

**TITLE**

by

**Kraig Andrews**

Ph.D. Disseration Prospectus

YEAR

\_\_\_\_\_  
Advisor

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

**ABSTRACT**

**TITLE HERE**

by

**Kraig J. Andrews**

August 2008

Advisor: Dr. Zhixain Zhou  
Major: Physics  
Degree: Doctor of Philosophy

Abstract here

## ACKNOWLEDGEMENTS

Acknowledgements here...

# Table of Contents

List of Figures . . . . .	iv
List of Tables . . . . .	v
<b>1 Introduction</b>	<b>1</b>
1.1 Birth of Integrated Circuits . . . . .	1
1.2 Graphene as a New Two-dimensional Material . . . . .	1
1.2.1 Properties of Graphene . . . . .	1
1.2.2 Band Structure of Graphene . . . . .	2
1.3 Two-dimensional Materials: Transition Metal Dichalcogenides . . . . .	3
1.3.1 Properties of Commonly Used transition metal dichalcogenides (TMDs) . . . . .	3
1.3.2 Current State of TMDs . . . . .	3
<b>2 Experimental Details</b>	<b>5</b>
2.1 Preperation . . . . .	5
2.1.1 Substrate Cleaning . . . . .	5
2.2 Exfoliation . . . . .	5
2.2.1 Oxygen Plasma . . . . .	5
2.2.2 Mechanical Exfoliation . . . . .	5
2.3 Device Synthesis . . . . .	5
2.3.1 Transfer . . . . .	5
2.3.2 Polycarbonate Pickup Method . . . . .	5
2.4 Characterization . . . . .	5
2.4.1 Optical Characterization . . . . .	5
2.4.2 AFM Characterization . . . . .	5
2.5 Device Fabrication . . . . .	5
2.5.1 Device Design . . . . .	5
2.5.2 Electron Beam Lithography . . . . .	5
2.5.3 Metal Deposition . . . . .	5
2.6 Electrical Measurements . . . . .	6
2.6.1 Measurement Devices . . . . .	6
<b>References</b>	<b>7</b>
<b>Appendices</b>	<b>11</b>

# List of Figures

1.1	Graphene honeycomb lattice . . . . .	2
1.2	Bandgap of graphene . . . . .	2
1.3	Layered TMD diagram . . . . .	3
1.4	Hexagonal lattice of TMD . . . . .	3
1.5	Band structures of MoS <sub>2</sub> . . . . .	4

# List of Tables

1.1	Band gaps of typical TMDs and other materials . . . . .	4
-----	---	---

# Chapter 1

## Introduction

### 1.1 Birth of Integrated Circuits

The development of microelectronics revolutionized the world in the latter half of the twentieth century. The term semiconductor, in the sense it is known today, first appears in literature in 1911 [1]. Initially, work on the subject was rather pessimistic. However, in the years following World War II breakthroughs began shed light on the possible applications and the underlying physics involved, such as the ideas of *intrinsic* and *extrinsic* semiconductors [2, 3, 4, 5].

The history of semiconductors and transistors is a well documented subject. The first transistor was constructed at Bell Labs in 1947 using polycrystalline germanium. Shortly thereafter one was developed using silicon. Throughout the following years, these devices were improved on by replacing polycrystalline with single crystals [6]. Then Jack Kilby demonstrated the first integrated circuit (IC) in 1958, for which he would win the Nobel Prize in physics [7, 8]. The scale of ICs grew rapidly in the subsequent years. Initially only a few transistors could fit on a chip (small-scale integration), in stark contrast to modern-day chips that contains billions of transistors [9, 10]. Growth continued at a rapid pace, but eventually it was realized that some limits, material and integration based, existed in silicon and other commonly used materials [11, 12]. In part, these limitations increased the interest in alternative materials. As a result widespread and renewed interest has led to a breadth information and results on a wide range of materials and their applications.

### 1.2 Graphene as a New Two-dimensional Material

Layered materials have existed for billions of years, and have been studied over the last few centuries [13, 14]. In recent decades the scientific study of graphite (3D) has led to new forms materials, such as carbon nanotubes (1D) and fullerenes (0D) [15, 16, 17]. However, only more recently have scientists began to understand the potential of such layered materials and their potential technological applications. After attempting unsuccessfully to synthesize few-layer graphite during the 1960s (only around 10-50 layers were able to be synthesized) a breakthrough was finally achieved [16]. This most notably began with the synthesis of monolayer graphene [18].

