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The growth of single and multilayer BN films on several substrates was investigated. A typical atomic layer deposition (ALD) process was demonstrated on $\mathrm{Si}(111)$ substrate with a growth rate of $1.1 \AA$ Å/cycle which showed good agreement with the literature value and a near stoichiometric $\mathrm{B} / \mathrm{N}$ ratio. Boron nitride films were also deposited by ALD on Cu poly crystal and $\mathrm{Cu}(111)$ single crystal substrates for the first time, and a growth rate of $\sim 1 \mathrm{ML} / \mathrm{ALD}$ cycle was obtained with a $B / N$ ratio of $\sim 2$. The realization of a $h-B N / C u$ heterojunction was the first step towards a graphene/h-BN/Cu structure which has potential application in gateable interconnects.

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#### Abstract

Mi Zhou


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## CHAPTER 1

## INTRODUCTION

This thesis is a compilation of the work done in the Surface Science Laboratory at the University of North Texas under the guidance of Dr. Jeffry Kelber. This thesis focuses on the growth of the boron nitride films by atomic layer deposition. Chapter 1 gives the motivation for this research and shows some scientific background information; Chapter 2 illustrates the experimental methods and the characterization techniques; Chapter 3 describes the experimental results in details and gives related discussion; Chapter 4 summarizes the results of this study and discusses the possible directions of the future work.

### 1.1 Graphene Properties and Fabrication Methods

According to Moore's law, the number of transistors on a single chip roughly doubles every two years, and the scale becomes smaller and smaller. As the dimensions of electronic devices continue to shrink, alternative semiconductor materials besides traditional Silicon are in strong demand for semiconductor fabrication. Graphene, a planar sheet of $\mathrm{sp}^{2}$ bonded carbon atoms with a hexagonal lattice structure, known as the thinnest and strongest material ever measured [2], has recently received intensive attention in both research area and semiconductor industry. As a single layer of graphite, graphene has exciting electronic properties such as high carrier mobility (10 times or even larger than Si depending on the underlying substrate) [1], which qualify graphene as a promising material in large-scale applications for high speed semiconductor devices. To fulfill this potential, a growth method for growing large-area-domain graphene on dielectric substrates needs to be achieved. Using a
dielectric with a similar lattice structure to help order carbon atoms during a chemical or physical vapor deposition process is a promising route to growth of high quality graphene layers on a variety of substrates [4, 5].

Conventionally, There are two methods to approach large domain graphene growth: 1). mechanically transfer graphene from a highly ordered pyrolytic graphite (HOPG) surface or a CVD grown graphene layers on metal to a pre-patterned dielectric surface (like $\mathrm{SiO}_{2} / \mathrm{Si}$ ) [6]; 2). Start from a $\operatorname{SiC}(0001)$ surface and evaporate the $\operatorname{Si}$ atoms out of the $\operatorname{SiC}(0001)$ surface at a temperature higher than 1500K, thus leaving either a monolayer or multi-layers of graphene on $\mathrm{SiC}(0001)$ surface [7]. Graphene layers transferred onto the $\mathrm{SiO}_{2}$ surface using the first method usually suffer from topographic corrugation and nanoscale charge pooling [8]. The mechanical transferring method also requires delicate operation and is time-consuming, therefore not suitable for industry application. The second method calls for high temperature treatment which is not compatible with many materials, and is also limited to SiC substrates. Growth of epitaxial graphene on $\mathrm{h}-\mathrm{BN}(0001)$ monolayers grown on $\mathrm{Ru}(0001)$ has been reported by Bjelkevig et al. [4]. The growth of graphene nanoflakes on $\mathrm{BN}(0001)$ nanocrystals has also been reported by Ding et al. [5]. This work explores the controlled growth of BN on other substrates to serve as a template for graphene growth.

### 1.2 Hexagonal Boron Nitride as a Template for Graphene Growth

The structures of hexagonal boron nitride and graphite are compared in Fig. 1.1 [9]. Hexagonal boron nitride has a graphene-like in-plane hexagonal lattice structure with both a similar in-plane lattice constant ( $2.50 \AA$ A for h-BN vs. $2.46 \AA$ for graphene) and a similar interlayer
distance to graphene ( $3.33 \AA$ vs. $3.35 \AA$ A , respectively) [9]. Hexagonal boron nitride is a III-V compound with a $\mathrm{B} / \mathrm{N}$ ratio of $1: 1$, therefore it is also iso-electronic to graphite.


Fig. 1.1 Similar structures of hexagonal boron nitride and graphite.

