Chemical Vapour Deposition Growth of Graphene and Hexagonal Boron Nitride, and a Study of the Electronic and Corrosion Inhibiting Properties of Hexagonal Boron Nitride

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To my parents and siblings

Abstract

Graphene is an allotrope of carbon in the form of a two-dimensional (2D) material with zero bandgap. Hexagonal boron nitride (hBN), also known as white graphite, is a wide bandgap 2D material that has found use as an insulating dielectric layer in ultra-high mobility graphene devices, 2D heterostructures and tunneling devices. In this thesis, we report the chemical vapor deposition (CVD) growth and characterization of graphene and monolayer hBN. The growth of graphene and hBN was performed separately in a tube furnace on Cu foils using methane (CH₄) and an ammonia borane (NH₃-BH₃) precursor, respectively. Raman spectroscopy confirmed that the CVD grown graphene is a monolayer of high quality. We have fabricated graphene field effect transistors and characterized their electrical properties to demonstrate material quality. Additionally, the CVD grown graphene was incorporated in a diverse range of applications, including large area graphene ion sensitive field effect transistors, suspended graphene varactors and an investigation of the role of hydrogenation on the electronic and thermal properties of graphene.

We employed a variety of techniques to characterize CVD grown hBN. The morphology of the as-grown film along with the optimization of growth conditions to yield high coverage of monolayer hBN was studied by scanning electron microscopy. X-ray photoelectron spectroscopy confirmed the presence of boron and nitrogen in the CVD grown film as well as the expected stoichiometry. The electron diffraction pattern of suspended hBN films displayed a hexagonal crystal structure. A prominent Stokes Raman shift at 1369 cm⁻¹ was observed in hBN transferred to Si/SiO₂ substrates, revealing that our CVD grown hBN is of monolayer form. The optical

properties of our hBN layers were probed by cathodoluminescence and UV-visible absorption spectroscopy.

We report the first observation of in-plane charge transport in large area CVD grown monolayer hBN using a variety of electrode geometries. Ni electrodes were used to provide electrical contacts. We have observed a quadratic scaling of current with voltage at high bias corresponding to a space charge limited conduction mechanism, with a room temperature mobility reaching up to 0.01 cm²/Vs at electric fields up to 100 kV/cm in the absence of dielectric breakdown. The observation of in-plane charge transport highlights the semiconducting nature of monolayer hBN, and identifies hBN as a wide-gap 2D crystal capable of supporting charge transport at high field.

Furthermore, we have examined the suitability of CVD grown monolayer hBN for inhibiting corrosion. Quantitative measurements of monolayer hBN as a Cu corrosion inhibitor were studied by use of cyclic voltammetry, Tafel analysis and electrochemical impedance spectroscopy. We have found that CVD grown monolayer hBN reduces the Cu corrosion rate by one order of magnitude compared to bare Cu, suggesting that this ultrathin layer can be employed as an atomically thin corrosion-inhibition coating.

The final contribution of this thesis is the growth of hBN directly on Si/SiO_2 substrate via CVD. The main focus of this work is to produce metal-free, large-area, continuous and uniform hBN dielectric films on Si-based substrates ready to incorporate into devices without any transfer processing. We have also examined the effect of carrier gas flow rate on the thickness and roughness of the grown film in atmospheric pressure CVD. We have succeeded to grow large area hBN films with the thickness of ~ 2 nm and rms roughness of 0.6 nm (over 1 μ m²) directly on Si/SiO₂ substrates via atmospheric pressure CVD.

Résumé

Le graphène est un allotrope de carbone sous forme d'un matériau bidimensionnel (2D) avec une bande interdite nulle. Le nitrure de bore hexagonal (hBN) connu sous le nom de graphite blanc, est un matériau à large bande 2D qui est utilisé comme une couche diélectrique isolante dans des dispositifs de graphène à ultra-haute mobilité, des hétérostructures 2D et des dispositifs de tunnel. Dans cette thèse, nous signalons la croissance par dépôt chimique en phase vapeur (CVD) et la caractérisation du graphène et de la monocouche hBN. La croissance du graphène et du hBN a été effectuée séparément dans un four à tubes sur des feuilles de cuivre (Cu) en utilisant, respectivement, le méthane (CH₄) et un précurseur d'ammoniac borane (NH₃-BH₃). La spectroscopie Raman a confirmé que le graphène cultivé par CVD est une monocouche de haute qualité. Nous avons fabriqué des transistors à effet de champ en graphène et nous avons caractérisé leurs propriétés électriques afin de démontrer la qualité du matériau. Par ailleurs, le graphène développé par CVD a été utilisé dans une large gamme d'applications, y compris des transistors à effet de champ à base de graphène à grande surface sensible aux ions, des varacteurs de graphène suspendus et aussi l'étude du rôle de l'hydrogénation sur les propriétés thermiques et électroniques du graphène.

Nous avons utilisé plusieurs techniques pour caractériser le hBN développé par CVD. La morphologie du film le plus développé ainsi que l'optimisation des conditions de croissance afin d'obtenir une couverture élevée de monocouche de hBN ont été étudiées par la microscopie électronique à balayage. La présence de bore et d'azote dans le film développé par CVD ainsi que leur stœchiométrie a été analysée par la spectroscopie photoélectronique par rayons X. Le

diagramme de diffraction d'électrons des films hBN en suspension montrait une structure hexagonale cristalline. Un changement important de Stokes Raman à 1369 cm⁻¹ a été observé dans le hBN transféré dans des substrats de Si/SiO₂, révélant que notre hBN développé par CVD est sous forme de monocouche. Les propriétés optiques de nos couches de hBN ont été sondées par la cathodoluminescence et la spectroscopie d'absorption UV-visible.

Nous rapportons la première observation du transport de charge en plan dans la grande surface de monocouche hBN développée par CVD en utilisant une variété de géométries d'électrodes. Des électrodes Ni ont été servies pour fournir des contacts électriques. Nous avons observé une échelle quadratique du courant avec une tension à un biais élevé correspondant à un mécanisme de conduction à un mécanisme de conduction limité de charge spatiale, avec une mobilité à température ambiante atteignant jusqu'à $0,01 \text{ cm}^2$ / Vs sur des champs électriques allant jusqu'à 100 kV / cm en l'absence de rupture diélectrique. L'observation du transport de charge en plan souligne la nature semi-conductrice du la monocouche hBN et identifie le hBN comme un cristal 2D à large intervalle capable de supporter le transport de charges dans un champ élevé.

Par ailleurs, nous avons examiné la pertinence de la nanoculture des monocouches hBN développée par CVD pour inhiber la corrosion. Les mesures quantitatives de la monocouche hBN comme inhibiteur de corrosion du Cu ont été étudiées par la voltamétrie cyclique, l'analyse de Tafel et la spectroscopie d'impédance électrochimique. Nous avons constaté que les monocouches hBN développées par CVD peuvent réduire le taux de corrosion du Cu d'un ordre de grandeur comparé à Cu nu, ce qui suggère que cette couche ultra-fine peut être employée comme un revêtement atomiquement mince inhibant la corrosion.

La contribution finale de cette thèse est avant tout la croissance de hBN directement sur le substrat Si/SiO₂ via CVD. L'objectif principal de ce travail est de produire des films diélectriques hBN sans métal, de larges surfaces, continues et uniformes sur des substrats à base de Si prêts à être intégrés dans des dispositifs sans aucun traitement de transfert. Nous avons également examiné l'effet du débit du gaz porteur sur l'épaisseur et la rugosité du film développé. Nous avons réussi la croissance des films hBN à grande surface avec une épaisseur d'environ 2 nm et une rugosité rms de 0,6 nm directement sur les substrats Si/SiO₂ par CVD en utilisant la pression atmosphérique.

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Contents

Chapter	1 Introduction	1
1.1	Motivation: From Graphene to Hexagonal Boron Nitride	1
1.2	Thesis Organization	4
1.3	Scholarly Contributions	5
1.3.1	Primary Original contribution	5
1.3.2	2 Publications Resulting from CVD Grown Graphene Described in this Thesis:	6
Chapter	2 Literature Review: Graphene and Hexagonal Boron Nitride	9
2.1	What Is Graphene?	10
2.2	Review of Graphene Synthesis	18
2.2.1	Mechanical Exfoliation	19
2.2.2	2 Liquid-phase Exfoliation	
2.2.3	3 Thermal Decomposition of Silicon Carbide (SiC)	21
2.2.4	4 Chemical Vapour Deposition	22
2.3	What Is Hexagonal Boron Nitride?	25

2	2.4	Review of Hexagonal Boron Nitride Synthesis	28
	2.4.1	Mechanical Exfoliation	28
	2.4.2	Liquid-Phase Exfoliation	28
	2.4.3	Chemical Vapor Deposition	29
Ch	apter	3 Synthesis and Characterization of Large Area High Quality Graphene	34
3	.1	Chemical Vapour Deposition of Large Area High Quality Graphene	35
3	.2	Transferring Graphene from Cu to Si/SiO ₂ Substrates	36
3	.3	Raman Spectroscopy	37
3	.4	Electronic Properties of Graphene Field Effect Transistor	40
3	.5	A Synopsis of Collaborative Work Using CVD Grown Graphene	43
3	.6	Conclusions	44
Ch	apter	4 Synthesis and Characterization of Monolayer Hexagonal Boron Nitride	45
4	.1	Chemical Vapour Deposition of Large Area Monolayer hBN	46
4	.2	Organic-free Suspension of hBN	48
4	.3	hBN Transfer from Cu to Other Substrates	49
4	.4	Characterization of CVD Grown Monolayer hBN	49
	4.4.1	Scanning Electron Microscopy	49
	4.4.2	X-ray Photoemission Spectroscopy	51
	4.4.3	Transmission Electron Microscopy and Selected-area Electron Diffraction	52
	4.4.4	Optical Microscopy and Atomic Force Microscopy	53
	4.4.5	Raman Spectroscopy	54
	4.4.6	Optical Properties of CVD Grown Monolayer hBN	55

4.5	Conclusions	57
Chapter	5 In-plane Charge Transport in Monolayer CVD Grown hBN	58
5.1	Introduction	59
5.2	Review of Charge Transport in hBN	60
5.3	Device Fabrication	63
5.4	Space Charge Limited Transport	64
5.4.2	1 2-point Measurements	65
5.4.2	2 4-point Measurements	67
5.4.3	3 Charge Carrier Mobility Estimation	68
5.5	Conclusions	71
Chapter	6 Anti-corrosion Property of Monolayer CVD Grown hBN on Copper	72
6.1	Introduction	73
6.1 6.2	Introduction Review of Monolayer Materials for Corrosion Inhibition	73 73
6.16.26.3	Introduction Review of Monolayer Materials for Corrosion Inhibition Sample Fabrication and Apparatus	73 73 74
6.16.26.36.4	Introduction Review of Monolayer Materials for Corrosion Inhibition Sample Fabrication and Apparatus Cyclic Voltammetry Measurements	73 73 74 75
 6.1 6.2 6.3 6.4 6.5 	Introduction Review of Monolayer Materials for Corrosion Inhibition Sample Fabrication and Apparatus Cyclic Voltammetry Measurements Copper Corrosion Rate Estimation	73 73 74 75 77
 6.1 6.2 6.3 6.4 6.5 6.6 	Introduction Review of Monolayer Materials for Corrosion Inhibition Sample Fabrication and Apparatus Cyclic Voltammetry Measurements Copper Corrosion Rate Estimation Electrochemical Impedance Spectroscopy	73 73 74 75 77
 6.1 6.2 6.3 6.4 6.5 6.6 6.7 	Introduction Review of Monolayer Materials for Corrosion Inhibition Sample Fabrication and Apparatus Cyclic Voltammetry Measurements Copper Corrosion Rate Estimation Electrochemical Impedance Spectroscopy Conclusions	73 73 74 75 77 79 81
 6.1 6.2 6.3 6.4 6.5 6.6 6.7 Chapter 	 Introduction Review of Monolayer Materials for Corrosion Inhibition Sample Fabrication and Apparatus Cyclic Voltammetry Measurements Copper Corrosion Rate Estimation Electrochemical Impedance Spectroscopy Conclusions 7 Direct CVD Growth of hBN on Dielectric Substrates 	73 73 74 75 77 79 81 83
 6.1 6.2 6.3 6.4 6.5 6.6 6.7 Chapter 7.1 	Introduction Review of Monolayer Materials for Corrosion Inhibition Sample Fabrication and Apparatus Cyclic Voltammetry Measurements Copper Corrosion Rate Estimation Electrochemical Impedance Spectroscopy Conclusions	73 73 74 75 77 79 81 83

xi

7.3 Chemical Vapour Deposition	Apparatus and Substrates
7.3.1 Low Pressure Chemical Vapo	our Deposition
7.3.2 Atmospheric Pressure Chemi	cal Vapour Deposition
7.4 Characterization	
7.4.1 Low Pressure Chemical Vapo	our Deposition
7.4.2 Atmospheric Pressure Chemi	cal Vapour Deposition
7.5 Discussion	
7.6 Conclusions	
Chapter 8 Conclusion and Future W	⁷ orks97
8.1 A Summary of the Main Find	ings
8.2 Future Works	
References	

List of Figures

absorbance was measured at 2.3 % per layer. The inset shows the sample design with several
apertures, taken form [8]. b) An optical image of graphene crystallites on 300 nm thick SiO_2
imaged with white light, taken from [28] 15
Figure 2-5: Ambipolar electric field in single-layer graphene. Application of a gate voltage
induces electrons or holes in graphene layer and consequently changes the position of its Fermi
level, taken from [17]
Figure 2-6: Raman spectra for different types of sp ² carbons, taken from [30]17
Figure 2-7: A schematic showing the comparison of the quality and cost of graphene made by
commonly used conventional methods 19
Figure 2-8: a, b) SEM images of early attempts for exfoliation of graphite plates with an AFM tip
on the Si (001) substrate, taken from [34]
Figure 2-9: Schematic of roll-to-roll CVD and transfer, taken from [70]
Figure 2-10: a) Schematic diagrams of crystal structures of graphite and h-BN, taken from [23].
b) TEM electron diffraction patterns of pristine hBN, taken from [74]
Figure 2-11: a) First-order Raman spectra of cubic and hexagonal boron nitride excited with λ_{exc} =
244 nm. The inset shows the crystal structure of the two BN structures, taken from [82]. b)
Raman spectra of atomically thin hBN excited with λ_{exc} = 514 nm. The left inset show changes in
integrated intensity $I_{\rm T}$ with the number of layers N. The right picture illustrates the phonon mode
(in-plane vibration) responsible for the Raman peak, taken from [83]
Figure 2-12: a) Schematic of an improved LPCVD, taken from [101]. b) schematic of CVD
system using a filter, taken from [102]

Figure 3-1: Schematic of the CVD system for graphene growth. Setup for growing graphene is composed of a quartz tube sitting in a split-tube furnace connecting from one side to CH₄ and H₂ sources and the other side to the diffusion and mechanical pumps. The pressure of system was monitored using a multi gauge controller using the convectron and ionization gauges. The flow of Figure 3-2: An optical microscope image of graphene transferred onto a Si substrate covered with 300 nm SiO_2 layer. The entire surface seen in the image is covered by the clean graphene except Figure 3-3: Raman spectrum of transferred CVD grown graphene onto a Si/SiO₂ substrate. The low D peak indicates the presence of high quality graphene. The G peak intensity is more than Figure 3-4: a) Output characteristic curve of CVD grown graphene field effect transistor. b) Transfer characteristic curve of CVD grown graphene field effect transistor. The drain voltage $V_{DS} = 100$ mV. The red curve is where the gate voltage V_{GS} is swept from -50 V to +50 V. For the blue curve, the V_{GS} sweep is from +50 to -50 V. c) Calculated FET mobility versus gate Figure 4-1: Schematic and photographs of the CVD system for hBN growth. Setup for growing hBN monolayer is composed of a quartz tube sitting in a split-tube furnace connecting from one side to the precursor and the other side to the diffusion and mechanical pumps. The pressure of system was monitored using a multi gauge controller using convectron and ionization gauges.