#### 1.2.1 Properties of Graphene

To date, graphene's properties have been the focus of much research, both theoretical and experimental. It has been one of the primary driving forces in study of 'relativistic' condensed matter physics due to its low dimensionality and its band structure that allows electrons to mimic relativistic particles confirming the appearance of several relativistic phenomena [19, 20, 21, 22]. In its most basic sense, graphene is

composed of a single layer of carbon atoms arranged in two-dimensional honeycomb lattice (see fig. 1.1) It has a Young's modulus of 100 GPa (several times more than steel) with a breaking force that is 13% of its Young's modulus [23, 24]. Its strength is due, in part, to its strong in-plane carbon (C) bonds. In addition, graphene can sustain elastic deformations of 20% due to its two-dimensional nature and it has high pliability [16]. These mechanical properties are of interest because graphene lies in the extreme ranges of many metrics considering its size and dimensionality.

Aside from its mechanical properties, graphene's transport properties were another reason why the material was so appealing. Graphene's mobility is several times that of silicon's. Experimental results have shown graphene mobility around  $15,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  with a potential theoretical limit of  $200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [25, 24]. The upper theoretical limit imposed on mobility is due to scattering, however, these high mobilities are achieved mainly because electrons in graphene act very much like photons in their mobility due to their lack of mass. This enables them to travel sub-micron distances without scattering [26]. In reality, there are other limiting factors that need to be considered such as the quality of graphene and scattering with the substrate, for example.

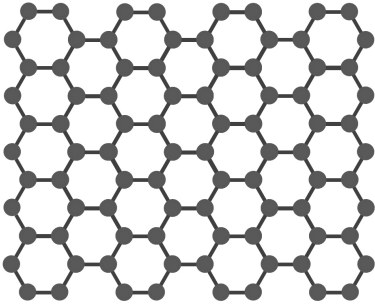


Figure 1.1: Graphene: a layer of carbon atoms in a honeycomb lattice.

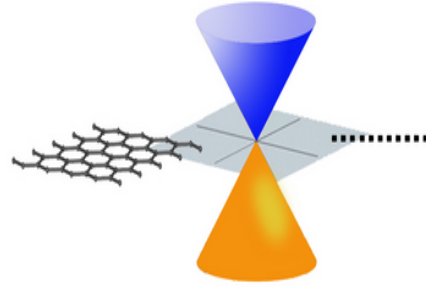


Figure 1.2: One of the most unusual features of graphene is that its conduction and valence bands meet at a point, meaning that in single-layer graphene there is no band gap (figure obtained from [27])

### 1.2.2 Band Structure of Graphene

Despite its impressive properties, the main drawback of graphene is its lack of bandgap. As this became known, the prospect of using graphene for the fabrication to ICs became unlikely. In graphene the conduction and valence bands touch at a single point as shown in fig. 1.2 [28]. Ultimately, the lack of a bandgap means that the current on/off ratio is low and is unappealing for logical circuit applications [29]. However, graphene exhibits some interesting properties as a result of having no bandgap, particularly as it pertains to its optical properties. The material's band structure allows for absorption of light over a large range of the electromagnetic spectrum, ranging from infrared ( $< 1.65 \text{ eV}$ ) to ultraviolet ( $> 3.2 \text{ eV}$ ), offering potential electronic-photonics device applications [30, 31, 32]. Since a direct use in logical circuits is not practical researchers have moved on to look for 'two-dimensional materials beyond graphene.' Several attempts at some derivatives of graphene-like materials have been studied, but for the most part they do not seem promising for use in logical circuits [33, 34]. As of late, research has been concentrated on two-dimensional materials, namely transition metal dichalcogenides, as a candidate for applications in ICs.



