer spacing distance to accommodate the electrons exerted from the cationic slab and the third criterion states that the cation should confine electrons loosely but not trap them. In our case all the stable electrene systems belongs to the cations from II-A group that provide a $[(M^{+2})_2(X^{-3})]^+$ cationic slab layer when the X is chosen from N, P, As and Sb (group V-A). The charge neutrality approach also explains why I-A group doesn't provide electrene systems with respect to II-A electrines. In the case of IA, metal atoms do not provide a cationic slab, which is necessary for electrene systems, due to their low oxidation state (M^{+1}). PED analysis and the decrease of the interlayer spacing between the layers indicate that the electrons are not loosely bound to cation but rather trapped by the crystal for I-A compounds (see Figure. 4.2.c. The larger interlayer space of II-A compounds than I-A compounds (c_b values in Table 4.1) acts as a host for electrons that compensates the charge of the positive slab. The bilayer form of prototypical Ca₂N has an interlayer spacing distance of 3.64 Å. The electrines found in this work range between 3.25 to 4.43 Å. The rest of the stable systems range between 1.68 to 2.4 Å obviously lower than that of electrene systems.

Table 4.1. Structural information on dynamically stable systems. a_m and a_b are the lattice constants of monolayer and bilayer structures, respectively. c_b indicates the distance between layers for bilayer structure. c_b/a_b is the ratio of the distance between the layers and the lattice constant of the bilayer system

Group	Material	a_m	a_b	c_b	c_b/a_b
II A	Mg ₂ C	3.55	3.68	1.68	0.46
II A	Ca ₂ C	3.91	3.90	3.25	0.83
II A	Sr ₂ C	4.16	4.13	3.82	0.92
II A	Ba ₂ C	4.23	4.15	4.11	0.99
II A	Ca ₂ N	3.62	3.59	3.64	1.01
II A	Sr ₂ N	3.87	3.84	4.01	1.04
II A	Ba ₂ N	4.01	4.01	4.43	1.10
II A	Sr ₂ P	4.45	4.45	3.92	0.88
II A	Ba ₂ P	4.64	4.63	4.40	0.95
II A	Ba ₂ As	4.76	4.73	4.30	0.90
II A	Ba ₂ Sb	5.04	5.02	4.22	0.84
I A	Na ₂ N	3.72	3.70	1.77	0.48
I A	K ₂ N	4.33	4.51	2.04	0.45
I A	Rb ₂ N	4.49	4.57	2.40	0.53
I A	Cs ₂ N	4.56	4.95	2.60	0.53
I A	Na ₂ P	4.34	4.37	1.76	0.40
I A	K ₂ P	5.07	5.17	2.18	0.42
I A	Rb ₂ P	5.31	5.46	2.30	0.42
I A	Rb ₂ As	5.41	5.56	2.32	0.41
I A	Cs ₂ As	5.66	5.86	2.40	0.41
I A	Li ₂ Sb	4.18	4.19	1.46	0.34
I A	K ₂ Sb	5.38	5.46	2.26	0.41
I A	Rb ₂ Sb	5.72	5.84	2.40	0.41

Consequently, five more stable electrene systems, Ba₂As, Ba₂Sb, Ba₂P, Sr₂P and Ba₂N were determined in addition to the previously reported Ca₂N and Sr₂N crystals, as a result of extensive electronic and vibrational character analysis. The calculated negative formation energy values depicted in Table 4.2 plainly demonstrate the experimental accessibility of these dynamically stable structures. Nonetheless, *ab-initio* molecular dynamics (MD) simulations within isothermal-isobaric (NPT) ensemble have also been conducted on monolayer Ba₂As, Ba₂Sb, Ba₂P and Ba₂N at 300 K (16 ps) and 500 K (7 ps), in order to shed more light on thermal stability of these structures. All these structures showed no sign of collapse up to 500K and preserved their initial geometry. The total energy, temperature, pressure, and RDF profiles shown in Appendix 2 clearly prove the thermodynamic stability of these structures, as well.

Table 4.2. Exfoliation energy of dynamically stable electrene systems

Structures	Exfoliation Energy (eV/Å ²)	Formation Energy (eV)
Ba ₂ As	-0.05	-2.06
Ba ₂ C	-0.03	2.06
Ba ₂ N	-0.05	-0.69
Ba ₂ P	-0.05	-1.99
Ba ₂ Sb	-0.04	-1.73
Ca ₂ C	-0.06	1.33
Ca ₂ N	-0.10	-1.59
Sr ₂ C	-0.04	1.88
Sr ₂ N	-0.08	-1.03
Sr ₂ P	-0.06	-1.95

Exfoliation energies (E_f) of these stable systems are then calculated by the formula of $E_f = (E_{1L} / A_{1L}) - (E_{bulk} / A_{bulk})$ and given in Table 4.2. Here E_{1L} and E_{bulk} are the total energies of monolayer and bulk materials and A_{1L} and A_{bulk} are the area of monolayer and area of bulk system, respectively. The lowest exfoliation energy is found for Ba₂C compound as 32 meV/Å². In general, low exfoliation energies (between 40 meV/Å² and 50 meV/Å²) are found for Ba containing compounds which are in the same order of black phosphorus (~43 meV/Å²).[191] The highest exfoliation energy is found for Ca₂N (102 meV/Å²) matches well with the previously reported values [11]. As noted by Druffel *et al.*[154] relatively higher exfoliation energies of the electrines with respect to other 2D materials such as graphene (20 meV/Å²) is due to the strong interaction between

positively charged layers and electron gas [11]. Thus, other electrene compounds reported here with lower exfoliation energies than that of Ca_2N are predicted to be easily exfoliated.

4.5. Anode Performance Assessment of Stable Electrenes

After the determination of stable electrene systems through phonon calculations, formation energies and ab-initio molecular dynamics simulations, we used two metrics to evaluate possible electrene candidates for battery applications. These metrics are adsorption energies of metal ions (Li, Na, K and Ca) on the selected adsorption sites and migration energy barrier of the adsorbed atom on the possible depicted paths, respectively. Adsorption energy (E_{Ad}) is calculated by using following formula: $E_{\text{Ad}} = E_{\text{AE}} - E_{\text{P}} - E_{\text{A}}$ where E_{AE} is the total energy of system with adsorbed element, E_{P} is the total energy of pristine system (E_{P}) and E_{A} is the energy per atom of the bulk phase of the intercalating metal. Most stable bulk structures, which is body centered cubic bulk structure is utilized for Li, Na, K, whereas face centered cubic is utilized for Ca to calculate E_{A} . One ion per $2 \times 2 \times 1$ supercell (25% coverage) are considered for adsorption on three selected sites (atop, fcc hollow, bcc hollow). Site 1 (bcc hollow) refers to a center of hexagonal position on top of non-metal (X) surrounded by metal atoms, site 2 (fcc hollow) and site 3 (atop) refer to positions on top of the metal atoms. Among these sites bcc hollow (Site 1) is found to be the most favorable position for all ion adsorption cases and (see Appendix 3) and for migration energy barriers (Appendix 4). Figure 4.5 shows the adsorption energies of Li, Na, K and Ca on considered electrene systems for Site 1. As is evident from Figure 4.4, three general results can be deduced:

- No ion (Li, Na, K, Ca) prefers to adsorb on carbide based electrenes.
- Li and Ca have positive adsorption energies for M_2X based electrenes and hence adsorption is not favorable for these elements.
- The adsorption strength of K is the strongest for all considered electrene systems.

A relatively strong binding energy of the metal ion means that material of interest might be a good anode material [192]. On the other hand, poor adsorption may result in clustering, adversely affects the performance of the battery [193]. Depending on the adsorbed species (Na or K) the predicted binding energies are in the range of 0 to -0.46 eV. Some systems have very weak binding energies. In general, binding energy of K and

Na in some systems is close to zero or comparable with room temperature. These systems, which are prone to K and Na clustering are Ba_2As , Ba_2P , Ba_2N and Ba_2Sb . For Ba_2N adsorption is slightly more favorable than rest of this group. On the other hand, K and Na adsorption on Ca_2N , Sr_2N and Sr_2P have relatively higher binding energy values. When we compare our adsorption results on Ca_2N and Sr_2N with a previous theoretical work [173], our adsorption energies (Na/ Ca_2N : -0.33 eV, K/ Ca_2N : -0.48 eV, Na/ Sr_2N : -0.18 eV, K/ Sr_2N : -0.39 eV) agree with their values (Na/ Ca_2N : -0.24 eV, K/ Ca_2N : -0.42 eV, Na/ Sr_2N : -0.13 eV, K/ Sr_2N : -0.31 eV). Our values indicate slightly stronger adsorption due to the inclusion of the van der Waals interactions in the methodology. It should be noted that binding energies for adsorption can be tuned by alloying, hydrogenation or defect engineering as demonstrated for other 2D materials [193, 194]. Therefore, adsorption results on freely suspended pristine electrenes indicate that electrenes can be possible candidates for K and Na anode electrodes.

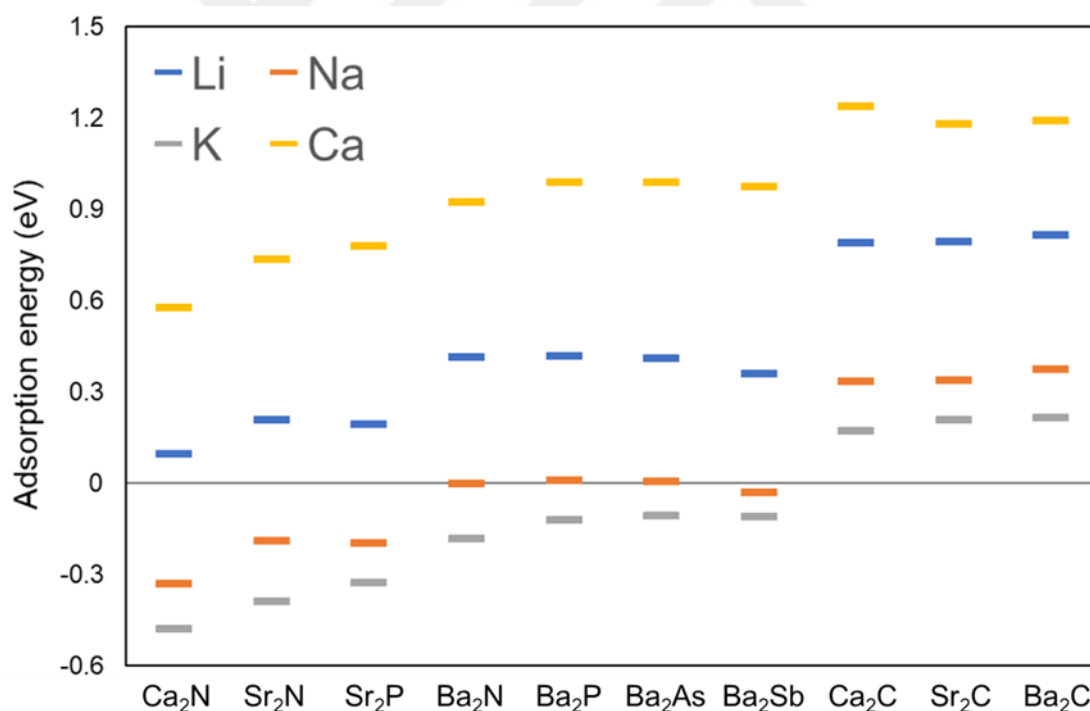


Figure 4.5. Adsorption energies of Na, K, Li and Ca on Site 1 of the dynamically stable electrene crystals

In addition to the strong binding energy, a low diffusion barrier, ensuring a high ionic mobility is required for fast charge and discharge of a battery [192]. To assess the

further potential of these systems, we investigate the diffusion barriers of stable electrene systems that demonstrate negative binding energies for Na and K for three possible paths depicted in Figure 4.6. In all systems, except K on Ba_2N , there is a local minimum between saddle points (see Appendix 4). This local minimum is observed for path 1 on site 2, where binding energy is the second most negative for all the systems. However, for Ba_2N the lack of local minimum on path 1 is due to the unfavorable adsorption on site 2. We find extremely low energy barriers for migration of Na and K. The calculated energy barrier values for all the considered electrene crystals are given in Fig. 5. In general, energy barriers of K are lower than Na. The migration energy barriers of K atom are between 0.005 and 0.016 eV, whereas they are between 0.012 and 0.032 eV for Na atom. Our values for the migration energy barriers of Na on Sr_2N system agree with the previous work of Hu *et al.* However, our result on Ca_2N is around 0.06 eV smaller possibly due to the difference in the computational methodology (inclusion of the van der Waals interaction corrections).

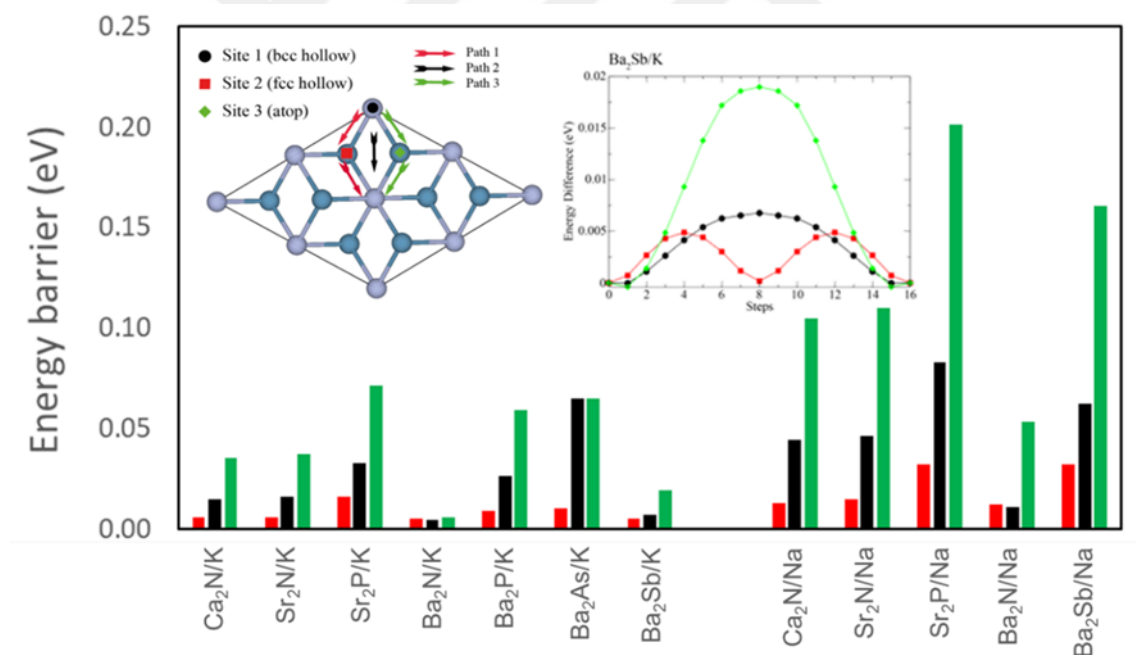


Figure 4.6. Diffusion energy barriers of K and Na on the dynamically stable systems for depicted migration paths. Inset shows diffusion energy profile example of K on Ba_2Sb

Migration energy barriers of commercial electrodes based on TiO_2 polymorphs are in the range between 0.35 and 0.65 eV [195-197], which are strikingly higher values than for considered electrene systems. Since high migration barriers are responsible for slow charge and discharge of a battery, 2D materials are started to be suggested as anode

materials for their lower migration energy barriers. For example, Li migration energy barrier on graphene is 0.33 eV [198], 0.084 eV on black phosphorous [199], 0.04 eV on Mo₂C [192], and 0.25 eV on MoS₂ [200]. The obtained migration energy barrier values of both K and Na for all considered electrenes are at least one order of magnitude lower than these 2D materials. These exceptionally low energy barriers may be attributed to 2D electron gas existing on surfaces of electrene systems which effectively smoothes the surface potential.[173] As Cakir *et al.*[192] performed on MXene systems, Arrhenius Law ($D \sim \exp(-E_a/k_b T)$) can be used to roughly compare the mobilities of the metal atoms at room temperature, where E_a is the migration energy barrier, k_b is the Boltzmann constant and T is the temperature. Smallest migration energy barriers (0.005 eV for K and 0.012 for Na on Ba₂N) and highest energy barriers (0.016 eV for K and 0.032 for Na on Sr₂P) can be considered to estimate mobility. According to above mentioned values, those electrene family may roughly demonstrate 2.0×10^5 (1.1×10^5) to 3.1×10^5 (2.4×10^5) times higher mobility than graphene and 2.5 (1.4) to 3.9 (3.0) times higher mobility than Mo₂C for K (Na) ion. These values indicate a very fast diffusion rates along the monolayer plane, a key enabler for efficient performance of a battery.

