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2D materials based heterostructures : a lithography free method.

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2D MATERIALS BASED HETEROSTRUCTURES: A LITHOGRAPHY FREE
METHOD

By

Adel Alruqi

B.S., Taif University, 2007
M.S., University of Louisville, 2015

A Dissertation
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A Dissertation Approved on

April 23rd, 2019

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ABSTRACT

2D MATERIALS BASED HETEROSTRUCTURES: A LITHOGRAPHY FREE METHOD

Adel Alruqi

April 23rd, 2019

Many properties of Two-dimensional (2D) materials are vastly different from those of their 3D counterparts. A large family of 2D materials ranging from gapless graphene to metallic NbSe₂ (also superconducting), semiconducting MoS₂, and insulating hexagonal boron nitride (h-BN) possessing a broad range of exciting new properties have emerged in recent years. Moreover, 2D materials provide the perfect platform to create laterally and vertically stacked heterostructures with intriguing properties. The physics of 2D materials based heterostructures is extremely interesting and novel 2D-heterostructured devices including tunneling diodes, tunneling transistors, photovoltaic cells, and light-emitting diodes have started to emerge.

In this work, we developed a novel lithography-free technique for the fabrication of 2D material-based electrical devices. We fabricated few-layer and multi-layer WS₂ devices using a transmission electron microscope (TEM) grid as a shadow mask, and its transport characteristics were studied by electrical measurements. WS₂ samples were synthesized by first depositing WO₃ followed by sulfurization and characterized by scanning tunneling microscopy (STM), atomic force microscopy (AFM), and Raman

spectroscopy. Hydrazine adsorption on WS_2 was studied by measuring the electrical resistances during adsorption (exposing to hydrazine vapor) and subsequent desorption (by pumping). WS_2 sample consisting of two layers showed a decrease of resistance upon exposure to hydrazine vapor and showed complete reversibility upon pumping. WS_2 sample with three layers showed a decrease of resistance during exposure but showed only partial recovery during desorption. In contrast, multi-layered (12 layers) WS_2 sample showed an initial decrease followed by a continued increase of the resistance upon exposure to hydrazine with little or no reversibility upon pumping. The charge transfer from N_2H_4 to WS_2 is believed to be responsible for the decrease of the resistance. Trapping of N_2H_4 molecules within the multilayers of WS_2 causing charge redistribution and possible chemical reactions is believed to be responsible for the increase in resistance during the adsorption and complete irreversibility of resistance during desorption. The experimental results are explained with the help of computational calculations carried out by employing the density functional theory (DFT) framework, as implemented in the Vienna Ab-initio Simulation Package (VASP).

Next, we extended our lithography-free technique for the fabrication of two-dimensional (2D) material based heterostructures. We fabricated graphene- WS_2 heterostructured devices again using a TEM grid as a shadow mask. Graphene was directly deposited on a Si/SiO_2 substrate by radio frequency (RF) plasma enhanced chemical vapor deposition (PECVD). WS_2 was synthesized as before. The temperature dependence of the resistance and magnetoresistance are measured for graphene, WS_2 , and graphene- WS_2 heterostructure. At low temperatures, the transport was found to follow the variable-range

hopping (VRH) process, where logarithmic R exhibits a $T^{-1/3}$ temperature dependence, an evidence for the 2D Mott VRH transport. The measured low-field magnetoresistance also exhibits a quadratic magnetic field dependence $\sim B^2$, consistent with the 2D Mott VRH transport.

Finally, a lithography-free technique was developed to fabricate Graphene/h-BN/Graphene tunnel junctions. Graphene and h-BN were directly deposited on a Si/SiO₂ substrate by RF-PECVD using CH₄ and ammonia borane as the precursors respectively. Tunnel diodes with varying barriers were fabricated by tuning the thickness of the h-BN layer thickness. The tunneling current was found to scale exponentially with the tunnel barrier thickness.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	iii
ABSTRACT.....	v
LIST OF TABLES	xii
LIST OF FIGURES	xiii
CHAPTER 01 INTRODUCTION	1
1.1 Two-dimensional Heterostructures	1
1.2 Background of Graphene	2
1.3 Band structure of graphene	5
1.4 Properties and potential applications of graphene.....	7
1.5 Synthesis of graphene.....	10
1.5.1 Mechanical exfoliation.....	11
1.5.2 Liquid phase exfoliation	12
1.5.3 Epitaxial growth on silicon carbides.....	13
1.5.4 Wet Chemical synthesis of graphene.....	14
1.6 Beyond Graphene Materials.....	16
1.7 History of Transition metal dichalcogenides (TMDCs).....	19

1.8	Synthesis of Transition metal dichalcogenides	23
1.8.1	Mechanical exfoliation.....	24
1.8.2	Chemical Vapor Deposition.....	24
1.8.3	Liquid Mechanical Exfoliation;	25
1.9	Modifications of Transition Metal Dichalcogenides and Graphene	26
1.9.1	Heterostructures	27
1.9.2	Doping;	28
1.9.3	Surface/Edge functionalization.....	30
1.10	Background of Hexagonal boron nitride	30
1.10.1	Structures of Hexagonal boron nitride.....	31
1.10.2	Synthesis of Hexagonal boron nitride	32
CHAPTER 02 CHEMICAL VAPOR DEPOSITION (CVD) OF 2D MATERIALS:		
SYNTHESIS AND CHARACTERIZATION		36
2.1	Introduction	36
2.2	Thermal evaporation and CVD Kinetics and transport.....	37
2.3	Plasma Enhanced Chemical Vapor Deposition (PECVD).....	47
2.4	Sample holder design	49
2.5	Characterization of Two-dimensional materials	50
2.5.1	Raman Spectroscopy.....	50

2.5.2	Scanning Electron Microscope	56
2.5.3	X-ray Photoelectron Spectroscopy	58
2.5.4	Atomic Force Microscopy	60
CHAPTER 03 LAYER DEPENDENT HYDRAZINE ADSORPTION PROPERTIES IN FEW LAYER WS ₂		64
3.1	Introduction	64
3.2	Experimental Methods for Device Fabrication	65
3.3	Surface and structural characterization of WS ₂	69
3.4	Current-Voltage Characteristics Study.....	72
3.5	Hydrazine adsorption of WS ₂	73
3.6	Theoretical Calculations and modeling.....	77
3.7	Conclusion.....	81
CHAPTER 04 SYNTHESIS OF PECVD GRAPHENE AND HEXAGONAL BORON NITRIDE (h-BN)		82
4.1	Introduction	82
4.2	Plasma Enhanced CVD (PECVD) of graphene	85
4.3	Plasma Enhanced CVD (PECVD) of Hexagonal Boron Nitride (h-BN).....	87
CHAPTER 05 GRAPHENE-WS ₂ HETEROSTRUCTURES BY A LITHOGRAPHY FREE METHOD: THEIR ELECTRICAL PROPERTIES.....		91

5.1	Introduction	91
5.2	Experiment Details and Results	93
5.3	Conclusion.....	106
CHAPTER 06 DIRECT FABRICATION OF GRAPHENE/h-BN/GRAPHENE		
TUNNEL JUNCTIONS.....		107
6.1	Introduction	107
6.2	Experiment Details and Results	108
6.3	Conclusion.....	114
REFERENCES		115
CURRICULUM VITAE.....		144

LIST OF TABLES

Table 3.1 The adsorption energy of WS ₂ layers exposed to N ₂ H ₄ molecule	79
Table 4.1 A summary of growth methods reported for 2D h-BN synthesized <i>via</i> CVD method.....	84

LIST OF FIGURES

Figure 1.1 Schematic illustration of graphitic materials with different dimensionalities, clockwise from top left, are 2D-graphene, 3D-graphite, 0D-fullerene, 1D-nanotube	3
Figure 1.2 (a) Left: the band structure of graphene in the honeycomb lattice. Right: magnified representation of the energy bands close to one of the Dirac points. (b) The hexagonal lattice of graphene, with the nearest neighbor δi and the primitive, a_i vectors being depicted. The Brillouin zone of graphene, with the Dirac points K and K' indicated	5
Figure 1.3 Commercial applications of graphene	9
Figure 1.4 Scheme showing the comparison of the quality and cost of graphene made by mostly used conventional techniques.	10
Figure 1.5 Schematic a representation of a series of steps followed in exfoliating graphene layers by using the scotch tape method.....	12
Figure 1.6 Schematic illustration of liquid phase exfoliation technique.....	13
Figure 1.7 Fundamentals of the graphene resultant of epitaxial thermal growth on SiC substrate.....	14
Figure 1.8 Schematic of the chemical route for the synthesis of graphene.....	15

Figure 1.9 The unique physical properties of 2D materials.....	17
Figure 1.10 Comparison of 2D materials in terms of number of published articles during a decade (The vertical axis is in log scale). KEY WORDS: "Graphene", "Hexagonal Boron Nitride", "Phosphorene", "Mxenes", "MoS2 or WS2 or MoSe2 or WSe2 or MoTe2", "Silicene or Germanene". SEARCH ENGINE: Google Scholar.....	18
Figure 1.11 Transition metals and three chalcogen elements (MX_2 is TMDs) in the periodic table.....	19
Figure 1.12 Structure of monolayer different transition metal dichalcogenides (TMD).....	20
Figure 1.13 Schematic of two zone quartz tube furnace used for CVD.....	24
Figure 1.14 Structure of h-BN (a) Stereogram (b) The 2D floor plan (a single layer) (c) few layer h-BN.....	32
Figure 2.1 (a) Schematic illustration of thermal evaporation process using resistive heating boat (b) Schematic diagram of thermal evaporator (c) Digital image of the inside of vacuum chamber setup (in current work).....	38
Figure 2.2 Schematic diagram of CVD reactor for sulfurization of tungsten oxide.....	45
Figure 2.3 CVD reactor for sulfurization of thermally evaporated oxides setup in our labatory.....	45
Figure 2.4 Mechanism of graphene growth involving the decomposition of CH_4/H_2 mixed into the plasma.....	48

Figure 2.5 Shows the sample holders that we have used to hold the TEM grid on the substrate during the process of (a) the WO_3 and graphene h-BN deposition (b) the gold deposition.....	49
Figure 2.6 Digital image of Raman spectroscopy System.....	50
Figure 2.7 The energy diagram describing the Rayleigh and Raman scattering.....	51
Figure 2.8 (a) Raman spectra of graphene on SiO_2/Si [1], (b) The Raman spectra for various layers of graphene on SiO_2/Si , (c) 2D band method is indicating the layer number of graphene.....	53
Figure 2.9 illustrates the schematic diagram for four Raman active modes of Transition metal dichalcogenide.....	54
Figure 2.10 Raman spectra of (a) WS_2 for from bulk to single layer layers and (b) few layers h-BN.....	55
Figure 2.11 Field Emission Scanning Electron microscope used in this work.....	56
Figure 2.12 Schematic illustration of internal components of SEM (left), Process flow chart of image formation using electron beam in SEM (right).....	57
Figure 2.13 Schematic of X-ray photoelectron spectroscopy.....	58
Figure 2.14 X-ray photoelectron spectroscopy system used during this research.....	59
Figure 2.15 (a) Schematic diagram of a typical AFM system (b) WS_2 AFM image and height profile.....	61

Figure 2.16 MFP-3D BIO AFM setup that we use for characterizing our samples (A) Top View camera for the purpose of alignment and for probe viewing (B) Atomic force microscope's head (C) sample area. (D) optical alignment for X and Y. (E) Hamamatsu video camera for viewing and recording in high resolution (F) Head stand (G) XY Mirror (H) Standard cantilever holder (I) cantilever (J) Quartz window (K) cantilever Clip (L) the tip.....	62
Figure 3.1 Temperature profile during sulfurization of tungsten oxide.....	67
Figure 3.2 WS ₂ based device fabrication scheme using a lithography-free technique.....	68
Figure 3.3 SEM images of few-layer and multi-layer WS ₂ samples thickness (a) 2 layers (b) 3 layers, and (c) 12 layers.....	69
Figure 3.4 AFM images and the height profile of few-layer and multi-layer WS ₂ samples (a) 2 layers (b) 3 layers (c) 12 layers.....	70
Figure 3.5 Raman spectra of WS ₂ samples with varying number of layers.....	71
Figure 3.6 I-V characteristic of WS ₂ samples with varying thicknesses.....	72
Figure 3.7 Schematic of hydrazine the absorption measurement setup.....	73
Figure 3.8 Instrumental setup used in this work for hydrazine adsorption.....	74
Figure 3.9 Resistive response to hydrazine at room temperature for WS ₂ samples with varying thicknesses.....	75

Figure 3.10 Relaxed structures of the monolayer (a), double-layer (b), and multi-layer (c) WS ₂ exposed to N ₂ H ₄ molecule. The numbers indicate the shortest distance between N ₂ H ₄ and WS ₂ layers, and the layer separations. The yellow, green, blue, and grey dots represent the S, W, N, and H atoms, respectively.....	78
Figure 3.11 The band structures of the pristine 3x3 WS ₂ monolayer (a), the monolayer WS ₂ with N ₂ H ₄ (b), the double-layer WS ₂ with N ₂ H ₄ (c), and multi-layer with N ₂ H ₄ (d), respectively. The red lines are the impurity states associated with the N ₂ H ₄ molecule.....	80
Figure 4.1 Home-built split ring radiofrequency plasma enhanced CVD system for graphene growth.....	86
Figure 4.2 The temperature profile for graphene growth on SiO ₂ /Si wafer.....	87
Figure 4.3 Home-built split ring radiofrequency plasma enhanced CVD system for h-BN growth.....	89
Figure 4.4 The temperature profile for the growth of hexagonal boron nitride (h-BN) on SiO ₂ /Si substrate.....	90
Figure 5.1 The scheme of Graphene-WS ₂ heterostructure device fabrication.....	94
Figure 5.2 Detailed scheme of Graphene-WS ₂ heterostructure device fabrication schematically describing each step.....	95
Figure 5.3 Detailed scheme of Graphene device fabrication for electrical characterization. Both schematic diagrams and real optical images are presented.....	96

Figure 5.4 (a) AFM image of the heterostructure region. (b) a blown-up image with clearly labelled regions. The isolated regions of the Si/SiO ₂ substrate, graphene, and WS ₂ are clearly shown. The height profiles for substrate-WS ₂ , substrate-graphene, and substrate-heterostructure interfaces are shown.....	97
Figure 5.5 (a) Raman spectrum of the graphene-WS ₂ lateral heterostructure with 632 nm laser excitation in an Invia Renishaw Raman spectrometer. In addition to the overlapped area, Raman spectra of individual graphene and WS ₂ regions are also shown (b) Optical image of the heterostructure with distinct regions of graphene, WS ₂ , and graphene-WS ₂ overlapped area. The positions where Raman spectra taken are denoted by open circles.....	98
Figure 5.6 Raman spectra of graphene and WS ₂ from isolated regions of the WS ₂ -graphene heterostructure. Each peak has been identified.....	100
Figure 5.7 I-V characteristics of WS ₂ , graphene, and graphene-WS ₂ heterostructure; Current, I for WS ₂ and graphene-WS ₂ heterostructure are shown in the left axis while that of graphene is shown in the right axis.....	101
Figure 5.8 Temperature dependence of the resistance, R(T) of graphene, WS ₂ , and graphene-WS ₂ heterostructure. The inset shows R(T) of graphene in an expanded scale.....	102
Figure 5.9 Mott VRH analysis of (a) Graphene (b) WS ₂ , and (c) Graphene-WS ₂ lateral heterostructure.....	103

Figure 5.10 Magnetoresistance of graphene, WS ₂ , and graphene-WS ₂ heterostructure at 20 K. The dotted lines for graphene and heterostructure represent the quadratic magnetic field dependence B^2	104
Figure 6.1 The scheme of Graphene/h-BN/Graphene tunnel junction fabrication.....	109
Figure 6.2 Raman spectra of graphene and h-BN with 632 nm laser excitation in an Invia Renishaw Raman spectrometer.....	110
Figure 6.3 (a) XPS survey plot of h-BN deposited by PECVD. (b) XPS peak of B1s (c) XPS peak of N1s.....	111
Figure 6.4 I-V characteristics of Graphene/h-BN/Graphene tunnel junctions for varying h-BN thicknesses.....	112
Figure 6.5 I-V characteristics with logarithmic I of Graphene/h-BN/Graphene tunnel junctions for varying h-BN thicknesses.....	113

CHAPTER 01

INTRODUCTION

1.1 Two-dimensional heterostructures

Two dimensional (2D) materials are of great interest in a wide variety of applications owing to their unique structural properties [2]. The crystal structure of these 2D materials is similar to bulk layered crystals, with weak van der Waals forces holding the layers together [3]. Particularly for device fabrication, 2D materials are of great significance when they are patterned laterally on substrates or stacked in the form of heterostructures [4]. When a 2D material is stacked with another 2D material, the resulting structure is a vertical 2D heterostructure. Nevertheless, the layers are mostly composed of different types of crystals, and their lattices are often not aligned.

