SYNTHESIS AND CHARACTERIZATION OF HEXAGONAL BORON NITRIDE FOR INTEGRATION WITH GRAPHENE ELECTRONICS

A Dissertation in
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by
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Hexagonal boron nitride (h-BN) has attracted increased interest as a dielectric material for graphene electronics. Traditional dielectrics, such as SiO\(_2\) or various high-k materials, can introduce scattering from charged surface states, impurities, surface optical phonons, and substrate roughness; significantly degrading the transport properties of graphene. Hexagonal boron nitride boasts several key advantages over SiO\(_2\) and high-k dielectrics. Most notably, it exhibits an atomically smooth surface that is expected to be free of dangling bonds, leading to an interface that is relatively free of surface charge traps and adsorbed impurities. Additionally, h-BN’s high energy surface optical phonon modes lead to reduced phonon scattering from the dielectric. Using h-BN (grown via CVD on copper foil) as a gate dielectric to quasi-freestanding epitaxial graphene (QFEG) devices, a >2.5x increase in intrinsic current gain cut-off frequency and a >3x increase in mobility over HfO\(_2\) gated devices is obtained.

In addition, this thesis presents the transfer-free deposition of boron nitride on sapphire and silicon for use as a supporting substrate to CVD-grown graphene. This is accomplished via a polymer-to-ceramic conversion process involving the deposition of polyborazylene at low temperature (≤400°C) and subsequent annealing at 1000°C to BN. Atomic force microscopy (AFM) confirms the deposition of an ultra smooth (RMS roughness <130pm) h-BN film without the need for a solution-based transfer process. However, x-ray photoelectron spectroscopy (XPS) shows that the stoichiometry is dependent on the initial polyborazylene deposition temperature. Despite a turbostratic structure and a boron-rich stoichiometry, CVD graphene transferred to boron nitride films deposited on Al\(_2\)O\(_3\) at a polyborazylene deposition temperature of 400°C is nearly strain-free and results in an improvement in mobility of >1.5x and >2.5x compared to CVD graphene transferred to bare Al\(_2\)O\(_3\) and SiO\(_2\), respectively, due to a low impurity density and reduced surface optical phonon scattering.
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Chapter 1
Introduction / Literature Review

1.1: Fundamental Properties and Characterization of Hexagonal Boron Nitride

Boron nitride (BN) is a III-V compound that can exist in hexagonal, cubic, or wurtzite crystalline structures, as well as in amorphous form. Of particular interest for this thesis is hexagonal boron nitride (h-BN), which is an insulating isomorph to graphite, which consists of sp$^2$ hybridized bonding resulting in layered hexagonal basal planes with lattice constants of $a_0=b_0=2.50\text{-}2.51\text{Å}$ and $c_0=2.66\text{-}2.67\text{Å}$, and having a space group of P6$_3$/mmc. In contrast to graphite, which displays an AB Bernal stacking, the stacking of h-BN sequence is AA', where B atoms of one plane are directly above the N atoms of the underlying plane. h-BN has been synthesized through various methods, such as metalorganic vapor phase epitaxy (MOVPE), pulsed laser deposition, atomic layer deposition (ALD), plasma enhanced chemical vapor deposition (PECVD), and various other thermal chemical vapor deposition (CVD) methods. Contrary to graphite, which is conductive, h-BN is electrically insulating with dielectric properties similar to SiO$_2$. Various electrical properties of interest for h-BN are shown in Table 1.1.1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive Index</td>
<td>1.7-1.8</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>5.8</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>3.7</td>
</tr>
<tr>
<td>Electrical resistivity (Ω-cm)</td>
<td>$10^{14}$ - $10^{17}$</td>
</tr>
<tr>
<td>Dielectric Breakdown Strength (V/cm)</td>
<td>$5 \times 10^6$</td>
</tr>
</tbody>
</table>
In addition to its insulating properties, h-BN is chemically inert in a wide variety of acids, solvents, and oxidizers. In fact, only heated phosphoric acid has been consistently shown to etch h-BN, where etch rates of ~8nm/min have been reported for a solution of 1:1 deionized (DI) water : phosphoric acid at 130°C.\textsuperscript{11} Additionally, dry etching with a CF\textsubscript{4}/O\textsubscript{2} plasma has been demonstrated.\textsuperscript{12} Owing to its high chemical resistance and thermal stability, h-BN is an attractive material for use as a chemically inert coating in hazardous environments.\textsuperscript{13} In-plane thermal conductivity has been reported as high as 390 W/m-K at room temperature, 280 times higher than SiO\textsubscript{2}, making h-BN an attractive dielectric material for heat generating electronic devices.\textsuperscript{13} Perhaps its most common application is as a dry lubricant, as with graphite, due to its weak inter-planar van der Waals bonds.

Similarly to graphite, h-BN has a strongly anisotropic coefficient of thermal expansion (CTE) due to its anisotropic bond strength. The CTE in the a-direction (in-plane) is negative (-2.90x10\textsuperscript{-6}K\textsuperscript{-1} at room temperature), while the CTE in the c-direction (inter-plane) is over ten times larger and positive (4.05x10\textsuperscript{-5}K\textsuperscript{-1} at room temperature).\textsuperscript{14} The change in lattice parameters as a function of temperature has been studied in detail by Paszkowics \textit{et al.}\textsuperscript{15} The large positive thermal expansion in the c-direction is due to weak van der Waals bonding between planes, and leads to the potential use of h-BN as a temperature calibrant.\textsuperscript{15}

The most commonly accepted phase diagram of boron nitride was calculated from thermodynamic properties of boron nitride phases by Solozhenko \textit{et al} in 1999 after refining their original work from 1988.\textsuperscript{16} It was found that the cubic phase of boron nitride (c-BN), rather than h-BN, is thermodynamically stable at ambient conditions.\textsuperscript{16} This is in contrast to the carbon phase diagram, where the hexagonal phase (graphite) is the stable phase at ambient conditions.\textsuperscript{17} The phase diagram of boron nitride is shown in Figure 1.1.1, where the dashed lines indicate the original calculations by Solozhenko \textit{et al} in 1988 and the solid lines indicate the refined diagram.
The h-BN/c-BN/liquid triple point occurs at 3480±10K at 5.9±0.1GPa while the h-BN/liquid/vapor triple point occurs at 3400±20K and 400±20Pa.\textsuperscript{16}

![Pressure-Temperature phase diagram of boron nitride.\textsuperscript{16}](image)

**Figure 1.1.1:** Pressure-Temperature phase diagram of boron nitride.\textsuperscript{16}

Interestingly, the above phase diagram indicates that c-BN is favorable at temperatures below $\sim$1600K ($\sim$1327°C). However, as detailed subsequently in Section 2, the growth temperature of h-BN on transition metals has been reported extensively well below the stability region of h-BN, typically between 750 and 1050°C. This may be explained by the sensitivity of the transition temperature with slight variations in the Gibbs free energy of the system, where Kern *et al* demonstrated significant shifting of the h-BN/c-BN transition temperature as a function of Gibbs free energy.\textsuperscript{18} Figure 1.1.2 shows the range of the transition temperature when a shift in free energy of $\pm$10meV/atom is implemented. When this change of free energy is considered, the transition temperature can vary between 1200-1800K (927-1527°C), where the
lower value is in range of typical h-BN growth temperatures. Small variations of the free energy may be caused by grain size, defects, or contamination or interaction with other elements (such as interaction with a transition metal substrate).

![Pressure-Temperature phase diagram of boron nitride at low pressure and temperature. The shaded region indicates the range over which the transition temperature varies depending on the shift in free energy of the phase.]()

**Figure 1.1.2**: Pressure-Temperature phase diagram of boron nitride at low pressure and temperature. The shaded region indicates the range over which the transition temperature varies depending on the shift in free energy of the phase.

Additionally, experimental attempts to grow c-BN on non-transition metals substrates at low temperatures (<1000°C) and pressures have been difficult, where boron nitride either forms exclusively as h-BN or as a mixture of h-BN and c-BN. This observation has been explained qualitatively by two empirical chemical rules known as the Ostwald and Ostwald-Volmer rules. The Ostwald rule proposes that when energy is withdrawn from a system with multiple energy states, the system will not reach the stable ground state directly, but instead must first pass through all intermediate states. Therefore, for the case of BN, the metastable hexagonal phase will often form despite the fact that the cubic phase is thermodynamically preferred. This rule is also apparent in the low pressure CVD synthesis of diamond, where the metastable cubic
(diamond) phase forms despite the fact that the hexagonal (graphitic) phase is thermodynamically preferred. Even further, the Ostwald-Volmer rule states that the less-dense phase (i.e., h-BN) is formed first.\footnote{20} For the case of diamond however, where the hexagonal (graphitic) phase is less dense, this rule is circumvented due to the preferential etching of non-diamond carbon phases by hydrogen and the Ostwald rule (rather than the Ostwald-Volmer rule) dominates. For boron nitride however, both rules are satisfied, leading often to the formation of the metastable hexagonal phase over the stable cubic phase. In addition, c-BN growth may be complicated by differences in the atomic attachment kinetics during growth along the (111) direction due to anisotropy of the (111) planes; where they are either N-terminated nor B-terminated, in contrast to diamond which is always C-terminated.\footnote{20} Also, the bonding energies and bond lengths of B-N, B-B, and N-N bonds are dissimilar in the cubic phase of boron nitride, further complicating CVD synthesis.\footnote{20}

Therefore, many factors come into play that can influence the experimentally obtained phase of boron nitride. Determination of the boron nitride phase can be easily accomplished through Raman spectroscopy. Typical first-order Raman spectra for cubic and hexagonal boron nitride are shown in Figure 1.1.3. Cubic boron nitride has one optical phonon mode that is Raman active. This mode splits into a transverse (TO) and longitudinal (LO) optical phonon due to the ionic character of BN, where the TO mode is located at ~1055 cm\textsuperscript{-1} and the LO at ~1304 cm\textsuperscript{-1}.\footnote{21} Hexagonal boron nitride, on the other hand, has one Raman active phonon that is mode located at ~1364 cm\textsuperscript{-1}. This optical phonon mode is an in-plane, doubly degenerate (TO/LO) mode with a E\textsubscript{2G} symmetry where the B and N atoms move in opposite directions.\footnote{21}
In summary, hexagonal boron nitride has dielectric properties similar to SiO$_2$, is chemically inert, and has a high thermal conductivity. Therefore, h-BN appears to be a suitable material for dielectric integration with microelectronics. Despite the fact that widely accepted phase diagrams indicate that c-BN is the stable phase at ambient conditions, c-BN has proven to be difficult to attain experimentally due to variation of the Gibbs free energy of BN synthesis. This therefore leads to the potential to easily synthesis the metastable hexagonal phase. Finally, Raman spectroscopy can be easily employed to determine the deposited phase.
1.2: CVD Growth of h-BN on Transition Metals

1.2.1: Bonding of h-BN to Transition Metal Surfaces

It has been well documented that ultra-thin (often monolayer) films of h-BN readily bind in a hexagonal structure to transition metals such as Rh, Ru, Pt, Ni, Pd, and Cu through a catalytic thermal CVD growth process. One of the first examples was by Nagashima et al., who demonstrated h-BN layers on Ni(111), Pd(111), and Pt(111) substrates through the thermal decomposition of borazine. They found through angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) that the bonding for h-BN films on Ni was stronger than for the other two substrates. This same group later realized through high resolution electron energy loss spectroscopy (EELS) that there was a level of hybridization between transition metal d and BN π states that was responsible for the differences in binding strength. Through X-ray photoelectron diffraction (XPD) and scanning tunneling microscopy (STM), Auwarter et al. showed that the structure of the h-BN film on Ni(111) surface is a commensurate (1x1) structure that is most stable when N atoms are bound directly over Ni atoms and B atoms over fcc hollow sites, leading to a slightly compressed film. This same structure was also found to be the case for h-BN on Cu(111). Through core-level spectroscopies, Preobrazhenski et al. studied the role of 3d states of Ni(111) and Cu(111) and found that the bonding strength of the h-BN/metal interface is dependent mainly on the strength of the metal 3d – h-BN π orbital hybridization. It was found that h-BN is strongly chemisorbed on Ni(111) while only weakly chemisorbed on Cu(111). Through density functional theory (DFT) calculations, Laskowski et al. investigated binding energies of h-BN on various transition metals, as shown in Table 1.2.1, and found a trend across the periodic table. Going across the 3d, 4d, and 5d rows of the periodic table, the binding energy of h-BN on transition metal surfaces decreases from left to right, with noble metals having the
lowest binding energies. Additionally, it was found that the highest binding energies were obtained for the 4d elements and the lowest for the 3d elements.\textsuperscript{29} It was found that for all cases a repulsive force acted on the N atoms while an attractive force acted on the B atoms, leading to vertical buckling of the h-BN lattice that is dependent on the binding energy.\textsuperscript{29}

\textbf{Table 1.2.1:} Local density approximation (LDA) of binding energies (ΔE) of h-BN on various transition metals, vertical metal-to-nitrogen distance (Z\textsubscript{MN}), and vertical boron-to-nitrogen distance (Z\textsubscript{BN}).\textsuperscript{29}

<table>
<thead>
<tr>
<th>Element</th>
<th>ΔE (eV)</th>
<th>Z\textsubscript{MN} (Å)</th>
<th>Z\textsubscript{BN} (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.32</td>
<td>2.14</td>
<td>0.11</td>
</tr>
<tr>
<td>Ni</td>
<td>0.27</td>
<td>2.12</td>
<td>0.11</td>
</tr>
<tr>
<td>Cu</td>
<td>0.19</td>
<td>3.10</td>
<td>0.02</td>
</tr>
<tr>
<td>4d</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>0.98</td>
<td>2.13</td>
<td>0.14</td>
</tr>
<tr>
<td>Rh</td>
<td>0.61</td>
<td>2.16</td>
<td>0.13</td>
</tr>
<tr>
<td>Pd</td>
<td>0.47</td>
<td>2.21</td>
<td>0.11</td>
</tr>
<tr>
<td>Ag</td>
<td>0.19</td>
<td>2.55</td>
<td>0.04</td>
</tr>
<tr>
<td>5d</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir</td>
<td>0.49</td>
<td>2.20</td>
<td>0.14</td>
</tr>
<tr>
<td>Pt</td>
<td>0.34</td>
<td>2.26</td>
<td>0.12</td>
</tr>
<tr>
<td>Au</td>
<td>0.16</td>
<td>2.95</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Therefore, the binding energy of h-BN on transition metals decreases with the filling of the valence d-band of the metal. This binding energy was found to play a critical role on the structure of h-BN films on various transition metals. High binding strength on transition metals with close lattice matches, such as on Ni (0.4\%), has been shown to result in a commensurate (1x1) h-BN structure, often with large h-BN domains.\textsuperscript{30,31} However, a high binding strength can complicate the h-BN structure when the lattice mismatch between film and substrate is significant. For example, strong 3d-π hybridization was found for Rh and Ru leading to high binding strengths, but the lattice mismatch between h-BN and these substrates is ~7\%.\textsuperscript{22,32} To compensate for the induced strain, the h-BN film forms a highly ordered corrugated bilayer.
structure consisting of an array of 2nm diameter holes with a periodicity of 3nm, called a “BN nanomesh”, due to a strong splitting of the h-BN $\sigma$ bands.\textsuperscript{22,32} Interestingly, other metals with large lattice mismatches, such as Pt(10.8\%)\textsuperscript{33} and Pd(~9\%),\textsuperscript{34} resulted in complete h-BN films rather than a nanomesh. In these cases, the h-BN film on these substrates accounted for the induced strain by forming two distinct structures; a 10x10 commensurate structure and an incommensurate structure rotated by 30°, where the rotated structure allowed for a reduced lattice mismatch.\textsuperscript{34} On the contrary, a low binding energy has different effects on the h-BN structure. Growth of h-BN films on Ag(111) substrates led to arbitrarily oriented nanocrystalline h-BN domains.\textsuperscript{35} This is due to the increased filling of the 4d band of Ag and is expected for other noble metals. Therefore, both the binding energy and lattice mismatch must be taken into account when choosing a suitable substrate for h-BN deposition.

### 1.2.2: CVD Growth of h-BN on Cu

Copper, having a lattice mismatch with h-BN of only 0.9\%,\textsuperscript{26} is one of the most common transition metal substrates for CVD synthesis of h-BN and, like Ni, forms strictly 1x1 commensurate h-BN layers. In this thesis, Cu substrates are used almost exclusively for synthesis of h-BN via CVD. Therefore, current results for CVD h-BN on Cu will be presented in detail in this section. Table 1.2.2 details the growth parameters used in several examples from literature.
Table 1.2: Growth parameters for CVD h-BN on Cu substrates from various references.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Precursor</th>
<th>Growth Temperature (°C)</th>
<th>Growth Pressure</th>
<th>Growth Time (min)</th>
<th>Additional Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Song et al\textsuperscript{36}</td>
<td>Ammonia Borane</td>
<td>1000</td>
<td>N/A</td>
<td>30-60</td>
<td>N/A</td>
</tr>
<tr>
<td>Preobranjenski et al\textsuperscript{36}</td>
<td>Borazine</td>
<td>750</td>
<td>2000L (exposure)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Kim et al\textsuperscript{37}</td>
<td>Borazine</td>
<td>750</td>
<td>Ambient</td>
<td>10-60</td>
<td>Post-Anneal at 1000°C</td>
</tr>
<tr>
<td>Kim et al\textsuperscript{38}</td>
<td>Ammonia Borane</td>
<td>1000</td>
<td>350mTorr</td>
<td>10-120</td>
<td>AB sublimation at 60-90°C</td>
</tr>
<tr>
<td>Lee et al\textsuperscript{39}</td>
<td>Ammonia Borane</td>
<td>1000</td>
<td>Ambient</td>
<td>30</td>
<td>Chemical polish of Cu foils</td>
</tr>
<tr>
<td>Guo et al\textsuperscript{40}</td>
<td>Ammonia Borane</td>
<td>1000</td>
<td>675mTorr</td>
<td>120</td>
<td>Varied AB weight, Cu foils in quartz enclosure</td>
</tr>
</tbody>
</table>

Growth of h-BN on Cu generally results in a polycrystalline film with domain sizes <10nm.\textsuperscript{36,37,40} Therefore, the crystallinity is not as high as h-BN films grown on Ni, where domains >1µm have been obtained.\textsuperscript{31} However, it was found that h-BN films grown on Ni foils are generally more leaky as a dielectric layer due to incomplete regions present at Ni grain boundaries.\textsuperscript{41} Therefore, growth of h-BN on Cu foils represents a more realistic and suitable approach for large scale device development. Additionally, growth of h-BN on Cu is not a self-limited growth process, unlike graphene growth on Cu, where the film thickness of h-BN grown on Cu can be easily controlled through tailoring of the growth parameters.\textsuperscript{36-38} The control of layer thickness is critical for gate dielectric applications, where the tunneling currents were found to be excessive for h-BN films less than four layers thick.\textsuperscript{42,43}

Kim et al revealed the nucleation behavior of h-BN on Cu foils through varying the ammonia borane (AB) sublimation temperature and growth time.\textsuperscript{38} At an AB sublimation temperature of 60°C, h-BN formed as small triangular domains that were randomly oriented due
to the weak chemisorption (low binding energy) of h-BN on Cu. Unlike graphene, which forms as hexagonal domains, triangles are more energetically favorable for h-BN growth as nitrogen-terminated edges have lower edge energy than boron-terminated edges and hexagon formation would ultimately lead to B-terminated edges.\textsuperscript{38} At higher AB sublimation temperatures, the domains became more asymmetric, presumably due to the increased concentration of gas-phase precursors at higher sublimation temperatures. Additionally, by studying the effects of growth time, it was found that monolayers form through the coalescence of triangular domains, as shown in Figure 1.2.1. Here, a complete monolayer is formed after ~40 minutes, as evidenced by the formation of wrinkling, as shown in Figure 1.2.1c. Wrinkling naturally occurs in CVD grown h-BN (and graphene) on Cu due to h-BN’s negative coefficient of thermal expansion, causing h-BN to expand upon cooling.\textsuperscript{14} After the initial monolayer is complete, additional (smaller) ad-layers nucleate over the original monolayer, as shown in Figure 1.2.1f. This indicates a growth mechanism similar to Stranski-Krastanov growth, where growth proceeds via a surface mediated layer-to-layer mechanism before changing to an island-like growth. This is most likely due to the strong adatom-surface interaction on the Cu surface and sharp decrease in the surface reactivity after the first h-BN layer.\textsuperscript{38} This also verifies that, unlike similar graphene growth on Cu, the growth of h-BN on Cu is not a self-limiting process.
Figure 1.2.1: (a-e) Nucleation behavior of h-BN film on Cu substrate as a function of growth time from 10-120 minutes. (f) Higher magnification image of (e).38

The surface morphology of the copper foil also plays a significant role in the nucleation and growth of h-BN. Often, impurity particles and unwanted cubic BN and amorphous BN allotropes can form as 3D particulates in the h-BN film, possibly forming through a Volmer-Weber nucleation along defects (such as vacancies, dislocations, and grain boundaries) on the Cu surface.39 Lee et al demonstrated a significant reduction in the density of such 3D particulates through the use of an extended pre-growth anneal and a pre-growth chemical polish, as shown in Figure 1.2.2.39 Thermal annealing was performed at 1020°C for 2 hours in an Ar atmosphere and resulted in an increase in the starting Cu grain size from ~30µm to ~120µm and a reduction in the RMS roughness from 2.42nm to 1.57nm.39 Chemical polishing was performed by rubbing the
copper foil with Cu etchant (Transcene, Type 1) following thermal annealing and resulted in a further improvement in RMS roughness (from 1.57nm to 1.10nm) over the thermally annealed samples. These results show that the starting Cu foil surface is essential for the suppression of 3D nanoparticles that form on surface defects.

![Figure 1.2.2: Optical images of (a) untreated, (b) thermally annealed, and (c) thermally annealed and chemically polished Cu foils. (d-f) Optical images of h-BN films grown on the respective Cu foil and transferred to SiO₂ substrates.](image)

To further elucidate the improvement in h-BN growth when using an enhanced starting Cu morphology, Raman spectroscopy was used and showed a suppression of defect peaks arising from boron carbon nitride (1304cm⁻¹) and amorphous BN “soot” (1336cm⁻¹) when the thermal anneal and chemical polishing steps were employed. Additionally, a reduction in the full width at half maximum (FWHM) of the E₂G peak (1367cm⁻¹) from 22.9cm⁻¹ to 14.8cm⁻¹ was observed.
for the untreated and thermally annealed/chemically polished sample, respectively. This indicates improved crystallinity and increased domain size, which was verified with transmission electron microscopy (TEM).\textsuperscript{39}

Similar 3D nanoparticles were also observed on h-BN films grown on Cu foil by Kim \textit{et al.}\textsuperscript{38} However, here the nanoparticles were postulated to form in the gas phase upon sublimation of ammonia borane. It was found that when a carrier gas flowed through the sublimator, a high density of nanoparticles (up to 50-100nm in diameter) were formed on the surface. The density of these nanoparticles increased with sublimation temperatures above 100°C. Therefore, the sublimation temperature was reduced to 60-90°C and no carrier gas was used (allowing the precursor to naturally diffuse into the growth zone).\textsuperscript{38} Again, using an electrochemical polishing (ECP) step improved the nucleation of h-BN on Cu foils, where nucleation was found on unpolished samples to occur preferentially on rolling lines (induced during manufacturing) of the Cu foil. The ECP step resulted in a more uniform nucleation over the Cu surface and a reduced density of nucleation sites. This ultimately led to an increase in h-BN domain size.\textsuperscript{38}

Despite the well documented research on h-BN growth on Cu substrates, the growth mechanisms of CVD grown h-BN are not fully understood and several growth-related issues exist which can impact graphene device performance such as: 1) impurity scattering from dangling bonds of 3D nanoparticles, 2) surface roughness scattering from wrinkles induced during growth, and 3) current leakage through nanocrystalline domain boundaries.

\textbf{1.3: Sublimation Properties of Ammonia Borane}

Ammonia borane (BH\textsubscript{3}NH\textsubscript{3}) is a white solid that is isoelectronic to ethane and contains a highly polarized electron-pair dative bond.\textsuperscript{44} The B-N bond results from a donation of the lone
pair electrons of ammonia to the 2p\textsubscript{z} orbital of borane and has a dissociation energy of 130kJ/mol.\textsuperscript{44,45} Ammonia borane (AB), being non-flammable and non-explosive under ambient conditions, has attracted considerable interest as a potential hydrogen (H\textsubscript{2}) storage material for automotive applications due to its high hydrogen content, having a gravimetric hydrogen density of 19.6 wt\% and a volumetric hydrogen density of 145 Kg/m\textsuperscript{3}, which can be extracted through various processes, such as thermolysis, hydrolysis, hydrothermolysis, and methanolysis.\textsuperscript{45} Of these, thermolysis (thermal decomposition) is the most common and practical method for generating hydrogen from AB, which can result in a generation of >9 wt\% hydrogen at moderate temperatures.\textsuperscript{45} The thermal decomposition of AB proceeds via multiple exothermic decomposition steps that correspond to both a weight loss and a release of hydrogen and/or various boron-nitrogen species. Preceding the exothermic decomposition steps, an endothermic process occurs near 101°C that can be attributed to the melting of AB.\textsuperscript{46} As shown in Figure 1.3.1, the exothermic decomposition steps occur at ~110°C, ~130°C, and ~1170°C.\textsuperscript{47} The first weight loss step at ~110°C results primarily in the release of H\textsubscript{2} with small traces of monomeric aminoborane (BH\textsubscript{2}NH\textsubscript{2}), leaving behind a solid polyaminoborane (PAB). This is followed by a second weight loss step at ~130°C, which results in a second hydrogen release from the PAB accompanied by a release of borazine (B\textsubscript{3}N\textsubscript{3}H\textsubscript{6}), which is a boron-nitrogen analog of benzene.\textsuperscript{48} Other reports have shown that additional boron-nitrogen species are released at the 130°C weight loss step as well, including monomeric aminoborane and diborane (B\textsubscript{2}H\textsubscript{6}).\textsuperscript{48-50} The second weight loss step results in residual solid polyiminoborane (PIB) that remains stable until further hydrogen abstraction begins at temperatures above 1170°C, which ultimately result in the formation of a semi-crystalline P6\textsubscript{3}/mmc (hexagonal) boron nitride phase.\textsuperscript{47}

Mass spectrometry results corroborate well with the above thermal decomposition model. As shown in Figure 1.3.2, the initial weight loss at ~110°C (Figure 1.3.2A) shows a large release of hydrogen (m/z = 2) accompanied by additional m/z values located at 27, 28, and 29 corresponding to aminoborane fragments. The second weight loss step (Figure 1.3.2B) also results in a hydrogen release but is accompanied by several additional species at higher m/z values. When compared to the mass spectrum of pure borazine (Figure 1.3.2C), which has distinct m/z peaks at 81, 80, 67, 63, 53, and 28, many similarities are observed indicating the generation of borazine at the second AB decomposition step. The complete mass spectrum is given in Table 1.3.1.
Figure 1.3.2: Mass Spectrum: (A) pyrolysis gases generated at 114°C scaled to impurity levels; (B) pyrolysis gases generated at 135°C scaled to impurity levels; (C) pure borazine. The m/z = 2 signal intensities in A and B are each about 2 orders of magnitude above their respective y-axis scales.
Table 1.3.1: Mass spectrum of the gas phase above BH$_3$NH$_3$ at elevated temperatures.$^{48}$

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>Assignment</th>
<th>Mass Number</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$H_2^+$</td>
<td>27</td>
<td>$^{11}$BNH$_2^+$, $^{10}$BNH$_3^+$, $^{11}$B$_2$H$_5^+$</td>
</tr>
<tr>
<td>11</td>
<td>$^{11}$B$^+$, $^{10}$BH$^+$</td>
<td>28</td>
<td>$^{11}$BNH$_3^+$, $^{10}$BNH$_4^+$</td>
</tr>
<tr>
<td>12</td>
<td>$^{11}$BH$^+$, $^{10}$BH$_2^+$</td>
<td>42</td>
<td>$^{11}$BH$_2$NH$_2$, $^{11}$BH$_2^+$</td>
</tr>
<tr>
<td>13</td>
<td>$^{11}$BH$_2^+$, $^{10}$BH$_3^+$</td>
<td>53</td>
<td>$^{11}$B$_2$N$_3$H$_3^+$</td>
</tr>
<tr>
<td>14</td>
<td>$^{11}$BH$_3^+$, N$^+$</td>
<td>62</td>
<td>$^{11}$B$_2$N$_2$H$^+$</td>
</tr>
<tr>
<td>24</td>
<td>$^{10}$BN$^+$, $^{11}$B$_2$H$_2^+$, $^{11}$B$_3^+$BH$_3^+$</td>
<td>63</td>
<td>$^{11}$B$_3$N$_2$H$_2^+$</td>
</tr>
<tr>
<td>25</td>
<td>$^{11}$BN$^+$, $^{10}$BNH+, $^{11}$B$_2$H$_3^+$</td>
<td>78</td>
<td>$^{11}$B$_3$N$_3$H$_3^+$</td>
</tr>
<tr>
<td>26</td>
<td>$^{11}$BNH$^+$, $^{10}$BNH$_2^+$, $^{11}$B$_2$H$_4^+$</td>
<td>80</td>
<td>$^{11}$B$_3$N$_4$H$_3^+$</td>
</tr>
</tbody>
</table>

Additionally, it was found by several groups that the decomposition of AB is strongly dependent on the thermal history and heating conditions.$^{48-50}$ It was found that the onset temperature for the first decomposition step is a function of the heating rate, where the starting temperature of decomposition increases from 82-107°C as heating rate increases from 0.05-1°C/min.$^{46}$ Additionally, the weight loss of the solid phase of AB is dependent on the heating rate. It was found that the first and second decomposition steps corresponded to an 8 and 15wt% loss, respectively, for a heating rate of 1°C/min. However, when the heating rate is increased to 5°C/min, the weight loss increases to 10 and 23wt% for the first and second decomposition steps, respectively.$^{48}$ Interestingly, it was observed through mass spectrometry that the evolution of hydrogen is independent of heating rate.$^{48}$ Instead, the increased weight loss was found to be due to the increased yield of boron-nitrogen species such as borazine, monomeric aminoborane, and diborane.$^{48}$ Table 1.3.2 shows the increase in product yield of these boron-nitrogen species with increasing heating rate.
**Table 1.3.2:** Yield of gaseous products of the thermal decomposition of ammonia borane at temperatures up to 500K calculated on the basis of thermogravimetric and mass spectrometric data for different runs.48

<table>
<thead>
<tr>
<th>Heating Rate</th>
<th>Product Yield (mol product/mol AB)</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;</th>
<th>BH&lt;sub&gt;2&lt;/sub&gt;NH&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Borazine</th>
<th>Diborane</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 K/min</td>
<td></td>
<td>2.2</td>
<td>0.12</td>
<td>0.035</td>
<td>0.020</td>
</tr>
<tr>
<td>1.5 K/min</td>
<td></td>
<td>2.2</td>
<td>0.16</td>
<td>0.050</td>
<td>0.025</td>
</tr>
<tr>
<td>5.0 K/min</td>
<td></td>
<td>2.2</td>
<td>0.21</td>
<td>0.065</td>
<td>0.040</td>
</tr>
<tr>
<td>Iso 363 K-1 K/min</td>
<td></td>
<td>2.2</td>
<td>0.12</td>
<td>0.040</td>
<td>0.020</td>
</tr>
</tbody>
</table>

Pressure was also found to be an important factor in the decomposition of AB. Sublimation of AB at ~90°C under an Ar background pressure ranging from ~35 Torr to atmospheric pressure resulted in an increase in the total weight loss (from 7 to 24wt%) with decreased pressure.49 The induction period of hydrogen evolution was also found to decrease with decreasing pressure, from 7 hours at atmospheric pressure down to 4 hours at low pressure.49 Additionally, mass spectrometry shows a dependence of the evolved species with pressure. Near ambient pressure, the primary emission was hydrogen (m/z = 2) with little detectable nitrogen-boron species. However, when the Ar background pressure was reduced to < 650 Torr, additional m/z values began to appear at 78 and 80 (borazine), 27-29 (aminoborane), 10-13 and 23-26 (diborane), and 42 (aminodiborane). It was found that the intensity of these boron-nitrogen species increases with decreasing pressure, as shown in Figure 1.3.3.49 It is reported that the increase in the boron-nitrogen species upon sublimation of AB at sub-ambient pressures may be a result of the increased breaking of dihydrogen bonding networks at higher sublimation rates.49
Figure 1.3.3: Mass spectrometry results as a function of time during thermal aging at 363K at pressures ranging from 52-1039 mbar. Mass spectrometry data is given for hydrogen (H₂), m/z = 2; unknown, m/z = 41; borazine (B₃N₃H₆), m/z = 78 and m/z = 80; monomeric aminoborane (BH₂NH₂), m/z between 27 and 29; diborane (B₂H₆), m/z between 10 and 13, and m/z between 23 and 26; aminodiborane (BH₂NH₂BH₃), m/z = 42; and boron (B⁺) m/z = 11.⁴⁹

The mechanism for the thermal decomposition of AB was studied via an in-situ ¹¹B magic angel spinning-nuclear magnetic resonance (MAS-NMR) technique at a decomposition
temperature of 88°C and external fields of 7.1T and 18.8T. The decomposition pathway can be described by induction, nucleation, and growth mechanisms, as shown in Figure 1.3.4.

Figure 1.3.4: The proposed dehydrogenation pathway of ammonia borane proceeds via induction, nucleation, and growth steps.

The induction period results in little to no hydrogen release but yields a mobile AB phase that is caused by disruptions of the dihydrogen bonding network, which are composed of bonds between amine protons and boron hydrides of adjacent AB molecules. Additionally, it was found that preheating of AB can result in a decreased induction period. The nucleation step then yields a reactive species from the mobile AB phase, identified as diammoniate of diborane \([(\text{NH}_3)_2\text{BH}_2]^+\text{[BH}_4^-\) (DADB). Growth then proceeds via a bimolecular reaction between DADB and AB to release the stored hydrogen and additional gas phase boron-nitrogen species. In other
words, hydrogen bonding is disrupted upon heating that allows for increased motion of AB groups during the “induction” step. The mobile phase converts into a new species, DADB, during “nucleation”. Once the DADB phase is formed, it reacts with the remaining AB during the “growth” step, which yields hydrogen and aminoborane. This study however, only examines the time-resolved hydrogen evolution at temperatures below the melting point of AB. However, these mechanisms give insight into the possible pathways for formation of boron-nitrogen species at higher temperatures, which may include additional breaking of the dihydrogen bonding network.

Sublimation of ammonia borane has been shown to occur in two distinct weight loss steps, where the first step results in evolution of hydrogen and the second results in additional hydrogen along with various boron-nitrogen species, such as borazine. Therefore, ammonia borane appears to be an excellent source for production of precursors for BN growth. However, the sublimation behavior of ammonia borane is highly sensitive to parameters such as heating rate and sublimation pressure. Therefore, significant attention must be placed on maintaining a consistent control of the ammonia borane sublimation process.

1.4: Polyborazylene as a Precursor to Boron Nitride

It was discussed in the previous section that ammonia borane can readily decompose to yield, among other gas-phase species, borazine (B₃N₃H₆). Fazen et al has shown that borazine can dehydropolymerize to a yield a soluble polymer, polyborazylene (B₃N₃H₄)x, in yields of 81-91% at temperatures as low as 70-110°C. Polyborazylene, which is soluble in ethers such as glyme and tetrahydrofuran (THF), can be thermally converted to boron nitride in yields of 89-99% through a two-dimensional cross-linking reaction. Polyborazylene is composed of linked borazine rings, as shown in Figure 1.4.1 in two configurations.
The chemical composition (hydrogen content) was found to be dependent on the temperature that borazine was heated to, as well as the reaction time. Hydrogen content was found to decrease with increased reaction times and temperature. At a maximum temperature of 500°C, an insoluble white powder was obtained with a chemical formula of BNH$_x$ (x≈1). The general thermal conversion reaction at 70°C is shown in Equation 1.4.1.

$$xB_3N_3H_6 \rightarrow (B_3N_3H_4)_x + xH_2$$

Equation 1.4.1

Polyborazylene was produced from liquid borazine at 70°C for 48-60 hours. The remaining polymer was soluble in ethers such as glyme and THF and was found to be moisture sensitive, readily decomposing in air. The average chemical formula for the polyborazylene made this way was B$_{3.0}$N$_{3.1}$H$_{3.6}$. Diffuse reflectance infrared fourier transform (DRIFT) spectroscopy was used to identify the presence of the B-N stretch mode near 1460cm$^{-1}$ and B-N-B
bending mode at ~900 cm\(^{-1}\), characteristic of borazine rings. Additionally, \(^{11}\)B nuclear magnetic resonance (NMR) was used to identify that a diborazine structure was responsible for the B-N bonds connecting adjacent borazine rings, indicating that the polymer proceeds via a dehydropolymerization reaction that forms a linked borazine ring structure.\(^{52}\)

Polyborazylene is expected to be an ideal chemical precursor to boron nitride, only having to lose hydrogen to form boron nitride. Fazen et al found that through pyrolysis of polyborazylene at 900-1450°C in argon or ammonia, boron nitride powder could be obtained at chemical yields of 89-99% with B:N ratios near 1:1.\(^{52}\) Equation 1.4.2 shows the ultimate conversion of polyborazylene to BN through pyrolysis at temperatures >900°C.

\[
(B_3N_3H_4)_x \rightarrow 3BN + 2H_2
\]

Equation 1.4.2\(^{53}\)

X-ray powder diffraction (XRD) showed the presence of turbostratic BN. Increasing the pyrolysis temperature resulted in an improvement in the crystallinity, as shown in Figure 1.4.2, where a temperature of 1450°C led to a sharp XRD peak near 26° 2θ for the (002) orientation and a d-spacing approaching 3.33 Å, consistent with bulk h-BN.\(^{54}\) Additionally, peaks near 42° 2θ and 54° 2θ indicate reflections associated with the (001) and (004) orientations, respectively.\(^{52}\) Not only did the increased pyrolysis temperature lead to enhanced crystallinity; the density of the BN films increased from 1.7 to 2.0 g/cm\(^3\) for pyrolysis temperatures of 900 and 1450°C, respectively.\(^{52}\)
The conversion of polyborazylene to boron nitride proceeds via two-step weight loss process, as shown with thermogravimetric analysis (TGA) in Figure 1.4.3. The first weight loss occurs between 125 and 300°C and corresponds to a 2% weight loss. Over the range of 300-700°C, little weight loss is observed. From 700°C up to 1100°C weight loss continues, corresponding to an additional 4% weight loss. Combining mass spectrometry with TGA shows that hydrogen is the primary species evolved at both steps. However, small concentrations of boron-nitrogen species were found to evolve from the polyborazylene in the first weight loss regime below 300°C.
Figure 1.4.3: Thermogravimetric analysis (TGA) of the polyborazylene to boron nitride conversion.52

One sample was heated to a temperature of 400°C, which lies just outside of the first weight loss step. Elemental analysis of this sample showed an empirical formula of $\text{B}_3\text{N}_3\text{H}_2$. The 1:1 B:N stoichiometry and reduced hydrogen content from polyborazylene indicates that hydrogen loss is primarily responsible for the observed weight loss.52

Figure 1.4.4 shows the possible polyborazylene to boron nitride conversion process. Following the formation of polyborazylene thermally from borazine at 70°C, two aligned (idealized) linear structures may then undergo an interchain dehydrocoupling at intermediate temperatures which results in the loss of hydrogen through the formation of a B-N cross-linked structure.52 The second hydrogen loss occurs only at higher temperatures from un-aligned (non-idealized) chain branched structures, forming boron nitride.52
Indeed, polyborazylene has been shown in literature to be an excellent candidate for boron nitride coatings. BN has been produced from spin coating polyborazylene on a variety of substrates, dip-coating on metallic substrates, and through CVD on transition metal substrates. Spin coating polyborazylene on silicon substrates and subsequent pyrolysis at 900-1250°C was performed by Chan et al. The thickness of the spin coated polyborazylene was found through optical ellipsometry to be ~950Å with a refractive index of ~1.67. It was found that the pyrolysis temperature played a significant role in the stoichiometry and morphology of the obtained BN films. Table 1.4.1 details the chemical composition (obtained through Rutherford backscattering spectrometry (RBS)) of the films studied by Chan et al. Samples prepared at 900°C resulted in a uniform and smooth morphology, but were boron-rich. In fact, the samples prepared at 900°C were more boron-rich than the starting polyborazylene film.
Unfortunately, no explanation for the observed differences in B/N ratios between samples is provided by Chan et al. When the pyrolysis temperature was increased to 1250°C, the B/N ratio became closer to unity and the hydrogen and oxygen content decreased compared to the sample prepared at 900°C. The pyrolysis step led to the incorporation of oxygen, which was not observed in the original polyborazylene film, for both pyrolysis temperatures. This was attributed to possible contamination during transfer to the annealing furnace, or from incorporation during annealing due to oxygen impurities in the furnace.