For practical battery applications, electrenes as an anode material should be capable of hosting high number of Na or K atoms. To check their capacity, we also performed full coverage calculations of Na and K atoms on the dynamically stable electrene candidates. Table 2 shows the adsorption energy values of electrene systems for %25 and %100 coverage. Although the highest adsorption energies are found for Sr₂N and Ca₂N systems, they have unfavorable adsorption energies towards full coverage of K atoms. Similarly, for Ba₂N system, adsorption becomes unfavorable upon full coverage, whereas full coverage Na adsorption is favorable for these systems. The reason for the restrained adsorption of K on these electrenes is the larger size of K atom compared to the lattice constant of the system. However, all larger electrenes (Sr₂P, Ba₂P, Ba₂As, and Ba₂Sb) shows favorable adsorption towards full coverage of K. The slight increase of adsorption energy upon increasing coverage in some systems are also due to the K-K or Na-Na interactions depending on the lattice constant of the adsorbent electrene system.

Because low migration energy barriers and high capacity is essential for battery applications, our numerical results point out that Ca₂N, Sr₂N, Ba₂N and Sr₂P are promising high rate electrode materials for Na and Sr₂P, Ba₂As, Ba₂P and Ba₂Sb are

promising for K ion batteries. Among them, Ba₂N shows excellent mobility for Na ion, while Ba₂As for K ion batteries.

Table 4.3. Adsorption energies (in eV/atom) of K and Na atoms on electrene systems

System	Single adsorption	%25 coverage	%100 coverage
Ba ₂ As/K	-0.12	-0.11	-0.19
Ba ₂ N/K	-0.22	-0.18	0.01
Ba ₂ N/Na	-0.00	-0.00	-0.14
Ba ₂ P/K	-0.13	-0.12	-0.18
Ba ₂ Sb/K	-0.11	-0.11	-0.20
Ba ₂ Sb/Na	-0.01	-0.03	0.01
Ca ₂ N/K	-0.44	-0.48	0.13
Ca ₂ N/Na	-0.38	-0.33	-0.30
Sr ₂ N/K	-0.46	-0.39	-0.02
Sr ₂ N/Na	-0.17	-0.19	-0.26
Sr ₂ P/K	-0.35	-0.32	-0.27
Sr ₂ P/Na	-0.18	-0.19	-0.23

4.6. Conclusion

To sum up, 50 possible electrene compounds of the form M₂X where M is group I-A or II-A metal and X is a non-metal element (C, N, P, As, and Sb) are studied in order to shed light on their thermal stability and potential to be an electrene. Out of these 50 compounds, 5 new stable electrene candidates are determined in addition to the previously known Ca₂N and Sr₂N. These 2D systems are Ba₂N, Sr₂P, Ba₂P, Ba₂As and Ba₂Sb and all these new electrines belong to group II-A compounds. Although 12 group I-A compounds are also found dynamically stable, these electron deficient compounds do not exhibit a confined electron gas as expected and their bilayers tend to stack together.

To assess the device performances of considered electrene systems, adsorption and migration properties of relevant atoms (Li, Na, K, and Ca) are calculated on stable electrene candidates. On the predicted electrene compounds, K adsorption is found stronger than Na, while Li and Ca atoms prefer clustering. Furthermore, NEB calculations

revealed very low migration energy barriers for K and Na atoms on stable electrene compounds, indicating very fast ion transport in battery applications. The migration energy barriers are found lower, while the adsorption is also found stronger for K atoms than Na. Especially the extremely low migration energy barriers than that of other 2D materials make considered electrene systems: Ba_2As , Ba_2P , Ba_2Sb , Sr_2P very promising for fast charging K ion batteries and Ca_2N , Sr_2N , Sr_2P for fast charging Na ion batteries.



5. CONCLUSIONS

In the first part of the thesis, presented research was motivated by the need of monolayer MoS_2 flakes for optoelectronics and nanoelectronics applications homogeneously grown over a substrate by a cost-effective method. Therefore, monolayer MoS_2 flakes were synthesized by applying CVD techniques. Several aspects of the growth procedure were investigated. Different growth configurations were performed and compared to find most favorable flake growth. It has been found that face-down approach yields larger flakes and higher coverage area with respect to horizontal growth configuration. Moreover, further growth experiments on the face-down growth scheme have been provided that local changes of S to Mo vapor ratio in the growth zone is a key factor for the change of shape, size and uniformity of the resulting MoS_2 formations.

Spectroscopic characterization of the grown monolayer flakes indicated significant residual stress effect in the grown flakes. Long term time dependent observations and transfer of the flakes to the fresh substrates revealed that flakes grown by face-down approach cracks due to this residual stress effect. The same effect has been attributed for heterogeneous intensity and photoluminescence peak center together with heterogeneous fluorescence lifetime distribution for the flakes.

To get rid of heterogeneous growth, heterogeneous PL intensity distribution inside the flakes, a new growth scheme has been adopted. Instead of using Si/SiO₂ substrates, which has no catalytic contribution to the growth, glass substrates containing Na as catalyst have been used by using same growth parameters optimized for face-down approach. This yields full coverage of the glass substrates with lower residual stress compared to Si/SiO₂. Moreover, it has been shown that transfer of the grown flakes completely removes that relatively low stress effect.

In the theoretical part of the thesis, DFT calculations have been performed to investigate new 2D materials. Extensive DFT calculations provided that electrene family derived from bulk electrides can be extended beyond Ca_2N to Ba_2As , Ba_2P , Ba_2Sb , and Sr_2P and Sr_2N . Adsorption energies of the Na, Ca, and K on these new electrines were found to be extremely low with very low diffusion energy barriers making electrines excellent candidates for battery anode applications.

6. FUTURE WORK

By using designed glass compositions, investigation of growth mechanism could be beneficial to understand the function of Na or other alkali elements on the quality of the monolayer flakes, their size and compositions. Moreover, Si/SiO₂ surfaces or other substrates that don't contain Na can be seeded with Na containing molecules to extend the homogeneity of the growth on these substrates.

Growth of other TMDs such as MoSe₂, WS₂ and WSe₂ can be optimized and many vertical heterostructures can be formed by either direct growth of heterolayers or by transfer techniques. Since transfer techniques provide residual molecules between the 2D layers, direct growth of the individual layers on top of each other might yield better results. Moreover, if a dielectric 2D material (such as h-BN) could be grown on glass substrates by benefiting from its catalytic properties and large area growth promotion, this dielectric layer can then be utilized as a suitable substrate for epitaxial growth of secondary layers.

DFT can be utilized to predict the properties of these heterostructures prior to synthesis.

REFERENCES

- [1] Landau, L., *Zur Theorie der phasenumwandlungen II*. Phys. Z. Sowjetunion, 1937. **11**(545): p. 26-35.
- [2] Landau, L.D., Lifshitz, E.M., and Pitaevskii, L. (1980) Statistical physics, part I. 1980, pergamon, Oxford.
- [3] Venables, J.A., Spiller, G.D.T., and Hanbucken, M., *Nucleation and growth of thin films*. Reports on Progress in Physics, 1984. **47**(4): p. 399.
- [4] Geim, A.K. and Novoselov, K.S., *The rise of graphene*, in *Nanoscience and Technology: A Collection of Reviews from Nature Journals*. 2010, World Scientific. p. 11-19.
- [5] Novoselov, K.S., Geim, A.K., Morozov, S.V., Jiang, D., Zhang, Y., Dubonos, S.V., Grigorieva, I.V., and Firsov, A.A., *Electric field effect in atomically thin carbon films*. Science, 2004. **306**(5696): p. 666-669.
- [6] Wallace, P.R., *The band theory of graphite*. Physical Review, 1947. **71**(9): p. 622.
- [7] Dresselhaus, M.S. and Araujo, P.T. (2010) Perspectives on the 2010 nobel prize in physics for graphene. 2010, ACS Publications.
- [8] Novoselov, K.S., Geim, A.K., Morozov, S., Jiang, D., Katsnelson, M., Grigorieva, I., Dubonos, S., Firsov, and AA, *Two-dimensional gas of massless Dirac fermions in graphene*. nature, 2005. **438**(7065): p. 197.
- [9] MEYER, J., *It's still all about graphene*.
- [10] Novoselov, K., Jiang, D., Schedin, F., Booth, T., Khotkevich, V., Morozov, S., and Geim, A., *Two-dimensional atomic crystals*. Proceedings of the National Academy of Sciences, 2005. **102**(30): p. 10451-10453.
- [11] Druffel, D.L., Kuntz, K.L., Woomer, A.H., Alcorn, F.M., Hu, J., Donley, C.L., and Warren, S.C., *Experimental Demonstration of an Electride as a 2D Material*. Journal of the American Chemical Society, 2016. **138**(49): p. 16089-16094.
- [12] Arguilla, M.Q., Katoch, J., Krymowski, K., Cultrara, N.D., Xu, J., Xi, X., Hanks, A., Jiang, S., Ross, R.D., and Koch, R.J., *Nas₂As₂: An exfoliatable layered van der waals zintl phase*. ACS nano, 2016. **10**(10): p. 9500-9508.
- [13] Arguilla, M., Cultrara, N., Baum, Z., Jiang, S., Ross, R., and Goldberger, J., *EuSn₂As₂: an exfoliatable magnetic layered Zintl–Klemm phase*. Inorganic Chemistry Frontiers, 2017. **4**(2): p. 378-386.
- [14] Liu, C.-C., Feng, W., and Yao, Y., *Quantum spin Hall effect in silicene and two-dimensional germanium*. Physical review letters, 2011. **107**(7): p. 076802.
- [15] Zhang, Y., Tan, Y.-W., Stormer, H.L., and Kim, P., *Experimental observation of the quantum Hall effect and Berry's phase in graphene*. nature, 2005. **438**(7065): p. 201.
- [16] Zhang, Y.W., Li, H., Wang, H.M., Liu, R., Zhang, S.L., and Qiu, Z.J., *On Valence-Band Splitting in Layered MoS₂*. Acs Nano, 2015. **9**(8): p. 8514-8519.
- [17] Mak, K.F., He, K.L., Shan, J., and Heinz, T.F., *Control of valley polarization in monolayer MoS₂ by optical helicity*. Nature Nanotechnology, 2012. **7**(8): p. 494-498.
- [18] Mak, K.F., Lee, C., Hone, J., Shan, J., and Heinz, T.F., *Atomically Thin MoS₂: A New Direct-Gap Semiconductor*. Physical Review Letters, 2010. **105**(13).
- [19] Geim, A.K. and Grigorieva, I.V., *Van der Waals heterostructures*. Nature, 2013. **499**(7459): p. 419-425.

- [20] Zeng, T., You, Y.C., Wang, X.F., Hu, T.S., and Tai, G.A., *Chemical Vapor Deposition and Device Application of Two-Dimensional Molybdenum Disulfide-Based Atomic Crystals*. Progress in Chemistry, 2016. **28**(4): p. 459-470.
- [21] Tong, X., Ashalley, E., Lin, F., Li, H., and Wang, Z.M., *Advances in MoS₂-based field effect transistors (FETs)*. Nano-Micro Letters, 2015. **7**(3): p. 203-218.
- [22] Chhowalla, M., Jena, D., and Zhang, H., *Two-dimensional semiconductors for transistors*. Nature Reviews Materials, 2016. **1**(11): p. 16052.
- [23] Jariwala, D., Sangwan, V.K., Lauhon, L.J., Marks, T.J., and Hersam, M.C., *Emerging device applications for semiconducting two-dimensional transition metal dichalcogenides*. ACS nano, 2014. **8**(2): p. 1102-1120.
- [24] Zappa, D., *Molybdenum dichalcogenides for environmental chemical sensing*. Materials, 2017. **10**(12): p. 1418.
- [25] Lee, J.Y., Shin, J.-H., Lee, G.-H., and Lee, C.-H., *Two-dimensional semiconductor optoelectronics based on van der Waals heterostructures*. Nanomaterials, 2016. **6**(11): p. 193.
- [26] Latini, S., Olsen, T., and Thygesen, K.S., *Excitons in van der Waals heterostructures: The important role of dielectric screening*. Physical Review B, 2015. **92**(24).
- [27] Xiao, J., Zhao, M., Wang, Y., and Zhang, X., *Excitons in atomically thin 2D semiconductors and their applications*. Nanophotonics, 2017. **6**(6): p. 1309-1328.
- [28] Lin, Z., Carvalho, B.R., Kahn, E., Lv, R., Rao, R., Terrones, H., Pimenta, M.A., and Terrones, M., *Defect engineering of two-dimensional transition metal dichalcogenides*. 2D Materials, 2016. **3**(2): p. 022002.
- [29] Santiago, Y. and Cabrera, C.R., *Electrochemistry and Surface-Analysis of Thin-Films of Mos₂*. Abstracts of Papers of the American Chemical Society, 1993. **205**: p. 251-Coll.
- [30] Santiago, Y. and Cabrera, C.R., *Surface-Analysis and Electrochemistry of Mos₂ Thin-Films Prepared by Intercalation-Exfoliation Techniques*. Journal of the Electrochemical Society, 1994. **141**(3): p. 629-635.
- [31] Eng, A.Y.S., Ambrosi, A., Sofer, Z., Šimek, P., and Pumera, M., *Electrochemistry of Transition Metal Dichalcogenides: Strong Dependence on the Metal-to-Chalcogen Composition and Exfoliation Method*. ACS Nano, 2014. **8**(12): p. 12185-12198.
- [32] Ramasubramaniam, A., Naveh, D., and Towe, E., *Tunable band gaps in bilayer graphene–BN heterostructures*. Nano letters, 2011. **11**(3): p. 1070-1075.
- [33] Li, Z., Meng, X., and Zhang, Z., *Recent development on MoS₂ 2-based photocatalysis: A review*. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 2017.
- [34] Chhowalla, M., Shin, H.S., Eda, G., Li, L.-J., Loh, K.P., and Zhang, H., *The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets*. Nature chemistry, 2013. **5**(4): p. 263.
- [35] Wilson, J.A., Di Salvo, F., and Mahajan, S., *Charge-density waves and superlattices in the metallic layered transition metal dichalcogenides*. Advances in Physics, 1975. **24**(2): p. 117-201.
- [36] Fang, H., Chuang, S., Chang, T.C., Takei, K., Takahashi, T., and Javey, A., *High-performance single layered WSe₂ p-FETs with chemically doped contacts*. Nano letters, 2012. **12**(7): p. 3788-3792.
- [37] Allain, A. and Kis, A., *Electron and hole mobilities in single-layer WSe₂*. ACS nano, 2014. **8**(7): p. 7180-7185.