### 1.3 Two-dimensional Materials: Transition Metal Dichalcogenides

Commonly referred to two-dimensional materials beyond graphene, TMD have garnered much interest. TMDs were studied previously, however, they have gained renewed interest due to their properties [35, 36, 37, 38]. TMDs consist of hexagonal layers of metal (M) atoms in between two layers chalcogen (X) atoms (see fig. 1.4, such that the stoichiometry of the material is  $MX_2$  [29]. The material is dependent on the type of transition metal, typically one of: molybdenum (Mo), tungsten (W), niobium (Nb), rhenium (Re), nickel (Ni), or vanadium (V), and two chalcogen atoms, typically one of: sulfur (S), selenium (Se), or tellurium (Te) [38, 39]. The most commonly studied variations of TMDs are molybdenum disulfide ( $MoS_2$ ), tungsten diselenide ( $WSe_2$ ), and tungsten disulfide ( $WS_2$ ). These materials are commonly stacked together involving van der Waals interactions between adjacent sheets and covalent bonding within each individual sheet (see fig. 1.3) [29]. TMDs exhibit a wide variety of properties, including either being a

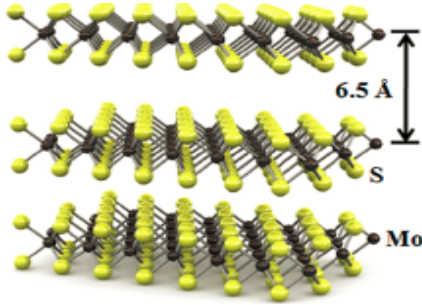


Figure 1.3: The atomic structure of a layered TMD, depicting  $MoS_2$ . Each sheet is composed of three atoms with Mo sandwiched in between two S atoms, S-Mo-S. (Figure obtained from [40])

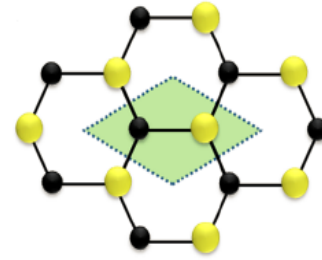


Figure 1.4: Top view of a TMD ( $MoS_2$ ) lattice. (Figure obtained from [40])

metal or insulator, and displaying the topological insulator effect, superconductivity, and thermoelectricity [41, 42, 43, 44].

#### 1.3.1 Properties of Commonly Used TMDs

As stated in sec. 1.2.2, one important property as it pertains to applications for logical circuits is the material's band structure. One of the main reasons TMDs have been so extensively studied lately is due to the fact that, unlike graphene, they do exhibit a band gap. The band gaps in some commonly used TMDs is interesting because of the transition from an indirect to a direct band gap as the layered thickness decreases. Fig. 1.5 illustrates this, for bulk and few-layer  $MoS_2$  there is an indirect band gap while for monolayer  $MoS_2$  there is a direct band gap. This unusual structure results in some unique optical and properties.

#### 1.3.2 Current State of TMDs

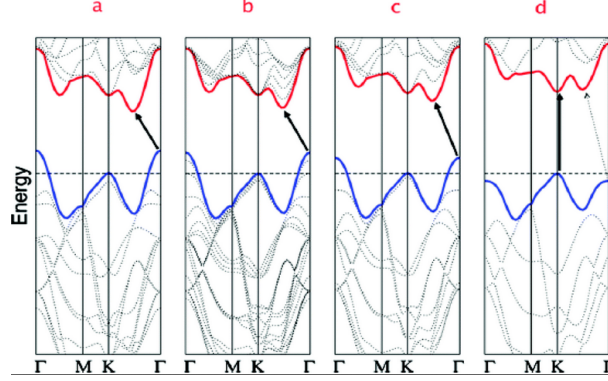


Figure 1.5: Calculated band structures of (a) bulk MoS<sub>2</sub>, (b) four-layer MoS<sub>2</sub>, (c) bilayer MoS<sub>2</sub>, and (d) monolayer MoS<sub>2</sub>. Here the solid arrows indicate the lowest energy transitions. (Taken from [45], originally appeared in [46])

2D material	theoretical $E_g$ (eV)	experimental $E_g$ (eV)
graphene	0	0
bilayer graphene	0	0
bulk <i>h</i> -BN	-	5.97 [47]
monolayer <i>h</i> -BN	-	6.07 [48]
few layer (2-5) <i>h</i> -BN	-	5.92 [49]
bulk MoS <sub>2</sub>	1.2 <sup>a,b</sup> [50, 51]	1.0-1.29 <sup>b</sup> [50, 51]
monolayer MoS <sub>2</sub>	~ 1.90 <sup>a,c</sup> [52]	~ 1.90 <sup>b</sup> [52]
bulk WS <sub>2</sub>	~ 1.30 <sup>a,b</sup> [50, 53]	~ 1.35 <sup>c</sup> [50, 53]
monolayer WS <sub>2</sub>	~ 2.10 <sup>a,c</sup> [54]	-

<sup>a</sup> Theoretical calculations based on first-principles calculations using density functional theory (DFT).