Such stacked structures are entirely different from the usual 3D semiconductor heterostructures. Each layer in 2D heterostructure tends to act simultaneously as the bulk material and the interface, reducing the amount of charge displacement within each layer. Nonetheless, the charge transfers between the layers can be significant which can, in turn, induce large electric fields, thereby offering exciting possibilities in band-structure engineering.

The physics of 2D materials and heterostructures is an exciting emerging domain in physics, which is also referred to as 2D physics [5]. The physics involved in the absence of long-range order, 2D excitons, commensurate-incommensurate transition, etc. play an important part in the development of novel heterostructure devices including light emitting

diodes, tunneling transistors, resonant tunneling diodes, etc. [5, 6]. It is anticipated that the ultimate length scale of such 2D materials, 2D heterostructures, and their corresponding unique properties can find potential application in device fabrication.

This thesis presents methods of synthesizing 2D materials and their heterostructures by thermal evaporation/conversion, chemical vapor deposition/plasma enhanced chemical vapor deposition techniques and fabricating electrical devices without the use of microfabrication. The electrical properties of these devices will also be discussed in detail.

1.2 Background of graphene

The layered materials of 2D materials have a unique property that differs from its bulk counterpart when it is reduced to its physical limit. Typically, graphene is the most studied 2D material, mainly because of its unique optoelectronic, electrochemical, and biomedical applications.

Carbon is categorized as a group-14 element in the periodic table; it is present in all organic compounds, the earth's crust, atmosphere, etc. Due to the flexibility of its chemical bonding, carbon-based systems indicate an unlimited number of various structures which have different physical properties. The well-known compounds with carbon structures are graphite, diamond, and amorphous carbon. Carbon has an atomic number of 6 with an electron configuration of $2s^2 2p^2$. Carbon tends to form covalent chemical bonds between its atoms with sp^1 , sp^2 , and sp^3 hybridization. The most known sp^2 hybridized carbon allotrope is graphite, and it is a layered structure having intralayer sp^2 hybridization and interlayer van der Waals interactions. We have four graphitic materials with different dimensionalities (see Figure 1.1). Graphene can be visualized as a

fundamental building block of graphitic materials. Graphene can be stacked to form 3D-graphite, rolled to form 1D-nanotubes and wrapped to form 0D-fullerene [7].

Figure 1.1 Schematic illustration of graphitic materials with different dimensionalities; clockwise from top left are 2D-graphene, 3D-graphite, 0D-fullerene, and 1D-nanotube [8].

Graphene is a universally known material used by scientists; it is a 2D nonmaterial that is made up of a planar sheet that is one atom thick. For a long time, it was considered a thermodynamically unstable material, and therefore it was generally believed that it could not exist as a free-standing material [9]. In 1947, Philip Wallace, a Canadian physicist, managed to illuminate the extraordinary electronic properties of graphene [10]. For decades, the material was considered for academic and theoretical purposes only; however, Geim, Novoselov, and co-workers transformed it into an elusive free-standing graphene

film, a breakthrough in graphene research that won them the Nobel Prize for Physics in 2010. Graphene is simply a 2D honeycomb lattice that consists of a monolayer of carbon atoms and is considered the basic structure of graphitic materials with distinct dimensions.

Scientific studies of the past 40 years have found that graphene is a good condensed matter, which is in line with (2+1) dimensional quantum electrodynamics. This study was responsible for making the graphene a successful theoretical model. The experiment conducted on graphene assured that the charge carriers somehow had no mass Dirac fermions. This feature made researchers take an interest in graphene.

Over seventy years ago, Landau and Peierls predicted that 2D crystals would be thermodynamically unstable and would not exist [11, 12]. Their theory postulated that the divergent contribution of the thermal fluctuations in low dimensional crystal lattice should result in the displacements comparable to their interatomic range. Experimental observation provided support for this theory.

Experimental discovery of graphene and other free-standing 2D atomic crystals (e.g., single-layer boron nitride) have helped researchers accomplish crystal growth on top of non-crystalline substrates and in liquid suspensions. Typically, one atomic plane is known as a 2D crystal, while a large number of layers is referred to as a thin film of a 3D material. In the case of graphene, 10 to 20 layers are generally considered to be 3D [13].

1.3 Band structure of graphene

Wallace was the first person to study the electronic energy band structure of graphene, using the tight binding method [10]. He explained the behavior as being semimetal because of a lack of an energy gap and between the valence and bands and vanishing density of states at the point where the conduction and valence bands touch at the Brillouin zone corners.

The touched point is referred to as the Dirac point, as indicated in Figure 1.2 (a). Undoped graphene has its Fermi level lie precisely at the Dirac point, which makes graphene a zero-bandgap semiconductor. This unique band structure provides the carriers with a constant Fermi velocity that allows graphene to be easily tuned from electron-like to hole-like via an external gate. The hexagonal arrangement of carbon atoms in graphene and the corresponding hexagonal Brillouin zone are shown in Figure 1.2 (b) and (c).

Figure 1.2 (a) Left: the band structure of graphene in the honeycomb lattice. Right: magnified representation of the energy bands close to one of the Dirac points [14]. (b) The

hexagonal lattice of graphene, with the nearest neighbor δi and the primitive a_i vectors being depicted. The Brillouin zone of graphene, with the Dirac points K and K' indicated.

Figure 1.2 indicates that the shape of graphene is a triangular lattice with a basis of two atoms for every unit cell; the lattice vectors are given by

$$\mathbf{a}_1 = \frac{a}{2}(3, \sqrt{3}), \quad \mathbf{a}_2 = \frac{a}{2}(3, -\sqrt{3}), \quad (1-1)$$

where $a \approx 1.42 \text{ \AA}$. On the other hand, the reciprocal-lattice is represented by the vectors

$$\mathbf{b}_1 = \frac{2\pi}{3a}(1, \sqrt{3}), \quad \mathbf{b}_2 = \frac{2\pi}{3a}(1, -\sqrt{3}) \quad (1-2)$$

The positions of Dirac points are represented by the vectors

$$K = \frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a}, \quad K' = \frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a}, \quad (1-3)$$

The three nearest neighbor vectors in real space are represented by

$$\delta_1 = \frac{a}{2}(1, \sqrt{3}), \quad \delta_2 = \frac{a}{2}(1, -\sqrt{3}), \quad \delta_3 = -a(1, 0) \quad (1-4)$$

The location of six second nearest neighbors is at $\delta'_1 = \pm a_1$, $\delta'_2 = \pm a_2$, $\delta'_3 = \pm(a_2 - a_1)$. The tight-binding Hamiltonian for each electron in graphene is given by

$$H = -t \sum_{\langle i,j \rangle, \sigma} (a_{\sigma,i}^\dagger b_{\sigma,j} + \text{H.c.}) - t' \sum_{\langle\langle i,j \rangle\rangle, \sigma} (a_{\sigma,i}^\dagger a_{\sigma,j} + b_{\sigma,i}^\dagger b_{\sigma,j} + \text{H.c.}) \quad (1-5)$$

The general energy bands derived from this Hamiltonian has the following form [10]:

$$E_{\pm}(k) = \pm t \sqrt{3 + f(k)} - t' f(k), \quad (1-6)$$

$$f(k) = 2 \cos(\sqrt{3}k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2}k_y a\right) + \cos\left(\frac{3}{2}k_x a\right), \quad (1-7)$$

Here, the plus sign applies to the upper (π^*), while the minus sign applies to the lower (π) band.

Normally, the absence of a bandgap in the energy dispersion of graphene indicates that the conduction in this particular material cannot be easily turned on or off using a gate voltage representing the Fermi level, which inhibits the use of graphene in an application of a conventional transistor.

1.4 Properties and potential applications of graphene

There are two carbons in each cell unit of a perfect graphene sheet. Each of the carbon atoms has four valence electrons, three of which are used in chemical bonding. The bonding energy of one C-C bond in graphene amounts to 4.93 eV [15]. The remaining 2p orbitals on each carbon atoms, which are perpendicular to the graphene planar structure, form highly delocalized π bonds. In a one-unit cell, there are two such electrons, corresponding to two π bands, π and π^* , with π corresponding to valence band and π^* corresponding to the conduction. Graphene has properties that can be broadly categorized.

Mechanical properties of graphene: graphene is extraordinarily light at 0.77 mg/m², and monolayer graphene has been experimentally proven to have second- and third-order elastic stiffness of $E^{2D} = 340 \pm 50 \text{ Nm}^{-1}$ and $D^{2D} = -690 \pm 120 \text{ Nm}^{-1}$, respectively. It also has an intrinsic length of $\sigma^{2D}_{\text{int}} = 42 \pm 4 \text{ Nm}^{-1}$. These correspond to Young's modulus of $E = 1.0 \pm 0.1 \text{ TPa}$ and a third-order elastic stiffness of $D = -2.0 \pm 0.4 \text{ TPa}$.

Electronic properties: The charge carriers in graphene have reduced effective mass due to no bandgap; graphene monolayer has an electrical conductivity of (4.84–5.30) 10³ W mK⁻¹ and charge mobility of 200,000 cm²V⁻¹s⁻¹ [16]. Graphene also exhibits an ability

to interact with all wavelengths of the light spectrum with an ability to absorb a 2.3% fraction of light. Graphene is also reported to have a thermal conductivity of 3000–5000 $\text{Wm}^{-1}\text{K}^{-1}$ [17, 18].

Graphene is believed to have the potential for the following applications: transparent layers of graphene electrodes act as good conductor of electricity; they can, therefore, be used in solar cells [19-21] and touch screens [22]. They also have a characteristic of reducing weight in lithium batteries, hence its use in the anode to provide a pathway for lithium ions to stick to the substrate. They are, therefore, used in micro cells for new generation power systems [23]. In supercapacitors, they can most probably be used as conductive plates due to their large surface area to mass ratio [24]—such an application can be a significant contribution due to an attribute of green energy solutions in electric vehicles, airplanes, and cars. Graphene has been successfully applied in the detection of glucose [25], cholesterol [26], hemoglobin [27], and cancer cells [28]. This is facilitated by its high sensitivity to changes in molecular activities since the carbon atoms in its structure are exposed to the surroundings.

Figure 1.3 Commercial applications of graphene [29].

Figure 1.3 shows the industrial applications of graphene; it has been applied widely in semiconductors, electronics and optoelectronics applications, and energy applications (mainly batteries/ultracapacitors), compared to different types of applications such as aerospace, composites, biomedical, and telecommunications [29]. The potential in graphene application encounters some challenges that need to be overcome to ensure successful technological and commercial applications. The problems include the high cost of large-scale synthesis as well as deficiency in knowledge of its electronic dependence.

1.5 Synthesis of graphene

Graphene can be prepared using different methods—the method used is reflected in the quality of the graphene produced. Currently, different methods are used to make varying shapes and qualities of graphene. This follows a discovery in the 1970s that carbon solidifies into thin coating layers of graphite on transition metals surfaces [30]. The methods, however, are not fully implementable in a vast industrial setup.

Figure 1.4 Scheme shows the comparison of the quality and cost of graphene made mostly through conventional techniques [31].

1.5.1 Mechanical exfoliation

This method was previously used to prepare single layers of high-quality graphene flakes on the substrate of choice [32]. Mechanical exfoliation is a practice in nanotechnology where crosswise force is initiated on the surface of layered structure materials. The suitability of the method lies on the fact that unpacked layers of highly ordered pyrolytic graphite (HOPG) are held together by weak van der Waals forces. In addition to this, the inner layer distance is $3.34 \text{ \AA}$, while their bond energy is 2 eV/nm^2 [33]. Therefore, it requires about $300 \text{ nN}/\mu\text{m}^2$ of an external force, which can be contained by adhesive tapes, to remove single layers of graphene from graphite [34]. Graphene accumulated on the adhesive tape is detached off using go-betweens such as scotch tape [32], ultrasonication [35], and an electric field [36] and even by a transfer printing technique [37, 38]. After successful detaching off processes, graphene obtained is transformed into SiO_2/Si by moderate pressing [32, 39] (Figure 1.4). Mechanical exfoliation is an easy-to-learn method that requires standard equipment for implementation; this property encouraged scientists to adopt it quickly. However, it is not applicable in an extensive industrial setup. The graphene flakes obtained from this method, however, display characteristics of optical microscopy, Raman spectroscopy, and AFM. They are also tiny with minimal width margins in μm .

Figure 1.5 Schematic representation of a series of steps followed in exfoliating graphene layers by using the scotch tape method [40].

1.5.2 Liquid phase exfoliation

This is a method that involves exfoliation of graphene from graphite layers by using a solvent with surface tension (γ) about 40 mJm^{-2} [41-43], which helps in increasing the total area of graphite crystallites. The most preferred solvents are N-methyl-2-pyrrolidone (NMP) [44], ortho-dichlorobenzene [45], and dimethylformamide (DMF) [46]. Sonication is applied to split graphite flakes into single graphene sheets. For acquiring different sizes and thicknesses of graphene, ultrasound treatment is used. Graphene sheets are eventually separated from the unexfoliated materials by centrifugation process.

Researchers have recently used this method to obtain liquid graphene and remove samples of their chemical vapor deposits. This has enabled further processing for practical application [47]. The graphene dispersion in a form that can be processed and applied to various substrates using spray coating, ink-jet printing, or spin coating [48, 49]. This method has a wide range of use; some of the ways include applying peeled off graphene as mechanical reinforcement for polymer-based composites [41], graphene dispersions as optical limiters, and films of graphene flakes as transparent conductors or sensors.

Figure 1.6 Schematic illustration of liquid phase exfoliation technique [50].

1.5.3 Epitaxial growth on silicon carbides

This method is highly preferred. It involves epitaxial thermal growth on a single crystalline silicon carbide (SiC). SiC is a polar material with two non-alike terminations, namely the Si-face, corresponding to the (0001) polar surface, and the C face (000 $\bar{1}$). For both terminations, the growth mechanism of graphene is driven by the same physical process: sublimation of Si at different temperatures at a rate much faster than C due to its higher vapor pressure [51]. The remaining C forms a graphene film on the surface. The

surface reconstructions and growth kinetics for Si and C faces are various graphene growth rates, growth morphologies, and electronic properties [52]. The method has several advantages; for example, the size of graphene produced can be matched to the substrate applied, and no transfer is necessary for device processing.

The shortcomings of this method, however, are notable. For example, the graphene formed is more delicate compared to the one resulting from exfoliation. This is due to the difference in SiC and graphene. It is also expensive since it requires very high temperatures in addition to the high cost of SiC.

Figure 1.7 Fundamentals of the graphene arising from epitaxial thermal growth on SiC substrate [53].

1.5.4 Wet chemical synthesis of graphene

This is a cheap way of producing graphene; it involves converting graphite into graphene oxide sheets in one large scale. Hummers' method [54] is applied to oxidize

graphite through the addition of oxidants nitric acid, sulfuric acid, and potassium permanganate to obtain graphene oxide. The graphene oxide sheets produced contain sp^3 hybridized atoms, which make it necessary to reduce the atoms. Various methods are used for the reduction process. They include thermal that involves the removal of oxide functional groups by heat treatment [55]. Reducing agents such as hydrazine [56], sodium borohydride [57], hydroquinone [57], and ascorbic acid [58] are also used, which have the advantage of giving rise to less hydrophilic graphite sheets due to the removal of oxygen atoms [59]. However, further research is required to improve the method due to its shortcomings, especially when some amount of functionalization groups such as oxygen, hydroxyl, and epoxy are not removed in the chemical reduction process.