- [38] Izyumskaya, N., DEMCHENKO, D.O., AVRUTIN, V., ÖZGÜR, Ü., and MORKOÇ, H., *Two-dimensional MoS₂ as a new material for electronic devices*. Turkish Journal of Physics, 2014. **38**(3): p. 478-496.
- [39] Wakabayashi, N., Smith, H., and Nicklow, R., *Lattice dynamics of hexagonal MoS₂ studied by neutron scattering*. Physical Review B, 1975. **12**(2): p. 659.
- [40] Wang, Q.H., Kalantar-Zadeh, K., Kis, A., Coleman, J.N., and Strano, M.S., *Electronics and optoelectronics of two-dimensional transition metal dichalcogenides*. Nature Nanotechnology, 2012. **7**(11): p. 699-712.
- [41] Velický, M. and Toth, P.S., *From two-dimensional materials to their heterostructures: An electrochemist's perspective*. Applied Materials Today, 2017. **8**: p. 68-103.
- [42] Fleischauer, P.D., Lince, J.R., Bertrand, P., and Bauer, R., *Electronic structure and lubrication properties of molybdenum disulfide: a qualitative molecular orbital approach*. Langmuir, 1989. **5**(4): p. 1009-1015.
- [43] Papageorgopoulos, C. and Jaegermann, W., *Li intercalation across and along the van der Waals surfaces of MoS₂ (0001)*. Surface science, 1995. **338**(1-3): p. 83-93.
- [44] Wypych, F. and Schöllhorn, R., *1T-MoS₂, a new metallic modification of molybdenum disulfide*. Journal of the Chemical Society, Chemical Communications, 1992(19): p. 1386-1388.
- [45] Wypych, F., Solenthaler, C., Prins, R., and Weber, T., *Electron diffraction study of intercalation compounds derived from 1T-MoS₂*. Journal of Solid State Chemistry, 1999. **144**(2): p. 430-436.
- [46] Fang, Y., Pan, J., He, J., Luo, R., Wang, D., Che, X., Bu, K., Zhao, W., Liu, P., and Mu, G., *Structure Re-determination and Superconductivity Observation of Bulk 1T MoS₂*. Angewandte Chemie, 2018. **130**(5): p. 1246-1249.
- [47] Huang, X., Zeng, Z.Y., and Zhang, H., *Metal dichalcogenide nanosheets: preparation, properties and applications*. Chemical Society Reviews, 2013. **42**(5): p. 1934-1946.
- [48] Eda, G., Yamaguchi, H., Voiry, D., Fujita, T., Chen, M., and Chhowalla, M., *Photoluminescence from Chemically Exfoliated MoS₂*. Nano Letters, 2011. **11**(12): p. 5111-5116.
- [49] Kuc, A., *Low-dimensional transition-metal dichalcogenides*. Chem. Modell, 2014. **11**(1).
- [50] Santosh, K., Longo, R.C., Addou, R., Wallace, R.M., and Cho, K., *Impact of intrinsic atomic defects on the electronic structure of MoS₂ monolayers*. Nanotechnology, 2014. **25**(37): p. 375703.
- [51] Xie, J., Zhang, H., Li, S., Wang, R., Sun, X., Zhou, M., Zhou, J., Lou, X.W., and Xie, Y., *Defect-rich MoS₂ ultrathin nanosheets with additional active edge sites for enhanced electrocatalytic hydrogen evolution*. Advanced materials, 2013. **25**(40): p. 5807-5813.
- [52] Shin, S., Jin, Z., Kwon, D.H., Bose, R., and Min, Y.S., *High Turnover Frequency of Hydrogen Evolution Reaction on Amorphous MoS₂ Thin Film Directly Grown by Atomic Layer Deposition*. Langmuir, 2015. **31**(3): p. 1196-1202.
- [53] Savan, A., Pflüger, E., Voumard, P., Schröer, A., and Simmonds, M., *Modern solid lubrication: recent developments and applications of MoS₂*. Lubrication Science, 2000. **12**(2): p. 185-203.

- [54] Santhosh, S. and Madhavan, A.A. *A review on the structure, properties and characterization of 2D Molybdenum Disulfide*. in *2019 Advances in Science and Engineering Technology International Conferences (ASET)*. 2019. IEEE.
- [55] Lu, C.-P., Li, G., Mao, J., Wang, L.-M., and Andrei, E.Y., *Bandgap, mid-gap states, and gating effects in MoS₂*. *Nano letters*, 2014. **14**(8): p. 4628-4633.
- [56] Lavrov, S., Shestakova, A., Avdizhiyan, A.Y., and Mishina, E., *Optical Characterization of the Structural Imperfection of Two-Dimensional MoS₂ Crystallites*. *Technical Physics Letters*, 2018. **44**(11): p. 1008-1009.
- [57] Kang, Y. and Han, S., *An origin of unintentional doping in transition metal dichalcogenides: the role of hydrogen impurities*. *Nanoscale*, 2017. **9**(12): p. 4265-4271.
- [58] Nan, H., Wang, Z., Wang, W., Liang, Z., Lu, Y., Chen, Q., He, D., Tan, P., Miao, F., and Wang, X., *Strong photoluminescence enhancement of MoS₂ through defect engineering and oxygen bonding*. *ACS nano*, 2014. **8**(6): p. 5738-5745.
- [59] Sercombe, D., Schwarz, S., Del Pozo-Zamudio, O., Liu, F., Robinson, B.J., Chekhovich, E.A., Tartakovskii, I.I., Kolosov, O., and Tartakovskii, A.I., *Optical investigation of the natural electron doping in thin MoS₂ films deposited on dielectric substrates*. *Scientific Reports*, 2013. **3**.
- [60] Kim, J.H., Kim, T.H., Lee, H., Park, Y.R., Choi, W., and Lee, C.J., *Thickness-dependent electron mobility of single and few-layer MoS₂ thin-film transistors*. *Aip Advances*, 2016. **6**(6).
- [61] Splendiani, A., Sun, L., Zhang, Y., Li, T., Kim, J., Chim, C.-Y., Galli, G., and Wang, F., *Emerging Photoluminescence in Monolayer MoS₂*. *Nano Letters*, 2010. **10**(4): p. 1271-1275.
- [62] Kuc, A., Zibouche, N., and Heine, T., *Influence of quantum confinement on the electronic structure of the transition metal sulfide T S₂*. *Physical Review B*, 2011. **83**(24): p. 245213.
- [63] Yun, W.S., Han, S., Hong, S.C., Kim, I.G., and Lee, J., *Thickness and strain effects on electronic structures of transition metal dichalcogenides: 2H-M X₂ semiconductors (M= Mo, W; X= S, Se, Te)*. *Physical Review B*, 2012. **85**(3): p. 033305.
- [64] Enyashin, A. and Seifert, G., *Electronic properties of MoS₂ monolayer and related structures*. *Наносистемы: физика, химия, математика*, 2014. **5**(4).
- [65] Klein, A., Tiefenbacher, S., Eyert, V., Pettenkofer, C., and Jaegermann, W., *Electronic band structure of single-crystal and single-layer WS₂: Influence of interlayer van der Waals interactions*. *Physical Review B*, 2001. **64**(20): p. 205416.
- [66] Albe, K. and Klein, A., *Density-functional-theory calculations of electronic band structure of single-crystal and single-layer WS₂*. *Physical Review B*, 2002. **66**(7): p. 073413.
- [67] Voß, D., Krüger, P., Mazur, A., and Pollmann, J., *Atomic and electronic structure of WSe₂ from ab initio theory: Bulk crystal and thin film systems*. *Physical Review B*, 1999. **60**(20): p. 14311.
- [68] Sattler, K.D., *Carbon Nanomaterials Sourcebook: Graphene, Fullerenes, Nanotubes, and Nanodiamonds*. Vol. 1. 2016: CRC Press.
- [69] Chen, J.-H., Jang, C., Xiao, S., Ishigami, M., and Fuhrer, M.S., *Intrinsic and extrinsic performance limits of graphene devices on SiO₂*. *Nature nanotechnology*, 2008. **3**(4): p. 206.

- [70] Banszerus, L., Schmitz, M., Engels, S., Dauber, J., Oellers, M., Haupt, F., Watanabe, K., Taniguchi, T., Beschoten, B., and Stampfer, C., *Ultrahigh-mobility graphene devices from chemical vapor deposition on reusable copper*. Science advances, 2015. **1**(6): p. e1500222.
- [71] Bolotin, K.I., Sikes, K., Jiang, Z., Klima, M., Fudenberg, G., Hone, J., Kim, P., and Stormer, H., *Ultrahigh electron mobility in suspended graphene*. Solid State Communications, 2008. **146**(9-10): p. 351-355.
- [72] Radisavljevic, B., Radenovic, A., Brivio, J., Giacometti, V., and Kis, A., *Single-layer MoS₂ transistors*. Nature Nanotechnology, 2011. **6**(3): p. 147-150.
- [73] Kim, S., Konar, A., Hwang, W.S., Lee, J.H., Lee, J., Yang, J., Jung, C., Kim, H., Yoo, J.B., Choi, J.Y., Jin, Y.W., Lee, S.Y., Jena, D., Choi, W., and Kim, K., *High-mobility and low-power thin-film transistors based on multilayer MoS₂ crystals*. Nature Communications, 2012. **3**.
- [74] Cui, X., Lee, G.-H., Kim, Y.D., Arefe, G., Huang, P.Y., Lee, C.-H., Chenet, D.A., Zhang, X., Wang, L., and Ye, F., *Multi-terminal transport measurements of MoS₂ using a van der Waals heterostructure device platform*. Nature nanotechnology, 2015. **10**(6): p. 534.
- [75] Bissessur, R., Kanatzidis, M.G., Schindler, J., and Kannewurf, C., *Encapsulation of polymers into MoS₂ and metal to insulator transition in metastable MoS₂*. Journal of the Chemical Society, Chemical Communications, 1993(20): p. 1582-1585.
- [76] Miller, D.A., *Optical physics of quantum wells*. Quantum Dynamics of Simple Systems," ed. G.-L. Oppo, SM Barnett, E. Riis, and M. Wilkinson (Institute of Physics, London, 1996), 1994: p. 239-266.
- [77] Yu, H., Cui, X., Xu, X., and Yao, W., *Valley excitons in two-dimensional semiconductors*. National Science Review, 2015. **2**(1): p. 57-70.
- [78] Amani, M., Lien, D.-H., Kiriya, D., Xiao, J., Azcatl, A., Noh, J., Madhupathy, S.R., Addou, R., Santosh, K., and Dubey, M., *Near-unity photoluminescence quantum yield in MoS₂*. Science, 2015. **350**(6264): p. 1065-1068.
- [79] Sanchez, O.L., Ovchinnikov, D., Misra, S., Allain, A., and Kis, A., *Valley Polarization by Spin Injection in a Light-Emitting van der Waals Heterojunction*. Nano Letters, 2016. **16**(9): p. 5792-5797.
- [80] Cao, T., Wang, G., Han, W., Ye, H., Zhu, C., Shi, J., Niu, Q., Tan, P., Wang, E., Liu, B., and Feng, J., *Valley-selective circular dichroism of monolayer molybdenum disulphide*. Nature Communications, 2012. **3**.
- [81] Withers, F., Del Pozo-Zamudio, O., Mishchenko, A., Rooney, A.P., Gholinia, A., Watanabe, K., Taniguchi, T., Haigh, S.J., Geim, A.K., Tartakovskii, A.I., and Novoselov, K.S., *Light-emitting diodes by band-structure engineering in van der Waals heterostructures*. Nat Mater, 2015. **14**(3): p. 301-306.
- [82] Eda, G. and Maier, S.A., *Two-dimensional crystals: managing light for optoelectronics*. Acs Nano, 2013. **7**(7): p. 5660-5665.
- [83] Xia, F., Wang, H., Xiao, D., Dubey, M., and Ramasubramaniam, A., *Two-dimensional material nanophotonics*. Nature Photonics, 2014. **8**(12): p. 899.
- [84] Rai, A., Movva, H., Roy, A., Taneja, D., Chowdhury, S., and Banerjee, S., *Progress in contact, doping and mobility engineering of MoS₂: An atomically thin 2D semiconductor*. Crystals, 2018. **8**(8): p. 316.
- [85] Şar, H., Özden, A., Yorulmaz, B., Sevik, C., Perkgoz, N.K., and Ay, F., *A comparative device performance assesment of CVD grown MoS₂ and WS₂*