<sup>b</sup> Indirect band gap semiconductor.

<sup>c</sup> Direct band gap semiconductor.

Table 1.1: Summary of the band gaps of typical monolayer, bilayer, and bulk TMDs and *h*-BN materials. Table adapted from ref. [29].

## Chapter 2

# Experimental Details

### 2.1 Preperation

#### 2.1.1 Substrate Cleaning

### 2.2 Exfoliation

#### 2.2.1 Oxygen Plasma

#### 2.2.2 Mechanical Exfoliation

### 2.3 Device Synthesis

#### 2.3.1 Transfer

#### 2.3.2 Polycarbonate Pickup Method

Polycarbonate (PC)

### 2.4 Characterization

#### 2.4.1 Optical Characterization

#### 2.4.2 AFM Characterization

### 2.5 Device Fabrication

#### 2.5.1 Device Design

#### 2.5.2 Electron Beam Lithography

#### 2.5.3 Metal Deposition

Polymethyl methacrylate (PMMA)

Polydimethylsiloxane (PDMS)

## **2.6 Electrical Measurements**

### **2.6.1 Measurement Devices**

# References

- [1] J Koenigsberger and J Weiss. Über die thermoelektrischen effekte (thermokräfte, thomsonwärme) und die wärmeleitung in einigen elementen und verbindungen und über die experimentelle prüfung der elektronentheorien. *Annalen der Physik*, 340(6):1–46, 1911.
- [2] G. Busch. Early history of the physics and chemistry of semiconductors-from doubts to fact in a hundred years. *European Journal of Physics*, 10:254–264, oct 1989.
- [3] KARL Lark-Horovitz. The present state of physics. *Am. Assoc. Advancement Sci., Washington, DC*, page 57, 1954.
- [4] A. H. Wilson. The theory of electronic semi-conductors. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 133(822):458–491, 1931.
- [5] A. H. Wilson. The theory of electronic semi-conductors. ii. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 134(823):277–287, 1931.
- [6] Donald A. Neaman. *Semiconductor Physics and Devices: Basic Principles*. McGraw-Hill, New York, NY, 3 edition, 2003.
- [7] Lidia Łukasiak and Andrzej Jakubowski. History of semiconductors. *Journal of Telecommunications and information technology*, pages 3–9, 2010.
- [8] Jack S. Kilby. Miniaturized electronic circuits. United States Patent Office, 1959. U.S. Patent 3,138,743, issued June 1964.
- [9] G. Moore. Cramming more components onto integrated circuits. *Electronics*, 38(8), 1965.
- [10] Peter Clarke. Intel enters billion-transistor processor era, October 2005. [Online; 13 accessed-December-2015].
- [11] James D. Meindl, Qiang Chen, and Jeffrey A. Davis. Limits on silicon nanoelectronics for terascale integration. *Science*, 293(5537):2044–2049, 2001.
- [12] Max Schulz. The end of the road for silicon? *Nature*, 399:729–730, 1999.
- [13] Joshua Golden, Melissa McMillan, Robert T Downs, Grethe Hystad, Ian Goldstein, Holly J Stein, Aaron Zimmerman, Dimitri A Sverjensky, John T Armstrong, and Robert M Hazen. Rhenium variations in molybdenite (mos 2): Evidence for progressive subsurface oxidation. *Earth and Planetary Science Letters*, 366:1–5, 2013.
- [14] Benjamin C Brodie. On the atomic weight of graphite. *Philosophical Transactions of the Royal Society of London*, pages 249–259, 1859.
- [15] H. W. Kroto, J. R. Heath, S. C. O’Brien, R. F. Curl, and R. E. Smalley. C60: Buckminsterfullerene. *Nature*, 318:162–163, 1985.