Figure 1.8 Schematic illustration of the chemical route for the synthesis of graphene [59].

Graphene arising from this method is used in different applications; for example, they are used as paper-like materials, polymer composites, energy storage materials, and transparent conductive electrodes.

Other methods used to produce graphene have not been discussed in this paper. Research, however, shows that they require some adjustments in terms of cost-effectiveness and large-scale applicability; this makes them suitable for adoption in industrial processes. These methods include electron beam irradiation of PMMA nanofibers [60], arc discharge of graphite [61], a thermal fusion of PAHs [62], and conversion of nondiamond [63].

1.6 Beyond graphene materials

Two-dimensional electronic materials cover a wide range of materials, including insulators, semiconductors, metal, and even superconductors (Figures 1–9) [64]. After the discovery of graphene, it remained to be the most studied 2D material structure for a long time [32]. Afterward, other exciting 2D materials and their properties were investigated, and their unique features were studied [65]. One groundbreaking 2D material other than graphene that gained popularity in a short time is hexagonal boron nitride (h-BN), which was predicted theoretically to induce a bandgap in graphene when graphene was deposited onto it [66]. This discovery resulted in a significant increase in experimental research on h-BN, and eventually, it was anticipated that h-BN could be an ideal substrate for graphene-based electronics [67]. Following graphene and h-BN, the investigations carried out on several other semiconducting 2D layers gave evidence that the band structure of a subset of the 2D materials family changed severely, as they were thinned to monolayer thickness

[68]. Formulated fabrication techniques ignited the interest of many in the electronics community [69]. Many researchers now emphasize novel semiconductors 2D materials, particularly transition-metal dichalcogenides (TMDs). Figure 1.10 shows the growth of research on 2D materials since the mid-2000s. Several layered materials are also being investigated alongside TMDs, such as monochalcogenides GaSe, mono-elemental 2D semiconductors (silicene, phosphorene, germanene), and MXenes (Figure 1.10).

Graphene

- Ambipolar conduction
- Best thermal conductivity (in plane)
- Record e^-/h^+ mobility

Bilayer Graphene

- Direct bandgap, controlled by E-field
- Potential for exciton condensate

Single-layer MoS₂

- Excellent semiconductor
- Suitable for scaled electronics
- Valleytronics

h-BN

- Outstanding dielectric and substrate
- Ideal passivation
- tunneling barrier

semi-metal (Graphene); semiconductor (MoS₂, WS₂); insulator (hBN); metal and superconductor

Figure 1.9 The unique physical properties of 2D materials [70].

The 2D materials display a rich array of physical properties and a versatile system of materials from semimetal to semiconductor, insulator, metal, and even superconductors.

Figure 1.10 Comparison of 2D materials in terms of the number of published articles during a decade (the vertical axis is in log scale). KEYWORDS: “Graphene,” “Hexagonal Boron Nitride,” “Phosphorene,” “Mxenes,” “MoS2 or WS2 or MoSe2 or WSe2 or MoTe2,” “Silicene or Germanene.” SEARCH ENGINE: Google Scholar [71].

1.7 History of transition metal dichalcogenides (TMDCs)

The transition metal dichalcogenides comprise a material that is referred to as transition metal atom, which is attached to two atoms from Group 16 (chalcogen) of the periodic table [72, 73]. Figure 1.8 shows about 44 different transition metal dichalcogenides (TMD) compounds through transition metals and three chalcogen elements.

H	<div>MX₂ M = Transition metal X = Chalcogen</div>																He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La - Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac - Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

Figure 1.11 Transition metals and three chalcogen elements (MX_2 is TMDs) in the periodic table [74].

For decades, they have been applied as additives to reduce friction through lubrication [75, 76]. However, with the advent of graphene in 2004 [32], they roused a new interest. TMDs have also been shown to have catalytic abilities [77, 78]. Monolayer MoS_2 has indicated that its edges are the highly active catalytic sites, while the basal plane is

catalytically inert [79-81]. Moreover, remarkable optical properties have been witnessed, such as room temperature photoluminescence effect in a single layer of WSe₂ [82, 83] and WS₂ [84].

Figure 1.12 Structure of monolayer different TMDs.

TMDs are unique compounds in which the bulk material is composed of individual layers of material, which are piled vertically to each other. Each layer has hexagonal orthorhombic symmetry [85-87] and can be seen as a layer of transition metal atoms sandwiched between two layers of chalcogen atoms (Figure 1.12).

In TMDs, it was discovered that these individual layers were capable of being separated through mechanical exfoliation method where a single layer TMD could be

synthesized [88-90]. This led to a steady increase in the publication of TMD systems. Monolayer TMDs can be of metallic, semiconducting, or insulating nature [73, 91, 92]. They have versatile properties and can be tuned in based on the number of layers existing in the specimen. The properties such as photoluminescence, band structures, conductivity, and vibrational modes can all be optimized by varying the layering number [84, 90, 93-98]. The monolayer form and tunable properties have made TMDs a very promising material in microelectronics and other fields. For example, a transition from indirect bandgap (in bulk) to direct bandgap (in single-layer form) is responsible for the photoluminescence (PL) effect at room temperature in monolayer TMDs [84, 88, 90]. The phonon modes can also be altered in single-layer sheets since the lack of inter-layer van der Waals interplay can modify the restoring forces of the lattice vibrations [89, 97, 99].

The most commonly known TMDs are the MX₂ grouping with M = Mo, W, and X = S, Se, Te. Molybdenum is made of 42 electrons having an electronic configuration of $1s^2 2s^2 p^6 3s^2 p^6 d^{10} 4s^2 p^6 d^5 5s^1$, and sulfur has 16 electrons with an electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^4$. In-plane bonding is covalent because of the 4d orbital of molybdenum and the 3p orbital of sulfur [100]. The out-of-plane bonding is the one that rouses considerable interest in TMDs. Each layer interacts with the adjacent layers through van der Waals forces. This attraction is fragile (15–20 meV/Å²) [101] when compared with the in-plane forces; this is the reason why TMDs can be fabricated in monolayer form.

TMDs bandgap is in the range of 1.0 eV to 2.5 eV in the monolayer form [74, 102, 103]. The bandgap of WS₂ increases as the number of layers decreases and this inverse relationship is because of a reduction in energy at the Γ point and an increase in energy at the K point in the energy dispersion relation [84]. Because the TMD group has a small

lattice mismatch and is a van der Waals material, several heterostructures are in a position of being synthesized [104-107]. The above structures enable bandgap engineering, absorption enhancement, and developed charge separation. The aforementioned remarkable features of TMDs render these materials sought-after for a wide variety of novel optoelectronic devices. So far, field effect transistors, photocatalysis, photovoltaics, and logic circuits have been studied. The physics in these monolayer compounds has been demonstrated to be very rich and have various device presentations at the laboratory scale [69, 95, 107-112]. A good example is the vertically accumulated heterostructures of graphene/h-BN, which have undergone synthesis [113, 114], and graphene/MoS₂/graphene and graphene/WS₂/graphene have been used to describe photoactive devices [115]. Theoretical considerations suggest that it is probable to obtain a direct bandgap layered material with the right mixture of alternated TMD sheets [116]; especially when the chalcogen atom is varied in the adjoining layers, the photogenerated electrons and holes could be isolated in adjacent layers [116]. WSe₂/MoS₂ heterojunctions [105, 117, 118], with photovoltaic behavior [117], have been lately developed by the immediate shift of TMD flakes.

The band alignments for several TMD, which are based on 2D heterojunctions, are potentially applied to the splitting of water [119]. Through thickness engineering, fabrication of quantum structures have been made simple due to the high sensitivity of the band offsets to the number of layers.

1.8 Synthesis of transition metal dichalcogenides

Transition metal dichalcogenides have a similar layer structure as graphene. Moreover, it is worth noting that a single monolayer of TMD is typically a layer of transition metal atoms, which is sandwiched between the two layers of the chalcogenides. Besides having this type of difference, the synthesis of monolayer TMDs naturally follow up the footsteps of graphene. Of the 44 theoretically predicted monolayer TMDs, only five are predicted to be unstable. Currently, the number of synthesized monolayer has risen drastically, and these include MoS_2 , WS_2 , MoSe_2 , and WSe_2 [120-123]; there are still more to be synthesized—some minelayers of TMDs have not been discovered experimentally due to some fundamental reasons.

Through theoretical calculation, it has been found that many TMDs have other crystal structures which are stable [73]. The fundamental reason why some TMDs have not been synthesized is because of the complexity in coming up with the technique of synthesis. If a well-developed recipe is not prepared for a TMD, it could take many experiments to carry a single synthesis. The outcome of the recipe can be determined through the following factors, which are the deposition of the chemical vapor, variables such as the sufficient volume flow rates, the precursor materials, temperature levels, and pressure. However, even if a recipe is well identified, the variations in the equipment such as loss of heat by insulation can still bring complications in the process of synthesizing the material.

1.8.1 Mechanical exfoliation

Mechanical exfoliation has been identified as the first methodology applied in the fabrication of graphene [32]. The limitation of this method is that it is only applicable to materials with a layered structure in heavy form. Typically, TMDs contain a layered structure in bulk form. In the process of mechanical exfoliation, the layers of the material can be removed by an adhesive backed tape [32, 97]—the process is referred to as the scotch tape method. The resulting material from mechanical exfoliation process is slightly small, although they can be about 100 μm [120] in the lateral dimension. Among the other methods of synthesis, mechanical exfoliation gives the lowest yields. It also requires considerable labor. The advantage of mechanical exfoliation is that it produces the highest quality crystal layers. Generally, the benefits generated from using mechanical exfoliation is that it has high mobility, the grain boundaries are much larger, and substrate of any kind can be used [124].

1.8.2 Chemical vapor deposition

Chemical vapor deposition (CVD) is one of the most fundamental methodologies which can be used to reproduce monolayer TMDs routinely.

Figure 1.13 Schematic illustration of two zone quartz tube furnace used for CVD [125].

The system usually assembles the quartz tube furnaces, the rate of volume flow matters, a sensor for pressure, and a vacuum system. The quartz tube furnace usually is made of a single and multi-zone stage of heating (see Figure 1.13).

CVD has many advantages when compared to mechanical exfoliation. The main advantage is that CVD is capable of producing large-scale monolayer films [121, 126, 127]. These films also have a uniform thickness because of the growth parameter, which is controlled. Upon development of a recipe, it can be applied concurrently, and monolayer can be successfully achieved. However, the development of the recipe can be somewhat complicated because CVD at some point scans more than 10 parameters, which can influence the monolayer growth. It is worth noting that growth is significantly affected by substrate preparation [128]. According to Arend M. van der Zande et al. “Improper cleaning of the substrate decreases material yield and produces misshapen layers” [128]. Lattice mismatch of substrate and TMDs can also affect the process of monolayer formation. Besides, when the temperatures are elevated, the substrate selection can be restricted.

1.8.3 Liquid mechanical exfoliation

Liquid mechanical exfoliation (LME) has several forms that have been implemented for the synthesis of monolayer TMDs. Lithium ions can be intercalated into the crystal lattice of TMDs to reduce the inter-layer interaction in bulk material [129, 130]. This is accomplished by the lithium-ion, expanding the interlayer spacing, which is found between successive layers, and it further makes the van der Waal forces weak. Lattice expansion of TMDs is evident in the lithium-ion battery anodes [131, 132]. The material is then suspended in a solvent after the lithium is used in expanding the space between the

layers. When applying lithium, deionized water is taken as the solvent liquid [129]. The following represents the equation of the reaction between lithium and water $2\text{Li(s)} + 2\text{H}_2\text{O(l)} \rightarrow 2\text{LiOH(aq)} + \text{H}_2\text{(g)}$ [129]. Lithium hydroxide formation helps in consuming any lithium present in the material; it also facilitates the process of exfoliation because of the expansion of the lattice by the lithium hydroxide bubbles. The solvent material mixture is usually sonicated for extended periods, which takes about 15 hours [133]. The number of layers of the resulting suspension can be affected by the different ultrasound frequency and temperature variations. After the sonication process, the samples are then centrifuged; this process divides materials in terms of the number of layers that each contains. The last stage of LME is to drop cast the suspension on the intended substrate. LME also has the advantage of applying any substrate. The inhibiting factor of LME is that it encounters less control in terms of the number of layers because of the flake restacking [134]. Through spin coating, the uniformity of layering number in samples can be improved. The other limitation is that the control of exact monolayer by LME parameters is very complicated. The outcome of a particular set of LME parameters results in various layering numbers to be produced as opposed to a specific number of layers.

1.9 Modifications of TMDs and graphene

The more 2D materials are mature, the more their inherent properties are altered. The methods that have been employed to tailor properties of the semiconductor are heterostructures, doping, and surface functionalization. For the development of 2D materials in advanced electronics, it is essential to develop a proper understanding of their properties. By functionalization of graphene using nitrogen in RF plasma, a metal-insulator transition was found in graphene [135]. Heterostructures of graphene have been

synthesized to take advantage of its long-range transport and massless Dirac fermions; however, the issue remains as to how to overcome its zero bandgap [136, 137]. Modification of graphene to encounter its limitations and tailor its properties was a natural progression.

1.9.1 Heterostructures

In consideration of the layered system, we have two types of heterostructures; these are stacked heterostructures that entail the successive vertical stacking of several 2D materials. In-plane (lateral) heterostructure are formed by bonding different compounds within the individual's planes. Stacked structures, on the other hand, can be prepared by combining various synthesis methods and the subsequent utilization of transfer techniques [107, 138]. One way of doing this is chemical etching of substrates to separate the substrate from the monolayer film [121]. The freed film can then be transferred on top of other monolayer films forming stacked heterostructures. Techniques including etching (chemical), electrostatic transfer, mechanical exfoliation, and chemical vapor deposition have been tried to produce stacked heterostructure [139]. Meanwhile, in-plane heterostructures have proven to be even more difficult to synthesize [140].

The objective of forming heterostructures is to join systems that have unique properties, which differ from the separated individual components. This reflects on the stacking or homo-structure, which TMDs automatically form for different layers of the same TMD. One such theoretical study reported that by stacking TMDs with the same transition metal, albeit different chalcogen atoms, the systems could maintain the direct bandgap electronic structure, which is otherwise only seen in monolayer TMDs [116].

When stacking the same TMDs is multiplied, the transition from direct to indirect bandgap occurs [84]. The direct bandgap has the advantage of being more effective in their use of photons. Band alignment of each material is another key benefit. When the different systems in heterostructures are brought in contact, the conduction band minimum (CBM) and the valence band maximum (VBM) of each material get adjusted up to equilibrium. In the real sense, the charges are exchanged between the materials, as their respective Fermi levels reach their equilibrium point. As a result, the CBM of the joined system may be within a single material, while the VBM may be in another material [116]. Layer separation in the CBM and VBM causes the electrons and holes to be physically separated. The separation results in a rise in the exciton lifetime, which is beneficial to photocatalysis, solar cells, photodetectors, and other junction devices

1.9.2 Doping

Doping refers to the incorporation of the atoms directly into the lattice of another material in small quantities. The only significant difference between doping and alloying is one material concentration. Dopant atoms are capable of increasing the number of electrons in a 2D material, while in the alloyed system the individual elements have the same concentration. The atoms in a MoS₂ layered system contain active sites within its edges [141]. After bond formation, there is still a contribution of the electrons to the system; this dopant is known as an n-type dopant or donor. The energy level of the dopant electrons is usually closer to the CBM of the original systems. Finite temperatures are capable of supplying energy used to excite the donated electrons into the CBM, where they are freely able to contribute to the conduction of the 2D system. On the other hand, the dopant atoms that contain fewer electrons are referred to as p-type (acceptors) and supply

holes into the VBM of the system. The added charge carriers raise the conductivity rate of the 2D system. Upon the addition of excess dopants, the Fermi level of the original system gets shifted toward the position of the dopant atoms. A study revealed that TMDs doped with potassium at the drain/source contacts in a FET create low contact resistance [142].