Figure 4-2: Organic free-suspension method of hBN. The hBN-coated Cu foils were floated in a
Cu etchant of 0.1 M $(NH_4)_2S_2O_8$ and monitored using transmission optical microscopy
Figure 4-3: SEM images of as grown hBN layer on Cu foil with the growth time of a) 5 min, b)
15 min, and c) 30 min
Figure 4-4 : X-ray photoelectron spectroscopy (XPS) analysis of hBN on Cu. a) Survey spectrum.
b) B1S spectrum, the experimental data points are fitted by the Gaussian function with the peak
position of 190.1 eV. c) N1S spectrum, the experimental data points are fitted by the Lorentzian
function with the peak position of 397.6 eV 51
Figure 4-5: a) TEM image of suspended hBN over Cu foil. b) Electron diffraction of hBN taken
from a suspended region with corresponding Miller-Bravais indices (hkil)
Figure 4-6: a) Photograph, b) Optical microscope and c) AFM images of hBN transferred onto a
Si/SiO ₂ substrate. The transferred hBN sheet is approximately 1 cm^2 in size. The step height of
hBN on SiO ₂ is 0.45 nm
Figure 4-7: Raman spectra of bulk BN and an hBN CVD monolayer transferred onto Si/SiO2
substrate. Symbols are experimental data and lines are corresponding Lorentzian fits 55
Figure 4-8: The optical properties of CVD grown monolayer hBN. a) UV-visible absorption
spectrum of hBN transferred to a quartz substrate, measured at room temperature. The blue line is
a Lorentzian fit. b) Cathodoluminescence spectrum of suspended hBN over Cu at 5 K 56
Figure 5-1: a) Energy-momentum dispersion for graphene, this is the spectrum of a zero-gap 2D
semiconductor that describes massless Dirac fermions with c $*$ 1/300 the speed of light. b)
Energy-momentum dispersion for hBN, a massive Dirac fermion is anticipated

Figure 5-2: Review of charge transport in hBN. a) Schematic of measurement set-up in CAFM along with an SEM image of platinum wire AFM tip (taken from [141]). b) Au/BN/Au and graphene/BN/graphene sandwiches to measure the tunneling current through the hBN flake (taken from [142]). c) Schematic of the BN nanotube unwrapping processes induced by plasma etching and TEM image of a hBN nanoribbon connected to the counter gold electrode (upper black part) and tungsten STM tip (bottom black part), the inset presents the experimental configuration (taken from [143]). d) SEM image of BNNT channel between Ni electrodes (taken Figure 5-3: a) Schematic and SEM image of CVD grown hBN device with 8 µm channel length and 100 μ m square Nickel electrodes. The substrate is n-doped Si covered by 300 nm SiO₂. b) Energy band diagram of Ni and hBN interface. E_F is the Fermi level of Ni. The energy difference between E_F and vacuum level is 5.3 eV [145]. In previous study, angle resolved photoelectron spectroscopy (ARPES) measurement on hBN and graphene transferred separately on the same substrates reveals that the π binding energy of hBN is about 2.5 eV lower than that of graphene [147]. From the Fermi level of graphene (4.5 eV) [148], one can estimate that the hBN Figure 5-4: a) 2-point I_s - V_s at various temperatures in vacuum (2×10⁻⁶ Torr) for a hBN device with channel length of 8 μ m. b) I_s - V_s^2 for the same device in panel c at various temperatures. We Figure 5-5: a) I-V curve of a device without hBN. Is-Vs (black curve- left axis) and Ig-Vs (Blue Curve- right axis) of the device without hBN (Only SiO₂) with $L = 8 \mu m$ and $W = 100 \mu m$. b)

Figure 5-6: Comparison of 2-point and 4-point measurements employing four electrodes with a
uniform spacing of 10 μ m. At most 6% of the measured voltage drop occurs at the contacts, with
the remaining voltage drop across the hBN channel
Figure 5-7: The estimated room temperature mobility of several hBN devices with 100 μ m width
and different channel lengths (4 μ m, 8 μ m, 10 μ m) along with their corresponding uncertainties.
Figure 5-8: α versus $1/T$ for several hBN devices. The voltage dependent of SCL current is given
by $I_s \propto V_s^{\alpha}$. The value of α is extracted at different temperatures from the $I_S - V_S$ curves of figure
5-4, a
Figure 6-1: Schematic of the custom built PTFE electrochemical cell. Bare Cu or hBN-Cu
samples were clasped in the PTFE cell with a 0.07 cm^2 area opening to the electrolytic solution.
Figure 6-2: (a) CV measurements for a 0.07 cm ² area bare Cu (red), hBN-Cu (blue) and scratched
hBN Cu (black) in a 0.1 M NaOH solution. Optical microscope images of hBN-Cu before (b) and
after (c) 30 consecutive CV sweeps. (d) Optical microscope image of scratched hBN-Cu after 30
CV sweeps. Scale bar is 100 μm in (b), (c) and (d)
Figure 6-3: Tafel plots of Cu (red) and hBN-Cu (blue) samples, with linear fits of cathodic and
Figure 6-3: Tafel plots of Cu (red) and hBN-Cu (blue) samples, with linear fits of cathodic and anodic curves (dashed line) giving the intersection at a potential V_{corr} and current density J_{corr} . 78
Figure 6-3: Tafel plots of Cu (red) and hBN-Cu (blue) samples, with linear fits of cathodic and anodic curves (dashed line) giving the intersection at a potential V_{corr} and current density J_{corr} . 78 Figure 6-4: EIS analysis of bare Cu and hBN-Cu in a 0.1 M NaOH electrolyte solution. Symbols
Figure 6-3: Tafel plots of Cu (red) and hBN-Cu (blue) samples, with linear fits of cathodic and anodic curves (dashed line) giving the intersection at a potential V_{corr} and current density J_{corr} . 78 Figure 6-4: EIS analysis of bare Cu and hBN-Cu in a 0.1 M NaOH electrolyte solution. Symbols are experimental data and lines are the corresponding model fits to a Randles equivalent circuit.
Figure 6-3: Tafel plots of Cu (red) and hBN-Cu (blue) samples, with linear fits of cathodic and anodic curves (dashed line) giving the intersection at a potential V_{corr} and current density $J_{corr.}$. 78 Figure 6-4: EIS analysis of bare Cu and hBN-Cu in a 0.1 M NaOH electrolyte solution. Symbols are experimental data and lines are the corresponding model fits to a Randles equivalent circuit. (a) Bode plot of impedance magnitude of Cu (red) and hBN-Cu (blue) samples. The Randles

 C_{dl} , charge-transfer resistance R_{ct} , and Warburg diffusion element W. (b) A Bode impedance phase plot of Cu (red) and hBN-Cu (blue) samples. (c) Nyquist impedance plots of Cu (red) and Figure 7-1: a) Schematic of the LPCVD system for hBN growth on Si/SiO₂ substrate. Setup for growing hBN layers is composed of a quartz tube sitting in a split-tube furnace connecting from one side to the precursor and the other side to the diffusion and mechanical pumps. The pressure of system was monitored using a multi gauge controller using convectron and ionization gauges. The flow of carrier gases (H_2 and Ar) was controlled by mass flow controller (Horiba). b) Experimental procedure with parameters (time, temperature, pressure, and gas flow rate), 89 Figure 7-2: a) Schematic of the APCVD system for hBN growth on Si/SiO₂ substrate. Setup for growing hBN layers is composed of a quartz tube sitting in a split-tube furnace connecting from one side to the precursor and the other side to the central exhaust ventilation of building. The flow of carrier gases (H₂ and Ar) was controlled by mass flow controller (Horiba). b) Figure 7-3: Characterization of hBN film grown on Si/SiO₂ using LPCVD with the growth time of 1 h. a) Raman spectrum of hBN film grown on Si/SiO₂ substrate. Inset shows the AFM image of the sample. The image size is 1 μ m × 1 μ m. XPS survey (b) and magnified XPS spectra of (c) B 1s and (d) N 1s. The peak binding energies for N 1s and B 1s are 397.9 eV and 190.4 eV, Figure 7-4: Characterization of hBN film grown on quartz substrate using LPCVD with the growth time of 1 h. a) UV-visible absorption spectrum of hBN grown on a quartz substrate, measured at room temperature. Inset shows the AFM image of the sample. The image size is 1

List of Tables

List of Terms

0D	Zero-Dimensional
1D	One-Dimensional
2D	Two-Dimensional
3D	Three-Dimensional
AB	Ammonia Borane
AFM	Atomic Force Microscopy
APCVD	Atmospheric Pressure Chemical Vapour Deposition
ARPES	Angle-Resolved Photoemission Spectroscopy
BNNR	BN Nanoribbon
BNNS	BN Nanosheet
BNNT	BN Nanotube
CAFM	Conductive Atomic Force Microscopy
CL	Cathodoluminescent
CR	Corrosion Rate
CV	Cyclic Voltammetry
CVD	Chemical Vapor Deposition

DMF	Dimethylformamide

EIS	Electrochemical Impedance Spectroscopy
FWHM	Full Width at Half Maximum
gFET	Graphene Field Effect Transistor
GO	Graphite Oxide
HARE	Helicon Activated Reactive Evaporation
hBN	Hexagonal Boron Nitride
HOPBN	Highly Oriented Pyrolytic Boron Nitride
HOPG	Highly Oriented Pyrolytic Graphite
IPA	Isopropanol Alcohol
ISFET	Ion Sensitive Field Effect Transistors
LEED	Low-Energy Electron Diffraction
LPCVD	Low Pressure Chemical Vapour Deposition
PMMA	Poly (Methyl Methacrylate)
PTFE	Polytetrafluoroethylene
Rad-OM	Radiation-mode Optical Microscopy
SAED	Selected Area Electron Diffraction
SCL	Space-Charge Limited
SEM	Scanning Electron Microscope
SiC	Silicon Carbide
STM	Scanning Tunnelling Microscopy
TEM	Transmission Electron Microscopy
TMD	Transition Metal Dichalcogenide

UV Ultra-Violet

XPS X-Ray Photoemission Spectroscopy

Chapter 1

Introduction

1.1 Motivation: From Graphene to Hexagonal Boron Nitride

The behavior of a nanostructured material is strongly influenced by its dimensionality [1]. In other words, the same material reveals diverse physical properties based on its structural arrangement, whether it be a zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D) form.

In this thesis, we are concerned with 2D material, which refers to a film with nanometer scale thickness and much larger lateral dimensions. The first 2D material that was isolated and transferred onto desired substrates is graphene [2], an atomically thick layer of carbon atoms arranged in a honeycomb structure. This ultra-thin sheet of carbon atoms is also the first 2D material studied in detail. Graphene is a gapless semimetal in which charge carriers behave like Dirac fermions with zero effective mass [3]. This results in unique properties including remarkably high charge carrier mobilities (see figure 1-1, a) [4], micrometer-scale ballistic transport [5], the half-integer quantum Hall effect [6,7] and optical transparency of > 97% [8]. Moreover, graphene is flexible and mechanically strong [9]. All these properties make graphene an excellent candidate for next generation electronics such as high frequency transistors [10], flexible displays [11], sensors [12] among other proposed applications.

In terms of graphene production, various methods have been reported so far. Chemical vapour deposition (CVD) is a comparatively facile and inexpensive route to produce large area high quality graphene. The evolution of price of bulk CVD grown monolayer graphene is illustrated in figure 1-1, b as reported by the Spanish company, Graphenea, including projections into the future. The price is associated with the cost of volume production as well as the transferring





Figure 1-1: a) Electron mobility versus bandgap in low electric fields for different materials, taken from [14]. b) The evolution of price of bulk CVD grown monolayer graphene reported by the Spanish company, Graphenea, modified from [13].

Hence, graphene is a promising material with high carrier mobility which can be prepared relatively with low cost compared to other semiconductors. To be clear, there is presently no competition for ultra large scale integration of transistors on silicon. However, graphene offers the possibility of economic production of large area electronic devices with a low-level of integration, such as macroscopic sensing field effect transistors. Here, in this thesis, we present the synthesis of large area high quality graphene on Cu foil using CVD. A variety of applications based on CVD grown graphene was demonstrated by colleagues in my research group. Importantly, band gap opening was shown by hydrogenation of graphene. A variety of results

have been obtained by incorporating CVD grown graphene into different applications which will be briefly summarized in a subsequent chapter.

We also conducted experiments on growth and characterizations of a 2D material which has a band gap in the UV i.e. hexagonal boron nitride (hBN). As seen in figure 1-2, a, in the family of 2D materials, hBN has the largest known band gap. It has been extensively used as an insulating layer in graphene electronics and 2D heterostructures [15], yet comparatively little is known about this layer itself. The number of publications reporting the properties and applications of hBN is much less than that of graphene (see figure 1-2, b). Therefore, the study of monolayer hBN is important.



Figure 1-2: a) Various 2D materials with their bandgaps and lattice constants. b) Comparison of 2D materials in terms of number of published articles during a decade, taken from [16].

1.2 Thesis Organization

This thesis is divided into eight chapters. The first chapter presents the motivation for graphene to hBN research, the thesis organization and scholarly contributions. Chapter two provides fundamental information from a literature review of graphene and hBN. The first part of chapter two introduces graphene including its band structure, optical and electronic properties, Raman spectrum and most importantly its synthesis by various methods. In the second part of chapter two, hBN is introduced along with its Raman spectrum. Different methods to synthesize hBN are then presented.

Chapter three presents the experimental procedure used in this thesis to grow graphene on Cu foils using CVD along with its transfer to insulating substrates. Then, the Raman spectrum, and the electrical properties of graphene through the field effect transistor measurements are discussed. Lastly, a summary of collaborative works using CVD grown graphene is provided.

Chapter four describes the experimental procedure to grow high quality large area monolayer hBN using CVD. A variety of techniques used to characterize the CVD grown hBN are also enclosed. All characterizations confirmed the presence of large area monolayer hBN. Chapter five reports the first observation of in-plane charge transport in large-area monolayer hBN grown by CVD. 2-point and 4-point measurements were carried out. We have observed a quadratic scaling of current with voltage at high bias corresponding to a space-charge limited conduction mechanism in monolayer hBN. Chapter six gives a comparative study of the corrosion inhibition properties of monolayer hBN on Cu. We found that CVD grown monolayer hBN reduces the Cu corrosion rate by one order of magnitude compared to bare Cu. Chapter seven describes the direct

CVD growth of hBN on insulating substrates. Large area hBN films with various thicknesses were grown on Si/SiO₂ substrates via low pressure CVD and atmospheric pressure CVD. Finally chapter eight summarizes the main finding of this research study along with future works.

1.3 Scholarly Contributions

The following publications have arisen from the research conducted in this thesis. In all cases, Prof. Thomas Szkopek and Prof. Mohamed Siaj contributed to the conception and the design of the experiments, supervised the work and edited the manuscripts.

1.3.1 Primary Original contribution

1) **F. Mahvash**, E. Paradis, D. Drouin, T. Szkopek, and M. Siaj, "Space-Charge Limited Transport in Large-Area Monolayer Hexagonal Boron Nitride," *Nano Lett.*, vol. 15, no. 4, pp. 2263–2268, Apr. 2015.

F.M. and M.S. designed the CVD system. F.M. performed the CVD, SEM, TEM, SAED, AFM, Raman and device fabrication. F.M. and T.S. performed the electrical measurements. E.P. and D.D. conducted the CL measurement. T.S. carried out the UV-Vis measurement. F.M., T.S. and M.S. analyzed the data and wrote the paper.

2) **F. Mahvash**, S. Eissa, T. Bordjiba, A. C. Tavares, T. Szkopek, and M. Siaj, "Corrosion resistance of monolayer hexagonal boron nitride on copper," *Sci. Rep.*, vol. 7, p. 42139, Feb. 2017.

F.M. and M.S. designed and built the CVD system. F.M. performed the CVD, AFM and Raman measurements and took the optical images. M.S. designed and built Polytetrafluoroethylene (PTFE) electrochemical cell. F.M, S.E. and T.B. performed the electrochemical measurements. F.M., T.S. and M.S. analysed data and wrote the manuscript. All authors reviewed the manuscript.

3) **F. Mahvash**, T. Szkopek, and M. Siaj, "Atmospheric pressure chemical vapour deposition of hexagonal boron nitride film on insulating substrate," In preparation.

F.M. performed the CVD and material characterization. T.S. and M.S. supervised the work.

1.3.2 Publications Resulting from CVD Grown Graphene Described in this Thesis:

In addition to the work cited above, the author of this thesis carried out the CVD growth of graphene used for a wide variety of works listed below. In addition to growing graphene, the author reviewed each of the manuscripts below and contributed to manuscript sections pertaining to graphene growth, transfer and processing.

1) M. AbdelGhany, **F. Mahvash**, M. Mukhopadhyay, A. Favron, R. Martel, M. Siaj, T. Szkopek, "Suspended graphene variable capacitor," *2D Mater.*, vol. 3, no. 4, p. 041005, 2016.

F.M. grew large area high quality graphene and performed spot Raman measurements.

 N. Hemsworth, F. Mahvash, P. L. Lévesque, M. Siaj, R. Martel, and T. Szkopek, "Measurement of electronic heat dissipation in highly disordered graphene," *Phys. Rev. B*, vol. 92, no. 24, p. 241411, Dec. 2015.

F.M. grew large area high quality graphene via CVD.

3) K. Bennaceur, J. Guillemette, P. L. Lévesque, N. Cottenye, **F. Mahvash**, N. Hemsworth, A. Kumar, Y. Murata, S. Heun, M. O. Goerbig, *et al.* "Measurement of topological Berry phase in highly disordered graphene," *Phys. Rev. B*, vol. 92, no. 12, p. 125410, Sep. 2015.

F.M. grew large area high quality graphene via CVD.

4) H. S. Skulason, D. L. Sounas, **F. Mahvash**, S. Francoeur, M. Siaj, C. Caloz, T. Szkopek, "Field effect tuning of microwave Faraday rotation and isolation with large-area graphene," *Appl. Phys. Lett.*, vol. 107, no. 9, p. 093106, Aug. 2015.

F.M. grew large area high quality graphene via CVD.

5) S. Eissa, G. C. Jimenez, **F. Mahvash**, A. Guermoune, C. Tlili, T. Szkopek, M. Zourob, M. Siaj, "Functionalized CVD monolayer graphene for label-free impedimetric biosensing," *Nano Res.*, vol. 8, no. 5, pp. 1698–1709, May 2015.

F.M. grew large area high quality graphene via CVD.

6) I. Fakih, S. Sabri, **F. Mahvash**, M. Nannini, M. Siaj, and T. Szkopek, "Large area graphene ion sensitive field effect transistors with tantalum pentoxide sensing layers for pH measurement at the Nernstian limit," *Appl. Phys. Lett.*, vol. 105, no. 8, p. 083101, Aug. 2014.

F.M. grew large area high quality graphene via CVD.

7) J. Guillemette, S. Sabri, B. Wu, K. Bennaceur, P. E. Gaskell, M. Savard, P. L. Lévesque, F. Mahvash, A. Guermoune, M. Siaj, *et al.* "Quantum Hall Effect in Hydrogenated Graphene," *Phys. Rev. Lett.*, vol. 110, no. 17, p. 176801, Apr. 2013.

F.M. grew large area high quality graphene via CVD.

8) I. Fakih, **F. Mahvash**, M. Siaj, and T. Szkopek, "Sensitive precise pH measurement with large-area graphene field effect transistors at the quantum-capacitance limit," *Phys. Rev. Applied*. Accepted.

F.M. grew large area high quality graphene via CVD.

9) J. Guillemette, N. Hemsworth, A. Vlasov, J. Kirman, F. Mahvash, P. L. Levesque, M. Siaj,
R. Martel, G. Gervais, S. Studenikin, A. Sachrajda, & T. Szkopek, "Giant magnetoresistance by
Pauli blockade in hydrogenated graphene," *Nat. Commun.* Submitted.