- monolayers*. Journal of Materials Science: Materials in Electronics, 2018. **29**(10): p. 8785-8792.
- [86] Mak, K.F., He, K., Lee, C., Lee, G.H., Hone, J., Heinz, T.F., and Shan, J., *Tightly bound trions in monolayer MoS₂*. Nat Mater, 2013. **12**(3): p. 207-211.
- [87] Lin, Y., Ling, X., Yu, L., Huang, S., Hsu, A.L., Lee, Y.-H., Kong, J., Dresselhaus, M.S., and Palacios, T., *Dielectric Screening of Excitons and Trions in Single-Layer MoS₂*. Nano Letters, 2014. **14**(10): p. 5569-5576.
- [88] Liu, K.-K., Zhang, W., Lee, Y.-H., Lin, Y.-C., Chang, M.-T., Su, C., Chang, C.-S., Li, H., Shi, Y., Zhang, H., Lai, C.-S., and Li, L.-J., *Growth of Large-Area and Highly Crystalline MoS₂ Thin Layers on Insulating Substrates*. Nano Letters, 2012. **12**(3): p. 1538-1544.
- [89] Feng, Y.L., Zhang, K.L., Wang, F., Liu, Z.W., Fang, M.X., Cao, R.R., Miao, Y.P., Yang, Z.C., Mi, W., Han, Y.M., Song, Z.T., and Wong, H.S.P., *Synthesis of Large-Area Highly Crystalline Monolayer Molybdenum Disulfide with Tunable Grain Size in a H-2 Atmosphere*. Acs Applied Materials & Interfaces, 2015. **7**(40): p. 22587-22593.
- [90] George, A.S., Mutlu, Z., Ionescu, R., Wu, R.J., Jeong, J.S., Bay, H.H., Chai, Y., Mkhoyan, K.A., Ozkan, M., and Ozkan, C.S., *Wafer Scale Synthesis and High Resolution Structural Characterization of Atomically Thin MoS₂ Layers*. Advanced Functional Materials, 2014. **24**(47): p. 7461-7466.
- [91] Zhan, Y., Liu, Z., Najmaei, S., Ajayan, P.M., and Lou, J., *Large-Area Vapor-Phase Growth and Characterization of MoS₂ Atomic Layers on a SiO₂ Substrate*. Small, 2012. **8**(7): p. 966-971.
- [92] Lin, Y.C., Zhang, W.J., Huang, J.K., Liu, K.K., Lee, Y.H., Liang, C.T., Chu, C.W., and Li, L.J., *Wafer-scale MoS₂ thin layers prepared by MoO₃ sulfurization*. Nanoscale, 2012. **4**(20): p. 6637-6641.
- [93] Pyeon, J.J., Kim, S.H., Jeong, D.S., Baek, S.H., Kang, C.Y., Kim, J.S., and Kim, S.K., *Wafer-scale growth of MoS₂ thin films by atomic layer deposition*. Nanoscale, 2016. **8**(20): p. 10792-10798.
- [94] Wang, X.S., Feng, H.B., Wu, Y.M., and Jiao, L.Y., *Controlled Synthesis of Highly Crystalline MoS₂ Flakes by Chemical Vapor Deposition*. Journal of the American Chemical Society, 2013. **135**(14): p. 5304-5307.
- [95] Liu, H.F., Wong, S.L., and Chi, D.Z., *CVD Growth of MoS₂-based Two-dimensional Materials*. Chemical Vapor Deposition, 2015. **21**(10-12): p. 241-259.
- [96] Das, S., Chen, H.Y., Penumatcha, A.V., and Appenzeller, J., *High Performance Multilayer MoS₂ Transistors with Scandium Contacts*. Nano Letters, 2013. **13**(1): p. 100-105.
- [97] Ganatra, R. and Zhang, Q., *Few-Layer MoS₂: A Promising Layered Semiconductor*. Acs Nano, 2014. **8**(5): p. 4074-4099.
- [98] Butler, S.Z., Hollen, S.M., Cao, L.Y., Cui, Y., Gupta, J.A., Gutierrez, H.R., Heinz, T.F., Hong, S.S., Huang, J.X., Ismach, A.F., Johnston-Halperin, E., Kuno, M., Plashnitsa, V.V., Robinson, R.D., Ruoff, R.S., Salahuddin, S., Shan, J., Shi, L., Spencer, M.G., Terrones, M., Windl, W., and Goldberger, J.E., *Progress, Challenges, and Opportunities in Two-Dimensional Materials Beyond Graphene*. Acs Nano, 2013. **7**(4): p. 2898-2926.
- [99] Xu, M.S., Liang, T., Shi, M.M., and Chen, H.Z., *Graphene-Like Two-Dimensional Materials*. Chemical Reviews, 2013. **113**(5): p. 3766-3798.

- [100] Ling, X., Lee, Y.H., Lin, Y.X., Fang, W.J., Yu, L.L., Dresselhaus, M.S., and Kong, J., *Role of the Seeding Promoter in MoS₂ Growth by Chemical Vapor Deposition*. Nano Letters, 2014. **14**(2): p. 464-472.
- [101] Li, X., Li, X., Zang, X., Zhu, M., He, Y., Wang, K., Xie, D., and Zhu, H., *Role of hydrogen in the chemical vapor deposition growth of MoS₂ atomic layers*. Nanoscale, 2015. **7**(18): p. 8398-8404.
- [102] Chen, W., Zhao, J., Zhang, J., Gu, L., Yang, Z.Z., Li, X.M., Yu, H., Zhu, X.T., Yang, R., Shi, D.X., Lin, X.C., Guo, J.D., Bai, X.D., and Zhang, G.Y., *Oxygen-Assisted Chemical Vapor Deposition Growth of Large Single-Crystal and High-Quality Monolayer MoS₂*. Journal of the American Chemical Society, 2015. **137**(50): p. 15632-15635.
- [103] Jeon, J., Jang, S.K., Jeon, S.M., Yoo, G., Jang, Y.H., Park, J.H., and Lee, S., *Layer-controlled CVD growth of large-area two-dimensional MoS₂ films*. Nanoscale, 2015. **7**(5): p. 1688-1695.
- [104] Shanshan, W., Merce, P., Harish, B., and Jamie, H.W., *Substrate control for large area continuous films of monolayer MoS₂ by atmospheric pressure chemical vapor deposition*. Nanotechnology, 2016. **27**(8): p. 085604.
- [105] van der Zande, A.M., Huang, P.Y., Chenet, D.A., Berkelbach, T.C., You, Y., Lee, G.-H., Heinz, T.F., Reichman, D.R., Muller, D.A., and Hone, J.C., *Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide*. Nature Materials, 2013. **12**(6): p. 554-561.
- [106] *Controlled synthesis of highly crystalline MoS₂ flakes by chemical vapor deposition*. J. Am. Chem. Soc., 2013. **135**: p. 5304.
- [107] Kang, K., Xie, S., Huang, L., Han, Y., Huang, P.Y., Mak, K.F., Kim, C.-J., Muller, D., and Park, J., *High-mobility three-atom-thick semiconducting films with wafer-scale homogeneity*. Nature, 2015. **520**(7549): p. 656-660.
- [108] Lee, Y.-H., Zhang, X.-Q., Zhang, W., Chang, M.-T., Lin, C.-T., Chang, K.-D., Yu, Y.-C., Wang, J.T.-W., Chang, C.-S., Li, L.-J., and Lin, T.-W., *Synthesis of Large-Area MoS₂ Atomic Layers with Chemical Vapor Deposition*. Advanced Materials, 2012. **24**(17): p. 2320-2325.
- [109] Dumcenco, D., Ovchinnikov, D., Marinov, K., Lazic, P., Gibertini, M., Marzari, N., Sanchez, O.L., Kung, Y.C., Krasnozhan, D., Chen, M.W., Bertolazzi, S., Gillet, P., Morral, A.F.I., Radenovic, A., and Kis, A., *Large-Area Epitaxial Monolayer MoS₂*. ACS Nano, 2015. **9**(4): p. 4611-4620.
- [110] Ji, Q.Q., Zhang, Y.F., Gao, T., Zhang, Y., Ma, D.L., Liu, M.X., Chen, Y.B., Qiao, X.F., Tan, P.H., Kan, M., Feng, J., Sun, Q., and Liu, Z.F., *Epitaxial Monolayer MoS₂ on Mica with Novel Photoluminescence*. Nano Letters, 2013. **13**(8): p. 3870-3877.
- [111] Cain, J.D., Shi, F., Wu, J., and Dravid, V.P., *Growth Mechanism of Transition Metal Dichalcogenide Monolayers: The Role of Self-Seeding Fullerene Nuclei*. ACS Nano, 2016. **10**(5): p. 5440-5445.
- [112] Shang, S.L., Lindwall, G., Wang, Y., Redwing, J.M., Anderson, T., and Liu, Z.K., *Lateral Versus Vertical Growth of Two-Dimensional Layered Transition-Metal Dichalcogenides: Thermodynamic Insight into MoS₂*. Nano Letters, 2016. **16**(9): p. 5742-5750.
- [113] Wang, S., Rong, Y., Fan, Y., Pacios, M., Bhaskaran, H., He, K., and Warner, J.H., *Shape Evolution of Monolayer MoS₂ Crystals Grown by Chemical Vapor Deposition*. Chemistry of Materials, 2014. **26**(22): p. 6371-6379.

- [114] Govind Rajan, A., Warner, J.H., Blankschtein, D., and Strano, M.S., *Generalized Mechanistic Model for the Chemical Vapor Deposition of 2D Transition Metal Dichalcogenide Monolayers*. ACS Nano, 2016. **10**(4): p. 4330-4344.
- [115] Nihan Kosku, P. and Mehmet, B., *Investigation of Single-Wall MoS₂ Monolayer Flakes Grown by Chemical Vapor Deposition*. Nano-Micro Letters, 2015. **8**(?).
- [116] Li, H., Wu, H., Yuan, S., and Qian, H., *Synthesis and characterization of vertically standing MoS₂ nanosheets*. Scientific Reports, 2016. **6**: p. 21171.
- [117] Ling, L., Wang, C., Zhang, K., Li, T., Tang, L., Li, C., Wang, L., Xu, Y., Song, Q., and Yao, Y., *Controlled growth of MoS₂ nanopetals and their hydrogen evolution performance*. RSC Advances, 2016. **6**(22): p. 18483-18489.
- [118] Lin, Z.Y., Zhao, Y.D., Zhou, C.J., Zhong, R., Wang, X.S., Tsang, Y.H., and Chai, Y., *Controllable Growth of Large-Size Crystalline MoS₂ and Resist-Free Transfer Assisted with a Cu Thin Film*. Scientific Reports, 2015. **5**.
- [119] Ayberk, Ö., Feridun, A., Cem, S., and Nihan Kosku, P., *CVD growth of monolayer MoS₂ : Role of growth zone configuration and precursors ratio*. Japanese Journal of Applied Physics, 2017. **56**(6S1): p. 06GG05.
- [120] Ferraro, J.R., *Introductory raman spectroscopy*. 2003: Elsevier.
- [121] Graves, P. and Gardiner, D., *Practical raman spectroscopy*. Springer, 1989.
- [122] Smith, G.P., McGoverin, C.M., Fraser, S.J., and Gordon, K.C., *Raman imaging of drug delivery systems*. Advanced drug delivery reviews, 2015. **89**: p. 21-41.
- [123] Luo, X., Zhao, Y.Y., Zhang, J., Xiong, Q.H., and Quek, S.Y., *Anomalous frequency trends in MoS₂ thin films attributed to surface effects*. Physical Review B, 2013. **88**(7).
- [124] Lee, C., Yan, H., Brus, L.E., Heinz, T.F., Hone, J., and Ryu, S., *Anomalous Lattice Vibrations of Single- and Few-Layer MoS₂*. ACS Nano, 2010. **4**(5): p. 2695-2700.
- [125] Molina-Sanchez, A. and Wirtz, L., *Phonons in single-layer and few-layer MoS₂ and WS₂*. Physical Review B, 2011. **84**(15): p. 155413.
- [126] Li, H., Zhang, Q., Yap, C.C.R., Tay, B.K., Edwin, T.H.T., Olivier, A., and Baillargeat, D., *From Bulk to Monolayer MoS₂: Evolution of Raman Scattering*. Advanced Functional Materials, 2012. **22**(7): p. 1385-1390.
- [127] Chakraborty, B., Matte, H., Sood, A., and Rao, C., *Layer-dependent resonant Raman scattering of a few layer MoS₂*. Journal of Raman Spectroscopy, 2013. **44**(1): p. 92-96.
- [128] Zhang, W.J., Huang, J.K., Chen, C.H., Chang, Y.H., Cheng, Y.J., and Li, L.J., *High-Gain Phototransistors Based on a CVD MoS₂ Monolayer*. Advanced Materials, 2013. **25**(25): p. 3456-3461.
- [129] Chakraborty, B., Bera, A., Muthu, D., Bhowmick, S., Waghmare, U.V., and Sood, A., *Symmetry-dependent phonon renormalization in monolayer MoS₂ transistor*. Physical Review B, 2012. **85**(16): p. 161403.
- [130] Yong, X., Zhan, W., Yongjie, Z., Peng, Z., Ruixue, W., Teng, J., Shiwei, W., Hong, W., Ying, Z., Tang, N., and Xiaohua, M., *Controllable growth of monolayer MoS₂ by chemical vapor deposition via close MoO₃ precursor for electrical and optical applications*. Nanotechnology, 2017. **28**(8): p. 084001.
- [131] Camacho-López, M.A., Escobar-Alarcón, L., Picquart, M., Arroyo, R., Córdoba, G., and Haro-Poniatowski, E., *Micro-Raman study of the m-MoO₃ to α-MoO₃ transformation induced by cw-laser irradiation*. Optical Materials, 2011. **33**(3): p. 480-484.
- [132] Dieterle, M. and Mestl, G., *Raman spectroscopy of molybdenum oxides*. Physical Chemistry Chemical Physics, 2002. **4**(5): p. 822-826.