Different methods have been developed for doping of the 2D materials. It has been indicated that graphene is capable of being doped with nitrogen, by using exact control of precursor material in CVD [143]. Plasma-assisted CVD [135] and chemisorption [144] have a similar characteristic. To bring atoms into the lattice of a system, one can increase the energy of the dopant atoms. Plasma-aided doping is significant since it can cover large area samples. Nevertheless, on the downside, plasma techniques can also cause degradation to the sample.

Upon introduction of a dopant atom into a system, it occupies a lattice site that would have been occupied by an atom from the original system; the process of taking over a lattice site by a dopant is known as substitutional doping. Moreover, a dopant atom can take the space between the lattice sites of a crystalline material, which is called interstitial doping. If the dopant atoms are not similar to the atomic radius close to their host system, charge carriers can see these dopant atoms as defect sites. Moreover, due to p-type dopants, lone pairs of electrons in the host system can induce magnetic moments [145, 146]. The final issue that dopant atoms can have is that they can be rejected from the host material if they exceed a certain amount. Which may be considered a form of precipitation.

1.9.3 Surface/Edge functionalization

Gas molecules usually interact with the 2D materials, as the dangling bonds on the edge and lone electron pairs atoms can easily be absorbed into the 2D system; the process by which elements are attached to the 2D system (surface/edges) is known as functionalization. During this process, the atoms do not need to be incorporated into a crystal structure of the sample. Li et al. found that functionalization could be enhanced by using lasers [147]. WS₂ nano-flakes have known to exhibit gas sensing capabilities, for example, through surface physical-absorption of NH₃ [148]. On top of being simple, functionalization has another essential role; when different atoms are attached to the 2D systems, several properties of the structure might change. Bandgaps engineering allows novel optical devices to be fabricated. The next crucial step in optoelectronics may be the realization of commercial products, such as photodetectors and gas sensors by surface functionalization.

1.10 Background of hexagonal boron nitride

Hexagonal boron nitride is a white, powdery substance that falls in the category of carbon system; it assumes a hexagonal structure in addition to a variety of differences from other forms of carbon. This raises suitability for its use in a wide range of applications. It has some structural similarities to graphite and graphene: an allotrope of graphite [149-152].

Boron nitride was discovered at the outset of the 19th century with several attempts devoted to preparing it. In 2005, a group from the University of Manchester, for instance, developed a two-dimension h-BN using mechanical exfoliation [65]. Elsewhere,

Nagashima et al. made an h-BN using epitaxial growth on metal surfaces method [153]. Boron nitride is synthetic III-V assuming different forms of existence. The structures range from hexagonal to crystalline, amorphous, cubic, and wurtzite [154]. Hexagonal form is the most prominent of them all and popularly known as white graphite. It consists of hexagonal layers with covalently bonded B and N (sp^2 -hybridization), structured on top of each other at a distance of 0.33 nm [155] and held by weak van der Waals forces [156]. Hexagonal boron nitride has a variety of outstanding characteristics. It has got a bandgap of about 5.9 eV, the heat conductivity of 600 to 1000 W m⁻¹ K⁻¹, and a refractive index of about 1.8 [157-160].

It is used in various ways in real-life applications. It is believed to be chemically stable, hence its use in oxidants, acids, and solvents. It has a property of good insulation with a dielectric trait such as SiO₂. Its bandgap, measured to be 6 eV [161], also makes it suitable to be used as an atomic flat insulating substrate or a tunneling dielectric barrier in 2D electronics as well as graphene [6, 67, 162]. It is also used as a stable coating in hazardous environments due to its strong covalent sp^2 B-N bonds, which results in high thermal and chemical stability, high mechanical strength, and thermal conductivity [163-165].

1.10.1 Structures of hexagonal boron nitride

In comparison to the formation of graphene, B and N atoms of a 2D hexagonal boron nitride are arranged in a form that resembles a honeycomb, as per the law of hexagonal lattice formation (Figure 1.10) [166-168]. The bond (B-N) length is 1.45 Å, formed through sp^2 hybridization. One adjacent N atom combines with three SP^2 orbits of

B atom to establish a strong α bond. Different but similar molecular structures of B-N bonds formed joins by a strong α bond. Weak van der Waals forces joined adjacent layers.

The distance between layers of h-BN is 0.33 nm, slightly lesser than that of graphite. The interlayers slide easily due to the large interlayer spacing as well as the small bonding force in the c-axis direction of h-BN [169-172].

Figure 1.14 Structure of h-BN (a) Stereogram (b) The 2D floor plan (a single layer) (c) Few layer h-BN [168, 173].

1.10.2 Synthesis of hexagonal boron nitride

Several methods have been successfully used to synthesize boron nitride. CVD is the most suitable method for the large-scale production of h-BN. Other methods include liquid phase and mechanical exfoliations. CVD can also be put to control since it utilizes the breakdown of antecedents.

Boron nitride nanosheet (BNNS) is prepared using two general approaches, namely (a) bottom-up, which involves the application of CVD and other deposition techniques and (b) top-down, which includes exfoliation methods. The most commonly used techniques

are pulsed laser deposition [174], chemical vapor deposition [175-179], chemical exfoliation [155, 180-185], and mechanical exfoliation [182, 186-189]. BNNS from exfoliation methods is normally crystalline in structure, although obtaining large amounts is very difficult (see below for a discussion of the methods).

1.10.2.1 Mechanical exfoliation

It is the simplest and the most efficient method, extended from the synthesis of graphene using adhesive tape [190]. From h-BN powder, small monolayers of h-BN—less than a substantial number of microns—have been isolated. Layers of more than 100 microns are prepared using synthetic highly oriented pyrolytic boron nitride (HOPBN) or mechanical cleavage [74, 191]. As indicated in Li et al. using entirely controlled low energy ball milling is another way of mechanical exfoliation of nanosheets [192]. The method has been used to prepare high quality and quantity of h-BN with reduced shortcomings of h-BN nanosheets.

1.10.2.2 Liquid phase exfoliation

This method utilizes the use of solvents in preparation of hexagonal boron nitride. It is exfoliated and dispersed in solvents such as 1, 2-dichloroethane [149], dimethylformamide (DMF) [193], or water [194]. A series of solution steps are followed to prepare substantial quantities of h-BN. The choice of solvent used is optimized to overcome the van der Waals forces amidst layers by ensuring that a solvent's surface energy matches that of h-BN. The best option is a solvent that can reduce the energy of exfoliation, subdue the van der Waals forces between layers, as well as end up in an

optimally defined dispersion, where the Hansen solubility parameter theory can assert the polar hydrogen bonding and the cohesive energy density. This method has several disadvantages. The number of single layers produced is minimal, while it is hard to control the number of layers. Relatively small adjacent size is also a disadvantage [195].

1.10.2.3 Chemical vapor deposition (CVD)

This method is currently the most common, mainly because of its viability in large-scale production of monolayer h-BN compared to the other ways. As early as 1995, an Oshima group reported that monolayer h-BN was epitaxially formed on Ni (111), Pd (111), and Pt (111) using borazine antecedents [153, 196, 197] at a high temperature of about 1000 °C under low-pressure CVD (LPCVD) and atmospheric pressure CVD (APCVD) with several precursors such as borazine, ammonia borane, and diborane with ammonia. Common substrates such as Pt, Cu, and Ni have been used to grow h-BN, although they need transfer process. Direct growth of h-BN on SiO₂/Si at high temperature (1000 °C) has been reported [198].

1.10.2.4 Physical vapor deposition (PVD)

It avoids the complex interrelation growth parameters involved in the CVD process. The B and N atoms join in an organized h-BN layered film by use of Ru (0001) substrate. Another approach uses a similar mechanism to produce films of h-BN on Au (111) substrate with a 60-degree rotation angle between interconnected triangular h-BN domains.

1.10.2.5 Pulsed laser deposition (PLD)

This method was adopted to reduce the growth of temperatures and achieve good stoichiometric h-BN. A high crystalline h-BN was produced from an amorphous form at 700 °C using the technique conducted by Glavin et al. In addition to this, a few monolayers of h-BN were achieved by Terry et al. on SiTiO₃ substrate with Ag films acting as the buffer layer. This method resulted in low crystalline h-BN as compared to liquid and CVD exfoliation [174].

Research in the field of hexagonal boron nitride continues being developed, and improvement efforts for large-scale and efficient synthesis methods are currently underway.

CHAPTER 02

CHEMICAL VAPOR DEPOSITION (CVD) OF 2D MATERIALS: SYNTHESIS AND CHARACTERIZATION

2.1 Introduction

As we discussed in Chapter 01, there are numerous ways to achieve 2D material systems. Many factors including temperature, pressure, gas flow, etc. need to be optimized to produce the desired 2D material. Growth and characterization of 2D materials have been highlighted for single layer films [69, 122, 199]. It is essential to subject prepared materials to controlled surface engineering to invoke more interesting properties, even though monolayers display different properties. One of the direct methods of achieving this is the use of heterostructures. In-plane and stacked heterostructures of TMDs have been reported [140]. Research progress on in-plane heterostructures, however, has been slower compared to stacked heterostructures due to numerous issues associated with the synthesis. It is essential to have good control and reproducibility especially in large-scale production of devices. The previous methods, however, had poor control since the synthesis was entirely based on CVD methods. We have developed a novel method to synthesize TMD/graphene heterostructures with good control using both thermal evaporation/conversion and CVD.

2.2 Thermal evaporation and CVD kinetics and transport

Thermal evaporation is a method that has been used for years in the synthesis of materials. In this method, a substrate is placed on the surface of a precursor. A boat is subjected to resistive heat to evaporate a precursor material toward a substrate over the initial precursor material, as shown in Figure 2.1. The atoms come into contact with the substrate and stick to the substrate. This method has various advantages, mainly the high level of control on the amount of material deposited on the substrate. It is also possible to carry out large-scale synthesis. Large-scale production might, however, be ineffective if depositions out of the substrate are not eliminated in the right direction.

Thermal evaporation is broken down into three main components: vacuum chamber environment, source evaporation or sublimation, and substrate adhesion. An experiment can demonstrate synthesis in a vacuum chamber. Evaporation in a vacuum environment has various advantages. It lowers the temperatures required in evaporating the original material; it also reduces the impurity that stems from the impurity atoms. Thermodynamics can also be used to prove that, in the course of the process, heat transfer from the evaporating source to the substrate is reduced.

Figure 2.1 (a) Schematic illustration of thermal evaporation process using resistive heating boat (b) Schematic diagram of thermal evaporator [200] (c) Digital image of the inside of vacuum chamber setup (in current work).

The first law of thermodynamics states that for all adiabatic processes between two specified states of a closed system, the net work done is the same regardless of the nature of the closed system and the process. The law can be re-branded according to the principle of heat conservation. It can be expressed as follows:

$$E_{in} - E_{out} = \Delta E_{system} \quad (2-1)$$

An analysis of the experiment can be demonstrated in two diverse situations. The first situation involves a sealed vacuum chamber disconnected from a pumping source with a trace leakage. In a different case, a closed vacuum chamber is connected to a pumping system. Transfer of the heat lost from the system through the boat takes place through conduction, convection, and radiation. Conduction involves the direct transfer of heat energy from adjacent strong atoms (atom has more energy) to the weaker atoms through contact. It is normally negligible due to reduced contact of adjacent atoms for the low-pressure system. The rate of heat conduction is represented by

$$Q_{cond} = k_t A \frac{\Delta T}{\Delta x} \quad (2-2)$$

where Q_{cond} is the time-dependent heat conduction in watts, k_t is the thermal conductivity of the material, A is the area normal to the direction of heat transfer, ΔT is the change in temperature from point y_1 to point y_2 (for this analysis, y_1 is the boat, and y_2 is the substrate), and k_t is thermal conductivity of air = 0.026 W/m×K. Transfer of heat from solids to adjacent liquids takes place through convection. It is, however, expected to be zero in both systems. In 1879, Stefanie established a relationship between the temperature of a solid

object to the power it emits as light; the experiment concluded the following formula—the Stefan-Boltzmann law:

$$Q_{rad_max} = \sigma AT_s^4 \quad (2-3)$$

where Q_{rad_max} is the maximum rate of radiation emitted. $\sigma = 5.670373 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$ is the Stefan-Boltzmann constant. T_s is the absolute temperature of the solid; A is the area. The formula is only applicable to blackbody structures since other actual world structures incorporate a constant ε in the formula as highlighted.

$$Q_{rad} = \varepsilon \sigma AT_s^4 \quad (2-4)$$

Radiation is only subject to the substrate in the vacuum. Vacuum is also necessary for the atoms to reach the substrate; the evaporated molecules collide the predecessor. A formula is devised for the average distance traveled by elements between two collisions. The resulting average distance is known as the mean free path and given by

$$\lambda = \frac{kT}{\sqrt{2}\pi P d^2} \quad (2-5)$$

where λ is the mean free path, k is the Boltzmann constant, T is temperature, P is pressure, and d is a molecular diameter of the atoms. One of the main demerits of the formula is that it does not take into account the collisions involving molecules with *diverse* molecular diameter. The average distance from the source to the substrate is usually less than 50 cm. The average free path can, however, be increased by lowering pressure. It has been noted that at a pressure of 10^{-5} Torr, the mean free path is over 500 cm. Increasing the pressure will lower the mean free path. The increased mean free path reduces the probability of gas

molecules coming into contact with the roughing pumps; therefore, materials are pulled off. For countering this effect, the ionization pumping technique is used to reduce the pressure to a much greater extent. Turbomolecular pumps transfer momentum from rotating blades to gas molecules. Molecules are eventually forced to leave the vacuum chamber by the direction of the transfer forces. In addition to a turbo molecular pump, oil pumps also apply the same mechanism but use oil instead of rotating blades to transfer the gas molecules to the vacuum system. It is notable that a vacuum is essential in thermal evaporation. Some conditions, however, need to be ensured. The balancing chamber conditions are observed during the selection of precursor material. Phase diagrams play a crucial role in optimizing composition. Different materials have different preferences in terms of temperature and pressure to determine their chemical composition. The correct pressure must, therefore, be maintained to prevent a change in the chemical composition. MoO_3 , for instance, might lose oxygen in evaporation and reach substrate as MO . For materials with higher melting points, it is advisable to use an electron beam for evaporation, where some precursors (e.g., tungsten) emit ultraviolet radiations due to the higher energy required. Powders, on the other hand, have a uniform distribution of gases in the vacuum; they also require less temperature to evaporate. Another critical factor in the process is monitoring the amount of substance formed on the substrate. A simple method of determining the amount of material formed is using calibration based on the time taken for materials to evaporate. A relationship between the time spent on evaporating material and the resultant material thickness can be established. A relationship between the intervals spent on vaporizing material to the thickness of the deposited material can be generated for a specific evaporation time and ex-situ thickness study (e.g., atomic force microscopy). It

is a straightforward and preferred method since it does not require the addition of electrons in the deposition chamber of the thermal evaporation system. This technique, however, reports inaccuracies in estimating the evaporation time; therefore, it is used as a way of confirming that other methods are working properly. Another technique uses crystal thickness sensors; it operates on the principle that, as materials are deposited on a crystal, the resonance frequency changes. Every sensor vibration calibration is based on the amount of material deposited on it; this makes it necessary to change the crystal sensors frequently. The readings obtained from this method should be verified using other methods such as ex-situ techniques. Electrical energy is converted into heat for the sake of precursor evaporation. The power applied to the boat can be expressed as follows:

$$W_e = VI \quad (2-6)$$

where V represents the potential difference, and I represents current. The following formula, devised by Knudsen [201], expresses the number of evaporating molecules as a function of time:

$$\frac{dN_e}{A dt} = P_e (2\pi m kT)^{-1/2} \quad (2-7)$$

N_e is the number of molecules, A is the surface area, m is the molecule mass, k is the Boltzmann constant, P_e is the partial pressure (pressure exerted by the evaporating atoms on the other atoms in the system), and T is the temperature. If we integrate and simplify equation (2-7), we will have the following:

$$N_e = A P_e (2\pi m kT)^{-1/2} \Delta t \quad (2-8)$$

where Δt represents the time needed to evaporate a given number of molecules.