F.M. grew large area high quality graphene via CVD.

Chapter 2

Literature Review: Graphene and Hexagonal Boron Nitride

Summary: This chapter is devoted to graphene and hexagonal boron nitride (hBN), the two isostructural extremes of band gap in the 2D materials family. Graphene is a gapless semimetal and hBN is an insulator with a band gap of 6.2 eV. The introduction of graphene starts by a brief history of its development. The band structure, optical and electronic properties of graphene are briefly described. Raman spectroscopy as a powerful tool to distinguish graphitic materials is presented. Then, we aim to provide a concise review of graphene's synthesis by various methods. In the second part of this chapter, hBN is introduced along with its Raman spectrum. Different methods to synthesize hBN are presented. Finally, we direct our attention to the synthesis of hBN on Cu foil using CVD with ammonia borane (AB) precursor.
2.1 What Is Graphene?

In simplest terms, graphene is an allotrope of carbon in an atomic-thick sheet shape. In fact, there are four graphitic materials with different dimensionalities as illustrated in figure 2-1: 3D-graphite, 2D-graphene, 1D-nanotube and 0D-fullerene. Graphene can be visualized as a basic building block of graphitic materials. Graphene can be stacked to form 3D-graphite, rolled to form 1D-nanotubes and wrapped to form 0D-fullerene [17], although this is not the means by which these other carbon allotropes are commonly synthesized.



Figure 2-1: Graphitic materials with different dimensionalities, clockwise from top left, are 2D-graphene, 3D-graphite, 0D-fullerene, 1D-nanotube, taken from [18].

Historically, graphite was firstly discovered in England in 1565 as a marking substance leading to the formation of pencils. In 1779, the carbon composition of graphite was discovered. In 1924, J. D. Bernal revealed the crystal structure of graphite using the recently discovered method of X-ray diffraction [19]. These measurements confirmed the hexagonal crystal structure with a lattice

constant of 2.46 Å and an interlayer spacing of 3.4 Å. The band structure of graphite and graphene was firstly calculated by the Canadian theorist Philip Russell Wallace in 1947 using tight binding approximation [20]. He used a graphene model as his starting point to study graphite, and predicted the zero band gap and relativistic behaviour of electrons in graphene. At that time, the existence of free-standing graphene seemed impossible.

In 1977, Grant and Haas reported the first electron diffraction pattern of graphene on a metal surface, which at the time was viewed as a nuisance interfering in the study of metal surfaces [21]. Single and bi layer graphene have been firstly grown on the surface of lanthanum hexaboride in 1977 by Oshima *et al.* using chemical vapour deposition (CVD) [22]. In the same year, the first angle-resolved photoemission spectroscopy (ARPES) measurement was performed on CVD grown graphene on transition metal carbide. The measurements showed the zero band gap and the linear electronic dispersions that approached a Dirac-like crossing in the vicinity of the Fermi level [23]. The CVD grown graphene, called monolayer graphite at the time, was also characterized using different techniques such as x-ray photoemission spectroscopy (XPS), low-energy electron diffraction (LEED), and scanning tunnelling microscopy (STM). Figure 2-2 illustrates an STM image of CVD grown graphene on TaC along with its LEED pattern.



Figure 2-2: An STM image for monolayer graphite (MG) on TaC (111). Inset is the LEED pattern of MG on TaC(111), taken from [23].

Interestingly, in 1985, a remarkably stable cluster consisting of 60 carbon atoms known as buckminsterfullerene was accidentally produced by vaporization of graphite using laser irradiation [24]. The next graphitic member to be discovered was the carbon nanotube. In 1999, Sumio Iijima announced in Nature the preparation of nanometre-size, needle-like tube of carbon produced by an arc-discharge evaporation of carbon similar to that used for fullerene synthesis [25].

Although graphene has been theoretically studied and epitaxially grown for many years earlier, the first electrical measurements of graphene in 2004 sparked a global explosion in graphene research. Andre Geim and co-workers at the University of Manchester were able to isolate a few layers of graphene from highly oriented pyrolytic graphite (HOPG) by repeated peeling using adhesive tape [2]. This is the first documented evidence of graphene being isolated and transferred onto desired substrates. They observed strong ambipolar field effect behaviour in graphene. In 2010, Andre Geim and Konstantin Novoselov were jointly awarded the Noble prize in physics for their pioneering research on 2D graphene.

As previously mentioned, the remarkable band structure of graphene has been theoretically and experimentally investigated. In a honeycomb lattice, each carbon atom is sp^2 -hybridized to form three σ bonds with their neighbours and a π -bond oriented in the z-direction (out of the plane). These π -bonds are then hybridized together to form what are referred to the π -bond and π^* -bond. The delocalization of π - π^* electrons are responsible for most of the peculiar electronic properties of graphene including being gapless. Figure 2-3, a illustrates the band structure of graphene. The valence and conduction bands formed respectively by π and π^* states have valley structure. These bands coincide at six corners of the hexagonal Brillouin zone, which are called Dirac or neutrality points. These six points can be classified as two in-equivalent points K and K' in momentum space due to their symmetry. Looking closely at the low energy regions (see figure 2-3, a) around the Dirac points, the linear cone-shaped band structure intersecting at the Dirac point is evident. This linear dispersion region is well-described by the Dirac equation for massless fermions [26]. That is, the effective mass of the charge carriers in this region is zero. An example of ARPES measurements for quasi free-standing monolayer graphene on 3C-SiC(111) indicative of the linear dispersion is shown in figure 2-3, b.



Figure 2-3: a) The band structure of graphene in the honeycomb lattice and zoom-in of the energy bands close to one of the Dirac points, taken from [3]. b) An example of ARPES measurement for quasi free-standing monolayer graphene on 3C-SiC(111)., taken from [27].

In terms of optical properties, a graphene layer was shown to absorb 2.3% of the incident white light [8] (see figure 2-4, a). This experimental investigation remarkably confirms the twodimensional nature and gapless electronic spectrum of graphene. In another study, the visibility of graphene on top of Si/SiO₂ substrates was investigated [28] and it was found that using monochromatic illumination, 300 nm and 100 nm thick SiO₂ are the most suitable substrates for graphene visual detection. Figure 2-4, b shows graphene viewed under normal, white-light illumination on top of Si substrate with 300 nm-thick SiO₂.



Figure 2-4: A photograph of a 50-mm aperture partially covered by graphene and its bilayer. The line scan profile shows the intensity of transmitted white light along the yellow line. Optical absorbance was measured at 2.3 % per layer. The inset shows the sample design with several apertures, taken form [8]. b) An optical image of graphene crystallites on 300 nm thick SiO_2 imaged with white light, taken from [28].

In terms of electronic properties, graphene exhibits ambipolar behaviour (see figure 2-5) and possesses very high charge carrier mobility at room temperature. Mobilities of 10,000–15,000 cm²/Vs were measured for exfoliated graphene on Si/SiO₂ substrates [3,4,14]. A charge carrier mobility in excess of 200,000 cm²/Vs at electron densities of $\sim 2 \times 10^{11}$ cm⁻² has been achieved in suspended exfoliated graphene [29]. Interestingly, exfoliated graphene on hBN, an atomically smooth and inert substrate, was shown to exhibit mobility of $\sim 100,000$ cm²/Vs at the electron density of $\sim 10^{11}$ cm⁻² [15].



Figure 2-5: Ambipolar electric field in single-layer graphene. Application of a gate voltage induces electrons or holes in graphene layer and consequently changes the position of its Fermi level, taken from [17].

Raman spectroscopy is a powerful tool that has been widely used to characterize graphitic materials. This technique can give valuable information such as the crystallite size, clustering of the sp^2 phase, the introduction of chemical impurities, and the number of graphene layers [30]. Raman spectra for various carbon nanostructures are illustrated in figure 2-6.



Figure 2-6: Raman spectra for different types of sp^2 carbons, taken from [30].

The Raman spectrum of graphene consists of two prominent distinct characteristic peaks known as G and G' (also called 2D). The G peak, which is common to all *graphitic* carbon systems corresponds to the primary in-plane vibration mode known as the E_{2g} phonon mode [31]. This band is highly sensitive to strain effects in sp² nanocarbons and can be used to probe any modification of graphene structure [32].

The G' peak is the strongest peak in graphene occurring at $\sim 2700 \text{ cm}^{-1}$. It originates from a second-order Raman process due to the in-plane breathing-like mode of the carbon rings [33]. This band has a strong dependence on any perturbation to the electronic and/or phonon structure

of graphene. For this reason, it provides information to differentiate single layer graphene from double-layer graphene [30].

In disordered graphene, another peak known as D peak at $\sim 1350 \text{ cm}^{-1}$ appears. This band known as the disorder or defect band also originates from a second-order Raman process but it must be activated by a defect or edge [31]. Therefore, the intensity of this band can give useful information on the level of defects in the sample.

2.2 Review of Graphene Synthesis

Several methods have been reported so far to synthesize graphene. Here, we aim to discuss the most common methods which include mechanical exfoliation, liquid exfoliation, reduction of graphene oxide, thermal decomposition of SiC substrates and chemical vapour deposition (CVD).

Each of the above methods has its own advantages as well as limitations. Figure 2-7 shows a comparison of different methods in terms of cost and quality. Quality is based on the charge carrier mobility, uniformity and being monolayers. Each method has also different applications. Some methods produce small graphene sheets while larger graphene films can be produced using CVD and thermal decomposition of SiC. As illustrated in that schematic, CVD is superior method to produce large area graphene films with lower cost.

Each technique is described individually along with some key remarks in subsequet sections.



Figure 2-7: A schematic showing the comparison of the quality and cost of graphene made by commonly used conventional methods.

2.2.1 Mechanical Exfoliation

The simplest form of mechanical exfoliation is to peel the atomic layers from the bulk material using adhesive tape. The detaching force is enough to break the weak van der Waals interactions between the layers and leave behind the remaining layer intact. This method was first reported by Novoselov and co-workers in 2004 to isolate graphene from HOPG [2]. In fact, the exfoliation of

graphene from HOPG dates back to 1999 where Lu *et al.* presented one approach to manipulate the individual sheets using scanning probe microscope tips (see figure 2-8) [34].



Figure 2-8: a, b) SEM images of early attempts for exfoliation of graphite plates with an AFM tip on the Si (001) substrate, taken from [34].

The exfoliation using adhesive tape provides small area high crystal quality sample (maximum $100 \ \mu\text{m}^2$ in size for graphene) with low cost and extremely low yield [35] which is suitable for the exploration of the intrinsic properties of 2D material [36]. In recent years, advance mechanical exfoliation techniques inspired by the Scotch tape method have been reported. Continuous mechanical exfoliation by a three-roll mill machine with a polymer adhesive has been used to peel the single layer of graphene [37]. Ball milling, either in wet or dry media, is another method generating a shear force to isolate graphene [38,39]. However as shown in figure 2-7, these methods do not provide that high quality graphene.

2.2.2 Liquid-phase Exfoliation

Liquid-phase exfoliation or wet-chemical exfoliation is the separation of individual sheets from stacked 2D crystals by means of sonication in various solvents or aqueous surfactant

solutions [40]. This method provides large quantities of dispersed nanosheets and has higher yield in comparison with mechanical exfoliation. Selection of solvent and the time of sonication play a crucial role in yield determination [41]. One main drawback of this method is that there is a trade-off between the lateral dimension size of graphene sheet and the number of layers.

Another method to isolate graphene which can be classified in this group is the oxidationexfoliation-reduction. First, graphite oxide (GO) is synthesized by the oxidation of graphite via one of three principle methods developed by Brodie [42], Staudemeier [43], or Hummers [44]. Then, graphene oxide can be produced easily by ultrasonic treatment of GO. Lastly, the reduction of graphene oxide is required. The oxidation in fact weakens the interlayer interaction of graphite and enhances its hydrophobicity. It also leads to severe structural damage to the graphene layer and produces pollution due to the release of NO_x gases during the synthesis [45]. However in 2010, Marcano *et al.* reported an improved synthesis based on the Hummers method which does not generate toxic gases [46]

The small graphene sheets produced by wet-exfoliation can be used in composites, transparent electrodes, functional coatings, conductive inks, batteries, supercapacitors and sensors [47].

2.2.3 Thermal Decomposition of Silicon Carbide (SiC)

The graphite formed by decomposing SiC was first reported by Badami in 1965 [48]. A decade later, Van Bommel *et al.* showed that a graphene layer (single layer of graphite) can be grown on hexagonal SiC in ultrahigh vacuum (UHV) at temperatures above $\sim 800 \,^{\circ}$ C [49]. The procedure is simple: a SiC substrate is annealed at high temperature under UHV. Since the vapour pressure

of carbon is negligible compared to silicon [50], silicon atoms at high temperature sublimate and leave behind carbon atoms on the surface. Subsequently, the carbon atoms rearrange to form graphene layers.

There has been a lot of work to understand the involved mechanism producing high quality graphene [51]. It was found that the annealing time and temperature and whether the graphene is grown on the C-face or Si-face of the substrates could affect the number and quality of graphene layers [52,53]. This approach appears to be promising since the graphene is grown directly on a semiconducting substrate obviating further transfer steps. Graphene produced by this method can be used as transparent and conductive electrodes.

2.2.4 Chemical Vapour Deposition

Historically, the concept of combining carbon with other materials leading to the graphitic formation was first patented in 1896 [54]. The first CVD grown graphene was reported on TiC substrates in 1990 by Oshima's group in Japan [55]. Since the discovery of Geim and Novoselov in 2004, graphene has been grown on various transition metals with different precursors [56–61]. This method has become the most promising approach which provides a large area high quality graphene required for tremendous applications.

The CVD growth process briefly involves the thermal decomposition of a hydrocarbon source such as methane on a heated substrate. The substrates are generally first heated in Ar/H_2 atmosphere to 900-1000 °C and then exposed to H_2 /hydrocarbon source mixture. The growth can be simplified into four basic steps: adsorption and decomposition of the hydrocarbon precursor, diffusion and/or dissolution of decomposed carbon species on the surface and into the bulk metal substrate, segregation of dissolved carbon atoms onto the metal surface, and subsequent nucleation and growth [62].

The substrate serving as a catalyst has a key role in determining the graphene growth mechanism. In the case of metal substrates having low solubility of carbon such as Cu (less than 0.001 atom% at 1000 °C [63]), the graphene growth mechanism is self-limited, i.e., the growth process effectively terminates once the substrates are fully covered by a graphene layer [64]. However, the self-limiting mechanism can be broken in some circumstances such as atmospheric pressure CVD [65], a slow cooling rate process [66] and high methane concentration in a low pressure CVD [67]. For substrates with greater carbon solubility such as Ni, controlling the number of graphene layers requires more effort. Moreover, the substrate morphology and surface orientation also affects the quality of graphene [68].

Although CVD is the most successful method for large area synthesis of graphene, potential challenges still exist. One challenge is that graphene is grown on transition metals and a transfer step is thus required for device application. This process might alter the graphene quality and a method to scale-up the transferred yield and area of graphene films in a uniform and effective manner is required. Recently, an interesting method of roll-to-roll CVD in collaboration with Samsung was reported. They were able to grow and transfer a very large scale graphene (30 inch across) as transparent electrodes [69]. In that method, graphene is grown on a large flexible Cu foil in the form of a roll-type substrate fitting inside a tubular furnace to maximize the scale and homogeneity of graphene. Subsequently, the graphene coated Cu foils automatically pass the etching process and transferring step. In 2013, Sony developed a new method of roll-to-roll CVD

and succeeded to produce graphene films more than 100 m in length [70]. A schematic of the roll-to-roll CVD and transfer is illustrated in figure 2-9.



Figure 2-9: Schematic of roll-to-roll CVD and transfer, taken from [70].

Another challenge is growing large area single crystal graphene which requires deeper comprehension of the elementary growth steps, especially the segregation process that directly determines density of graphene grains [62]. Concerning this problem, Li *et al.* demonstrated CVD synthesis of graphene single crystals with dimensions of up to 0.5 mm in a Cu-foil enclosure using methane [71]. They believe that the increase in domain size is due to a lower

partial pressure of methane inside the Cu enclosure which leads to a reduced density of nucleation.

2.3 What Is Hexagonal Boron Nitride?

Boron nitride is a synthetic III-V compound discovered in early 19th century. This material exists in different crystalline structures; hexagonal, cubic and wurtzite or in amorphous form [72]. The hexagonal form is the most common and the primary focus of this thesis. Hexagonal boron nitride (hBN) is also a layered material and it is known as white graphite. Each layer is constructed out of boron and nitrogen atoms bonded covalently in a honeycomb lattice structure and the layers are joined together with an inter-layer spacing of ~ 0.33 nm by weak van der Waals interaction [73]. It is also colloquially called "graphene's sister" since it has a similar hexagonal lattice with a modest lattice mismatch of 1.7% (see figure 2-10, a). Its hexagonal structure has been identified using X-ray and electron diffraction. An example of electron diffraction pattern of hBN is shown in figure 2-10, b.



Figure 2-10: a) Schematic diagrams of crystal structures of graphite and h-BN, taken from [23]. b) TEM electron diffraction patterns of pristine hBN, taken from [74].

Contrary to graphene, hBN is an insulator with dielectric properties similar to SiO₂. Its band gap was measured to be ~ 6 eV [75]. Therefore, it often serves as an atomic flat insulating substrate or a tunneling dielectric barrier in graphene and other 2D electronics [15,76,77]. It is chemically inert in a wide variety of acids, solvents and oxidizers [78]. Due to the strong covalent sp² B-N bonds, hBN has high thermal and chemical stability, high mechanical strength and thermal conductivity [79–81]. Hence, it is an attractive material for use as a chemically inert coating in hazardous environments.