Table 1.4.1: Composition and thickness of spin coated polyborazylene on silicon and boron nitride prepared from pyrolysis of polyborazylene.53

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>B/N</th>
<th>O/B</th>
<th>Atomic fraction of H</th>
<th>Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyborazylene</td>
<td>1.18</td>
<td>N/A</td>
<td>0.33</td>
<td>1500</td>
</tr>
<tr>
<td>BN prepared at 900°C</td>
<td>1.37</td>
<td>0.21</td>
<td>0.10</td>
<td>800</td>
</tr>
<tr>
<td>BN prepared at 1250°C</td>
<td>1.09</td>
<td>0.14</td>
<td>0.09</td>
<td>900</td>
</tr>
</tbody>
</table>

Interestingly, the samples prepared at 1250°C showed the presence of surface features, unlike the samples prepared at 900°C which were visually smooth. The surface features were pits covering ~15% of the film surface and were ~0.5μm in diameter and 2-7nm deep.53 Figure 1.4.5 shows an SEM image of the surface features resulting from the 1250°C pyrolysis of polyborazylene on silicon. Cross-sectional SEM revealed that the surface pits did not correspond to a void in the BN film, as the BN was found to be present at the bottom of the pits. The surface pitting was attributed to the decomposition of the native silicon oxide at high temperatures.53 Upon removal of the native oxide via a hydrofluoric (HF) acid solution prior to polyborazylene deposition, the pitting was reduced by nearly 75%.
Figure 1.4.5: Top-view SEM image of a boron nitride film prepared on a silicon substrate through pyrolysis of polyborazylene at 1250°C showing the presence of surface features. 53

In another study, boron-rich films were obtained by pyrolysis of spin-coated polyborazylene on Si and SiO$_2$/Si by Kho et al. 55 These films were produced by pyrolysis at 5°C/min in a quartz tube furnace in vacuum or an Ar atmosphere up to 900 or 1100°C, where the final pyrolysis temperature was held for 2hrs, resulting in BN films with thicknesses of 0.15-2.0µm. 55 The morphology of the films pyrolyzed at 900°C, studied by AFM, indicated RMS surface roughness values of 0.213 and 0.415nm for films pyrolyzed under an Ar atmosphere or under vacuum, respectively. 55 The increased roughness under vacuum was attributed to a more aggressive evaporation of volatile species during pyrolysis. Increasing the pyrolysis temperature to 1100°C resulted in rougher surface and pyrolysis above 1200°C resulted in the formation of pitting, due to the vaporization of the native silicon oxide at high temperatures, similarly to those observed by Chan et al.
X-ray diffraction (XRD) was used to investigate the crystallinity of the films prepared by pyrolysis of polyborazylene and is shown in Figure 1.4.6. It was found that at 900°C, the BN (002) peak near 26° 2θ was very broad, indicating a nearly amorphous structure. At 1100°C however, the BN (002) peak became narrower and stronger in intensity, indicating that the film pyrolyzed at 1100°C is more crystalline than the film pyrolyzed at 900°C. A d-spacing of 3.48Å was found, which is slightly larger than the d-spacing of well ordered hexagonal boron nitride reported at 3.33Å, \(^{54}\) indicating a turbostratic structure.

![Figure 1.4.6: XRD pattern of BN film pyrolyzed from spin-coated polyborazylene indicate an improvement in crystallinity upon increasing pyrolysis temperatures from (a) 900°C to (b) 1100°C.\(^{55}\)](image-url)
Secondary ion mass spectrometry (SIMS) was used to study the chemical composition of these films. For the samples pyrolyzed at 900°C, N/B ratios of ~0.75 were obtained, showing a boron-rich stoichiometry. Additionally, it was found that the silicon and boron atoms were interdiffused in a region of thickness ~0.15µm for the 900°C samples, and a very broad region of thickness ~0.90µm for the 1000°C films. It was found that films deposited on the SiO₂/Si substrates did not have the inter-diffusion region. Figure 1.4.7 shows the SIMS depth profile of a 900°C sample and the cross-sectional TEM image of an 1100°C sample. From the electron diffraction patterns obtained during cross-sectional TEM, the film was verified to be turbostratic.

Figure 1.4.7: (a) SIMS depth profile of BN film prepared from spin coated polyborazylene film at 900°C on Si shows a boron-rich stoichiometry and interdiffusion of Si and B atoms. (b) Cross-sectional TEM image of BN film prepared from spin coated polyborazylene film at 1100°C on Si showing inter-diffusion of Si and B atoms over a ~0.9µm thick region.
Growth of boron nitride from a polyborazylene precursor was also demonstrated on nickel substrates by Shi et al.\textsuperscript{31} Here, borazine was used as the precursor to polyborazylene deposition at 400°C on polycrystalline Ni foils in an ambient background pressure of N\textsubscript{2}.\textsuperscript{31} Following deposition of polyborazylene at 400°C, a post-growth anneal was performed to facilitate dehydrogenation of the polyborazylene to yield h-BN. The samples were heated at a rate of 5°C/min to a temperature of 1000°C and maintained at this temperature for 1 hr. Thickness was dependent on the polyborazylene deposition time and the flow rate of borazine into the tube furnace, where a borazine flow rate of 1 sccm for 30 minutes and 10 sccm for 1 hour resulted in a final h-BN thickness of 5nm and 50nm, respectively.\textsuperscript{31} Figure 1.4.8 shows the XRD and TEM results from a 50nm and 5nm, respectively, h-BN film prepared by polyborazylene deposition and subsequent annealing.

**Figure 1.4.8:** (a) XRD spectra of an h-BN film grown on a nickel substrate showing a sharp (002) peak indicating high crystallinity. (b) Plan-view TEM of a wrinkle shows a cross-sectional view, providing the d-spacing and layer thickness. (c) Plan-view TEM showing h-BN surface and crystallinity.\textsuperscript{31}
XRD analysis shows a sharp (002) peak with high intensity, indicating that the h-BN films are highly crystalline. Some areas of the h-BN film transferred to the holey carbon grid had tears or wrinkles which folded upwards to reveal the cross-section of the film. Here, a d-spacing of 3.50Å was found, which is slightly greater than that reported for bulk h-BN (3.33Å), although the d-spacing found from the XRD analysis was 3.30Å. Plan-view TEM shows a single crystal h-BN domain with a high degree of order and an in-plane lattice spacing of 2.50Å, in good agreement with the reported bulk value for h-BN.⁵⁴ XPS was used to characterize the stoichiometry of the 5nm thick sample and indicates a B/N ratio of 1.12. A large oxygen peak was present in the XPS spectra, indicating high oxygen content, although the exact concentration was not reported. Fourier transfer infrared (FTIR) and Raman spectroscopy of the 50nm thick sample (used for a stronger signal) also show indicative peaks associated with h-BN.³¹

In summary, through a dehydropolymerization process, polyborazylene has been shown to be a suitable precursor to boron nitride films on various substrates. Growth has been demonstrated to proceed from spin coating substrates with polyborazylene directly as well as through CVD methods where polyborazylene is deposited from a borazine vapor source. In both cases, boron nitride films of excellent chemical yield have been obtained. However, interdiffusion of silicon and boron remains an issue for growth on Si substrates, and B-rich films appear to be a common problem in synthesis of h-BN from polyborazylene.

1.5: Fundamental Properties and Synthesis of Graphene

Graphene is a zero-gap semiconductor composed of a single monolayer of sp² bonded carbon and is a material of increasing interest to the scientific and technical communities. Due to its linear electronic band structure, charge carriers behave as relativistic particles having zero
Consequently, graphene demonstrates many exceptional properties including high electron and hole mobilities (theoretically >200,000 cm$^2$V$^{-1}$s$^{-1}$), high thermal conductivity (>5x10$^3$ Wm$^{-1}$K$^{-1}$), and high saturation current/velocity (>3x10$^7$cm/s). Proven applications include radio-frequency (RF) field-effect transistors (FETs) and transparent conductors. Additionally, graphene exhibits a symmetric, ambipolar field effect that makes it attractive for use as an RF mixer. Table 1.5.1 details various electronic properties of graphene compared to several commonly used semiconductors.

<table>
<thead>
<tr>
<th>Property</th>
<th>Si</th>
<th>Ge</th>
<th>GaAs</th>
<th>AlGaN/GaN 2DEG</th>
<th>Graphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$ at 300K (eV)</td>
<td>1.1</td>
<td>0.67</td>
<td>1.43</td>
<td>3.3</td>
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</tr>
<tr>
<td>$m^*/m_e$</td>
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<td>0.55</td>
<td>0.067</td>
<td>0.19</td>
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<tr>
<td>$\mu_e$ at 300K (cm$^2$/V-s)</td>
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<td>3900</td>
<td>4600</td>
<td>1500-2000</td>
<td>~200,000</td>
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<tr>
<td>$v_{sat}$ (x10$^7$ cm/s)</td>
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<td>0.6</td>
<td>2</td>
<td>3</td>
<td>~4</td>
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</tbody>
</table>

Synthesis of graphene is accomplished by several methods. The earliest report of isolated graphene was obtained by Geim and Novoselov in 2004 through the mechanical exfoliation of highly oriented pyrolitic graphite (HOPG). This technique produces the highest quality graphene, resulting in the highest reported mobilities. However, due to the size limitations of these flakes (usually no more than 10µm across), this technique is not suitable for large scale industrial applications. Large area graphene of high quality has also been achieved through chemical vapor deposition (CVD) on transition metals such as Ni(111) and Cu(111). However, the interaction with graphene and the conductive substrate results in a high level of n-type doping and degradation of graphene’s electronic properties. Therefore, a solution based transfer of the graphene film from the transition metal to an insulating substrate is required and
can induce pinholes, tears, and wrinkling into the final graphene film. Chemical vapor deposition of graphene onto sapphire has also been demonstrated.\(^6\) This method however usually results in thick graphitic films. Finally, graphene can be formed on silicon carbide (SiC) via the sublimation of silicon at high temperatures and the subsequent rearrangement of the remaining carbon atoms into graphene. Known as “epitaxial graphene” (EG), this technique has been shown to produce uniform, large area, and high quality graphene for high frequency applications with an intrinsic current gain cutoff frequency \(f_T\) approaching 300GHz.\(^6\) However, degradation of epitaxial graphene’s electronic properties is induced from step-edges of the SiC substrate. For this thesis, h-BN integration with graphene is confined to quasi-freestanding epitaxial graphene (QFEG) and CVD graphene transferred from transition metals. Therefore, this literature review will only focus on these two synthesis methods.

### 1.5.1: Growth of Epitaxial Graphene

Graphene growth via sublimation proceeds through the thermal desorption of silicon atoms and the subsequent rearrangement of the residual carbon atoms. The carbon required to produce one layer of graphene is equivalent to approximately three bi-layers of SiC.\(^7\) Sublimation is generally performed at high vacuum or in a background of inert gas at temperatures between 1200-1800°C. Graphene σ-states begin to appear in photoemission spectra at growth temperatures as low as 1100°C, though π-bands do not appear until 1250-1300°C.\(^7\) Epitaxial graphene synthesis via the thermal desorption of silicon from SiC is generally performed in either an ultra-high vacuum (UHV) chamber via direct current resistive heating, or in a RF induction furnace. The benefit of the UHV chamber is that in-situ characterization techniques, such as LEED and scanning tunneling microscopy (STM) can be easily incorporated
with the system to monitor graphene formation.\textsuperscript{71} The RF furnace, on the other hand, is useful because hydrogen etching (which is universally used prior to graphene synthesis to remove polishing damage) can be performed in the same chamber without the need for a second system.\textsuperscript{71} In addition, van der Pauw Hall effect measurements indicate that graphene produced in the RF furnace generally show higher carrier mobilities than UHV produced material.\textsuperscript{71} Typically, SiC is etched at atmospheric pressure for 5-30 minutes at 1500-1600°C under 5-10\% hydrogen and 90-95\% argon.\textsuperscript{71,72} Similar basic growth mechanisms are observed from group to group. Synthesis of graphene from the sublimation of SiC can be done on either the silicon terminated face (SiC(0001)) or the carbon terminated face (SiC(000\bar{1})) of SiC. The mechanisms of graphene formation on these two polar faces are significantly different.\textsuperscript{70,71,73}

Graphene growth on the Si-face is much slower compared to the C-face, and is considered to limit itself to one to a few layers.\textsuperscript{70,73} The number of graphene layers grown on the Si-face is sensitive to the growth temperature and relatively independent of the growth time.\textsuperscript{70} In addition, graphene grown on the Si-face is rotated 30° relative to the substrate while C-face grown graphene may have multiple orientational phases.\textsuperscript{70,73} According to Tromp \textit{et al.}\textsuperscript{74} when heating the SiC substrate, the Si-face goes through a sequence of surface reconstructions as shown in Equation 1.5.1.

\[
(3\times3) \rightarrow (1\times1) \xrightarrow{1000^\circ C} (\sqrt{3}\times\sqrt{3}) \xrightarrow{1080^\circ C} (6\sqrt{3}\times6\sqrt{3}) + \text{Graphene}
\]

\textit{Equation 1.5.1}\textsuperscript{74}

These surface transitions have been verified through STM and LEED.\textsuperscript{70,73} Upon heating above 1200°C, the (6\sqrt{3}\times6\sqrt{3})R30 reconstruction phase (which will be abbreviated as (6\sqrt{3})) appears. This layer is believed to contain a mixture of sp\textsuperscript{2} and sp\textsuperscript{3} bonded carbon (and up to 30\%
Si adatoms) and is the precursor to graphene formation on the Si-face. Graphene grows epitaxially, rotated 30° and commensurate to the \((6\sqrt{3})\) periodicity. Subsequent graphene layers then follow a regular AB Bernal stacking sequence, i.e. two graphene sheets on top of each other with one rotated 60° about the z-axis, which is the most common stacking arrangement of graphite.

The interaction between the substrate and the \(6\sqrt{3}\) reconstruction results in a distortion of the \(\pi\)-bands that induce a band gap. As a result, this \(6\sqrt{3}\) “buffer” layer grown on the Si-face does not show the relativistic properties of graphene. The linear dispersion of the band structure (characteristic of isolated graphene) only appears when the second layer is formed. It is believed that the silicon atoms bound to the \(6\sqrt{3}\) reconstruction have unsatisfied dangling bonds which influences and degrades the electronic properties of the initial graphene layer and also explains the high degree of order between the substrate and graphene. This layer is covalently bonded to the SiC substrate and induces charge into the subsequent graphene layers, which become heavily n-doped \((n=1x10^{13} \text{cm}^{-2})\). Therefore, graphene on the Si-face tends to have lower mobilities compared to C-face growth, where the graphene layers are weakly bound to the substrate and do not exhibit Bernal stacking (discussed later).

There is significant evidence that suggests that graphene nucleation on the Si-face occurs along the \((1\overline{1}00)\) plane, which is the terrace step edge on the SiC(0001) face. The amount of carbon required to produce one layer of graphene is contained in approximately three bi-layers of SiC. In addition, different steps of SiC have different desorption rates, leading to a “step bunching” effect that results in a roughened SiC surface, and thus a rough graphene film. The receding step mechanism is shown in Figure 1.5.1.
Figure 1.5.1: Formation process (from left to right) of graphene via the retraction of 3 bi-layer SiC steps. Steps having different retraction speeds lead to step bunching and consequent graphene islands and “fingers”. 78

Robinson et al showed through TEM analysis that graphene grows significantly thicker on the (1\(\bar{1}00\)) step edges and does not seem to have a thickness limit, as shown in Figure 1.5.2. 79 The graphitic Bernal stacking at these locations would compromise the 2D properties of graphene, causing local areas of decreased mobility. In addition, these areas are believed to contain a higher density of structural defects compared to growth on the (0001) plane. Therefore, these local areas of thicker material degrade the electronic properties of the entire film. 79
Figure 1.5.2: TEM micrographs of graphene on the (1\overline{1}00) step edge of SiC at 1425°C. a) Layer thickness appears to not be self-limiting from this face. b) Graphene layer termination suggests that the formation of graphene from step edges is the result of step erosion. c) Growth defects which produce discontinuous regions within a graphene layer.\(^{79}\)

Unlike graphene growth on the Si-face, C-face (SiC(000\overline{1})) sublimation is not self-limiting and occurs at much faster rates where the thickness increases with both time and temperature.\(^{70}\) C-face surface reconstruction is not well understood and the surface is believed to contain a mixture of domains (such as (2x2), (3x3), and (√3x√3)) prior to graphene production.\(^{70}\) Above 1200°C, the hexagonal graphene LEED pattern is fully developed, and like Si-face growth, is rotated 30° relative to the SiC surface.\(^{70}\) However, there is no evidence of a (6√3x6√3)R30 diffraction pattern.\(^{70,75}\) Due to the lack of the (6√3) surface reconstruction, the interaction between the graphene and the SiC(000\overline{1}) face is much weaker than the respective interaction on the Si-face.\(^{75}\) In addition, the stacking between graphene layers does not follow the
AB Bernal stacking sequence observed on the Si-face. Instead, rotational faults between layers give rise to a large inter-layer spacing.\textsuperscript{70} Therefore, each graphene layer acts as an isolated graphene sheet, rather than a multi-layer graphitic structure. Consequently, the 2D properties of each layer are preserved, explaining the high mobilities obtained from C-face graphene.\textsuperscript{75}

Another difference between Si-face and C-face growth is the nucleation mechanisms. It was previously stated that graphene nucleates from step edges on the Si-face. Camara et al suggests that C-face graphene growth initializes from defects from which silicon is easily desorbed.\textsuperscript{80,81} Figure 1.5.3 shows an SEM image of graphene nucleating from a defective site. This defect could be a crystallographic defect such as a dislocation or it could be an imbedded particle or a scratch.\textsuperscript{80} Unlike Si-face growth where steps recede and produce step bunches with significantly larger step heights, leading to surface roughening of both the SiC substrate and the graphene layers, AFM has shown that the pre-graphitized step density of SiC is preserved during C-face sublimation.\textsuperscript{70} Therefore, it can be concluded that graphene does not form from receding step edges, but rather in islands propagating from local areas of enhanced growth (i.e. defective regions).\textsuperscript{75,80,81} Because of this nucleation mechanism, the main issue associated with C-face graphene growth is that the thickness is non-uniform across the wafer. Local areas of enhanced growth will result in thicker graphene regions, making device patterning difficult.\textsuperscript{80,81}
Figure 1.5.3: SEM images of a monolayer graphene island grown on the C-face of an 8° off-axis 4H-SiC substrate. The nucleation occurs from a defect.80

In summary, sublimation from the Si-face of SiC results in one to few layer graphene with relatively uniform thickness while C-face sublimation results in multi-layer graphene with a non-uniform thickness. However, because of the formation of a $(6\sqrt{3})$ surface reconstruction for Si-face growth prior to growth, the graphene layers are strongly influenced by the properties of the interfacial region between the graphene and the substrate. Consequently, the mobilities are much lower for Si-face graphene than reported for exfoliated graphene and graphene grown on the C-face of SiC. In addition, enhanced growth rates at step edges of Si-face SiC results in local areas of thickness non-uniformity, and thus degraded electronic properties.
1.5.2: Quasi-Freestanding Epitaxial Graphene

As mentioned in the previous section, growth of epitaxial graphene on the Si-face (0001) of SiC results in the formation of a $(6\sqrt{3} \times 6\sqrt{3}) R30^\circ$ buffer layer, where about 30% of its carbon atoms are covalently bound to the SiC substrate, as shown in Figure 1.5.4a. Upon further sublimation, the first electrically active graphene layer forms above the $6\sqrt{3}$ buffer layer, as shown in Figure 1.5.4b. This layer is heavily influenced from being in close proximity with the $6\sqrt{3}$ buffer layer and experiences significant electron doping ($n \approx 10^{13} \text{cm}^{-2}$) as well as remote charged impurity scattering, significantly degrading epitaxial graphene’s transport properties. However, this covalent bonding between the SiC substrate and the $6\sqrt{3}$ buffer layer can be passivated through a process known as hydrogen intercalation. Here, hydrogen atoms terminate the interfacial Si bonds and decouple the $6\sqrt{3}$ buffer layer from the SiC substrate, forming electronically isolated single layer (Figure 1.5.4c) or bi-layer (Figure 1.5.4d) quasi-freestanding epitaxial graphene (QFEG).
Figure 1.5.4: Side-view model of (a) $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ buffer layer, (b) as-grown epitaxial graphene monolayer, (c) decoupling of $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ buffer layer after hydrogen intercalation to form monolayer QFEG, and (d) decoupling of the monolayer after hydrogen intercalation to form bi-layer QFEG.\textsuperscript{82}

Following thermal sublimation of SiC to form epitaxial graphene, hydrogenation can be performed through annealing at 600-1200°C near atmospheric pressure for 30-120 minutes in molecular hydrogen.\textsuperscript{82,83} At lower temperatures only partial hydrogenation occurs, while at higher temperature (>900°C) the buffer layer is fully decoupled from the SiC substrate.\textsuperscript{83} Following hydrogenation, Robinson et al found a complete elimination of the Raman D-peak of graphene (~1360cm\textsuperscript{-1}) and significant improvements in the transport properties over as-grown epitaxial graphene, where improvements in mobility of ~2.5x (from 800 to 2000cm\textsuperscript{2}/V-s at a carrier density of ~1x10\textsuperscript{13}cm\textsuperscript{-2}), transistor current saturation of ~1.7x (from 750 to >1300mA/mm), transconductance of ~2.3x (from 175 to >400mS/mm), and extrinsic cut-off frequency ($f_T$) improvements of ~3.2x (from 2.3 to 7.3 GHz-μm) were obtained.\textsuperscript{83} By decoupling the graphene from its native substrate, the improvement in transport properties is a result of reduced scattering from the SiC substrate, primarily from remote charged impurities and (to a lesser degree) surface
optical phonons. The mechanisms for hydrogen intercalation of epitaxial graphene remain unclear, although Riedl et al propose that hydrogen may either pass directly through the graphene layer, through grain boundaries, or through defects.\textsuperscript{82} Additionally, it was found that the hydrogen intercalation of QFEG remains stable over presumably indefinite periods of time in ambient conditions.\textsuperscript{82}

Interestingly, the majority carrier type of QFEG changes from n-type (found in as-grown epitaxial graphene) to p-type. For as-grown epitaxial graphene, n-type doping is a result of bonding of the $6\sqrt{3}$ buffer layer to Si atoms which results in a density of interface states that is positively charged, thus acting as donor-like states that electrostatically induce a negative charge in graphene.\textsuperscript{84} Therefore, despite the fact that Fermi statistics yield a theoretical doping value of $n_0=6.1 \times 10^{10} \text{cm}^{-2}$, an electron doping over two orders of magnitude larger than $n_0 (>1 \times 10^{13} \text{cm}^{-2})$ is typically observed.\textsuperscript{84} When the $6\sqrt{3}$ buffer layer is intercalated by hydrogen however, the density of positively charged states is passivated.\textsuperscript{84} P-type doping is thus induced in QFEG through the intrinsic spontaneous polarization of the hexagonal SiC substrate, where the polarization vector opposes the primary c-axis direction. This polarization of the SiC substrate acts as a sheet of acceptor-like states which induce p-type doping in QFEG, typically on the order of ~$5-10 \times 10^{12} \text{cm}^{-2}$.\textsuperscript{84} Although these interface states act to dope the QFEG just as the negatively charged interface states dope the non-hydrogen intercalated EG, a dramatic decrease in remote charged impurity scattering is found for QFEG samples. The reduction in remote charged impurity scattering leads to a 2-3x increase in transport properties, suggesting that passivation of dangling bonds within the buffer layer is a key step to improved transport properties for epitaxially grown graphene and highlighting the importance of buffer layer passivation through hydrogen intercalation. Additionally, a reduction in surface optical phonon scattering is found for QFEG.
1.5.3: CVD Graphene on Transition Metals

In contrast to epitaxial graphene, where the carbon source is intrinsically present in the SiC substrate, the carbon precursor for CVD graphene on transition metals is typically a hydrocarbon such as methane (CH$_4$). Synthesis typically takes place at temperatures between 900-1050°C and pressures usually no more than a few hundred millitorr.\textsuperscript{66,67} Though graphene has been successfully synthesized on various transition metal surfaces, Cu and Ni remain the most common and well understood. CVD synthesis of graphene on Ni substrates typically results in the formation of multi-layer graphene, where the layer thickness is often non-uniform over the sample surface.\textsuperscript{66} Contrarily, graphene growth on Cu substrates appears to be self-limiting to one or two layers and results in a uniform thickness over large areas.\textsuperscript{67} This contrast between Cu and Ni substrates is due to their different solid solubilities of carbon atoms, where carbon solubility in Ni and Cu is ~0.9 and ~0.0001 atomic % at 900°C, respectively.\textsuperscript{85} This leads to two different growth mechanisms for graphene growth via CVD on Ni and Cu. The two possible growth mechanisms are surface segregation and precipitation, and surface absorption, as detailed in Figure 1.5.5.
Figure 1.5.5: Schematic of graphene growth using different C isotopes to reveal the growth mechanisms of CVD graphene on Ni and Cu. The two possible mechanisms are (a) surface segregation and precipitation, such as for graphene growth on Ni, and (b) surface absorption, such as for graphene growth on Cu.85

Through carbon isotope labeling, Li et al were able to reveal the growth mechanisms of CVD graphene on Ni and Cu.85 Here, they introduced normal methane (\(12\text{CH}_4\)) and methane containing the \(13\text{C}\) isotope (\(13\text{CH}_4\)) at separate times during the growth process. Due to the fact that \(12\text{C}\) and \(13\text{C}\) have slightly different Raman modes, Raman mapping could easily be used to identify the presence of graphene deposited with \(12\text{CH}_4\) or \(13\text{CH}_4\). As shown in Figure 1.5.5, if surface segregation and precipitation occur, both \(12\text{C}\) and \(13\text{C}\) isotopes will diffuse into the metal, segregate randomly, and precipitate upon cooling. This would result in a graphene film where the \(12\text{C}\) and \(13\text{C}\) isotopes are randomly mixed.85 This mechanism is expected for metals having high carbon solubility, such as Ni, and generally leads to multilayer graphene due to the high amount of carbon diffused into the metal. For a metal that does not have high carbon solubility, such as
Cu, the carbon atoms will not diffuse into the metal, and instead will grow via surface absorption. This mechanism will result in a graphene film with discrete areas of each carbon isotope, depending on the dosing sequence, and is expected to result in one to few layer graphene.\textsuperscript{85} Utilizing Raman mapping of graphene films grown with the carbon isotope labeling method, Li et al were indeed able to show that graphene growth on Ni occurs via surface segregation and precipitation, and growth on Cu occurs via surface absorption.\textsuperscript{85} Therefore, due to its self-limiting growth via surface absorption, Cu is generally accepted as the preferred substrate for CVD graphene synthesis.

Often, graphene growth on Cu results in domain sizes limited to a few tens of micrometers.\textsuperscript{85,86} These domain boundaries contain defects that disrupt the sp\textsuperscript{2} bonding nature of graphene and were found to easily react with surface adsorbates or deposited dielectric materials, thus making them detrimental to graphene’s transport properties.\textsuperscript{86} In another work, Li et al demonstrated that by using a Cu enclosure, large domains could be obtained.\textsuperscript{87} The enclosure was formed by bending a 25\textmu m thick Cu foil in half and crimping the three remaining sides. Graphene growth on the outside of the Cu enclosure resulted in domain sizes similar to those reported previously. However, graphene growth on the inside of the enclosure resulted in a lower density of graphene nuclei and, consequently, domains up to 0.5mm in diameter.\textsuperscript{87} Li et al propose that this contrast in domain size from the outside of the Cu enclosure to the inside is due to a reduced partial pressure of methane due to an improved growth environment, where Cu vapor is in a static equilibrium and reduces the partial pressure of all other gas-phase species.\textsuperscript{87}

In summary, synthesis of graphene via CVD on transition metals can proceed via different growth mechanisms depending on the choice of transition metal substrate. It was found that growth via surface absorption on Cu results in uniform and self-limiting one-to-few layer graphene. Additionally, use of a copper enclosure resulted in an improvement in the domain size of graphene films. Here, a copper overpressure resulted in a decreased methane partial pressure,
ultimately leading to a reduced nuclei density and domains approaching 0.5mm. Mobilities >4000cm²/V-s were obtained from the large domain CVD graphene film. However, these mobilities remain significantly less than those obtained from exfoliated graphene. Therefore, continued work is required in the area of CVD graphene synthesis on Cu.

1.6: Dielectric – Graphene Scattering Mechanisms

One of the key limitations to the realization of graphene’s full potential comes from its interaction with dielectric interfaces, which act to limit the excellent charge transport properties of graphene. Typically, top-gated graphene field effect transistors (GFETs) are fabricated with SiO₂ or one of various high-k gate dielectrics. Such dielectrics are usually grown either by atomic layer deposition (ALD) or deposited via electron-beam physical vapor deposition, creating an imperfect electrical interface between graphene and dielectric. This low quality interface introduces extrinsic scattering from charged surface states, remote impurities, remote surface optical phonons (SOP), and substrate roughness, significantly degrading the transport properties of graphene. Besides these extrinsic scattering mechanisms induced by the dielectric environment, intrinsic scattering from acoustic and optical phonons in graphene must be taken into account as well. Therefore, the dominant scattering mechanism will depend on the quality of the graphene as well as its surrounding dielectric environment. Additionally, depending on the carrier concentration and temperature, the dominate scattering mechanism can vary between several mechanisms. Therefore, understanding charge scattering in graphene is a powerful tool for understanding growth and integration of graphene with other materials. The subsequent sections detail the primary scattering mechanisms induced in ideal monolayer graphene from the surrounding dielectric environment.
1.6.1: Surface Roughness Scattering

Surface roughness scattering is an intrinsic scattering mechanism found in graphene samples, which can be exacerbated by choice of substrate or top-gate dielectric. Graphene, being a 2D material, is naturally extremely flexible. Because of this, microscopic corrugations in the form of ripples with lateral sizes of several nanometers and heights of up to 1 nanometer are present on suspended graphene’s surface, as observed with transmission electron microscopy (TEM). Upon placing graphene on a substrate, such as SiO$_2$, the ripples can be enhanced in size due to increased wrinkling induced from the surface roughness of the underlying substrate.

Local perturbations in the graphene sheet resulting from ripples will cause a local change in the in-plane inter-atomic distances and the angles between the chemical bonds of nearest neighbor atoms. This leads to a change in the nearest-neighbor hoping behavior of electrons and, consequently, induces an electrostatic potential that fluctuates across the rippled graphene sheet. This potential increases with increased size of the ripple, where the magnitude of the vector potential can be described by Equation 1.6.1, where $z$ and $R$ are the height and radius of the ripple, respectively, and $a$ is the lattice constant, and $v_F \approx 10^6$ is the Fermi velocity.

$$\langle V_q V_{-q} \rangle \approx \left( \frac{\hbar v_F}{a} \right)^2 \frac{z^4}{R^2}$$

Equation 1.6.1

This potential induced from microscopic rippling in the graphene sheet then leads to a reduction in the mean-free path of electrons, as described by Equation 1.6.2, where $\tau$ is the mean-
free path, \( N(E_F) = \frac{2k_F}{\pi \hbar v_F} \) is the density of states at the Fermi level, and \( \langle V_q V_{-q} \rangle \) is the vector potential described in Equation 1.6.1.

\[
\frac{1}{\tau} \approx \frac{2\pi}{\hbar} N(E_F) \langle V_q V_{-q} \rangle
\]

Equation 1.6.2 \(^{101}\)

Ultimately, the contribution of these microscopic ripples to the total resistivity of graphene increases with increasing height and decreasing ripple radius, as shown in Equation 1.6.3.

\[
\delta \rho \approx \frac{\hbar}{4e^2} \frac{z^4}{R^2 a^2}
\]

Equation 1.6.3 \(^{101}\)

Intrinsic rippling in graphene thus creates a long-range scattering potential, similar to Coulombic scatterers, that results in a degradation of the mobility that is independent of carrier concentration. Rippling in a suspended graphene sheet is dynamic and can vary based on thermal fluctuations. However, once the graphene sheet is transferred (or deposited) onto a substrate, the van der Waals forces between the graphene and substrate pin the ripples, making the rippled configuration static. \(^{101}\) In addition, further perturbations in the graphene sheet can be induced by the substrate, where the size of the substrate-induced rippling is dependent on the substrate’s surface roughness. Therefore, based on the previously shown equations, a rougher substrate
surface would be expected to induced increased resistivity and decreased mobility to the graphene sheet. In this way, surface roughness scattering can be considered as both an intrinsic as well as extrinsic scattering mechanism, where choice of substrate can lead to enhanced surface roughness scattering and can thus be considered an extrinsic source of additional scattering.

### 1.6.2: Surface Optical Phonon Scattering

Surface optical phonon scattering is an extrinsic scattering mechanism that can be an important source of scattering for graphene samples after integration with a dielectric. Use of typical dielectrics (which are usually highly polar materials) with graphene and other 2D electronics results in electrostatic coupling of the charge carriers in graphene to the long-range polarization fields present at the graphene-dielectric interface. The induced electrostatic potential is primarily caused by high frequency (low energy) surface optical phonon modes (SOP) that propagate longitudinally and continuously over the dielectric surface in periods comparable to the material’s lattice constant. Scattering in graphene from SOPs is temperature dependent, where the contribution is negligible at low temperatures but significantly degrades graphene transport at room temperature. Fratini et al show that SOPs couple with the charge carriers of graphene with a coupling parameter that is proportional to the dielectric phonon frequency, as shown in Equation 1.6.4. Here, $g$ is the coupling strength, $\beta = (\varepsilon_s - \varepsilon_\infty)/(\varepsilon_s + 1)/(\varepsilon_\infty + 1)$ is a combination of the known dielectric constants of the substrate, $v_F \approx 10^6$ cm/s is the Fermi velocity, and $\omega_s$ is the lowest surface optical phonon mode (meV) of the dielectric, and $a$ is the lattice spacing.
This coupling strength is directly proportional to the phonon energy. However, the scattering rate (inverse of scattering time) is directly proportional to the coupling strength ($g$) and $e^{-\omega_s/T}$, giving a non-monotonic dependency of scattering rate on SOP energy that decreases exponentially for larger SOP modes, as shown in Equation 1.6.5, where $\tau_{SO}$ is the time between scattering events (seconds) associated with SOP scattering and $T$ is the temperature (K). Therefore, the transport properties of graphene will be degraded most by materials with a lower SOP mode, despite the fact that the coupling strength is weaker for lower SOP modes. Additionally, materials with multiple SOP modes (SiO$_2$ for example has a SOP mode at 59meV and 155meV) will experience the highest contribution from SOP scattering from the material’s lowest SOP mode.

\[
\frac{1}{\tau_{SO}} \propto g e^{-\omega_s/T}
\]

Equation 1.6.5$^{100}$

From this explanation, it can be shown that the conductivity of single layer graphene is inversely proportional to the scattering rate ($\frac{1}{\tau_{SO}}$) in Equation 1.6.6, where $n_F$ is the Fermi function for electrons. For bilayer graphene, the integral of Equation 1.6.6 will have an additional factor
(2ω/t┴, where t┴ =0.35eV is the interlayer hoping parameter) arising from the parabolic band dispersion.

\[ \sigma = \frac{e^2}{h} \int d\omega |\omega| R_{tr}^{-1}(\omega)\left(-\frac{dn_F}{d\omega}\right) \]

Equation 1.6.6

Figure 1.6.1 shows the resistivity, calculated from Equation 1.6.6, of single layer graphene vs. temperature at a constant SOP mode of 100meV. The inset shows conductivity vs. SOP energy for a constant temperature of 300K and shows the comparison to bilayer graphene (dotted line).