The following equation represents the number of atoms that reach distance Y:

$$N = N_0 e^{\left(\frac{-Y}{\lambda}\right)} \quad (2-9)$$

where λ is the mean free path, and N_0 represents the number of molecules in the course of covering distance N. Simplifying the equation gives the following:

$$N_0 = N_e \quad (2-10)$$

If we integrate formulae (2-8) and (2-9), we obtain an equation that expresses the number of atoms reaching distance Y in terms of temperature and pressure, hence the following equation:

$$N = A P_e (2\pi m kT)^{-1/2} \Delta t e^{\left(\frac{-Y}{\lambda}\right)} \quad (2-11)$$

At this point, we introduce the factor of a mean free path in equation (2-11) and integrate it with equation (2-5). The resulting equation is

$$N = A P_e (2\pi m kT)^{-1/2} \Delta t \frac{1}{e^{\left(\frac{\sqrt{2}\pi P d^2 Y}{kT}\right)}} \quad (2-12)$$

Equation (2.12) shows some factors that directly control the rate of deposition in thermal evaporation. Increasing the rate of deposition increases the number of atoms that reach the substrate. On the other hand, there is an inverse relationship between pressure and mean free path, as seen in equation (2.12). Increasing the pressure inside the chamber

will cause a decrement in the number of atoms that pass through distance Y due to a decrease in the mean free path.

For the formation of films, it is crucial that the atoms that reach the substrate also correctly adhere to the substrate. In this regard, the excess energy of atoms has to be transferred to the substrate upon contact between atoms and the substrate. There are several mechanisms via which the atoms can adhere to the substrate surface. Mechanical adhesion is a process that favors the trapping of atoms on the surface of substrates owing to the surface irregularities of the substrate. One instance of surface irregularities include cavities on the substrate surface generated by etching or photolithography process. Furthermore, van der Waals forces might also be responsible for adhesion via electrostatic interaction. Other than adhesion to substrate via the abovementioned mechanisms, atoms might also diffuse through the substrate surface; however, this phenomenon can only occur when the substrate is heated, since heating provides the energy of the deposited atoms required for the diffusion.

As shown in Figures 2.2 and 2.3, the chemical vapor process entails a series of transport of vapor phase chemicals, temperature control, and removal of unused precursors and by-products. Transportation in the reactor can be turbulent or laminar depending on location in the chamber. The flow of material is viewed as continuous when the mean free atoms in the furnace are much lower than the dimensions of the furnace. On the contrary, when the mean free path is comparable to the aspects of the furnace, the flow is no longer continuous. Knudsen number is used to determine the expected results.

Figure 2.2 Schematic diagram of CVD reactor for sulfurization of tungsten oxide.

Figure 2.3 CVD reactor for sulfurization of thermally evaporated oxides setup in our laboratory.

Knudsen number is a ratio of the chamber size to the mean free path. The process of approximating is considered valid when the value of the Knudsen number is greater than 1. On the other hand, when the value is less than 1, the process is discontinuous:

$$\vec{J}_c = n\vec{u} \quad (2-13)$$

Equation (2-13) defines transport of material across area (A) and through volume (V). The variables represent the following: n = molecular density and $\vec{u}$ = velocity. This equation might be taken to be convection if the velocity is taken to be the overall velocity of gas flow. Diffusion is caused by the thermal motion of molecules and cannot, therefore, be assumed to be net. This method, however, does not cater for diffusion in a case where there is variability in aspects such as temperature and material concentration. The total motion will be parallel to the slope of decline of diffusion:

$$\begin{aligned} \vec{J}_{dx} &= -D \frac{dn}{dx} \hat{i} \\ \vec{J}_{dy} &= -D \frac{dn}{dy} \hat{j} \\ \vec{J}_{dz} &= -D \frac{dn}{dz} \hat{k} \end{aligned} \quad (2-14)$$

However, the diffusion flux equations are only valid for continuous models. In case of a discontinuous model, a different model is generated to arrive at the constant diffusion D:

$$D(Knudsen) = cL/3 \quad (2-15)$$

where variable c represents the mean thermal velocity of the molecules. The following partial differential equations give time dependence of diffusion:

$$\frac{\delta n}{\delta t} = D \nabla^2 n \quad (2-16)$$

where ∇^2 is the Laplacian operator

$$\nabla^2 = \frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2} \quad (2-17)$$

In a CVD reactions system, flux caused by diffusion and convection should be accounted for. Appropriate ratios of precursor materials ought to be supplied at the right time and place. If an interface layer subsists on the surface of a substrate, diffusion will dominate on the surface of the substrate.

2.3 Plasma enhanced chemical vapor deposition (PECVD)

PECVD is a popular method that has been extensively used in the synthesis of materials that contain carbon. PECVD technique is used to deposit a thin film from a gas state (vapor) to a solid state on a substrate. This technique is reinforced by its numerous advantages, which include formation in a considerably pure atmosphere; it also requires relatively lower temperatures. It involves high growth selectivity and also maintains control of the pattern formed by Nano-structures. Using PECVD method for the direct production of graphene and h-BN on insulating substrates such as SiO₂/Si helps minimize quality degradation as well as the additional defects caused by the transfer process. Plasma provides an environment dominated by molecule, ions, and a mixture of radicals from a single hydrogen hydrocarbon feedstock. Use of plasma in such a case provides an environment that helps achieve a higher growth rate and a lower deposition temperature than in the thermal CVD method. CVD method still yields higher quality graphene than PECVD [202, 203].

Figure 2.4 Mechanism of graphene growth involving the decomposition of CH_4/H_2 mixed into the plasma.

Figure 2.4 illustrates the graphene growth mechanism, which is a process that entails methane and hydrogen mixed plasma and CH_x radicals; these are generated after the decomposition of methane. The CH_x radicals in gaseous state recombine with each other once they have floated a particular distance; an SP^2 structure was formed on a substrate via metastable carbon atoms and molecules. It is vital to select a suitable source of carbon and regulate its amount in the feedstock mixture of gases to ensure high-quality growth. Large-scale production of graphene involves supplying a large amount of gas. Most PECVD processes, on the other hand, take place under low pressure so that a relatively long mean free path of electrons can be achieved. Different sources of plasma for the synthesis of graphene in the PECVD method have been successfully experimented

despite displaying different reactor configurations; such sources include microwave plasma [203], DC discharges [204], and radiofrequency plasma [205].

2.4 Sample holder design

These holders were custom built by machine shop at the physics department of the University of Louisville. All three holders were designed for the deposition of graphene, h-BN (PECVD), WO_3 , and gold (thermal evaporation).

Figure 2.5 Sample holders that we used to hold the TEM grid on the substrate during the process of (a) the WO_3 and graphene h-BN deposition and (b) the gold deposition.

The only difference between graphene holder and h-BN is the hole size on the cap; however, dimensions of both holders are the same (24 mm x 47 mm x 3 mm for W x L x H, respectively). We chose these dimensions for the sample holders so that they could easily fit into the quartz reactor inside the tube furnace. For graphene and WO_3 growth, the cap holder consists of three different hole sizes (diameter) (i.e., 300 μm , 500 μm , and 1000 μm , respectively), whereas for h-BN synthesis, the hole sizes of the holder are 5.5 mm, 4.5 mm, and 5.5 mm, respectively. The holder used for gold deposition has the following dimensions: 46 mm x 71 mm x 3 mm, and all hole sizes are the same (i.e., 2.5 mm) to match the holes of the mask used for gold deposition. All sample holders are made up of stainless-steel material so that they can withstand high temperatures and are thus suitable for both low- and high-temperature experiments.

2.5 Characterization of 2D materials

2.5.1 Raman spectroscopy

Figure 2.6 Digital image of the Raman spectroscopy system.

Raman spectroscopy is an inelastic spectroscopic technique of scattering monochromatic light primarily from a laser source; Rayleigh scattering, on the contrary, is elastic. Inelasticity of dispersion means that photons coming from the laser upon interaction with a sample will have their frequency changed. The sample eventually absorbs and re-emits them at either a higher or a lower frequency according to the original monochromatic frequency in a Raman effect. Both Raman and Rayleigh scattering involves a transition of molecules from the ground electronic state to a virtual state. The energy transition in Rayleigh and Raman is better illustrated using a Jablonski diagram [206] (Figure 2.7).

Figure 2.7 The energy diagram describing the Rayleigh and Raman scattering.

However, Raman scattering takes a different dimension, in that a molecule emits either a stoke or an anti-stoke compared to an incident photon. At room temperature, molecules are at ground state. Thus, the possibility of obtaining a stoke is higher than that of obtaining an anti-stoke. In a Raman spectrum, the frequency difference ($\Delta \nu$), commonly known as Raman shift, provides details of rotational, vibrational, and other

frequencies of transition. Raman shift is what appears on an abscissa of the Raman spectrum.

Raman spectroscopy has a variety of applications. It has been used in tracking molecular structures and crystallinity as well as in the study of solid, liquid, and gaseous substances to identify different polymorphs and unknown materials. It has also been used in evaluating the modulus of residual stress and monitoring the direction of orientation of molecules.

Raman spectroscopy is the most profound tool in the fields of (2D) materials and graphene. It is applied to characterize some structural properties such as defect density, strain, and the number of layers. It has been used in understanding the behavior of electrons and photons in graphene [207]. Laser excitation in graphene causes a shift in energy, resulting in two main peaks in Raman spectroscopy: G (1580 cm^{-1}) is most fundamental in a plane vibrational mode, involving sp^2 hybridized carbon atoms in graphene. The second peak is 2D (2690 cm^{-1}), resulting from a double photon lattice vibrational process. The D (1350 cm^{-1}) band is known as the disorder band or the defect band. It represents ring breathing from sp^2 carbon rings that must be adjacent to a defect or a graphene edge. The final band is defective and not visible in high-quality graphene due to crystal symmetries [208] (see Figure 2.8 (a)).

In a graphene sample, as the number of layers increases, the position of the G band moves to lower frequencies. This is mainly because the G band position is strongly sensitive to strain effects while it also indicates the number of graphene layers [209]. The G band position is also sensitive to doping and can, therefore, be used in the examination of drugs doping levels. Both the line width and the frequency of the end of a G band are

utilized in examining the doping levels. A 2D band is, on the other hand, useful in differentiating between single and multiple layers of less than four layers in graphene (Figure 2.8 (c)). The distinction depends on both the band's position and the band's shape. In a different case, both 2D and G bands can be used to detect the band layers of defect-free single layers of graphene. The defect-free, separate layers of graphene are confirmed with the ratio I_{2D}/I_G of these bands being equal to 2 and due to a lack of a D band and a sharp symmetric 2D. This is verified by a closer analysis of the peak intensity of the G and the 2D bands.

Figure 2.8 (a) Raman spectra of graphene on SiO₂/Si [1], (b) The Raman spectra for various layers of graphene on SiO₂/Si, (c) 2D band method indicating the layer number of graphene [210].

Figure 2.9 Schematic illustration of four Raman active modes of transition metal dichalcogenide [211].

Figure (2.9) exhibits the vibrational modes of TMDs. The first-order active peak E_{1g} does not allow the backscattering geometry on a basal plane [82]. The second-order peak E_{2g}^2 is below 100 cm^{-1} , which makes it very low [82]. The notch filters would eliminate the wave numbers near the laser. TMDs undergo significant variations in their vibrational spectrums, which explain the changes in their physical properties. Raman modes shift, as the number of corresponding layers of MX_2 ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{S}, \text{Se}$) decreases.. Analyzing the separation of E_{2g}^1 and A_{1g} modes can be utilized in determining the layers of MoS_2 and WS_2 [89]. The in-plane E_{2g}^1 and the out-of-plane A_{1g} are the two main modes in determining the number of layers of WS_2 . The bilayer difference of A_{1g} and E_{2g}^1 for MoS_2 is 21.5 cm^{-1} , while for monolayers the difference is 19.5 cm^{-1} [89]. WS_2

displays a difference of about 63 cm^{-1} for bilayer and 60 cm^{-1} for monolayer [98], which is similar to MoS_2 for these modes (Figure 2.10). It has, however, been proven that the outright positioning of the Raman modes for both WS_2 and MoS_2 depends on the wavelength of the laser excitation [97, 98].

A thorough academic examination of h-BN upon considering polarization was published in 1966 by Geick et al., showing h-BN to have four active optical modes after two single Raman lines [212]. One in-plane mode and one shear mode derive from the additive effect of two in-plane modes, and two shear modes occur on the same Raman shift due to the high symmetry of h-BN. The two Raman active modes arise in either of the following two ways: shear mode (low-frequency phonon) or in-plane mode E_{2g} (high-frequency phonon) [213, 214] (Figure 2.10 (b)).

Figure 2.10 Raman spectra of (a) WS_2 from bulk to single layers [215] and (b) a few layers h-BN [216].

2.5.2 Scanning electron microscope

Figure 2.11 Field emission scanning electron microscope used in this work.

Specimen surfaces are observed using the scanning electron microscope. Secondary electrons are reflected from the specimen surface upon irradiation by a fine electron beam. The fine beam of electrons is referred to as the electron probe. Acquisition of an image from the detected secondary electrons as well as a two-dimensional scanning of the electron probe over a specimen surface can be used in observation of the topography of the specimen surface.

Figure 2.12 Schematic illustration of internal components of SEM (left), The process flow chart of image formation using electron beam in SEM (right) [217].

The scanning electron microscope method has been widely used in the observation of Nano and micro lengths. This method is profoundly preferred since it is rapid and not invasive. It is, therefore, useful for examining internal structures. This method has also shown a range of advantages, some of which involve the diminishing of transferred and synthesized 2D materials on a wide range of substrates, detecting ruptures, folds, impurities, and voids.

2.5.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface characterization technique for material composition, and it is a highly important approach to analyze 2D functionalized samples of materials. In this method, mono-energetic Al K α x-rays or Mg K α x-rays are excited on the surface of a sample, which results in the emission of photoelectrons from the surface. An electron energy analyzer is used to measure the energy of the emitted photoelectrons. From the binding energy and intensity of a photoelectron peak, the chemical state, the identity of an element, and the quantity of a detected element are determined. In a three-step model, Step 1 of the process involves electron excitation when a photon with an energy of $h\nu$ impinges on the surface. Afterward, the electron becomes free by overcoming a vacuum barrier with a kinetic energy E_{kin} that can be analyzed with the help of energy analyzer, as shown in Figure 2.13.

Figure 2.13 Schematic illustration of X-ray photoelectron spectroscopy [218].

The kinetic energy can be converted into a binding energy scale using the following formula:

$$E_{bin} = E_{photon} - (E_{kin} + \phi) \quad (2.18)$$

E_{bin} is the binding energy of the electron; E_{photon} is the energy of the X-ray photons being used; E_{kin} is the kinetic energy of the electron, as measured by the instrument; and ϕ is the work function dependent on both the spectrometer and the material. ϕ is a constant and barely needs to be adjusted; it accounts for the kinetic energy lost by a photoelectron, as it gets absorbed by the instrument detector. X-ray photoelectron spectroscopy can be used to characterize the chemical state of an element as well as for identifying elemental compositions, owing to their particular binding energies. This is facilitated by the fact that its chemical environment influences the binding energy of the core level of the electron.

Figure 2.14 X-ray photoelectron spectroscopy system used during this research.

2.5.4 Atomic force microscopy

Atomic force microscopy is a type of a very high-resolution scanning probe microscope (SPM) invented in 1986 by Binnig, Quate, and Gerber. It is used to measure friction, height (thickness of 2D materials), and magnetism of samples by using a probe. This method is applied to a variety of materials, ranging from conductors to semiconductors and insulators [219]. It is capable of performing force spectroscopy by measuring samples' stiffness, young modulus, and other properties that require mutual separation [220]. Through raster scanning, AFM can form a three-dimensional image. AFM consists of a cantilever with a probing tip made of either silicon nitride or silicon. It operates based on Hooke's law. According to Hooke's law, AFM contains a cantilever with a tip used to scan a specimen by deflection of the cantilever as per the force between the sample and the tip. The force between the probing tip and the sample has a range of 10^{-11} to 10^{-6} N. Particular types of probes are used to measure different properties. The kind of force measured by AFM depends on the situation in question [221]. The forces measured include van der Waal forces, capillarity, electrostatic, and Casimir forces.