However, unlike graphene with a zero bandgap, hexagonal boron nitride is a wide band-gap insulator with a bandgap of 5.97 eV [10]. The iso-structural and iso-electronic properties with graphene make hexagonal boron nitride a promising epitaxial template for graphene growth; and the totally different electronic properties enables hexagonal boron nitride as a possible modifier by serving as a template for graphene growth on conducting (e.g., metal, Si ) substrates and permitting the formation of graphene-insulator-metal (semiconductor) structures for various device applications. C. R. Dean et al. also reported a 10 times enhanced carrier mobility of graphene transferred onto a hexagonal boron nitride surface comparing to a $\mathrm{SiO}_{2}$ surface [11].

The CVD growth of boron nitride by thermal decomposition of borazine typically renders a surface inert after completion of the first BN monolayer [12, 13]. To obtain controlled film thickness, atomic layer deposition (ALD) growth of hexagonal boron nitride thin films was adopted in this study on various (111)-oriented substrates. Since boron nitride is a wide-
bandgap dielectric material with a dielectric constant of 4.1, the integration of graphene and hexagonal boron nitride on copper also provides potential interconnect application in the back end of line (BEOL), such as gateable interconnects device as illustrated in Fig. 1.2.


Fig. 1.2 A graphene/BN/Cu stacking structure for application of gateable interconnects.

## CHAPTER 2

## EXPERIMENTAL METHODS

### 2.1. Equipment Description: The UHV System

In this study, both the thin film growth and characterization were carried out under an ultra-high vacuum (UHV) condition. The Omicron UHV system used for this study was shown in Fig. 2.1. The system consists of three major chambers: the UHV/scanning tunneling microscopy (STM) chamber, the introduction/transfer chamber, and the deposition chamber.


Fig. 2.1 The UHV system for thin films study with in-situ capability of AES, LEED and STM.

The UHV/STM chamber is pumped by a combination ion/titanium sublimator pump and yields typical working pressures of $\sim 5 \times 10^{-10}$ Torr. The UHV chamber can also be pumped by a turbo molecular pump for roughing under high gas loads, such as Ar ion sputtering. The intro/transfer chamber and the deposition chamber were pumped down by turbo pumps to a
base pressure of $1 \times 10^{-8}$ Torr and $1 \times 10^{-6}$ Torr, respectively. After a cleaning process with repeated cycles of Ar ion sputtering and annealing the substrate sample to 1000 K in the UHV chamber, the atomic layer deposition (ALD) growth of boron nitride films was carried out on the sample in the deposition chamber by alternatively introducing $\mathrm{BCl}_{3}$ and $\mathrm{NH}_{3}$ doses to the heated sample surface [14]. Then the thin films sample was transferred through the intro/transfer chamber under vacuum condition to the UHV/STM chamber where it was characterized by in-situ Auger electron spectroscopy (AES) by PHI and low energy electron diffraction (LEED) by Omicron. However, due to the insulating characteristic, the boron nitride films couldn't provide a detectable tunneling current and thus it was difficult to be characterized by STM/scanning tunneling spectroscopy (STS).

### 2.2 Film Deposition Techniques

### 2.2.1 Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) is among the most commonly used film deposition techniques. In a typical CVD process, the substrate is dosed with one or more gas-phase precursors at a certain temperature. Thermal reactions or decomposition take place on the substrate surface and produce a uniform product film on top of it. Usually the by-products (if any) are also gaseous which can be easily removed by purging or pumping down. Compared to physical vapor deposition (PVD), it has advantages such as low operating temperature, high purity, conformality.

### 2.2.2 Atomic Layer Deposition (ALD)

Atomic layer deposition (ALD) is a particular type of CVD process where the different precursors are dosed to the heated sample surface alternatively in one ALD cycle. As a result of the separation of different doses, it allows for a layer by layer self-limiting growth mode of ultra-thin films including boron nitride, thus enabling an accurate thickness control and a not-so-sensitive-to-pressure processing window for thin film growth.


Fig. 2.2 An illustration for four steps of a typical ALD cycle.