Figure 1.6.1: Resistivity vs temperature for a SOP mode of 100meV. Inset: Conductivity vs SOP energy for a constant temperature of 300K. The dotted line indicates bilayer graphene.
The contribution of SOP scattering to the low-field mobility was determined by Perebeinos et al and is shown in Equation 1.6.7.\textsuperscript{105} Here, \( z_0 \approx 3.5\text{Å} \) is the van der Waals distance between the graphene and the dielectric substrate, \( N_{\text{SOP}} \) is the occupation number of the SOPs, \( \beta \approx 0.0115 \) is a global fitting parameter, and \( k_0 \approx \sqrt{\left(\frac{2\omega_{\text{SOP}}}{v_F}\right)^2 + \alpha n} \), where \( \alpha \approx 10.5 \).\textsuperscript{105} Additionally, the low-field mobility is a non-monotonic function of the carrier density, \( n \), and the \( F_v^2 \) term describing the magnitude of the polarization field is called the Frohlich coupling parameter and is analogous to the coupling strength, \( g \), detailed previously in Equation 1.6.4 by Fratini et al.\textsuperscript{100}

\[
\mu_{\text{SOP}} \approx \beta \frac{\hbar v_F e v_F \exp(k_0 z_0)}{e^2 F_v^2 N_{\text{SOP}} \sqrt{n}}
\]

\textit{Equation 1.6.7\textsuperscript{105}}

The total mobility of single layer graphene on various substrates can then be approximated by summing the extrinsic mobility contributions from all SOP modes of the dielectric, as well as the mobility contributions from the intrinsic acoustic phonons and optical phonons of graphene, \( \mu_{\text{ac}} \) and \( \mu_{\text{op}} \), respectively.\textsuperscript{105} Therefore, the total mobility can be approximated by the Boltzmann transport equation (BTE) and yield Equation 1.6.8.

\[
\mu^{-1} = \mu_{\text{ac}}^{-1} + \mu_{\text{op}}^{-1} + \sum \mu_{\text{SOP}}^{-1}
\]

\textit{Equation 1.6.8\textsuperscript{105}}
Therefore, literature has shown that the scattering induced into graphene from SOPs is primarily dependent on the SOP mode, where lower SOP energies will result in a greater degradation in the transport properties of graphene. To compare different dielectric materials, the lowest surface optical phonon mode (which will have the highest contribution to SOP scattering) for various dielectric materials are shown in Table 1.6.1.

**Table 1.6.1:** Lowest surface optical phonon modes for various dielectrics.

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<tr>
<th>Dielectric Material</th>
<th>Lowest Surface Optical Phonon Energy (meV)</th>
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<td>h-BN</td>
<td>169.7</td>
<td>Serrano et al&lt;sup&gt;106&lt;/sup&gt;</td>
</tr>
<tr>
<td>SiC</td>
<td>116</td>
<td>Fratini et al&lt;sup&gt;100&lt;/sup&gt;</td>
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<tr>
<td>AlN</td>
<td>83.6</td>
<td>Konar et al&lt;sup&gt;104&lt;/sup&gt;</td>
</tr>
<tr>
<td>ZrSiO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>60</td>
<td>Perebeinos et al&lt;sup&gt;107&lt;/sup&gt;</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>59.98</td>
<td>Konar et al&lt;sup&gt;104&lt;/sup&gt;</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>55.01</td>
<td>Konar et al&lt;sup&gt;104&lt;/sup&gt;</td>
</tr>
<tr>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>25.02</td>
<td>Konar et al&lt;sup&gt;104&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

**1.6.3: Charged Impurity Scattering and Dielectric Screening**

Dangling bonds and absorbed impurities at or near the dielectric-graphene interface can introduce scattering in the form of long-range, unscreened, Coulombic scatterers.<sup>98,99,104</sup> Scattering from charged impurities results in a conductivity that is linearly dependent on the carrier concentration, leading to a constant mobility away from the Dirac point for both monolayer and bilayer graphene.<sup>98</sup> Additionally, charged impurity scattering results in mobilities that are independent of temperature due to the unique dispersion relationship in graphene.<sup>98</sup> The distance between the graphene layer and the remote charged impurities also has an effect on conductivity, as shown in Figure 1.6.2, where the charged impurities are considered as an impurity layer located a distance d from the graphene-dielectric interface.
Figure 1.6.2: Effect of the ratio of charge carrier density (n) to impurity concentration (n_i) on the conductivity of graphene as a function of distance (d) between the graphene layer and the 2D impurity layer.\(^{98}\)

Equation 1.6.9 gives the scattering rate, calculated by Konar et al, due to charged impurities \(\left(\frac{1}{\tau_{\text{imp}}(k)}\right)\), where \(n_{\text{imp}}\) is the density of charged impurities at or near the graphene-dielectric interface and \(\varepsilon_{\text{avg}}\) is the average dielectric constant of the environment surrounding the graphene layer, i.e. \(\varepsilon_{\text{avg}} = (\varepsilon_{\text{top}} + \varepsilon_{\text{bottom}})/2\).\(^{104}\)

\[
\frac{1}{\tau_{\text{imp}}(k)} = \frac{n_{\text{imp}}}{\pi \hbar} \left(\frac{e^2}{2\varepsilon_0 \varepsilon_{\text{avg}}}\right)^2 F(\alpha) \frac{F(k)}{\varepsilon(k)}
\]

Equation 1.6.9\(^{104}\)
Therefore, it is apparent that the contribution of charge impurities to the scattering rate is not only a function of the charged impurity concentration, but also a function of the dielectric environment around graphene. Additionally, from Equation 1.6.9, it is clear that the scattering rate can be significantly reduced through the use of a high-k dielectric with graphene electronics, in a phenomena known as dielectric screening. However, despite the ability to screen charged impurity scattering, high-k dielectrics ultimately lead to increased scattering due to their lower SOP modes, as shown in Figure 1.6.3.

Figure 1.6.3: Scattering rate vs SOP absorption energy for various dielectrics. Higher dielectric constants result in increased scattering from SOPs.

Figure 1.6.4 shows the modeled mobility for five different dielectric materials, where the solid red line indicates the expected mobility enhancement if SOP scattering were completely...
neglected. Here the mobility ($\mu = \sigma/ne$) is calculated from the conductivity ($\sigma(T) = \frac{e^2}{h}2v_Fk_F\tau$), where $\tau$ is obtained from Equation 1.6.9 and $k_F$ is the Fermi wave vector. The modeled improvement in mobility due to dielectric screening of charged impurities is effectively countered by the increased SOP scattering (filled circles), where a constant temperature of 300K, impurity density of $n_{imp}=5\times10^{11}\text{cm}^{-2}$, and a carrier concentration of $n=10^{12}\text{cm}^{-2}$ were used. Here the total mobility, taking SOP scattering and charged impurity scattering into account, is calculated from $\tau_{tot} = (\tau_{SOP}^{-1} + \tau_{imp}^{-1})^{-1}$.\textsuperscript{104}

![Figure 1.6.4](image.png)

**Figure 1.6.4:** Mobility of graphene for five different dielectric substrates. The solid red line indicates the modeled behavior of increased mobility with increasing dielectric constant. However, when SOP scattering (filled circles) is taken into consideration, the mobilities are significantly reduced.\textsuperscript{104}
Due to the fact that SOP scattering is temperature dependent and charge impurity scattering is temperature independent, the expected degradation in mobility of high-k dielectrics due to SOP scattering is expected to decrease at lower temperatures. Figure 1.6.5 shows this effect.

**Figure 1.6.5:** Mobility of graphene on various substrates as a function of temperature. At low temperatures, dielectric screening allows high-k materials to experience high mobilities. However, at higher temperatures SOP scattering begins to degrade mobility.\(^{104}\)
At low temperatures, the use of a high-k dielectric can result in mobility improvements of ~4x (using ZrO$_2$) due to the reduced contribution from SOP scattering and the enhanced contribution from dielectric screening, where ZrO$_2$, Al$_2$O$_3$, HfO$_2$, AlN, and SiO$_2$ have dielectric constants of 24.0, 12.53, 22.0, 9.14, and 3.9, respectively. However, at room temperature, the mobilities of graphene on the high-k dielectrics are significantly degraded compared to lower-k dielectrics, such as SiO$_2$ and AlN, due to the increased scattering from SOPs in high-k materials.$^{104}$

1.7: Hexagonal Boron Nitride as a Dielectric Material for Graphene Devices

One promising dielectric for potential integration with graphene is hexagonal boron nitride (h-BN), an insulating isomorph of graphene with a lattice mismatch of approximately 1.7%.$^{108}$ Though it has dielectric properties similar to SiO$_2$ ($\varepsilon \approx 4$, $V_{\text{Breakdown}} \approx 0.7 \text{ V/nm}$),$^{109}$ h-BN has several key advantages. One of these advantages is an atomically smooth surface. Not only does the h-BN surface have a reduced surface roughness, having an RMS roughness of 50pm for exfoliated h-BN (compared to 250pm for SiO$_2$),$^{110}$ but it is also expected to be free of dangling bonds due to its strong in-plane covalent bonding and weak inter-planar van der Waals bonds.$^{111}$ Therefore, compared to other dielectrics, the interface between graphene and h-BN is expected to exhibit a low density of charge traps and adsorbed impurities that may act as remote ionized impurity scatterers. Another advantage to h-BN is that it possesses high energy surface optical phonon modes,$^{109}$ as shown in comparison to other common dielectrics in Figure 1.7.1.
Figure 1.7.1: Graphical representation of Table 1.6.1 showing a comparison of the lowest surface optical phonon modes of various dielectrics.

Therefore, h-BN is expected to incorporate less remote surface optical phonon scattering into graphene compared to high-k dielectrics and SiO$_2$. Both ionized impurities and surface optical phonons can induce scattering in graphene, as described in Section 1.6. Therefore, h-BN theoretically has a significant advantage to high-k dielectrics, despite the fact that it has a dielectric constant similar to SiO$_2$. 
1.7.1: Novel Properties of Graphene/h-BN Heterostructures

Heterostructures composed of various 2D conducting, semi-conducting, and insulating materials have attracted considerable interest in recent years. Of these 2D material systems, the graphene/h-BN heterostructures have become one of the most important and well documented, due to h-BN being an insulating isomorph of graphene. Besides the well documented benefits of reduced charge carrier scattering in graphene, the use of h-BN as a supporting substrate has resulted in reports of novel electrical properties, such as a fractional quantum Hall effect with an anomalous Landau gap\textsuperscript{112} and unique superlattice Dirac points.\textsuperscript{113} Additionally, it has been shown that the mean free path of electrons in graphene encapsulated in h-BN can be on the order of several micrometers due to the reduced scattering from the h-BN dielectric environment.\textsuperscript{114}

Theoretical computation methods, such as density functional theory (DFT) and local density approximation (LDA) have been used to model the electronic structure of graphene/h-BN heterostructures.\textsuperscript{108,115} It was found that total energies of the heterostructures is dependent on the stacking geometries of h-BN and graphene layers and can influence the electronic structure of the superlattice. Sakai et al investigated several stacking geometries and found that the configuration analogous to AB stacking of graphite, where the B atoms of h-BN are directly under the C atoms of graphene and the N atoms are directly under the center of the hexagonal graphene ring (denoted as the Ab configuration), was the most stable among various configurations.\textsuperscript{115} Even more, Giovannetti et al found that this stacking sequence resulted in the opening of a bandgap in graphene of 53meV at the Dirac point, leading to a finite effective mass for Dirac fermions in graphene.\textsuperscript{108} This is due to the interaction of graphene with the h-BN substrate, which has inequivalent B and N sublattices. Consequently the symmetry between graphene’s two equivalent carbon sublattices is broken, resulting in the formation of a bandgap, which has significant implications for improving the cut-off frequency of graphene-based electronics. Alternative
stacking configurations of graphene/h-BN also induce bandgaps, however these were smaller than that obtained with the Ab configuration. Additionally, Sakai et al found that a superlattice of alternating bilayer h-BN and graphene layers in the Ab configuration resulted in an electron effective mass of 0.015$m_e$. Interestingly, this effective mass is less than that of freestanding bilayer graphene ($m_e^\# = 0.019m_e$). The reduced effective mass and formation of a bandgap in graphene indicate excellent potential for novel semiconducting devices using Ab configured graphene/h-BN superlattices.

Experimentally, it was found through scanning tunneling microscopy (STM) that the local electronic properties of graphene varied depending on substrate choice. It was found that graphene on h-BN had a more homogeneous adhesion compared to graphene on SiO$_2$, where several areas were partially suspended locally, causing the STM tip to vibrate and become unstable. Additionally, the RMS roughness measured via STM for graphene on SiO$_2$ and h-BN was 1.5-2.0Å and 0.02-0.17Å, respectively. Importantly, it was found that the charge density distribution of graphene on SiO$_2$ was significantly more inhomogeneous than for graphene on h-BN, as shown in Figure 1.7.2, where a ~3.5x (RMS) increase in the charge density distribution values were found. This suggests that a smaller density of charged impurities is present on the graphene/h-BN sample compared to the graphene/SiO$_2$ sample. Additionally, differential conductance spectra obtained from STM indicates reduced electron-phonon and electron-electron scattering in the graphene/h-BN sample. However, the differential conductance spectra does not suggest an opening of a bandgap, as predicted previously, due to the random orientations obtained experimentally.
Figure 1.7.2: (a,b) Topography of graphene on h-BN (a) and SiO₂ (b). (c,d) Charge density maps of graphene on h-BN (c) and SiO₂ (d).

Ahn et al report significant differences between the electronic interaction of graphene and h-BN and the interaction of graphene and SiO₂ through use of Raman spectroscopy. Here, it was demonstrated that Raman spectroscopy can be a simple and effect tool for detecting changes in Fermi velocity ($v_F$), strain, and charge carrier doping in graphene. It was observed that the Raman signal of graphene on h-BN was primarily affected by changes in $v_F$ and strain and that little doping occurred, unlike for graphene on SiO₂. The Raman 2D vs G peak and the 2D/G vs G peak for graphene on h-BN and SiO₂ are shown in Figure 1.7.3a and 1.7.3b, respectively.
Figure 1.7.3: (a) Correlation between the Raman 2D vs G peaks of graphene on h-BN (crosses) and SiO$_2$ (open circles). The blue and red colored data indicate two separate samples and the brown squares indicate Raman spectra of graphene on SiO$_2$ taken from various references. The inset shows the trajectories associated with compressive strain ($e_C$), tensile strain ($e_T$), hole doping ($e_H$), and Fermi velocity reduction ($e_{FVR}$). (b) 2D/G ratio vs G peak for graphene on h-BN and SiO$_2$.\textsuperscript{117}

The $v_F$ reduction is a result of van der Waals interlayer interactions, due to modulation in the dispersion of π and π* bands, and was found to only effect the 2D peak of graphene since the $E_{2G}$ (G peak) of graphene is not affected to a first-order approximation.\textsuperscript{117} Interestingly, the reduction in $v_F$ was not observed for graphene on SiO$_2$ due to reduced van der Waals interaction. However, apparent from Figure 1.7.3a, the hole doping in the graphene on h-BN samples is considerably less than that on SiO$_2$. Additionally, the 2D/G ratio of the graphene on h-BN samples in Figure 1.7.3b indicates similar values to that of charge-neutral graphene (denoted by
the green dot) while the 2D/G ratio of SiO$_2$ samples is much less, indicating hole doping, where the 2D/G ratio is sensitive to small changes in carrier concentration.\textsuperscript{117} Both the graphene on h-BN and SiO$_2$ samples are affected by strain, where the films were found to be slightly compressed at strains of $\sim$0.1\%.\textsuperscript{117} Importantly, these results indicate that Raman spectroscopy can be a useful tool for rapid analysis of the electronic interactions between graphene and various dielectric materials in terms of relative charge doping, strain, and $v_F$ reduction.

1.7.2: Effects of h-BN Dielectrics on Graphene Transport

Indeed, it has been shown extensively in the literature that h-BN, as a supporting substrate, can significantly improve the transport properties of exfoliated and CVD grown graphene compared to SiO$_2$ and high-k dielectrics.\textsuperscript{109,118,119} Wang et al demonstrated the fabrication of graphene field effect transistors (GFET) using h-BN/Graphene/h-BN heterostructures using exfoliated h-BN and bilayer graphene.\textsuperscript{110} The transport properties of these devices were then compared to GFETs fabricated with exfoliated bilayer graphene on thermally grown SiO$_2$ gated with a 16nm thick ALD deposited Al$_2$O$_3$ gate dielectric.\textsuperscript{110} A cross sectional schematic of both GFET structures is shown in Figure 1.7.4a.
Figure 1.7.4: Schematic cross-section of (a) the h-BN/graphene/h-BN GFET and (b) the \( \text{Al}_2\text{O}_3/\text{graphene/SiO}_2 \) GFET. (c) RF performance of both GFET structures showing their respective cut-off frequencies.\textsuperscript{110}

Compared to the \( \text{Al}_2\text{O}_3/\text{graphene/SiO}_2 \) GFET, the h-BN/graphene/h-BN GFET showed an improvement in transconductance of 70% (\( g_m \) increase from 140 mS/mm to 238 mS/mm) and an increase in transistor cutoff frequency (at a back-gate voltage of -30V) of nearly 2x (\( f_T \) increase from 18 to 33 GHz, where the gate length (\( L_G \) was 450nm) compared to the \( \text{SiO}_2 \) supported, \( \text{Al}_2\text{O}_3 \) gated GFET after an open-short de-embedding procedure.\textsuperscript{110} The extracted mobilities for the \( \text{Al}_2\text{O}_3/\text{graphene/SiO}_2 \) GFET and the h-BN/graphene/h-BN GFET were found to be 1200 and 6500 cm\(^2\)/V-s, respectively.\textsuperscript{110} Additionally, transfer curves (I\( _{DS} \) vs V\( _{GS} \)) of the h-BN/graphene/h-BN GFET indicate negligible doping effects from the surrounding h-BN dielectrics, as shown in Figure 1.7.5. Alternatively, the \( \text{Al}_2\text{O}_3/\text{graphene/SiO}_2 \) GFET not only
shows reduced current density and transconductance, but also a shift in the minimum conduction point, indicating hole doping from the dielectric environment.\textsuperscript{110}

\textbf{Figure 1.7.5:} DC characterization ($I_{DS}$ vs $V_{GS}$) of (a) h-BN/graphene/h-BN GFET and (b) Al$_2$O$_3$/graphene/SiO$_2$ GFET at $V_{DS} = 1V$.\textsuperscript{110}

Kim \textit{et al} also investigated the use of an h-BN supporting substrate for graphene synthesized via CVD.\textsuperscript{120} Here, h-BN flakes were exfoliated onto SiO$_2$ and CVD graphene was transferred over the h-BN flakes and SiO$_2$ substrate to compare GFETs fabricated on both substrates. Figure 1.7.6 shows the effective mobility vs carrier concentration (controlled through backgating) of CVD graphene on exfoliated h-BN and SiO$_2$. Use of h-BN results in a 3-4x increase in effective mobility compared to the SiO$_2$ substrate. Additionally, it was found that GFET channel scaling resulted in considerably higher mobilities, where scaling from 2µm to 500nm resulted in a $>10x$ increase in mobility for GFETs on h-BN at a carrier concentration of
$10^{12}\text{cm}^2$, due to the decreased resistance and increased channel current in short-channel devices.\textsuperscript{120}

**Figure 1.7.6:** Comparison of effective mobility as a function of carrier concentration between CVD GFETs on h-BN and SiO$_2$ substrates. Additionally, the effect of gate length scaling is shown.\textsuperscript{120}

Several other groups have also reported similar enhancement of transport properties of graphene (both exfoliated and CVD-grown) using h-BN dielectrics over SiO$_2$ and high-k dielectrics, as detailed in Table 1.7.1.
Table 1.7.1: Comparison of graphene transport data from various groups utilizing h-BN dielectrics.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Graphene Synthesis</th>
<th>h-BN Synthesis</th>
<th>Gate Length</th>
<th>$g_m$ (mS/mm)</th>
<th>$\mu$ (cm$^2$/V-s)</th>
<th>$n$ ($cm^{-2}$)</th>
<th>$\mu$ Increase over SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wang et al$^{110}$</td>
<td>Exfoliation</td>
<td>Exfoliation</td>
<td>450nm</td>
<td>238</td>
<td>6500</td>
<td>N/A</td>
<td>&gt;5x</td>
</tr>
<tr>
<td>Kim et al$^{120}$</td>
<td>CVD</td>
<td>Exfoliation</td>
<td>500nm</td>
<td>1040</td>
<td>18000</td>
<td>$10^{12}$</td>
<td>3-4x</td>
</tr>
<tr>
<td>Gannet et al$^{119}$</td>
<td>CVD</td>
<td>Exfoliation</td>
<td>N/A</td>
<td>N/A</td>
<td>28800</td>
<td>N/A</td>
<td>3-4x</td>
</tr>
<tr>
<td>Meric et al$^{121}$</td>
<td>Exfoliation</td>
<td>Exfoliation</td>
<td>500nm</td>
<td>400</td>
<td>10000</td>
<td>$2.2 \times 10^{11}$</td>
<td>&gt;2x</td>
</tr>
<tr>
<td>Dean et al$^{109}$</td>
<td>Exfoliation</td>
<td>Exfoliation</td>
<td>N/A</td>
<td>N/A</td>
<td>25000</td>
<td>N/A</td>
<td>&gt;3x</td>
</tr>
<tr>
<td>Lee et al$^{39}$</td>
<td>CVD</td>
<td>CVD</td>
<td>2µm</td>
<td>N/A</td>
<td>573</td>
<td>$2 \times 10^{11}$</td>
<td>3x</td>
</tr>
</tbody>
</table>

In all examples listed in Table 1.7.1, the h-BN layer used for the gate dielectric was multi-layer with thicknesses generally >10nm. This is due to the fact that excessive tunneling currents have been reported for h-BN dielectrics less than four layers thick.$^{42,43}$ In these reports, it was found through conductive atomic force microscopy (CAFM) that mono-, bi-, and tri-layer h-BN samples show significant conduction, even at low bias, due to direct tunneling. At four layers however, the films are insulating at low bias and show a sharp increase in conduction upon breakdown, where breakdown voltage increases with increasing thickness as shown in Figure 1.7.7.$^{43}$ Lee et al showed that the average breakdown voltage field (the voltage at which the current reached $10^{11}$A normalized by thickness) of the insulating h-BN films was 7.94MV/cm, which is similar to that of SiO$_2$ (8-10MV/cm).$^{43}$
Therefore, literature has consistently shown that h-BN as a supporting and gate dielectric can be advantageous for graphene device development, leading to significant improvements in graphene’s transport properties over conventional dielectrics. However, when used as a gate dielectric, the thickness of the h-BN layer needs to be considered as tunneling currents can become problematic for atomically thin films (<4 layers). Additionally, focus to-date has been limited to h-BN integration with CVD or exfoliated graphene. The effects of h-BN on epitaxial graphene, which is more conducive to large scale high performance electronics and commercialization, have not yet been investigated.
Chapter 2

Equipment and Experimental Procedures

2.1: Experimental Materials and Substrate Cleaning Process

Hexagonal boron nitride was grown via CVD on copper foils, silicon, and sapphire substrates. In all cases, ammonia borane (NH$_3$BH$_3$) was used as the precursor for h-BN growth. The ammonia borane used in this study was purchased from Sigma Aldrich (part #682098) and had a listed purity of 97%. For all growths (unless stated otherwise), 200mg of ammonia borane was loaded into the sublimator in disposable aluminum carrier boats. The sublimation conditions and procedure will be discussed in the next section.

For growth of h-BN on copper substrates, 25µm thick 99.999% (metals basis) pure Cu foils (Alfa Aesar, part #10950) were used. Table 2.1.1 details the cleaning procedure for sample preparation, where room temperature (RT) is considered to be ~20°C. A simple solvent clean with acetone at 70°C for 10 minutes followed by isopropyl alcohol (IPA) at room temperature for 2 minutes was used to remove organic contamination from the Cu surface. Following a DI water bath, the samples were placed in acetic acid (Glacial, JT Baker, part #9503-05) diluted to 20% in DI water to remove the native copper oxide. The samples were held in the dilute acetic acid at 70°C for 10 minutes, then placed in a DI water bath for 2 minutes to remove residual acetic acid. The Cu samples were blown dry with nitrogen and loaded into the tube furnace via a quartz sample boat immediately after cleaning to reduce re-growth of the native copper oxide. The size of the copper foils varied depending on the desired use of the h-BN films. For general materials characterization and process optimization, 1x1cm$^2$ samples were used for eventual transfer to arbitrary substrates for various characterizations. For development of quasi-
freestanding epitaxial graphene (QFEG) devices utilizing h-BN gate dielectrics, samples as large as 5x5cm$^2$ were grown.

<table>
<thead>
<tr>
<th>Step</th>
<th>Chemicals</th>
<th>Temperature</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetone</td>
<td>70°C</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>IPA</td>
<td>RT</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>DI Water</td>
<td>RT</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>Acetic Acid (20%)</td>
<td>70°C</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>DI Water</td>
<td>RT</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 2.1.1: Cleaning procedure for copper foils

For direct growth of h-BN on silicon and sapphire substrates, a variation on the cleaning procedure was implemented and is shown in Table 2.1.2. The solvent cleaning, using acetone and IPA, was again used for initial removal of organic residues from the substrates. However, a more aggressive cleaning step utilizing Nanostrip 2x (Cyantek, part #539400), which is a stabilized mixture of sulfuric acid and hydrogen peroxide compounds, was used to remove stubborn organics and ionic contamination. For the sapphire samples, the cleaning process was complete after the Nanostrip 2x step and a subsequent DI water bath. For the silicon samples however, the native oxide had to be removed via a hydflouric acid step. Therefore, a 10:1 buffered oxide etch (BOE) (JT Baker, part #5175-03) solution was utilized, where the Si samples were soaked for 1 minute before being immediately placed in DI water bath to remove residual BOE solution. Both the sapphire and Si samples were dried with nitrogen and placed immediately in the tube furnace to reduce re-growth of silicon’s native oxide and general exposure to ambient conditions.
### Table 2.1.2: Cleaning procedure for Si and Al₂O₃ substrates

<table>
<thead>
<tr>
<th>Step</th>
<th>Chemicals</th>
<th>Temperature</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetone</td>
<td>70°C</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>IPA</td>
<td>RT</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>DI Water</td>
<td>RT</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>Nanostrip 2x</td>
<td>90°C</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>DI Water</td>
<td>RT</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>HF: 10:1 BOE (Si only)</td>
<td>RT</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>DI Water</td>
<td>RT</td>
<td>2</td>
</tr>
</tbody>
</table>

### 2.2: Boron Nitride CVD Furnace Design and Operation

Boron nitride was grown via CVD in hot-wall tube furnaces, utilizing quartz tubes. Two tube furnaces, with a 3” and 1” nominal tube diameter, were utilized for film growth for this thesis. The 3” tube furnace employed for this work was a Lindberg/Blue M STF-55666C 3-zone tube furnace with a maximum temperature of 1100°C. This furnace had a heating length of 36” and can accommodate a maximum tube diameter of 6”. The 3” tube furnace was used for large scale growth, such as for integration with 75mm quasi-freestanding epitaxial graphene (QFEG) wafers. Additionally, this furnace was used for all the direct growth runs on sapphire and silicon. The 1” tube furnace used in this work was a single zone Lindberg/Blue M “Mini-mite”. This furnace had a heating length of 12” and a maximum temperature of 1100°C. The 1” furnace was utilized (due to its split hinge design) for its faster cooling rate, allowing a higher through-put of samples. Therefore, this furnace was used for h-BN growth on 1x1cm² copper foils where a large number of runs were required for process-property analysis.

Both furnaces used an identical process flow, where the schematics and associated component list are shown in Appendix A. The process consists of a single ultra high purity (UHP) carrier gas source (H₂/N₂, 15% H₂), which splits to feed into two mass flow controllers (MFC). One MFC feeds directly into the furnace and acts as a dilution flow to dilute the ammonia borane.
precursor. The second MFC feeds into a “sublimator”, which consists of a KF-40 flanged tee wrapped in heat tape and contains the solid ammonia borane precursor. The heating of the sublimator is controlled via a Watlow SD31 PID controller, where the sublimation temperature of ammonia borane was maintained at 135°C for all growth runs. Table 2.2.1 details the operation procedure for the sublimation of ammonia borane. This temperature control process, as well as a constant sublimation pressure of ~100 Torr (maintained via a needle valve downstream of the sublimator), was kept standard for all growth runs, since the heating rate and sublimation pressure have been shown to affect the sublimation kinetics of ammonia borane, as detailed in Section 1.3.

**Table 2.2.1:** Temperature set points and operating procedure of Watlow SD31 PID controller for ammonia borane sublimation process.

<table>
<thead>
<tr>
<th>Step</th>
<th>Set Temperature (°C)</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>55</td>
<td>Initiated with 35 minutes left in pre-growth anneal</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>Set when sublimation temperature reaches 80°C upon overshoot</td>
</tr>
<tr>
<td>3</td>
<td>110</td>
<td>Initiated with 10 minutes left in pre-growth anneal</td>
</tr>
<tr>
<td>4</td>
<td>135</td>
<td>Set when sublimation temperature reaches 135°C upon overshoot</td>
</tr>
</tbody>
</table>

Heating of the sublimator begins when there is 35 minutes remaining in the pre-growth anneal (sample annealing will be discussed in the next section). The first input temperature to the Watlow SD31 PID controller is 55°C. The heating tape, being rated for high temperatures (up to 700°C), easily overshoots this temperature despite the fact that the input power to the heat tape is restricted via a variable temperature switch (McMaster.com part #35655K89). The sublimator temperature will overshoot to ~80°C, at which point the Watlow SD31 can be reset to 80°C. This temperature is held to remove residual water from the sublimator until there is 10 minutes remaining in the pre-growth anneal. At this point, sublimation is initiated by setting the Watlow
SD31 PID controller to 110°C, where the temperature will quickly jump to >135°C due to the exothermic reactions at ~110°C and ~125°C caused by the first and second weight loss steps, respectively, as discussed in Section 1.3. Once a temperature >135°C is reached, the Watlow SD31 is reset to 135°C and maintained at this temperature for the duration of the growth run. During the initial sublimation ramp, the sublimator is vented to the roughing pump via a vent line, as shown in Appendix A. This allows the initial hydrogen release, which results in a large spike in pressure (usually to >600 Torr) to stabilize. Once the sublimator pressure has returned to ~100 Torr and the pre-growth furnace anneal is complete, the ¼ turn valve to the vent line can be shut off and the ¼ turn valve to the furnace can be opened, where the gas-phase precursors mix with the dilution gas line and subsequently flow into the tube furnace for BN growth. All gas lines downstream of the sublimator and leading up to the tube furnace are heated with heat tape at a constant temperature of 150°C to prevent condensation of the gas-phase precursors on the insides of the ¼ stainless steel tubing.

2.3: CVD Growth Processes

2.3.1: Growth of h-BN on Copper Substrates

Hexagonal boron nitride is grown on 25µm thick, 99.999% pure Cu foils via a catalytic thermal CVD method utilizing a single ammonia borane (NH₃BH₃) precursor similar to previously reported methods. After cleaning, described in Section 2.1, the 10x10mm² Cu foils are loaded into a 25mm diameter tube furnace on a quartz boat. A pre-growth anneal is performed at 1000°C and 350mTorr for 2 hours to remove any additional oxide that may have re-grown following cleaning and to increase the grain size of the starting Cu surface via a thermal surface
reconstruction. For many growth runs, the Cu foils were encapsulated in a Cu enclosure by wrapping the boat and samples with 99.8% purity (Alfa Aesar, part #13382), shown in Figure 2.3.1. This resulted in a gas-phase Cu overpressure during the pre-growth anneal and growth processes, which led to a reduction in the amount of copper loss from the sample surface and an improvement in the starting grain size. Additionally, the Cu overpressure was used to improve the growth of h-BN, which will be discussed in later sections.

![Figure 2.3.1](image)

**Figure 2.3.1:** (a) Six 10×10mm² Cu foils on quartz boat over large Cu foil. (b) Large Cu foil folded over Cu samples to form enclosure. (c) Copper enclosure in 1” quartz tube furnace.

After the pre-growth anneal, the ammonia borane was introduced following sublimation, as described in Section 2.2. The growth time, pressure, and temperature were varied to give a range of parameters for a complete systematic study of h-BN growth via CVD on Cu foils. The parameter ranges are listed in Table 2.3.1. The parameters had a significant effect on the thickness of the h-BN films and will be discussed in detail in later sections.
Table 2.3.1: Growth parameter ranges for CVD growth of h-BN on Cu foils.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth Temperature</td>
<td>800 - 1050°C</td>
</tr>
<tr>
<td>Growth Pressure</td>
<td>0.250 – 5.0 Torr</td>
</tr>
<tr>
<td>Growth Time</td>
<td>2.5 – 60 mins</td>
</tr>
</tbody>
</table>

After growth is completed, the ammonia borane source is isolated from the process furnace by shutting off the ¼ turn valve to the tube furnace and opening the ¼ valve to the vent line. The furnace is shut off and the samples are allowed to slowly cool to room temperature under H₂/N₂ (15% H₂) flow. Figure 2.3.2 shows a pressure/temperature profile of a typical growth run, shown here with a two hour pre-growth anneal at 1000°C, a 30 minute growth at 1000°C, and a pressure of 0.25 Torr.

Figure 2.3.2: Pressure/Temperature profile of a typical growth run for BN synthesis on copper.
2.3.2: Growth of h-BN on Silicon and Al₂O₃

In addition to the catalytic growth of h-BN on transition metal substrates for use as a top-gate dielectric in graphene electronics, boron nitride films were also deposited onto Si(111) and Al₂O₃(0001) substrates directly, using a transfer-free deposition method. This method involves the initial deposition of a hydrogenated polymer precursor known as polyborazylene (B₃N₃Hₓ) and the subsequent ceramic conversion to boron nitride. This direct deposition method provides a means to deposit an h-BN supporting dielectric for CVD grown graphene that can also act as a back-gate dielectric when deposited on highly doped, conductive Si. Polyborazylene is synthesized from borazine through a dehydropolymerization process, detailed in Section 1.4, where initial hydrogen loss occurs between 125 and 300°C by means of a two-dimensional cross-linking reaction of B-H and N-H groups, forming the polymer polyborazylene. Upon further heating, a second hydrogen loss reaction occurs between 700-1100°C from unaligned chain branches of polyborazylene, forming h-BN. In this work, ammonia borane was again used as the precursor material to borazine upon sublimation at 135°C. The deposition of polyborazylene was performed under 100 Torr of H₂/N₂ (15% H₂) carrier gas at two temperatures, 250°C and 400°C. These two temperatures were selected to represent one temperature within the first hydrogen loss regime and one slightly above the regime. Growth time of the polyborazylene film was varied for desired film thickness. A post deposition anneal was then performed at 1 Torr H₂/N₂ (15% H₂), 1000°C for one hour to facilitate the ceramic conversion, via the second hydrogen loss process, to boron nitride. A pre-growth anneal was performed prior to growth at the polyborazylene deposition temperature, unless otherwise noted, for 30 minutes. Additionally, h-BN films were deposited directly at 1000°C, without the use of a polyborazylene deposition step, for comparison. Table 2.3.2 details the deposition conditions used for the direct growth of h-BN on
Si and Sapphire substrates. Typical pressure/temperature growth profiles for each of the four synthesis conditions are shown in Appendix B.

Table 2.3.2: Description of various direct BN growth conditions

<table>
<thead>
<tr>
<th>Polyborazylene Deposition Temperature (°C)</th>
<th>Pre-growth Anneal (°C)</th>
<th>Post-Growth Anneal (°C)</th>
<th>Growth time (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>1000</td>
<td>N/A</td>
<td>5-20</td>
</tr>
<tr>
<td>400</td>
<td>400</td>
<td>1000</td>
<td>10-30</td>
</tr>
<tr>
<td>250</td>
<td>250</td>
<td>1000</td>
<td>60-120</td>
</tr>
<tr>
<td>250</td>
<td>1000</td>
<td>1000</td>
<td>60-120</td>
</tr>
</tbody>
</table>

2.4: Transfer Process

For general materials characterization and integration as a top-gate dielectric to QFEG, the as-grown h-BN films (grown on Cu foils) have to first be decoupled from the Cu foil substrate and then transferred to arbitrary substrates or QFEG ohmic level devices for characterization or device integration, respectively. This transfer process, detailed in Figure 2.4.1, is also used in this work for transfer of CVD graphene (grown on Cu foils) to direct growth BN on Si or Al₂O₃ and is similar to previously reported techniques for transfer of CVD grown graphene from Cu.⁶⁷
Figure 2.4.1: Process detailing the major steps for transfer of h-BN or graphene grown on copper substrates

Using a spin bench, the transfer process begins first by coating the h-BN on Cu films with photoresist (950 PMMA A3, MicroChem). The spin bench is operated at 4000rpm for 45 seconds. Following resist application, the samples are soft baked at 105°C for 1 minute. The samples are then placed upside down in a TVA TePla M4L plasma etcher to remove any h-BN (or graphene) that may have grown on the backside of the copper substrate. Removal of this backside film will help to expedite etching of the Cu foil. The etching recipe utilizes flow rates of 150 sccm O₂ and 50 sccm He, a pressure of 600mTorr, a plasma power of 150 sccm, and an etch time of 1 minute. After PMMA application and back-side etching, the Cu substrate is removed using a ferric chloride solution (CE-100, Transene Company). The time required for this step can vary drastically from <15 minutes to several hours depending on how effectively the backside film was removed and whether or not any PMMA was accidentally coated to the backside of the sample. After the Cu foil is completely etched away, the remaining PMMA/h-BN film is then
transferred via a SiO$_2$ transfer wafer to a water bath to remove residual etchant, followed by a 10% hydrochloric acid bath (JT Baker, product #9539-05) diluted in DI water, followed by a second water bath to remove residual HCl. After the final water bath, the PMMA/h-BN film can be carefully transferred to the cleaned final substrate. The sample is then dried on a hot plate at 50°C for 10 minutes then 90°C for 10 minutes to remove residual water trapped between the film and the substrate. The PMMA is then removed with acetone at room temperature for 30 minutes, followed by IPA at room temperature for 2 minutes to remove residual acetone. Finally, the transferred h-BN film is heated again on a hot plate to 50°C for 10 minutes then 90°C for 10 minutes to drive off residual IPA. If necessary, removal of residual PMMA and water from the transfer process may be accomplished via a post-transfer anneal at 400°C for 20 minutes in a rapid thermal annealer under an H$_2$/N$_2$ (15% H$_2$) environment.