The nature of the tip of an AFM determines the mechanism with which it illuminates its specimen. There are two main classifications: (a) the static mode and (b) the dynamic mode. The static mode, which is commonly known as contact mode (the tip and the sample are very close), involves illumination of a sample at depth to prevent the tip of the cantilever from submerging. The repulsive force at depth keeps the firm at a constant focus with the specimen [222]. The tip is controlled by static deflection. This method has the advantages of high scan speed, the ability to scan rough images despite the extreme change in topography, and a high atomic resolution. In contrast, the method has the

disadvantage of the possibility of distorting the face of a 2D sample due to the high lateral force involved in the mechanism. Tapping mode is known as AC mode, and the tip is controlled by oscillation amplitude. In non-contact mode, the cantilever has no contact with the sample surface. Van der Waals forces in the oscillated tip of the cantilever maintain decreased resonance that sustains a distance between the sample and the tip. The tip is controlled by resonance frequency. A topographic image is finally achieved by plotting an x, y plot of the distance between the image and a tip. A non-contact mode has the advantage of utilizing low force, hence minimal chances of distorting the image; on the downside, it is carried out in an ultrahigh vacuum setup to acquire a high resolution; this setup usually is not ideal. Finally, the tip-sample separation limits the lateral resolution, leading to an overall lower lateral resolution. AC mode works between the contact and non-contact modes. The tapping mode is the best choice for our sample; its advantages include high lateral resolution, no damage to samples, and ambient conditions. The tapping mode, however, shows a slower scan speed compared to the contact mode.

Figure 2.15 (a) Schematic diagram of a typical AFM system [218] (b) WS2 AFM image and height profile [223].

Figure 2.15 (a) represents the basic principle of the AFM. In general, a sharp tip mounted at the free end of a cantilever beam is used to scan the sample's surface line by line. The interaction forces between the tip and the surface cause the cantilever to bend. A laser beam focused on the backside of the cantilever then detects the deflection of the cantilever and the beam is then reflected onto a photodetector. This configuration makes it easy to monitor the deflection of the cantilever through observing the position changing of the laser spot on the photodetector. In most of the AFM configurations, a feedback loop is then utilized to maintain the tip-surface interaction at a constant set-point value.

Figure 2.16 MFP-3D BIO AFM setup that we used for characterizing our samples: (A) Top view camera for alignment and probe viewing (B) Atomic force microscope's head (C) Sample area (D) Optical alignment for X and Y (E) Hamamatsu video camera for viewing

and recording in high resolution (F) Headstand (G) XY Mirror (H) Standard cantilever holder (I) Cantilever (J) Quartz window (K) Cantilever Clip (L) The tip.

CHAPTER 03

LAYER DEPENDENT HYDRAZINE ADSORPTION PROPERTIES IN FEW LAYER WS₂

3.1 Introduction

Two-dimensional materials are desirable for sensing applications considering their high surface-to-volume ratio, a wide range of chemical compositions and the unique thickness-dependent properties [224-226]. Graphene and graphene oxide have been widely utilized for chemical and biological sensing applications [227-229]. TMDs show extreme sensitivity to various gas molecules [230-232]. WS₂ exhibits high thermal stability and wide operation temperature range as lubricants, it shows the potential to outperform other 2D crystals in FETs applications due to its favorable band structure [233]. Zhou et al. theoretically predict the possible gas sensing properties of single layer WS₂ considering the moderate interaction of the 2D materials with several gas species [234]. Recently WS₂ sensors in the form of thin films, multilayer photoresponsive FET, Pd-loaded nanosheets, metallic 1T-WS₂, and Ag nanowires functionalized nanosheets have been tested at room temperature NH₃, H₂, NO₂, and different vapor gas sensors [235-239]. Here we show the layer dependent adsorption/desorption properties of WS₂.

3.2 Experimental Methods for Device Fabrication

The initial step of the experiment involved the selection of the substrate then cleaning it using organic solvents. The cleaning methods used in our experiments consist of the following steps: cleaning of the substrate with acetone in an ultrasonic bath for 10 minutes, ultrasonication of substrates using isopropanol for 5 minutes, and finally the treatment of the substrate with de-ionized (DI) water in an ultrasonic bath for 10 minutes. The substrate was then dried by blowing ultra-high purity compressed N_2 onto it. For all our experiments, we utilized Si/SiO₂ substrate. The substrate used particularly for WS₂ synthesis had an oxide layer with thickness of 300 nm and a lateral dimension of 10 by 10 mm. The p-type silicon wafers were purchased from the University of Wafer.

After the substrates were cleaned, they were transferred to the sample holders, as described in section 2.4. The Si/SiO₂ substrates were well adjusted in the sample holder, and then the square patterned copper TEM grids were fixed on the top of substrates. Our custom-built substrate holder was made in such a way to ensure maximum contact between the substrates and the TEM grids. After the TEM grid was adjusted on the substrates, the grid was held in its place by using cap holder with hole as described in section 2.4. Whereupon, the substrate holder, was transferred to the thermal evaporation chamber. Once the substrate was inside, the chamber was evacuated and the pressure inside the chamber was decreased to 10^{-6} Torr. The chamber pressure was always kept constant since an ultrahigh vacuum was required to achieve reproducible films. Once the said pressure was reached, the WO₃ powdered precursor (WO₃, alfa aesar 99.99%), was evaporated and

subsequently deposited in on to the substrate through the grids, in the form of patterned films. The deposition on all three samples was done in the same way, as described above.

Three samples of different thickness i.e. 1 nm (10 Å), 2 nm (20 Å) and 5 nm (50 Å) were deposited and the thickness of the material was determined with the help of crystal thickness sensor, equipped inside the thermal evaporator. After the desired deposition was achieved, the substrate holder was removed and thereafter the substrates and the TEM grids were taken off very carefully. It can be seen from Figure 3.2, that the deposition was successfully done in the form of patterned thin film.

Immediately after the thermal evaporation was done, the samples were directly transferred to the CVD reactor for sulfurization of patterned WO₃ films. Figure 2.2 in the previous chapter, illustrates the CVD process of sulfurization. The quartz tube furnace was evacuated before the start of evaporation experiment to make sure there are no air molecules inside the furnace. In a two-zone setup, sulfur flakes (S, Sigma-Aldrich 99.99%) were put into the alumina boat and were placed inside the low-temperature zone while the patterned WO₃ film samples were placed in the high-temperature zone of the quartz tube. Sulfur flakes were gradually heated to 120 °C with the help of the heating belt. On the other hand, the substrate zone was heated to 700 °C at the ramp-up rate of 15 °C/min and the furnace temperature was controlled using a temperature controller. Here it is important to mention that the boat containing sulfur flakes was kept 6 cm away from the high-temperature furnace in order to prevent it from any heat coming from the furnace. Since the melting point of sulfur is low (around 115 °C under atmospheric conditions), the experiment was conducted very carefully and in a very controlled manner. We made sure

that the sulfur was evaporated with the help of the heat belt, only when the substrate temperature was reached 700 °C. A mixture of Ar/H₂ in the ratio of 60:40 was used as carrier gas with a flow rate of 50 standard cubic per centimeters (sccm). This also provides an inert atmosphere during the reaction process for avoiding any side reaction. Once the reaction was finished, the carrier gas flow was kept on, to cool down the samples. Temperature profile during sulfurization of tungsten oxide is showing in Figure 3.1. Using this technique, the WO₃ samples were successfully converted to WS₂ which was later characterized using various methods, as shall be described in the following section.

Figure 3.1 Temperature profile during sulfurization of tungsten oxide.

Gold was deposited to create contacts on patterned WS₂ film for the sake of device fabrication, as shown in Figure 3.2. TEM grid was cut down and adjusted on the sample holder to make a gold mask, in the similar way as described above, the characteristics of sample holder used for gold deposition are already described in section 2.4.

Figure 3.2 WS₂ based device fabrication scheme using a lithography-free technique.

Figure 3.2 shows the sequential processes of fabricating WS₂ based device. First, using a square TEM grid WO₃ (~1 nm, 2 nm, and 5 nm) was deposited by thermal evaporation followed by sulfurization. In order to define the electrical contacts on each sample, a customized straight TEM grid was carefully aligned so that WS₂ layers are exposed after gold deposition as masked by the bar.

3.3 Surface and structural characterization of WS₂

The surface of CVD prepared WS₂ was characterized using SEM and AFM techniques while the structure and composition were studied using Raman technique. Figure 3.3 shows the SEM images of each WS₂ sample taken by an FEI Nova 600 field emission scanning electron microscope. Although this microscope can operate at accelerating voltages of up to 30 kV, the low acceleration voltage of 5 kV was used for the imaging of the WS₂ samples.

Figure 3.3 SEM images of few-layer and multi-layer WS₂ samples thickness (a) 2 layers (b) 3 layers, and (c) 12 layers.

This helped to enhance the surface probing capabilities and to increase the contrast difference between thin 2D layers of WS₂ and the substrate. As evident from Figure 3.3, the contrast difference between WS₂ regions and the substrate increases with the layer thickness. Furthermore, for the thickest layer (Fig. 3.3 c), the edges of the square WS₂ region are clearly defined.

Figure 3.4 AFM images and the height profile of few-layer and multi-layer WS₂ samples
(a) 2 layers (b) 3 layers (c) 12 layers.

Figure 3.4 shows the AFM images taken by Asylum Research MFP-3D-Bio Atomic Force Microscope. The AFM topography images were acquired in tapping mode in air using Si tips with a typical tip radius of 25 nm, a tip length of ~240 μm , spring constant rang 1.8-12.5 N/m and frequency range 58-97 kHz (Asylum Research probe, Model ASYELEC.01-R2). The AFM images in Figure 3.4 show the surface and height profile of each sample. The average thicknesses of samples were found to be 1.41 nm, 2.46 nm, and 9.19 nm with number of layers being 2, 3, and 12 layers respectively.

Figure 3.5 Raman spectra of WS₂ samples with varying number of layers.

WS₂ films were characterized by Raman spectroscopy using in a Renishaw InVia confocal microscope-based Raman spectrometer with a spectral resolution better than 1 cm⁻¹. We used 647 nm laser excitations, keeping the laser power under 0.2 mW at all times. Raman spectra show the in-plane phonon mode E_{2g}¹(Γ) and the out-of-plane phonon mode A_{1g}(Γ). The frequency difference and the intensity ratio between E_{2g}¹(Γ) and A_{1g}(Γ) peaks are key indications for determining the number of layers of WS₂ sample. For λ_{exc} = 647 nm, the frequency difference between E_{2g}¹(Γ) and A_{1g}(Γ) modes and the intensity ratio shown in Figure 3.5 (b) seem to follow systematic changes with the number of layers.

3.4 Current-Voltage Characteristics Study

Figure 3.6 I - V characteristic of WS_2 samples with varying thicknesses.

Figure 3.6 shows the I - V characteristics of WS_2 samples with varying thicknesses. The resistance of the thickest sample is several orders of magnitude lower than that of other two samples as expected. The I - V for the 2 few layer samples are also shown in an expanded scale as an inset. All 3 samples show linear ohmic behavior in the measured voltage range.

3.5 Hydrazine adsorption of WS₂

WS₂ films for hydrazine adsorption were synthesized on Si/ SiO₂ substrate in home-made CVD system as described in section 3.1. Three different samples with different thicknesses of WS₂ films were tested. The resistance of WS₂ during hydrazine adsorption was measured using a chip carrier supporting the WS₂ sample as shown in Figure 3.7 at room temperature.

Figure 3.7 Schematic of hydrazine the absorption measurement setup.

The following procedure was practiced during the process:

- Before starting the experiment, the sample was kept under vacuum for at least 30 mins.
- After that, the pump valve was closed, and then the liquid vapors were introduced.
- When the vacuum level reached the desired pressure, the liquid-vapor supply was terminated.
- Finally, the sample chamber was evacuated. The same process was repeated for different values of pressures.

Figure 3.8 Instrumental setup used in this work for hydrazine adsorption.

Figure 3.9 shows the resistive response of each sample when exposed to hydrazine at room temperature. The downward arrows in each figure indicate where hydrazine was introduced for the specified pressure while the upward arrow indicates when the hydrazine was pumped out.

Figure 3.9 Resistive response to hydrazine at room temperature for WS₂ samples with varying thicknesses.

Figure 3.9 (a) shows the time dependence of the resistance of the WS₂ sample with 2 layers during adsorption and desorption of hydrazine. When hydrazine was admitted to a pressure of 12 Torr, the resistance is seen to decrease from the initial value of ~760 MΩ down to ~ 460 MΩ. Upon pumping, the resistance recovers to the original value. Next, when hydrazine was admitted to a pressure of 13 Torr, resistance dropped to a lower value of ~160 MΩ and again recovers back upon pumping. Finally, admission of hydrazine to a pressure of 14 Torr causes the resistance to a much lower value of ~ 30 MΩ yet recovers back to the initial value upon pumping. The decrease of resistance due to hydrazine exposure can be explained as due to the charge transfer process from the adsorbed N₂H₄ molecules to the WS₂. The full recovery of the resistance during the pumping suggests that for 2 layers thick WS₂, hydrazine can be completely desorbed at room temperature. Figure 3.9 (b) shows the time dependence of the resistance of the WS₂ sample with 3-4 layers during adsorption and desorption of hydrazine. When hydrazine was admitted to a pressure of 12 Torr, the resistance is seen to decrease from the initial value of ~8.2 MΩ down to ~ 6 MΩ. Interestingly, the resistance value does not recover back to the initial value upon pumping and saturates at a lower value at ~ 7.8 MΩ. Further exposure to hydrazine to higher pressure causes a higher decrease of resistance, but only recovers to a lower value upon pumping. The partial recovery of the resistance during the pumping suggests that for 3-4 layers thick WS₂, hydrazine can only be partially desorbed at room temperature. In contrast, Figure 3.9 (c) shows completely different behavior of resistance when the multi-layered WS₂ sample was exposed to hydrazine. When hydrazine was admitted to a pressure of 12 Torr, the resistance shows a sudden decrease in resistance as in the first 2 samples,

but then starts to increase. When pumping was introduced at that point, the resistance does not show any significant change. Next when hydrazine was introduced to a pressure of 13 Torr, again the resistance shows an initial decrease followed by an eventual increase. Again, pumping has a minimal effect on the resistance value. Similar trend continues for the hydrazine exposure to a pressure of 13 Torr. The results suggest initial charge transfer from N_2H_4 to WS_2 causing the resistance to drop, but the trapping of N_2H_4 molecules within the multilayers of WS_2 causes charge redistribution, and possible chemical reactions may be responsible for the increase in resistance during the adsorption and complete irreversibility of resistance during desorption.

3.6 Theoretical Calculations and modeling

In order to explain the observed resistive responses during adsorption and desorption of hydrazine on WS_2 samples with varying number of layers, theoretical calculations and modeling were performed using the density functional theory (DFT) as implemented in the Vienna Ab-initio Simulation Package (VASP) [240]. Figure 3.10 shows the fully relaxed monolayer (Figure 3.10 (a)), the double-layer (Figure 3.10 (b)), and the multi-layer WS_2 (Figure 3.10 (c)) exposed to N_2H_4 molecule. The shortest distances ($\sim 3.5 \text{ \AA}$) of N_2H_4 to the WS_2 layers clearly show a physical adsorption nature. The corresponding adsorption energy per N_2H_4 gas molecule is listed in Table 3.1. They are in the range of -0.009 to -0.47 eV, conforming their physical adsorption. In particular, the adsorption energy in the case of multilayer with an optimized separation distance of $8 \text{ \AA}$ (-0.4713 eV) is almost four times as lower as that in the case of the monolayer (-0.0977 eV). This indicates that it will

need more energy to remove N_2H_4 molecules from multi-layer WS_2 than from monolayer WS_2 , consistent with our experimental observation that the change of the resistance during the pumping/degassing processes depend on the number of WS_2 layers (see Figure 3.9 (a) and (b)). Furthermore, it is also found that the optimized separation distance between WS_2 layers after exposed to N_2H_4 molecule is 9.37 Å in the double-layer, about 1.37 Å larger than that in the multi-layers. In particular, if the multi-layer WS_2 with the separation distance is close to that of bulk WS_2 (~6-7 Å), the N_2H_4 molecules strongly interact with WS_2 layers. They either form chemical bonds with S atoms or break W-S bonds, leading to a distortion in WS_2 layers and therefore a change in the electronic structures, which might explain our experimental observation for resistance changes in the sample with the thickness of 9.19 nm (see Figure 3.9 (c)).