A typical cycle consists of four sequential pulses as illustrated in Fig. 2.2: a). Precursor A pulse; b). Purge pulse; c). Precursor B pulse; d). Purge pulse. During the precursor A pulse, the precursor A is absorbed onto the sample surface which is pre-heated to a certain temperature, and a certain amount of dose is needed to guarantee a saturated chemical absorption of
precursor A. During the following purge pulse, the excessive precursor $A$ is either pumped down (in our case) or purged with inert gases like $N_{2}$ or $A r$, leaving a saturated $A$ absorbate layer on the surface which will react with the precursor $B$ in the succeeding precursor $B$ pulse. Then the excess precursor $B$ and the gaseous by-product are removed by another purge pulse, producing a single layer of desired product film in an ideal case. In this way, the thickness of the thin films can be effectively monitored by conveniently varying the number of ALD cycles; A conformal deposition can be achieved due to the layer by layer growth mode; ALD process is also not very sensitive to the pressure change as a result of its self-limiting growth feature. These features promise ALD of broad applications in the constantly shrinking electronic devices.
$\mathrm{BCl}_{3}$ and $\mathrm{NH}_{3}$ were used here as precursor " A " and " B " [14], and each ALD cycle is also called one $A B$ cycle. The overall chemical reaction involved in the ALD growth of boron nitride films is based on the CVD reaction: $\mathrm{BCl}_{3}+\mathrm{NH}_{3} \rightarrow \mathrm{BN}+3 \mathrm{HCl}$. This process has been previously reported in the literature [14] and used to grow polycrystalline, stoichiometric BN films on various substrates. The two half chemical reactions are shown in equation 2.1 and 2.2, respectively, where * indicates a surface species.

$$
\begin{align*}
& \mathrm{BNH}_{2}{ }^{*}+\mathrm{BCl}_{3} \rightarrow \mathrm{BNBCl}_{2}{ }^{*}+\mathrm{HCl}  \tag{2.1}\\
& \mathrm{BCl}^{*}+\mathrm{NH}_{3} \rightarrow \mathrm{BNH}_{2}^{*}+\mathrm{HCl} \tag{2.2}
\end{align*}
$$

Both the $\mathrm{BCl}_{3}$ and $\mathrm{NH}_{3}$ doses were conducted at a pressure 1.5 Torr with a dosing time of 12 mins , which gave a total dose of $6 \times 10^{6} \mathrm{~L}$ for each half cycle. For different substrates, the dosing temperatures were usually different. The thickness of grown BN films can be roughly calculated from the attenuation of the substrate Auger signals by the deposited BN films.

### 2.3 Characterization Techniques

### 2.3.1. Auger Electron Spectroscopy (AES)

Auger electron spectroscopy (AES) is a widely used analytical technology for surface study based on Auger emission effect. The emission process of an Auger electron, which involves three electrons within one atom, was shown in Fig. 2.3.

(a)

(b)

Fig. 2.3 The illustration of an Auger emission: a three-electron process in an atom. (a). the formation of a vacancy in the core level from the electron collision; (b). the emission of an Auger electron after adsorbing a photon produced by an electron migration to the core level.

The electron collision process introduced by electron beam bombardment normal to the sample surface is indicated by Fig. 2.3 (a). When one of the core level ( $K$ shell) electrons is subjected to collision with an incident electron (typically with an energy of $1 \mathrm{keV} \sim 10 \mathrm{keV}$ ), a vacancy will form in the K shell due to the core electron ejection and the atom state will become unstable as a result of the core vacancy. Therefore an electron from a higher energy level (e.g. $L_{1}$ shell) will migrate and fill the core vacancy and release a certain amount of energy
in the form of a photon. The generated photon has an energy equal to the difference between the binding energies for $K$ shell and $L_{1}$ shell ( $h v=E_{K}-E_{L 1}$ ). If the photon energy is higher than the binding energy of a even higher level (e.g. $L_{2,3}$ shell), an electron from $L_{2,3}$ shell can absorb this energy and escape from $L_{2,3}$ shell with a detectable kinetic energy (KE), as shown in Fig. 2.3 (b). The emitted electron from $L_{2,3}$ shell is called an Auger electron and such an example of Auger emission illustrated in Fig. 2.3 is denoted as $K L_{1} L_{2,3}$. The kinetic energy of the Auger electron is expressed as equation 2.3.

$$
\begin{equation*}
K E=E_{K}-E_{L 1}-E_{L 2,3}-U(1,2) \tag{2.3}
\end{equation*}
$$

where $U$ is the screened coulombic repulsion between the two final state holes. Often $U \sim 0$, but not always, especially for nanoclusters. Since the orbital energies are unique for a specific atom, the kinetic energy measured from the Auger electrons will yield information about the chemical composition of the sample surface. As a result of the low kinetic energy of the emitted Auger electrons, AES is very surface sensitive and can only be used to analyze a sample surface to a depth of a few nanometers, which is the range where the Auger electrons still have enough energy to escape after suffering the inelastic scattering from the solid surface. The secondary electrons generated in the Auger emission process will give a continuously increasing background signal and make the Auger features too small to be handily analyzed. For the convenience of data analysis, the Auger spectrum is usually plotted as a derivative form, $\mathrm{dN} / \mathrm{dE}$, instead of directly plotted as $\mathrm{N}($ electron counts)/E(electron kinetic energy).