2.5: Integration of h-BN with Graphene Devices

For large area development of h-BN top gated quasi-freestanding epitaxial graphene (QFEG) devices, a 75mm epitaxial graphene wafer (Figure 2.5.1a) is grown via the sublimation of silicon from 6H-SiC (0001) at 1625°C for 15 minutes under 1 Torr argon (Ar) background pressure. The wafer is then exposed to 600 Torr hydrogen (H$_2$) at 1050°C for 120 minutes to intercalate hydrogen at the graphene/SiC(0001) interface, leading to the formation of QFEG. Radio frequency field-effect transistor structures and Van der Pauw (VdP) Hall crosses are fabricated using standard ultra-violet photolithography. Transistors (Figure 2.5.1b) utilize two-finger gates, 2x(10x1)µm (WxL) with 750nm source-drain spacing, while VdP structures (Figure 2.5.1c) are 5x5µm$^2$ squares and often incorporate SiC step edges known to effect carrier density and mobility. Source/drain contacts (Ti/Au 10/50nm) are prepared using an oxygen plasma
pretreatment of the underlying graphene, as detailed in previous work,\textsuperscript{123} and deposited via electron beam physical vapor deposition (Kurt J. Lesker, Lab-18). For wafer scale dielectric integration, h-BN is deposited on 50x50mm$^2$ Cu foils in a 75mm diameter horizontal tube furnace and subsequently transferred to a 75mm QFEG wafer previously patterned with ohmic level device structures. The transferred h-BN dielectric layer is patterned and etched via a magnetically enhance reactive ion etch (MERIE) (Applied Materials, P5000) using a CHF$_3$/CF$_4$ mixture to clear the ohmic contacts of h-BN.

**Figure 2.5.1:** (a) Optical image of a 75mm quasi-freestanding epitaxial graphene wafer with CVD h-BN gated transistors and Van der Pauw Hall crosses. (b) FESEM image of an h-BN gated graphene FET structure. (c) FESEM image of an h-BN coated Van der Pauw Hall cross. False coloration has been added to FESEM images for enhancement.

Graphene devices were also fabricated for CVD graphene grown on copper substrates and transferred to h-BN directly grown on silicon or sapphire. Here, the graphene was grown in a 50mm diameter tube furnace (MTI, OTF-1200X) with a maximum temperature of 1200°C. The
copper substrates were cleaned via the same process used for growth of h-BN on copper and placed in the tube furnace on an alumina sample boat connected to a spool system with tungsten wire for post-growth extraction. Following a pre-growth anneal at 1000°C and 1 Torr for 30 minutes under an H₂ flow of 20 sccm and an Ar flow of 180 sccm, growth was initiated by flowing 60 sccm CH₄ (after reducing the Ar flow to 120 sccm to retain the same total flow rate). Growth proceeded at 1000°C and 1 Torr for 15 minutes. After completion of the growth process, the samples were extracted via the spool system to allow for quenching to precipitate the carbon from the copper foil to form graphene. Upon transfer, as detailed in Section 2.4, devices were fabricated via the same UV photolithography process as was used for fabrication of QFEG devices. However, for these samples, no gate dielectric or gate contacts were employed.

2.6: Characterization Techniques

For general materials characterization of h-BN films grown on Cu substrates, h-BN is deposited on 10x10mm² Cu foils in a 25mm diameter horizontal tube furnace and subsequently transferred to Si(111) substrates for further characterization. These films were characterized prior to transfer (as-grown) with Raman spectroscopy (WiTec CRM200) at an incident laser wavelength of 488nm for bonding and structural information and scanning electron microscopy (SEM) (Leo 1530 FESEM) with an accelerating voltage of 5kV for morphological analysis. Following transfer, the films on Si(111) are again characterized with Raman and SEM, and additionally with optical ellipsometry (Gaertner L116C), assuming a bulk refractive index of h-BN of 1.67, for thickness measurements and atomic force microscopy (AFM) (Bruker Icon) with a scan rate of 0.5 Hz and a resolution of 512 points per line for surface roughness measurements. Select h-BN films were also transferred to 3mm diameter 200 mesh lacey carbon TEM grids for
high-resolution transmission electron microscopy (HRTEM) (JEOL 2010F) for structural analysis. Additionally, select h-BN films, both as-grown on copper and transferred to Si(111) substrates, were characterized with x-ray photoelectron spectroscopy (XPS) (Kratos Axis Ultra) utilizing an Al Kα x-ray source with energy of 1486eV for chemical bonding and stoichiometry analysis. For electrical breakdown measurements of h-BN films grown on Cu, the films were transferred to Si/SiO₂(300nm)/Ti(10nm)/Au(500nm) substrates. Contacts (Ti/Au 20/100nm) with nominal sizes of 500, 250, and 125μm were deposited over the h-BN film using a shadow mask and the Lab-18 e-beam evaporator. Breakdown measurements were then performed with a Keithley 4200 semiconductor characterization system. Figure 2.6.1 shows an SEM image of the shadow masked contacts deposited on an h-BN film.

**Figure 2.6.1:** SEM image of shadow masked contacts deposited on an h-BN film transferred to an Au/Ti/SiO₂/Si substrate for breakdown analysis.
For direct growth of h-BN on Si(111) and sapphire substrates, SEM and AFM were again used to characterize the as-grown morphology and surface roughness, respectively, of the films and optical ellipsometry was used for thickness measurement. Also, chemical bonding and stoichiometry were again investigated using XPS. Cross-sectional TEM analysis was performed by the JEOL 2010F TEM after sample preparation by focus ion beam (FIB) milling. Cross-plane thermal transport properties of thin film h-BN films were measured using time-domain thermoreflectance (TDTR), which is a femtosecond laser pump-probe based approach to monitor time-resolved, temperature-induced changes in optical reflectivity. For TDTR preparation, each sample was coated with ~70nm of aluminum metal to serve as a thermo-reflectance transducer. For each sample, data was acquired at five randomly chosen spots (laser beams focused down to ~50µm diameter). Analysis of TDTR data was performed using a nonlinear least-squares application to Cahill’s frequency domain model. For this analysis, the physical properties of the aluminum layer were held constant. The aluminum thickness was quantified by picosecond acoustics and bulk aluminum thermal properties were assumed. For data fitting to the thermal diffusivity model, heat capacities of bulk sapphire, silicon, and h-BN were used. For each sample, data sets were statistically analyzed to obtain average ± standard deviation values. Raman spectroscopy was used to investigate strain and Van der Waals interactions that lead to Fermi velocity reduction of transferred graphene on various dielectrics. Raman data was obtained through 20µm line scans utilizing a WiTec CRM200 at an incident laser wavelength of 488nm. Using the same contacts shown in Figure 2.6.1, electrical breakdown measurements were performed on h-BN films directly grown on conductive Si(111) with a Keithley 4200 semiconductor characterization system. Hall mobility and hole concentration of transferred CVD graphene was obtained with a Nanometrics 4-point probe Hall mobility measurement system. Van der Pauw test structures with 10x10µm² Hall crosses and Ti/Au (10/50nm) contacts were prepared via standard UV photolithography techniques.
For electrical characterization of h-BN gated GFETs on QFEG wafers, room temperature Hall effect measurements of VdP test structures are taken before transfer, immediately after transfer, and after a 400°C anneal with a Nanometrics Hall mobility measurement system, while temperature dependent Hall mobility measurements of VdP test structures are again obtained with a Lakeshore cryogenic probe station. RF testing of graphene FETs was performed with a Keithley 4200 semiconductor characterization system. For electrical characterization of h-BN top gated QFEG devices, a large h-BN film thickness was used to guarantee adequately low leakage currents. Britnell et al have shown that exfoliated single crystal h-BN demonstrates negligible tunneling currents when a thickness of only 4 layers is used. However, the CVD grown h-BN films used in this study resulted in $V_{\text{Breakdown}} < 1\text{V}$ for thicknesses up to 20nm, possibly due to pinholes, domain boundaries, or non-uniformities in the transferred films. Therefore, a thickness of 50nm was used where leakage currents measured at $V_{gs}=1\text{V}$ were found to be $<1\times10^{-10} \text{A/µm}^2$.

Gas-phase precursors evolved during the sublimation of ammonia borane was analyzed with mass spectrometry (Dymaxion Dycor, DM200M) to investigate the chemistry of the evolved species upon sublimation (135°C) and at direct growth temperatures (250, 400, 1000°C). Additionally, thermogravimetric analysis (TGA) (TA Instruments, TGA Q5000) was used to study the weight loss behavior of ammonia borane upon sublimation. The result of the TGA study is shown in Appendix C.

2.7: Scattering Model

Following electrical characterization of h-BN and high-k gated devices on QFEG, modeling of the carrier concentration as a function of impurity density was employed to identify the regimes where h-BN dielectrics had an advantage over conventional dielectrics and where
they did not. The physics of both intrinsic and extrinsic scattering mechanisms were taken into account to explain the dependencies of temperature and carrier density on the Hall mobility of QFEG devices having h-BN or various other dielectric coatings. For this work, modeling was primarily performed by Matthew Hollander (Penn State, Electrical Engineering) and is detailed in a previous work.\textsuperscript{127}

The intrinsic scattering mechanisms of graphene that affect carrier transport are due to electron-phonon interactions, where the phonon modes that require consideration are acoustic and optical phonons. The contributions of these intrinsic scatterers are calculated as a scattering rate using Fermi’s Golden rule.\textsuperscript{102} The acoustic phonon scattering rate \( \frac{1}{\tau_{ac}(k)} \) for an electron in state (k) is calculated by summing over all possible values in k-space and is given in Equation 2.7.1.\textsuperscript{102} Here, \( k_B \) is the Boltzmann’s constant, T is the temperature, \( \varepsilon_k = \hbar v_f |k| \) is the kinetic energy where \( k \) is the wave vector and \( \hbar \) is the reduced Planck constant, \( D_{ac} = 16 \text{eV} \) is the acoustic deformation potential, \( v_F = 10^6 \text{m/s} \) is the Fermi velocity, \( \sigma_m = 7.6 \times 10^{-8} \text{g/cm}^2 \) is the 2D mass density of graphene and \( v_p = 20 \text{ km/s} \) is the acoustic phonon (sound) velocity in graphene. Acoustic phonon scattering is treated as quasi-elastic, where both emission and absorption are taken into account.\textsuperscript{102}

\[
\frac{1}{\tau_{ac}(k)} = \frac{D_{ac}^2 k_B T}{2\hbar^3 v_F^2 \sigma_m v_p^2} \times \varepsilon_k
\]

Equation 2.7.1\textsuperscript{102}

For intrinsic optical phonon scattering in graphene, again the scattering rate \( \frac{1}{\tau_{op}(k)} \) for an electron in state (k) is the sum of all possible values in k-space and is given in Equation
2.7.2 Here, $D_0 = 25.6 \text{eV/Å}$ is the optical deformation potential, $\hbar \omega_0 = 160 \text{meV}$ is the optical phonon energy for the zone edge transverse optical (TO) mode (which was the strongest coupling strength with electrons), and $N_{\text{op}} = \frac{1}{\hbar \omega_0} e^{\frac{\hbar \omega_0}{e F T}} - 1$ is the optical phonon number. The ± is for phonon absorption and emission, respectively.

$$\frac{1}{\tau_{\text{op}}(k)} = \frac{D_0^2 (N_{\text{op}} + \frac{1}{2} \pm \frac{1}{2})}{2 \hbar^2 v_F^2 \sigma \omega_0} \times [\epsilon_k \pm \hbar \omega_0]$$

Equation 2.7.2

Extrinsic scattering from surface optical phonons (SOP) of the surrounding dielectric environment, detailed in Section 1.6.2, are a result of the polar nature of dielectric surfaces and produce an electric field that couples to the carriers in graphene. This type of scattering is temperature dependent and is a dominant mechanism for mobility degradation at higher temperatures. Equation 2.7.3 gives the scattering rate for SOPs ($\frac{1}{\tau_{\text{SOP}}(k)}$), where $k_0 \approx \sqrt{\left(\frac{2 \omega_{\text{SOP}}}{v_F}\right)^2 + \alpha n_z}$, $z_0$ is the van der Waals distance between the dielectric and the graphene layer, $F_v^2 = \frac{\hbar \omega_{\text{SOP}}}{2 \pi} \left(\frac{1}{\epsilon_\infty + 1} - \frac{1}{\epsilon_0 + 1}\right)$ is the Fröhlich coupling parameter, $\hbar \omega_{\text{SOP}}$ is the SOP mode energy, $\epsilon_0$ and $\epsilon_\infty$ are the low and high frequency dielectric constants, respectively, of the polar dielectric, $N_{\text{SOP}}$ is occupation number of the SOPs, and $\beta$ is used as fitting parameter.

$$\frac{1}{\tau_{\text{SOP}}(k)} = \frac{e^2 F_v^2 N_{\text{SOP}} \sqrt{n_s}}{\beta \hbar \exp(k_0 z_0)} \times \frac{1}{\epsilon_k}$$

Equation 2.7.3
Extrinsic scattering from ionized impurities or charged surface states at or near the dielectric-graphene interface, detailed in Section 1.6.3, result in a mobility that is independent of carrier concentration as well as temperature. Here, the effects of short range and long-range scatterers in bilayer graphene (QFEG) are grouped into a single fitting parameter that varies linearly with carrier density, similar to the approach of Konar et al.\textsuperscript{104} Equation 2.7.4 gives the scattering rate for ionized impurities \( \left( \frac{1}{\tau_{\text{imp}}(k)} \right) \), where \( n_{\text{imp}} \) is the sheet density of impurities at or near the graphene-dielectric interface and \( \varepsilon_{\text{avg}} = (\varepsilon_{\text{top}} + \varepsilon_{\text{bottom}})/2 \) is the average relative dielectric constant of the two dielectrics surfaces surrounding graphene.\textsuperscript{104} Using this approach, the effective impurity density \( (n_{\text{imp}}) \) can be calculated before and after integration of graphene with a dielectric material to investigate the changes in scattering due to changes in dielectric coating. Additionally, it should be noted that this approach will not give absolute impurity densities unless the samples closely approximate ideal monolayer graphene. However, this approach is useful for studying the relative change in scattering due to charged impurities before and after dielectric integration when long-range scatterers dominate \( (n_{\text{imp}} > 1.5 \times 10^{12} \text{cm}^{-2}) \).\textsuperscript{127}

\[
\frac{1}{\tau_{\text{imp}}(k)} = \frac{n_{\text{imp}}}{\pi \hbar} \left( \frac{e^2}{2 \varepsilon_0 \varepsilon_{\text{avg}}} \right)^2 \frac{F(a)}{\varepsilon(k)}
\]

\textbf{Equation 2.7.4}\textsuperscript{104}

To summarize the values of various parameters used in this work for the modeling of the above scattering mechanisms, Table 2.7.1 details several key values.
Table 2.7.1: List of relevant parameters for modeling of scattering physics for dielectric-graphene interactions.\(^{127}\)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acoustic Deformation Potential ((D_{ac}))</td>
<td>4.8eV</td>
</tr>
<tr>
<td>Optical Deformation Potential ((D_{o}))</td>
<td>25.6eV/Å</td>
</tr>
<tr>
<td>Intrinsic Optical Phonon Energy ((\hbar\omega_0))</td>
<td>160meV</td>
</tr>
</tbody>
</table>
| Surface Optical Phonon Energy (\(h\omega_{SOP}\)) | SiC: 116meV  
HfO\(_2\): 25.5meV  
h-BN: 120meV |
| Relative Dielectric Constants                  | SiC: \(\varepsilon_0=9.7, \varepsilon_\infty=6.5\)  
HfO\(_2\): \(\varepsilon_0=18, \varepsilon_\infty=5.03\)  
h-BN: \(\varepsilon_0=4.0, \varepsilon_\infty=3.5\) |

The total scattering time (in seconds) can then be calculated by combining the scattering times of all the above mechanisms, as shown in Equation 2.7.5.

\[
\tau_{tot} = (\tau_{ac}^{-1} + \tau_{op}^{-1} + \tau_{SOP}^{-1} + \tau_{imp}^{-1})^{-1}
\]

Equation 2.7.5

The mobility can then be determined from the total scattering time through Equation 2.7.6.

\[
\mu = \frac{e\nu_F^2\tau_{tot}}{E_F}
\]

Equation 2.7.6\(^{128}\)

By applying these models to temperature dependent Hall mobility measurements, the extent of the remote charged impurity scattering and remote SOP scattering for various dielectric materials can be studied. An effective remote impurity concentration, \(n_{imp}\), and a remote phonon scattering fitting parameter, \(\beta\), can be extracted from the data and used to examine various carrier concentration and temperature regimes.
Growth of h-BN films on copper substrates has been reported extensively in literature, as detailed previously in Section 1.2.2. However, a detailed study on the effect of growth conditions on the growth rate, morphology, chemistry, and structure of h-BN films has not been demonstrated. This chapter examines the growth rate as a function of time, pressure, and ammonia borane flow rate, as well as presents the use of Raman for thickness estimation and strain quantification. The chemical properties of both as-grown h-BN films on Cu and h-BN films transferred to Si are examined with x-ray photoelectron spectroscopy (XPS) and the structure of h-BN films grown on Cu is examined with transmission electron microscopy (TEM). Additionally, a novel growth process that maintains a copper overpressure is presented and shown to result in an improvement in morphology, chemical composition, and structure. Finally, a possible model describing the observed growth of h-BN films is presented. Many of the results presented in this chapter are also published elsewhere\textsuperscript{129,130} or are in preparation for publishing\textsuperscript{131}.

### 3.1: Characterization and Effect of Process Conditions on Growth Rate and Morphology

As discussed in Section 1.2.2, initial reports of h-BN growth on Cu substrates suggested that h-BN growth proceeds similarly to graphene growth on Cu, where the growth rate decreases rapidly after the formation of one to a few layers due to a significant reduction in the surface reactivity of borazine on BN compared to the bare Cu substrate.\textsuperscript{36} Therefore, growth of h-BN on Cu was believed to be self-limiting, like graphene, to one to a few layers.\textsuperscript{36} However, more recent reports demonstrate that the growth of h-BN on Cu is not self-limiting, where multi-layer films
were easily obtained.\textsuperscript{37–40} Additionally, it was found that h-BN film thickness proceeds linearly with growth time, indicating that gas-phase precursors readily nucleate on BN, despite the reduced surface reactivity.\textsuperscript{30} In the present work, we confirm that the growth of h-BN on Cu is non-self limiting.

### 3.1.1: Effect of Process Conditions on h-BN Growth Rate

Figure 3.1.1a shows the dependence of the h-BN film thickness on the ammonia borane (AB) carrier gas flow, which is the percentage of the total H\textsubscript{2}/N\textsubscript{2} gas flow diverted to the sublimator. Here, the temperature, pressure, and growth time were held constant at 1000°C, 250mTorr, and 15 minutes, respectively. Only a slight increase in the growth rate is observed, from 0.86nm/min at 1\% AB flow to 1.04nm/min at 10\% AB flow. The slope of this curve normalized by the growth time (15 minutes) gives the growth rate as a function of carrier gas flow and was found to be 0.027nm/(min\%\%). This indicates that the carrier flow rate through the sublimator minimally affects the h-BN growth rate. Instead the growth rate is most likely limited by the sublimation rate of the ammonia borane, where an increase in flow rate through the sublimator does not result in a significant increase in the concentration of gas phase BN precursors (such as borazine) in the total inlet flow. Therefore, the overall partial pressure of BN precursors in the furnace remains relatively constant regardless of flow rate ratio.
Figure 3.1.1: (a) Thickness vs. ammonia borane carrier gas flow demonstrates only a minor increase in growth rate with increased ammonia borane carrier gas flow. (b) Thickness vs. growth time for three different pressures at a constant temperature of 1000°C indicates a linear increase in film thickness with time and an increase in growth rate (slope) with increasing pressure.

Figure 3.1.1b shows the dependence of the h-BN film thickness on the growth time and reactor pressure. Three different pressures were studied: the base pressure at 250 mTorr, 500 mTorr, and 5 Torr. From the slopes of these curves, it is found that the growth rate increases nearly linearly with increasing pressure, from a minimum of 0.6nm/min at 250 mTorr to a maximum of 2.3nm/min at 5 Torr. This is expected, as an increase in pressure would lead to an increase in the density of BN precursors in the gas-phase, such as borazine and diborane.
Additionally, film thickness increases nearly linearly with growth time after 5 minutes for all three pressures. The linear increase in growth rate with increased pressure, and the linear increase in film thickness with increased time indicate that the growth of h-BN on Cu foils is not self-limiting, but rather diffusion controlled where the growth rate at constant temperature is limited by the flux of precursors to the surface and not by the reaction kinetics. However, clearly the growth rate is much higher during the first 5 minutes of growth, as evident by the 5 Torr data, where the film thickness rapidly reaches 73.1nm after only 5 minutes of growth. To a lesser degree, this is also true for the 250 and 500mTorr data, where the y-intercept of the linear fit is located at non-zero values of 2.14 and 8.69nm, respectively, indicating that with increased pressure, the initially higher growth rate is more pronounced. It has been reported previously that the growth rate of h-BN decreases significantly after the formation of the first few layers due to a decrease in the surface reactivity of BN compared to the bare Cu surface. However, this would not explain the rapid increase in growth rate within the first few minutes at 5 Torr, since the film is measured to be ~73nm, far greater than a few h-BN layers. Instead, this initial high growth rate is likely due to the rapid drop off in gas-phase BN precursors after the first few minutes of ammonia borane sublimation, as shown with mass spectrometry in Figure 3.1.2.
Figure 3.1.2: Mass spectrometry analysis of diborane and borazine concentrations (normalized to the total sampling pressure) sampled from the growth region of the h-BN furnace at 1000°C. The first point for each curve represents the moment when the ammonia borane carrier flow was introduced into the furnace.

Here, the mass spectrometer was configured to sample the gas-phase chemistry in the hot-zone of the tube furnace at 1000°C. This allows the data to represent the growth environment around the Cu substrate. Figure 3.1.2 shows the relative concentrations (normalized to the total sampling pressure) of two common precursors to BN growth: borazine (B₃N₃H₆) and diborane (B₂H₆). The first point of each data set represents the moment when the ammonia borane carrier gas flow was delivered to the tube furnace. Unlike processes that use gas-phase precursors, such as pure borazine which can be easily controlled and held constant, the growth process used in this study utilized a solid precursor, ammonia borane, which sublimes and depletes with time.
Within the first 5 minutes of growth, the concentrations of borazine and diborane decrease by 87% and 85%, respectively. After this initial drop-off, the precursor concentrations level out and remain nearly constant for the remaining sampling time. This large concentration of gas-phase precursors upon initial sublimation of ammonia borane may explain the rapid growth rate in the first few minutes of h-BN growth and the subsequently reduced and linear growth rate after a growth time of 5 minutes, as observed in Figure 3.1.1. Therefore, use of a solid source precursor clearly has the disadvantage of producing varying amounts of gas-phase precursors, and thus non-uniform growth rates, with time. To mitigate this, the use of a pressure-based mass flow controller (MFC), such as the MKS 1150C, could be used in future experiments to regulate the amount of gas-phase precursors introduced into the furnace after sublimation of ammonia borane. Another alternative for future work would be to utilize a liquid or gas phase precursor, such as borazine or diborane and ammonia.

3.1.2: h-BN Surface Morphology

Figures 3.1.3a and b show scanning electron microscopy (SEM) images of h-BN films of various thicknesses as-grown on Cu and transferred to Si, respectively. The most clearly recognizable surface feature of these films is the presence of wrinkles across the film surface, similar to those observed elsewhere. The wrinkles result from the anisotropic thermal expansion of h-BN, where a negative coefficient of thermal expansion (CTE) exists in the plane of bonding. This negative CTE causes the h-BN film to expand during cooling while the copper substrate shrinks, inducing a compressive stress in the h-BN film. This compressive stress results in local areas of film de-lamination in the form of wrinkles. Following transfer of the film (Figure 3.1.3b), the as-grown morphology is essentially preserved as the large wrinkles are still apparent.
These wrinkles were measured with AFM to be approximately 6-10nm high for 10nm thick films and increase in height with increasing film thickness. Additionally, the width of the wrinkles shown in Figure 3.1.1 increase ultimately by >4x (from 17.3nm to 70.1nm) when increasing film thickness from ~3nm to ~20nm. The variation in total film thickness that results from wrinkling presents a challenge to graphene device fabrication, as h-BN wrinkles will result in a non-uniform electric field when used as a gate dielectric, and induce surface roughness scattering when used as a supporting substrate to CVD or exfoliated graphene. This phenomenon is also observed in transferred CVD grown graphene, where wrinkling is significantly reduced by incorporating an additional PMMA application step following initial transfer in order to relieve stress in the film. Similar modifications to our current process may also benefit from this additional step and provide improved transfer morphology of CVD grown h-BN films.
Figure 3.1.3: (a) FESEM images of as-grown h-BN films on the Cu substrate indicate the presence of stress induced wrinkling which increases in size with film thickness. (b) FESEM images of h-BN films transferred to Si (111) substrates show that the wrinkles induced during growth on Cu translate to the transferred film morphology. The inset text gives growth time and thickness.

In addition to stress-induced film wrinkling, another feature is observed in the SEM images of Figure 3.1.3. Small, particle-like three-dimensional (3D) formations are distributed uniformly across the film surface. These 3D features appear to nucleate randomly and increase in
density ultimately by >14x (from ~40(±19) nuclei/μm² to ~568(±55) nuclei/μm²) when increasing film thickness from ~3nm to ~20nm (see Figure 3.1.5). To examine these 3D nuclei further, plan-view TEM was performed on a 20nm thick film with a high density of these formations and is shown in Figure 3.1.4.

![Figure 3.1.4: (a) SEM image of 20nm h-BN film grown on Cu foil without the use of a copper enclosure shows a high density of 3D nuclei. (b) Plan-view TEM image of a 3D nuclei shows that the h-BN planes propagate normal to the Cu surface and form in an “onion-like” structure. (c) D-spacing measurement of the layers in the 3D nuclei show a d-spacing matching h-BN.](image)

Plan-view TEM (Figure 3.1.4b) indicates that the 3D nuclei are h-BN layers growing perpendicular to the Cu substrate surface, in contrast to the underlying film, which propagates parallel to the growth surface (shown subsequently in Figure 3.2.5). Furthermore, these h-BN layers appear to wrap around themselves and produce an “onion-like” formation. The d-spacing measurement of these layers is shown in Figure 3.1.4c and gives a d-spacing of 0.355nm, close to that of bulk h-BN (0.333nm), indicating that the 3D nuclei are indeed composed of h-BN layers. The exact growth mechanism of these 3D nuclei are not fully understood, however two possible
mechanisms may be at play. One possibility is that the 3D features form in the gas-phase and “rain” onto the growing h-BN film; the other possibility is that the 3D features are nucleating on the h-BN film surface, likely from defective domain boundaries. In the case of gas-phase nucleation, the density of these 3D particulates would be expected to increase linearly with time. As shown in Figure 3.1.5, however, the increase in 3D nuclei density increases exponentially, indicating a higher growth rate of these features at higher film thicknesses. This may indicate that the 3D features are nucleating at defective domain boundaries, where the crystallinity of the h-BN films may be degrading with increasing thickness (as verified in Section 3.2). These features are notably similar to BN fullerenes, where literature has shown that BN fullerenes form more preferentially from turbostratic BN, which displays small domain sizes and a high density of defects and dangling bonds compared to well-ordered h-BN, which again indicates decreased crystallinity of these films at higher thicknesses.

Figure 3.1.5: Density of 3D nuclei versus h-BN film thickness indicates that the nucleation rate of these 3D features increases with increasing thickness, possibly due to increased density of defects and domain boundaries at higher film thickness.
The presence of oxygen impurities in the as-grown BN film (discussed subsequently in Section 3.1.3) further corroborates the theory that the observed 3D nuclei present on the h-BN film surface are BN fullerene structures. BN fullerenes are composed of hexagons and pentagons that would ultimately form thermodynamically unfavorable B-B and N-N bonds. Therefore BN fullerenes require the incorporation of substitutional oxygen into the BN lattice to form stable B-O bonds at the pentagon and hexagon boundaries.\textsuperscript{133}

It is also possible that both proposed mechanisms, gas-phase and surface nucleation, may be contributing to the growth of these features and further research is required to fully understand their exact growth mechanisms. What can be assumed, however, is that these formations will negatively impact graphene device performance. An obvious adverse effect would be increased surface roughness scattering when these films are used as a supporting substrate to CVD or exfoliated graphene. Additionally, having the basal plane normal to the rest of the h-BN film, these 3D nuclei will have dangling bonds at the terminations of the in-plane σ-bonds. It is expected that impurities will readily absorb at these sites and may lead to reduced resistivity of the h-BN film when used as a gate dielectric and lead to increased impurity scattering when used as a supporting substrate. Therefore, a reduction or elimination of these surface defects would presumably be highly beneficial to the dielectric performance of CVD grown h-BN films. Section 3.2 will discuss a novel technique that leads to a significant reduction in the formation of 3D nuclei.
3.1.3: Effect of Transfer Process on Chemical Stability of h-BN

X-ray photoelectron spectroscopy (XPS) was utilized for analysis of the chemical composition and bonding properties of h-BN, both as-grown on Cu substrates and transferred to Si. The high resolution B1s and N1s core level peaks (Figure 3.1.6a and b) are located at approximately 190.4eV and 398.1eV, respectively, matching reported values for bulk h-BN, which give the N1s peak at 398.1eV and the B1s peak at 190.1eV. Additionally, the measured atomic percentages indicate excellent stoichiometry with a B/N ratio of 1.01. Both the B1s and the N1s core level peaks exhibit no shift in peak position or full width at half maximum (FWHM) after transfer, as shown in Table 3.1.1, indicating negligible degradation of the primary B-N bonding configuration.

<table>
<thead>
<tr>
<th></th>
<th>B1s</th>
<th></th>
<th>N1s</th>
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<tr>
<td></td>
<td>Peak Position (eV)</td>
<td>FWHM (eV)</td>
<td>Peak Position (eV)</td>
<td>FWHM (eV)</td>
</tr>
<tr>
<td>As-Grown</td>
<td>190.39</td>
<td>1.25</td>
<td>398.09</td>
<td>1.21</td>
</tr>
<tr>
<td>Transferred</td>
<td>190.43</td>
<td>1.25</td>
<td>398.03</td>
<td>1.26</td>
</tr>
</tbody>
</table>

Upon deconvolution, two peaks are found to make up the B1s spectra. The main peak at ~190.4eV (red peak in Figure 3.1.6a) is the main bonding configuration of the film and correlates to a boron atom bonded to three nitrogen atoms in the typical h-BN lattice structure. The second peak at ~191.5eV (blue peak in Figure 3.1.6a) correlates to a boron atom bonded to one or two nitrogen atoms as well as one or two oxygen atoms. Since oxygen has a higher electronegativity
than nitrogen, this bonding configuration will result in the formation of a peak shifted to higher binding energies. Therefore, this peak implies that there is partial bonding of oxygen to boron and can be assigned to a \( \text{BN}_x \text{O}_y \) configuration. Additionally, the oxygen content of these films was found to increase upon transfer. Prior to transfer, the as-grown oxygen content was measured to be 5.46%. Upon transfer, the oxygen content increased to 8.40%. This amounts to an increase in oxygen contamination of nearly 54%, consistent with the increase in the intensity of the peak at \(~191.5\text{eV}\). The oxygen contamination may occur during the transfer step, where several water baths are utilized. It is unlikely that oxygen atoms are replacing nitrogen atoms as substitutional impurities in the h-BN lattice during the transfer process, instead the oxygen atoms are likely bonding to dangling bonds present at domain terminations or defect sites.
Figure 3.1.6: XPS spectra of as-grown h-BN films on copper foil and after transfer to Si. (a) High resolution XPS spectra of the B1s core level peak. The peak ~192eV (blue peak) was found to increase from the as-grown film to the transferred film indicating an increase in oxygen contamination. (b) High resolution XPS spectra of the N1s core level peak shows negligible change upon transfer. (c, d) Low resolution XPS survey spectra for transferred and as-grown h-BN. The as-grown film contains very little oxygen and carbon contamination, while the transferred h-BN shows an increase in both the carbon and oxygen peaks.
It is apparent from the transferred low resolution spectra (Figure 3.1.6c) that the C1s peak has increased in intensity significantly from the as grown spectra (Figure 3.1.6d), where the measured concentration of carbon increased from 5.25% to 14.89%. However, unlike previous reports for hybrid h-BN/graphene domains,\textsuperscript{137} the carbon peaks associated with B-C-N bonding (located at \textasciitilde 188eV for the B1s spectra and \textasciitilde 400eV for the N1s spectra) are not apparent following transfer of the h-BN films studied here. Instead, the increase in carbon is likely due to residual photoresist on the h-BN surface. Often, a peak located at approximately 710eV is present in the low resolution XPS spectra of the transferred h-BN film that is indicative of the Fe2p peak, which correlates to an iron impurity, presumably located at the h-BN/Si interface. Residual iron impurities are likely due to the ferric chloride etchant used to remove the Cu substrate during the transfer process. However, use of a 10% HCl bath during the transfer process effectively removed residual iron. Therefore, no Fe2p peak is observed for the samples presented here. Additionally, the Si2p peak is from the Si substrate utilized in XPS investigations. Non-labeled peaks in the spectra are secondary peaks of already established elements.

3.1.4: Use of Raman Spectroscopy for Film Thickness Estimation and Quantification of Strain

Correlating the as-grown Raman spectra to the h-BN film thickness, measured \textit{via} ellipsometry after transfer to Si(111), indicates that there is a dependence of the Raman spectra on the thickness of the film, as shown in Figure 3.1.7. The FWHM as well as the relative intensity of the peak located at approximately 1366cm\textsuperscript{-1}, originating from the E\textsubscript{2g} phonon mode of h-BN,\textsuperscript{138} are both shown to increase with film thickness, following a log-log power law dependency. Here, a constant laser power (WiTec Raman system set at 150mW) and an integration time of 3 seconds
were used for all samples to isolate the dependence of the Raman signal on film thickness. This relationship offers the possibility to estimate approximate h-BN film thickness with Raman spectroscopy (given a standard laser power and integration time) directly after growth on Cu foils without the need to transfer to silicon substrates for ellipsometry measurements.

Figure 3.1.7: Log-log plots of Raman data obtained with the WiTec Raman system at PSU showing (a) the as-grown h-BN $E_{2g}$ Raman peak intensity vs. h-BN film thickness, and (b) the as-grown full width half maximum (FWHM) of the h-BN $E_{2g}$ Raman peak vs. h-BN film thickness.

Additionally, Raman spectroscopy verifies that the h-BN film experiences a compressive stress during cooling which is partially relaxed upon transfer. Raman was first performed on the as-grown h-BN film on Cu. The same film was then transferred to the QFEG wafer where Raman
scans were taken over Hall crosses and over etched regions (bare SiC). The use of the same h-BN film for Raman analysis was critical to rule out effects of thickness variations between different samples. Figure 3.1.8 clearly demonstrates a red-shift in peak position from the as-grown (1373 cm\(^{-1}\)) to transferred h-BN film over SiC (1370 cm\(^{-1}\)). Additionally, both peak positions are blue-shifted from the \(E_{2g}\) phonon mode of bulk h-BN \(E_{2g}\) \(\omega^0\) located at 1366 cm\(^{-1}\),\(^{138}\) indicating these h-BN films are compressively strained. The shift in Raman \(E_{2g}\) peak position from its bulk value \((\Delta \omega_{E_{2g}})\) provides a means to quantify strain induced in the as-grown and transferred h-BN films via:\(^{139}\) \(
abla \omega_{E_{2g}} = -2\omega^0 \gamma_{E_{2g}} \varepsilon\), where \(\gamma_{E_{2g}}\) is the Grüneisen parameter for the Raman-active \(E_{2g}\) phonon mode of h-BN \((\gamma_{E_{2g}} = 0.89)^{140}\) and \(\varepsilon\) is the strain tensor.

![Figure 3.1.8: High resolution Raman spectra of as-grown h-BN on the copper substrate compared to transferred h-BN on a SiC substrate and over QFEG.](image-url)
From the above relationship, it was found that the as-grown and transferred h-BN films are compressively strained by 0.29% and 0.16%, respectively, indicating a relaxation of compressive strain upon transfer. Given that the as-grown and transferred film is of identical thickness, the shift in the $E_{2g}$ peak may be directly attributed to strain relaxation of h-BN during the transfer process from the as-grown copper substrate to the supporting SiC/QFEG substrate. The stress relaxation (~3 cm$^{-1}$ shift in the $E_{2g}$ peak position) associated with the removal of the Cu substrate corresponds to a 42.9% decrease in compressive strain upon transfer. This corroborates well with reports that the h-BN film is weakly chemisorbed to the supporting Cu substrate, suggesting that removal of the chemisorbed substrate would lead to a relaxation of the induced stress. The overall blue-shifted Raman peaks observed here have also been reported for as-grown atomically thin h-BN films and h-BN nanotubes and are attributed to a hardening of the $E_{2g}$ phonons due to an increase in h-BN’s lattice constant from the lack of interaction from neighboring sheets. However, for this study, Raman was performed on multilayer films (approximately 50nm) to obtain a high intensity Raman signal and to provide pin-hole free dielectric layers for device applications. Thus, the upward shift from h-BN’s bulk Raman frequency observed here is presumably due to substrate induced compressive stress; although substrate induced charge carrier doping cannot be ruled out. The Raman spectra of the h-BN film over a graphene Hall cross clearly shows the spectral contribution from the under-lying graphene. The $E_{2g}$ phonon mode of graphene, or G-Peak, is apparent at 1591 cm$^{-1}$. Additionally, a shoulder on the h-BN peak, corresponding to the overlapping D-peak of graphene (attributed to defects in QFEG), is observed at approximately 1355 cm$^{-1}$. The smaller peaks in the spectral noise are remnants from the background subtraction processing of the raw data.
3.2: Use of a Copper Overpressure for Improved Growth and Proposed h-BN Growth Mechanisms

Recently, graphene has been synthesized on copper via CVD in a copper enclosure, which resulted in monolayer graphene with domain size increases of ~30x and a lower density of adlayers compared to non-enclosed graphene growth. This is reported to be a result of a lower partial pressure of methane (leading to a reduced density of nucleation sites) as well as an improved growth environment through creation of a static Cu overpressure inside the copper enclosure. In the present work, this basic idea was also investigated for the growth of h-BN on Cu. Although the growth mechanisms of graphene and h-BN on Cu are believed to be different, both h-BN and graphene benefit from improved initial copper surface morphology. Here, a Cu enclosure was utilized to provide the Cu overpressure. This enclosure was simply made by wrapping a large sheet of copper (made from the same 99.98% purity 25µm Cu foil used for the substrate material) around a quartz boat holding up to six 10x10mm² Cu foils, as shown previously in Figure 2.3.1. The copper enclosure was utilized during the two hour pre-growth anneal and the subsequent growth process. The results presented in this chapter were also in preparation for publishing elsewhere at the time this thesis was submitted.