- [133] Najmaei, S., Liu, Z., Zhou, W., Zou, X., Shi, G., Lei, S., Yakobson, B.I., Idrobo, J.-C., Ajayan, P.M., and Lou, J., *Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers*. Nat Mater, 2013. **12**(8): p. 754-759.
- [134] *Role of kinetic factors in chemical vapor deposition synthesis of uniform large area graphene using copper catalyst*. Nano Lett., 2010. **10**: p. 4128.
- [135] Gao, J., Yip, J., Zhao, J., Yakobson, B.I., and Ding, F., *Graphene Nucleation on Transition Metal Surface: Structure Transformation and Role of the Metal Step Edge*. Journal of the American Chemical Society, 2011. **133**(13): p. 5009-5015.
- [136] Chen, C.Y., Qiao, H., Xue, Y.Z., Yu, W.Z., Song, J.C., Lu, Y., Li, S.J., and Bao, Q.L., *Growth of large-area atomically thin MoS₂ film via ambient pressure chemical vapor deposition*. Photonics Research, 2015. **3**(4): p. 110-114.
- [137] Ohring, M., *Chapter 3 - Thin-Film Evaporation Processes*, in *Materials Science of Thin Films (Second Edition)*. 2002, Academic Press: San Diego. p. 95-144.
- [138] Li, J. and Östling, M., *Scalable fabrication of 2D semiconducting crystals for future electronics*. Electronics, 2015. **4**(4): p. 1033-1061.
- [139] Senthilkumar, V., Tam, L.C., Kim, Y.S., Sim, Y., Seong, M.-J., and Jang, J.I., *Direct vapor phase growth process and robust photoluminescence properties of large area MoS₂ layers*. Nano Research, 2014. **7**(12): p. 1759-1768.
- [140] Wu, D., Huang, H., Zhu, X., He, Y., Xie, Q., Chen, X., Zheng, X., Duan, H., and Gao, Y., *E'' Raman Mode in Thermal Strain-Fractured CVD-MoS₂*. Crystals, 2016. **6**(11): p. 151.
- [141] Niehues, I., Blob, A., Stiehm, T., Schmidt, R., Jadriško, V., Radatović, B., Čapeta, D., Kralj, M., de Vasconcellos, S.M., and Bratschitsch, R., *Strain transfer across grain boundaries in MoS₂ monolayers grown by chemical vapor deposition*. 2D Materials, 2018. **5**(3): p. 031003.
- [142] Guo, H.Y., Lu, N., Wang, L., Wu, X.J., and Zeng, X.C., *Tuning Electronic and Magnetic Properties of Early Transition-Metal Dichalcogenides via Tensile Strain*. Journal of Physical Chemistry C, 2014. **118**(13): p. 7242-7249.
- [143] Conley, H.J., Wang, B., Ziegler, J.I., Haglund, R.F., Pantelides, S.T., and Bolotin, K.I., *Bandgap Engineering of Strained Monolayer and Bilayer MoS₂*. Nano Letters, 2013. **13**(8): p. 3626-3630.
- [144] Gao, J., Li, B., Tan, J., Chow, P., Lu, T.-M., and Koratkar, N., *Aging of Transition Metal Dichalcogenide Monolayers*. ACS Nano, 2016. **10**(2): p. 2628-2635.
- [145] *Controlled preferential oxidation of grain boundaries in monolayer tungsten disulfide for direct optical imaging*. ACS Nano, 2015. **9**: p. 3695.
- [146] Costa, D., Levy, F., Schmid, P., and Tissot, P., *Chemical-Composition of Thin MoS₂ Films as a Function of Their Thickness and of Aging Conditions*. Helvetica Physica Acta, 1987. **60**(5-6): p. 839-839.
- [147] Yang, P., Zou, X., Zhang, Z., Hong, M., Shi, J., Chen, S., Shu, J., Zhao, L., Jiang, S., and Zhou, X., *Batch production of 6-inch uniform monolayer molybdenum disulfide catalyzed by sodium in glass*. Nature communications, 2018. **9**(1): p. 979.
- [148] Chen, J., Zhao, X., Tan, S.J.R., Xu, H., Wu, B., Liu, B., Fu, D., Fu, W., Geng, D., Liu, Y., Liu, W., Tang, W., Li, L., Zhou, W., Sum, T.C., and Loh, K.P., *Chemical Vapor Deposition of Large-Size Monolayer MoSe₂ Crystals on Molten Glass*. Journal of the American Chemical Society, 2017. **139**(3): p. 1073-1076.

- [149] Wang, Z., Xie, Y., Wang, H., Wu, R., Nan, T., Zhan, Y., Sun, J., Jiang, T., Zhao, Y., and Lei, Y., *NaCl-assisted one-step growth of MoS₂-WS₂ in-plane heterostructures*. Nanotechnology, 2017. **28**(32): p. 325602.
- [150] Şar, H., Özden, A., Demiroğlu, İ., Sevik, C., Perkgoz, N.K., and Ay, F., *Long-Term Stability Control of CVD-Grown Monolayer MoS₂*. physica status solidi (RRL)–Rapid Research Letters: p. 1800687.
- [151] Yorulmaz, B., Özden, A., Şar, H., Ay, F., Sevik, C., and Perkgoz, N.K., *CVD growth of monolayer WS₂ through controlled seed formation and vapor density*. Materials Science in Semiconductor Processing, 2019. **93**: p. 158-163.
- [152] Taghipour, N., Hernandez Martinez, P.L., Ozden, A., Olutas, M., Dede, D., Gungor, K., Erdem, O., Perkgoz, N.K., and Demir, H.V., *Near-Unity Efficiency Energy Transfer from Colloidal Semiconductor Quantum Wells of CdSe/CdS Nanoplatelets to a Monolayer of MoS₂*. ACS nano, 2018. **12**(8): p. 8547-8554.
- [153] Bay, M., Özden, A., Ay, F., and Perkgoz, N.K., *Bandgap tuning of Monolayer MoS₂ (1-x) Se_{2x} alloys by optimizing parameters*. Materials Science in Semiconductor Processing, 2019. **99**: p. 134-139.
- [154] Druffel, D.L., Woomer, A.H., Kuntz, K.L., Pawlik, J.T., and Warren, S.C., *Electrons on the surface of 2D materials: from layered electrides to 2D electrenes*. Journal of Materials Chemistry C, 2017.
- [155] Dye, J.L., *Electrons as Anions*. Science, 2003. **301**: p. 607-608.
- [156] Dye, J.L., *Electrides: Early Examples of Quantum Confinement*. Accounts of Chemical Research, 2009. **42**(10): p. 1564-1572.
- [157] Mani, R.G., Smet, J.H., von Klitzing, K., Narayanamurti, V., Johnson, W.B., and Umansky, V., *Zero-resistance states induced by electromagnetic-wave excitation in GaAs/AlGaAs heterostructures*. Nature, 2002. **420**(6916): p. 646-650.
- [158] Ohtomo, A. and Hwang, H.Y., *A high-mobility electron gas at the LaAlO₃/SrTiO₃ heterointerface*. Nature, 2004. **427**(6973): p. 423-426.
- [159] Ellaboudy, A., Dye, J.L., and Smith, P.B., *Cesium 18-crown-6 compounds. A crystalline ceside and a crystalline electride*. Journal of the American Chemical Society, 1983. **105**(21): p. 6490-6491.
- [160] Ichimura, A.S., Dye, J.L., Camblor, M.A., and Villaescusa, L.A., *Toward Inorganic Electrides*. Journal of the American Chemical Society, 2002. **124**(7): p. 1170-1171.
- [161] Matsuishi, S., Toda, Y., Miyakawa, M., Hayashi, K., Kamiya, T., Hirano, M., Tanaka, I., and Hosono, H., *High-Density Electron Anions in a Nanoporous Single Crystal: [Ca₂₄Al₂₈O₆₄]_{4+4e⁻}*. Science, 2003. **301**(5633): p. 626.
- [162] Zhang, Y., Xiao, Z., Kamiya, T., and Hosono, H., *Electron Confinement in Channel Spaces for One-Dimensional Electride*. The Journal of Physical Chemistry Letters, 2015. **6**(24): p. 4966-4971.
- [163] Wang, J., Hanzawa, K., Hiramatsu, H., Kim, J., Umezawa, N., Iwanaka, K., Tada, T., and Hosono, H., *Exploration of Stable Strontium Phosphide-Based Electrides: Theoretical Structure Prediction and Experimental Validation*. Journal of the American Chemical Society, 2017. **139**(44): p. 15668-15680.
- [164] Lee, K., Kim, S.W., Toda, Y., Matsuishi, S., and Hosono, H., *Dicalcium nitride as a two-dimensional electride with an anionic electron layer*. Nature, 2013. **494**(7437): p. 336-340.
- [165] Walsh, A. and Scanlon, D.O., *Electron excess in alkaline earth sub-nitrides: 2D electron gas or 3D electride?* Journal of Materials Chemistry C, 2013. **1**(22): p. 3525-3528.

- [166] Zhang, X., Xiao, Z., Lei, H., Toda, Y., Matsuishi, S., Kamiya, T., Ueda, S., and Hosono, H., *Two-Dimensional Transition-Metal Electride Y₂C*. Chemistry of Materials, 2014. **26**(22): p. 6638-6643.
- [167] Oh, J.S., Kang, C.-J., Kim, Y.J., Sinn, S., Han, M., Chang, Y.J., Park, B.-G., Kim, S.W., Min, B.I., Kim, H.-D., and Noh, T.W., *Evidence for Anionic Excess Electrons in a Quasi-Two-Dimensional Ca₂N Electride by Angle-Resolved Photoemission Spectroscopy*. Journal of the American Chemical Society, 2016. **138**(8): p. 2496-2499.
- [168] Medvedeva, J.E. and Freeman, A.J., *Hopping versus bulk conductivity in transparent oxides: 12CaO·7Al₂O₃*. Applied Physics Letters, 2004. **85**(6): p. 955-957.
- [169] Kim, S.W., Toda, Y., Hayashi, K., Hirano, M., and Hosono, H., *Synthesis of a Room Temperature Stable 12CaO·7Al₂O₃ Electride from the Melt and Its Application as an Electron Field Emitter*. Chemistry of Materials, 2006. **18**(7): p. 1938-1944.
- [170] Kitano, M., Inoue, Y., Yamazaki, Y., Hayashi, F., Kanbara, S., Matsuishi, S., Yokoyama, T., Kim, S.-W., Hara, M., and Hosono, H., *Ammonia synthesis using a stable electride as an electron donor and reversible hydrogen store*. Nature Chemistry, 2012. **4**: p. 934.
- [171] Miyakawa, M., Kim, S.W., Hirano, M., Kohama, Y., Kawaji, H., Atake, T., Ikegami, H., Kono, K., and Hosono, H., *Superconductivity in an Inorganic Electride 12CaO·7Al₂O₃:e*. Journal of the American Chemical Society, 2007. **129**(23): p. 7270-7271.
- [172] Hosono, H., *Two classes of superconductors discovered in our material research: Iron-based high temperature superconductor and electride superconductor*. Physica C: Superconductivity, 2009. **469**(9): p. 314-325.
- [173] Hu, J., Xu, B., Yang, S.A., Guan, S., Ouyang, C., and Yao, Y., *2D Electrides as Promising Anode Materials for Na-Ion Batteries from First-Principles Study*. ACS Applied Materials & Interfaces, 2015. **7**(43): p. 24016-24022.
- [174] Chen, G., Bai, Y., Li, H., Li, Y., Wang, Z., Ni, Q., Liu, L., Wu, F., Yao, Y., and Wu, C., *Multilayered Electride Ca₂N Electrode via Compression Molding Fabrication for Sodium Ion Batteries*. ACS Applied Materials & Interfaces, 2017. **9**(8): p. 6666-6669.
- [175] Hou, J., Tu, K., and Chen, Z., *Two-Dimensional Y₂C Electride: A Promising Anode Material for Na-Ion Batteries*. The Journal of Physical Chemistry C, 2016. **120**(33): p. 18473-18478.
- [176] Inoshita, T., Jeong, S., Hamada, N., and Hosono, H., *Exploration for Two-Dimensional Electrides via Database Screening and Ab Initio Calculation*. Physical Review X, 2014. **4**(3): p. 031023.
- [177] Zhang, Y., Wang, H., Wang, Y., Zhang, L., and Ma, Y., *Computer-Assisted Inverse Design of Inorganic Electrides*. Physical Review X, 2017. **7**(1): p. 011017.
- [178] Tada, T., Takemoto, S., Matsuishi, S., and Hosono, H., *High-Throughput ab Initio Screening for Two-Dimensional Electride Materials*. Inorganic Chemistry, 2014. **53**(19): p. 10347-10358.
- [179] Ming, W., Yoon, M., Du, M.-H., Lee, K., and Kim, S.W., *First-Principles Prediction of Thermodynamically Stable Two-Dimensional Electrides*. Journal of the American Chemical Society, 2016. **138**(47): p. 15336-15344.

- [180] Peng, L., Zhu, Y., Chen, D., Ruoff, R.S., and Yu, G., *Two-Dimensional Materials for Beyond-Lithium-Ion Batteries*. Advanced Energy Materials, 2016. **6**(11): p. 1600025-n/a.
- [181] Hwang, J.-Y., Myung, S.-T., and Sun, Y.-K., *Sodium-ion batteries: present and future*. Chemical Society Reviews, 2017. **46**(12): p. 3529-3614.
- [182] Kresse, G. and Hafner, J., *Ab initio molecular dynamics for liquid metals*. Physical Review B, 1993. **47**(1): p. 558-561.
- [183] Perdew, J.P., Burke, K., and Ernzerhof, M., *Generalized Gradient Approximation Made Simple*. Physical Review Letters, 1996. **77**(18): p. 3865-3868.
- [184] Blöchl, P.E., *Projector augmented-wave method*. Physical Review B, 1994. **50**(24): p. 17953-17979.
- [185] Kresse, G. and Joubert, D., *From ultrasoft pseudopotentials to the projector augmented-wave method*. Physical Review B, 1999. **59**(3): p. 1758-1775.
- [186] Togo, A. and Tanaka, I., *First principles phonon calculations in materials science*. Scripta Materialia, 2015. **108**: p. 1-5.
- [187] Henkelman, G., Uberuaga, B.P., and Jónsson, H., *A climbing image nudged elastic band method for finding saddle points and minimum energy paths*. The Journal of Chemical Physics, 2000. **113**(22): p. 9901-9904.
- [188] Guan, S., Yang, S.A., Zhu, L., Hu, J., and Yao, Y., *Electronic, Dielectric, and Plasmonic Properties of Two-Dimensional Electride Materials $X(2)N$ ($X=Ca, Sr$): A First-Principles Study*. Scientific Reports, 2015. **5**: p. 12285.
- [189] Baroni, S., de Gironcoli, S., Dal Corso, A., and Giannozzi, P., *Phonons and related crystal properties from density-functional perturbation theory*. Reviews of Modern Physics, 2001. **73**(2): p. 515-562.
- [190] Li, Y.-L., Wang, S.-N., Oganov, A.R., Gou, H., Smith, J.S., and Strobel, T.A., *Investigation of exotic stable calcium carbides using theory and experiment*. Nature Communications, 2015. **6**: p. 6974.
- [191] Sansone, G., Maschio, L., Usvyat, D., Schütz, M., and Karttunen, A., *Toward an Accurate Estimate of the Exfoliation Energy of Black Phosphorus: A Periodic Quantum Chemical Approach*. The Journal of Physical Chemistry Letters, 2016. **7**(1): p. 131-136.
- [192] Cakr, D., Sevik, C., Gulseren, O., and Peeters, F.M., *Mo₂C as a high capacity anode material: a first-principles study*. Journal of Materials Chemistry A, 2016. **4**(16): p. 6029-6035.
- [193] Hardikar, R.P., Das, D., Han, S.S., Lee, K.-R., and Singh, A.K., *Boron doped defective graphene as a potential anode material for Li-ion batteries*. Physical Chemistry Chemical Physics, 2014. **16**(31): p. 16502-16508.
- [194] Xie, Y., Dall'Agnese, Y., Naguib, M., Gogotsi, Y., Barsoum, M.W., Zhuang, H.L., and Kent, P.R.C., *Prediction and Characterization of MXene Nanosheet Anodes for Non-Lithium-Ion Batteries*. ACS Nano, 2014. **8**(9): p. 9606-9615.
- [195] Lindström, H., Södergren, S., Solbrand, A., Rensmo, H., Hjelm, J., Hagfeldt, A., and Lindquist, S.-E., *Li⁺ Ion Insertion in TiO₂ (Anatase). 2. Voltammetry on Nanoporous Films*. The Journal of Physical Chemistry B, 1997. **101**(39): p. 7717-7722.
- [196] Lunell, S., Stashans, A., Ojamäe, L., Lindström, H., and Hagfeldt, A., *Li and Na Diffusion in TiO₂ from Quantum Chemical Theory versus Electrochemical Experiment*. Journal of the American Chemical Society, 1997. **119**(31): p. 7374-7380.