The thickness of an overlayer A on a substrate B can be calculated from the attenuation of peak-to-peak intensity for the substrate $B$ by the overlayer $A$. The formulas were given by equation 2.4 and 2.5 [15],

$$
\begin{align*}
& I_{B}=I_{B}^{\infty} e^{-d_{A} / \lambda_{A}\left(E_{B}\right) \cos \theta}  \tag{2.4}\\
& I_{A}=I_{A}^{\infty}\left[1-e^{-d_{A} / \lambda_{A}\left(E_{A}\right) \cos \theta}\right] \tag{2.5}
\end{align*}
$$

where $I_{B}$ and $I_{B}^{\infty}$ are the intensity and atomic sensitivity factors for the substrate B, respectively, $d_{A}$ is the thin film thickness, $\lambda_{A}\left(E_{B}\right)$ is the inelastic mean free path (IMFP) for a photoelectron from substrate $B$ passing through overlayer $A$, and $\cos \theta$ is the angle between the surface normal and the axis of the analyzer; $I_{A}$ and $I_{A}^{\infty}$ are the intensity and atomic sensitivity factors for the overlayer $A$, respectively, $\lambda_{A}\left(E_{A}\right)$ is the IMFP for a photoelectron from the overlayer A. The IMFPs were calculated from the TPP-2M equations [15, 16]. Equations 2.4 and 2.5 were then plotted vs. thickness with the point at which the two line cross equal to the thickness of the overlayer A.

### 2.3.2. Low Energy Electron Diffraction (LEED)

Low energy electron diffraction (LEED) is a useful tool for study the surface structure of a material based on the wave-particle duality nature of the electrons. In a LEED experiment, a collimated electron beam with a low energy ( $20^{\sim} 200 \mathrm{eV}$ ) is normally directed to the sample surface. According to the wave-particle duality, the incident electrons can be considered as waves propagating normally towards the sample. The wavelength of the electron waves, $\lambda$, is determined by equation 2.6, where $h$ is the Planck constant, p is the momentum of the electrons and V is the accelerating voltage of the electron gun. For an electron with a kinetic energy of 150 eV , the wavelength is $\sim 1 \AA$, which corresponds to the inter-atomic distances in a solid.

$$
\begin{equation*}
\lambda=\frac{h}{p} \approx \sqrt{\frac{150}{V}} \AA \tag{2.6}
\end{equation*}
$$

The incident electrons are strongly back-scattered by the electrons in the surface atoms, which can also be viewed as waves being reflected backwards, from another angle. The surface atoms interacting with the incident electrons are simplified to a one dimensional model and the electron diffraction process is shown in Fig. 2.4.


Fig. 2.4 The electron diffraction on the surface atoms.

As the electron beam is backscattered at an angle $\theta$ by the surface atoms, as shown in Fig. 2.4, a path difference $d$ is generated between the backscattered electrons from two adjacent surface atoms and causes the interference which can be described by Bragg's Law in equation 2.7.

$$
\begin{equation*}
d=a \sin \theta=n \lambda \quad \text { where } n=1,2,3 \ldots \tag{2.7}
\end{equation*}
$$

As shown in Fig. 2.5, a typical LEED system includes two major parts: 1). the electron gun which generates the electron beam incident normally onto the sample surface; 2). the hemispherical fluorescent screen which accepts the backscattered electrons and displays the LEED pattern caused by the constructive interference.

The information which can be abstracted from a LEED pattern includes: 1). qualitatively, the LEED spot positions provide the information on the size, symmetry, long-range order and rotational alignment of adsorbate with respect to the substrate; 2 ). quantitatively, the plot of LEED spot intensities vs. electron beam energy (so called I-V curves) provide information on atomic positions.


Fig. 2.5 Schematic diagram of a typical LEED experiment.

## CHAPTER 3

## EXPERIMENTAL RESULTS AND DISCUSSIONS

In this paper, I present experimental results for BN formation by atomic layer deposition (ALD) on $\mathrm{Si}(111)$, and $\mathrm{Cu}(111)$.