- [16] Ruben Mas-Balleste, Cristina Gomez-Navarro, Julio Gomez-Herrero, and Felix Zamora. 2d materials: to graphene and beyond. *Nanoscale*, 3:20–30, 2011.
- [17] Sumio Iijima. Helical microtubules of graphitic carbon. *Nature*, 354:56–58, 1991.
- [18] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov. Electric field effect in atomically thin carbon films. *Science*, 306(5696):666–669, 2004.
- [19] A. K. Geim and K. S. Novoselov. The rise of graphene. *Nature Materials*, 6:183–191, 2007.
- [20] K.S. Novoselov, A. K. Geim, S.V. Morozov, D. Jiang, M.I. Katsnelson, I.V. Grigorieva, S.V. Dubonos, and A.A. Firsov. Two-dimensional gas of massless dirac fermions in graphene. *Nature*, 438:197–200, 2005.
- [21] L. Zhang, Y. Zhang, J. Camacho, M. Khodas, and I. Zaliznyak. The experimental observation of quantum hall effect of  $l=3$  chiral quasiparticles in trilayer graphene. *Nat. Phys.*, 7:953–957, 2011.
- [22] J. R. Williams, L. DiCarlo, and C. M. Marcus. Quantum hall effect in a gate-controlled p-n junction of graphene. *Science*, 317(5838):638–641, 2007.
- [23] Simone Bertolazzi, Jacopo Brivio, and Andras Kis. Stretching and breaking of ultrathin mos2. *ACS Nano*, 5(12):9703–9709, 2011. PMID: 22087740.
- [24] Deji Akinwande, Nicholas Petron, and James Hone. Two-dimensional flexible nanoelectronics. *Nature Communications*, 5, 2014.
- [25] A. Dargys and J. Kundrotas. *Handbook on physical properties of Ge, Si, GaAs, InP*. Science and Encyclopedia Publishers, Vilnius, Lithuania, 1994.
- [26] K.S. Novoselov and A.K. Geim. The rise of graphene. *Nature Materials*, 6:183–191, 2007.
- [27] Berkley Labs. Bilayer graphene gets a bandgap, June 2009. [Online; 23 accessed-December-2015].
- [28] P. R. Wallace. The band theory of graphite. *Phys. Rev.*, 71:622–634, May 1947.
- [29] Mingsheng Xu, Tao Liang, Minmin Shi, and Hongzheng Chen. Graphene-like two-dimensional materials. *Chemical Reviews*, 113(5):3766–3798, 2013. PMID: 23286380.
- [30] F.N. Xia, T. Mueller, Y.M. Lin, A. Valdes-Garcia, and P. Avouris. Ultrafast graphene photodetector. *Nat. Nanotechnol.*, 4:839–843, 2009.
- [31] Feng Wang, Yuanbo Zhang, Chuanshan Tian, Caglar Girit, Alex Zettl, Michael Crommie, and Y. Ron Shen. Gate-variable optical transitions in graphene. *Science*, 320(5873):206–209, 2008.
- [32] T.J. Echtermeyer, L. Britnell, P.K. Jasnós, A. Lombardo, R.V. Gorbachev, A.N. Grigorenko, A.K. Geim, A.C. Ferrari, and K.S. Novoselov. Strong plasmonic enhancement of photovoltage in graphene. *Nat. Commun.*, 2:458, 2011.
- [33] Kyoaburo Takeda and Kenji Shiraishi. Theoretical possibility of stage corrugation in si and ge analogs of graphite. *Phys. Rev. B*, 50:14916–14922, Nov 1994.
- [34] S. Cahangirov, M. Topsakal, E. Aktürk, H. Şahin, and S. Ciraci. Two- and one-dimensional honeycomb structures of silicon and germanium. *Phys. Rev. Lett.*, 102:236804, Jun 2009.
- [35] R. F. Frindt and A. D. Yoffe. Physical properties of layer structures: Optical properties and photoconductivity of thin crystals of molybdenum disulphide. *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 273(1352):69–83, 1963.

