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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.

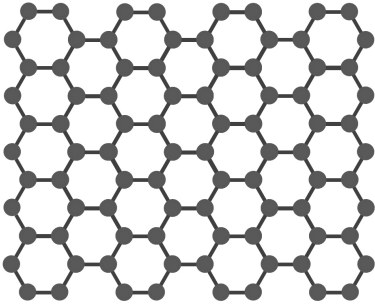


Figure 1.1: Graphene: a layer of carbon atoms in a honeycomb lattice.

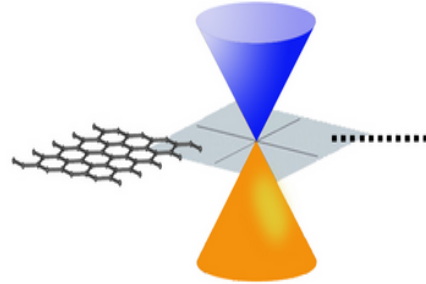


Figure 1.2: One of the most unusual features of graphene is that its conduction and valence bands meet at a point, meaning that in single-layer graphene there is no band gap (figure obtained from [27])

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

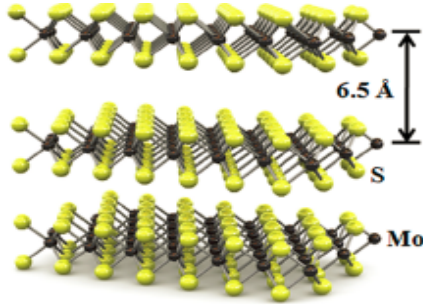


Figure 1.3: The atomic structure of a layered TMD, depicting MoS_2 . Each sheet is composed of three atoms with Mo sandwiched in between two S atoms, S-Mo-S. (Figure obtained from [40])

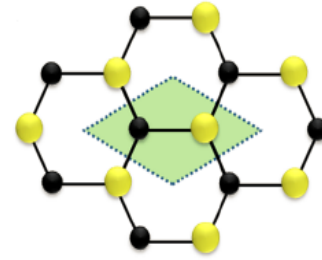


Figure 1.4: Top view of a TMD (MoS_2) lattice. (Figure obtained from [40])

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

1.4 Hall Effect

Give a brief overview of the history

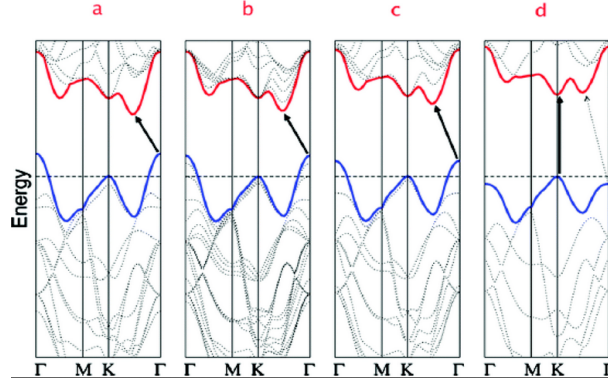


Figure 1.5: Calculated band structures of (a) bulk MoS₂, (b) four-layer MoS₂, (c) bilayer MoS₂, and (d) monolayer MoS₂. Here the solid arrows indicate the lowest energy transitions. (Taken from [45], originally appeared in [46])

2D material	theoretical E_g (eV)	experimental E_g (eV)
graphene	0	0
bilayer graphene	0	0
bulk h -BN	-	5.97 [47]
monolayer h -BN	-	6.07 [48]
few layer (2-5) h -BN	-	5.92 [49]
bulk MoS ₂	1.2 ^{a,b} [50, 51]	1.0-1.29 ^b [50, 51]
monolayer MoS ₂	$\sim 1.90^{\text{a,c}}$ [52]	$\sim 1.90^{\text{b}}$ [52]
bulk WS ₂	$\sim 1.30^{\text{a,b}}$ [50, 53]	$\sim 1.35^{\text{c}}$ [50, 53]
monolayer WS ₂	$\sim 2.10^{\text{a,c}}$ [54]	-

^a Theoretical calculations based on first-principles calculations using density functional theory (DFT).

^b Indirect band gap semiconductor.

^c 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].

1.4.1 Overview

1.4.2 Theoretical Background

Some useful references for this section [55, 56, 57, 58, 59, 60]

Chapter 2

Experimental Details

2.1 Substrate Preperation

2.1.1 Photolithography

2.1.2 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

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

2.6 Electrical Measurements

2.6.1 Measurement Devices

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Appendices

DFT density functional theory

IC integrated circuit

Mo molybdenum

MoS₂ molybdenum disulfide

Nb niobium

Ni nickel

Re rhenium

S sulfur

Se selenium

Te tellurium

TMD transition metal dichalcogenides

V vanadium

W tungsten

WS₂ tungsten disulfide

WSe₂ tungsten diselenide