Figure 3.10 Relaxed structures of the monolayer (a), double-layer (b), and multi-layer (c) WS_2 exposed to N_2H_4 molecule. The numbers indicate the shortest distance between N_2H_4 and WS_2 layers, and the layer separations. The yellow, green, blue, and grey dots represent the S, W, N, and H atoms, respectively.

Table 3.1 The adsorption energy of WS₂ layers exposed to N₂H₄ molecule.

System	E_a (eV)
Monolayer WS ₂ exposed to N ₂ H ₄ molecules	-0.0977
Double-layer WS ₂ exposed to N ₂ H ₄ molecules	-0.1863
Multilayer WS ₂ exposed to N ₂ H ₄ molecules	-0.4713

Figure 3.11 shows the calculated electronic band structures for the pristine WS₂ monolayer (Figure 3.11 (a)), the monolayer WS₂ exposed to N₂H₄ gas molecules (Figure 3.11 (b)), the double-layer WS₂ exposed to N₂H₄ (Figure 3.11 (c)), and the multi-layer WS₂ exposed to N₂H₄ (Figure 3.11 (d)), respectively. Comparing to the pristine WS₂, there is an impurity state (indicated by the red lines) associated with N₂H₄ molecules pinning into the band gap, independent of the number of WS₂ layers. Since this state is below the Fermi level, it clearly exhibits an *n*-type behavior, which can generate more electrons jumping to the empty conduction bands and reduce the resistance. These results demonstrate that the electronic band structures of WS₂ near the Fermi level very sensitive to the explosion of N₂H₄ gas molecules, in agreement with the experimental observation that a reeducation of the resistance occurred after the WS₂ layers are exposed to N₂H₄ gas molecules (Figure 3.11).

Figure 3.11 The band structures of the pristine 3x3 WS₂ monolayer (a), the monolayer WS₂ with N₂H₄ (b), the double-layer WS₂ with N₂H₄ (c), and multi-layer with N₂H₄ (d), respectively. The red lines are the impurity states associated with the N₂H₄ molecule.

3.7 Conclusion

In summary, few-layer and multi-layer WS₂ devices fabricated using a simple lithography-free technique were exposed to hydrazine at varying pressures and their electrical resistances were monitored during adsorption and subsequent desorption. WS₂ sample consisting of 2-layers showed a decrease of resistance upon exposure to hydrazine vapor and showed complete reversibility upon pumping. WS₂ sample with 3-4 layers showed a decrease of resistance during exposure, but showed only partial recovery during desorption. In contrast, multi-layered (12 layers) WS₂ sample showed an initial decrease followed by a continued increase of the resistance upon exposure to hydrazine with little or no reversibility upon pumping. The charge transfer from N₂H₄ to WS₂ is believed to be responsible for the decrease of the resistance. Trapping of N₂H₄ molecules within the multilayers of WS₂ causing charge redistribution and possible chemical reactions may be responsible for the increase in resistance during the adsorption and complete irreversibility of resistance during desorption. The experimental results are further supported by the computational calculations carried out by employing the density functional theory (DFT) framework, as implemented in the Vienna Ab-initio Simulation Package (VASP). It was found to exist an impurity state in the band structure of WS₂ associated with N₂H₄ molecules below the Fermi level exhibiting an *n*-type behavior. The adsorption energy per N₂H₄ gas molecule conforms the physical adsorption nature of N₂H₄ in WS₂ and the optimized separation distance between layers in multilayers is almost four times as lower as that in the case of the monolayer indicating it requires more energy to remove N₂H₄ molecules from multi-layer WS₂ than from monolayer WS₂.

CHAPTER 04

SYNTHESIS OF PECVD GRAPHENE AND HEXAGONAL BORON NITRIDE (h-BN)

4.1 Introduction

Carbon can form various types of layer structures when it is in form of sp^2 carbon, which is the most stable elementary form at room temperature. Graphene is a 2D allotrope of carbon wherein the carbon atoms are densely packed in a regular hexagonal pattern. Inspired by the graphene structure, there has been recently a lot of research on similar 2D structures for a wide variety of significant applications. One particularly important analog to graphene is 2D hexagonal boron nitride (h-BN). In 2D h-BN structure, B and N atoms are arranged in a form like a honeycomb which is an attribute of hexagonal lattice formation. Both graphene and h-BN are of great importance in the application related to micro and nanoelectronics.

So far, wide various approaches have been reported for the preparation of 2D graphene which includes chemical exfoliation from bulk graphite [241-243], mechanical exfoliation from pyrolytic graphite [244, 245] and thermal decomposition using 4H-SiC substrates [246, 247], etc. On the other hand, various versatile methods have reported of boron nitride synthesis. 2D Boron nitride is usually prepared using two common approaches which include bottom-up approach which involves vapor transport reactions

(CVD) and top-down approach which is deal with exfoliation methods. However, for the growth of 2D graphene and h-BN, the most commonly used method remains to be chemical vapor deposition as this method ensures large scale production of h-BN and graphene with high reproducibility. However, thermal CVD methods that have been utilized for of graphene growth always involve high processing temperatures (1000-1600 °C) [248-250] which makes them very complex and therefore limits the application of graphene in devices formation related to electronics and optoelectronics. Moreover, the as-prepared graphene films are required to be separated from the metal substrates first and later transferred to some insulating substrates, like dielectrics, for further electronic processing [251]. Similar to graphene, h-BN can be prepared using thermal CVD method but the set-back again is the high processing temperature which limits its large-scale applications. Table 4.1 demonstrates the reported growth of h-BN using CVD methods. It can be seen that all the methods reported so far, required high synthesis temperature in the range of 900-1400 °C. Here we introduce a low temperature, plasma enhanced chemical vapor deposition (PECVD) through which 2D graphene and h-BN was grown on SiO₂/Si substrate at temperature of 650 °C and 700°C, respectively. This reduces the complexity of 2D growth and ensures a simple and reproducible method as compared to other high processing CVD methods.

Also, it's a direct approach for thin film growth for 2D materials on SiO₂/Si substrates. Most previous reported methods involved growth on the substrates other than SiO₂/Si as can be seen from table 4.1, therefore, it is required to transfer the films to SiO₂/Si which is an extra step that adds to the complexity of overall growth procedure. Our PECVD

approach for graphene and h-BN can be further expanded to the substrates other than SiO₂/Si.

Table 4.1 A summary of growth methods reported for 2D h-BN synthesized *via* CVD method [252].

Substrate	CVD route	Growth temp. (°C)	Precursor
SiO₂	LPCVD	1000	Ammonia borane
Cu foil	LPCVD	1000	Ammonia borane
Cu foil	APCVD	1050, 1065	Ammonia borane
Ni film	APCVD	1000	Borazine
Pt foil	LPCVD	1100	Ammonia borane
Cu foil	APCVD	1000	Ammonia borane
Sapphire	LPCVD	1400	Ammonia borane
Cu–Ni	LPCVD	1050–1085	Ammonia borane
Fe foil	LPCVD	900,1100	Borazine
Fe–Ni	LPCVD	900–1100	B, N-Solid source
Pt foil	APCVD	1000	Ammonia borane
SiO₂, quartz	LPCVD	1000	Ammonia borane

4.2 Plasma Enhanced CVD (PECVD) of graphene

For our experiments, we synthesized graphene using a home-built split ring radiofrequency (13.56 MHz, Max. power 600W) plasma enhanced chemical vapor deposition (PECVD) system on SiO₂/Si wafers, as demonstrated in Figure 4.1. Before the synthesis, the substrate was cleaned using ultrasonication in acetone, isopropyl alcohol and DI water for 10 min each and subsequently dried using a nitrogen (N₂) blow gun. Thereafter, the substrate was placed inside the quartz tube furnace. Then the quartz tube reactor was evacuated to a point where the pressure reached 2 mTorr and then heated at a ramp rate of 25 °C/min to 650 °C alongside the introduction of gas mixture: Ar/H₂ (40 vol % argon, 60 vol % H₂) at a flow rate of ~20 sccm. Once the furnace was around 400 °C, the plasma was started at the power of 50W, then when the furnace reached 650 °C under the plasma ambience, it was kept in this state for 20 minutes. After that, the Ar/H₂ mixture and the RF plasma were turned off simultaneously. Thereafter, pure CH₄ (99.8%) with a flow rate of ~5 sccm was introduced into the growth chamber, immediately after which plasma (~40W) was reintroduced into the setup and the growth was allowed to take place for 40 minutes. The samples were then cooled down to room temperature with a rate of 25 °C/min. The temperature profile for the growth experiment is shown in Figure 4.2.

Figure 4.1 Home-built split ring radiofrequency plasma enhanced CVD system for graphene growth.

Figure 4.2 The temperature profile for graphene growth on SiO₂/Si wafer.

4.3 Plasma Enhanced CVD (PECVD) of Hexagonal Boron Nitride (h-BN)

In order to synthesize h-BN, once again we utilized our RF (13.56 MHz, Max. power 600W) PECVD system, as demonstrated in Figure 4.3. The growth substrate used in this process was SiO₂/Si wafer. In this setup, two heating zones were used, a low-temperature zone for ammonia borane complex powder (H₃N-BH₃, Sigma-Aldrich, 97%) and a high-temperature zone

for the substrate. The substrate zone was heated using the temperature-controlled furnace, and the low-temperature zone carrying ammonia borane was heated slowly using heat belt to make sure both zones can reach the desired temperatures simultaneously. The cleaning of the substrate was performed in the same manner as reported above. Once the substrates were clean, the h-BN was grown directly on the SiO₂/Si substrate in the form of fully covered uniform planar film. By using a substrate holder with a TEM grid mask, h-BN was grown in the form of square-patterns onto SiO₂/Si substrate. Once, the substrate was placed inside the quartz tube furnace, the tube was evacuated to ~2 mTorr and at this point it was subjected to heating at a ramp rate of 25 °C/min to 700 °C alongside the introduction of gas mixture: Ar/H₂ (40 vol % argon, 60 vol % H₂) at a flow rate of ~50 sccm. Once the furnace temperature reached 400 °C, the plasma was initiated at the power of 100W, and the temperature was further increased up to 700 °C under the plasma. At this point, the reactor zone containing ammonia borane complex powder has reached 110 °C. The setup was maintained under this state for 45 minutes of growth time. Once the desired growth time was achieved, the RF plasma was turned off.

Later The samples were then cooled down to room temperature under Ar/H₂ flow with the rate of 50 sccm. The inert atmosphere was maintained inside the furnace to avoid any oxidation. The temperature profile of the growth is shown in Figure 4.4.

Figure 4.3 Home-built split ring radiofrequency plasma enhanced CVD system for h-BN growth.

Figure 4.4 The temperature profile for the growth of hexagonal boron nitride (h-BN) on SiO₂/Si substrate.

CHAPTER 05

GRAPHENE-WS₂ HETEROSTRUCTURES BY A LITHOGRAPHY FREE METHOD: THEIR ELECTRICAL PROPERTIES

5.1 Introduction

Researchers have attempted to stack a combination of metallic (graphene etc.), insulating (h-BN etc.) and semiconducting (MoS₂ etc.) 2D materials to enable functional devices. This includes; (i) adding some functionality into such 2D structures [135, 253-255], (ii) stacking them vertically or arrange laterally [256-258], (iii) combining into nanocomposite to optimize many inherent properties such as optical absorption etc [259, 260].

These strategies suggest that an ideal 2D material for next generation of functional devices should meet the following important criteria: They must be (i) a single layer of atoms (for fastest conduction of electrons), (ii) be highly stable and high-temperature stability (up to 600 °C) for devices application such as high-temperature memory, (iii) possess a small and tunable band gap for using in logic and high speed switching devices and, (iv) scalable in both synthesis and processing with the ability to integrate with existing technology etc.

Heterostructures have been the essential elements in semiconductor industry. The newly developed monolayer 2D materials offer a platform that allows creation of heterostructures with a variety of properties. Many physical properties have been explored

on van der Waals heterostructures that created by monolayers of multiple 2D materials with vertically layer-by-layer or stitched together seamlessly in-plane lateral heterojunctions [261-265]. Since these heterostructures utilize the van der Waals interlayer interaction, lattice matching is no longer a significant factor. The interface is atomically sharp, and the junction can be as thin as two atomic layers to reach the ultimate limits. Such stacks are very different from the traditional 3D semiconductor heterostructures, as each layer acts simultaneously as the bulk material and the surface, reducing the amount of charge displacement within each layer. In addition, these structures are flexible and stable with compatible fabrication thin-film technologies. In recent years, there have been many studies on graphene-2D materials heterostructures demonstrating novel charge transport properties across the interface [264, 266, 267]. Such graphene-TMDs structures have been introduced for various device applications and also been of particular interest in the spectroscopy community [264, 268-270]. For example, many groups demonstrated the vertical tunneling transistors with high on-off ratios and large current densities that used TMDs thin layers as tunneling barriers and graphene as one or both electrodes [261, 264, 266, 271].

We have developed a lithography-free, dry process for fabricating WS₂ and graphene devices (including a graphene-WS₂ lateral heterostructure) using a copper transmission electron microscope (TEM) grid as a shadow mask. This technique, which is free of the possible contamination of graphene and WS₂ during lithographic process, is simple to implement.

In this study, we synthesized single crystalline WS_2 by sulfurization of WO_3 thin films, while graphene was directly deposited by RF-plasma enhanced chemical vapor deposition. Graphene- WS_2 heterostructured device was fabricated with Au electrical contacts using a lithography-free technique and a series of transport measurements of resistance and magnetoresistance were carried out.

5.2 Experiment Details and Results

We compare transport properties of graphene, WS_2 , and graphene- WS_2 lateral heterostructure samples. Graphene was directly deposited on Si/SiO₂ substrate using RF-plasma enhanced CVD technique developed in our laboratory [272], more details in chapter 4 (section 4.2). WS_2 samples were fabricated by first depositing 2 nm thick WO_3 layer by thermal evaporation followed by sulfurization and more details were provided in section 3.2. In both cases, electrical contacts were defined using a modified TEM grid.

Figure 5.1 The scheme of Graphene-WS₂ heterostructure device fabrication.

Figure 5.1 shows the sequential processes of fabricating graphene-WS₂ heterostructure based device. First, graphene was deposited using PECVD on a Si/SiO₂ substrate through a mask with a circular opening. Next, using a square TEM grid, WO₃ (~2 nm) was deposited by thermal evaporation covering the graphene area followed by sulfurization.

Figure 5.2 Detailed scheme of Graphene-WS₂ heterostructure device fabrication schematically describing each step.

In order to define the electrical contacts on the heterostructure, a customized straight-bar TEM grid was carefully aligned so that edge regions consist of graphene and WS₂ while middle region consists of overlapped graphene-WS₂. The dimension of the fabricated graphene-WS₂ heterostructured device is around 30 μm . A sequential explanation of this process can be found in Figure 5.2 which describes the step-wise process flow.

Figure 5.3 Detailed scheme of Graphene device fabrication for electrical characterization. Both schematic diagrams and real optical images are presented.

Figure 5.3 shows the fabrication process of the graphene device. First, graphene was deposited using PECVD on a Si/SiO₂ substrate through a mask with a circular opening (sample holder as described in section 2.4) and after that, aligning a customized straight-bar TEM grid for gold deposition to create the electrical contacts. Detailed scheme of WS₂ device fabrication has been represented in Chapter 3 (section 3.2).

Figure 5.4 (a) AFM image of the heterostructure region. (b) a blown-up image with clearly labeled regions. The isolated regions of the Si/SiO₂ substrate, graphene, and WS₂ are clearly shown. The height profiles for substrate-WS₂, substrate-graphene, and substrate-heterostructure interfaces are shown.