### 3.1. Boron Nitride Growth on $\mathrm{Si}(111)$ Substrate

3.1.1. Demonstration of ALD Boron Nitride Growth on $\mathrm{Si}(111)$


Fig. 3.1 AES Spectra of clean $\mathrm{Si}(111)$ and after sequential dosing of $\mathrm{BCl}_{3}$ and $\mathrm{NH}_{3}$ at 550 K .

As a traditional semiconductor material, Si has been under a lot of studies over the years and is a well understood system, which makes Si a good starting point for trying out the ALD growth of boron nitride films. The Auger electron spectra (AES) of alternative dosing with $\mathrm{BCl}_{3}$ and $\mathrm{NH}_{3}[14]$ in a typical ALD process were shown in Fig. 3.1. Before the ALD process, the Si(111) substrate was cleaned by alternating Ar ion sputtering and annealing until the carbon and oxygen level were not reducible by further ion bombardment. Estimated $O$ and $C$ coverages
at this point (eq.2.4 and eq.2.5) are 0.04 and 0.15 monolayer, respectively. Then $\mathrm{BCl}_{3}$ was introduced in the deposition chamber at 550 K with a dosing amount of $5.4 \times 10^{8} \mathrm{~L}(100 \mathrm{mTorr}$, 1h) and followed by pumping down the excess $\mathrm{BCl}_{3}$. After the $\mathrm{BCl}_{3}$ dose, the Auger spectrum indicated there was a B peak at 170 eV and a Cl peak at 182 eV and the Si peak was attenuated, which indicated the adsorption of $\mathrm{BCl}_{3}$ onto the $\mathrm{Si}(111)$ surface. Following the $\mathrm{BCl}_{3}$ dose, a $\mathrm{NH}_{3}$ dose of $5.4 \times 10^{8} \mathrm{~L}$ was carried out also at 550 K followed by pumping down the excess of $\mathrm{NH}_{3}$ and the gaseous byproduct. After the $\mathrm{NH}_{3}$ dose, the Auger spectrum indicated a significant decrease of the Cl peak and an appearance of the N peak@388eV as well as a further attenuation of the Si signal, which demonstrated the self-limiting growth of ALD process.

### 3.1.2. Multiple Cycles of Boron Nitride on $\mathrm{Si}(111)$



Fig. 3.2 (a). The thickness of; and (b). the $B / N$ ratio of 5,10 , and 15 AB cycles of BN on $\mathrm{Si}(111)$ by ALD.

To obtain the growth rate and $B / N$ atomic ratio of the ALD grown BN films, thicker films were put down on $\mathrm{Si}(111)$ substrate. As shown in Fig. 3.2(a), the thicknesses of the boron nitride films after 5,10 , and 15 AB cycles of ALD deposition were $6 \AA, 10.4 \AA$, and $23 \AA$, respectively. The linear fit gave an average growth rate of $1.1 \AA$ /AB cycle( $0.5 \mathrm{ML} / \mathrm{AB}$ cycle)
which had good agreement with the literature value of $0.96 \AA$ / $A B$ cycle [14]. As shown in Fig. 3.2(b), the $B / N$ ratio values for the $5,10,15 A B$ cycles of the deposited boron nitride films were $0.9,1.3$, and 1.5 , respectively, which indicated the $\mathrm{B} / \mathrm{N}$ ratio of boron nitride films on $\mathrm{Si}(111)$ was generally around 1.0 but became more boron rich with increasing the thickness of the films. However, there was a lack of long range order for the ALD BN films on $\operatorname{Si}(111)$ due to the relatively large in-plane lattice mismatch between $\operatorname{Si}(111)$ and $\mathrm{h}-\mathrm{BN}(3.84 \AA$ for $\mathrm{Si}(111)$ [17] and $2.50 \AA$ for $\mathrm{h}-\mathrm{BN}$ [18], respectively) and also there will be $\mathrm{Si}(111)-7 \times 7$ surface reconstruction when heating up the sample during ALD process.

### 3.2. Boron Nitride Growth on Cu

To obtain a h-BN/Cu heterojunction by ALD process was the first step to achieve the graphene/h-BN/Cu structure which provides potential applications in switchable gated devices on interconnects. The ALD growth of boron nitride films was carried out both on polycrystalline Cu I substrate ( $\mathrm{Cu}($ poly $)$ ) and $\mathrm{Cu}(111)$ single crystal substrate.