- [197] Olson, C.L., Nelson, J., and Islam, M.S., *Defect Chemistry, Surface Structures, and Lithium Insertion in Anatase TiO₂*. The Journal of Physical Chemistry B, 2006. **110**(20): p. 9995-10001.
- [198] Uthaisar, C. and Barone, V., *Edge Effects on the Characteristics of Li Diffusion in Graphene*. Nano Letters, 2010. **10**(8): p. 2838-2842.
- [199] Li, W., Yang, Y., Zhang, G., and Zhang, Y.-W., *Ultrafast and Directional Diffusion of Lithium in Phosphorene for High-Performance Lithium-Ion Battery*. Nano Letters, 2015. **15**(3): p. 1691-1697.
- [200] Jing, Y., Zhou, Z., Cabrera, C.R., and Chen, Z., *Metallic VS₂ Monolayer: A Promising 2D Anode Material for Lithium Ion Batteries*. The Journal of Physical Chemistry C, 2013. **117**(48): p. 25409-25413.



APPENDIX-1

In this work, 532 nm CW laser with 1 mW laser power is used for PL and Raman maps. 485 nm pulsed laser with 80 MHz repetition rate (12.5 ns) is used for the lifetime mapping. We used 0.9 mW pulsed laser power (maximum output of our pulsed laser) considering having a better signal to noise ratio. IRF FWHM of the photon counting detector (MPD brand) is 49 ps at the wavelength of 670 nm.

Normalized decay curves of the Points 1 to Point 8 was given in Figure A1.1 below.

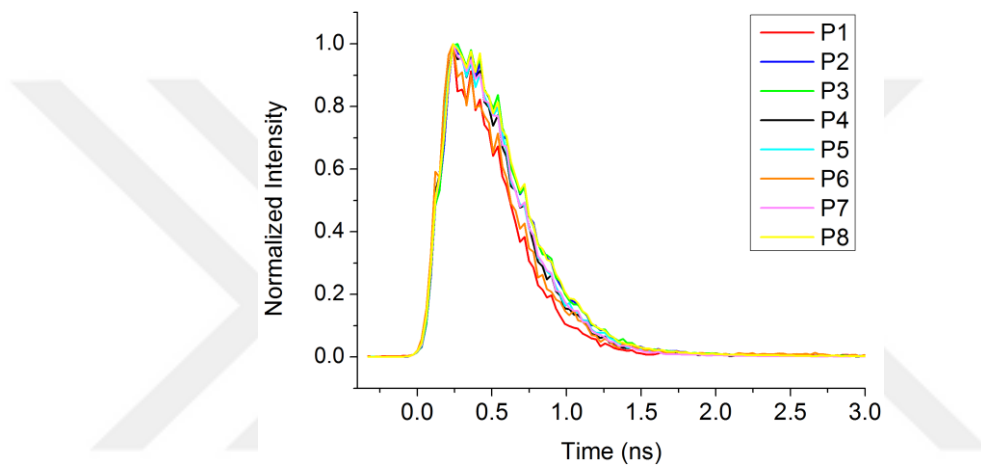


Figure A1.1 Normalized decay curves and corresponding lifetimes of the points taken from the film region. Color code refers to color of the cross marks on the film.

Fitting is performed with the Control FOUR program of the WITEC company by using exponential decay function:

$$y = y_0 + \sum_{i=0}^{n-1} Amp_i e^{\frac{-x-x_0}{t_i}}$$

n : Exponential decay order

y_0 : Offset

x_0 : Center

Amp_i : Amplitude

t_i : Decay constant

Fitting procedure was explained by using two different points on the film region as an example. Lifetime data lies between 0 to 12.5 ns as can be seen below. Shaded areas in the figure indicate selected fitting region, where it ranges from 0.6 ns to 3 ns. We applied $n = 1$ exponential decay fit (single component decay) and neglect the lifetime data smaller than 0.6 ns to prevent the effect of fast transitions. Due to the nature of the mapping procedure and subsequent data analysis limitations, this value was chosen large enough to prevent any interference with the fast transition region. This means that, fast transition zone could change point to point (shrinks or enlarges in nanoseconds unit) due to the probed microstructure on the film. Since we are not able to change this value simultaneously during the fitting of 375 x 375 data point, to be on the safe side fitting started from 0.6 ns.

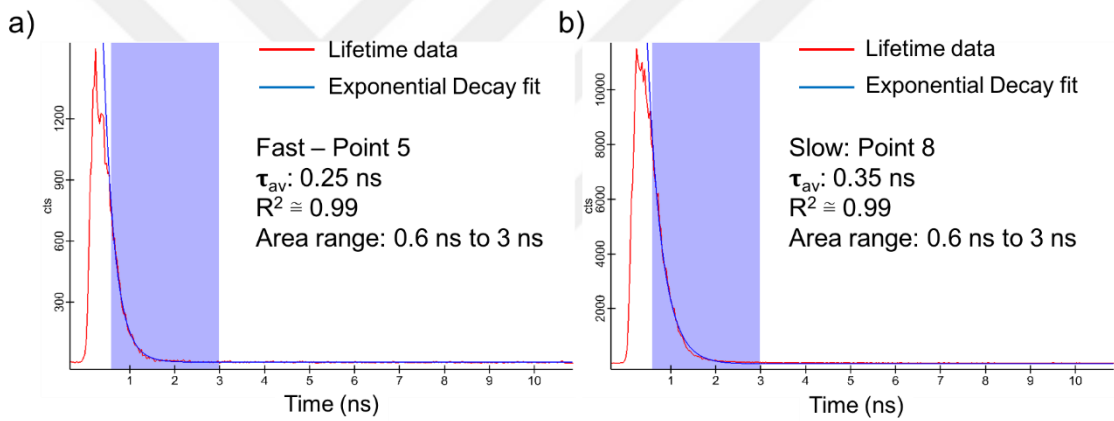
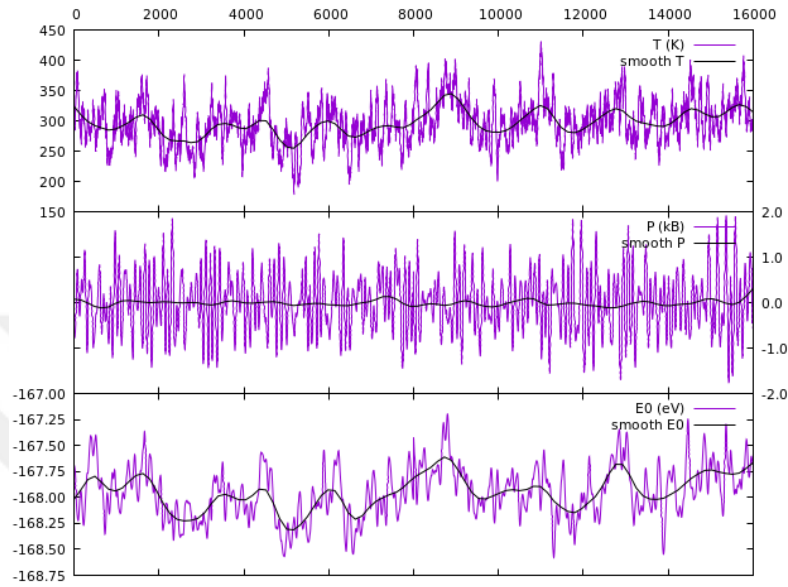


Figure A1.2 Lifetime decay data (red curves) and exponential fits (red curves) within the range of 0.35 ns to 4 ns (shaded area). a) point 5: bilayer to three layer, and b) point 8: monolayer.

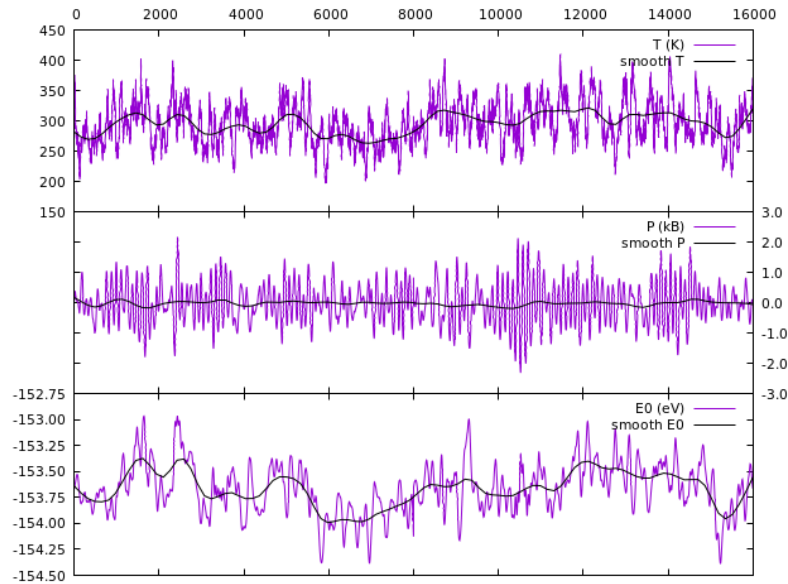
APPENDIX-2

Figures below show the temperature, pressure, total energy curves and radial distribution functions of NPT ensemble ab-initio MD calculations

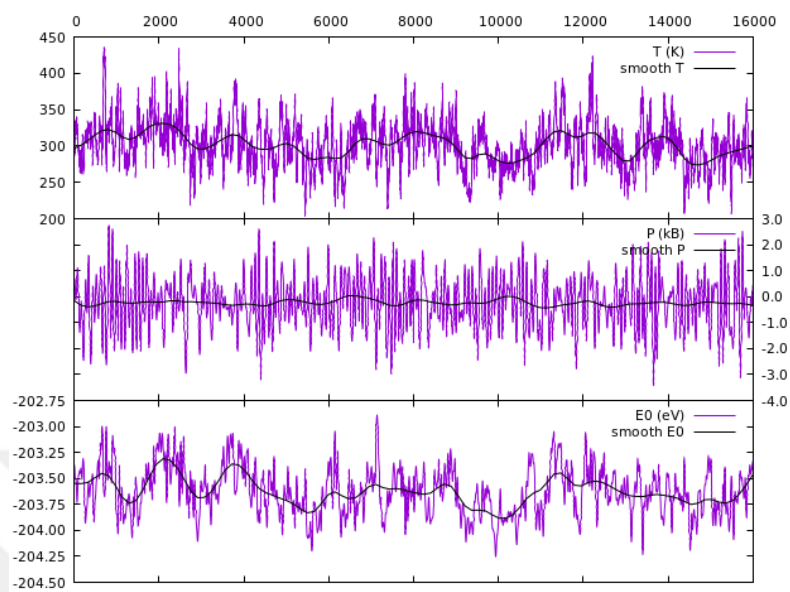
Ba₂As (300K):



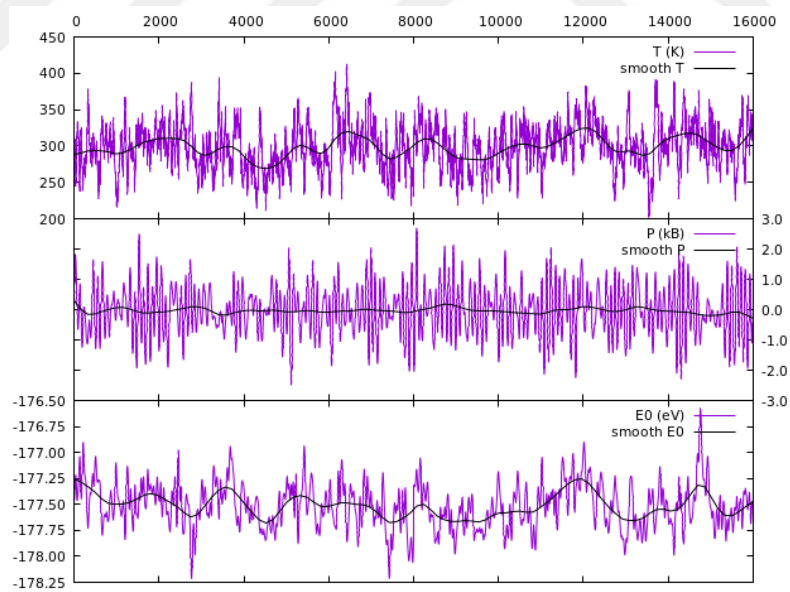
Ba₂Sb (300K):



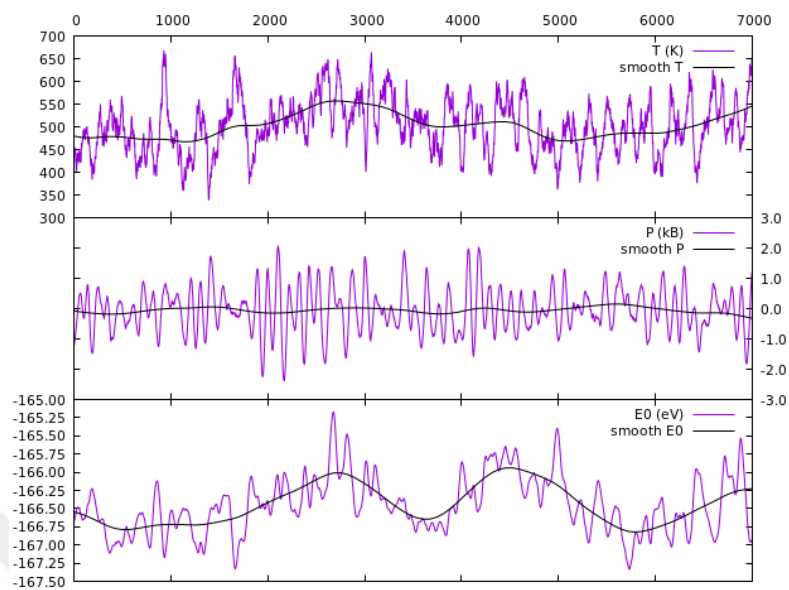
Ba₂N (300K):