Figure 5.4 shows the AFM images taken by Asylum Research MFP-3D-Bio Atomic Force Microscope. The AFM topography images were acquired in tapping mode in air using Si tips with a typical tip radius of 25 nm, tip length of ~240 μm, spring constant range 1.8-12.5 N/m and frequency range 58-97 kHz (Asylum Research probe, Model ASYELEC.01-R2). The AFM images in Figure 5.4 show the surface and height profile of

the heterostructure region. Figure 5.4 (a) clearly shows the isolated regions of the Si/SiO₂ substrate, graphene, and WS₂. A blown-up image of the heterostructure is shown in Figure 5.4 (b). The height profiles for substrate-WS₂, substrate-graphene, and substrate-heterostructure interfaces are also shown. The average thickness of graphene was found to ~3.69 nm which is typical for graphene nanowalls grown by plasma enhanced CVD technique [272], while WS₂ layer thickness being ~ 2.9 nm corresponding to ~ 3-4 layers. The thickness of the heterostructure was found to be ~6.6 nm in agreement with individual graphene and WS₂ thicknesses.

Figure 5.5 (a) Raman spectrum of the graphene-WS₂ lateral heterostructure with 632 nm laser excitation in an Invia Renishaw Raman spectrometer. In addition to the overlapped area, Raman spectra of individual graphene and WS₂ regions are also shown (b) Optical

image of the heterostructure with distinct regions of graphene, WS₂, and graphene-WS₂ overlapped area. The positions where Raman spectra taken are denoted by open circles.

Figure 5.5 (a) shows the Raman spectrum of the graphene-WS₂ lateral heterostructure with 632 nm laser excitation in an Invia Renishaw Raman spectrometer. For comparison, Raman spectra of individual graphene and WS₂ regions are also shown in the figure. Figure 5.5 (b) shows the optical image of the heterostructure with distinct regions of graphene, WS₂, and graphene-WS₂ overlapped area. The positions where Raman spectra taken are denoted by open circles. The heterostructure (overlapped region) shows the Raman peaks characteristic of graphene and WS₂. The peaks at 1350 cm⁻¹, 1590 cm⁻¹, 1630 cm⁻¹, and 2600 cm⁻¹ are characteristic of D, G, D', and 2D bands of graphene. G (1580 cm⁻¹), a primary in-plane vibrational mode involving the sp² hybridized carbon atoms that comprises the graphene sheet. 2D or G' (2690 cm⁻¹), a second-order overtone of the D band corresponding the result of a two-phonon lattice vibrational process. The D (1350 cm⁻¹) band is known as the disorder band associated with the defects of graphene. The D'-band (around 1630 cm⁻¹) is associated with edges and structural disorder in graphene films [273]. The PECVD technique allows the growth of graphene on both conductive and insulated substrates with almost the same quality. In addition to the graphene related Raman peaks, we observe 2 distinct Raman peaks at ~ 351 cm⁻¹ (E_{2g}¹) and 417 cm⁻¹ (A_{1g}) characteristic of WS₂ [274]. The A_{1g} mode is an out-of-plane vibration involving only the chalcogen atoms while the E_{2g}¹ mode involves in-plane displacement of transition metal (W) and chalcogen atoms (S). More details of the Raman spectra for graphene and WS₂ are showing in Figure 5.6.

Figure 5.6 Raman spectra of graphene and WS₂ from isolated regions of the WS₂-graphene heterostructure. Each peak has been identified.

Figure 5.7 I-V characteristics of WS₂, graphene, and graphene-WS₂ heterostructure; Current, I for WS₂ and graphene-WS₂ heterostructure are shown in the left axis while that of graphene is shown in the right axis.

Figure 5.7 shows the I-V characteristics of WS₂, graphene, and graphene-WS₂ lateral heterostructure; The devices for graphene and WS₂ were also fabricated using the lithography-free technique described before. Current, I for WS₂ and Graphene-WS₂ heterostructure are shown in the left axis while that of graphene is shown in the right axis. The resistance of graphene is several orders of magnitude lower than that of WS₂ and graphene-WS₂ heterostructures. All 3 samples show linear ohmic behavior in the measured voltage range. Graphene with zero band gap shows the highest conductivity (highest current at a given voltage) compared to WS₂ which is a semiconductor. The Graphene-WS₂ heterostructure shows intermediate conductivity as expected due to the partial shunting of WS₂ with graphene.

Figure 5.8 Temperature dependence of the resistance, $R(T)$ of graphene, WS_2 , and graphene- WS_2 heterostructure. The inset shows $R(T)$ of graphene in an expanded scale.

Figure 5.8 shows the temperature dependence of the resistance for graphene, WS_2 , and graphene- WS_2 heterostructure. Since the resistance of graphene is several orders of magnitude lower than that of WS_2 and graphene- WS_2 heterostructures, $R(T)$ of graphene is also shown in an expanded scale as an inset. The temperature dependence of the resistance for all 3 samples show typical semiconducting behavior, with an exponential increase of the resistance at low temperature. The behavior can be described in the frameworks of Mott VRH model which describes low temperature conductance in strongly disordered systems with localized charge-carrier states, especially in low dimensional

system. The conductance satisfies the equation $R=R_0 \exp(T_0/T)^{1/(1+d)}$, where d is the dimension of the sample and $T_0 = 13.8/(k_B N(E_F) \xi^2)$, k_B is the Boltzmann constant, $N(E_F)$ is the density of states at the Fermi energy, and ξ is the localization length [275]. Figure 5.9, we plot the low-temperature dependent resistance curve via different exponent referring to dimensions 0, 1, 2. As seen from the fits, $d = 2$ gives the best fitting, reflecting the intrinsic 2d attributes of graphene, WS₂, and even for graphene-WS₂ heterostructure. In our previous study [272], for PECVD grown graphene, electrical transport was explained as due to hopping conduction and thermally activated conduction mechanisms with the density of states of graphene given by, $N(E) = (2E/(\pi \hbar^2 v_F^2))$ (assuming $v_F \sim 1 \times 10^6$ m/s⁻¹) and the carrier density given by, $n = E_F^2/(2\pi \hbar^2 v_F^2)$. In contrast, for WS₂, $N(E) = (4\pi g_v m^*/h^2)$, where $m^* = 0.34m_0$ represents the electron effective mass and $g_v = 2$ is the valley degeneracy [276].

Figure 5.9 Mott VRH analysis of (a) Graphene (b) WS₂, and (c) Graphene-WS₂ lateral heterostructure.

Figure 5.10 Magnetoresistance of graphene, WS₂, and graphene-WS₂ heterostructure at 20 K. The dotted lines for graphene and heterostructure represent the quadratic magnetic field dependence B^2 .

Finally, Figure 5.10 shows the magnetoresistance characteristics of graphene, WS₂, and graphene-WS₂ heterostructure at 20 K with the magnetic field B applied perpendicular to each sample. Here, the magnetoresistance is defined as $\Delta R/R = [R(B) - R(B = 0)]/R(B = 0)$. Clearly, WS₂ doesn't show any appreciable magnetoresistance at 20 K, whereas graphene and graphene-WS₂ heterostructure show a quadratic dependence on magnetic field B . In the wave-function shrinkage model [277-280], the quadratic magnetoresistance is attributed to the contraction of the electronic wave function at traps in a magnetic field leading to a reduction of hopping probability. Quantitatively, in the wave-function shrinkage model, the magnetoresistance in the Mott VRH regime can be expressed as

$\Delta R = \alpha_{Mott} B^2$, where the pre-factor α_{Mott} is given by, $\alpha_{Mott} = e^2 \xi^4 / (36 \hbar^2) (T_{Mott} / T)$, where T_{Mott} is a characteristic temperature [281]. The negative MR results for graphene and graphene-WS₂ can also be argued as due to the quantum interference effects. In such systems, the conductivity is generally described in the framework of weak localization theory [254]. The low-temperature data are analyzed according to WL theory developed for graphene. These results provide exclusive evidences that the 2D Mott VRH transport is the dominant transport mechanism at low temperatures for graphene and graphene-WS₂ heterostructure.

5.3 Conclusion

A lithography free technique was developed to fabricate graphene-WS₂ heterostructure devices using a transmission electron microscope (TEM) grid as a shadow mask. Graphene was directly deposited on a Si/SiO₂ substrate by radio frequency (RF) plasma enhanced chemical vapor deposition. WS₂ was synthesized by first depositing WO₃ followed by sulfurization. At low temperatures, for all samples, the transport is found to follow the variable-range hopping (VRH) process, where logarithmic R exhibits a $T^{-1/3}$ temperature dependence, an evidence for the 2D Mott VRH transport. The measured low-field magnetoresistance also exhibits a quadratic magnetic field dependence $\sim B^2$, consistent with the 2D Mott VRH transport.

CHAPTER 06

DIRECT FABRICATION OF GRAPHENE/h-BN/GRAPHENE TUNNEL JUNCTIONS

6.1 Introduction

A detailed account of two-dimensional (2D) materials was introduced in Chapter 1 [282-288]. Graphene is metallic, while h-BN is a wide band gap semiconductor thus making them both unsuitable for electronics applications which require small and (preferably) tunable band gap materials [289].

Hexagonal boron nitride (h-BN) is an important 2D material and is particularly useful as the dielectric layer in functional heterostructures [290]. Graphene in combination with h-BN offer exciting possibilities of initiating a novel class of atomically-thin stacked heterostructures [65, 291]. Graphene and h-BN have very similar crystal structures with quite similar lattice constants. Nevertheless, unlike graphene, h-BN is categorized as an insulator that possesses a large energy bandgap of 6 eV [67, 292]. Previous reports have mostly focused on the utilizing thick layers of BN as either substrate for graphene-based electronics [293-295] or as a dielectric material in coupled 2D electron gases [296]. Moreover, Hexagonal boron nitride has also been utilized as a barrier for tunneling devices by sandwiching it in-between two graphene layers [297]. It is highly desirable to extend these results to graphene-based tunneling devices where h-BN can serve as a tunneling barrier offering significant potential for new and interesting applications e.g. tunneling devices for flexible electronics.

In this study, we investigated the electrical properties of three tunnel diodes wherein h-BN acts as a barrier layer between two graphene layers. We demonstrate that h-BN effectively plays the role of an efficient tunnel barrier and we also found in our study that the transmission probability of the h-BN barrier reduces exponentially with the thickness of h-BN. The current-voltage (I-V) plots of these devices exhibit a linear correlation at low bias and also show an exponential dependence at higher voltages. The slope of the linear range in each sample (differential conductance at zero bias) decreases exponentially with the increase of the h-BN thickness. Unlike in the previous studies involving cumbersome processes including transfer of graphene and h-BN followed by microfabrication processes, we have created vertically stacked tunnel junctions by directly depositing graphene, h-BN, and graphene sequentially on an arbitrary substrate using a PECVD technique. This simple architecture doesn't require any microfabrication step and the electrical contacts could be directly defined on the bottom and top graphene layers.

Here, graphene and h-BN were directly deposited by RF-plasma enhanced chemical vapor deposition. In the case of graphene, CH_4 gas was used whilst ammonia borane was used for h-BN synthesis.

6.2 Experiment Details and Results

We synthesized Graphene/h-BN/Graphene tunnel junctions with varying h-BN thickness directly on Si/SiO₂ substrates. First, graphene was deposited on the entire substrate using PECVD with pure CH_4 (99.8%) at a flow rate of ~5 sccm as the carbon source. Next, using a circular shadow mask with a diameter ~ 4.5 mm, h-BN was deposited

on graphene on a selected narrow region again using PECVD, but with ammonia borane (borane-ammonia complex powder, Sigma-Aldrich, 97%) as the B and N source.

Figure 6.1 The scheme of Graphene/h-BN/Graphene tunnel junction fabrication.

In this process, Ammonia borane was sublimed using a heating tape with 110°C for the source zone and carried into the growth chamber using a gas mixture of Ar/H₂ (40 vol % argon, 60 vol % H₂) at a flow rate of ~50 sccm. The temperature was maintained at 700 °C and more details about the synthesis could be found in section 4.3. Next, a second smaller circular mask with diameter ~ 2.5 mm was carefully placed over the h-BN region and graphene was deposited by PECVD as in the first step. The thickness of the h-BN layer was tuned by varying the deposition time of h-BN for different for 3 samples; 15 min, 30

min and 45 min. The electrical contacts were defined on the top graphene layer and the bottom graphene layer. The fabrication process is shown in schematically Figure 6.1.

Figure 6.2 Raman spectra of graphene and h-BN with 632 nm laser excitation in an Invia Renishaw Raman spectrometer.

Figure 6.2 (a) and (b) show the Raman spectrum of graphene and h-BN respectively taken with 632 nm laser excitation in an Invia Renishaw Raman spectrometer. Figure 6.2 (b) shows the Raman peaks characteristic of graphene. The peaks at 1350 cm⁻¹, 1590 cm⁻¹, 1630 cm⁻¹, and 2600 cm⁻¹ are characteristic of D, G, D', and 2D bands of graphene. G (1580 cm⁻¹), a primary in-plane vibrational mode involving the sp² hybridized carbon atoms that comprises the graphene sheet. 2D or G' (2690 cm⁻¹), a second-order overtone of the

D band corresponding the result of a two-phonon lattice vibrational process. The D (1350 cm^{-1}) band is known as the disorder band associated with the defects of graphene. The D'-band (around 1630 cm^{-1}) is associated with edges and structural disorder in graphene films [273]. Figure 6.2 (a) shows the Raman spectrum of h-BN consisting of a peak at $\sim 1380\text{ cm}^{-1}$ which is assigned to the h-BN high-frequency vibrational mode (E_{2g}).

Figure 6.3 (a) XPS survey plot of h-BN deposited by PECVD. (b) XPS peak of B1s (c) XPS peak of N1s.

Figure 6.3 shows the X-ray photoemission spectra of h-BN grown by PECVD. The survey spectrum, Fig. 6.3 (a) clearly shows the peaks corresponding to B1s and N1s core electrons. In addition, the spectrum consists of peaks due to C1s and O1s core electrons. The C1s peak is due to the contamination from carbon resulting from the previous synthesis of graphene in the reactor Figure 6.3 (b) and (c) show the individual peaks, B1s, and N1s respectively of the XPS spectra. B1s and N1s exhibit energy positions at 198.6 eV and 406.8 eV, respectively, which are consistent with the reported XPS characteristic lines for h-BN. Stoichiometry calculation based on the XPS data gives a B/N ratio of 1.08, suggesting an almost equal composition of B and N elements.

Figure 6.4 I-V characteristics of Graphene/h-BN/Graphene tunnel junctions for varying h-BN thicknesses.

Figure 6.4 shows the I-V characteristics of Graphene/h-BN/Graphene samples with 3 different h-BN thicknesses. The I-V curves of all three samples show exponential dependence of the current, I on the voltage, V at higher biases. The zero-bias conductivity (slope of the linear range about $V = 0$) for the three samples were estimated to be $1.760 \text{ G}\Omega^{-1}$, $0.356 \text{ G}\Omega^{-1}$, and $0.0253 \text{ G}\Omega^{-1}$ from thinnest to thickest h-BN tunnel barrier respectively. The results indicate the exponential dependence of the zero-bias conductivity with the BN barrier thickness.

Figure 6.5 I-V characteristics with logarithmic I of Graphene/h-BN/Graphene tunnel junctions for varying h-BN thicknesses.

In Figure 6.5, we plot I-V, plot with logarithmic I to demonstrates the exponential dependence of the tunnel current on bias voltages. Interestingly, for the graphene/BN/graphene tunnel junctions, the exponential dependence seems to scale with barrier thickness.

6.3 Conclusion

In summary, a lithography free technique was developed to fabricate Graphene/h-BN/Graphene tunnel junctions. Graphene and h-BN were directly deposited on a Si/SiO₂ substrate by radio frequency (RF) plasma enhanced chemical vapor deposition using CH₄ and ammonia borane as the precursors respectively.

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6. “Direct fabrication of Graphene/h-BN/Graphene tunnel junctions”. Adel Alruqi, Rong Zhao, Jacek Jasinski, Gamini Sumanasekera. (To be submitted soon.)
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