The production of hBN for possible applications requires reliable analytical characterization. As previously mentioned, boron nitride has different phases. Determination of the boron nitride phase can be accomplished through Raman spectroscopy [82]. Typical first-order Raman spectra for cubic and hexagonal boron nitride are shown in figure 2-11, a. Cubic boron nitride has one optical phonon mode which splits into a transverse (TO) and longitudinal (LO) optical phonon. On the other hand, hBN exhibits a strong characteristic peak occurring at ~ 1364 cm⁻¹ which is due to the in plane vibration (E_{2g} phonon mode) and is analogous to the G peak in graphene. Moreover, an enhancement by a factor of 2–5 was found in the Raman susceptibility of hBN under UV excitation as compared to visible excitation.

In another study, Raman properties of mono- and few-layer hBN obtained by micromechanical cleavage of high-quality hBN crystals have been investigated using visible excitation [83]. It was reported that the Raman intensity is proportional to the number of hBN layers, as expected. As shown in figure 2-11, b, bulk hBN exhibits a strong characteristic peak located at 1366 cm⁻¹. In addition to lowering their intensity, the Raman peak is usually blue-shifted in monolayers and

red-shifted in bilayers with respect to its position in bulk hBN. The blue shifting is explained to be the result of the hardening of the E_{2g} phonon mode due to a slightly shorter B-N bond expected in isolated monolayers.



Figure 2-11: a) First-order Raman spectra of cubic and hexagonal boron nitride excited with λ_{exc} = 244 nm. The inset shows the crystal structure of the two BN structures, taken from [82]. b) Raman spectra of atomically thin hBN excited with λ_{exc} = 514 nm. The left inset show changes in integrated intensity I_T with the number of layers *N*. The right picture illustrates the phonon mode (in-plane vibration) responsible for the Raman peak, taken from [83].

The visibility of the hBN monolayer on top of Si substrates with different thickness of oxide was also examined [83]. Generally, atomically-thin hBN exhibits little optical contrast due to its large band gap. For the commonly used ~ 300 nm SiO₂ thickness, BN monolayers show a white-light contrast of <1.5%, which makes them undetectable by the human eye [83]. However it can be detectable under an optical microscope with optical filters.

2.4 Review of Hexagonal Boron Nitride Synthesis

The most common techniques to synthesize hBN are mechanical exfoliation, liquid-phase exfoliation and CVD. As noted previously, CVD is the best known method to produce large area hBN with high quality.

2.4.1 Mechanical Exfoliation

The simple and effective method using adhesive tape to isolate graphene from HOPG was further extended to work for a variety of 2D materials such as hBN [1]. hBN monolayers less than a couple of microns in size have been isolated from hBN powder [1]. Larger hBN layers (more than 100 μ m) have been prepared by mechanical cleavage of synthetic highly oriented pyrolytic boron nitride (HOPBN) [15,84]. Li *et al.* reported another way of mechanical peeling of hBN nanosheets by use of fully controlled low energy ball milling [85]. Large quantities of high quality hBN nanosheets with very small amounts of point defect have been prepared.

2.4.2 Liquid-Phase Exfoliation

Liquid-phase exfoliation is a solution-processing route to produce large quantities of hBN nanosheets. hBN has been successfully exfoliated and dispersed in various solvents such as dimethylformamide (DMF) [86], 1,2-dichloroethane [87] and even water [88]. Low yield of single layers, uncontrollable layer number, and relatively small lateral size are the shortcomings of this method [40].

2.4.3 Chemical Vapor Deposition

The CVD growth of hBN dates back to 1995 when Oshima's group reported monolayer hBN epitaxially formed on Ni (111), Pd (111), and Pt (111) using a borazine precursor [23,89,90]. This technique has been widely used more recently since it is easier to achieve controllable and large scale fabrication of monolayer hBN in comparison with other methods. hBN monolayers or multilayers have been grown on various metal substrates such as Cu, Ni, Ir, Pt, Ge foils at high temperature of about 1000 °C using low pressure CVD (LPCVD) and atmospheric pressure CVD (APCVD) with several precursors (ammonia borane, borazine, diborine with ammonia) [91–96].

Here, we consider the CVD growth of hBN on Cu foil using ammonia borane $[H_3N-BH_3]$ (AB). The Cu is an inexpensive typical substrate for CVD growth of layered materials. The AB complex having a 1:1 ratio of boron and nitrogen is an inexpensive, air stable solid, and has sufficient volatility to serve as a CVD precursor for hBN thin films. Its vapour pressure has been estimated to be ~10⁻⁴ Torr at room temperature [97].

To synthesize hBN on Cu using the AB complex, two heating zones are required, one for the substrates which is typically 1000 °C and a second zone for decomposing the precursor. The thermally activated decomposition of AB takes place in the temperature range of 77–137 °C producing hydrogen gas, a solid monomeric aminoborane (BH₂NH₂) and borazine ((HBNH)₃) [98]. The borazine gas is the main product for hBN growth. The carrier gases Ar/H_2 are also used. Prior to introduction of precursor inside the growth chamber, the Cu foils are typically annealed to etch the oxide layer and increase the grain size of the starting Cu surface via a thermal surface reconstruction [99].

In 2010, Song *et al.* reported the large area synthesis of hBN films consisting of two to five atomic layers on Cu foils using APCVD [100]. They investigated the optical and mechanical properties of the hBN film. Two years later, the large area monolayer hBN was grown on Cu using LPCVD for the first time by Kim *et al.* [91]. They showed that hBN growth under low pressure is preferentially surface reaction limited, which is similar to graphene growth on Cu under low pressure [65]. It was also observed that the initial crystal of hBN is a triangle and by increasing the growth time the crystal domains extend in area and merge with each other, resulting in a complete layer covering the Cu surface. The morphology of the Cu surface affects the location and density of hBN nucleation.

In another study, a method for controlling the growth of triangular hBN domains on the Cu (100) plane was investigated using an improved LPCVD process (see figure 2-12, a) [101]. The Cu foils were placed inside an extra small quartz tube with the dead end facing upstream towards the gas source to stabilize the gas flow over the Cu substrate, reducing the growth rate of hBN. They found that the triangular hBN domains are more likely to be oriented under these conditions. The dependence of coverage rate of hBN domains on the weight of AB was also investigated.



Figure 2-12: a) Schematic of an improved LPCVD, taken from [101]. b) schematic of CVD system using a filter, taken from [102].

It was previously mentioned that the decomposition of AB produces a solid compound of aminoborane. This compound should not come into contact with the Cu during the hBN growth since it results in BN nanoparticles and harms the hBN quality [91,103]. Han *et al.* grew a clean and high quality hBN layer free of BN particles by simply employing filter paper to prevent the introduction of monomeric aminoborane onto the Cu substrate (see figure 2-12, b) [102].

In 2014, a similar concept of Cu enclosure, which resulted in large graphene single crystals, was investigated for the growth of hBN on Cu [104]. This process enhanced structural, chemical, and dielectric properties of hBN films. An \sim 11 times reduction of 3-dimensional fullerene-like h-BN surface features, a reduction of carbon and oxygen contamination of 65% and 62%, respectively,

and a greater then 2-fold increase in hBN grain size was observed. In fact, the Cu enclosure reduces the flux of BN precursors to the Cu substrate, which eventually improves the film crystallinity. Additionally, they proposed that the growth of hBN on Cu proceeds via the nucleation of nanocrystalline islands over an original monolayer in accord with the Stranski–Krastanov growth mode [105].

Recently, the role of Ar/H₂ background pressure (P_{TOT}) on the optical, chemical, and electrical properties of CVD grown hBN was investigated [106]. They found that the films grown at $P_{TOT} \leq 2.0$ Torr with well-controlled precursor flux are uniform in thickness, highly crystalline, and consist solely of hBN. At larger P_{TOT} , with constant precursor flow, the resulting hBN is more amorphous, disordered, and contains regions of sp³-hybridization.

A summary of all these studies previously mentioned, along with relevant experimental details and the characterization techniques employed, is provided in table 2-1.

Technique	Layer			DC
Experimental details	number	Characterization	Remarks	Kef.
$\begin{array}{c} APCVD\\ T_{substrate} = 1000\ ^{\circ}C\\ T_{precursor} = 120\text{-}130\ ^{\circ}C\\ Ar/H_2\\ 20\ \text{min Substrate annealing at}\\ 600\ ^{\circ}C\\ Growth\ time = 30\text{-}60\ \text{min} \end{array}$	2-5	SEM, AFM, HRTEM, SAED, EELS, XPS, Raman spectroscopy, Uv-vis spectroscopy	2D elastic modulus in the range of 200-500 N/m was measured for the hBN film.	[100]
LPCVD $T_{substrate} = 1000 \circ C$ $T_{precursor} = 60-90 \circ C$ H_2 Growth time = 10 -120 min	1	SEM, AFM, TEM, EELS, UV-vis spectroscopy	The hBN growth under LPCVD is self-limiting to one monolayer. Initial flake is triangle. The condition of the growth substrate affects the hBN nucleation sites and density.	[91]
$LPCVD$ $T_{substrate} = 1000 \circ C$ $T_{precursor} = 120 \circ C$ Ar/H_2 10 min substrate annealing Growth time = 2 h	1-4	SEM, XRD, XPS, HRTEM, SAED,AFM	An improved LPCVD for controllably fabricating triangular hBN domains was demonstrated by using a small quartz tube to reduce the gas flow. The size and coverage rate of hBN domain are well controlled by tuning the amount of AB.	[101]
LPCVD $T_{substrate} = 1050 \circ C$ $T_{precursor} = 130 \circ C$ H_2 1 h substrate annealing Growth time = 1 h Using filter paper	1	SEM, Raman spectroscopy, XPS, UV-Vis, HRTEM, AFM	Synthesis of wafer-scale high- quality single-layer hBN without BN nanoparticles by incorporating a simple filter system.	[102]
LPCVD $T_{substrate} = 1000 \circ C$ $T_{precursor} = 135 \circ C$ H_2 / N_2 2 h substrate annealing Growth time = 2.5-30 min Using Cu enclosure	1	SEM, Optical ellipsometry, AFM, HRTEM, XPS	The Cu enclosure process resulted in increase of hBN grain size. The growth of hBN on Cu proceeds similarly to the Stranski–Krastanov growth mode	[104]
LPCVD, MPCVD, APCVD $T_{substrate} = 1000 ^{\circ}C$ $T_{precursor} = 95 ^{\circ}C$ H_2 / Ar 2 h substrate annealing Growth time = 25 min	1-multi	SEM, AFM, XPS, FTIR spectroscopy, Raman spectroscopy, STM, UV-vis spectroscopy	Films grown at Ar/H_2 background pressure (P_{TOT}) ≤ 2.0 Torr are uniform in thickness, highly crystalline, and consist solely of hBN. At larger P_{TOT} , h-BN is more amorphous.	[106]

Table 2-1: All the published studies concerning the CVD growth of hBN on Cu foil using the solid precursor of ammonia borane [H₃N–BH₃].

Chapter 3

Synthesis and Characterization of Large Area High Quality Graphene

Summary: In this chapter, we talk about the experimental procedure to grow graphene on Cu foils using CVD. The growth of graphene is comparatively simple and therefore it is important as a stepping stone to the growth of hBN, which is the focus of this thesis. The transfer of graphene from Cu foils to Si/SiO_2 substrates is also presented. The Raman spectroscopy indicative of the high quality monolayer graphene is shown. The electrical properties of graphene through the field effect transistor are explained. Lastly, a summary of collaborative works using the CVD grown graphene is provided.

3.1 Chemical Vapour Deposition of Large Area High Quality Graphene

Graphene was grown on Cu foils using a methane (CH₄) precursor in a custom built low pressure CVD system illustrated in figure 3-1 [57]. The Cu foil with a thickness of 25 μ m (99.8 %, Sigma Aldrich) was selected as a substrate due to the low solubility of carbon in Cu which facilitates the high percentage coverage of single-layer graphene [63,107].

The initial step is cleaning the substrates. After cutting the Cu foils into squares of 2 cm × 2 cm, they were immersed in lukewarm 100 % acetic acid for 15 min to remove the Cu oxide following by washing with copious amount of deionized water and subsequently rinsing with isopropanol alcohol (IPA). The substrate was then placed inside the 120 cm long quartz tube with a diameter of 3.5 cm inside a miniature tube furnace. One side of the quartz tube is connected to ultra-high purity precursor (CH₄, 99.97 %) and carrier gas (H₂, 99.999 %) while the other side is attached to the vacuum pumps. The growth chamber was pumped down to ~ 1×10^{-5} Torr and the furnace temperature was set to 980 °C. 10 sccm of H₂ was introduced to the system, which increased the pressure to 1 Torr. When the furnace temperature reached 980 °C (~ 40 min), the H₂ flow rate was reduced from 10 sccm to 7 sccm and 2 sccm of CH₄ was added to the growth chamber. The total pressure of the system was again 1 Torr. After 90 min, the introduction of CH₄ was stopped and the substrates were cooled down rapidly (~ 10 min) under the flow of H₂.



Figure 3-1: Schematic of the CVD system for graphene growth. Setup for growing graphene is composed of a quartz tube sitting in a split-tube furnace connecting from one side to CH_4 and H_2 sources and the other side to the diffusion and mechanical pumps. The pressure of system was monitored using a multi gauge controller using the convectron and ionization gauges. The flow of gases (H_2 and CH_4) was controlled by mass flow controllers (Horiba).

3.2 Transferring Graphene from Cu to Si/SiO₂ Substrates

The transfer was carried out by a simple and well-known method using a poly (methyl methacrylate) (PMMA) handle. PMMA was spin coated onto the surface of graphene on Cu. The sample was next baked at 100 °C for 1 minute to stiffen the PMMA handle. Then, it was immersed in a Cu etchant of 0.1 M ammonium persulfate to etch away the Cu. After approximately 1 hour, the sample was taken out of the etchant smoothly and the side without PMMA was washed with a gently squeezed deionized water bottle. Then, the sample was again placed back into the Cu etchant. The rinse removes all the damaged graphene grown on the "back side" of the Cu since both sides of Cu are covered by graphene.

After completely dissolving the Cu, the graphene layer covered by PMMA was gently transferred to a deionized water bath using a clean glass slide to wash away the etchant residues. Then, the sample floating on deionized water was scooped by heavily doped Si covered with 300 nm of thermal oxide. It was found that using monochromatic illumination, 300 nm thick SiO₂ on Si is the most suitable substrate for graphene visual detection [28]. The sample was then kept in a desiccator to dry for 48 hours. The final step is to remove the PMMA. This step was done by immersing the sample in either warm acetone or 1-2-dichlorethane [108] for 48 hours. Finally the sample was rinsed in deionized water and IPA as well as blow drying by N₂. An optical microscope image of graphene transferred onto a Si/SiO₂ substrate is shown in figure 3-2.



Figure 3-2: An optical microscope image of graphene transferred onto a Si substrate covered with 300 nm SiO_2 layer. The entire surface seen in the image is covered by the clean graphene except in a few small areas in which the graphene has been torn.

3.3 Raman Spectroscopy

Raman spectroscopy is a fast and powerful spectroscopic technique to characterize materials, particularly graphene. Since graphene has a zero band gap, the Raman resonant processes in

graphene are always active and enhance the Raman scattering [32]. Raman resonant happens when the incident (or scattered) photon energy exactly matches the energy difference between the initial and excited electronic states of the material. Hence, the observation of intense Raman peaks in graphene is a very straightforward task.

Raman measurements (Renishaw inVia) were conducted on CVD grown graphene transferred from Cu onto a Si/SiO₂ substrate. A 514.5 nm laser excitation at a power of 8 mW was used. The measurements were carried out using 50× microscope objective with 0.75 numerical aperture. The Raman spectrum of transferred graphene is shown in figure 3-3 and the spectrum is characteristic of spot measurements recorded over the 1 cm² area of the sample.



Figure 3-3: Raman spectrum of transferred CVD grown graphene onto a Si/SiO₂ substrate. The low D peak indicates the presence of high quality graphene. The G peak intensity is more than twice lower than 2D peak intensity which specifies the monolayer graphene.

The Raman spectrum of graphene shows a G peak at ~ 1591 cm⁻¹, a 2D peak at ~ 2688 cm⁻¹ and a D peak at 1353 cm⁻¹. The shape and position of G and 2D peaks along with their intensity ratio (I_{2D}/I_G) indicate that our CVD grown graphene is monolayer [32]. To explain in details, the G peak position can be correlated to the number of graphene layers by the following equation:

$$\omega_{\rm G} = 1581.6 + 11/(1 + n^{1.6})$$
 Equation 3-1

where ω_{G} is the band position in wavenumber, and n is the number of layers present in the sample [109]. This equation indicates that as the number of layers increase the band shifts to lower wavenumber. Moreover, it was found that the G peak intensity increases in an almost linear relation with increased layers. It is worth to mention that the position and full width at half maximum (FWHM) of G peak can also be affected by the doping level of graphene on various substrates. For example, it was reported that the free-standing monolayer graphene has a G peak at 1580 cm⁻¹ with FWHM of 14 cm⁻¹ whereas the same monolayer graphene supported on SiO₂ substrate exhibits a G peak at 1587 cm⁻¹ with FWHM of 6 cm⁻¹ [110].

The sharp 2D band of our spectrum is fitted perfectly to a single Lorentzian with FWHM of 30 cm⁻¹. This is a simple and efficient way to distinguish single layer graphene since the 2D band of multilayer graphene has higher wavenumber, becomes broader (for example, FWHM ~ 50 cm⁻¹ for bilayer), asymmetric and is fitted to four or more Lorentzians [111].

A very weak D peak has been also observed which indicates that the transferred graphene has low defects. We can also estimate the crystallite size L_a of our CVD grown graphene from the intensity ratio of D peak over G peak using the following equation:

$$L_{a}(nm) = (2.4 \times 10^{-10}) \lambda_{laser}^{4} \left(\frac{I_{D}}{I_{G}}\right)^{-1}$$
 Equation 3-2

where λ_{laser} is the excitation laser wavelength in nm used in Raman experiment [112]. In our CVD graphene, $(I_D/I_G) \sim 0.06$, $\lambda_{\text{laser}} = 514.5$ nm, and $L_a \sim 280$ nm.