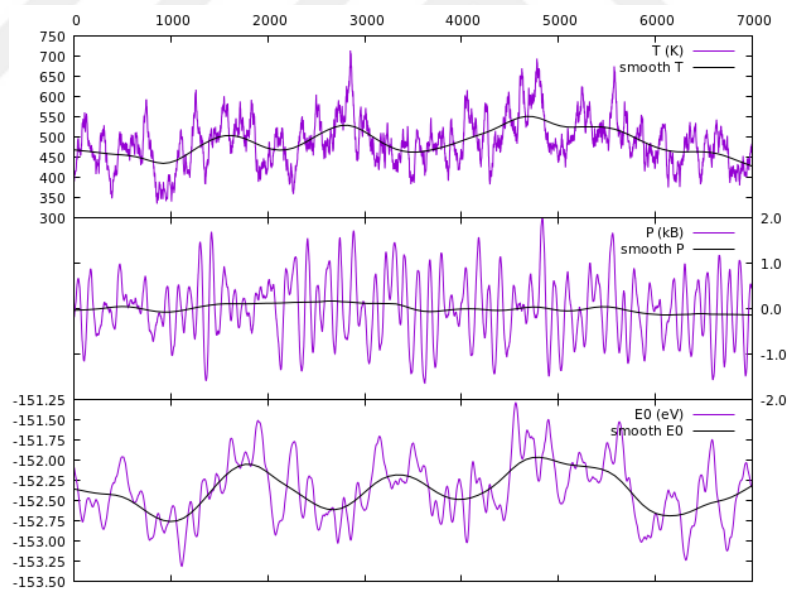
Ba₂P (300K):



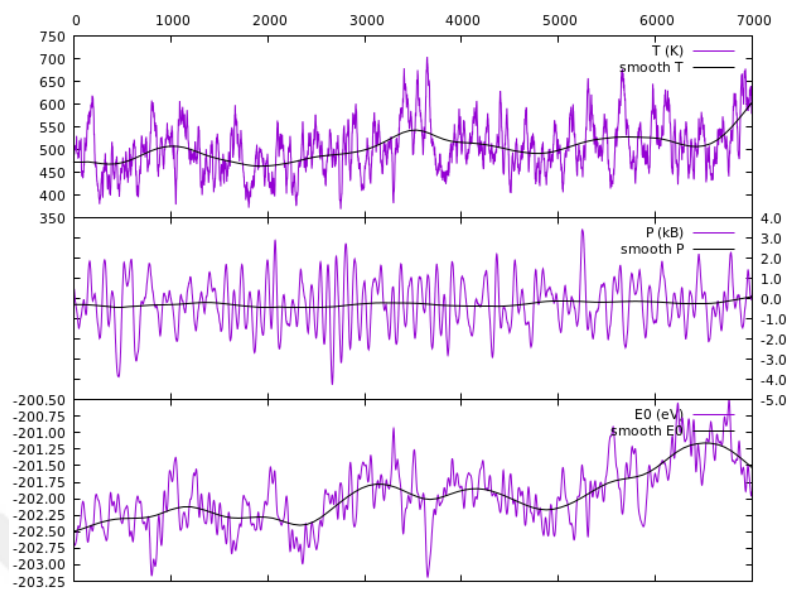
Ba₂As (500K):



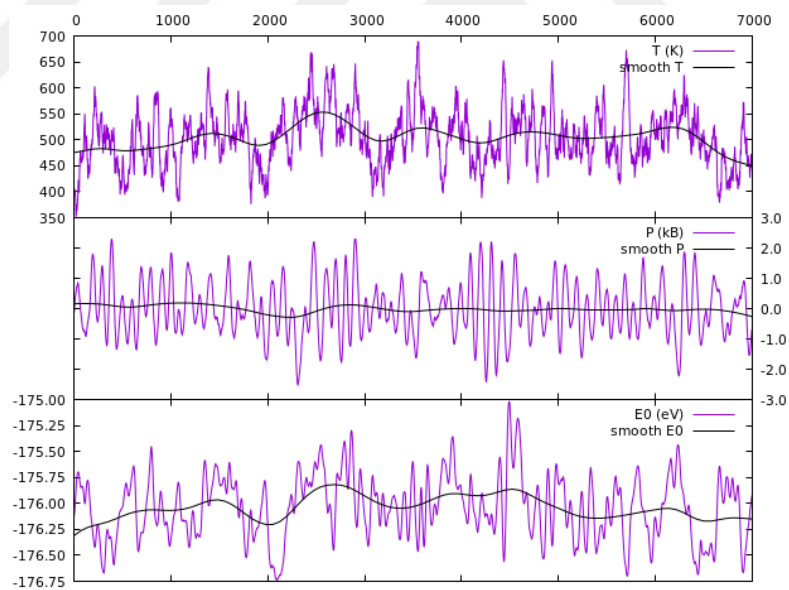
Ba₂Sb (500K):



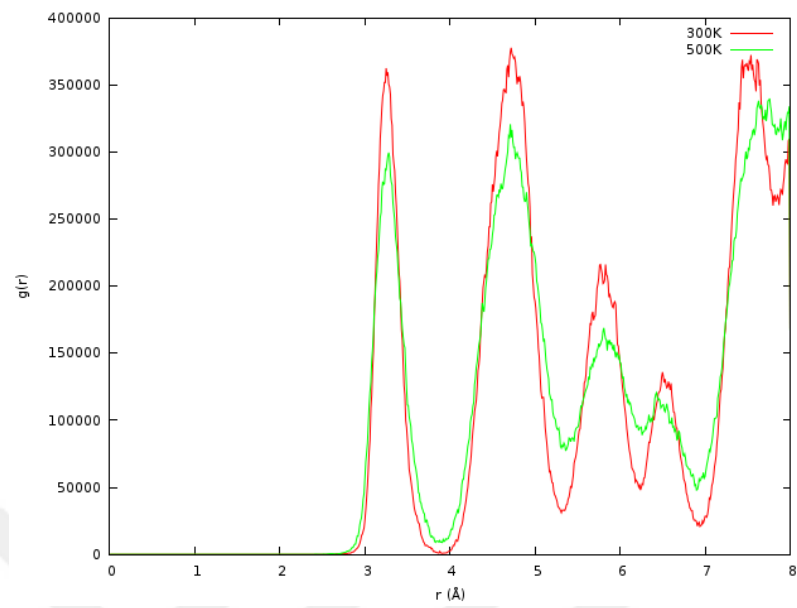
Ba₂N (500K):



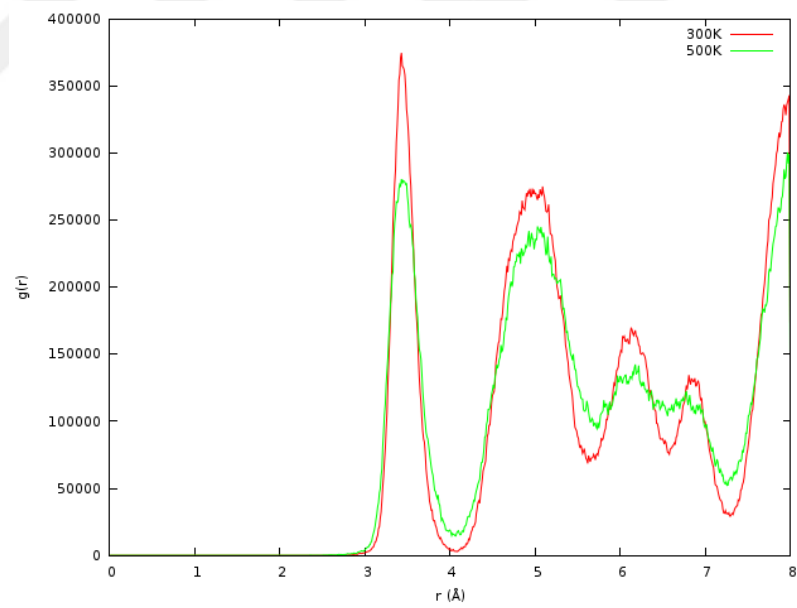
Ba₂P (500K):



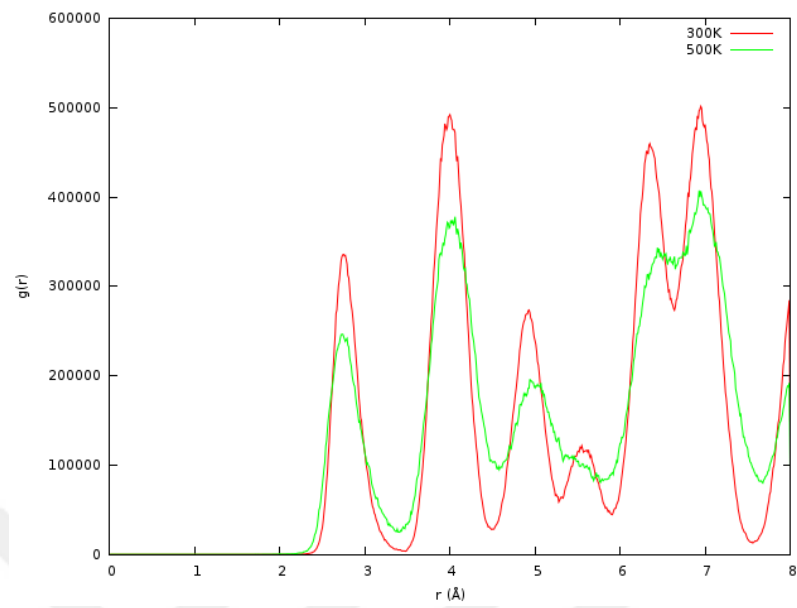
Ba₂As (rdf):



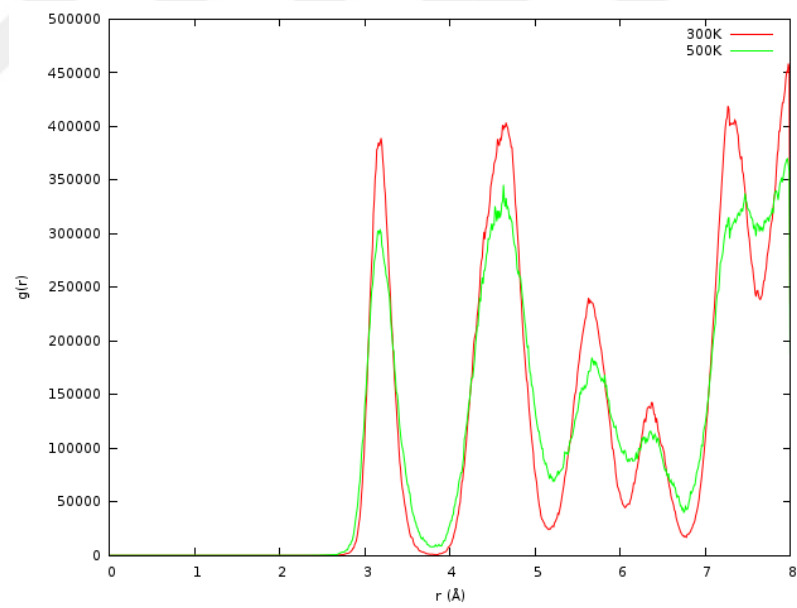
Ba₂Sb (rdf):



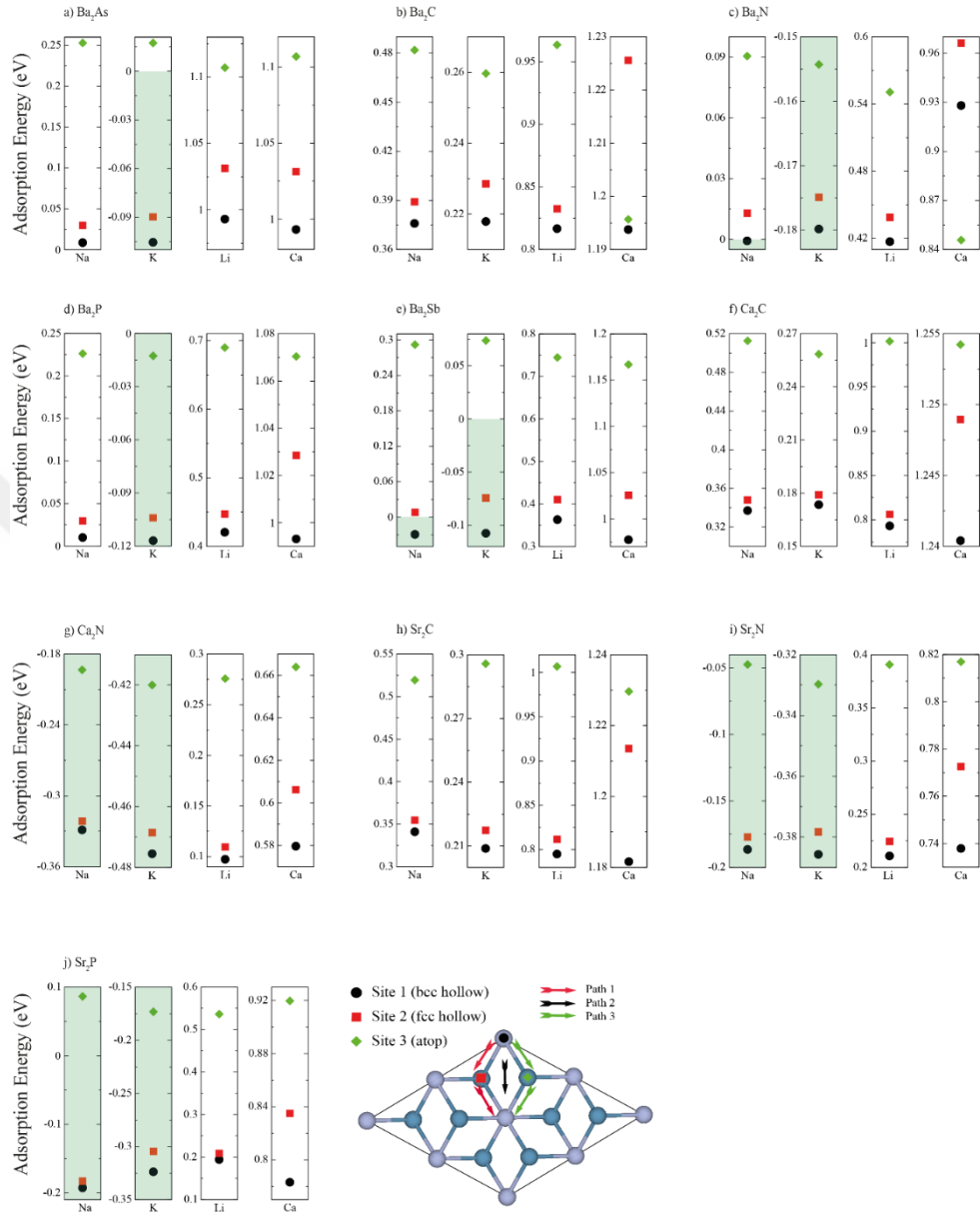
Ba₂N (rdf):