- [36] R. Fivaz and E. Mooser. Mobility of charge carriers in semiconducting layer structures. *Phys. Rev.*, 163:743–755, Nov 1967.
- [37] L. F. Mattheiss. Band structures of transition-metal-dichalcogenide layer compounds. *Phys. Rev. B*, 8:3719–3740, Oct 1973.
- [38] J.A. Wilson and A.D. Yoffe. The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties. *Advances in Physics*, 18(73):193–335, 1969.
- [39] AF Wells. Structural inorganic chemistry. Oxford Univ. Press, 1984.
- [40] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis. Single-layer mos<sub>2</sub> transistors. *Nat. Nano.*, 6:147–150, 2011.
- [41] Murong Lang, Liang He, Faxian Xiu, Xinxin Yu, Jianshi Tang, Yong Wang, Xufeng Kou, Wanjuan Jiang, Alexei V. Fedorov, and Kang L. Wang. Revelation of topological surface states in bi<sub>2</sub>se<sub>3</sub> thin films by in situ al passivation. *ACS Nano*, 6(1):295–302, 2012. PMID: 22147687.
- [42] Hong Bin Zhang, Hai Lin Yu, Ding Hua Bao, Shu Wei Li, Cheng Xin Wang, and Guo Wei Yang. Magnetoresistance switch effect of a sn-doped bi<sub>2</sub>te<sub>3</sub> topological insulator. *Advanced Materials*, 24(1):132–136, 2012.
- [43] Wenjie Xie, Xinfeng Tang, Yonggao Yan, Qingjie Zhang, and Terry M. Tritt. Unique nanostructures and enhanced thermoelectric performance of melt-spun bisbte alloys. *Applied Physics Letters*, 94(10):–, 2009.
- [44] F. R. Gamble and B. G. Silbernagel. Anisotropy of the proton spinlattice relaxation time in the superconducting intercalation complex tas<sub>2</sub>(nh<sub>3</sub>): Structural and bonding implications. *The Journal of Chemical Physics*, 63(6):2544–2552, 1975.
- [45] Seunghyun Lee and Zhaohui Zhong. Nanoelectronic circuits based on two-dimensional atomic layer crystals. *Nanoscale*, 6(22):13283–13300, 2014.
- [46] Andrea Splendiani, Liang Sun, Yuanbo Zhang, Tianshu Li, Jonghwan Kim, Chi-Yung Chim, Giulia Galli, and Feng Wang. Emerging photoluminescence in monolayer mos<sub>2</sub>. *Nano letters*, 10(4):1271–1275, 2010.
- [47] Yoichi Kubota, Kenji Watanabe, Osamu Tsuda, and Takashi Taniguchi. Deep ultraviolet light-emitting hexagonal boron nitride synthesized at atmospheric pressure. *Science*, 317(5840):932–934, 2007.
- [48] Ki Kang Kim, Allen Hsu, Xiaoting Jia, Soo Min Kim, Yumeng Shi, Mario Hofmann, Daniel Nezich, Joaquin F Rodriguez-Nieva, Mildred Dresselhaus, Tomas Palacios, et al. Synthesis of monolayer hexagonal boron nitride on cu foil using chemical vapor deposition. *Nano letters*, 12(1):161–166, 2011.
- [49] Li Song, Lijie Ci, Hao Lu, Pavel B Sorokin, Chuanhong Jin, Jie Ni, Alexander G Kvashnin, Dmitry G Kvashnin, Jun Lou, Boris I Yakobson, et al. Large scale growth and characterization of atomic hexagonal boron nitride layers. *Nano letters*, 10(8):3209–3215, 2010.
- [50] Kin Fai Mak, Changgu Lee, James Hone, Jie Shan, and Tony F Heinz. Atomically thin mos<sub>2</sub>: a new direct-gap semiconductor. *Physical Review Letters*, 105(13):136805, 2010.
- [51] E Gourmelon, O Lignier, H Hadouda, G Couturier, JC Bernede, J Tedd, J Pouzet, and J Salardenne. Ms<sub>2</sub> (m= w, mo) photosensitive thin films for solar cells. *Solar energy materials and solar cells*, 46(2):115–121, 1997.

- [52] E Fortin and WM Sears. Photovoltaic effect and optical absorption in mos 2. *Journal of Physics and Chemistry of Solids*, 43(9):881–884, 1982.
- [53] Agnieszka Kuc, Nourdine Zibouche, and Thomas Heine. Influence of quantum confinement on the electronic structure of the transition metal sulfide t s 2. *Physical Review B*, 83(24):245213, 2011.
- [54] Yandong Ma, Ying Dai, Meng Guo, Chengwang Niu, Jibao Lu, and Baibiao Huang. Electronic and magnetic properties of perfect, vacancy-doped, and nonmetal adsorbed mose 2, mote 2 and ws 2 monolayers. *Physical Chemistry Chemical Physics*, 13(34):15546–15553, 2011.



# Appendices

**IC** integrated circuit

**TMD** transition metal dichalcogenides

**Mo** molybdenum

**W** tungsten

**Nb** niobium

**Re** rhenium

**Ni** nickel

**V** vanadium

**S** sulfur

**Se** selenium

**Te** tellurium

**MoS<sub>2</sub>** molybdenum disulfide

**WSe<sub>2</sub>** tungsten diselenide

**WS<sub>2</sub>** tungsten disulfide

**DFT** density functional theory