### 3.2.1. Boron Nitride Growth on Cu(poly)

The ALD growth of boron nitride films was first investigated on $\mathrm{Cu}($ poly $)$ for the potential application of gated Cu interconnects with a graphene/BN/Cu(poly) stacking structure. The Cu(poly) substrate used in this study was provided by Intel Corp. and the structure is 150 nm poly Cu by physical vapor deposition (PVD) on $\mathrm{Ta} / \mathrm{TaN} / \mathrm{Si}(100)$ wafer. A clean Cu poly surface was achieved by repeated cycles of Ar ion sputtering and annealing at a relatively low temperature, 800 K , since it was getting close to the failure temperature of the $\mathrm{Ta} / \mathrm{TaN}$ diffusion
barrier. Then $3 A B$ cycles of boron nitride films were deposited by ALD process at $750 \mathrm{~K}\left(6 \times 10^{6}\right.$ L/dose, with a dosing pressure of 1.5 Torr) onto the clean Cu poly crystal substrate and its chemical composition was investigated by Auger electron spectroscopy.


Fig. 3.3 AES spectra of BN films on Cu poly crystal substrate by ALD.

As shown in Fig. 3.3, after deposition, the Cu peaks were largely attenuated by the grown boron nitride film. An oxygen peak was also observed in the Auger spectrum, indicating partial oxidation of the BN film. The calculated thickness from the attenuation of the Cu peak at 58 eV by BN was 6.07 ML for the boron nitride films after 3AB cycles of ALD deposition, and a slightly boron rich $\mathrm{B} / \mathrm{N}$ ratio of 1.7. The Auger data demonstrated the capability of growing near stoichiometric boron nitride films on Cu poly crystal with some oxidation from the ambient.

### 3.2.2. Boron Nitride Growth on $\mathrm{Cu}(111)$

Cu interconnect structures tend to have (111) texture [19].-i.e., large grains with (111) orientation. Also, due to the relatively small in-plane lattice mismatch between $\mathrm{Cu}(111)$ and h $\mathrm{BN}, \mathrm{Cu}(111)$ is theoretically a good template for epitaxially growing hexagonal boron nitride films, thus a good supporting substrate for realizing the graphene/h-BN heterojunction. The
study of $\mathrm{h}-\mathrm{BN}$ growth on $\mathrm{Cu}(111)$ is a relatively easy way to approach the heterojunction structure and it's also of import to look at the growth mode of BN on a highly ordered Cu surface.

The dosing temperature was proved to be an important parameter for gaining a good BN growth rate during the ALD process and it usually differs on different substrates. To optimize the thermal condition, several boron nitride depositions by ALD were carried out on $\mathrm{Cu}(111)$ at different temperatures. According to the thickness data from AES, no BN was picked up after ALD at 550K, which indicated 550 K was too low a temperature to initiate the ALD process; the situation was improved by increasing the dosing temperature to 650 K but still a relatively low growth rate of $\sim 0.3 \mathrm{ML} /$ cycle; and dosing at 750 K yielded a growth rate of >2ML/cycle, which revealed a chemical vapor deposition (CVD) growth mode rather than an ALD one; however, by lowering the dosing temperature to 700-725K, a growth rate of $\sim 1 \mathrm{ML} /$ cycle was achieved for the boron nitride deposition on $\mathrm{Cu}(111)$.

### 3.2.2.1. Mono-layer of BN on $\mathrm{Cu}(111)$

To understand the growth mode of boron nitride films on a highly ordered $\mathrm{Cu}(111)$ surface, two sequential $A B$ cycles of $B N$ were put down on cleaned $C u(111)$ by $A L D$ at 725 K . The first $A B$ cycle was divided into " $A$ " dose $\left(\mathrm{BCl}_{3}\right)$ and " $B$ " dose $\left(\mathrm{NH}_{3}\right)$, and after each dose the sample was transferred from the deposition chamber back into the UHV chamber to be characterized by low energy electron diffraction (LEED) and AES. The second AB cycle was a continuous process which had no transferring back and forth between chambers.

The Auger electron spectra illustrated in Fig. 3.4 showed the BN growth process on $\mathrm{Cu}(111)$ and the LEED images in Fig. 3.5 provided some clues for the changes on the sample surface structure.


Fig. 3.4 AES spectra of BN films by ALD on Cu(111).


Fig. 3.5 LEED image of (a). clean Cu(111); (b). 0.5ML BN on Cu(111); (c). 1.4ML BN on Cu(111); (d). 1.3ML BN on $\mathrm{Cu}(111)$ after 30 min anneal@1000K.