3.2.1: Effect of Copper Enclosure on h-BN Growth Rate

For comparison, h-BN films were grown with and without the use of a copper enclosure for various growth times, but were otherwise grown under the same conditions (1000°C, 250mTorr) and were subjected to a 2 hour pre-growth anneal at 1000°C, 250mTorr in H₂/N₂ (15% H₂). Figure 3.2.1 shows the h-BN film thickness as a function of growth time for films
grown with (enclosed) and without (non-enclosed) the use of a copper enclosure. The use of a copper enclosure during h-BN growth resulted in a 53.7% decrease in growth rate, from 0.66nm/min to 0.30nm/min.

![Figure 3.2.1: Thickness vs. growth time for h-BN films grown of copper foils with and without the use of a copper enclosure. Utilization of a copper enclosure during h-BN growth leads to a ~2x decrease in the growth rate of h-BN on copper.](image)

This reduction in growth rate can be explained by the gas-phase environment surrounding the Cu substrates during growth. Dalton’s law states that the total pressure of a mixture of gases is equal to the sum of the partial pressures of the individual gases in the mixture, such that: $P_{tot} = P_1 + P_2 + P_3 + \ldots$. For the growth configuration utilizing the copper enclosure, it can be
assumed to be an open system where the total pressure inside the copper enclosure is equal to the total pressure outside of the enclosure. Additionally, the total pressure of the non-enclosed configuration and the enclosed configuration can be assumed to be equal, being held constant at 250mTorr. Given that the vapor pressure of Cu is relatively high for a transition metal (7.5x10^5 Torr at 1000°C),\textsuperscript{146} the nearly static partial pressure of copper inside the enclosure would be significantly higher than that above Cu samples without a copper enclosure. Therefore, in order to satisfy Dalton’s equation, the partial pressures of the remaining gas-phase species, including BN precursors such as borazine and diborane, would be reduced compared to the environment surrounding the films grown in the non-enclosed configuration. A reduced partial pressure of BN precursors would thus directly lead to a reduction in growth rate, as observed, since the impingement flux of gas-phase precursors would decrease with reduced precursor partial pressure. This is illustrated in Equation 3.2.1, where \( \Phi \) is the impingement flux (molecules/cm\(^2\)-s), \( P_i \) is the partial pressure of gas species (Torr), \( M \) is the molecular weight of gas species, and \( T \) is the temperature (°C).

\[
\Phi = 3.513 \times 10^{22} \frac{P_i}{(MT)^{1/2}}
\]

Equation 3.2.1\textsuperscript{147}

3.2.2: Effect of Copper Enclosure on h-BN Morphology and Domain Size and Proposed Growth Model

The reduced flux of h-BN precursors, described in the previous section, would lead to a reduction in adatom surface density, \( n_a \) (cm\(^{-2}\)), by: \( n_a = \tau_s \Phi \), where \( \tau_s \) (s\(^{-1}\)) is the adatom
lifetime. Additionally, the adatom surface density is directly proportional to the nucleation rate, $\dot{N}$ (nuclei/cm$^2$-s). The grain diameter, $l_g$ (cm), is then given by: $l_g \propto (\dot{G}/\dot{N})^{1/3}$, where $\dot{G}$ (cm/s) is the linear growth rate of the grain. This suggests then that a decrease in partial pressure of BN precursors through the use of a copper enclosure should enhance the domain size of the h-BN film, which is highly desirable since small domain sizes are often reported for growth of h-BN on Cu foils and can lead to increased leakage currents. Figure 3.2.2 shows SEM images detailing the evolution of grain size with growth time, as a function of film thickness (measured via optical ellipsometry) for h-BN films grown using a copper enclosure.

**Figure 3.2.2**: 50,000x FESEM images of h-BN films grown via CVD on copper foils at various growth times and subsequently transferred to Si(111) substrates. The h-BN film thickness increases progressively from (a) to (d).
The 2D island growth is easily discernible with SEM, where islands increase in size and decrease in density as the coalesced film thickness increases. At a film thickness of \( \sim 10 \text{nm} \), grains appear to be nearly coalesced and individual islands become more difficult to distinguish. Figure 3.2.3 shows 2x1\( \mu \text{m}^2 \) AFM scans of the same films observed with SEM in Figure 3.2.2. Again, the transition from small grains in high density to larger grains in low density with increasing thickness is apparent. However, height quantification via AFM shows that the islands are thicker in the centers than at the edges, indicating nucleation of new nano-domains over the existing islands.

![AFM scans](image)

**Figure 3.2.3:** (a-d) 2x1\( \mu \text{m}^2 \) AFM scans of h-BN films grown via CVD on copper foils and subsequently transferred to Si(111) substrates. The h-BN film thickness and the RMS roughness increases progressively from (a) to (d).

Interestingly, the shape of the h-BN grains observed in Figure 3.2.2 and 3.2.3 appears circular, unlike previous reports of triangular h-BN domains observed for monolayer h-BN growth on Cu.\(^{38,40}\) As described in Section 1.2, Kim et al.\(^{38}\) suggested that triangles are more energetically favorable for h-BN growth since nitrogen-terminated edges have lower edge energy than boron-terminated edges. Unlike graphene, where hexagon domains are preferred, single crystal h-BN domains nucleate as triangles since hexagon formation would ultimately lead to
non-energetically favorable B-terminated edges. However, for the multilayer h-BN films shown in Figures 3.2.2 and 3.2.3, h-BN triangular domains are not observed, suggesting that the circular islands are likely composed of many nanocrystalline triangular domains. To understand the growth mechanisms of the films presented in this thesis, the growth time was reduced further in an attempt to grow a monolayer h-BN film. Figure 3.2.4 shows SEM images taken of an h-BN film as-grown on Cu after 2.5 minutes of growth with the use of a Cu enclosure. Figure 3.2.4a is a low magnification image showing three different Cu grains. Figure 3.2.4b shows a high magnification image of Grain 1 (top left corner of Figure 3.2.4a) and shows several randomly oriented triangular h-BN domains nucleating over a complete monolayer, as apparent from the wrinkling of the underlying monolayer. Figure 3.2.4c shows a zoomed-in image of one of these secondary triangular h-BN domains with a length (tip of triangle to center of base) of approximately 195nm. The triangular domains observed on Grain 1 appear to nucleate preferentially from surface wrinkles, likely due to defects or dangling bonds at wrinkle edges. It is believed that the surface wrinkling results during post-growth cooling of the sample, due to induced strain resulting from copper’s negative coefficient of thermal expansion (CTE). However, Figure 3.2.4b suggests that the wrinkling of this particular grain may occur during growth, since h-BN nucleation appears to initiate at wrinkle edges. This may be due to the orientation of this particular grain. It has been previously reported that the (111) face of Cu is an ideal substrate for graphene and h-BN growth due to their close lattice match, where Cu(111) has a lattice constant of 2.56Å and h-BN has a lattice constant of 2.50Å, leading to a lattice mismatch of only 2.3%. However, Cu(100) has a lattice constant of 3.61Å, giving a lattice mismatch with h-BN of 30.8%. Therefore, for a polycrystalline Cu foil, the local lattice mismatch will vary depending on grain orientation. It is possible that for Grain 1 of Figure 3.2.4a, the orientation is not (111), but rather (100), (110), etc; leading to a larger lattice mismatch that may
result in wrinkling during growth. Since the wrinkles propagate in random directions, h-BN domains nucleating from these wrinkles will be randomly oriented, as shown in Figure 3.2.4b.

In contrast, inspection of Grain 2 of Figure 3.2.4a indicates morphological differences between different Cu grains. Figures 3.2.4d and e show high magnification images from Grain 2 (bottom left corner of Figure 3.2.4a). Unlike Grain 1, where the h-BN triangular domains were randomly oriented, h-BN grown on Grain 2 shows preferential nucleation of h-BN triangles from crystallographic Cu step-edges. The wrinkling observed in Figure 3.2.4d indicates that again, these domains are forming over a complete monolayer. Interestingly however, the density of wrinkles in Grain 2 is significantly less than in Grain 1, where the overall length of observable wrinkles was measured to be 26.63µm in Grain 1 (Figure 3.2.4b) and 10.37µm in Grain 2 (Figure 3.2.4d), indicating a 61% higher wrinkle density in Grain 1. It is likely that Grain 2 is a Cu(111) grain, where a small lattice mismatch exists. Closer inspection of the SEM images reveals that the triangular domains do not nucleate at the large wrinkle observed in Grain 2, indicating that film wrinkling of Grain 2 occurred only during cooling to compensate for the mismatch in CTE between h-BN and Cu. In this case, nucleation of secondary triangular domains over the original monolayer occurs at crystallographic step-edges rather than at wrinkle edges, as shown in Figure 3.2.4e. The step-edges likely provide energetically favorable nucleation sites due to an increased density of dangling bonds, even for growth of the second h-BN layer. This suggests that improved orientation texturing of h-BN monolayers and bi-layers can be controlled through selection of the Cu orientation. It is difficult to determine the orientation of Grains 1 and 2 based on morphological observation alone. A technique such as orientation imaging microscopy (OIM) would be required for precise indexing. However, RMS surface roughness limits (typically <1nm) prevent its use for the Cu foils used in this thesis.
**Figure 3.2.4:** FESEM images of an h-BN film grown with a copper enclosure for a growth time of 2.5 minutes. (a) Low magnification FESEM image showing multiple Cu grain orientations. (b, c) High magnification images of Grain 1 showing the formation of triangular domains oriented randomly over an h-BN monolayer. (d,e) High magnification images of Grain 2 showing the formation of triangular domains nucleating preferentially from Cu step-edges over an h-BN monolayer.
Based on the observed morphological features, a potential nucleation and growth model can be proposed. Figure 3.2.4 verifies that the h-BN films grown for this thesis do initially nucleate as triangular single-crystal domains. It is widely believed that the first monolayer forms rapidly due to the high surface reactivity and diffusion rate of borazine on Cu (as well as the high initial precursor concentrations observed in Figure 3.1.2).\(^{24}\) However, the surface reactivity of BN precursors such as borazine on h-BN (compared to Cu) is poor.\(^{24}\) This would lead to a dramatic reduction in surface diffusion of BN precursors, and thus a reduction of h-BN domain size, over the initial h-BN monolayer. This corroborates with the work shown by Kim et al.,\(^{38}\) whom show that the size of the triangular domains decrease significantly after the formation of a complete monolayer. It is apparent from the work of Kim et al.\(^{38}\) and the results shown in this thesis (Figure 3.2.4) that single crystal triangular domains can form even after the initial monolayer. Additionally, Figure 3.2.4d shows that even after the formation of the original monolayer, subsequent h-BN triangles nucleate from Cu surface features such as step-edges. This suggests that these triangular domains retain some binding energy to the Cu substrate for at least the first two (possibly more) layers. It is likely that this binding energy decreases exponentially with increasing layer thickness however, and may explain the transition from the single-crystal triangular domain growth to the circular island growth observed in Figures 3.2.2 and 3.2.3. After the first few h-BN layers, the binding energy between impinging BN precursors and the Cu substrate is negligible and subsequent h-BN growth nucleates as nanocrystalline domains (possibly at domain edges or defects) rather than large single-crystal h-BN triangles, due to the decreased adatom diffusion. These nanocrystalline domains eventually nucleate off of each other and form the small circular islands observed for multi-layer h-BN in Figures 3.2.2 and 3.2.3.

This suggests that h-BN growth on Cu proceeds similarly to the Stranski-Krastanov growth mode,\(^{147}\) where island growth becomes favorable over layer-by-layer growth after the first few layers. Stranski-Krastanov growth occurs when the first few layers of a material are more
strongly bound to the substrate surface than to each other. When subsequent layer-substrate binding is reduced, island formation occurs as atoms are more strongly bound to each other than to the substrate. At this point, subsequent atoms impinging on the initial h-BN layers are limited by their reduced diffusion mean free path and are most likely to encounter other impinging atoms and nucleate into nanocrystalline clusters. Additional adatoms attach to these clusters and result in the formation of small individual nanocrystalline islands in high density, as shown in Figure 3.2.2a and 3.2.3a. From these figures, it is apparent that the nanocrystalline islands (~20nm) are much smaller than the initial single-crystal triangular domains (~200nm) shown in Figure 3.2.4, verifying the decrease in surface reactivity and diffusion at multi-layer thicknesses. As the density of these nanocrystalline islands increases, the mean free path of diffusion becomes equal to or less than the separation distance of individual islands. Therefore, the probability of an atom attaching to an already existing island becomes greater than the probability of it forming a new nucleation site. As the size of the islands increase, neighboring islands will begin to coalesce and create larger islands with a reduced surface density, as observed in Figures 3.2.2b,c and 3.2.3b,c. Since the probability of adatoms attaching to island edges would be higher than for nucleating a new layer on top of an existing island, the lateral growth rate would be higher than the vertical growth rate. This ultimately will lead to the coalescence of the larger islands and formation of a continuous film, as shown in Figure 3.2.2d and 3.2.3d.

This proposed growth method may explain the structure of h-BN films grown on Cu and transferred to insulating substrates, as observed with cross-sectional TEM in Figure 3.2.5 for films grown with the use of a copper enclosure. For a 5nm h-BN film transferred to Al2O3 (Figure 3.2.5a), highly planar and laminar growth of nine h-BN layers with high crystallinity and atomically sharp interfaces is observed. The first few layers appear highly continuous due to the nucleation of large single-crystal triangular domains. Additionally, a small dip in the top three layers is present and indicates a separation of two h-BN islands that are in the process of
coalescing, consistent with the proposed growth model. Interestingly, for the 15nm thick sample (Figure 3.2.5b), there is clearly a point after approximately 15 layers where the h-BN film transitions from highly planar to a less ordered turbostratic structure. After ~15 layers, not only do the h-BN domains decrease in apparent size, but the orientation of the c-plane becomes significantly more random. This sharp transition in apparent growth mode likely occurs at the point in the proposed growth model when the nanocrystalline h-BN islands fully coalesce into a continuous film. At this point, lateral growth is essentially quenched as islands are fully coalesced and the density of island edges is negligible. This may then lead to subsequent h-BN growth proceeding via nucleation of randomly oriented nanoclusters over the fully coalesced h-BN film, resulting in the formation of turbostratic BN layers.

Figure 3.2.5: Cross-sectional TEM images of h-BN films grown on Cu and transferred to insulating substrates. (a) ~5nm h-BN film transferred to Al₂O₃ shows laminar growth of nine crystalline h-BN layers and coalescence of h-BN islands. (b) ~15nm h-BN film transferred to SiO₂ shows that after ~15 layers, the film becomes turbostratic with a more random orientation.
It should be noted that the nine h-BN layers shown in Figure 3.2.5a appear much more laminar and continuous than the first ~15 layers of Figure 3.2.5b, where h-BN layers often appear to overlap each other and small breaks in the first layer propagate into subsequent layers. This may be due TEM sampling at different local grain orientations. It is impossible to determine with exact certainty the orientation of the Cu grain that these h-BN films were grown on, since these films were transferred from their native Cu substrates. However, it is hypothesized that the reduced order of the first few layers in Figure 3.2.5b may be a result of stitching of randomly oriented triangular domains (nucleated at wrinkle edges), such as observed in Grain 1 of Figure 3.2.4a. Conversely, the highly laminar and continuous layers observed in Figure 3.2.5a may be a result of the formation of oriented triangular domains (nucleated at crystallographic Cu step edges), such as observed in Grain 2 of Figure 3.2.5a, where stitching of complete layers would be enhanced due to the preservation of the crystallographic orientation of h-BN over large areas.

Based on the morphological features observed with SEM and the structural features observed with TEM, a 3-step growth model can be hypothesized. To simply illustrate the growth model based off the experimental observations presented previously, a basic cross-sectional illustration of the proposed model is presented in Figure 3.2.6. It is suggested in this thesis that growth of h-BN on Cu substrates proceeds first through the nucleation of large triangular domains on the Cu surface (red layers in Figure 3.2.6). These triangular domains persist through the first few layers until the interactions between subsequent adatoms and the Cu substrate is quenched. Similarly to the Stranksi-Krastanov growth mode, island growth (green layers in Figure 3.2.6) begins due to the reduced binding energy of subsequent adatoms to the Cu surface. These circular islands, consisting of nanocrystalline domains, increase in diameter and decrease in density as they coalesce with each other with increasing film thickness. After the islands fully coalesce, subsequent growth proceeds via random nucleation of BN nanoclusters, from which turbostratic BN growth proceeds (yellow layers in Figure 3.2.6).
**Figure 3.2.6:** Proposed nucleation and growth model for h-BN films on Cu substrates. The blue area is the Cu substrate; the red layers correspond to h-BN formed through growth of triangular domains; the green layers are h-BN formed through nucleation and coalescence of h-BN islands; and the yellow layers represent h-BN formed from nucleation of disordered nanoclusters resulting in turbostratic BN.

Therefore, the growth of h-BN on Cu only produces uniform, laminar layers for a short time before disordered turbostratic growth dominates. Interestingly, the use of a copper enclosure to control the partial pressure of BN precursors during growth appears to play a role as to when the h-BN islands will fully coalesce, and thus transition to turbostratic BN growth. Figure 3.2.7 shows SEM images of ~5, 10, and 20nm thick h-BN films grown without (Figure 3.2.7a-c) and with (Figure 3.2.7d-f) the use of a copper enclosure. For the ~5nm thick films, the h-BN islands
can be easily observed for both growth configurations. However, the use of a Cu enclosure results in a >2.3x increase in h-BN island size at similar film thicknesses (~5nm), where the islands are an average of 177.20nm (±3.61nm) for the enclosed growth and 75.83nm (±5.99nm) for the non-enclosed growth. This is due to the increased flux of BN precursors on the Cu surface for the non-enclosed growth, where the diffusion mean free path (L) is decreased by: \( \approx (D/\Phi)^{1/6} \), where \( D \) is the diffusion coefficient and \( \Phi \) is the impingement flux described by Equation 3.2.1. Therefore, the probability of adatoms forming new nucleation sites, rather than attaching to existing nuclei, is increased compared to the enclosed growth. This then results in a higher density of h-BN islands, which then coalesce at reduced thicknesses compared to the enclosed growth. This is most apparent from the ~10nm thick films of Figure 3.2.7, where the non-enclosed film has completed coalesced and individual islands are not observed. Here, the h-BN film has likely completely transitioned to the turbostratic growth mode. Additionally, the surface is uniformly covered with the 3D nuclei described in Section 3.1.2. In comparison, the enclosed sample appears to be in the final stages of coalescence and individual grains are still partially visible. Additionally, the density of 3D nuclei is strikingly reduced relative to the non-enclosed sample. At ~20nm, the non-enclosed sample is similar in morphology to the ~10nm sample, only with increased wrinkle width due to the increased thickness, and contains again a high density of 3D nuclei. Interestingly however, the enclosed sample remains nearly free of 3D nuclei even at a film thickness of ~20nm, where the density of 3D nuclei of this film compared to the ~20nm thick film grown without a Cu enclosure decreased by ~11x (from ~568±55 nuclei/\( \mu m^2 \) to ~52±15 nuclei/\( \mu m^2 \)). Additionally, surface wrinkling is dramatically reduced. Therefore, not only does the use of a copper enclosure during growth result in enhanced h-BN island size; it also appears to significantly reduce or even eliminate the formation of 3D nuclei and reduce surface wrinkling. This is, again, likely due to the improved crystallinity at high film thickness due to the decreased partial pressure of BN precursors and thus, a reduced impingement rate. Additionally, a decrease
in the partial pressure of oxygen impurities (as discussed subsequently in Section 3.2.3) would be expected to reduce the formation of BN fullerenes, which require oxygen incorporation, and may be another possible mechanism for the decrease in 3D nuclei with the use of a Cu enclosure.

Figure 3.2.7: (a-c) 50,000x SEM images of h-BN films with increasing thickness (~5, 10, and 20nm, respectively) grown without the use of a copper enclosure show a high density of 3D particle nucleation and a high degree of film wrinkling. (d-f) 50,000x SEM images of h-BN films of similar thicknesses grown using a copper enclosure show a larger apparent domain size and a reduced density of 3D particle formation.
The use of plan-view high resolution transmission electron microscopy (HRTEM) on ~20nm thick h-BN films grown without and with the use of copper enclosure was employed to investigate the structural and crystallographic differences between the two growth configurations. For the film grown without the copper enclosure (Figure 3.2.8a), HRTEM analysis indicates that the film is nanocrystalline with domain sizes on the order of only a few nanometers. This nanocrystalline texturing is also apparent in the selected area diffraction pattern (SAD), shown in Figure 3.2.8c, where broad rings and weak diffraction spots are observed. Additionally, the film shows areas where the c-axis propagates perpendicular to the growth surface, similar to the HRTEM analysis of the 3D nuclei shown previously in Figure 3.1.4. In contrast, h-BN grown with a copper enclosure (Figure 3.2.8b) exhibits a higher degree of order and texturing in the film and increased domain size. The spots in the SAD pattern (Figure 3.2.8d) also appear much sharper compared to the non-enclosed growth, indicating that the crystallinity of the film is improved. In both cases the d-spacing is approximately ~0.21nm, as measured directly from the TEM image (Figure 3.2.8c), with the calculated Fast Fourier Transform (FFT) pattern (inset of Figure 3.2.8c) matching the inter-atomic distance in the (0001) plane of bulk h-BN. However, even for the sample utilizing the Cu enclosure, the domain size observed with plan-view HRTEM is still quite small (~5nm), making orientation indexing difficult from the SAD patterns since the smallest aperture for SAD analysis is 125nm in diameter. Such small domain sizes could be detrimental to graphene-based devices, since domain boundaries and the addition of adsorbates at domain boundaries can lead to enhanced conduction. However, based on the proposed growth model of Figure 3.2.6 and the cross-sectional TEM observations of Figure 3.2.5, these ~20nm thick films are likely composed mostly of nanocrystalline/turbostratic BN structures, where a transition to turbostratic BN growth was found to occur after ~15 layers.
Figure 3.2.8: (a, b) Plan view HRTEM of an h-BN film grown without and with the use of a Cu enclosure, respectively. (c, d) Diffraction patterns corresponding to (a) and (b), respectively; indicate that the use of a Cu enclosure during growth resulted in higher degree of crystallographic texturing and larger domains. (e) High magnification image of (b) showing the commensurate hexagonal structure. Inset shows the calculated FFT pattern from the TEM image of (e) and was used to measure d-spacing.

These results show that use of a Cu enclosure during growth of h-BN on Cu substrates results in an overall enhancement of the crystalline domain size and a reduction in the formation of unwanted 3D nucleation and wrinkling. This occurs due to the reduction in the partial pressure of BN precursors as described previously. However, these results also suggest that the Cu enclosure may not be needed if the partial pressure could be reduced by alternative
techniques, such as incorporation of a pressure-based MFC to accurately control the concentration of gas-phase precursors introduced into the system. Unfortunately, at the time of this work, such a growth configuration was not available. However, the Cu enclosure accurately details the benefits of reduced precursor partial pressure for h-BN growth.

3.2.3: Chemical and Bonding Analysis via XPS of Enclosed vs. Non-Enclosed h-BN Growth

X-ray photoelectron spectroscopy (XPS) was utilized to study the effect of the copper enclosure on the chemical properties of h-BN. Here, two sets of films were grown under similar conditions (T=1000°C, P=250mTorr) to similar thicknesses (~10nm); but either with or without the use of a copper enclosure. XPS was performed on as-grown h-BN films on copper substrates as well as on h-BN films transferred to Si substrates. Table 3.2.1 details the concentrations of B, C, N, and O, as well as the B/N ratios, for these h-BN films.

Table 3.2.1: Relative concentrations (%) of boron, nitrogen, carbon, and oxygen as measured with XPS for growth of h-BN on copper substrates with and without the use of a copper enclosure during growth. Use of a Cu enclosure results in a reduction of both carbon and oxygen impurities.
For both growth configurations, the as-grown and transferred B/N ratios are within 10% of unity, indicating highly stoichiometric films. However, with the use of a copper enclosure, the carbon content was reduced by 62% (from 5.3% to 2.0%) and the oxygen content was reduced by 65% (from 5.5% to 1.9%) compared to h-BN films grown without a copper enclosure. Additionally, the B1s high resolution spectra (Figure 3.2.9) indicate the presence of oxygen bonding in the h-BN lattice, as evident by the peak at ~192eV (blue peak). The contribution of this peak to the total area of the B1s spectra indicates the degree of bonding between oxygen and boron atoms in the film. For the B1s spectra of the non-enclosed h-BN film (Figure 3.2.9a), 94.1% of the B1s spectra is attributed to B-N bonding (190.45eV) while B-O bonding (191.52eV) contributes the remaining 5.9%. For the case of the enclosed h-BN film (Figure 3.2.9b) however, B-N bonding (190.46eV) contributes to 98.7% of the B1s spectra, while B-O bonding (191.80eV) is responsible for only 1.1%. This indicates that for oxygen actually bonded to boron atoms, the enclosed growth results in an 81% reduction in B-O bonding. These results contribute to the notion that the copper enclosure creates a static gas-phase Cu overpressure in the growth environment. This not only leads to a reduction in the partial pressure of the gas-phase BN precursors, as discussed previously, but also in other gaseous impurity species, such as oxygen from leaks in the vacuum system or hydrocarbons from back-streamed pump oil. These results suggest that the use of a copper enclosure, and thus a copper overpressure, during growth of h-BN on Cu substrates can significantly reduce contamination from impurity elements. Additionally, since B-O bonding likely occurs at unsatisfied bonds at defects or domain boundaries, the increase in domain size (detailed previously) is likely another possibility for the observed decrease in B-O bonding with the Cu enclosed growth. As mentioned in Section 3.1.2, 3D surface features are likely composed of BN fullerene structures, which require oxygen to form thermodynamically. Therefore, the decrease in oxygen content with use of a Cu enclosure may be responsible for the decreased density of 3D nuclei, observed in Figure 3.2.7.
Figure 3.2.9: XPS B1s spectra of as-grown h-BN on copper foils grown (a) without a copper enclosure and (b) with a copper enclosure. Bonding of oxygen in the BN lattice (BN$_x$O$_y$) is represented by a higher energy peak ~192eV (blue peak). With use of a copper enclosure, the presence of this peak is significantly reduced.

The XPS results of Table 3.2.1 also show that upon transfer, in both cases the carbon and oxygen content increase significantly. It was discussed in section 3.1 that the increase in oxygen content upon transfer is a result of the transfer process, which utilizes several water baths that could lead to oxygen bonding at defect sites or domain boundaries. In Figure 3.1.5, it was found
that the BN$_x$O$_y$ peak at ~192eV, associated with B-O bonding increased upon transfer. However, peaks expected to be associated with B-C bonding (~188eV) were not observed. Again, the transferred B1s spectra (not shown) for both h-BN films grown with and without the use of a Cu enclosure indicate no presence of B-C bonding, despite the observed increase in carbon composition. Interestingly however, the high resolution C1s spectra (Figure 3.2.10) indicate otherwise. For the as-grown film grown without the use of a Cu enclosure, shown in Figure 3.2.10a, the primary peak associated with the C1s spectra is located at 284.8eV (red peak) and is indicative of C-C bonding, most likely from residual photoresist or adventitious carbon on the h-BN surface. This peak accounts for 63.5% of the as-grown C1s spectra for the non-enclosed growth. However, a second peak located at 285.7eV (blue peak) contributes 36.5% of the C1s spectra. This peak is associated with C-B bonding and has been reported elsewhere for hybridized graphene/h-BN films, where C-B and C-N bonding was reported to occur at the boundaries between h-BN and graphene domains. Interestingly, this peak was not observed for the film grown with the Cu enclosure (Figure 3.2.10c), indicating that negligible bonding between B and C atoms occurs during h-BN growth when utilizing a Cu enclosure. Again, this is likely due to the decreased partial pressure of impurity species in the Cu enclosure growth environment. However, both films showed distinctly different C1s spectra upon transfer, as shown in Figure 3.2.10b and d, where the C-B peak (blue peak) located at ~286eV was observed in both cases. Additionally, a third peak located at ~289eV is present. This peak is indicative of C-N bonding, as reported again for graphene/h-BN hybridized films. This indicates that the transfer process results in partial bonding of carbon, likely from the photoresist, to both B and N atoms of the h-BN film.
Figure 3.2.10: XPS C1s spectra of h-BN as-grown on Cu foils (a, c) and transferred to Si (b, d) for films grown without a copper enclosure (a, b) and with a copper enclosure (c, d). With the use of copper enclosure, the as-grown C1s peak is significantly less intense than for the film grown without a copper enclosure. For both cases, the C1s peak increases and gains additional peaks after transfer due to residual photoresist on the h-BN surface.

Similarly to oxygen incorporation, it was found that the contributions of C-B and C-N bonding to the transferred C1s spectra were reduced for the h-BN film grown using a Cu
enclosure, as shown in Table 3.2.2. These results indicate a 20% decrease in C-N bonding and a 26% decrease in C-B bonding in the transferred h-BN films with the use of a Cu enclosure. Carbon bonding likely occurs at domain boundaries and defects, as shown with TEM in the reports of hybridized graphene/h-BN films.\textsuperscript{137} The reduction in C-B and C-N bonding observed with the use of a Cu enclosure is likely a result of increased domain size, as detailed previously. Larger h-BN domains will result in a decrease in the density of domain boundaries and consequently, unsatisfied bonds. Therefore, the incorporation of impurities at these sites should be reduced, as observed with XPS. It is interesting that the C-B and C-N bonding is only observed in the C1s spectra and not the B1s or N1s spectra. It is likely that the contribution of C-B and C-N bonding is greatly overshadowed by the primary B-N bonding configuration, and therefore is not detectable in the B1s or N1s spectra.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
 & \textbf{Without Cu Enclosure} & & \textbf{With Cu Enclosure} & \\
 & \textbf{As-Grown} & \textbf{Transferred to Si} & \textbf{As-Grown} & \textbf{Transferred to Si} \\
\hline
C-C (184.8eV) & 63.51 & 61.85 & 100 & 71.05 \\
\hline
C-N (\textasciitilde289eV) & N/A & 11.47 & N/A & 9.16 \\
\hline
C-B (\textasciitilde286eV) & 36.49 & 26.68 & N/A & 19.79 \\
\hline
\end{tabular}
\caption{Component contribution (\%) of various carbon bonding configurations after deconvolution of C1s spectra for as-grown and transferred h-BN films grown with and without the use of Cu enclosure.}
\end{table}

In conclusion, the use of a copper enclosure during the pre-growth anneal and growth of h-BN films has been shown to be highly beneficial for h-BN synthesis. The Cu enclosure creates a nearly static copper overpressure directly above the Cu substrates. This Cu overpressure reduces the partial pressure of all other gas species in the growth environment, including the BN
precursors (such as borazine and diborane) and impurity gases. The reduction in BN precursors results in a reduction in growth rate as well as an enhancement of h-BN domains due to a reduced flux of precursor to the Cu substrate. Additionally, a possible growth model was proposed where h-BN proceeds via the nucleation of islands over an original monolayer (Stranski-Krastanov growth mode). Upon full coalescence of h-BN islands, further nucleation proceeds as random nano-domains, resulting in the formation of turbostratic BN as evidenced by cross-sectional TEM. It was found that the use of a copper enclosure, which promotes larger h-BN islands, fully coalesces at larger thicknesses than non-enclosed growth, leading to a film with a higher crystallinity. Finally, it was found that the use of a Cu enclosure reduces the incorporation of oxygen and carbon impurities, as evident through XPS. The reduction in impurity concentrations found in the enclosed films are likely a result of two mechanisms: 1) a reduced flux of impurity gas species to the Cu substrate due to an increased copper partial pressure, and 2) a reduced h-BN domain boundary density due to enhanced h-BN domain size, where impurities are likely to bond.

3.3: Electrical Properties of h-BN Films Grown on Copper

Electrical breakdown measurements were performed between two 125µm Au/Ti pads (100nm/20nm) deposited on h-BN films grown on Cu foils and transferred to Au/Ti/SiO₂/Si (100nm/20nm/300nm/bulk) substrates, as described in Section 2.6. Here, we investigate the insulating behavior of the films as a function of thickness and growth configuration (with or without a Cu enclosure). It has been previously reported that bulk h-BN typically has a breakdown field in the range of 2-6×10⁶ V/cm. However, breakdown fields reported for exfoliated h-BN have been reported at 10-15×10⁶ V/cm, due to the pristine single crystal nature of exfoliated h-BN flakes. In these reports, it was found that exfoliated h-BN flakes less than 4 layers experienced significant tunneling currents. However, the breakdown characteristics of h-
BN films grown on Cu have not been thoroughly explored. For these experiments, the breakdown field was considered to be the voltage field (V/cm) where the current density reached 10 A/cm².

Figure 3.3.1 shows the log-log plots of current density versus voltage field for h-BN films grown with a copper enclosure. The breakdown curves for the thinner h-BN films (up to ~5nm) show significant leakage (current density of ~4 A/cm² at 1x10⁵ V/cm) with no distinguishable breakdown point, behaving similarly to a short. This is most likely due to the fragility of these films; where pinholes, tears, and defects are easily introduced during the transfer process. Therefore, a high density of conduction paths are likely to be introduced into these films, leading to the shorting behavior. For thicker h-BN films (~10 and ~20nm) however, the breakdown characteristics are typical of insulating films. These films are more stable during transfer and presumably have a lower density of pinholes and tears introduced during transfer that act as conduction paths; however many of the tested devices on both samples still showed shorting behavior, indicating not all areas were free of film damage. Note that the dotted black lines beside the breakdown curves of the ~10nm and ~20nm thick h-BN films represents the standard deviations of the optical ellipsometry measurements used for thickness quantification, where a standard deviation of 0.42nm and 0.91nm was obtained for the ~10nm and ~20nm thick films, respectively. The breakdown fields (assuming the average thickness values) were found to be similar for both the ~10nm and ~20nm thick h-BN films, where breakdown occurred at 1.24x10⁶ and 1.34x10⁶ V/cm, respectively. This is expected for h-BN films of similar quality since the breakdown field is normalized to thickness. However, the current density at low fields for the ~10nm thick film was found to be significantly higher than for the ~20nm thick film, where current densities at 1x10⁵ V/cm were 8.4x10⁻⁶ and 3.4x10⁻⁹ A/cm², respectively, indicating a current density over three orders of magnitude higher for the ~10nm thick film. This may be attributed to the fact that the h-BN film thickness is not uniform. Through AFM measurements of a ~10nm thick h-BN film, a maximum peak-to-valley value was found to be ~18nm for a film
measured with optical ellipsometry at a nominal thickness of ~10nm. This large peak-to-valley value is due to the formation of large surface wrinkles (peaks) and the presence of low areas between h-BN islands (valleys), such as shown previously in the AFM scan of Figure 3.2.3d. Therefore, breakdown likely occurs in the low valleys of the film where the local thickness is much less than the nominal film thickness measured with optical ellipsometry. For the ~10nm thick film, the low thickness locally at “valleys” leads to enhanced tunneling and thus increased leakage currents compared to the ~20nm thick film, where the film thickness at “valleys” would be increased relative to the 10nm thick film, leading to reduced tunneling. For both the ~10nm and ~20nm thick h-BN films, current leakage and eventual breakdown likely occur through domain boundaries, where nanocrystalline domains (observed through HRTEM previously in Figure 3.2.8) lead to a high density of domain boundaries. This is in contrast to single crystal exfoliated h-BN flakes, which have high breakdown strengths (10-15x10^6 V/cm)^42,43 due to an absence of domain boundaries.
Figure 3.3.1: Current density vs. voltage field showing the breakdown characteristics of h-BN films grown to various thicknesses in a copper enclosure. Up to ~5nm, the h-BN films exhibit high leakage currents. At ~10nm and ~20nm, the h-BN films are insulating with breakdown ~$1.5 \times 10^6$V/cm, where the 20nm film shows lower leakage compared to the 10nm film. The dotted lines of the ~10nm and ~20nm curves indicate the standard deviation of the thickness measurements.

Breakdown analysis was also performed on h-BN films of similar thicknesses, but grown under different growth configurations. Figure 3.3.2 shows the log-log plots of current density vs. voltage field for ~20nm thick h-BN films grown with or without the use of a copper overpressure and shows a significant difference between the two growth configurations.
Figure 3.3.2: Current density vs. voltage field showing the breakdown characteristics of 20nm h-BN films grown with and without the use of a copper enclosure. The breakdown characteristics of two 30nm thick high-k dielectrics, Al$_2$O$_3$ and HfO$_2$, are also shown. The h-BN film grown with the copper enclosure shows similar leakage currents and only a slightly lower breakdown field compared to high-k dielectrics, while the h-BN film grown without the copper enclosure shows significantly higher leakage currents and a reduced breakdown field.
For the ~20nm h-BN film grown with the Cu enclosure (also shown in Figure 3.3.1), breakdown occurs at 1.34x10^6 V/cm. Conversely, for the ~20nm thick h-BN film growth without the Cu enclosure, breakdown occurs at 7.09x10^5 V/cm. This indicates an increase in h-BN breakdown field of 89% when grown with the use of a Cu enclosure. Additionally, the current density at a voltage field of 1x10^5 V/cm increases by over four orders of magnitude (from 3.4x10^-9 to 2.04x10^-5 A/cm^2) when h-BN is grown without the use of a Cu enclosure. This indicates that the density of conduction paths is significantly increased in the h-BN film grown without the use of a Cu enclosure. This could be a result of an increased density of domain boundaries due to the decreased crystallinity observed in Section 3.2.2, or an increase in conductivity due the increased carbon content of the h-BN film grown without a Cu enclosure.