3.4 Electronic Properties of Graphene Field Effect Transistor

The electronic properties of CVD grown graphene has been investigated through the field effect transistor. To fabricate a graphene field effect transistor (gFET), the source and drain contacts (5 nm Cr/50 nm Au) were thermally evaporated through a shadow mask (20 μ m thick TEM grid) atop the transferred graphene into the highly doped Si substrate with 300 nm of oxide. Channel widths *W* of 305 μ m and channel lengths *L* of 50 μ m were defined. The highly doped Si substrate acts as a back-gate electrode. Prior to electrical measurement, the sample was annealed inside a variable environment probe station overnight in vacuum at 420 K. Measurements were performed with a semiconductor parameter analyzer (Agilent B1500A) in vacuum (5×10⁻⁶ Torr) at room temperature.

The output and transfer curves of a representative sample are illustrated in figure 3-4 a and b, respectively. For the transfer curve, the forward and backward gate voltage sweeps were also measured to study the hysteresis. The leakage current through 300 nm-thick SiO_2 was measured to be in the pA range.

The typical behavior of a gFET was observed in which graphene's conduction (drain-source current) is at its minimum where its Fermi level is placed. This point is frequently referred as the neutrality point or Dirac point [14]. The Fermi level for an intrinsic graphene is theoretically

placed at the conduction and valence bands intersection and it occurs at $V_{GS} = 0$ V. The charge carrier density and the type of charge carrier (electrons or holes) in the channel are governed by the potential differences between the channel and the gate electrode (doped Si). Application of a positive gate voltages promotes electron accumulation in the channel (n-type channel), and negative gate voltages results in a p-type channel. Hence, a gFET exhibits ambipolar conduction having the two branches of the transfer characteristics separated by the Dirac point.



Figure 3-4: a) Output characteristic curve of CVD grown graphene field effect transistor. b) Transfer characteristic curve of CVD grown graphene field effect transistor. The drain voltage $V_{DS} = 100$ mV. The red curve is where the gate voltage V_{GS} is swept from -50 V to +50 V. For the blue curve, the V_{GS} sweep is from +50 to -50 V. c) Calculated FET mobility versus gate voltage for the backward sweep, the maximum mobility is ~ 1500 cm²/Vs.

If the Dirac point of a graphene is in the positive (negative) range of gate voltage, the Fermi level of graphene is in the valence (conduction) band and consequently the graphene is p-type (n-type). Here, the Dirac point voltage V_{NP} for the forward sweep calculated by a parabolic fit to the current I_{DS} equals to -4 V and is shifted to -0.9 V for the backward sweep. Therefore, we can conclude that our CVD grown graphene is slightly n-type. The shifting of the Dirac point is often

observed in gFETs and it varies depending on the sweeping voltage range, sweeping rate, and ambient conditions [113]. In general, the hysteresis is presumably due to the charge transfer from neighbouring adsorbates (such as a water molecule) or charge injection into the trap sites located on the dielectric substrate. Vacuum treatment and annealing as well as introduction of a hydrophobic polymer layer between graphene and SiO₂ were found to effectively suppress the hysteresis [73], [74].

For a small V_{DS}, the current-voltage characteristics of a gFET can be expressed as:

$$I_{DS} \cong \frac{W}{L} \mu C_G (V_{GS} - V_{NP}) V_{DS} \qquad \text{Equation 3-3}$$

where C_G is the capacitance of the gate dielectric layer per unit area. μ is the charge carrier mobility. V_{NP} is the Dirac point voltage. *L* and *W* are the channel length and width, respectively. A key figure of merit for a gFET is mobility. The field effect mobility can be calculated by transconductance defined as $g_m = \frac{dI_{DS}}{dV_{GS}}$ at fixed source drain voltage V_{DS} using the following equation:

$$\mu = \frac{Lg_m}{WC_G V_{DS}}$$
 Equation 3-4

In our experiment, C_G , the capacitance of the gate dielectric layer per unit area, is calculated to be 11.5 nF/cm⁻² for 300 nm thick SiO₂. The extracted field effect mobility versus the gate voltage is illustrated in figure 3-4, c. The maximum mobility of ~ 1500 cm²/Vs at the electron density of $n = 3.5 \times 10^{11}$ cm⁻² has been obtained which is similar to previously reported field effect mobility for CVD grown graphene atop of SiO₂ [57].

3.5 A Synopsis of Collaborative Work Using CVD Grown Graphene

The large area high quality CVD graphene grown by the author has been incorporated in several projects. These projects are briefly described as follows:

Graphene has zero band gap. One way to open up a gap in graphene is hydrogenation. The chemical bonding of hydrogen adatoms on a graphene layer produces CH_x and changes the properties of the resultant layer, which is known as hydrogenated graphene. The hydrogenated graphene samples have been prepared by exposing the high quality large area CVD grown graphene to an atomic hydrogen beam [114]. The disorder induced by hydrogenation was also controlled and characterized by Raman spectroscopy. Having a clean and high quality graphene as a starting material is an important point for controlling the amount of induced disorder. The quantum Hall effect in the hydrogenated graphene having a charge carrier mobility of less than 10 cm²/Vs has been observed [114]. The electronic heat dissipation has also been investigated in millimeter scale pristine CVD grown graphene and highly disordered graphene at temperatures T = 0.3-3 K [115]. Interestingly, in another study, it was found that the topological part of the Berry phase, proportional to the pseudospin winding number, is robust in the presence of hydrogenation in large-scale graphene [116]. The observation of a giant positive magnetoresistance in millimetre scale hydrogenated graphene with magnetic field oriented inplane was also reported.

Large area graphene ion sensitive field effect transistors (ISFETs) with tantalum pentoxide sensing layers have been fabricated. It was found that the ISFETs with tantalum pentoxide attain near-Nernstian performance with pH sensitivities reaching up to 55 mV/pH over pH 3 through

pH 8 [117]. The combination of large area, high charge carrier mobility, and cost-effective processing makes graphene an ideal charge transport layer in solid state sensors. Moreover, the detection limit of graphene based ISFETs was enhanced by encapsulating the graphene with ultra-thin layers of parylene and consequently improving the gate capacitance approaching the quantum limit.

Large area suspended graphene varactors, reaching a 55% tuning range with a 10 V actuation voltage was demonstrated [118]. The modulation of microwave isolation was demonstrated experimentally by gate voltage using a gated, large area graphene device loaded in a hollow waveguide [119]. CVD grown monolayer graphene transferred onto glass substrates was also examined as an electrode material for electrochemical biosensing applications [120].

3.6 Conclusions

In this chapter, we succeeded to grow large area and continuous graphene on Cu foils using CVD. The Raman spectroscopy confirmed that the CVD grown graphene is a monolayer of high quality. Additionally, our graphene is large area with sufficient quality which resulted in significant outcomes in many applications. It has enabled the world's first investigations of quantum Hall effects in the lowest mobility material ever reported and the first Nernstian limited graphene pH sensor.

Chapter 4

Synthesis and Characterization of Monolayer Hexagonal Boron Nitride

Summary: In this chapter, the experimental procedure to grow high quality large area monolayer hexagonal boron nitride (hBN) using CVD is provided. An entirely organic-free method to suspend monolayer hBN is described. The method to transfer hBN from Cu foil to desired substrates is explained. A field emission scanning electron microscope (SEM) was used to optimize the growth conditions to yield high coverage of monolayer hBN. Complete hBN coverage over the Cu substrate was obtained for a 30 min growth time. A B/N ratio of 1.1 was measured via X-ray photoemission spectroscopy (XPS) analysis, verifying stoichiometry in accord with hBN. Selected area electron diffraction (SAED) pattern of suspended hBN gives the expected hexagonal structure with a lattice constant of $a = 2.488 \pm 0.016$ Å. The thickness
of the hBN layer was measured to be less than 0.45 nm by atomic force microscopy (AFM). The Raman peak of CVD grown hBN was observed at 1369 cm⁻¹ which is indicative of a monolayer. A strong absorption peak was observed at 5.83 eV for hBN at 300 K on a quartz substrate. The cathodoluminescence (CL) spectrum of suspended hBN over Cu shows significant emission at energies of 2.6 eV and 2.8 eV below bandgap. This result suggests that monolayer hBN used in this work is polycrystalline, and may incorporate impurity atoms.

4.1 Chemical Vapour Deposition of Large Area Monolayer hBN

The hBN layers were synthesized at low-pressure (600 mTorr) and high furnace temperature (1000 °C) using a CVD method similar to that previously reported [91]. The low pressure CVD (LPCVD) was used to obtain monolayer hBN as reviewed in Chapter 2. The schematic and photograph of the home-built CVD system is shown in figure 4-1. The growth substrate and precursor used were 25 µm thick Cu foils (99.8 %, Alfa Aesar) and ammonia borane (AB, 97 % Sigma Aldrich), respectively. After washing the Cu foils with warm 100% acetic acid (60 °C) for 15 minutes followed by rinsing with deionized water and isopropanol alcohol (IPA), they were placed in a quartz tube (20 cm long and 2.5 cm diameter) with one end closed, as shown in figure 4.1. This small quartz tube was placed in the center of another 120 cm long tube (3.5 cm diameter) with its dead-end facing the flow of precursor and carrier gases. In this way, high quality hBN layer can be obtained. The AB precursor was also placed inside a 12.5 cm long quartz tube (1.5 cm diameter) with a dead end to minimize the introduction of unwanted by-products into the growth chamber.



Figure 4-1: Schematic and photographs of the CVD system for hBN growth. Setup for growing hBN monolayer is composed of a quartz tube sitting in a split-tube furnace connecting from one side to the precursor and the other side to the diffusion and mechanical pumps. The pressure of system was monitored using a multi gauge controller using convectron and ionization gauges. The flow of carrier gases (H_2 and Ar) was controlled by mass flow controllers (Horiba).

The temperature of the furnace was set to 1000 °C while the whole system was under vacuum $(5 \times 10^{-5} \text{ Torr})$. To avoid the oxidation of Cu foils, ultra high purity (99.999 %) carrier gases of H₂ (5 sccm) and Ar (5 sccm) were introduced into the growth chamber through the course of the temperature ramp. This introduction would increase the pressure of the system to 1 Torr. After annealing the Cu foils at 1000 °C in Ar/H₂ atmosphere (1 Torr) for 15 minutes, the carrier gas flow was reduced to obtain a pressure of 350 mTorr (2 sccm H₂ and 2 sccm Ar). In the meantime, the AB was heated using a heating belt and the temperature of heating belt was monitored using thermocouple thermometer. When the temperature reached 60 °C, the precursor vapour was introduced into the growth chamber. The heating of the precursor continued at a low rate (~ 3 °C/min) until 100 °C was reached. This changed the pressure of system to be 600 mTorr. After 30

min, the precursor heating and flow into the chamber were stopped. The furnace was cooled down rapidly (15 min) to room temperature in Ar/H_2 atmosphere.

For further characterisation and device fabrication, the CVD grown hBN must be transferred from Cu foils to desired substrates, or the hBN must be suspended

4.2 Organic-free Suspension of hBN

The hBN-coated Cu foils were floated in a Cu etchant of 0.1 M $(NH_4)_2S_2O_8$ and monitored using transmission optical microscopy as illustrated in figure 4-2 over the course of a few hours to observe the formation of etch pits. The sample was then placed in a deionized water bath to stop further etching and allowed to dry in air. This entirely organic free-method was first developed by Ledwosinska *et al.* for graphene suspension [121], and is applied here to hBN for the first time. In this method, clean hBN was suspended over Cu and there was no step of the process where hBN was in physical contact with any chemical apart from the inorganic Cu etchant and deionized water.



Figure 4-2: Organic free-suspension method of hBN. The hBN-coated Cu foils were floated in a Cu etchant of $0.1 \text{ M} (\text{NH}_4)_2 \text{S}_2 \text{O}_8$ and monitored using transmission optical microscopy.

4.3 hBN Transfer from Cu to Other Substrates

The transfer is similar to the procedure previously explained for graphene transfer. Firstly, PMMA was spin coated onto the surface of h-BN-coated Cu. Next, the sample was baked at 100 °C for 1 minute to stiffen the PMMA handle. It was then immersed in a 0.1 M ammonium persulfate solution. After completely etching the Cu away, the hBN layer covered by PMMA was gently transferred to a deionized water bath to wash away the etchant residues. Then, the sample floating on deionized water must be placed on the target substrate. The selected target substrates were quartz and heavily doped Si covered with 300 nm of thermal oxide in this work. The samples were kept in a desiccator to dry for 48 hours. The final step is to remove the PMMA from the top of the hBN film. This step was done by dissolving the sample in warm acetone for 48 hours followed by rinsing in deionized water and IPA.

4.4 Characterization of CVD Grown Monolayer hBN

Various methods were employed to characterize the grown hBN. In the following, the results indicating a monolayer thickness of hBN are separately presented.

4.4.1 Scanning Electron Microscopy

A field emission SEM (JEOL JSM7600F) was used to study the morphology of the as-grown films and optimize growth conditions to yield high coverage of monolayer hBN. An accelerating voltage of 2 kV and working distance of 13 mm were used with a detector which collects both back-scattered electrons and secondary electrons. Figure 4-3 shows the SEM images of pristine hBN on Cu with different growth times. In figure 4-3, a, the growth time is 5 min and the initial

stage of formation of triangular hBN islands around nucleation sites is readily apparent. These nucleation sites (white spots) appear to be impurities that probably segregate out from the Cu. For the CVD growth of graphene on Cu, Taira *et al.* investigated the graphene nucleation sites in real space using radiation-mode optical microscopy (Rad-OM) [122]. They found that graphene grains nucleate from carbon impurities present in the Cu foil. In our case, we do not know the exact origin and composition of the nucleation sites. Figure 4-3, b shows the hBN triangles nucleated for 15 min growth time, which are typically randomly oriented. Figure 4-3, c is related to the sample with 30 min growth time. The image is characteristic of the complete hBN coverage over the Cu substrate. The observed wrinkles are related to the stress developed upon cooling from the growth temperature and the negative coefficient of thermal expansion for hBN [123].



Figure 4-3: SEM images of as grown hBN layer on Cu foil with the growth time of a) 5 min, b) 15 min, and c) 30 min.

4.4.2 X-ray Photoemission Spectroscopy

X-ray photoemission spectroscopy (XPS) was carried out on hBN coated Cu (30 min growth time) using XPS (PHI 5600-ci) with monochromatic aluminium K α X-rays for chemical bonding and stoichiometry analysis. The survey spectrum is illustrated in figure 4-4, a, which indicates the presence of B and N atoms in the layer. The B/N ratio of 1.1 was derived, verifying a stoichiometry close that of hBN.



Figure 4-4 : X-ray photoelectron spectroscopy (XPS) analysis of hBN on Cu. a) Survey spectrum. b) B1S spectrum, the experimental data points are fitted by the Gaussian function with the peak position of 190.1 eV. c) N1S spectrum, the experimental data points are fitted by the Lorentzian function with the peak position of 397.6 eV.

The existence of additional carbon and oxygen atoms stems from the exposure of the hBN film to air prior to XPS measurement and carbon impurities in the Cu foil. The observation of silicon peak could be due to the silicon impurities present in the Cu foil as well [124].

The high-resolution core level peaks of B 1s and N 1s were measured at 190.1 eV and 397.6 eV respectively (figure 4-4,b and c). These peaks are in accord with those previously reported for monolayer and bulk hBN [101,125].

4.4.3 Transmission Electron Microscopy and Selected-area Electron Diffraction

TEM and SAED were carried out on a suspended hBN over Cu using JEOL JEM-2100F at 200 kV. A bright-field TEM image and SAED spectrum of suspended hBN on Cu foil are shown respectively in figure. 4-5, a and b. The bright-field TEM image reveals a continuous, large-area, electron transparent layer. The SAED measurement gives the expected (10-10) and (11-20) diffraction peaks of hBN with a lattice constant $a = 2.488 \pm 0.016$ Å. Diffraction peaks from two crystalline orientations are seen, indicative of either a folded monolayer or the presence of two grains within the selected area (120 nm spot size) of the SAED.



Figure 4-5: a) TEM image of suspended hBN over Cu foil. b) Electron diffraction of hBN taken from a suspended region with corresponding Miller-Bravais indices (hkil).

4.4.4 Optical Microscopy and Atomic Force Microscopy

A photograph of hBN transferred to a Si/SiO₂ substrate is shown in figure 4-6, a, highlighting the centimeter scale dimensions of the large area hBN. Figures 4-6, b and c illustrate an optical image and an AFM image of the same sample, respectively.

The optical reflection image shows a uniform monolayer transferred to a Si substrate with 300 nm thick SiO2 for enhanced visible reflection contrast of 2-3% in the visible region [126]. The AFM image was acquired in air using silicon nitride cantilevers operated in Bruker's ScanAsyst which is a self-optimized PeakForce Tapping mode. The AFM image shows that the films were uniform with some PMMA residue originating from the transfer process. The thickness of the hBN layer is less than 0.45 nm, which is slightly larger than the layer spacing of bulk hBN and in good agreement with the expected thickness measured by AFM for monolayer hBN [91,102].



Figure 4-6: a) Photograph, b) Optical microscope and c) AFM images of hBN transferred onto a Si/SiO_2 substrate. The transferred hBN sheet is approximately 1 cm² in size. The step height of hBN on SiO₂ is 0.45 nm.

4.4.5 Raman Spectroscopy

Raman measurements were conducted on bulk hBN and CVD grown hBN transferred from Cu to a Si/SiO₂ substrate. Raman spectroscopy (Renishaw inVia) was performed with 514.5 nm laser excitation and a 1800 line/mm grating (with a spectral resolution of ~ 1.3 cm^{-1}) at a power of 20 mW using 50x microscope objective with 0.75 numerical aperture. Unlike graphene, which has unusually bright Raman Stokes peaks owing to strong resonant enhancement of Raman scattering [127], the wide gap of hBN suppresses the resonant enhancement of Raman scattering under visible excitation and necessitates higher pump powers.