The clean $\mathrm{Cu}(111)$ gave a sharp low energy Auger electron peak at $58 \mathrm{eV}(\mathrm{Cu}$ MNN) and 3 high energy peaks ranging from 780 eV to $950 \mathrm{eV}(\mathrm{Cu}$ LMM). The sharp (1x1) LEED pattern in Fig. 3.5(a) confirmed a clean and highly ordered $\mathrm{Cu}(111)$ surface with significant sulfur contamination ( 0.5 ML ) due to segregation of $S$ from the bulk.

After the first $A B$ cycle, 0.5 monolayer of $B N$ was picked up with a $B / N$ atomic ratio of 2.9 according to the AES calculation. The significant Cl peak was consistently observed after the ALD process and even from exposure to the ambient in the deposition chamber in the absence of $\mathrm{BCl}_{3}$ or $\mathrm{NH}_{3}$. This indicated that Cl adsorption on the $\mathrm{Cu}(111)$ surface was a constant problem, only partially ameliorated by purging with Ar. P. J. Goddard et al. has shown that Cl absorbs on $\mathrm{Cu}(111)$ with a high sticking probability and a high coverage even at room temperature which leads to the formation of a sequential of well-ordered phases depending on different coverages, such as (6V3x6V3)R30 [20]. In this study, as shown in Fig. 3.5(b), a typical (6V3x6V3)R30 LEED pattern with 6-fold outer main spots and 6-fold inner triplet spots which have rotated 30 degree with respect to the main spots was observed after the first $A B$ cycle, which was possibly due to the surface $\mathrm{Cu}-\mathrm{Cl}$ adsorption.

After the second $A B$ cycle of growth, the $B N$ thickness from the AES calculation increased to 1.4 ML with a decreased $\mathrm{B} / \mathrm{N}$ ratio of 2.3. As shown in Fig. 3.5(c), $\mathrm{A}(6 \mathrm{~V} 3 \times 6 \mathrm{~V} 3) \mathrm{R} 30$ LEED pattern was still observed but had weakened intensities for both the 6 -fold outer spots and the 6 -fold triple inner dots, which was due to the reflected electron signal attenuation along the progress of the ALD process and provided a proof of forming a continuous boron nitride film on top of $\mathrm{Cu}(111)$. The weak intensities of the Cu and $\mathrm{Cu}-\mathrm{Cl}$ related LEED spots in

Fig. 3.5(c), together with the Cl peak drop in Fig. 3.4, indicated that the $\mathrm{Cu}-\mathrm{Cl}$ occurred at the $\mathrm{BN} / \mathrm{Cu}$ interface even during the very first dose of $\mathrm{BCl}_{3}$.

The deposited boron nitride films sitting on $\mathrm{Cu}(111)$ then went through 30 minutes of annealing at 1000 K , the Auger spectra showed the film composition remained almost the same(with a BN thickness of 1.3 ML and a $\mathrm{B} / \mathrm{N}$ ratio of 2.5 ) except for the decrease of the Cl peak, revealing a desorbing process which released the Cl adsorbate from the $\mathrm{Cu} / \mathrm{BN}$ interface under thermal condition [20]. The disappearance of the ( $6 \sqrt[V]{ } 3 \times 6 \mathrm{~V} 3$ )R30 LEED pattern in Fig. 3.5(d) further confirmed this desorbing process, leaving a (1x1) LEED pattern from $\mathrm{Cu}(111)$ and the 1.3ML BN films above. There was no obvious bifurcation in the (1x1) LEED pattern due to the relatively small in-plane lattice mismatch of $2.3 \%$ between $\mathrm{h}-\mathrm{BN}(0001)$ and $\mathrm{Cu}(111)(2.50 \AA$ for h-BN [18] and 2.56Å for $\mathrm{Cu}(111)$ [21]), comparing with the previous report in our group of the bifurcated LEED spots for $h-B N(0001)$ on $\operatorname{Ru}(0001)(2.71 \AA$ for $R u(0001))$ which is due to the in-plane lattice match of 7.7\% [4].