For comparison, the breakdown characteristics of two high-k dielectrics typically used as dielectrics in graphene devices (Al_2O_3 and HfO_2) were plotted with the h-BN results. Both of these high-k dielectrics were ~30nm thick and deposited via e-beam evaporation. It was found that the current densities were very similar up to ~1x10^6 V/cm, indicating that the leakage currents for h-BN films grown with the use of a Cu enclosure are on par with these two high-k dielectrics. As expected however, the breakdown fields for the high-k dielectrics were slightly higher than the h-BN film, where breakdown of the Al_2O_3 and HfO_2 films occurred at 1.76x10^6 and 2.32x10^6 V/cm, respectively, due to their superior dielectric strength. This indicates that h-BN dielectrics grown on Cu foils with the use of a Cu enclosure have breakdown strengths only moderately lower than these common high-k dielectrics, where its breakdown strength was found to be ~24% and ~42% less than Al_2O_3 and HfO_2, respectively.
Chapter 4

Integration of Hexagonal Boron Nitride as a Top-Gate Dielectric for Quasi-Freestanding Epitaxial Graphene Electronics

Although the benefits of h-BN/graphene systems have been demonstrated previously, current focus has been limited to h-BN integration with CVD or exfoliated graphene, as detailed in Section 1.7. The effects of h-BN on epitaxial graphene, which is more conducive to large scale development than exfoliated graphene and more easily processed than CVD graphene, have not yet been investigated. Epitaxial graphene has been shown to produce uniform, large area, and high quality graphene for high frequency applications with an intrinsic current gain cutoff frequency ($f_T$) approaching 300GHz. In addition, epitaxial graphene has been further enhanced by hydrogen intercalation, where the interfacial (buffer) layer present in epitaxial graphene is passivated by hydrogen, forming a “quasi-freestanding” epitaxial graphene (QFEG) which leads to mobility improvements of approximately 2.5x and extrinsic $f_T$ improvements of >3x.

This thesis presents the results of the first 75mm QFEG wafer with CVD h-BN top-gated graphene field effect transistors (GFETs). This chapter presents electrical characterization that indicates CVD h-BN integration with QFEG results in significantly less remote surface optical phonon scattering and introduces less charged impurities to the system relative to HfO$_2$ based dielectrics. Additionally, the overall benefit of h-BN relative to HfO$_2$ dielectrics is found to be critically dependent on the initial impurity density of the QFEG samples; which results in unique limitations not typically observed in h-BN integration with exfoliated or CVD grown graphene. On high mobility QFEG samples (>2000 cm$^2$/V-s at a carrier density of 1x10$^{13}$ cm$^{-3}$) with low remote charged impurity densities, h-BN gate dielectrics are shown to effectively preserve mobilities >3000 cm$^2$/V-s at room temperature, ultimately leading to intrinsic transistor cutoff frequencies of 33.5 GHz for 750nm gate lengths. However, for low mobility QFEG samples
(<1500 cm$^2$/V-s at similar carrier densities) with a high density of remote charged impurities, Coulombic scattering dominates transport and the benefits of h-BN are quenched relative to HfO$_2$ due to h-BN’s low dielectric constant. It was found that the initial mobility of the QFEG system was highly influenced by the local SiC morphology of each Van der Pauw (VdP) device, where step-edges induce additional remote impurities and surface optical phonon scattering. The results presented in this chapter are also published elsewhere.$^{127,129}$

4.1: Room Temperature Hall Effect Measurements

Following growth of h-BN on Cu substrates, the films were transferred, via the process described in Section 2.4, to quasi-freestanding epitaxial graphene (QFEG) substrates with pre-fabricated ohmic-level devices and prepared via the processes described in Section 2.5. It should be noted that the h-BN films used in this study were grown without the use of the copper enclosure described in Section 3.2. The studies presented in this chapter were performed prior to the development of the copper enclosure growth configuration.

Room temperature Hall Effect measurements, shown in Figure 4.1.1, were performed prior to h-BN integration on the as-grown QFEG Hall crosses (Pre-Transfer), immediately after h-BN integration (Post-Transfer), and after a 400°C anneal in H$_2$/N$_2$ (15% H$_2$) for 20 minutes (Post-Anneal). Despite the presence of stress induced wrinkling and 3D surface particulates observed in AFM and SEM in Section 3.1, room temperature Hall effect measurements indicate that the carrier mobility and concentration of the QFEG are minimally affected upon integration with the h-BN dielectric over-layer, although this is partially a result of the initial low mobilities inherent to the epitaxial graphene system (~1500 cm$^2$/V sec at 1x10$^{13}$ cm$^{-2}$). Upon transfer, the QFEG experiences an average increase in hole concentration of approximately 5x10$^{11}$ cm$^{-2}$ (<5 ±
2%), which is coupled with a 14 (±3)% decrease in average Hall mobility, from 1741 cm²/V-s to 1499 cm²/V-s. Hole doping of the graphene is attributed to the presence of residual water at the h-BN/QFEG interface subsequent to h-BN transfer. After a 20 minute anneal to remove residual photoresist and water at 400°C in H₂/N₂ (15% H₂), the carrier concentration returns to as-grown values, which indicates that the h-BN itself does not significantly induce hole doping within the QFEG; however, Hall mobility remains an average of 9 (±5)% below its original value.

![Figure 4.1.1:](image)

**Figure 4.1.1:** (a) Room temperature Hall mobility vs. carrier concentration obtained before h-BN integration, after h-BN transfer, and after annealing at 400°C for 20 minutes in H₂/Ar (15% H₂) shows minimum degradation of the carrier mobility. Inset: SEM micrograph of Van der Pauw test structure after transfer and patterning of h-BN dielectric layer. (b) Normalized $\mu/\mu_0$ vs. $n/n_0$ plot of (a) showing the change in mobility and carrier concentration for QFEG devices immediately after h-BN transfer and after the 400°C anneal. Here, $\mu_0$ and $n_0$ are the original as-grown mobilities and carrier concentrations, respectively, of the QFEG wafer.
These results were consistent for h-BN films with thicknesses from 10 to 50nm indicating that doping induced by the h-BN layer is independent of thickness for multilayer h-BN. The degradation in mobility is likely a result of the addition of impurities at the dielectric/graphene interface during the transfer process (such as oxygen impurities bonding at defects and domain boundaries from the DI water baths, as previously observed with XPS in Figure 3.1.6) which act to increase remote charged impurity scattering within the QFEG.\textsuperscript{90,91} Another possible mechanism for local mobility degradation may be surface roughness scattering at the dielectric/graphene interface due to the stress-induced wrinkling of the h-BN film. Overall however, these results indicate only a small decrease in the ambient Hall mobility of QFEG upon integration with h-BN, unlike reports of significant mobility degradation upon integration with HfO\textsubscript{2} dielectrics.\textsuperscript{89}

4.2: Temperature Dependent Hall Effect Measurements

Temperature dependent Hall mobility data was utilized to study the scattering mechanisms induced into QFEG by the dielectric over-layer. Here, h-BN gated QFEG devices were compared to devices gated with the high-k dielectric HfO\textsubscript{2}. Figure 4.2.1a plots the temperature dependent Hall mobility before and after h-BN integration and confirms an increase in remote charged impurity scattering. This is shown by a reduction in the temperature independent portion of the curve after h-BN integration, which is dominated by remote charged impurity scattering.\textsuperscript{104} In another work,\textsuperscript{127} physics based modeling of the temperature dependent transport data indicates remote charged impurity scattering as the dominant scattering source in these samples and that integration of CVD h-BN can introduce up to $6 \times 10^{12}$ additional impurities/cm$^2$ at the dielectric-graphene interface, although this value was found to be roughly 4x less than that introduced by HfO\textsubscript{2} dielectrics and can be as low as $3 \times 10^{12}$ cm$^2$. In this way, h-
BN integration can be beneficial in reducing the number of additional remote charged impurity scatterers. The effect of impurity concentration, which varies from device to device, will be discussed in Section 4.4.

**Figure 4.2.1:** (a) Hall mobility *versus* temperature before and after h-BN integration shows minimal change in the surface optical scattering as well as the incorporation of additional remote charged impurity scattering. (b) Temperature dependent Hall mobility shows the potential of h-BN in preserving high mobilities for QFEG due to reduced introduction of charged impurity and remote surface optical phonon scattering compared to HfO₂. Here, \( N_{sh} \) is the sheet carrier density (cm\(^{-2}\)) and \( n_{imp} \) is the approximate remote charged impurity density extracted using techniques adapted from Konar *et al.*\(^{104}\)
Temperature dependent Hall Effect measurements indicate little contribution from remote surface optical phonon scattering after h-BN integration (Figure 4.2.1b). For a high mobility (low $n_{\text{imp}}$) h-BN coated QFEG sample (red curve), exhibiting mobilities greater than 3000 cm$^2$/V-s and with a low impurity density of $3.7 \times 10^{12}$ cm$^2$, the ultimate decrease in mobility from the low temperature, impurity limited regime to the high temperature, phonon limited regime is only 4.4% and can be explained as a result of intrinsic phonon scattering within the graphene. The method presented by Konar et al. was adapted here to show that for a fixed carrier concentration and charged impurity density of $9.3 \times 10^{12}$ cm$^{-2}$ and $3.7 \times 10^{12}$ cm$^{-2}$, respectively, (given an acoustic deformation potential of 4.8 eV, optical deformation potential of 25.6 eV/A, and intrinsic optical phonon energy of 140 meV) the expected change in mobility due to optical and acoustic phonon scattering from 5 – 400K is approximately 5%, which matches well with our experimental results and indicates that phonon-carrier coupling is weak for the h-BN/graphene system. These results are similar to results published elsewhere for un-coated QFEG samples, which exhibit minimal temperature dependence of Hall mobility and confirm that pristine QFEG samples exhibit minimal remote surface optical phonon scattering from surface modes within the substrate. Importantly, our results show that even with h-BN integration, the limited effect of remote surface optical phonon scattering is preserved, suggesting that h-BN introduces little additional remote surface optical phonon scattering. Alternatively, for a low mobility (high $n_{\text{imp}}$) h-BN coated sample (blue curve), exhibiting mobilities ~1100 cm$^2$/V-s and with an approximate fixed impurity density of $1.1 \times 10^{13}$ cm$^2$, the decrease in mobility is 7.7% for the same temperature range and, following similar analysis, indicates an increase in remote surface optical phonon scattering for this sample. However, the change in temperature dependence before and after dielectric integration (Figure 4.2.1a) is minimal and again indicates that h-BN introduces negligible additional remote surface optical scattering. Instead, the increased contribution from remote surface optical phonons in both the as-grown and h-BN coated sample is thought to
originate from the SiC substrate, where an increased SiC step-edge density was found for this particular sample and is thought to lead not only to a higher density of remote charged impurities, evidenced by the reduction in the temperature independent mobility (remote charged impurity dominated), but also to increased phonon scattering and reduced room temperature mobility. Degradation of transport properties with presence of step-edges for epitaxial graphene (will be discussed in more detail in Section 4.4) is a well known phenomenon and has been reported elsewhere.\textsuperscript{124}

In contrast, the HfO\textsubscript{2} coated QFEG sample (green curve) exhibits a 14.5% degradation in temperature dependent mobility, which fits well with expected results and verifies that the use of high-k dielectrics induces additional remote surface optical phonon scattering compared to h-BN dielectrics. Modeling of the temperature dependent data indicates that remote surface optical scattering contributes \textasciitilde15\% of the total mobility reduction in these samples.\textsuperscript{127} Despite this increase in remote surface optical phonon scattering, as well as remote charged impurity scattering, the ability of the HfO\textsubscript{2} to screen the carriers from remote charged impurities results in an average increase in carrier mobility when initial as-grown mobility is heavily dominated by remote charged impurity scattering.\textsuperscript{104} However, for QFEG samples exhibiting a high initial mobility (phonon limited regime), the increased surface optical phonon scattering from HfO\textsubscript{2} results in a large degradation in mobility compared to h-BN. Therefore, QFEG’s mobility is limited by HfO\textsubscript{2} for high mobility QFEG samples and benefits from HfO\textsubscript{2} for low mobility QFEG samples.\textsuperscript{91,104} In contrast, the benefit of h-BN is most evident in the high mobility QFEG (phonon limited) regime. Additionally, we note that Figure 4.2.1b shows a small increase in Hall mobility with temperature for the HfO\textsubscript{2} coated sample before decreasing at higher temperatures. This increase in mobility occurred in conjunction with a decrease in the carrier density and is attributed to the presence of temperature activated traps in the HfO\textsubscript{2} over-layer which capture charge carriers and lead to an increase in mobility. Similar behavior has been reported for un-
coated epitaxial graphene where an increase in Hall density and subsequent decrease in Hall mobility were reported and attributed to donor traps in the SiC substrate.\textsuperscript{103}

4.3: RF Characterization

RF characterization of CVD grown h-BN and HfO\textsubscript{2} gated GFETs confirms that the use of h-BN dielectrics can be effective in preserving the transport properties of high mobility QFEG samples. Though Britnell \textit{et al} suggests that exfoliated single crystal h-BN flakes show negligible tunneling currents at thicknesses of only 4 layers,\textsuperscript{42} CVD h-BN used here resulted in significant leakage currents and $V_{\text{breakdown}}<1\text{V}$ for thicknesses up to 20nm, as described in Section 3.3 for non-enclosed h-BN growth on Cu, which is likely due to pin-holes, non-uniformities, and grain boundary conduction in the transferred films. Therefore, for GFET characterization, an h-BN thickness of $\sim50\text{nm}$ was used to ensure sufficiently low gate leakage currents (measured to be $<1\times10^{-10}\text{A/\mu m}^2$ at $V_{gs}=1\text{V}$). Figure 4.3.1a plots drain current as a function of gate voltage ($V_{ds}=-1\text{V}$) for typical h-BN and HfO\textsubscript{2} gated GFETs and shows the characteristic p-type transfer curve of QFEG graphene for h-BN gated GFETs, where hole doping of the QFEG is a result of the intrinsic spontaneous polarization charge of the hexagonal SiC substrate.\textsuperscript{84} Alternatively, HfO\textsubscript{2} gated GFETs exhibit slightly n-type behavior and $V_{\text{Drac}}$ much nearer to 0 V, which is attributed to n-type doping by the HfO\textsubscript{2} over-layer that competes with the substrate induced hole doping.\textsuperscript{83} The heavily p-type behavior of the h-BN gated devices leads to increased drain currents over the range of evaluated gate voltages compared to HfO\textsubscript{2} gated GFETs. Besides increased drain currents, the shift in transfer curve also leads to reduced transconductance over the same voltage range, evidenced as a decrease in the on-off ratio. Despite this reduction in transconductance, the intrinsic RF performance for h-BN gated GFETs can be up to 2.4x that of HfO\textsubscript{2} gated GFETs,
although ultimate performance is found to be highly dependent on initial mobility of the QFEG sample. Figure 4.3.1b plots the small signal current gain for three different GFETs as a function of frequency after de-embedding the pad parasitics using a short-open-load-thru compensation.

Figure 4.3.1: (a) Drain current as a function of gate voltage for h-BN and HfO$_2$ gated GFETs. The p-type doping of the h-BN gated GFET shifts the minimum conductivity point in the positive direction while use of an HfO$_2$ gate leads to a minimum conductivity point close to zero volts. (b) Intrinsic RF performance of h-BN and HfO$_2$ gated GFETs. For the high mobility QFEG sample with low impurity density, the small degree of remote surface optical scattering from use of h-BN dielectrics leads to excellent RF performance.
The results show that for low mobility QFEG, use of h-BN top-gates shows no benefit compared to HfO$_2$ dielectrics, producing current gain cutoff frequencies of 5.4 GHz (4.1 GHz-µm) compared to 13.8 GHz (10.4 GHz-µm) for HfO$_2$ coated GFETs, where the significant decrease in RF performance for h-BN coated GFETs is partially attributed to the reduction in transconductance caused by the p-type shift of the transfer curve. Alternatively, for high mobility QFEG, use of h-BN leads to cutoff frequencies as high as 33.5 GHz (25.12 GHz-µm), which is the highest $f_T\cdot L_g$ product reported for h-BN coated graphene transistors and is attributed to a reduced contribution from remote surface optical phonon scattering and a lower density of remote charged impurities relative to HfO$_2$ coated GFETs that act to preserve the excellent transport properties of QFEG.

4.4: Effect of Impurity Concentration on Dielectric – Graphene Scattering

Through modeling detailed elsewhere,\textsuperscript{127} we find that HfO$_2$ integration with QFEG leads to an impurity density increase of 2.8x10$^{13}$ cm$^{-2}$ while integration of h-BN with QFEG led to an impurity density increase of 5.6x10$^{12}$ cm$^{-2}$, indicating a 5x higher incorporation of remote charged impurities compared to h-BN. However, as observed previously in Figure 4.2.1b, the mobilities are higher for the HfO$_2$ coated sample than for the h-BN coated sample with high n$_{imp}$. This is despite the fact that this h-BN coated sample (with high n$_{imp}$) had a 66% lower total impurity concentration than the HfO$_2$ coated sample. This is due to the ability of HfO$_2$ to screen remote charged impurities given its high dielectric constant (4x higher than h-BN), which offsets the additional impurities introduced from the HfO$_2$ film. However, as impurity concentration decreases, surface optical phonon scattering begins to contribute more to the overall scattering rate and the ability of HfO$_2$ to screen impurities begins to lose out to scattering from surface
optical phonons due HfO$_2$’s low energy surface optical phonon modes; which induce stronger electron-phonon coupling, as described in Section 1.6.2. In this regime, h-BN outperforms HfO$_2$ due to its high energy surface optical phonon modes, where h-BN and HfO$_2$ have surface optical phonon energies of 120meV and 25.5meV, respectively. However, apparent from the temperature dependent Hall mobility data (Figure 4.2.1b), the effective impurity density can change drastically from device to device over the wafer. We correlate this to local impurity incorporation from the SiC substrate; or more accurately, from the SiC step edges. Although the SiC substrates used for QFEG synthesis had a nominal miscut of zero degrees relative to the (0001) plane, a slight miscut naturally exists and leads to a terraced morphology, as shown in Figures 4.4.1a and b. These SiC step-edges naturally bunch together during the high temperature sublimation step in epitaxial graphene synthesis, forming terraces 1-10µm wide with step heights up to 10nm, and have been cited as a source of additional scattering. Additionally, it was found that while the terrace planes exhibit primarily monolayer graphene for epitaxial graphene and bi-layer graphene for QFEG (where the second layer forms after hydrogen passivation and conversion of the 6√3 buffer layer to graphene), multi-layer graphene exists at the step-edges due to faster nucleation and growth. Through the use of optical profilometry, it was found that nearly all of VdP test structures include step-edges in the active region, as shown in Figure 4.4.1b. However, the extent of the step-bunching was found to vary from device to device, where some VdP test structures had a high density of step-edges while others had a low density of step-edges in the active region, as shown in Figure 4.4.1c. By correlating the ultimate change in step height (total distance traveled along the c-axis) to the measured Hall mobility and carrier concentration, Hollander et al. show that an increase in step density (high ultimate change in step height) directly leads to a reduction in mobility (Figure 4.4.1d). However, the expected dependency of mobility on hole concentration was not found to correlate to the observed decrease in Hall mobility with increased step-edge density, as shown in Figure 4.4.1e. This suggests that
additional scattering is being introduced at step-edges. Additionally, it was previously reported that moving from a sample with a high step-edge density to one with a low step-edge density led to a reduction in $n_{imp}$ of up to $1.7 \times 10^{12}$ cm$^{-2}$ and a significant reduction in surface optical phonon scattering.$^{127}$

Figure 4.4.1: (a) SEM image of Van der Pauw test structure used for Hall mobility analysis. (b) Optical profilometry image of Van der Pauw test structure showing the presence of step edges running through the device. (c) Height profile showing the contrast in geometry between various step edges. (d) Hall mobility vs. absolute change in step height shows a decrease in mobility for devices having higher step heights. (e) Hall mobility vs carrier density. The simulated dependency on carrier density indicates that the increase in hole doping is not the only cause of the degraded mobility.
The additional impurity and surface optical phonon scattering at step-edges may be a result of incomplete hydrogen passivation at the step-edge, possibly due to the increased graphene thickness, where hydrogen passivation has been clearly shown to reduce both remote charged impurity incorporation and surface optical phonon scattering.\textsuperscript{127} Another possible explanation for the increased surface optical phonon scattering at step edges may be decreased phonon energies for phonons propagating along the c-axis of SiC.\textsuperscript{127} The different impurity concentrations obtained through modeling of the temperature dependent Hall mobility (Figure 4.2.1) can thus be effectively explained by impurity incorporation from the SiC step edges. A low density of SiC steps will result in a low impurity density regime where h-BN can excel due to its reduced incorporation of extrinsic impurities and its negligible contribution to surface optical phonon scattering. Conversely, a high density of SiC steps will result in a high impurity density regime where Coulombic scattering dominates and HfO\textsubscript{2} outperforms h-BN due to its dielectric screening properties.

Evident from this discussion, the impurity concentration of the dielectric/graphene system plays a key role in the observed benefits of the dielectric over-layer. Through physics-based models similar to those developed by Konar \textit{et al},\textsuperscript{104} the Hall mobility as a function of impurity concentration could be predicted. Here, modeling was performed by Matthew Hollander of Penn State Electrical Engineering and the details of the model are published elsewhere.\textsuperscript{127} It was found that the benefit of h-BN compared to HfO\textsubscript{2} is critically dependent on the impurity concentration of the dielectric/graphene system. As suggested previously, Figure 4.4.2a shows that two regimes exist where the use of either h-BN or HfO\textsubscript{2} can result in higher Hall mobilities. For comparison, both dielectrics over-layers on QFEG were compared to exfoliated graphene on SiO\textsubscript{2}, as reported by Chen \textit{et al}.\textsuperscript{97} At impurity concentrations >5x10\textsuperscript{11} cm\textsuperscript{-2}, HfO\textsubscript{2} is the superior dielectric material due to its ability to screen charged impurities. However, at impurity concentrations <5x10\textsuperscript{11} cm\textsuperscript{-2}, h-BN begins to surpass HfO\textsubscript{2} due to the increased contribution of
surface optical phonon scattering to the total scattering rate, where h-BN’s high energy surface optical phonon modes result in overall reduced scattering.

Figure 4.4.2: (a) Modeled dependency of Hall mobility on impurity concentration for QFEG gated with h-BN and HfO₂, as well as exfoliated graphene gated with SiO₂.⁹⁷ (b) Expected percent increase in mobility for h-BN gated QFEG compared to HfO₂ and SiO₂ as a function of impurity concentration.

Figure 4.4.2b shows the simulated percent change in QFEG Hall mobility when using h-BN as a dielectric compared to HfO₂ and SiO₂. At an impurity concentration of \(10^{13}\) cm\(^{-2}\), HfO₂ is a superior dielectric, due to its dielectric screening abilities, and h-BN has only a minimum benefit over SiO₂. However, at an impurity concentration of \(10^{12}\) cm\(^{-2}\), h-BN shows a benefit over both HfO₂ and SiO₂ as impurity scattering begins to contribute less to the total scattering rate. Finally, at an impurity concentration of \(10^{11}\) cm\(^{-2}\), h-BN shows a nearly 300% and 125% increase
in mobility over HfO$_2$ and SiO$_2$, respectively, due to the increased contribution of surface optical phonon scattering to the total scattering rate at low impurity densities. Therefore, modeling mobility as a function of impurity concentration clearly shows that the benefit of h-BN as a dielectric for QFEG-based devices is critically dependent on the impurity concentration of the system. Additionally, due to epitaxial graphene’s unique morphology, improvements in the growth of EG and QFEG (that lead to a reduction in the step-edge density) should allow for reduced intrinsic impurity densities; and thus a regime where h-BN dielectrics are a valid candidate for EG or QFEG-based device development.
Chapter 5

Direct Growth of Boron Nitride Dielectrics on Insulating and Conductive Substrates via a Polyborazylene to Boron Nitride Conversion Process

As discussed in Section 1.7, exfoliated h-BN and transferred CVD h-BN have been shown to be excellent candidates as a supporting substrate and gate dielectric to CVD graphene.\textsuperscript{39,110,118,119} Additionally, it was shown in the previous chapter (Chapter 4) that transferred CVD h-BN can be highly beneficial as a top-gate dielectric to epitaxial graphene, although the benefits were found to be highly dependent on the impurity concentration of the graphene-dielectric system.\textsuperscript{129} The observed improvements in graphene transport properties (relative to high-k dielectrics and SiO\textsubscript{2}) with the use of h-BN is a result of h-BN dielectrics introducing reduced Coulombic and surface optical phonon scatterers to the graphene-dielectric interface (see Section 1.6 and 1.7). Besides graphene, h-BN is also of interest as a substrate for development of other 2D layered materials, such as transition metal dichalcogenides (TMDCs),\textsuperscript{150} where h-BN’s close lattice match makes it an ideal candidate as a substrate for growth and integration. Despite the advantages of h-BN over high-k dielectrics and SiO\textsubscript{2}, exfoliated h-BN is not suitable for large scale development, and CVD of h-BN on metal substrates requires a transfer process that can be difficult to perform with repeatable success.\textsuperscript{67} This transfer process often results in a rough h-BN surface due to stress induced wrinkling of the film during growth on the transition metal surface, where surface roughness and wrinkling increase with film thickness, as shown previously in Section 3.2.2 (see Figures 3.2.2 and 3.2.3).\textsuperscript{129} Additionally, the formation of tears and pinholes can easily occur during the transfer process, leading to difficulty in producing continuous films over large areas and causing shorting issues for h-BN films <10nm thick, as shown previously in Figure 3.3.1. Contamination issues can also arise during the solution-based
transfer process, usually in the form of residual iron from the ferric chloride solution used to etch copper and nickel, carbon from residual photoresist, or oxygen from the DI water baths used in the transfer process. Therefore, a deposition process that can grow high-quality, ultra-smooth, transfer-free h-BN with controllable thicknesses directly on a variety of insulating and conductive supporting substrates would be highly beneficial for graphene and TMDC development. Here, we present a direct deposition process of h-BN on Al₂O₃(0001) and conductive Si(111) that involves the initial deposition of the hydrogenated polymer precursor polyborazylene (B₃N₃Hₓ) and its subsequent conversion to boron nitride, as discussed in Section 1.4. Direct deposition provides a means to synthesize an h-BN supporting dielectric for CVD-grown graphene and TMDCs that can also act as a back-gate dielectric when deposited on highly doped, conductive Si. Here we explore the effects of the initial polyborazylene deposition temperature on the chemical composition as measured by X-ray photoelectron spectroscopy (XPS), the surface morphology and roughness as characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM), and the film structure as examined by cross-sectional transmission electron microscopy (TEM) for h-BN films grown directly on Al₂O₃(0001) and/or Si(111) substrates. The results presented in this chapter are also published elsewhere.¹⁵¹

5.1: Effect of Polyborazylene Deposition Temperature on Surface Morphology and Roughness

Initial attempts to deposit h-BN directly on Al₂O₃ and Si using high temperature growth conditions at 1000°C (Figures 5.1.1a and b, respectively) resulted in thick h-BN films with a high surface roughness not suitable for device development. Therefore, a two-step deposition process, similar to the 2-step growth of h-BN on Ni substrates reported elsewhere,³¹ was developed to
reduce surface roughness. The process consists of depositing a film of polyborazylene onto a substrate at low temperatures followed by a high temperature anneal at 1000°C to convert the polyborazylene to h-BN.\textsuperscript{31} As discussed in Section 1.4, polyborazylene is synthesized from borazine (B\textsubscript{3}N\textsubscript{3}H\textsubscript{6}) through a dehydropolymerization process, where initial hydrogen loss occurs between 125°C and 300°C by means of a two-dimensional cross-linking reaction of B-H and N-H groups, forming polyborazylene (B\textsubscript{3}N\textsubscript{3}H\textsubscript{x}).\textsuperscript{52} Upon further heating, a second hydrogen loss reaction occurs between 700-1100°C from unaligned chain branches of polyborazylene, forming h-BN (see Figures 1.4.3 and 1.4.4).\textsuperscript{52} Ammonia borane was used as the precursor material to borazine upon sublimation at 135°C (thermogravimetric analysis (TGA) data of ammonia borane sublimation is shown in Appendix C). The deposition of polyborazylene was performed under 100 Torr of H\textsubscript{2}/N\textsubscript{2} (15% H\textsubscript{2}) carrier gas at two temperatures, 250°C and 400°C. These two temperatures were selected to represent a temperature within the first hydrogen loss regime and one slightly above the regime. Growth time of the polyborazylene film was varied for desired film thickness. A post-growth anneal was then performed at 1 Torr H\textsubscript{2}/N\textsubscript{2} (15% H\textsubscript{2}), 1000°C for one hour to facilitate the ceramic conversion, via the second hydrogen loss process, to boron nitride.

Figure 5.1.1 shows the 2x1µm\textsuperscript{2} AFM images of h-BN films obtained from the direct growth process for different growth temperatures and different substrates. The high temperature growth (1000°C, 100 Torr, 10 minutes) without the use of an initial polyborazylene deposition resulted in high surface roughness, where a root-mean-square (RMS) roughness of >3nm was measured with AFM, as shown in Figure 5.1.1a and b. Using optical ellipsometry for the h-BN film grown on Si at this temperature, the h-BN film thickness was found to be ~25nm. Using an initial polyborazylene deposition of 400°C (400°C, 100 Torr, 10 minutes) followed by a post-growth anneal at 1000°C resulted in a ~8nm film with a reduction in surface roughness of >13x (RMS roughness: 3.3nm to 0.24nm) from the high temperature growth process to the 2-step
growth process, as shown in Figure 5.1.1c and d. Additionally, a >16x decrease in RMS roughness (4.0nm to 0.24nm) was found when this sample was compared to an h-BN film of similar thickness grown via CVD on a copper substrate and transferred to Si(111) (see Figure 3.2.3d). Further reducing the polyborazylene deposition temperature to 250°C (250°C, 100 Torr, 120 minutes) led to a highly uniform film with an RMS roughness of 130pm and thickness of ~2nm on the Al₂O₃ sample. Here, a >25x reduction in RMS roughness (3.3nm to 0.13nm) was observed over the high temperature deposition (Figure 5.1.1e) and a >9x decrease in RMS roughness (1.2nm to 0.13nm) was observed over a transferred h-BN film of similar thickness (see Figure 3.2.3b). To the author’s knowledge, the RMS roughness of 130pm on Al₂O₃ for the 250°C polyborazylene deposition is the lowest reported RMS roughness for non-exfoliated h-BN. Interestingly however, when the same conditions are used for h-BN growth on Si(111), partial film voiding occurs, as shown in Figure 5.1.1f. This has been observed previously for spin coated polyborazylene on Si after high temperature annealing and was attributed to degradation of the underlying native oxide. Therefore, a pre-growth anneal at 1000°C and 100 Torr in an H₂/N₂ environment was performed to remove any native oxide on the Si surface prior to growth at 250°C. Similar annealing conditions are commonly used in the Si integrated circuit industry for thermal removal of native oxide. This resulted in an increased RMS roughness of the film to approximately 1nm, shown in Figures 5.1.1g and h. This roughening may result from several possible mechanisms. One possibility is that an initial deposition of BN during the 1000°C pre-growth anneal may occur due to desorption and re-deposition of residual BN from the furnace walls; acting as a seed layer with a rough morphology, as similarly observed for the 1000°C BN deposition shown in Figures 5.1.1a and b. An alternative possibility is that the Si and Al₂O₃ substrate surfaces may reconstruct and roughen during the 1000°C pre-growth anneal. This roughening of the substrate surface may translate to the morphology of the deposited polyborazylene film. Although further analysis is required to fully understand the surface
roughening resulting from the high temperature pre-growth anneal, what can be concluded is that the film voiding on the Si sample was successfully eliminated through use of this high temperature pre-growth treatment, as shown in Figure 5.1.1h.

**Figure 5.1.1:** AFM scans of h-BN directly grown on Al$_2$O$_3$(0001) and Si(111) at various deposition conditions. (a,b) Growth of h-BN on Al$_2$O$_3$ and Si, respectively, at 1000°C without the use of an initial polyborazylene deposition. (c,d) Growth of h-BN on Al$_2$O$_3$ and Si, respectively, using an initial polyborazylene deposition temperature of 400°C. (e,f) Growth of h-BN on Al$_2$O$_3$ and Si, respectively, using a polyborazylene deposition temperature of 250°C. (g,h) Growth of h-BN on Al$_2$O$_3$ and Si, respectively, using an initial polyborazylene deposition temperature of 250°C and a pre-growth anneal of 1000°C. Note that the scale bar for (a, b) is 20 nm while the scale bar for (c-h) is 4 nm.
For comparison, Figure 5.1.2a, b, and c show 2x1µm² AFM scans of bare Si(111), Al₂O₃(0001), and SiO₂, respectively. The measured RMS value of the Al₂O₃ substrate (0.42nm) is approximately 43% and 70% higher than the h-BN directly grown on Al₂O₃ at 400°C and 250°C (without a pre-growth anneal), respectively. Likewise, the measured RMS value of the SiO₂ substrate (0.25nm) is approximately 4% and 49% higher than the h-BN directly grown on Al₂O₃ at 400°C and 250°C (without a pre-growth anneal), respectively. Although the Si(111) RMS roughness (0.17nm) is less than any of the h-BN films obtained, these results show that the h-BN films grown on Al₂O₃ using a polyborazylene deposition at 400°C and 250°C (without a pre-growth anneal) result in smoother surfaces than SiO₂ and the high-k dielectric Al₂O₃.

**Figure 5.1.2:** 2x1um² AFM scans of various substrates for comparison to direct growth BN films: (a) Si (111), (b) Al₂O₃ (0001), (c) 300nm dry oxide. The correlating RMS roughness values are shown for each substrate material.

The morphology of the h-BN films grown on Si(111) is also observed through scanning electron microscopy (SEM), as shown in Figure 5.1.3. Here, SEM was only achievable on h-BN films grown on the conductive Si substrates. Excessive surface charging was observed for h-BN.
films grown on insulating Al₂O₃(0001) making imaging via SEM for these samples difficult. Again, the variation in surface morphology with different growth conditions can be observed. Growth at 1000°C results in a rough surface morphology while growth using the polyborazylene deposition at 400°C followed by a post-growth anneal at 1000°C resulted in a significant improvement in the apparent surface roughness.

**Figure 5.1.3:** SEM images of h-BN directly grown on Si(111) at different deposition temperatures. (a) 1000°C without a polyborazylene deposition. (b) Polyborazylene deposition temperature of 400°C. (c) Polyborazylene deposition temperature of 250°C without a pre-growth anneal. (d) Polyborazylene deposition temperature of 250°C with a 1000°C pre-growth anneal.
The voiding observed with AFM for the film grown at 250°C without a pre-growth anneal is again observed in Figure 5.1.3c. With the use of a 1000°C pre-growth anneal, the film voiding is eliminated, however the surface roughness increases, as shown in Figure 5.1.3d. A lower magnification image of the sample grown at 250°C without a pre-growth anneal is shown in Figure 5.1.4 and indicates that the film surface pitting is composed of many aligned triangular or hexagonal structures, indicating a reaction with the underlying single crystal Si(111) surface. This is likely caused by degradation of a SiO$_2$ layer between the Si substrate and h-BN film during the high temperature (1000°C) post-growth anneal.

**Figure 5.1.4:** 50,000x SEM image of h-BN film grown on Si(111) at a polyborazylene deposition temperature of 250°C without a post-growth anneal. The surface pits appear as oriented triangular and hexagonal structures.

It should be noted that all Si(111) substrates were treated with an HF (10:1 BOE) dip for 1 minute (followed by rinsing with DI water and drying with a nitrogen gun) prior to loading in the tube furnace. However, some native oxide may have re-grown on the sample surface while loading into the tube furnace. Another possibility for oxygen contamination could be from
impurity oxygen present in the tube furnace during growth, possibly from residual water vapor or from micro-leaks in the vacuum system. As discussed in Section 2.2, the tube furnace employed for this work did not utilize a high vacuum pump (such as a turbo molecular pump), but rather employed only a mechanical roughing pump which was capable of reaching a system base pressure of ~10mTorr. Therefore, it is highly likely that a residual impurity partial pressure of oxygen exists during growth of these films, despite the fact that the hydrogen introduced to the system (15%) should reduce leaks at o-ring seals.