A Raman spectrum of the transferred hBN on SiO_2/Si substrate is shown in figure 4-7 and the spectrum is characteristic of spot measurements recorded over the 1 cm² area of the sample. A single Stokes peak originating from the E_{2g} phonon mode, analogous with the G-peak in graphene, is observed in both the bulk hBN reference (BN powder from Momentive) and CVD grown hBN [128]. Compared to the Raman peak of bulk hBN located at 1365 cm⁻¹, the Raman

peak of CVD grown hBN was observed at a blue shifted 1369 cm⁻¹. The blue shift of our CVD hBN is consistent with the blue shifted Raman peak position previously reported for exfoliated monolayer hBN [126]. The Raman peaks of bulk hBN and CVD grown hBN monolayer have FWHM of 12 cm⁻¹ and 16 cm⁻¹, respectively. It was reported that the E_{2g} phonon mode of hBN powder broadened as the crystallite size decreased [129]. The small FWHM of our CVD grown hBN monolayer can be attributed to the micrometer-scale domain size [130].



Figure 4-7: Raman spectra of bulk BN and an hBN CVD monolayer transferred onto Si/SiO₂ substrate. Symbols are experimental data and lines are corresponding Lorentzian fits.

4.4.6 Optical Properties of CVD Grown Monolayer hBN

The optical properties of CVD grown monolayer hBN were examined by UV-visible absorption spectroscopy and cathodoluminescence (CL). UV-visible absorption spectroscopy was performed with a Fourier transform spectrometer (Bruker v80) in nitrogen with a deuterium lamp and GaP

photodiode. The measured absorbance of monolayer hBN at 300 K on a quartz substrate, with instrument response and quartz absorption subtracted, is illustrated in figure 4-8, a. A strong absorption peak was observed at 5.83 eV. Quasi-particle bandstructure calculations predict that monolayer hBN has a direct gap of 6.0 eV [131], in relative agreement with our measurement. Further work is required to understand the optical absorption spectrum of monolayer hBN, including the possible role of many-body effects.



Figure 4-8: The optical properties of CVD grown monolayer hBN. a) UV-visible absorption spectrum of hBN transferred to a quartz substrate, measured at room temperature. The blue line is a Lorentzian fit. b) Cathodoluminescence spectrum of suspended hBN over Cu at 5 K.

The CL spectrum of suspended hBN over Cu taken at 5 K is shown in figure 4-8, b. The spectrum shows significant emission at energies 2.6 eV and 2.8 eV below bandgap. Monocrystal hBN CL emission is primarily concentrated at the 5.8 eV band edge with a shoulder extending down to 3.8 eV [132], while luminescence peaks far below the absorption edge have been

routinely observed in hBN quantum dots [133], polycrystalline hBN [134], and hBN powders [135] and attributed to transitions involving impurity atoms or structural defects. We conclude that the monolayer hBN used in this work is polycrystalline (micrometer-scale domain size), and may incorporate impurity atoms.

4.5 Conclusions

In this chapter, we presented the CVD synthesis of high quality large area monolayer hBN. For the first time, an entirely organic-free method to suspend monolayer hBN was described. The hBN layers were characterized with a variety of techniques. A B/N ratio of 1.1 was measured via XPS analysis. SAED pattern of suspended hBN gives the expected hexagonal structure. The thickness of the hBN layer was measured by AFM. The Raman spectroscopy indicates that our hBN is a monolayer. A strong absorption peak was observed at 5.83 eV for hBN at 300 K on a quartz substrate. The CL spectrum of suspended hBN over Cu shows significant emission at energies of 2.6 eV and 2.8 eV below bandgap.

Chapter 5

In-plane Charge Transport in Monolayer CVD Grown hBN

Summary: We report in this chapter the first observation of in-plane charge transport in largearea monolayer hBN, grown by CVD. 2-point and 4-point measurements were carried out. The quadratic scaling of current with voltage at high bias corresponds to a space-charge limited conduction mechanism, with a room temperature mobility reaching up to $0.01 \text{ cm}^2/\text{Vs}$ at electric fields up to 100 kV/cm with a complete absence of dielectric breakdown. The agreement between 2-point and 4-point measurements indicates that the contact resistance is low and that the voltage drop is predominantly across the channel and not at the contacts.

5.1 Introduction

Monolayer graphene is a gapless semimetal with a linear energy-momentum dispersion shown in figure 5-1, a. In fact, the charge carriers in graphene mimic Dirac relativistic particles with zero rest mass and have an effective speed of light $c^* \approx 10^6$ m/s [26]. The massless Dirac fermion spectrum arising within the π and π^* bands in graphene has been theoretically and experimentally investigated by many researchers around the world.

In contrast, monolayer hBN is a widegap semiconductor because of the broken sub-lattice symmetry arising from the difference in boron and nitrogen *p*-orbital energies. The energy-momentum dispersion of hBN is shown in figure 5-1, b. A massive Dirac fermion spectrum is anticipated, although there is no experimental evidence for the Dirac nature of charge carriers in hBN. Instead, exfoliated few-layer hBN has found use as an insulating dielectric layer in 2D crystal heterostructures, including vertical tunneling transistors [136] and high-mobility graphene devices [5]. The low density of dangling bonds and ultra-flat surface of hBN has enabled observation of a fractional quantum Hall sequence in graphene [137] and the first experimental observation of Hofstadter's butterfly [138]. Bulk hBN is also of interest as an ultra violet light emitting semiconductor owing to its wide bandgap (5.97 eV) [132,139]. However, the problem of efficient charge carrier injection remains, with demonstrations of light emission restricted to photoluminescence and cathodoluminescence [135].



Figure 5-1: a) Energy-momentum dispersion for graphene, this is the spectrum of a zero-gap 2D semiconductor that describes massless Dirac fermions with c * 1/300 the speed of light. b) Energy-momentum dispersion for hBN, a massive Dirac fermion is anticipated.

5.2 Review of Charge Transport in hBN

Charge transport in hBN has received comparatively little attention, as hBN is generally considered to be an insulator, although the semiconducting nature of hBN is anticipated theoretically [140]. Electron tunneling through exfoliated mono-, bi-, and tri-layer hBN on gold-coated mica was investigated using conductive atomic force microscopy (CAFM) [141]. A platinum wire tip was used to avoid loss of conductivity due to wear. A schematic of the measurement set-up in CAFM along with an SEM image of platinum wire AFM tip are illustrated in figure 5-2,a. The barrier height for tunneling and dielectric breakdown strength of hBN were estimated to be $3.03 \text{ eV} (\pm 0.3)$ and 7.94 MV/cm, respectively.

In another study, Britnell *et al.* from Manchester university (Novoselov group) investigated electron tunneling through few-layer hBN along the *c*-axis with different conducting materials

(graphite, graphene, and gold) on either side of the barrier layer [142]. Several types of device, in the form of Au/BN/Au, graphene/BN/graphene, and graphite/BN/graphite sandwiches, as illustrated in figure 5-2, b were fabricated. Micromechanical cleavage was used to isolate the flakes of hBN and graphene. They found the linear I–V curves at low bias along with an exponential dependence at higher bias (> 0.5 V). Moreover, the measured tunnel current was exponentially dependent on the BN barrier thickness, as expected for quantum tunneling.

Charge transport has also been observed through ultra-short hBN nanoribbons produced by unwrapping multi-walled hBN nanotubes [143]. They showed that the few- and single-layered BN nanoribbons (BNNRs), mostly terminated with zigzag edges, can be produced by unwrapping multiwalled hBN nanotubes through plasma etching. The electrical transport of the BNNRs was studied using a scanning tunneling microscopy (STM)-TEM holder integrated in the HRTEM. As illustrated in figure 5-2, c, a BNNR was first attached onto a counter gold electrode, then the STM tungsten tip was moved to contact with the sample. The authors explained the measurement configuration as a tandem circuit including an Au/BN Schottky junction, a resistor (BNNR), and another BN/W Schottky junction. A conductance of 104 S/m and a carrier mobility of 59 cm²/Vs were measured in BNNR without application of gate bias.

An early seminal work reported non-linear hole transport and field effect in BN nanotube (BNNT) bundles [144]. An SEM image of a BNNT channel is illustrated in figure 5-2, d. Ni electrodes were used, and it was hypothesized that the metal electrode work function played an important role in charge injection at the metal-BN interface.



Figure 5-2: Review of charge transport in hBN. a) Schematic of measurement set-up in CAFM along with an SEM image of platinum wire AFM tip (taken from [141]). b) Au/BN/Au and graphene/BN/graphene sandwiches to measure the tunneling current through the hBN flake (taken from [142]). c) Schematic of the BN nanotube unwrapping processes induced by plasma etching and TEM image of a hBN nanoribbon connected to the counter gold electrode (upper black part) and tungsten STM tip (bottom black part), the inset presents the experimental configuration (taken from [143]). d) SEM image of BNNT channel between Ni electrodes (taken from [144]).

In this thesis, we have experimentally investigated the in-plane charge transport in large-area monolayer hBN grown by CVD.

5.3 Device Fabrication

The in-plane charge transport properties of CVD grown hBN transferred onto a doped Si covered by 300 nm SiO₂ substrates were measured. The transferred hBN was first characterized with a variety of techniques as described in chapter 4. Ni contact electrodes suitable for 2-point and 4point measurements were fabricated atop the transferred hBN. A positive tone photoresist (LOR 1811) was patterned onto the CVD grown hBN transferred to Si/ SiO₂ substrates by photolithography. Ni electrodes (50 nm) with 4 μ m, 8 μ m and 10 μ m separation and 100 μ m width were defined using e-beam evaporation. The lift-off process was performed by immersing the samples in warm acetone. A schematic and a representative SEM image of an hBN device are shown in figure 5-3, a. We used Ni electrodes for efficient charge injection into the valence band of hBN (figure 5-3, b). The Ni work function (5.3 eV) [145,146] is in relatively good alignment, as compared to other commonly available metals, with the hBN work function (7 eV) as determined by photoemission spectroscopy of hBN on monocrystalline Ni [147]. Prior to electrical characterization, the hBN devices were annealed for 10 minutes at 770 K in an Ar environment.



Figure 5-3: a) Schematic and SEM image of CVD grown hBN device with 8 μ m channel length and 100 μ m square Nickel electrodes. The substrate is n-doped Si covered by 300 nm SiO₂. b) Energy band diagram of Ni and hBN interface. E_F is the Fermi level of Ni. The energy difference between E_F and vacuum level is 5.3 eV [145]. In previous study, angle resolved photoelectron spectroscopy (ARPES) measurement on hBN and graphene transferred separately on the same substrates reveals that the π binding energy of hBN is about 2.5 eV lower than that of graphene [147]. From the Fermi level of graphene (4.5 eV) [148], one can estimate that the hBN valence band $E_V = 7$ eV and consequently the conduction band $E_C = 1.19$ eV.

5.4 Space Charge Limited Transport

Electrical measurements were performed in vacuum $(2 \times 10^{-6} \text{ Torr})$ in a variable environment probe station at various temperatures with a semiconductor parameter analyzer (Agilent B1500A). 2-point and 4-point measurements were carried out. Charge conduction was observed in a total of 18 hBN devices. The charge carrier mobility was also estimated. Results indicative of space charge limited (SCL) transport mechanism are presented in the following sections.

5.4.1 2-point Measurements

Upon application of a source-drain voltage, conduction in the hBN monolayer was observed. Figure 5-4, a illustrates the I_s - V_s characteristic of a representative hBN device in logarithmic scale at various temperatures. Gate leakage current I_g was also monitored throughout all measurements, and never exceeded 1% of the hBN channel current. Control experiments with Ni electrodes atop Si/SiO₂ alone gave I_s no greater than 200 fA at $V_s = 20$ V (see figure 5-5, a), allowing us to rule out leakage current in the Si/SiO₂ substrate. Charge conduction was observed in a total of 18 hBN devices. The measured conduction curves were reproducible, eliminating irreversible dielectric breakdown as the conduction mechanism.



Figure 5-4: a) 2-point I_s - V_s at various temperatures in vacuum (2×10⁻⁶ Torr) for a hBN device with channel length of 8 µm. b) I_s - V_s^2 for the same device in panel c at various temperatures. We observe the linear dependence of I_s with V_s^2 that is consistent with SCL transport.

The nature of the charge transport mechanism is revealed by the I_s - V_s characteristic. As seen in figure 5-4, a, $I_s \propto V_s$ as expected in the low bias regime ($V_s < 5$ V). The room temperature

resistivity inferred in the low-bias regime is typically ~ 100 Ω -cm, comparable to that of low impurity doped Si. However, as V_s increases, the observed transport characteristic follows $I_s \propto V_s^{\alpha}$ with 1.75 < α < 2.5. As shown in figure 5-4, b, for a representative hBN device, we found $I_s \propto V_s^2$. The quadratic scaling of current with voltage is consistent with the Mott-Gurney theory for SCL conduction, where mobile charge density is supported by the electric potential difference across source and drain. Charge traps modify the power law from that of a pure quadratic, with a non-trivial dependence upon charge trap energy distribution [149]. It is worth to mention that the channel current was also measured upon application of gate voltage and no field-effect was observed. The measured conductance at differing back-gate voltages is presented in figure 5-5, b.



Figure 5-5: a) I-V curve of a device without hBN. I_s -V_s (black curve- left axis) and I_g -V_s (Blue Curveright axis) of the device without hBN (Only SiO₂) with $L = 8 \mu m$ and $W = 100 \mu m$. b) Back gate dependence of a hBN device. $L = 8 \mu m$ and $W = 100 \mu m$.

5.4.2 4-point Measurements

To ensure that the nonlinear charge transport originates from SCL in monolayer hBN and is not due to a high contact resistance originating from inefficient carrier injection as sometimes observed in organic semiconductors [150], 4-point measurements were also performed. The device geometry consists of four square electrodes arranged linearly and equidistantly. As illustrated in figure 5-6, the agreement between 2-point and 4-point measurements indicates that the contact resistance is low and that the voltage drop is predominantly across the channel and not at the contacts. We repeated such comparative measurements for a total of four 4-point devices with similar results.



Figure 5-6: Comparison of 2-point and 4-point measurements employing four electrodes with a uniform spacing of 10 μ m. At most 6% of the measured voltage drop occurs at the contacts, with the remaining voltage drop across the hBN channel.

5.4.3 Charge Carrier Mobility Estimation

The Si substrate was used as a back-gate, and the absence of any field-effect is consistent with an SCL transport mechanism. For a 2D film with negligible trap density, the SCL current is given by [151]

$$I_s = \zeta \varepsilon_0 \varepsilon_r \mu \frac{V_s^2}{L^2} W, \qquad \text{Equation 5-1}$$

where ζ is a dimensionless parameter related to the capacitive coupling of the electrodes, $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m, ε_r is the effective dielectric constant for field lines from source and drain to the channel, and μ is the mobility of the carriers of SCL current. We have estimated the room temperature mobility of several devices in figure 5-7, using equation 1 with $\zeta = 0.70$ for the strip contact geometry [151] and $\varepsilon_r = 3$ as the average effective dielectric constant of oxide ($\varepsilon_r = 3.9$), vacuum ($\varepsilon_r = 1.0$) and the hBN layer ($\varepsilon_r = 3-4$ [152]). An uncertainty in mobility of ~ 40 % is estimated based on uncertainty in ε_r and ζ . The maximum room temperature hBN mobility organic semiconductors [153]. It is worth noting that the maximum electric field applied within the film is approximately 100 kV/cm, yet there is no indication of dielectric breakdown.



Figure 5-7: The estimated room temperature mobility of several hBN devices with 100 μ m width and different channel lengths (4 μ m, 8 μ m, 10 μ m) along with their corresponding uncertainties.

The quadratic behaviour of current versus voltage and unambiguously low contact resistance are indicative of the SCL transport. The carrier type cannot be determined definitively from our experiments, but is most likely to be hole type based on the better alignment of the Ni electrochemical potential with the hBN valence band as compared to the hBN conduction band (see figure 5-3, b).

As illustrated in figure 5-4, a, conduction at fixed bias decreases as temperature is reduced, consistent with a mobility that is more likely limited by impurity or defect scattering rather than phonon scattering. A similar temperature dependence of mobility limited by charged impurity scattering is not necessarily trivial, as predicted for the closely related 2D material graphene [154].

As explained previously, the voltage dependence of SCL current is given by $I_s \propto V_s^{\alpha}$. The value of α was extracted at different temperatures from the $I_s - V_s$ curves of figure 5-4, a. We found that α increases as device temperature T decreases as seen in figure 5-8. This behaviour is in accord with space charge conduction in solids, with an observed trend of $\alpha = (\frac{T_c}{T}) + 1$ where T_c is a characteristic temperature relating to the charge trap distribution as firstly described by A. Rose in 1954 [149].



Figure 5-8: α versus 1/T for several hBN devices. The voltage dependent of SCL current is given by $I_s \propto V_s^{\alpha}$. The value of α is extracted at different temperatures from the $I_s - V_s$ curves of figure 5-4, a.

We return to the linear conduction regime observed at low bias. The low bias conductance G = 0.21 nA/V for a representative device (figure 5-4, a) at room temperature corresponds to a sheet conductance $\sigma_{2D} = 16.8$ pA/V. Making use of the mobility $\mu = 0.01$ cm²/Vs inferred from the

space charge limited regime, the estimated carrier density is $p = \sigma_{2D}/e\mu = 10^{10}/\text{cm}^2$. This low charge density may originate from structural defects and impurity atoms that are electrically active and whose presence is clear from CL measurements (see section 4-4-6 in chapter 4).