### 3.2.2.2. Multiple Cycles of Boron Nitride Films on $\mathrm{Cu}(111)$

For demonstrating the capability of tuning the BN thickness by ALD, which is different from the first-monolayer-terminated CVD growth of BN from borazine [12, 13], a thicker BN film was also grown on $\mathrm{Cu}(111)$. After several cycles of alternative Ar ion sputtering and annealing at 1000 K until the $\mathrm{Cu}(111)$ surface gave a sharp (1x1) pattern in LEED, 3 AB cycles of boron nitride films were put down on the clean $\mathrm{Cu}(111)$ surface at $700 \mathrm{~K}\left(6 \times 10^{6} \mathrm{~L} /\right.$ dose $)$. The Auger spectrum showed a boron nitride film with a thickness of 4 ML and a $\mathrm{B} / \mathrm{N}$ ratio of 2.4 , which gave an average growth rate of $1.3 \mathrm{ML} / \mathrm{AB}$ cycle. No obvious LEED pattern was observed
after deposition of BN films even after annealing at 1000 K due to the non-ordered or amorphous structure of the as-deposited BN films.

Comparing with the monolayer of BN film, the appearance of a relatively small Cl Auger peak after the 3 AB cycle of ALD process in Fig. 3.6 can be explained as due to the attenuation of Cl adsorbate peak at the $\mathrm{Cu} / \mathrm{BN}$ interface caused by a thicker BN film. And no LEED pattern was observed for multiple layers of BN since it was more difficult to thermally order a thicker amorphous film. The Cl rich Cu surface indicated the Cl ligands from $\mathrm{BCl}_{3}$ in the " A " dose were not completely removed by exposure to $\mathrm{NH}_{3}$ during the " B " dose, which provided possible explanations for the boron richness of the films.


Fig. 3.6 AES Spectra of multiple layers of BN films on $\mathrm{Cu}(111)$ by ALD.

## CHAPTER 4

## SUMMARY AND CONCLUSIONS

### 4.1 Summary and Conclusions

Hexagonal boron nitride (h-BN) was considered to be a proper template for growing graphene, which is a promising semiconductor material. Previous published paper from our group has reported the electron doping effect from underlying transition metal substrate to graphene in a graphene/h-BN/Ru(0001) structure [4].

In this study, the growth of boron nitride films by atomic layer deposition (ALD) method was investigated on Si and Cu substrates for the first time. This ALD growth method was developed by J. D. Ferguson et al. [14] where $\mathrm{BCl}_{3}$ and $\mathrm{NH}_{3}$ were alternatively dosed onto the surface of $\mathrm{ZrO}_{2}$ particles at 500 K during the process.

An typical ALD process of BN films growth was demonstrated on $\mathrm{Si}(111)$ substrate at 550 K , and a growth rate of $1.1 \mathrm{~A} /$ cycle showed good agreement with the literature value. The $B / N$ ratio for the grown BN films on $\mathrm{Si}(111)$ was $\sim 1$ but increased with the thickness of BN films. The grown BN films on $\mathrm{Si}(111)$ didn't show a long-range order due to the relatively large inplane lattice mismatch between $\mathrm{Si}(111)$ and BN .

The ALD growth of BN films was also carried out on both $\mathrm{Cu}($ poly $)$ and $\mathrm{Cu}(111)$ substrates. The dosing temperature was optimized for boron nitride growth on $\mathrm{Cu}(111)$ to a range of $700 \mathrm{~K} \sim 725 \mathrm{~K}$ and a growth rate of $\sim 1 \mathrm{ML} / \mathrm{AB}$ cycle was obtained. The BN films grown on Cu were boron rich with a $B / N$ ratio of $\sim 2$.

The ALD growth of BN films on Si and Cu substrates with a tunable thickness, specifies that the ALD growth method developed by Ferguson et al. can be transferred on to other
substrates and thus opening up opportunities for interesting material study for combinations of BN with different substrates.

### 4.2 Future Work

More work will be done towards studying the electronic properties of the BN films on metal substrates such as band gap width.

Since the boron nitride films grown by ALD using $\mathrm{BCl}_{3}$ and $\mathrm{NH}_{3}$ as precursors were usually boron rich on $\mathrm{Cu}(111)$ substrate which is possibly caused by strong surface $\mathrm{Cu}-\mathrm{Cl}$ adsorption and uncompleted Cl reduction by $\mathrm{NH}_{3}$, other methods need to be explored so as to get a more stoichiometric ratio of BN film, such as a CVD growth by thermal decomposition of Ammonia Borane $\left(\mathrm{NH}_{3} \mathrm{BH}_{3}\right)$ to produce a large area of $h$ - BN films even on amorphous supporting substrates [22].

Once a uniform and stoichiometric h-BN film with good electronic properties is obtained, physical vapor deposition (PVD) growth of graphene by a mini e-beam evaporator will be applied onto the BN films to achieve a graphene/BN/Cu for the gateable interconnects application.

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