5.2: Effect of Polyborazylene Deposition Temperature on Chemical Composition

X-ray photoelectron spectroscopy (XPS) was used to investigate the bonding of boron nitride grown at different polyborazylene deposition temperatures. The following four sections (Section 5.2.1 – 5.2.4) investigate the deconvoluted B1s, N1s, O1s, and C1s spectra, respectively, of h-BN grown on Al$_2$O$_3$(0001) and Si(111) substrates using the four growth conditions described previously. The binding energies of all spectra were obtained after charge correction of the C1s line to adventitious C-C bonding at 284.8eV. Unless specifically noted, all subsequent discussion of peak assignment and component concentrations will reflect XPS analysis of h-BN films grown on Al$_2$O$_3$ substrates. This will be done for simplicity since h-BN films grown on Si(111) substrates were, except where noted, similar in chemical composition to those grown on Al$_2$O$_3$. Additionally, the intensities of the spectra for the different growth conditions are arbitrary, since the intensity is a function of film thickness.
5.2.1: B1s XPS Analysis

The B1s XPS spectra of h-BN directly grown under various conditions on Al₂O₃(0001) (left column) and Si(111) (right column) is shown in Figure 5.2.1. The sample grown on Al₂O₃ at 1000°C without the polyborazylene deposition shows an intense B1s peak with two components. The primary peak at 190.25eV, accounting for 69.8% of the main B1s line, is indicative of the h-BN structure where the core boron atom is bonded to three nitrogen atoms in the planar hexagonal configuration and can be written as [BN₃]. This value is close to the B1s peak of bulk h-BN reported by Moulder et al between 190.4-190.5eV. The smaller shoulder at 191.01eV indicates the presence of oxygen and occupies 30.2% of the main B1s line. Pure B₂O₃ has been previously reported to be located between 193.0-193.6eV. This intermediate peak between the h-BN [BN₃] peak and the reported B₂O₃ peak was similarly observed by Guimon et al and was attributed to the core boron atom bonding to nitrogen and oxygen, where oxygen may be a substitutional element in place of nitrogen, forming a BNₓOᵧ ternary species. Oxygen incorporation may be from interdiffusion with the Al₂O₃ substrate (and native oxide of Si), or due to oxygen impurities in the gas phase as has been commonly reported in the literature. Additionally, a broad peak at 198.62eV corresponds to a π-π* plasmon shake-up peak, which is indicative of sp² bonded hexagonal boron nitride and is not found in the cubic phase. A B/N ratio of 1.07 was obtained for this sample, indicating a film with a stoichiometry of nearly 1:1.

For the sample grown on Al₂O₃ with a polyborazylene deposition temperature of 400°C, shown in Figure 5.2.1, four distinct components appear after deconvolution of the B1s peak. The primary [BN₃] bonding configuration is found at 190.65eV and accounts for 42.7% of the B1s spectrum. Additionally, two shoulders at energies lower than the [BN₃] peak are found at 188.86eV and 187.60eV. Elemental boron-boron bonding has been reported previously in the range of 187.3-187.7eV. Here, the peak at 187.60eV accounts for 17.2% of the B1s
spectrum and can be attributed to elemental boron with no bonds to nitrogen atoms due to boron-boron bonding in either interstitial or interlayer positions, or at defective domain boundaries. Bonding with nitrogen atoms creates a higher binding energy compared to elemental boron-boron bonding due to the core boron atom bonding with the higher electronegative element nitrogen. Therefore, the peak inbetween the h-BN [BN$_3$] and the B-B configuration, located at 188.86eV (25.7% of the B1s spectrum), can be attributed to either a [BN$_2$] configuration, with boron bonded to two nitrogen atoms, or a [BN] configuration with boron bonded to one nitrogen atom. In other words, the intermediate peak corresponds to a single or double nitrogen vacancy (V$_N$). A similar peak was reported by Guimon $et$ $al$, where after 4 keV Ar$^+$ sputtering, a peak at 189.2eV appeared. Likewise, Schild $et$ $al$ reported the emergence of a peak at 188.8eV after sputter cleaning of c-BN samples. In both cases this peak was attributed to preferential sputtering of nitrogen atoms, leaving behind a boron-rich surface. Additionally, a peak at 191.98eV again is attributed to substitutional oxygen contamination in the form of a BN$_x$O$_y$ ternary species and accounts for 14.5% of the B1s spectrum. Due to the elemental boron bonding, nitrogen vacancies, and substitutional oxygen bonding, a B/N ratio of 1.92 was obtained for this sample, indicating a highly boron-rich film. Interestingly, the presence of B-B bonding in this film may result in a reduction of free electrons in the material by compensating for the difference in valence between nitrogen and oxygen, where the oxygen impurities will induce additional valence electrons. Therefore, despite the fact that this film is highly non-stoichiometric, the B-B bonding may act to create a more charge-neutral dielectric material (compared to direct-growth BN films containing oxygen contamination but no B-B bonding) which may result in reduced electrostatic doping to graphene.

The sample grown on Al$_2$O$_3$ at a polyborazylene deposition temperature of 250°C without the use of a pre-growth anneal resulted in the presence of two components assigned to h-BN [BN$_3$] (190.64eV) and BN$_x$O$_y$ (191.73eV). Interestingly, for this sample the BN$_x$O$_y$ peak
accounts for 57.7% of the B1s spectra, indicating significant oxygen incorporation. Electron energy loss spectroscopy (EELS) (not shown) indicates that for the majority of these samples, interdiffusion between the substrate and the h-BN layer occurs up to 5nm. Given that this sample is approximately 2nm, the additional oxygen incorporation is likely induced from the Al₂O₃ substrate and substitutional bonding occurs during the high temperature anneal. The nitrogen vacancy peak and B-B bonding peak are not observed for this sample, possibly due to oxygen occupying vacancy sites. However, the additional substitutional oxygen contamination results in a B/N ratio of 1.51. Unlike the h-BN films grown at 1000°C and 400°C, a disparity in chemical composition was found between samples grown on Al₂O₃ and Si. For the sample grown at 250°C without the use of a pre-growth anneal on Si(111), the BN₃O₂ peak located at 191.98eV accounts for only 16.9% of the B1s spectra, in contrast to 57.7% for the h-BN film grown on Al₂O₃ under this growth condition. These results show that the h-BN film grown on Si(111) at 250°C without a pre-growth anneal results in a 71% reduction in B-O bonding. This is likely a result of interdiffusion of oxygen from the Al₂O₃ substrate into the h-BN film grown on sapphire, where electron energy loss spectroscopy (EELS) (discussed in Section 5.4) indicates oxygen interdiffusion up to 5nm for the films grown on Al₂O₃. Therefore, the low thickness of this film (~2nm) would contain significant oxygen contamination from the Al₂O₃ substrate while the samples thicker than 5nm (grown at 1000°C and 400°C) would contain less oxygen incorporation. Additionally, the sample grown on Si(111) would be expected to contain less oxygen contamination since the Si substrate nominally contains no oxygen to diffuse into the h-BN sample (though a native oxide likely exists), in agreement with XPS analysis. In this case, oxygen incorporation in h-BN films on Si(111) is likely induced from a combination of oxygen impurities in the gas-phase and low levels of native oxide remaining on the Si substrate.

Similarly to the sample grown at 250°C without a pre-growth anneal, the sample grown on Al₂O₃ at a polyborazylene deposition temperature of 250°C with the use of a 1000°C pre-
growth anneal resulted in two components after deconvolution assigned to h-BN [BN₃] (190.61eV) and BNₓOᵧ (191.78eV). However, here the BNₓOᵧ peak is significantly reduced compared to the sample grown at 250°C without a pre-growth anneal, accounting for 17.7% (compared to 57.7%) of the B1s spectrum, despite the fact that these films were of similar thickness (~2nm). This may be attributed to the 1000°C pre-growth anneal, where hydrogen from the H₂/N₂ (15% H₂) environment may act to reduce the Al₂O₃ surface (or in the case of the Si sample, reduce or remove the native oxide), leaving an oxygen-deficient interface for polyborazylene deposition. This would intuitively result in a reduced interdiffusion of oxygen into the BN film. Alternatively, a BN seed layer may be deposited during the 1000°C pre-growth anneal that acts to reduce interdiffusion between the Al₂O₃ substrate and the h-BN layer. Unlike the sample grown at 400°C however, the lower energy peaks corresponding to nitrogen vacancies and B-B bonding are absent and the B/N ratio was found to be 1.01, indicating excellent stoichiometry. This may again be a result of the BN seed layer grown during the high temperature anneal, which may act to promote further BN bonding and reduce B-B bonding. Further analysis is required, however, to fully understand the mechanisms responsible for interdiffusion between BN and substrate.
Figure 5.2.1: XPS spectra of B1s core level binding energies for h-BN films directly grown on Al$_2$O$_3$(0001) and Si(111). Component peaks were deconvoluted using a Gaussian fit. Peak positions are given after performing a charge correction of the C1s core level peak to 284.8eV.
5.2.2: N1s XPS Analysis

The N1s XPS spectra of h-BN directly grown under various conditions on Al₂O₃(0001) (left column) and Si(111) (right column) is shown in Figure 5.2.2. The N1s peak for bulk h-BN was reported by Moulder et al between 398.1-398.2eV.¹³⁶ For growth on Al₂O₃ at 1000°C without the use of a polyborazylene deposition, a peak at 398.40eV is present and indicative of boron nitrogen bonded to three boron atoms in a hexagonal structure. Additionally, the π-π* “shake-up peak”, also observed in the B1s spectra for the 1000°C sample, is located at 406.75eV. For the h-BN films grown with a polyborazylene deposition at 400°C, 250°C without a pre-growth anneal, and 250°C with a pre-growth anneal, the N1s peak was measured at 398.12eV, 398.26eV, and 398.27eV, respectively, for h-BN films grown on Al₂O₃. Interestingly, the N1s peaks for all growth conditions contain only one component in the main N1s line. Nitrogen-carbon bonding has been reported by Ci et al to manifest as a broad peak located at ~400eV of the N1s line.¹³⁷ This peak is absent in the N1s spectra of all samples examined in this thesis, indicating negligible nitrogen-carbon bonding. Unlike the B1s spectra of these films, which all showed some level of oxygen bonding, additional components of the N1s line that may indicate nitrogen-oxygen bonding were not observed. This has also been reported in the literature for oxygen containing c-BN¹⁵⁶ (cubic) and h-BN films,¹⁵⁴ where an oxygen incorporation was found in the B1s peak, but was not observed the N1s peak. This may be due to the higher relative intensity of the N1s peak compared to the B1s peak. Therefore, impurity peaks associated with nitrogen-impurity bonding may be suppressed by the large signal of the N1s peak. Conversely, boron-impurity peaks would be more identifiable in the B1s peak, which has a comparatively weaker signal.
Figure 5.2.2: XPS spectra of N1s core level binding energies for h-BN films directly grown on Al₂O₃(0001) and Si(111). Component peaks were deconvoluted using a Gaussian fit. Peak positions are given after performing a charge correction of the C1s core level peak to 284.8eV.
5.2.3: O1s XPS Analysis

The O1s XPS spectra of h-BN directly grown under various conditions on Al2O3(0001) (left column) and Si(111) (right column) is shown in Figure 5.2.3. Here the O1s spectra of the h-BN films grown on Al2O3 (often containing two components) is dissimilar than the O1s spectra of the h-BN films grown on Si (comprised of a singlular component). This is due to the fact that the signal from Al-O bonding associated with the Al2O3 substrate, reported at ~531.9eV,136 is detectable in the thinner h-BN films. For the samples grown with a polyborazylene deposition of 250°C with and without the 1000°C pre-growth anneal, the Al2O3 substrate peak is located at 131.14eV and 130.96eV, respectively; and the contribution from this peak to the total O1s spectra is 77.6% and 80.36%, respectively, due to the small film thickness of ~2nm. The additional component peak located at 532.09eV and 532.01eV for the 250°C h-BN samples with and without the pre-growth anneal, respectively, is attributed to the BNxOy bonding configuration, as additionally observed in the B1s spectra. Guimon et al154 also observed a similar peak located at 532.4eV in the O1s spectra of oxygen containing CVD-grown h-BN and likewise attributed this peak to BNxOy bonding. For the sample grown with a polyborazylene dpeosition at 400°C, the signal from the Al2O3 substrate located at 531.50eV is reduced, contributing only 26.7% to the total O1s spectra. Meanwhile the BNxOy peak located at 532.56eV contributes the majority of the O1s spectrum (73.3%) due to the increased signal from a thicker BN film (~8nm). Following this trend, the film grown at 1000°C without the polyborazylene deposition was absent of the Al2O3 substrate peak, where only the BNxOy peak located at 533.00eV was observed. This film was measured with optical ellipsometry to be ~25nm thick, sufficiently thick enough to suppress the substrate signal. The peak position of B2O3 has been reported to lie between 533.0eV and 533.3eV.156 Therefore, the peak observed here may be attributed to B2O3, however the peak associated with B2O3 bonding was not observed in the B1s spectra (Figure 5.2.1).
Figure 5.2.3: XPS spectra of O1s core level binding energies for h-BN films directly grown on Al₂O₃(0001) and Si(111). Component peaks were deconvoluted using a Gaussian fit. Peak positions are given after performing a charge correction of the C1s core level peak to 284.8eV.
5.2.4: C1s XPS Analysis

The C1s XPS spectra of h-BN directly grown under various conditions on Al₂O₃(0001) (left column) and Si(111) (right column) is shown in Figure 5.2.4. In all cases, the primary peak is attributed to C-C bonding of adventitious carbon. This peak has been well established in literature and is located at 284.8eV. Therefore, this peak was used as a calibration standard, where the XPS data was shifted to center this peak at 284.8eV to accommodate for charge shifting induced in the h-BN film during XPS analysis. A shoulder at higher energies is observed for all spectra on both Al₂O₃ and Si ranging between a minimum of 285.52eV to a maximum of 286.72eV. Bepete et al. extensively studied the C1s spectra of graphene films containing h-BN domains synthesized via CVD. They observed several small shoulders at higher energies than the adventitious carbon peak. A peak located at 285.1eV was assigned to C-N bonding at graphene-BN domain boundaries, while one peak located at 286.6eV and another weak and broad peak located at 289.1eV were assigned to C-O bonding. For the C1s results presented in this thesis, the shoulder at high energies varies between samples and is located between the reported C-N and C-O bonding. Therefore, it is difficult to assign the proper bonding configuration. It is also possible that both the reported C-N peak at 285.1eV and the C-O peak at 286.6eV are present here, but overlapping with each other. Additionally, the h-BN samples grown at 250°C with and without a pre-growth anneal on Si show a peak at lower energies located at 283.36eV and 282.76eV, respectively. Bepete et al. observed a similar peak located at 282.5eV assigned to C-B bonding at graphene-BN domain boundaries. Therefore, some carbon-boron bonding and carbon-nitrogen bonding may exist in these films, although the B1s spectra of both films did not show significant bonding to carbon, indicating the overall concentration of B-C and N-C bonds is low.
Figure 5.2.4: XPS spectra of C1s core level binding energies for h-BN films directly grown on Al₂O₃(0001) and Si(111). Component peaks were deconvoluted using a Gaussian fit. Peak positions are given after performing a charge correction of the C1s core level peak to 284.8eV.
Table 5.2.1 shows the B, N, O, and C atomic percentages and B/N ratios for h-BN grown on both Al₂O₃(0001) and Si(111) for all four growth conditions. In three of the four cases, the atomic concentrations and B/N ratios are comparable between both substrates. However, the sample grown at 250°C without the use of a pre-growth anneal shows significant variance between the films grown on Al₂O₃ and Si. Unlike the sample grown on Al₂O₃, the film grown on Si shows significantly reduced oxygen contamination and excellent stoichiometry with a B/N ratio of 1.00. Clearly, oxygen contamination from interdiffusion with the substrate is reduced with use of an Si substrate. However, the overall oxygen content is reduced in comparison to the other h-BN films grown on Si. This may explain the pitting observed with AFM in Figure 1f. Due to the small thickness of this sample (~2nm), it is possible that oxygen from the gas-phase environment diffuses through the BN layer and reacts with the Si substrate to form SiO₂, rather than reacting with the newly formed polyborazylene film. During the 1000°C post-growth anneal however, this SiO₂ layer decomposes and results in surface pitting.

Table 5.2.1: Atomic concentrations of boron, nitrogen, oxygen, and carbon and B/N ratios as measured with XPS of h-BN films grown at various conditions on Al₂O₃(0001) and Si(111).

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<th>h-BN on Al₂O₃(0001)</th>
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<th>O</th>
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<tr>
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<td>6.16%</td>
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</tbody>
</table>
The exact mechanisms for the variance in stoichiometry and bonding configurations between different growth conditions is not fully understood, although boron-rich stoichiometries have been reported previously for boron nitride films synthesized from polyborazylene.\textsuperscript{53,55} To rule out the effect of variance in gas-phase chemistry on film stoichiometry, mass spectrometry was used. Here, the concentrations of various gas-phase BN precursors (produced from sublimation of ammonia borane at 135°C) were obtained for furnace temperatures of 250, 400, and 1000°C. The results, shown in the Figure 5.2.5, show that the concentrations of borazine, diborane, and BH\textsubscript{2} remain independent of temperature. Therefore, the observed differences in stoichiometry at these growth temperatures is not due to the gas-phase chemistry in the CVD environment. Instead, nitrogen may be lost during the high temperature annealing process required to form BN. Indeed, Chan et al demonstrated an increase in the B/N ratio, from 1.18 to 1.37, from spin coated polyborazylene to BN upon annealing to 900°C.\textsuperscript{53} It is broadly accepted that the formation of BN from polyborazylene at high temperatures results in the loss of hydrogen during cross-linking of unaligned chain branch structures.\textsuperscript{52} It is possible that some B-B bonding may occur during this process, where the bonding energy of B-B bonds has been reported to be 38\% less than that of B-N bonds (310 and 500 KJ/mol, respectively),\textsuperscript{20} resulting in a loss of nitrogen locally and the formation of a boron-rich film. Another possible cause of boron rich films is from the oxygen bonding observed in the B1s spectra of Figure 5.2.1. Oxygen likely incorporates into the BN films as substitutional impurities, likely taking the place of nitrogen. Therefore, many boron bonding sites are satisfied by oxygen impurities rather than nitrogen. The exact mechanisms remain unclear, however the answer may lie in a combination of processes such as those outlined here.
Figure 5.2.5: Mass spectra of indicative m/z values for various gas-phase species involved in the sublimation of ammonia borane sampled at furnace temperatures of 250, 400, and 1000°C. (a) Nitrogen, N₂ and N (m/z = 28 and 14, respectively); aminoborane (m/z = 27); and hydrogen (m/z = 2); (b) borazine (m/z = 80); (c) BH₂ (m/z = 13); and (d) diborane (m/z = 25). The temperature of the furnace has a negligible effect on the concentration of the various gas-phase species involved in the CVD of boron nitride.
5.3: Cross-Sectional TEM Analysis

The structures of these films were characterized with cross-sectional TEM. Figure 5.3.1 shows the cross-sections of h-BN films grown on Al₂O₃ substrates only, since the structures on both Al₂O₃ and Si(111) were nearly identical. The sample grown directly at 1000°C is shown in Figure 5.3.1a and suggests that the initial h-BN layers grow nearly parallel to the Al₂O₃ surface. After ~5nm however, the c-axis orientation of the h-BN layers becomes highly random, and is likely the cause of the rough film surface. The film thickness is ~25nm after only 10 minutes of growth, indicating a comparitively large growth rate of 2.5nm/min. Additionally, the film is polycrystalline with domain sizes <5nm. The small domain size is likely a result of stress induced in the h-BN layers due to both the mismatch in coefficient of thermal expansion (CTE) between BN and the substrate (where h-BN has a negative CTE, leading to expansion and compressive stress incorporation in the BN film upon cooling),¹⁴ and to the large lattice mismatch between Al₂O₃ and h-BN of 46%, where Al₂O₃ and h-BN have c-plane lattice constants of 4.67Å and 2.50 Å, respectively.¹⁶⁰ For the sample grown with the polyborazylene deposition step at 400°C (Figure 5.3.1b), a ~5nm film was obtained after 10 minutes of growth indicating a growth rate of 0.5nm/min. This film is significantly less crystalline than the film grown at 1000°C; although some layering of nano-crystalline domains can be observed, indicating a turbostratic structure. For the films grown at 250°C without a pre-growth anneal (Figure 5.3.1c), and 250°C with a pre-growth anneal (Figure 5.3.1d), the crystallinity is decreased even further and the films appear nearly amorphous with no long range order. The poor crystallinity obtained in the films grown with the initial polyborazylene deposition can be attributed to the nature of the initial polyborazylene film, which consist primarily of unaligned chain branches that likely bond with only short-range order upon conversion to BN,⁴⁷ although growth at 400°C appears to promote more order than at 250°C.
Figure 5.3.1: Cross sectional TEM micrographs of h-BN films grown on Al₂O₃ at (a) 1000°C without an initial polyborazylene deposition, (b) a polyborazylene deposition temperature of 400°C, (c) a polyborazylene deposition temperature of 250°C without the use of a pre-growth anneal, and (d) a polyborazylene deposition temperature of 250°C and with the use of a 1000°C pre-growth anneal.

In agreement with Chan et al.⁵³ and Kho et al.⁵⁵, the use of EELS indicates that an interdiffusion layer is present at the h-BN/substrate interface for all four samples, where aluminum and oxygen from the Al₂O₃ substrate diffused into the h-BN layers. For the thicker films, grown at higher temperatures (Figures 5.3.1a and b), the interface region was found to be ~3-5 nm in width, as shown with EELS in Figure 5.3.2 for the 1000°C sample grown on Al₂O₃. This indicates that for the ~2 nm thick samples (Figures 5.3.1c and d), significant fractions of the h-BN film are likely to be BNₓOᵧ, corresponding to XPS measurements showing the atomic concentrations of oxygen to be higher in these films (Table 5.2.1). Interestingly however, XPS shows somewhat reduced incorporation of oxygen in the BN sample grown at 250°C on Al₂O₃ with the use of a pre-growth anneal, shown previously in Table 5.2.1 and Figure 5.2.1, indicating that a BN seed layer or hydrogen reduction of Al₂O₃ during the pre-growth anneal may act to
partially reduce oxygen interdiffusion. Similar results were observed for the films grown on Si(111) in this study, where Si was interdiffused in the BN layer.

Figure 5.3.2: EELS results showing the core-loss signal vs. scan length for the BN sample grown at 1000°C on Al₂O₃ without an initial polyborazylene deposition shows an interdiffusion region of ~5nm at the BN/Al₂O₃ interface. Inset: scanning transmission electron microscopy (STEM) image showing scan location.

5.4: Thermal Conductance Measurements

Thermal conductivity of h-BN films grown using the conditions described in this chapter were investigated for their thermal interface conductance with the time-domain thermoreflectance (TDTR) method, which is sensitive to the inter-atomic bonding and ordering in the thin-film structure as well as interface roughness. Analysis was performed by Jamie J. Gengler, Andrey A.
Voevodin, and William C. Mitchel of the Air Force Research Lab (AFRL). Table 5.4.1 summarizes results of the TDTR measurements, while data fitting examples are provided in supplemental Figure 5.4.1. For thicker h-BN films produced by a direct one-step growth at 1000°C, it was possible to extract the film cross-plane thermal conductivity. It was interesting to observe for these films that the h-BN thermal conductivity was very low. Conductivities of about 600 Wm⁻¹K⁻¹ along base planes and 30 Wm⁻¹K⁻¹ in cross base plane directions are normally expected for bulk h-BN crystals. For thin ordered h-BN, these are reduced by a factor of two, where recent evaluations of suspended exfoliated few layer h-BN films had shown 250 Wm⁻¹K⁻¹ for in-plane thermal conductivity of 5ML h-BN films.¹⁶¹ The results of our TEM studies show that h-BN films from 1000°C direct-growth are nanocrystalline and randomly oriented (Figure 5.3.1a), which critically influences their overall thermal conductivity. From previous experiments and transport modeling with nanocrystalline hexagonal solids within the transition metal dichalcogenide family, it is possible to expect several orders of magnitude reduction in thermal conductivity of disordered hexagonal structures with weak cross-plane bonding characteristics.¹⁶² Thermal conductivity values reported in this paper for nanocrystalline hexagonal thin films of MoS₂, WS₂, and WSe₂ are of the same order of magnitude as in Table 5.4.1 found here for h-BN direct-growth films.
Table 5.4.1: Results of TDTR studies of h-BN films directly grown on silicon and sapphire substrates at different growth conditions.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Growth Condition</th>
<th>Thickness (nm)</th>
<th>Interface Thermal Conductance (MWm$^{-2}$K$^{-1}$)*</th>
<th>BN Thermal Conductivity (Wm$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(111)</td>
<td>1000°C</td>
<td>25</td>
<td>17 ± 1</td>
<td>0.46 ± 0.01</td>
</tr>
<tr>
<td>Si(111)</td>
<td>400°C</td>
<td>7</td>
<td>51 ± 2</td>
<td>-</td>
</tr>
<tr>
<td>Si(111)</td>
<td>250°C no anneal</td>
<td>2</td>
<td>65 ± 2</td>
<td>-</td>
</tr>
<tr>
<td>Si(111)</td>
<td>250°C with anneal</td>
<td>2</td>
<td>72 ± 2</td>
<td>-</td>
</tr>
<tr>
<td>Al$_2$O$_3$(0001)</td>
<td>1000°C</td>
<td>25</td>
<td>20 ± 1</td>
<td>0.57 ± 0.02</td>
</tr>
<tr>
<td>Al$_2$O$_3$(0001)</td>
<td>400°C</td>
<td>7</td>
<td>58 ± 1</td>
<td>-</td>
</tr>
<tr>
<td>Al$_2$O$_3$(0001)</td>
<td>250°C no anneal</td>
<td>2</td>
<td>98 ± 6</td>
<td>-</td>
</tr>
<tr>
<td>Al$_2$O$_3$(0001)</td>
<td>250°C with anneal</td>
<td>2</td>
<td>88 ± 3</td>
<td>-</td>
</tr>
</tbody>
</table>

*Effective conductance, including thermal transport through film thickness and interfaces.

Films grown from polyborazylene were much thinner, making direct measurements of their thermal conductivity impossible as the TDTR penetration depth was two orders of magnitude deeper. Instead, for such thin h-BN films thermal effects were interpreted as changes in an overall interface conductance between the top aluminum transducer layer applied for TDTR analysis and the underlying sapphire or silicon substrates. Such effective thermal interface conductance incorporates thermal transport in the h-BN film as well as its interface resistances with the substrate and aluminum layer. A similar procedure was recently used with graphene layers. From this perspective, there is a clear trend in Table 5.4.1 that the thinner h-BN films grown at 400°C and 250°C provide better effective thermal interface conductance. In all cases it was several times higher than that of the conductance measured for thicker films produced at 1000°C.
Figure 5.4.1: TDTR data and models for two thin film h-BN samples studied.

The observation of higher effective thermal interface conductances for smaller thickness h-BN films can be understood as a decreased resistance of phonon transport through the film thickness. In addition, polyborazylene growth yields better ordered h-BN films near the substrate surface region, which would be expected to reduce phonon scattering at the interface. It remains to be determined how crystallinity within the h-BN film and its structural alignment at the interfaces affects thermal conductance. As one indicator, a well ordered 5nm thick h-BN film produced by direct growth on a copper foil and transferred to sapphire shows an effective thermal interface conductance of $101 \pm 5 \text{ MWm}^{-2}\text{K}^{-1}$. This is higher than values in Table 5.4.1, indicating that ordering within the h-BN film may contribute to the observed improvement of the effective thermal conductance with the polyborazylene growth.
Chapter 6

Direct Growth Boron Nitride as a Supporting Substrate for CVD Graphene

In Chapter 5, a two-step growth method involving the low temperature deposition (250°C and 400°C) of polyborazylene and the subsequent high temperature conversion (1000°C) to boron nitride was presented for synthesis of h-BN films on Al₂O₃(0001) and Si(111) substrates. This chapter explores the electrical properties of these films and the impact these films have on the transport properties of transferred CVD graphene as a supporting dielectric. Current-voltage (I-V) measurements were used to study the electrical breakdown behavior of these films as a function of deposition conditions. Additionally, Raman spectroscopy was used to study the electronic interactions between the graphene and supporting dielectric through analysis of graphene’s G and 2D Raman peaks. Finally, the effect of the h-BN supporting substrates on the transport properties of transferred CVD graphene was examined via Hall mobility measurements. The results presented in this chapter are also published elsewhere.¹⁵¹

6.1: Breakdown Analysis of Direct Growth BN Films

Figure 6.1.1 shows the breakdown characteristics of h-BN films grown on conductive N-type (As) Si(111) substrates (resistivity <0.005) normalized to voltage field to account for thickness variation between samples. Here, I-V measurements were performed between two 125µm diameter Au/Ti (100/20nm) pads and converted to resistivity (Figure 6.1.1a) and current density (Figure 6.1.1b). The films grown with an initial polyborazylene deposition step of 250°C and 400°C resulted in breakdown fields of 1.8x10⁶V/cm and 2.5x10⁶V/cm, respectively; where breakdown was defined as the voltage field at which the threshold current density reached 100
A/cm². For the sample directly grown on Si(111) at 1000°C without the polyborazylene deposition, the breakdown field was 6.1x10⁶ V/cm at a threshold current density of 80A/cm². Additionally, the 1000°C sample shows several current “spikes” in the curve that correspond to the creation of conduction paths across the film that become annihilated due to conduction-induced heating, as similarly observed in breakdown of cubic BN films.¹⁴⁹

Figure 6.1.1: Log-log plots of (a) resistivity and (b) current density vs. voltage field for breakdown analysis of h-BN films grown on conductive Si(111) substrates for different growth temperatures indicate an increased conductivity with decreased growth temperature.
The reduced resistivity for the films grown with the polyborazylene deposition may be correlated to the films chemistry and structure. For the 400°C film, B-B bonding was observed through XPS (Section 5.2.1) and would be expected to lead to an overall increase in conductivity compared to the 1000°C film. Despite this, the 400°C film still displayed higher resistivities at comparable voltage fields than the film grown at 250°C with an anneal. This is likely due to the fact that the reduced thickness of the 250°C film led to increased incorporation of substitutional oxygen impurities from interdiffusion with the native oxide, as discussed in Section 5.3; thus resulting in increased conductivity due to the fact that oxygen has an extra valence electron compared to nitrogen. In contrast, the extra valence electrons induced from oxygen impurities in the 400°C film would be compensated for by the B-B bonding; resulting in reduced conductivity.

For all cases, the breakdown voltages obtained are similar to those reported previously for bulk BN films, where a range between 2-6x10⁶ V/cm has been observed. However, breakdown fields reported for exfoliated h-BN have been reported at 10-15x10⁶ V/cm, due to the pristine single crystal and chemically pure nature of exfoliated h-BN flakes, in contrast to the h-BN films presented in this thesis, which display reduced breakdown and resistivity due to the fact that they are nearly amorphous and incorporate oxygen impurities and B-B bonding.

6.2: Use of Raman Spectroscopy for Analysis of CVD Graphene – Dielectric Interactions

As discussed in Section 1.7.1, Raman spectroscopy is a powerful tool for analysis of graphene’s structure, quality, and electronic properties. It has been well established in literature that the 2D, G, and D peak positions of graphene can indicate the degree of charge doping, strain, and van der Waals interactions between graphene and substrate. Ahn et al. showed that
by simply plotting the 2D and G peak positions of exfoliated graphene on h-BN and SiO₂, that these effects can be modeled and estimated through vector decomposition (see Figure 1.7.3).

Figure 6.2.1 shows the Raman 2D vs. G peak positions for CVD graphene transferred to various dielectric substrates, including: h-BN grown directly on Al₂O₃(0001) and Si(111) under the four growth conditions described in Chapter 5 (8 samples total), a 5nm h-BN film grown on Cu foil with a copper enclosure (as described in Section 3.2) and transferred to Al₂O₃, bare 300nm SiO₂ (Dry oxide), and bare Al₂O₃(0001). In all cases, the acquired Raman data was obtained from 20µm line scans over the transferred graphene surface using a 488nm laser. The error bars shown in Figure 6.2.1 indicate the standard deviations associated with the 20µm line scans. Nominally, strain-free and charge-neutral graphene is located at G and 2D peak positions of 1581.6cm⁻¹ and 2676.9cm⁻¹, respectively, as indicated by the light blue circle in Figure 6.2.1.¹⁶⁶

The experimentally observed 2D and G peak positions for transferred CVD graphene samples presented here show significant deviation from the position of strain-free and charge-neutral graphene, which is expected due graphene’s interaction with the underlying substrate. Interestingly, the 2D and G peak positions of CVD graphene transferred to h-BN vary drastically from each other and appear dependent on the growth conditions of the h-BN films. Additionally, the substrate used for h-BN deposition does not seem to alter the Raman spectra, where similar peak positions were found for both h-BN grown on Al₂O₃ (squares) and Si (triangles) for the same growth conditions. The one exception to this, however, is the h-BN growth at 250°C without a pre-growth anneal, where growth on Al₂O₃ and Si resulted in variance in Raman peak positions, resulting in G, 2D peak positions of 1584.9cm⁻¹, 2696.1cm⁻¹ and 1582.0cm⁻¹, 2682.7cm⁻¹, respectively. This is expected however, since this growth condition was found in Chapter 5 to result in the most disparity in chemical and morphological properties between the two substrate materials, where growth on Si resulted in surface pitting (see Section 5.1) but significantly reduced oxygen incorporation (see Section 5.2) compared to growth on Al₂O₃. In
contrast, all other BN growth conditions resulted in similar morphological and chemical properties for both substrates investigated.

**Figure 6.2.1:** Raman 2D frequency vs. G frequency of CVD graphene transferred to various substrates. Like colors indicate identical growth conditions. Squares indicate CVD graphene transferred to h-BN films grown on Al₂O₃(0001) while triangles indicate CVD graphene transferred to h-BN films grown on Si(111). Circles indicate CVD graphene transferred to alternative substrates.

Figure 6.2.2 shows the vector analysis correlating graphene’s 2D (ω₂D) and G (ωG) peak positions to tensile and compressive strain (e_T and e_C, respectively), Fermi velocity reduction (e_FVR), and hole doping (e_H), based on the work of Lee et al. and Ahn et al. As discussed in Section 1.7.1, even weak Van der Waals forces between graphene and its dielectric environment
can lead to perturbation of graphene’s electronic band structure through breaking of symmetry between neighboring C atoms in graphene.\textsuperscript{108} The modulation of the electronic structure will manifest as a reduction in the Fermi velocity ($v_F$) of charge carriers in graphene. This Fermi velocity reduction (FVR) was found to only effect the 2D peak of graphene since the G peak of graphene, originating from the $E_{2G}$ phonon, is not affected to a first-order approximation.\textsuperscript{117,165} Therefore, any reduction in $v_F$ of graphene will manifest as an upward shift in the 2D peak along the $e_{\text{FVR}}$ vector shown in Figure 6.2.2, where the values shown indicate $\Delta v_F/v_F$ (\%) and are negative to indicate a decrease from the intrinsic $v_F$ of graphene ($\approx 10^6$ m/s).\textsuperscript{117,165} Raman spectroscopy is also useful in characterizing strain ($\varepsilon$) in a wide variety of materials, since changes in lattice constant due to strain will result in alterations to the respective phonon frequencies.\textsuperscript{167} Lee et al\textsuperscript{166} then extracted the contribution of strain ($\varepsilon$) for given points in the $\omega_G$-$\omega_{2D}$ space, forming a simple vector model for $e_T$ and $e_C$, as explained elsewhere.\textsuperscript{166} Finally, the vector associated with hole doping ($e_H$) was formed from in-situ Raman analysis data obtained by Das et al,\textsuperscript{168} where hole doping was controlled through electrical gating.

Since both electron and hole doping will lead to an increase in $\omega_G$,\textsuperscript{166} the results presented in Figure 6.2.2 show that the contribution of charge doping to the Raman spectra of the samples investigated here is negligible. It was also observed by Ahn et al\textsuperscript{166} that hole doping of exfoliated graphene on h-BN was negligible, although hole doping was found for exfoliated graphene on SiO$_2$, in contrast to the transferred CVD graphene on SiO$_2$ shown in Figure 6.2.2. A possible explanation for this will be proposed later. Therefore, the $\omega_G$ and $\omega_{2D}$ positions of the transferred CVD graphene investigated in this thesis can be vector decomposed into contributions from strain ($e_T$, $e_C$) and Fermi velocity reduction ($e_{\text{FVR}}$) only. Based on the vector analysis, the effect of the underlying substrate on the transferred CVD graphene can be quantified in terms of strain and FVR for the various h-BN growth conditions, as well as for other common substrates (SiO$_2$, Al$_2$O$_3$, and transferred h-BN).
Figure 6.2.2: Raman 2D frequency vs. G frequency of CVD graphene transferred to various substrates. The data is identical to that shown in Figure 6.2.1, but vector decomposed to correlate peak shifting to tensile and compressive strain ($e_T$ and $e_C$, respectively), Fermi velocity reduction ($e_{FVR}$), and hole doping ($e_H$), using methods reported by Ahn et al.\textsuperscript{117} The inset shows the expected trajectories of 2D and G peak positions affected by $e_T$, $e_C$, $e_{FVR}$, and $e_H$. 
Table 6.2.1 shows the positions for the various substrates investigated here as well as the approximate strain and FVR induced into the transferred CVD graphene. Based on these results, possible effects that the supporting substrate has on the overlying graphene can be proposed. Apparent from Figure 6.2.2, the h-BN films grown directly on Al₂O₃ and Si at 1000°C without a polyborazylene deposition (green symbols) and at 250°C with a pre-growth anneal (pink symbols) resulted in extensive tensile strain, with an average of 0.34% and 0.24% tensile strain, respectively. This is due to the fact that these samples resulted in large RMS surface roughnesses, as discussed in Section 5.1 (see Figure 5.1.1), where the transferred graphene layer is stretched across the rough surface. Interestingly, the FVR for these samples was low compared to the other growth conditions, where the 1000°C and 250°C sample with a pre-growth anneal resulted in a FVR of -2.0% and -4.0%, respectively. This is particularly unexpected since the h-BN samples grown at 1000°C showed the highest degree of crystallinity (see Figure 5.3.1). Ahn et al.117 showed that exfoliated h-BN supporting dielectrics resulted in an increase in FVR compared to amorphous SiO₂ due to the crystalline nature of h-BN, which would induce periodic perturbations to the graphene band structure. However, here the 1000°C h-BN sample shows lower FVR than the amorphous BN samples (grown with the polyborazylene deposition). This again may be due to the surface roughness. Since the graphene film would be partially suspended over the rough h-BN surface, a large percentage of the graphene film would not be in contact with the h-BN surface, reducing the van der Waals interactions between the graphene and substrate. In this case, the tensile strain resulting from the partial suspension over the substrate would primarily contribute to the shift in Raman peak position, as observed in Figure 6.2.2, and would be expected to show similar FVR to the rough amorphous samples grown at 250°C with a pre-growth anneal. The h-BN film grown on a Cu foil and transferred to Al₂O₃ (purple circle) also induces tensile stress (0.14%) to the graphene layer. Likewise, this film was also found to have a high surface roughness. However, this film shows significant FVR compared to the direct grown
h-BN samples with high surface roughness previously discussed. This may be a result of the improved crystallinity, where these films were found to have much higher crystallographic texturing and domain sizes compared to the direct growth h-BN films (see Figure 3.2.5a), and thus may not only induce strain from surface roughness but also induce periodic perturbations to the graphene band structure over several nm ranges.