5.5 Conclusions

In conclusion, we have observed for the first time space-charge limited conduction in large-area monolayer hBN prepared by CVD. Our work highlights the wide-gap semiconducting nature of monolayer hBN in contrast with the more typical application of hBN as a passive dielectric layer in 2D crystal heterostructures. hBN is thus far the only 2D crystal known to support space charge limited current, which is an important step toward the goal of UV light emitting diodes and laser diodes, by demonstrating that charge can be injected into and transported through hBN. Further work is required to optimize charge injection from metal electrodes to hBN and to improve the quality of CVD grown hBN monolayers. The future development of hBN devices with a stable charge density compensated by impurity dopants or field effect will enable hBN to be applied to UV optoelectronic devices and will also enable fundamental studies of the massive Dirac fermions that are predicted to carry charge in hBN.

Chapter 6

Anti-corrosion Property of Monolayer CVD Grown hBN on Copper

Summary: We have previously shown the in-plane conduction in large area CVD grown monolayer hBN. Here, this chapter is related to the out-of-plane conduction of monolayer hBN. We studied the corrosion resistance of Cu with CVD grown hBN by use of cyclic voltammetry, Tafel analysis and electrochemical impedance spectroscopy (EIS) in a 0.1 M NaOH solution. We found that CVD grown hBN reduces the Cu corrosion rate by one order of magnitude compared to bare Cu.

6.1 Introduction

Previous work has shown that hBN has high thermal and chemical stability [155,156], and monolayer hBN is impermeable to oxygen diffusion even at high temperatures in an oxidizing atmosphere and air [157,158]. In other studies, the electrochemical analyses reveal that the hBN nanosheet coating (15-20 layers) can increase open circuit potential and suppress the oxidation of the underlying Cu foil [159,160]. These results together suggest hBN may be suitable as a corrosion inhibiting coating, where high quality, continuous hBN layers without pinholes and tears are required for such an application.

6.2 Review of Monolayer Materials for Corrosion Inhibition

The suitability of an atomic monolayer for inhibiting corrosion has been established in studies of graphene, a material sharing the same layered hexagonal crystal structure as hBN. Graphene layers on Ni and Cu can serve as barriers to electrochemical corrosion in aqueous media [161]. An increase in the resistance to electrochemical degradation exceeding one order of magnitude has been observed in graphene-coated Cu [162]. In another study, the corrosion-inhibiting behavior of single-layer and multilayer graphene was quantitatively investigated [163], where it was found that Cu foils with a graphene monolayer experience a ~ 7 fold reduction in corrosion rate as compared to bare Cu. The electrically insulating nature of hBN, in contrast with the semi-metallic nature of graphene, is anticipated to favor hBN as a corrosion inhibiting layer by suppressing electron transfer even in a long term. Recently, the long-term barrier characteristics of hBN and graphene have been investigated theoretically and experimentally by exposing them to an ambient environment for 160 days [164].

In this thesis, we report quantitative measurements of monolayer hBN grown by CVD as a Cu corrosion inhibitor by use of cyclic voltammetry, Tafel analysis and electrochemical impedance spectroscopy (EIS) in a 0.1 M NaOH solution.

6.3 Sample Fabrication and Apparatus

The hBN monolayers were grown on Cu foils as previously described in chapter 4. Upon the completion of growth, a portion of the CVD grown hBN on Cu samples was directly used in electrochemical measurements and the other portions were characterized by Raman spectroscopy, AFM, optical reflection microscopy, TEM and SAED. The results of these characterization techniques were presented in chapter 4.

Electrochemical measurements were conducted with a standard three-electrode configuration in a custom built polytetrafluoroethylene (PTFE) cell filled with a 0.1 M NaOH (Sigma Aldrich) solution at room temperature. A schematic of the PTFE cell is illustrated in figure 6-1. Two types of samples were measured: bare Cu foils and Cu foils with an hBN monolayer grown directly on the surface by CVD and designated hBN-Cu. In all measurements, bare Cu or hBN-Cu foils with a 0.07 cm² area were used as the working electrode, a Pt wire was used as a counter electrode and Ag/AgCl (from BASi) was used as a reference electrode. All electrochemical measurements were carried out using a potentiostat/galvanostat (Autolab PGSTAT302N). The voltage sweep rate of 20 mV/s was used for all the measurements.



Figure 6-1: Schematic of the custom built PTFE electrochemical cell. Bare Cu or hBN-Cu samples were clasped in the PTFE cell with a 0.07 cm^2 area opening to the electrolytic solution.

6.4 Cyclic Voltammetry Measurements

Cyclic voltammetry (CV) was first used to investigate the surface electrochemistry of the Cu and hBN-Cu samples. Figure 6-2, a illustrates the CV measurements of bare Cu, hBN-Cu and hBN-Cu with a purposefully introduced scratch, in a 0.1 M NaOH electrolyte solution. Two anodic current peaks and two cathodic current peaks were observed for bare Cu due to two Cu redox reactions [165]. The anodic peaks at cell potentials of -0.3 V and -0.1 V are due to the forward reactions and the cathodic peaks at -0.4 V and -0.75 V are attributed to the reverse reactions. The two principle Cu redox reactions are,

$$2Cu + 2OH \leftrightarrow Cu_2O + H_2O + 2e$$
, (1)

$$Cu_2O + 2OH \leftrightarrow 2CuO + H_2O + 2e$$
, (2)

However, no peaks were found for hBN-Cu samples. The anodic and cathodic currents were suppressed by over three orders of magnitude in comparison with bare Cu samples. There were no measureable cathodic or anodic peaks signaling Cu oxidation after 30 consecutive CV sweeps. These results indicate that hBN is effective in protecting Cu from oxidation and isolating the Cu from the electrolytic solution. The same hBN-Cu sample was mechanically scratched to expose bare Cu and the CV measurements were repeated. As shown in figure 6-2, a, the anodic and cathodic peaks of Cu reappeared in the hBN-Cu sample with a mechanically scratched surface.



Figure 6-2: (a) CV measurements for a 0.07 cm^2 area bare Cu (red), hBN-Cu (blue) and scratched hBN Cu (black) in a 0.1 M NaOH solution. Optical microscope images of hBN-Cu before (b) and after (c) 30 consecutive CV sweeps. (d) Optical microscope image of scratched hBN-Cu after 30 CV sweeps. Scale bar is 100 µm in (b), (c) and (d).

Optical images were taken of the sample surfaces before and after CV measurements. Figures 6-2, b and c show the hBN-Cu sample before and after 30 CV sweeps, respectively. The hBN-Cu surface was unchanged after 30 consecutive CV sweeps. However, the oxidation of Cu was directly observed after 30 CV sweeps in the areas of Cu exposed by a mechanical scratch, as clearly seen in the optical image of figure 6-2, d. Notably, the striations in the Cu foil visible in figure 6-2, b-d that result from the cold roll manufacturing process of thin foils do not inhibit the formation of a continuous hBN layer over the Cu foils. The CVD hBN forms a conformal layer over the Cu surface, indicating that corrosion can be inhibited on Cu surfaces with some texturing.

6.5 Copper Corrosion Rate Estimation

We quantitatively determined the corrosion rate (CR) of our samples. The corrosion of Cu includes both oxidation and reduction reactions, and the CR is accordingly determined by the kinetics of both anodic and cathodic reactions [166]. For uniform surface corrosion, the CR is related directly to the corrosion current density, J_{corr} through the simple relation [167]:

$$CR = \frac{J_{corr}K EW}{\rho}$$
, Equation 6-1

where $K = 3272 \text{ mm/A}\cdot\text{cm}\cdot\text{year}$ is the corrosion rate constant, and *EW* and ρ are the equivalent weight and mass density of the corroding species, respectively. The current density under an electrochemical potential difference *V* can be modeled by the Butler-Volmer equation, in which the kinetics of the electron-transfer reaction are assumed to dominate [168]:

$$J = J_{corr} \left(e^{\frac{\ln 10 (V - V_{corr})}{\beta_a}} - e^{-\frac{\ln 10 (V - V_{corr})}{\beta_c}} \right), \qquad \text{Equation 6-2}$$

where V_{corr} is the potential at which the rate of anodic and cathodic processes are equal, and β_a and β_c are the anodic and cathodic Tafel constants, respectively.

A Tafel analysis of the logarithm of current density J versus potential V for both reactions was used to infer the corrosion current $J_{\text{corr.}}$, as shown in figure 6-3. The intersection of the linear fits to anodic and cathodic branches gives an estimate of $J_{corr} = (1.22 \pm 0.22) \times 10^{-8} \text{ A/cm}^2$ for hBN-Cu and $J_{corr} = (3.08 \pm 0.03) \times 10^{-7} \text{ A/cm}^2$ for bare Cu. These values are the average values over three samples \pm standard deviation. The corrosion current of hBN-Cu is approximately one order of magnitude less than that of bare Cu. Noting the mass density $\rho = 8.94 \text{ g/cm}^3$ and equivalent weight EW = 31.7 g of Cu, the extracted average CR for Cu was $(3.57 \pm 0.03) \times 10^{-3} \text{ mm/year}$, which is in accord with literature values [163,169]. A CR of $(1.41 \pm 0.25) \times 10^{-4} \text{ mm/year}$ was obtained for hBN-Cu, which is approximately one order of magnitude less than that of bare Cu.



Figure 6-3: Tafel plots of Cu (red) and hBN-Cu (blue) samples, with linear fits of cathodic and anodic curves (dashed line) giving the intersection at a potential V_{corr} and current density J_{corr} .

6.6 Electrochemical Impedance Spectroscopy

The corrosion inhibition in hBN-Cu was further validated by electrochemical impedance spectroscopy (EIS). The impedance $Z = Z_0(\cos \varphi + j \sin \varphi)$ from electrolyte to electrode versus frequency was measured by application of a 10 mV sinusoidal AC potential and a DC potential of 0.1 V versus Ag/AgCl to the working electrode, over a frequency range of 0.1 Hz to 10 kHz. A Bode plot of impedance magnitude ($|Z| = Z_0$, figure 6-4, a), a Bode plot of impedance phase φ (figure 6-4, b) and Nyquist plots of impedance (figures 6-4, c) are presented for both hBN-Cu and Cu samples under identical experimental conditions. Measured data points are indicated with symbols.



Figure 6-4: EIS analysis of bare Cu and hBN-Cu in a 0.1 M NaOH electrolyte solution. Symbols are experimental data and lines are the corresponding model fits to a Randles equivalent circuit. (a) Bode plot of impedance magnitude of Cu (red) and hBN-Cu (blue) samples. The Randles equivalent circuit shown in the inset comprises of solution resistance R_s , double-layer capacitance C_{dl} , charge-transfer resistance R_{ct} , and Warburg diffusion element W. (b) A Bode impedance phase plot of Cu (red) and hBN-Cu (blue) samples. (c) Nyquist impedance plots of Cu (red) and hBN-Cu (blue) sample. Inset, Nyquist impedance plot of Cu.

The impedance of both samples (hBN-Cu and Cu) were fit to a Randles circuit model, indicated with solid lines, consistent with previous studies of bare Cu [170] and graphene-coated Cu [163]. The Randles circuit is shown in the inset of figure 6-4, a, including an active electrolyte resistance R_s in series with the parallel combination of the double-layer capacitance C_{dl} and the impedance of a Faradaic reaction. The behavior of C_{dl} at the metal/liquid interface is typically modeled with a constant phase element (CPE) due to the inhomogeneity of the surface under investigation [168]. The impedance of a Faradaic reaction includes an active charge-transfer resistance R_{cl} and a Warburg diffusion element W. The impedance parameters extracted from the fitted curves are listed in table 6-1.

Specimen	$\mathbf{R}_{\mathrm{s}}\left(\Omega ight)$	C_{dl}^{a}		\mathbf{R}_{ct} (k Ω)	W (µS s ^{1/2})
		n	$Y_0 (\mu S s^n)$		~
hBN-Cu	657	0.92	0.16	924	1.05
Cu	833	0.88	0.75	141	10.7

Table 6-1: Impedance parameters in Randle equivalent circuit for Cu and hBN-Cu samples.

a: C_{dl} is modeled with a CPE.

As is evident in figure 6-4, the most prominent difference between hBN-Cu and Cu is the increased electrochemical impedance of hBN-Cu versus Cu. In particular, the charge-transfer resistance R_{ct} of hBN-Cu is significantly greater than that of Cu, leading to a slower cathodic reaction rate. The Warburg impedance W, which we attribute to oxygen diffusion from the bulk solution to the active Cu surface, is higher for hBN-Cu than for Cu, that is to say oxygen diffusion to the Cu surface is slower for hBN-Cu than for Cu, as expected. It is worth noting that

the higher Warburg impedance was also found in graphene-coated Cu [163]. Additionally, in another study, the tightly packed self-assemble monolayers on Cu have prevented the oxygen diffusion to the Cu surface and consequently effaced the Warburg element in the Randles circuit [170].

The double layer capacitance C_{dl} of hBN-Cu is ~ 5 times smaller than that of hBN-Cu. The CPE exponent *n* for both samples is close to 1, indicating behavior close to that of a capacitor. The reduction in capacitance for hBN-Cu can be understood as arising from the introduction of the hBN monolayer as a dielectric layer with capacitance 0.35-0.70 μ S s (over the 0.07 cm² sample area) [171] in series with the usual double layer capacitance. Additionally, the hBN-Cu and Cu samples have surfaces that may be dressed by different Stern layers, contributing to a potential further change in double layer capacitance. The Nyquist plots of both hBN-Cu and Cu samples consist of two distinct phases with the expected semicircle and linear regions as shown in figure 6-4. The semicircle corresponding to low frequencies is kinetically controlled while it is mass transfer that dominates impedance in the linear region of the high frequency range.

6.7 Conclusions

We have investigated the suitability of CVD grown monolayer hBN for Cu corrosion inhibitor by use of cyclic voltammetry, Tafel analysis and EIS. We found that CVD grown monolayer hBN reduces the Cu corrosion rate by one order of magnitude compared to bare Cu. The chargetransfer resistance R_{ct} of hBN-Cu is significantly greater than that of Cu, leading to a slower reaction rate. The presented analysis demonstrates that an hBN monolayer acts as a Cu corrosion inhibitor with better performance than graphene and other corrosion inhibiting
layers [162,172,173]. This behavior could be a result of insulating nature of hBN which suppresses the electrochemical reactions.

Chapter 7

Direct CVD Growth of hBN on Dielectric Substrates

Summary: In this chapter, the experimental procedure to grow hBN on Si/SiO₂ and quartz substrates using LPCVD and APCVD with the precursor of AB complex is presented. The presence of hBN layers was confirmed using Raman spectroscopy. Thick and rough hBN films on Si/SiO₂ substrates via LPCVD were obtained. Due to the high roughness, the grown hBN film may not be suitable for incorporation into device fabrication in nanoelectronics. Therefore, APCVD growth was investigated. We have found that the grown hBN film via APCVD is thinner and smoother with smaller crystallite size. The carrier gas flow rate also affects the CVD grown hBN film roughness and thickness. Large area hBN films with the thickness of ~ 2 nm and rms roughness of 0.6 nm (over 1 μ m²) were grown directly on Si/SiO₂ substrates via APCVD.

7.1 Introduction

hBN has gained a lot of attention as an appealing dielectric substrates to graphene electronics. Standard dielectrics substrates such as SiO_2 have been shown to degrade the performance of graphene devices due to the scattering from the charged surface states, impurities, substrate roughness and surface optical phonons [3,15,17,154]. In contrast, hBN is chemically inert and has a flat surface with the lack of dangling bonds leading to a clean interface without charge traps and impurities. Additionally, hBN has higher energy surface optical phonon modes in comparison with SiO_2 which minimize the phonon scattering from the dielectric [14].

To fabricate such devices, exfoliated hBN or CVD grown hBN was used in most published works. In fact, CVD growth of hBN on transition metals such as Cu and Ni has been considered as a crucial step towards commercial realization of large area hBN. The incorporation of CVD grown hBN from transition metals into devices requires an inevitable transfer step which may alter the quality of the hBN, and equally importantly, contaminate the hBN with organic residues that are difficult to remove. Therefore, there is a growing need to obtain hBN dielectrics that are straightforward to be integrated into devices while retaining their quality. The CVD growth of hBN directly on silicon substrate can be a promising approach.

7.2 Literature Review

Direct growth of hBN on SiO_2 substrates dates back to 1996 using helicon activated reactive evaporation (HARE) where a helicon plasma source was coupled with an electron beam

evaporator to enhance the growth [174]. hBN thin films (up to 100 nm in thickness) were deposited in a mixture of Ar and N_2 gases in the course of boron evaporation.

A simple and efficient approach for the direct synthesis of BN nanosheets (BNNSs) on Si/SiO₂ substrates with the thickness of less than 5 nm was reported by thermal CVD using B, magnesium oxide (MgO), and iron oxide (FeO) powders as precursors under ammonia (NH₃) gas flow [175]. The systematic procedure for controlling the size, shape, and wettability of BNNSs was also established.

Few- to multi-layer nanocrystalline hBN was directly grown on amorphous Si/SiO_2 and quartz substrates using LPCVD technique with a single precursor of solid ammonia–borane (AB) (NH_3-BH_3) under a constant flow of Ar/H₂ at a pressure of 1.1 Torr [176]. In another study, it was emphasized that the boron/oxygen bond facilitates the formation of large-area, continuous thin films of hBN on Si-based dielectric (SiO₂ and quartz) substrates, obviating the need for metal catalysts [177]. A summary of all prior studies concerning the growth of hBN on Si/SiO₂ is provided in table 7-1, including notes on the various characterization techniques employed.

Here we have shown that the hBN film grown on Si/SiO_2 using LPCVD is thick and rough. The thinner and smoother hBN film with smaller crystallites can be obtained via. This is the first study of hBN growth on insulating substrate using APCVD. We have also presented a comparative study on the effect of carrier gas flow rates in thickness and roughness of resultant hBN film in APCVD.

Generally, thin film grown via APCVD has poor step coverage and non-uniform thickness [178]. The mechanism of growth in APCVD is mass transport limited. However, LPCVD results in a thin film with excellent purity, uniformity and step coverage [178]. The mechanism in LPCVD is surface reaction limited and it requires vacuum system. For the case of hBN film, more works are required to understand the involved mechanism in APCVD and LPCVD.