Ba₂P (rdf):

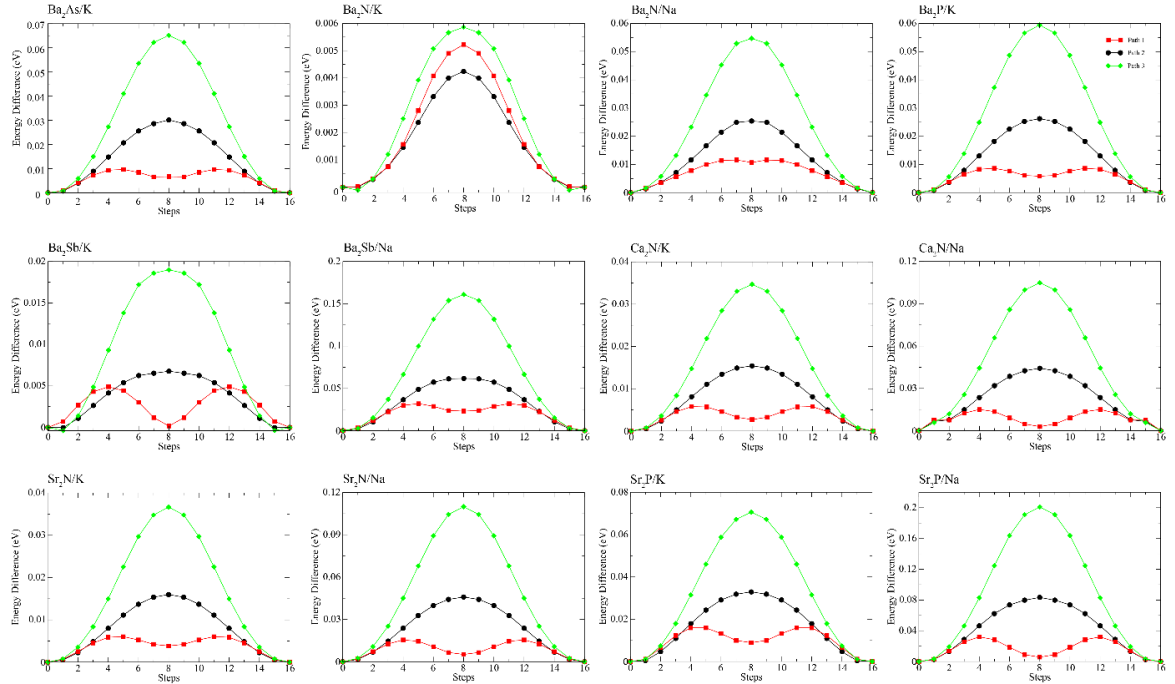


APPENDIX-3



Adsorption energies for Na, K, Li and Ca on the selected sites of the dynamically stable electrene crystals for a) Ba_2As , b) Ba_2C , c) Ba_2N , d) Ba_2P , e) Ba_2Sb , f) Ca_2C , g) Ca_2N , h) Sr_2C i) Sr_2N and j) Sr_2P . Selected sites are depicted right below corner of the figure. Green color indicates an adsorption energy below 0 eV (favorable adsorption).

APPENDIX-4



Diffusion barrier profiles of K and Na on the dynamically stable systems having negative binding energies.

RESUME

Name Surname: Ayberk ÖZDEN

Foreign Language: English

Birth Place and Date: Çorlu / 02.01.1985

E-mail: ozden.ayberk@gmail.com

EDUCATION

2013 – Current	Eskişehir Technical University	Ph.D.
2009-2012	Augsburg University	M.Sc.
2003-2008	Anadolu University	B.Sc.

SCI PUBLICATIONS

1. M. Bay, A. Özden, F. Ay, N. K. Perkgöz, “ Bandgap Tuning of Monolayer MoS₂(1-x)Se_{2x} alloys by optimizing parameters” ” Materials Science in Semiconductor Processing, 2019
2. H. Şar*, A. Özden*, İ. Demiroğlu, C. Sevik, N.K Perkgöz, F. Ay,, “Long-Term Stability Control of CVD Grown Monolayer MoS₂” Pysica Status Solidi (RRL), 2019
3. B. Yorulmaz, A. Özden, H. Sar, C. Sevik, F. Ay, N. K. Perkgoz “CVD Growth of Monolayer WS₂ Through Controlled Seed Formation and Vapor Density” Materials Science in Semiconductor Processing, 2019
4. T. Kocabaş*, A. Özden*, İ. Demiroğlu, D. Çakır, C. Sevik “Determination of Dynamically Stable Electrenes Towards Ultra Fast Charging Battery Applications” The Journal of Physical Chemistry Letters, 2018
5. N. Taghipour, P. L. H. Martinez, A. Özden, M. Olutas, , D. Dede, K. Gungor, O. Erdem, N. K. Perkgoz and H. V. Demir “Near-Unity Efficiency Energy Transfer from Colloidal Semiconductor Quantum Wells of CdSe/CdS Nanoplatelets to A Monolayer of MoS₂” ACS Nano, 2018
6. H. Şar, A. Özden, B. Yorulmaz, C. Sevik, N. K. Perkgoz, F. Ay “A Comparative Device Performance Assesment of CVD Grown MoS₂ and WS₂ Monolayers ” Journal of Materials Science: Materials in Electronics, 2018.

7. A. Özden, F. Ay, C. Sevik, N. K. Perkgöz, “CVD Growth of Monolayer MoS₂: The Role of Growth Zone Configuration and Precursors Ratio” Japanese Journal of Applied Physics, 2017
8. A. Kandemir, A. Özden, T. Çağın, C. Sevik, “Thermal Conductivity Engineering of Bulk and One-Dimensional Si-Ge Nanoarchitectures” Science and Technology of Advanced Materials, 2017
9. A. Özden, H. Şar, A. Yeltik, B. Madenoğlu, C. Sevik, F. Ay, N. K. Perkgöz, “CVD grown 2-D MoS₂ layers: A photoluminescence and fluorescence lifetime imaging study” Physica Status Solidi (RRL), 2016
10. U. Yorulmaz, A. Özden, N. K. Perkgöz, F. Ay, C. Sevik, “Vibrational and Mechanical Properties of Single Layer MXene structures: A first-principles investigation” IOP Nanotechnology, 2016
11. M. Demirtaş, A. Özden, Ethem Açıkaş, F. Ay, “Extensive Mode Mapping and Novel Polarization Filter Design for ALD grown Al₂O₃ Ridge Waveguides” Optical and Quantum Electronics, 2016
12. S.Sarikurt, A. Özden, A. Kandemir, C. Sevik, A. Kinaci, J. Haskins, T. Çağın, “Tailoring Thermal Conductivity of Silicon/Germanium Nanowires Utilizing Core-Shell Architecture”, Journal of Applied Physics, 2016
13. A. Özden, A. Kandemir, F.Ay, N. K. Perkgöz, C. Sevik, “Thermal Conductivity Suppression in Nanostructured Si and Ge Nanowires”, Journal of Electronic Materials, 1594-1600, 2016
14. A. Özden, M. Demirtaş, F.Ay, “Polarization Insensitive Single Mode Al₂O₃ Rib Waveguide Design for Applications in Active and Passive Optical Waveguides”, Journal of the European Optical Society Rapid Publications, 10(15005), 2015
15. A. Ullrich, S. Hohenberger, A. Özden, S. Horn, “Synthesis of iron oxide/manganese oxide composite particles and their magnetic properties”, Journal of Nanoparticle Research, 2014

* Equal contribution

CONFERENCES AND WORKSHOPS

1. A. Özden, H. Şar, C. Odacı , C. Sevik, F. Ay, N. K. Perkgöz “Time Dependent Structural Analysis of CVD Grown MoS₂ Flakes With Different Configurations” Solid State Devices and Materials 2017, Sendai, Japan, 2017, Short Talk
2. H.Şar, A. Özden, C. Odacı, C. Sevik, N. K. Perkgöz, F. Ay, “Investigation of Long Term Electrical Transport Stability of MoS₂ Flakes” Solid State Devices and Materials 2017, Sendai, Japan, 2017, Short Talk
3. A. Özden, U. Savacı, H. Şar, C. Sevik, N. K. Perkgöz, S. Turan, F. Ay, “Evolution of 2D MoS₂ Structures as a Function of the Hydrogen Flow Rate” 13th Nanoscience and Nanotechnology Congress, Antalya, Turkey, 2017. Oral Presentation
4. H.Sar, A. Özden, B. Yorulmaz, C. Sevik, N.K. Perkgöz, F. Ay, “A Comparative Study on Transport Properties of 2D MoS₂ and WS₂ Field Effect Transistors” 13th Nanoscience and Nanotechnology Congress, Antalya, Turkey, 2017. Oral Presentation
5. A. Özden, B. Yorulmaz, H. Şar, C. Sevik, F. Ay, N. K. Perkgöz “CVD Formation of Hetero of Hetero 2D MoS₂-WS₂ Flakes” 13th Nanoscience and Nanotechnology Congress, Antalya, Turkey, 2017. Oral Presentation
6. A. Özden, F. Ay, C. Sevik, N. K. Perkgöz. Controlling Flake Size and Shape of MoS₂ Monolayers Grown by Chemical Vapor Deposition. 29th International Microprocesses and Nanotechnology Conference, Kyoto Japan, 2016. Oral Presentation
7. A. Özden, U. Yorulmaz. C. Sevik. Dynamical and Mechanical Stability of MXene Crystals, 12th Nanoscience and Nanotechnology Congress, 3-5 June, Gebze Technical University, Turkey. Oral Presentation, 2016
8. A. Özden, F. Ay. Chemical Vapour Deposition of MoS₂ Flakes and Their Characterization with Raman and Photoluminescence Spectroscopy, 12th Nanoscience and Nanotechnology Congress, 3-5 June, Gebze Technical University, Turkey. Poster Presentation, 2016

9. H. Şar, A. Özden, O. Balcı, C. Kocabaş, N. K. Perkgöz, F. Ay, C. Sevik, „Systematic Characterization of MoS₂ CVD Growth on Transferred and As-grown Graphene”, European MRS, Fall Meeting, Lille, France Poster Presentation, 2016
10. A. Özden, B. Madenoğlu, A. Yeltik, C. Sevik, F. Ay, N. K. Perkgöz. “A Comparative Study of CVD Grown Monolayer MoS₂ Flake Formations: Electrical and Optical Properties” European MRS, Fall Meeting, Lille, France. Poster Presentation, 2016
11. M. Bay, A. Özden, A. Yeltik, C. Sevik, F. Ay, N. K. Perkgöz, “Controllable CVD Growth of Monolayer MoS₂ (1-X)-Se_{2x} Alloys: Size and Bandgap Tuning” European MRS, Fall Meeting, Lille, France. Poster Presentation, 2016
12. B. Madenoğlu, A. Özden, T. Özmen, F. Ay, N. K. Perkgöz, C. Sevik, “Controlled Growth of Two Dimensional WS₂ Structures Using CVD” European MRS, Fall Meeting, Lille, France. Poster Presentation, 2016
13. S. Sarıkurt, A. Özden, C. Sevik, A. Kinaci, J. B. Haskins, T. Cagin, “Cross-Sectional Size and Interface Roughness Effects on Thermal Conductivity of Ge/Si Core/Shell Nanowires”, TMS 2015, 144th ANNUAL MEETING & EXHIBITION, Orlando, FL, USA, Poster Presentation, 2015
14. M. Demirtaş, A. Özden, F. Ay, "Systematic Approach to Determine Optimal Design Geometry for ALD grown Al₂O₃ Ridge Waveguide Amplifiers"16. Ulusal Optik, Elektro-Optik ve Fotonik Çalıştayı, p.56, Ankara Üniversitesi, Poster Presentation, 2015
15. M. Demirtaş, E. Açıkbaş, A.Özden, F. Ay, "Thickness Dependency of Single Mode, Wavelength and Polarization Insensitive Region of Al₂O₃ Ridge Waveguides", Workshop on Photonics Fundamentals and Applications, IZTECH, Turkey, Poster Presentation, 2015
16. A. Özden, M. Demirtaş, E. Açıkbaş, F. Ay, "Monolithic TE Mode Selective Filters on Thermal Oxide for Integrated Optical Circuits", Workshop on Photonics Fundamentals and Applications, IZTECH, Turkey, Poster Presentation, 2015,
17. M. Demirtaş, A. Özden, F. Ay, “Modelling of Polarization and Wavelength Insensitive Single Mode Al₂O₃ Rib Waveguides for Active and Passive Applications” XXIII International Workshop On Optical Wave And Waveguide Theory And Numerical Modelling, p. 103, City University London, UK,. Poster Presentation, 2015

18. M. Demirtaş, A. Özden, F. Ay, “Assessment of ALD Grown Al₂O₃ as a Host Material for Active and Passive Waveguide Applications”, 16. Ulusal Optik, Elektro-Optik ve Fotonik Çalıştayı, p.13, Kocaeli Üniversitesi, Poster Presentation, 2014
19. A. Özden, M. Demirtaş, F. Ay, “Al₂O₃ Ridge Waveguide Design for Applications in Active and Passive Optical Waveguides”, 16. Ulusal Optik, Elektro-Optik ve Fotonik Çalıştayı, p.35, Kocaeli Üniversitesi, Poster Presentation, 2014
20. M. Demirtaş, A. Özden, F. Ay, "Optimization of ALD grown Al₂O₃ Host Material for Use in Integrated Optical Circuits", 10th Nanoscience and Nanotechnology Congress, Nano-TR-X, p. 138, 17-21 June 2014, Istanbul, Turkey. Yeditepe University, Oral Presentation, 2014
21. A. Ullrich, S. Hohenberger, A. Özden, N. Rölle, S. Horn, “Synthesis of transition metal oxide core-shell and composite nanoparticles and their magnetic properties” NANOTECH DUBAI 2015, Dubai, UAE 2015
22. A. Ullrich, S. Hohenberger, A. Özden, S. Horn “Core-Shell and Composite Nanoparticles of Transition Metal Oxides: Synthesis and Magnetic Characterization” Second International Conference on Nanostructured Materials and Nanocomposites, Kottayam, India 2014