Table 6.2.1: Raman peak positions ($\omega_G$ and $\omega_{2D}$) as well as approximate strain ($\varepsilon$) and Fermi velocity reduction (FVR) induced in transferred CVD graphene from various dielectric substrates. Data is based on results from Figure 6.2.2.

| Dielectric Substrate          | $\omega_G$ (cm$^{-1}$) | $\omega_{2D}$ (cm$^{-1}$) | $\varepsilon$(%) | FVR(%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain-Free Graphene</td>
<td>1581.6</td>
<td>2676.9</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1585.5</td>
<td>2701.4</td>
<td>-0.17</td>
<td>-7.1</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1587.1</td>
<td>2701.9</td>
<td>-0.24</td>
<td>-5.8</td>
</tr>
<tr>
<td>BN: Transferred</td>
<td>1578.3</td>
<td>2683.9</td>
<td>0.14</td>
<td>-6.3</td>
</tr>
<tr>
<td>BN on Al$_2$O$_3$: 1000°C</td>
<td>1574.1</td>
<td>2666.8</td>
<td>0.32</td>
<td>-2.6</td>
</tr>
<tr>
<td>BN on Al$_2$O$_3$: 400°C</td>
<td>1581.4</td>
<td>2685.4</td>
<td>0.01</td>
<td>-3.7</td>
</tr>
<tr>
<td>BN on Al$_2$O$_3$: 250°C no anneal</td>
<td>1584.9</td>
<td>2696.1</td>
<td>-0.14</td>
<td>-5.4</td>
</tr>
<tr>
<td>BN on Al$_2$O$_3$: 250°C with anneal</td>
<td>1576.4</td>
<td>2675.8</td>
<td>0.23</td>
<td>-4.4</td>
</tr>
<tr>
<td>BN on Si: 1000°C</td>
<td>1573.5</td>
<td>2662.6</td>
<td>0.35</td>
<td>-1.3</td>
</tr>
<tr>
<td>BN on Si: 400°C</td>
<td>1583.6</td>
<td>2688.0</td>
<td>-0.08</td>
<td>-3.1</td>
</tr>
<tr>
<td>BN on Si: 250°C no anneal</td>
<td>1582.0</td>
<td>2682.7</td>
<td>-0.02</td>
<td>-2.2</td>
</tr>
<tr>
<td>BN on Si: 250°C with anneal</td>
<td>1576.1</td>
<td>2673.1</td>
<td>0.24</td>
<td>-3.6</td>
</tr>
</tbody>
</table>

The alternative substrates, SiO$_2$ (blue circle) and Al$_2$O$_3$ (black circle), both resulted in compressive stress (-0.17% and -0.24%, respectively) and large FVR (-7.1% and -5.8%, respectively). The compressive stress likely arises from strong adhesion of the graphene to these dielectrics. It has been shown previously that exfoliated graphene on SiO$_2$ substrates experience strong compressive stress and deformation due to ultra-strong adhesion forces with the underlying substrate. It is possible that graphene may have strong adhesion to Al$_2$O$_3$ as well, based on the shift of $\omega_G$-$\omega_{2D}$ along $\varepsilon_C$, as shown in Figure 6.2.2. The reduction in Fermi velocity was expected
for the single crystal Al$_2$O$_3$ substrate, however not for the SiO$_2$ substrate. As mentioned previously, Ahn et al.$^{117}$ found that for exfoliated graphene on SiO$_2$, FVR was minimal (due to SiO$_2$'s amorphous nature) and hole doping was experienced, in contrast to the results shown here (see Figure 1.7.3). It is not fully understood why the results found here for CVD graphene on SiO$_2$ vary from those found by Ahn et al.$^{117}$ One possibility may be due to differences in the CVD graphene used here compared to exfoliated graphene.

The samples grown with a polyborazylene deposition of 250°C without a pre-growth anneal (orange symbols) were found to result in the most variation in $\omega_G$ and $\omega_{2D}$ peak positions between the Al$_2$O$_3$ (square) and Si (triangle) substrates. The sample grown on Si resulted in a negligible compressive strain of -0.02% and a reduced FVR of -2.2%. The low surface roughness (<130 pm) of this film induces negligible strain while its amorphous structure is expected to induce minimal van der Waals interactions to the graphene layer, thus resulting in low FVR. However, it should be noted that this film experienced surface pitting (see Figure 5.1.1); therefore the Raman line scan for this sample was taken in a region where surface pitting was not observed locally. Although this sample resulted in $\omega_G$ and $\omega_{2D}$ positions comparable with strain-free charge-neutral graphene, this sample is unfortunately unsuitable for graphene device development due to the surface pitting observed across the film surface. In contrast, the BN sample grown on Al$_2$O$_3$ resulted in a compressive strain of -0.14% and a FVR of -5.4%. It is not fully understood why this sample shows such contrast to the sample grown on Si under the same conditions, as the relatively high FVR is not expected for an amorphous material. However, based on results in Chapter 5, it is known that this film is much different chemically than the film grown on Si. Therefore, the increase in FVR may be due to the fact that this sample was found to have significant oxygen contamination. If these impurities possess a high density of dangling bonds, they may be inducing electrostatic perturbations to graphene’s band structure and increasing the FVR.
The samples grown at a polyborazylene deposition of 400°C (red symbols) show negligible strain and low FVR for both BN films grown on Al\textsubscript{2}O\textsubscript{3} (square) and Si (triangle), where the strain was 0.01\% and -0.08\% and FVR was -3.7\% and -3.1\% for these films, respectively. The amorphous nature of these films results in minimal van der Waals interaction with the graphene layer and minimally degrades the FVR. Additionally, the presence of both B-B bonding and BN\textsubscript{x}O\textsubscript{y} bonding (as observed with XPS in Section 5.2) likely results in an overall compensation of valence; resulting in negligible electrostatic interaction from free electrons, further leading to a low FVR. Even more interesting is that the strain induced into graphene is nearly negligible and comparable to strain-free graphene, likely due to low adhesion between graphene and BN. This indicates that the amorphous BN grown with a polyborazylene deposition of 400°C may be an excellent candidate for CVD graphene integration due to the introduction of minimal FVR and negligible strain, as observed with Raman spectroscopy.

6.3: Effect of Supporting Substrate on CVD Graphene Hall Mobility

Figure 6.3.1 shows the Hall mobility as a function of charge carrier density for CVD graphene transferred to the various substrates. The direct growth h-BN samples on Al\textsubscript{2}O\textsubscript{3} (grown under the various conditions detailed in Chapter 5) were used as supporting substrates for transferred CVD graphene. For comparison, CVD graphene was also transferred to additional substrates; these included an h-BN film with a thickness of ~5nm grown on Cu and transferred to Al\textsubscript{2}O\textsubscript{3}, a bare Al\textsubscript{2}O\textsubscript{3}(0001) substrate, and a bare 300nm SiO\textsubscript{2} substrate. It should be noted that the graphene on h-BN Hall mobility data presented here is only for h-BN films grown or transferred onto Al\textsubscript{2}O\textsubscript{3} (0001) substrates. For films on Si(111), the conductive Si substrate resulted in shorting issues between the contacts and substrate due to device fabrication issues.
Figure 6.3.1: (a) Hall mobility vs. hole concentration of CVD graphene transferred to h-BN dielectrics synthesized at various growth conditions, as well as bare Al$_2$O$_3$ and SiO$_2$ substrates. Dotted curves indicate the simulated dependency of mobility on carrier density at various impurity densities based on modeling for the h-BN/graphene system described by Hollander et al.$^{127}$ (b) Log-log plot of graphene Hall mobility vs. RMS surface roughness of the underlying h-BN dielectric, as measured by AFM. (c) Log-log plot of graphene Hall mobility vs. oxygen content of the underlying h-BN dielectric, as measured by XPS. The symbols shown in (b) and (c) correspond to the legend given in (a) and represent the average of the mobilities obtained for each sample.
From the Hall mobility measurements of Figure 6.3.1a, it is clear that the underlying dielectric substrate (and the various growth conditions of the h-BN substrates) play a significant role in the transport properties of the transferred CVD graphene film. For comparison to the h-BN samples described previously, CVD graphene was also transferred to 300nm SiO$_2$ and a high-k dielectric (Al$_2$O$_3$). The graphene sample transferred to bare Al$_2$O$_3$(0001) (orange circles) shows an average mobility of $4218 \pm 849$ cm$^2$/V-s at a hole concentration of $1.9 \times 10^{12} \pm 4.5 \times 10^{11}$ cm$^{-2}$, while the graphene sample transferred to the SiO$_2$ substrate (brown hexagons) shows an average mobility of $2559 \pm 124$ cm$^2$/V-s at a hole concentration of $3.5 \times 10^{12} \pm 3.5 \times 10^{11}$ cm$^{-2}$. Both Al$_2$O$_3$ and SiO$_2$ have low surface optical phonon energies, reported at 55.01 and 59.98 meV, respectively. Therefore, both substrates are expected to experience significant phonon-electron coupling, resulting in surface optical phonon scattering. In a separate work, however, it was found that impurity scattering is the dominant scattering mechanism for h-BN gated epitaxial graphene devices, accounting for $>90\%$ of the total scattering processes for h-BN coated epitaxial graphene. Though the samples detailed here show reduced carrier densities compared to epitaxial graphene, these samples are likely similarly dominated primarily by impurity scattering. Given that the dielectric constants of Al$_2$O$_3$ and SiO$_2$ are 12.5 and 3.9, respectively, the higher dielectric constant of Al$_2$O$_3$ will act to screen charged impurities that would induce Coulombic scattering to graphene, as described by Konar et al. Therefore, the effective impurity density of the graphene/Al$_2$O$_3$ system is reduced (due to its higher dielectric constant) compared to graphene/SiO$_2$, resulting in reduced Coulombic scattering and higher mobilities for the graphene/Al$_2$O$_3$ system. Based on temperature dependent Hall Effect measurements and subsequent modeling described by Hollander et al., it was found that the effective impurity concentration is approximately $5.5 \times 10^{11}$ cm$^{-2}$ for a graphene/SiO$_2$ system with the mobilities and sheet densities shown in Figure 6.3.1a. Unfortunately, the impurity density of the graphene/Al$_2$O$_3$ system cannot be extracted without temperature-dependent Hall mobility analysis. The variation
in mobility for these two samples can be effectively described by impurity scattering, since surface roughness scattering can be ruled out as both substrates display a similar surface roughness (see Figure 5.1.1). Additionally, the compressive strain and high Fermi velocity reduction (FVR) observed with Raman spectroscopy was similar for these two samples (Figure 6.2.2) and likely further limits the mobility for both substrates.

The dotted lines in Figure 6.3.1a represent the simulated dependency of mobility on carrier density for given impurity densities of the h-BN/graphene system, based on modeling described by Hollander et al.\textsuperscript{127} The model assumes an acoustic deformation potential of 4.8eV\textsuperscript{102} and an optical deformation potential of 25.6eV/A\textsuperscript{102} for the CVD graphene and that the surface optical phonon modes (taken as 160meV) of all h-BN films are equal.\textsuperscript{127} It should also be noted that this model does not take into account surface roughness scattering. These results show that the observed variation in mobility between graphene on the various h-BN samples cannot be described by changes in carrier density alone. Based on this modeling, the change in mobility as a function of h-BN growth condition can be effectively described by impurity concentration. The graphene devices on h-BN films grown at an initial polyborazylene deposition temperature of 400°C (red square) resulted in an average mobility of 6425 (±975) cm\textsuperscript{2}/V-s at a hole concentration of 1.1x10\textsuperscript{12} (±3.0x10\textsuperscript{11}) cm\textsuperscript{2} and reached a maximum mobility of nearly 8000 cm\textsuperscript{2}/V-s. Modeling of these mobilities resulted in extraction of impurity densities ranging from 2.0x10\textsuperscript{11} cm\textsuperscript{2} to 3.0x10\textsuperscript{11} cm\textsuperscript{2}. In contrast, the h-BN films grown at the various other growth conditions result in reduced mobility and increased hole density, leading to increased impurity densities ranging from 4.5x10\textsuperscript{11} cm\textsuperscript{2} to 6.5x10\textsuperscript{11} cm\textsuperscript{2}. In other works,\textsuperscript{127,150} we found that the benefits of h-BN dielectrics on epitaxial graphene were heavily dependent on the charged impurity density, where impurity concentrations >5x10\textsuperscript{11} cm\textsuperscript{2} resulted in a charged impurity dominated scattering regime where high-k dielectrics outperformed h-BN due to their ability to screen Coulombic scatterers. On the other hand, for impurity concentrations <5x10\textsuperscript{11} cm\textsuperscript{2}, surface
optical phonon scattering begins to contribute more significantly to the total scattering rate. In this scattering regime, the increased phonon-electron coupling induced by high-k dielectrics (having low surface optical phonon modes) limit the mobility of charge carriers in graphene, while h-BN gated devices benefit from h-BN’s high surface optical phonon modes. Interestingly, the models described in these previous works appear to hold true for the CVD graphene investigated in this work, as shown in Figure 6.3.1a, where the high-k dielectric Al₂O₃ outperforms h-BN samples with high impurity densities, while the h-BN samples with low impurity densities (grown at 400°C) outperform Al₂O₃.

Unfortunately, the model used for impurity density extraction in Figure 6.3.1a does not take into account surface roughness scattering, where significant variation between h-BN growth conditions was observed previously in Chapter 5 (see Figure 5.1.1). Increased interfacial surface roughness has not only been shown in literature to directly induce scattering in graphene;¹⁰¹ but also induces strain in graphene (as validated with Raman spectroscopy in Figure 6.2.2), which has been shown to further reduce mobility.¹⁷⁰,¹⁷¹ Therefore, the average mobilities of the transferred graphene on the various h-BN samples is plotted against RMS surface roughness, as measured with AFM, in Figure 6.3.1b. A trend is observed for four of the five samples; however the sample grown at 250°C without a pre-growth anneal results in a low average mobility (2445 (±535) cm²/V-s at a hole concentration of 5.8x10¹² (±1.1x10¹²) cm⁻²) despite the fact that this sample displayed the lowest RMS roughness (130pm) of all the h-BN samples. To understand this, the average mobilities were also plotted against the oxygen concentration of the h-BN films, as measured with XPS, in Figure 6.3.1c. It is likely that substitutional oxygen bonding contributes significantly to the overall impurity density of the graphene/dielectric system since oxygen possesses an extra valence electron than nitrogen, resulting in an increased density of dangling bonds that would induce Coulombic scattering to graphene. Therefore, the oxygen concentration of the h-BN films can be correlated directly to impurity density. From Figure 6.3.1c, graphene’s
mobility is found to decrease with increasing oxygen content, where the sample grown at 250°C without a pre-growth anneal (light blue cross) is dominated by impurity scattering due to its high concentration of substitutional oxygen impurities. Again however, outliers in the observed trend are found. The sample grown at 1000°C without a polyborazylene deposition (green triangle) was found to have an average mobility of 2407 (±478) cm²/V-s at a hole concentration of 4.9x10¹² (±8.3x10¹¹) cm⁻², while the transferred h-BN sample (pink “X”) was found to have an average mobility of 2123 (±243) cm²/V-s at a hole concentration of 4.6x10¹² (±8.3x10¹¹) cm⁻², despite the fact that these samples had relatively low oxygen impurity concentrations. The results of Figures 6.3.1b and 6.3.1c suggest that two scattering mechanisms are at play for graphene transferred to the h-BN films investigated here. Scattering can be dominated by surface roughness (and strain) as evident in the rough h-BN sample grown at 1000°C (RMS roughness >3nm) and the transferred h-BN sample (RMS roughness >1.5nm), or by impurity density as evident by the ultra-smooth but highly oxygen-rich (>50%) sample grown at 250°C without a pre-growth anneal. Another option is a combination of the two scattering mechanisms, as evident by the h-BN film grown at 250°C with a pre-growth anneal (blue diamond), where the mobility (3098 (±281) cm²/V-s at a hole concentration of 3.1x10¹² (±5.6x10¹¹) cm⁻²) was found to similarly lie at intermediate points in the trend lines of both Figures 6.3.1b and 6.3.1c. In this case, the moderate roughness and moderate oxygen contamination lead to contributions from both scattering mechanisms. Further work is required to model the exact impurity concentrations of these samples while taking into account the effects of surface roughness scattering. Based on these results, however, it is apparent that when h-BN is synthesized under conditions that result in both low surface roughness and low oxygen contamination, the beneficial effects of h-BN’s high energy surface optical phonon modes can be realized. This was achieved in the present work for h-BN synthesis at an initial polyborazylene deposition temperature of 400°C; where an RMS surface roughness of 240pm resulted in nearly strain-free transferred graphene (as observed with
Raman spectroscopy in Figure 6.2.2), while a low oxygen content of <6 atomic % resulted in low impurity densities (<3x10^{11} \text{cm}^{-2}) which allow h-BN’s high energy surface optical phonon modes to benefit graphene devices. With use of the 400°C polyborazylene-to-BN synthesis conditions, transferred CVD graphene devices resulted in an increase in average mobility of 52% and 151% and a reduction in hole doping of 75% and 224% over the Al₂O₃ and SiO₂ substrates, respectively, with a maximum mobility reaching nearly 8000 cm²/V-s. These results also suggest that even use of nearly amorphous BN, as shown with cross-sectional TEM in Chapter 5 (see Figure 5.3.1), can benefit graphene electronics.
Chapter 7

Conclusions and Future Work

This thesis has demonstrated the synthesis and characterization of hexagonal boron nitride through two primary techniques: growth on copper foil, which can be transferred to arbitrary substrates, and direct-growth on various substrates using a two-step polyborazylene-to-ceramic conversion. The chemical, structural, morphological, and electrical properties of these h-BN films, synthesized via both techniques, have been investigated in detail as a function of growth conditions and presented in the previous chapters. Additionally, the effect of these h-BN films on the transport properties of graphene, where h-BN grown on Cu was used a top-gate dielectric to quasi-freestanding epitaxial graphene (QFEG) and h-BN grown directly on Al₂O₃ and Si was used as a supporting substrate to CVD-grown graphene (transferred from Cu foil), was thoroughly explored. Despite the many interesting results found during this research, many questions remain unanswered, requiring additional work to obtain a more detailed understanding of these films and their influence as dielectric materials on the transport properties of graphene and other two-dimensional materials, such as transition metal dichalcogenides (TMDCs). Therefore, this chapter acts to summarize the major findings of this thesis as well as present areas where additional research is required to further the knowledge and range of possible applications for hexagonal boron nitride dielectrics.

7.1: Hexagonal Boron Nitride Growth on Copper

Growth of h-BN films on 25µm thick 99.999% (metals basis) pure copper foils was investigated in Chapter 3 of this thesis. In Section 3.1, growth rate was found to increase with
increasing reactor pressure and found to change negligibly with ammonia borane flow rate, indicating that the partial pressure of gas-phase BN precursors is limited by the sublimation rate of ammonia borane and remains constant with sublimator flow rate. Additionally, it was found through mass spectrometry that an 87% and 85% drop-off in the concentrations of the gas-phase BN precursors borazine and diborane, respectively, occurred during the first 5 minutes of growth due to the non-linear sublimation rate of ammonia borane with time. Raman spectroscopy was used to correlate as-grown h-BN film thickness to the intensity and full width half maximum (FWHM) of the E$_{2G}$ phonon mode of h-BN, located at $\sim$1364cm$^{-1}$, where a power law relationship was found for both quantities. This provides a simple technique to quantify the film thickness of as-grown h-BN films on Cu without the need to transfer for optical ellipsometry or AFM measurements.

SEM and AFM analysis revealed the presence stress-induced wrinkling of the h-BN films that result from the coefficient of thermal expansion mismatch between h-BN and Cu. Additionally, Raman was used to show a blue-shift in peak position of the E$_{2G}$ phonon mode upon transfer of the h-BN film to arbitrary substrates. This was found to correlate to a $\sim$42% decrease in compressive strain from the as-grown to transferred h-BN film, where the as-grown film was partially chemisorbed to the Cu substrate. Besides surface wrinkling, three-dimensional surface features that increased in density and size with increasing h-BN thickness were also observed in the h-BN morphology. Plan-view transmission electron microscopy (TEM) was used to investigate these 3D features and found that they were composed of h-BN layers propagating perpendicular to the growth plane.

Transfer of the as-grown h-BN films from the Cu foil to arbitrary substrates was accomplished via a ferric chloride based transfer process to remove the native Cu substrate. X-ray photoelectron spectroscopy was used to examine the impact of the transfer process on the chemical properties of the h-BN films. It was found that the primary B1s and N1s core level
peaks did not degrade upon transfer, however a small shoulder at higher binding energies of the B1s spectra indicates oxygen content increases by 54% upon transfer. It is likely that oxygen is bonding at domain boundaries or defects, rather than substitutionally as the B/N ratio remained near 1:1 following transfer. Incorporation of oxygen is likely from the de-ionized water baths used during the transfer process to remove residual ferric chloride etchant. Additionally, the C1s peak was found to increase upon transfer due to residual photoresist on the h-BN film surface. Evidence of bonding, though only slight, was observed as C-B and C-N shoulders on the C1s spectra, where carbon likely is bonding at defects or domain boundaries of the top h-BN surface.

Section 3.2 investigated the use of a copper enclosure during growth of h-BN on Cu foils. It was found that the Cu enclosure acted to reduce the partial pressure of gas-phase BN precursors through the creation of a static Cu vapor overpressure above the Cu foil samples. This not only resulted in a decreased growth rate compared to h-BN growth without a Cu enclosure, but also in an increased domain and island size through a reduced flux of BN precursors to the Cu substrate. Additionally, it was found that the concentrations of oxygen and carbon impurities were reduced by 65% and 62%, respectively, with the use of a copper enclosure during h-BN growth. Again, this was attributed to a reduction in the partial pressure of impurity gases (such as water vapor, oxygen leaks, or back-streamed pump oil) in the h-BN growth environment due to the presence of a copper overpressure. Additionally, the slowed growth of h-BN with a Cu enclosure allowed for the growth mechanisms to be thoroughly studied. It was found that h-BN growth on Cu initiates as large (~200nm length) triangular domains. These domains were found to nucleate over an initial h-BN monolayer either from surface wrinkles or from crystallographic step edges, depending on Cu grain orientation. This suggests that Cu orientation can be used to promote well ordered and textured BN films. Unfortunately, indexing of the Cu grains was not possible due to the rough surface of the Cu foils. However, it is clear that the triangular domains retain a binding energy to the Cu surface, even though an initial monolayer was present. When this binding
energy eventually decays with increased layer thickness however, the h-BN domains no longer form as single crystal domains, but rather as small randomly oriented nano-crystalline domains that increase in density and diameter with increasing film thickness. This suggests that h-BN growth on Cu foils proceeds via a Stranski-Krastanov growth mode, where initial layers are strongly bound to the substrate and form in a layer-by-layer growth mode, while subsequent layers are more strongly bound to each other than to the substrate and thus form as islands. These islands eventually coalesce, upon which additional layers may form as randomly oriented nano-clusters and propagate as poorly ordered turbostratic BN. Cross-sectional TEM analysis was used to verify the proposed growth model and showed well ordered and laminar h-BN layers, as well as the coalescence of islands, at a thickness of 5nm. However, at a thickness of >10nm, a clear transition from layered growth to turbostratic growth was observed, indicating that the crystallinity of these films decreases significantly after full coalescence of h-BN islands. The turbostratic growth likely leads to randomly oriented h-BN layers and is likely the cause of the 3D features observed previously in Section 3.1. It was found that the copper enclosure allows for improved island size with reduced density; therefore, full coalescence of these islands occurs at larger film thicknesses compared to h-BN growth without a Cu enclosure, thus resulting in improved crystallinity, improved domain size, and a significant reduction in the density of 3D surface features. Because of these improvements, h-BN films grown with a Cu enclosure were found to result in an 89% increase in breakdown strength and a decrease in current density of nearly four orders of magnitude at a voltage field of $1 \times 10^5$ V/cm for ~20nm thick films.

Future work for growth of h-BN on Cu substrates includes improved control of gas-phase BN precursors. Based on the mass spectroscopy data previously discussed, the concentration of gas-phase BN precursors drops significantly after only a few minutes of growth. Also, the growth rate was invariable with flow rate through the sublimator, resulting in poor control of gas-phase BN precursor partial pressure. The results of Section 3.2 show that by decreasing the partial
pressure of gas-phase precursors through use of a copper enclosure, an improvement in the crystallinity, morphology, chemistry, and electrical properties of h-BN films was observed. Therefore, decreasing the partial pressure of gas-phase BN precursors through alternative ways will likely lead to similar results. Unfortunately, in this thesis work, the BN precursor partial pressure was limited and controlled through ammonia borane’s sublimation rate, requiring novel approaches to control partial pressures, i.e. – the copper enclosure. However, use a pressure-based mass flow controller (MFC), such as the MKS-1150 or MKS-1152, would likely be highly beneficial in controlling the partial pressure of BN precursor. With a pressure-based MFC, the ammonia borane can be sublimated upstream of the MFC. The “reservoir” of gas-phase BN precursors produced from the sublimation of ammonia borane can then be held at a constant temperature in the sublimator for long periods of time. The MFC can then regulate the flow of these precursors into the tube furnace, thus providing a means to maintain a constant concentration of gas-phase precursors, as well as allowing for precise control of the partial pressure of these precursors. With such a set-up, the growth mechanisms and film properties can be studied in detail as a function of precursor partial pressure, which was not possible for this thesis work. Additional future work involves study of h-BN growth on alternative transition metal substrates. It was shown in Section 1.2 that the binding energy between h-BN and its substrate varied for different transition metals. Going across the 3d, 4d, and 5d rows of the periodic table, the binding energy of h-BN on transition metal surfaces decreases from left to right, with noble metals having the lowest binding energies. Therefore, binding energy decreases with increased filling of the valence d-band. Additionally, it was found that the highest binding energies were obtained for the 4d elements and the lowest for the 3d elements. Since it was suggested in Section 3.2 that a shift from single crystal triangular domains to nanocrystalline islands occurred due to a reduction in h-BN/Cu binding energy with increased film thickness, it would be assumed that h-BN growth on transition metals with higher h-BN/metal binding energies would result in
improved texturing and crystallinity compared to growth on Cu, which was shown by Laskowski *et al.*<sup>29</sup> to be relatively weak due to increased filling of the valence d-band. The author suggests investigation of h-BN growth on Co, Pd, Zr, and Ti due to their comparatively large binding energies, similar lattice constants, and similar crystallographic structures (HCP) to h-BN.

### 7.2: Integration of Transferred h-BN with Quasi-Freestanding Epitaxial Graphene

Hexagonal boron nitride films grown on Cu foils were transferred to quasi-freestanding epitaxial graphene (QFEG) samples with pre-fabricated ohmic level devices, as discussed in Chapter 4. In Section 4.1 it was found that despite the presence of wrinkles on the h-BN surface, only a ~9% decrease in room temperature mobility and a negligible increase in hole doping was observed after transfer of h-BN followed by a post-transfer anneal at 400°C (see Figure 4.1.1). This suggests that the h-BN film minimally degrades the room temperature mobility and introduces minimal hole doping. Temperature dependent measurements were presented in Section 4.2 to investigate the scattering mechanisms of h-BN gated QFEG compared to QFEG devices gated with the high-k dielectric HfO<sub>2</sub>. Additionally, RF characterization was investigated in Section 4.3 to compare the performance of h-BN and HfO<sub>2</sub> gated QFEG FETs. It was found from these two sections that h-BN induces reduced remote charged impurity scattering and negligible remote surface optical phonon scattering to the QFEG/dielectric system compared to high-k dielectrics, allowing for excellent preservation of QFEG’s transport properties. However, it was shown that the benefit of CVD h-BN over high-k dielectrics is highly dependent on the initial carrier mobility of the QFEG sample, where remote impurity scattering in low mobility QFEG (high impurity density) can mask the potential benefits of h-BN dielectrics. In this case, high-k dielectrics outperform h-BN due to dielectric screening of charge impurities. Alternatively, for
high carrier mobility QFEG, h-BN effectively preserves carrier mobilities \( > 3,000 \text{ cm}^2\text{/V-s} \) at room temperature and results in intrinsic cutoff frequency improvements of 2.4x over HfO\(_2\) gated QFEG FETs. As discussed in Section 4.4, step-edges associated with epitaxial graphene synthesis result in unique limitations to QFEG transport not observed with CVD and exfoliated graphene, where step-edges were found to induce additional impurity and surface optical phonon scattering to the system. Modeling performed by Matthew Hollander verifies that charged impurity scattering is the primary scattering mechanism in these films, contributing >90% to the total scattering rate.\(^{127}\) However, it was found that for QFEG devices having a low step-edge density (and thus a reduced impurity density), surface optical phonon scattering begins to contribute more significantly to the total scattering rate. In this regime \((n_{\text{imp}} < 5 \times 10^{11} \text{ cm}^{-2})\), h-BN can outperform HfO\(_2\) due to its high surface optical phonon energies. Conversely, HfO\(_2\) excelled at high impurity densities \((n_{\text{imp}} > 5 \times 10^{11} \text{ cm}^{-2})\) due to its ability to screen impurities with its high dielectric constant. Therefore, it was shown that the benefit of h-BN vs. HfO\(_2\) is highly dependent on the impurity density (contributed to primarily by QFEG step-edge density and dielectric integration) of the QFEG/dielectric system. With improvements in the growth of epitaxial graphene leading to reduction of step-edges, as well as reduction of impurity contamination from the h-BN transfer process, CVD h-BN may prove to be an excellent dielectric for QFEG and other types of graphene due to its low contributions to surface optical phonon scattering.

Future work for integration of h-BN with QFEG involves the re-evaluation of QFEG devices utilizing h-BN films grown on Cu with a Cu enclosure, as described in Section 3.2. The h-BN/QFEG integration work performed for this thesis was done prior to the research involving growth of h-BN with a Cu enclosure. It was found in Section 3.2 that use of a Cu enclosure resulted in improvements in the chemical, structural, and dielectric properties of h-BN films grown on Cu foil. Because of these improved properties, it would be expected that these films would introduced even further reduced impurity and surface optical phonon scattering to the h-
BN/QFEG system. Therefore, it is likely that the transport properties of the underlying QFEG would be further enhanced compared to the results shown in Chapter 4, which utilized h-BN films grown without a Cu enclosure. Additional future work may involve novel approaches to dielectric integration with QFEG utilizing multiple dielectric materials. As discussed in Section 4.4, at low intrinsic impurity densities h-BN can be a significantly superior dielectric material to high-k dielectrics (such as HfO₂) due to its low contribution of impurity and surface optical phonon scattering to the QFEG/dielectric system. However, high-k dielectrics are desirable for their scalability and improved capacitance (C), given by: \( C = \frac{\varepsilon_0 k A}{d} \) where \( \varepsilon_0 \) is the permittivity of free space, \( k \) is the dielectric constant, \( A \) is the contact area, and \( d \) is the dielectric thickness. The equivalent oxide thickness (EOT) shows how thick an SiO₂ dielectric would need to be to achieve the same capacitance as a high-k dielectric and is given by: \( EOT = t_{\text{high-k}} \left( \frac{k_{\text{SiO}_2}}{k_{\text{high-k}}} \right) \), where \( t_{\text{high-k}} \) is the thickness of the high-k dielectric and \( k_{\text{SiO}_2} \) (~4) and \( k_{\text{high-k}} \) (~17) are the dielectric constants of SiO₂ and the high-k dielectric, respectively. Therefore, a novel stacked gate dielectric using h-BN and HfO₂ (or another high-k dielectric) may result in optimal device performance and scalability utilizing the benefits of both dielectrics. A thin (monolayer or bi-layer) h-BN film could be transferred to QFEG, where the h-BN would introduce negligible surface optical phonon scattering and minimal impurity scattering to the h-BN/QFEG interface. A high-k dielectric such as HfO₂ could then be deposited via e-beam or ALD over the existing h-BN film. With this configuration, the net EOT for the stacked gate dielectric would be:

\[
EOT = \left[ t_{\text{high-k}} \left( \frac{k_{\text{SiO}_2}}{k_{\text{high-k}}} \right) + t_{\text{h-BN}} \left( \frac{k_{\text{SiO}_2}}{k_{\text{h-BN}}} \right) \right] / 2,
\]

where \( t_{\text{h-BN}} \) is the h-BN thickness and \( k_{\text{h-BN}} \) (~4) is the h-BN dielectric constant. Since the thickness of the high-k dielectric (several nanometers) would be significantly larger than the h-BN monolayer (or bi-layer), the EOT of the stacked dielectric would be only slightly reduced compared to the high-k dielectric alone, allowing for improved capacitance and scaling from the high-k dielectric while introducing...
reduced surface optical phonon scattering and impurity scattering to the dielectric/QFEG system from the h-BN interfacial layer.

7.3: Direct Growth Boron Nitride as a Substrate to CVD Graphene

Boron nitride was deposited via CVD directly on Si(111) and Al₂O₃(0001) substrates using a polyborazylene to BN conversion process, as described in Chapter 5. This direct growth process allows for the use of h-BN as a supporting substrate to CVD-grown graphene. Initial results show that by using a two-step growth process involving the low temperature (250°C and 400°C) deposition of a polyborazylene film and the subsequent ceramic conversion to BN through a 1000°C anneal, ultra-smooth h-BN films down to <130pm RMS roughness can be successfully deposited with a uniform thickness controllable down to a few nanometers. To the author’s knowledge, this surface roughness is the lowest reported roughness of non-exfoliated BN and represents a >25x reduction in RMS roughness over h-BN films grown at 1000°C without the polyborazylene to BN conversion. Control of the stoichiometry appears to be difficult during the polyborazylene to BN conversion, where boron-rich films were obtained at polyborazylene deposition temperatures of 250°C and 400°C, as measured with XPS. Additionally, surface pitting occurred for h-BN samples grown at 250°C on Si. Use of a pre-growth anneal prior to polyborazylene deposition at 250°C resulted in an absence of these surface pits on Si as well as an improved stoichiometry for growth on both Si and Al₂O₃; however the resulting h-BN films experienced a ~7.7x increase in RMS surface roughness from ~0.130nm up to ~1.0nm. Furthermore, films synthesized from an initial polyborazylene deposition were found with cross-sectional TEM to be nearly amorphous with only short-range order.
In Chapter 6, Raman spectroscopy was utilized to quantify changes in strain and Fermi velocity reduction (FVR) of transferred CVD graphene as a function of the underlying dielectric substrate. It was found that the BN films with a high surface roughness (grown at 1000°C, 250°C with a pre-growth anneal, and h-BN transferred from Cu) displayed significant tensile strains induced in the graphene and that transferred CVD graphene on bare SiO₂ and Al₂O₃ resulted in strong compressive strains and FVR (likely from high adhesion strengths). The amorphous BN films grown with an initial polyborazylene deposition of 400°C resulted in nearly strain-free graphene, due to its low surface roughness and low adhesion, as well as low FVR as a result of negligible Van der Waals interactions, due to its amorphous structure, with the overlying graphene. These results suggest that these ultra-smooth and nearly amorphous BN films may be excellent candidates for CVD graphene integration as a supporting dielectric. Indeed, when used as a supporting substrate, the films grown at a polyborazylene deposition temperature of 400°C showed the best potential for improved transport properties of transferred CVD graphene, resulting in a 52% and 151% increase in mobility compared to CVD graphene on a bare sapphire and SiO₂ substrates, respectively. The extracted impurity density of \(<3 \times 10^{11} \text{cm}^{-2}\) for graphene transferred to this sample suggests surface optical phonon scattering contributes significantly to the overall scattering rate, where h-BN excels compared to high-k dielectrics due to its high surface optical phonon modes. This suggests that even amorphous/turbostratic BN can benefit graphene electronics. Continued efforts to improve the B/N ratio while maintaining a low RMS roughness in these films are in progress. Additionally, more work is required to form an improved scattering model that takes into account the effects of surface roughness scattering.

Future work includes continued efforts to improve the B/N ratio while maintaining a low RMS roughness in these films. Polyborazylene deposition at additional temperatures (500°C, 600°C, 700°C, etc), as well as various post-growth anneal temperatures (1100°C, 1200°C, 1300°C, etc), may lead to an optimized growth condition for the polyborazylene-to-BN synthesis.
technique. Additionally, a detailed study of the temperature dependent transport properties of transferred CVD graphene on these films, as well as modeling of the scattering mechanisms and extraction of impurity densities and surface optical phonon scattering constants, would be significant in understanding the exact mechanisms that account for the observed electronic differences between various BN growth conditions. Fabrication of gated graphene Hall bars and FETs based on CVD graphene transferred to direct-growth BN substrates and utilizing transferred h-BN, direct-growth h-BN, and various high-k materials as gate dielectrics can lead to a comprehensive understanding of possible device configurations exploiting these materials for future applications in the micro-electronics industry. Another area of interest for future work is a detailed investigation of direct-growth on additional substrates using the two-step polyborazylene-to-BN conversion process. Though the author has synthesized BN films on additional substrates such as SiC, SiO$_2$, and QFEG; the results were not fully investigated and thus, were not presented in this thesis. Initial results suggest that growth on these substrates results in similar morphologies and structures to those grown on the Al$_2$O$_3$ and Si substrates presented in Chapter 5 and 6. Therefore, for applications requiring BN films on other substrates, it is likely possible to produce similar results using the previously described techniques, however future work is required to verify this. Finally, integration of other 2D materials, such as TMDCs, was not investigated in this thesis. As these materials become more and more understood and useful to the scientific and technical communities, a suitable dielectric material will be needed for device development. Boron nitride films synthesized via the two-step growth method described in this thesis may very well act as an ideal substrate for TMDC integration, leading to similar benefits as observed for graphene.
References


Appendix A

Boron Nitride Tube Furnace Schematics

Boron Nitride CVD Reactor Flow Diagram
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Equipment List Corresponding to BN CVD Reactor Flow Diagram
Appendix B

Pressure / Temperature Profiles for Direct Growth Processes

Direct Growth: 1000°C

Direct Growth: 400°C
Appendix C

Thermogravimetric Analysis (TGA) of Ammonia Borane (NH$_3$BH$_3$)
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