Technique	Characterization	Remarks	Ref.
Helicon activated reactive evaporation Substrates: Glass, Si, SiO ₂ Precursor: B, N ₂	IR spectroscopy, refractive indices measurement	hBN and cBN have been grown at different operating conditions.	[174]
Thermal CVD Substrate: Si/ SiO ₂ Precursor: B, MgO, FeO, NH ₃	SEM, TEM, EELS, Raman, AFM, XPS, contact angle measurement, EDS	BN nanosheets less than 5 nm in thickness have been grown. A smooth BN coating was obtained at 900 °C.	[175]
LPCVD Substrate: Si/ SiO ₂ & quartz Precursor: AB H ₂ /Ar [1.1 Torr]	XPS, AFM, Raman, TEM, UV-vis spectroscopy	Few- to multi-layer nanocrystalline hBN was obtained. The crystallite size is ~ 25 nm.	[176]
LPCVD Substrate: Si/ SiO ₂ & quartz Precursor: AB H ₂ [5-10 Tor]	Raman, XPS, AFM, UV-vis spectroscopy	The boron/oxygen bonds facilitate the hBN growth on oxide surface.	[177]
LPCVD and APCVD Substrate: Si/ SiO ₂ & quartz Precursor: AB H ₂ /Ar	Raman, XPS, AFM, UV-vis spectroscopy, ellipsometry	The first APCVD growth of hBN. Smoother and thinner hBN films have been obtained using APCVD with increased carrier gas flow rates.	this work

Table 7-1: All the studies concerning the growth of hBN on SiO₂ surface.

7.3 Chemical Vapour Deposition Apparatus and Substrates

hBN films were grown on the surface of Si/SiO₂ and quartz using LPCVD and APCVD. Prior to the growth, the substrates were cleaved into 1 cm \times 1 cm squares. The quartz was then cleaned by sonication in acetone and IPA, 15 min each, followed by rinsing with deionised water and blow drying by N₂ gas.

7.3.1 Low Pressure Chemical Vapour Deposition

The hBN layers were synthesized at low-pressure and high furnace temperature (1000 °C) using a LPCVD method similar to that previously described for the growth of hBN on Cu foils in chapter 4. The AB complex was used as a precursor. After cleaning the substrates, they were placed inside the 120 cm long quartz tube with a diameter of 3.5 cm sitting in a split tube furnace and the system was evacuated to 5×10^{-5} Torr. The furnace was heated to 1000 °C in a mixture of Ar/H₂ atmosphere (2 sccm H₂ and 2 sccm Ar). The schematic of the custom built LPCVD system is illustrated in figure 7-1, a. The system is the same as the one for the growth of hBN on Cu (see chapter 4). The only difference is that the substrates here were not placed inside the small quartz tube. Once the furnace temperature reached 1000 °C, the heated AB precursor was introduced into the growth chamber. The hBN synthesis took place at a pressure of 600 mTorr, and the growth time was varied from 15 to 60 min followed by fast cooling. Figure 7-1, b illustrates a graph giving the evolution of temperature, gas flow rates and pressure of system.

7.3.2 Atmospheric Pressure Chemical Vapour Deposition

The growth was conducted in an APCVD system also using an AB precursor (see figure 7-2, a). The difference between the APCVD and LPCVD systems is that there is no diffusion and mechanical pumps for the APCVD system. After placing the substrates inside the growth chamber, a mixture of Ar/H_2 gas was fed into the growth chamber. The furnace was heated to 1000 °C. The growth time was fixed to 1 h. The flow rate of Ar/H_2 was varied from 5 sccm to 15 sccm. Figure 7-2, b illustrates a graph giving the evolution of temperature and gas flow rates.

7.4 Characterization

hBN layers were grown atop of Si/SiO₂ and quartz substrates using two different methods; LPCVD and APCVD. The substrates were ~ cm in size and the hBN layers fully covered the substrates, as made evident by the slightly changed green color of the Si/SiO₂ substrate. The asgrown hBN layers were characterized using Raman spectroscopy, AFM, XPS, spectroscopic ellipsometry and UV-visible absorption spectroscopy. Raman spectroscopy (Renishaw inVia) was performed with 514.5 nm laser excitation and a 1800 lines/mm grating (with a spectral resolution of ~ 1.3 cm⁻¹) at a power of 20 mW using 50x microscope objective with 0.75 numerical aperture. The AFM image was acquired in air using silicon nitride cantilevers operated in Bruker's ScanAsyst. XPS was carried out using XPS (PHI 5600-ci) with monochromatic aluminium K α X-rays. Spectroscopic ellipsometry was performed using a Sopra, GES5-E. UVvisible absorption spectroscopy was carried out using UV-Vis-NIR Lambda 750. The results are presented in the following sections separately.



Figure 7-1: a) Schematic of the LPCVD system for hBN growth on Si/SiO_2 substrate. Setup for growing hBN layers is composed of a quartz tube sitting in a split-tube furnace connecting from one side to the precursor and the other side to the diffusion and mechanical pumps. The pressure of system was monitored using a multi gauge controller using convectron and ionization gauges. The flow of carrier gases (H₂ and Ar) was controlled by mass flow controller (Horiba). b) Experimental procedure with parameters (time, temperature, pressure, and gas flow rate),



Figure 7-2: a) Schematic of the APCVD system for hBN growth on Si/SiO₂ substrate. Setup for growing hBN layers is composed of a quartz tube sitting in a split-tube furnace connecting from one side to the precursor and the other side to the central exhaust ventilation of building. The flow of carrier gases (H_2 and Ar) was controlled by mass flow controller (Horiba). b) Experimental procedure with parameters (time, temperature and gas flow rate).

7.4.1 Low Pressure Chemical Vapour Deposition

A thick and large area hBN film was grown on Si/SiO₂ substrates using LPCVD with a growth time of 1 h. Figure 7.3 a shows the AFM image and Raman spectrum of hBN films grown on Si/SiO₂. The spectrum is characteristic of spot measurements recorded over the 1 cm² area of the sample. A single Stokes peak at 1372 cm⁻¹ with FWHM of 60 cm⁻¹ was observed which is attributed to the in-plane vibration mode of B-N bond. The grown film is rough. The root mean squared roughness R_q was measured to be ~ 13.4 nm over 1 μ m² via AFM. The thickness of the film t_{hBN} was estimated to be ~ 240 nm by spectroscopic ellipsometry.

XPS was carried out on hBN coated Si/SiO₂ substrates for chemical bonding and stoichiometric analysis. The survey spectrum is illustrated in figure 7-3, b, which indicates the presence of B and N atoms in the layer. A B/N ratio of 1.03 was determined, verifying that the stoichiometry of the film is in excellent agreement with that of hBN. The existence of additional carbon and oxygen atoms stems from the exposure of hBN film to air prior to XPS measurement. The high resolution core level peaks of B 1s and N 1s were measured at 190.4 eV and 397.9 eV, respectively (figure 7-3,c and d) which are in good agreement with the reported results of the hexagonal BN phase in the literature [179].



Figure 7-3: Characterization of hBN film grown on Si/SiO₂ using LPCVD with the growth time of 1 h. a) Raman spectrum of hBN film grown on Si/SiO₂ substrate. Inset shows the AFM image of the sample. The image size is 1 μ m × 1 μ m. XPS survey (b) and magnified XPS spectra of (c) B 1s and (d) N 1s. The peak binding energies for N 1s and B 1s are 397.9 eV and 190.4 eV, respectively.

The hBN film grown on quartz using LPCVD and a 1 hr growth time was characterized by Raman spectroscopy and UV-visible absorption spectroscopy. Figure 7-4, a illustrates the absorbance spectrum along with an AFM image. The quartz background was subtracted using a

quartz blank. A sharp absorption peak at 6.1 eV has been observed, which is in excellent agreement with the literature value for hBN [180].

A rough film was obtained on quartz, as was observed on SiO_2/Si , with a roughness of ~ 8 nm over 1 μ m². We could not estimate the thickness of as grown film on quartz using ellipsometry due to inadequate index contrast between hBN and quartz. The Raman spectrum shown in figure 7-4, b affirms the presence of hBN film via the presence of the E_{2g} Stokes peak at 1374 cm⁻¹ with FWHM of 37 cm⁻¹.



Figure 7-4: Characterization of hBN film grown on quartz substrate using LPCVD with the growth time of 1 h. a) UV-visible absorption spectrum of hBN grown on a quartz substrate, measured at room temperature. Inset shows the AFM image of the sample. The image size is 1 μ m. The root mean squared roughness R_q was calculated to be ~ 8 nm over 1 μ m². b) Raman spectra of a clean quartz substrate and hBN film grown on a quartz substrate.

7.4.2 Atmospheric Pressure Chemical Vapour Deposition

The hBN film was grown by APCVD only on Si/SiO₂ substrates. We have conducted the growth with different carrier gas flow rates with fixed growth time. We have used (5 sccm of H_2 + 5 sccm of Ar), (10 sccm of H_2 + 10 sccm of Ar) and (15 sccm of H_2 + 15 sccm of Ar). Figure 7-4 illustrates the AFM images and Raman spectra of as-grown hBN films on Si/SiO₂ substrates using APCVD with the different carrier gas flow rates.



Figure 7-5: Characterization of hBN film grown on Si/SiO₂ using APCVD with the growth time of 1 h and variable carrier gas flow rates. AFM image and Raman spectrum of hBN film grown on Si/SiO₂ substrate in 5 sccm of H₂ and 5 sccm of Ar (a), 10 sccm of H₂ and 10 sccm of Ar (b), 15 sccm of H₂ and 15 sccm of Ar (c) . The image size is 1 μ m. The root mean squared roughness R_q was calculated over 1 μ m² using Nanoscope analyzer. Thickness of the film t_{hBN} was estimated using spectroscopic ellipsometry.

The thickness of each film was estimated using spectroscopic ellipsometry. A single Stokes peak located at ~ 1374 cm⁻¹ corresponding to the E_{2g} vibration mode of hBN is observed. This peak has FWHM of 63 cm⁻¹, 57 cm⁻¹ and 88 cm⁻¹ for samples in a,b and c, respectively. The smaller peak at ~ 1450 cm⁻¹ is assigned as the third order Si transverse optical (TO) phonon which is due to the underlying Si/SiO₂ substrate [181]. We have found that the hBN film is smoother and thinner as the carrier gas flow rate increases. Moreover, FWHM of peaks has been changed which is indicative of different crystallite size.

The chemical composition and stoichiometry of the grown hBN film were further verified via XPS. A B/N ratio of 1.03 was found for all three sets of samples confirming the stoichiometry of the hBN. Moreover, the high resolution core level peaks of B 1s and N 1s were measured at 190.4 eV and 397.9 eV, respectively for all the samples.

7.5 Discussion

We have observed different Raman shift for our hBN film in the range of 1370-1375 cm⁻¹. The shifting of hBN Raman peak has been observed in literature. It was found that the Raman peak frequency would shift to a higher frequency under a compressive stress [82]. It was reported that monolayer hBN exhibits a blue shifted Raman peak in comparison to its position in bulk hBN [126]. Interestingly, Nemanich *et al.* found that the high-frequency E_{2g} phonon mode in hBN shifted to higher frequency and broadened as the crystallite size decreased [129]. They established relationships between the hBN frequency shift, the broadening of the mode, and the crystallite size. Hence, we can speculate that changing from LPCVD to APCVD decreases the hBN crystallite size. In APCVD, the hBN peak is slightly shifted to higher frequency as the

carrier gas flow rate increased. This may suggest that the crystalline size of hBN shrank. Using 15 sccm carrier gases, we have estimated a crystallite size of ~ 4 nm based on the reported dependence of Raman shift and crystallite size however the AFM measurements gives the crystallite size average of ~ 18 nm.

We have observed a decrease in hBN film thickness as the carrier gas flow rate increased. Moreover, as the film grew thicker, it roughened due to surface irregularities and multiple grain boundaries.

7.6 Conclusions

In this chapter, we succeeded to grow hBN on Si/SiO₂ and quartz substrates using LPCVD and APCVD without the aid of any metal catalyst. LPCVD growth resulted in thick and rough hBN films on Si/SiO₂ substrates. We have found that the grown hBN film via APCVD is thinner, smoother and has smaller crystallite size in comparison with hBN film grown via LPCVD. Moreover, the carrier gas flow rate affects the CVD grown hBN film roughness and thickness in APCVD. Large area hBN films with the thickness of ~ 2 nm and rms roughness of 0.6 nm (over 1 μ m²) were grown directly on Si/SiO₂ substrates via APCVD.

Chapter 8

Conclusion and Future Works

Summary: In this chapter, the main findings of the research conducted in this thesis are summarized. We close the chapter, and the thesis, with a list of future work suggested by our research findings.

8.1 A Summary of the Main Findings

We succeeded in growing large area high quality graphene and hBN on Cu foils using CVD. Our CVD grown graphene was of sufficient quality to contribute to significant advances in many projects which as follows:

- Observation of quantum Hall effect in millimeter-scale hydrogenated graphene, with a mobility less than 10 cm²/Vs [114].
- Measurement of the electronic heat dissipation of hot electrons in highly disordered millimeter scale graphene at temperatures T = 0.3-3 K [115].
- Robustness of the topological part of the Berry phase against introduction of disorder by hydrogenation in large-scale graphene [116].
- Observation of a giant positive magnetoresistance in millimeter scale hydrogenated graphene with magnetic field oriented in-plane.
- Fabrication of a Ta₂O₅/graphene ISFET that performs near the Nernstian limit of response with pH sensitivities of 55 mV/pH [117].
- Detection limit enhancement of graphene based ISFETs via graphene encapsulation by ultra-thin layers of parylene at the quantum capacitance limit.
- Demonstration of large area suspended graphene varactors, reaching a 55% tuning range with a 10 V actuation voltage [118].
- Demonstration of field effect tuning of microwave frequency Faraday rotation in magnetically biased large-area graphene in a hollow circular waveguide [119].

• Examination of CVD grown monolayer graphene supported on glass substrate as an electrode material for electrochemical biosensing applications [120].

We have shown a variety of techniques including SEM, TEM, SAED, AFM, XPS, Raman, UV-Vis spectroscopy and cathodoluminescence to confirm the presence of monolayer hBN on Cu.

A seminal contribution of this thesis is the first observation of space-charge limited conduction in large-area, monolayer hBN prepared by CVD [182]. Our work highlights the wide-gap semiconducting nature of monolayer hBN in contrast with the more typical application of hBN as a passive dielectric layer in 2D crystal heterostructures. hBN is thus far the only 2D crystal known to support space charge limited current. This is an important step towards the goal of UV light emitting diodes, laser diodes and fundamental studies of massive Dirac fermions, by demonstrating that charges can be injected into and transported through hBN.

Moreover, the suitability of monolayer hBN for inhibiting corrosion has been investigated [183]. We presented the quantitative measurements of monolayer hBN as a Cu corrosion inhibitor by use of cyclic voltammetry, Tafel analysis and electrochemical impedance spectroscopy. The result of this investigation showed that CVD grown hBN monolayers can serve as corrosion-inhibiting layers. We have found that CVD grown monolayer hBN reduces the Cu corrosion rate by one order of magnitude compared to bare Cu.

We have also successfully grown hBN films on insulating substrates via LPCVD and APCVD. The main focus of the work was to produce metal-free, large-area, continuous, and uniform hBN dielectric films on Si-based substrates without any transfer-associated processes. Thick and rough hBN film on Si/SiO₂ substrates via LPCVD has been obtained. We have found that the grown hBN film via APCVD is thinner, smoother and has smaller crystallite size. Moreover, the carrier gas flow rate affects the CVD grown hBN film roughness and thickness in APCVD. The large area hBN films with the thickness of ~ 2 nm and rms roughness of 0.6 nm (over 1 μ m²) have been grown on Si/SiO₂ substrates via APCVD.

8.2 Future Works

The research conducted in this thesis leaves many questions and further investigations. The future work will consist of:

1) Optimize the charge injection into the hBN: Further work is required to optimize charge injection from metal electrodes to hBN and to improve the quality of CVD grown hBN monolayers. The future development of hBN devices with a stable charge density compensated by impurity dopants or field effect will enable hBN to be applied to UV optoelectronic devices and will also enable fundamental studies of the massive Dirac fermions that are predicted to carry charge in hBN.

2) Investigate a method to enhance the production of large area hBN without pinholes: We found that CVD grown hBN reduces the Cu corrosion rate by one order of magnitude compared to bare Cu. The practical adoption of hBN monolayers as atomically thin anti-corrosion coatings entails further development of facile synthesis techniques for large area hBN without any pinholes. Moreover, thorough investigation of pinhole and tear density over areas exceeding 1 cm² and further investigations of mechanical stability are required before hBN passivation against corrosion can be considered practical.

3) Fabricate heterostructures of 2D materials on CVD grown hBN substrates.

Exfoliated hBN has been shown to be a superior substrate to Si/SiO₂ for graphene electronic devices due to the flat surface of hBN and less charge inhomogeneity [184–186]. Similarly, it was reported that transition metal dichalcogenide (TMD) 2D materials such as MoS₂ transferred onto hBN exhibits excellent device quality [187]. It was also found that the optical properties of MoS₂ are improved when they are stacked onto the hBN layers [188]. Most work to date has used exfoliated 2D materials or/and the CVD grown ones on transition metals. To fabricate the stack, a direct transfer is required which can trap impurities or residues at the interface between the individual layers during the transfer [189]. Moreover, for the case of CVD grown layers, a transfer step is also needed which is tedious and effectively non-scalable to form the heterostructure. In contrast, the direct growth of 2D materials on top of each other appears to be an alternative way to form clean heterostructures. In this thesis, we succeeded in growing hBN directly on Si/SiO₂ substrates. The next step is the growth of another 2D material on top of the hBN. Our work emphasizes the ability of growing hBN without the use of any transition metal. It can be more interesting to grow hBN on graphene/graphite as well. This direct and versatile fabrication approach of another 2D material/hBN heterostructures may have potential in electronic and optoelectronic applications.

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