ATOMIC LAYER DEPOSITION OF H-BN(0001) ON TRANSITION METAL SUBSTRATES, AND IN SITU XPS STUDY OF CARBONATE REMOVAL FROM LITHIUM GARNET SURFACES

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The direct epitaxial growth of multilayer BN by atomic layer deposition is of critical significance for two-dimensional device applications. X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) demonstrate layer-by-layer BN epitaxy on two different substrates. One substrate was a monolayer of RuO$_2$(110) formed on a Ru(0001) substrate, the other was an atomically clean Ni(111) single crystal. Growth was accomplished atomic layer deposition (ALD) cycles of BCl$_3$/NH$_3$ at 600 K substrate temperature and subsequent annealing in ultrahigh vacuum (UHV). This yielded stoichiometric BN layers, and an average BN film thickness linearly proportional to the number of BCl$_3$/NH$_3$ cycles. The BN(0001)/RuO$_2$(110) interface had negligible charge transfer or band bending as indicated by XPS and LEED data indicate a 30° rotation between the coincident BN and oxide lattices. The atomic layer epitaxy of BN on an oxide surface suggests new routes to the direct growth and integration of graphene and BN with industrially important substrates, including Si(100). XPS and LEED indicated epitaxial deposition of h-BN(0001) on the Ni(111) single crystal by ALD, and subsequent epitaxially aligned graphene was deposited by chemical vapor deposition (CVD) of ethylene at 1000 K. Direct multilayer, in situ growth of h-BN on magnetic substrates such as Ni is important for spintronic device applications.

Solid-state electrolytes (SSEs) are of significant interest for their promise as lithium-ion conducting materials but are prone to degradation due to lithium carbonate formation on the surface upon exposure to atmosphere, adversely impacting Li ion conduction. In situ XPS monitored changes in the composition of the SSE Li garnet (Li$_{6.5}$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$, LLZTaO)
upon annealing in UHV and upon Ar\textsuperscript{+} ion sputtering. Trends in core level spectra demonstrate that binding energy (BE) calibration of the Li 1s at 56.4 eV, yields a more consistent interpretation of results than the more commonly used standard of the adventitious C 1s at 284.8 eV. Annealing one ambient-exposed sample to >1000 K in UHV effectively reduced surface carbonate and oxygen, leaving significant amounts of carbon in lower oxidation states. A second ambient-exposed sample was subjected to 3 keV Ar\textsuperscript{+} ion sputtering at 500 K in UHV, which eliminated all surface carbon, and reduced the O 1s intensity and BE. These methods present alternative approaches to lithium carbonate removal than heating or polishing in inert atmospheres and are compatible with fundamental surface science studies. In particular, the data show that sputtering at mildly elevated temperatures yields facile elimination of carbonate and other forms of surface carbon. This is in contrast to annealing in either UHV or in noble gas environments, which result in carbonate reduction, but with significant remnant coverages of other forms of carbon.
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By

Jessica C. Jones
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Thank you to my advisor Dr. Jeffry Kelber, for his mentorship over the years and invaluable insight. He not only taught me about the operations of the lab, but in how to laugh when the lab does not go the way you would like. I must also thank my committee for agreeing to read and review this document.

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I must thank my husband, Daniel, who has given me unconditional support throughout my time at UNT. He has tolerated me pulling many late nights and working weekends. He always takes care of me. Coming home from a long day to dinner cooked and an ear to listen, means so much. I can never thank him enough for the support and love he gives me every day.
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CHAPTER 1
INTRODUCTION

1.1 Motivation

The number of transistors on a chip has doubled every year since the 1960’s (Moore’s law), but this trend is reaching fundamental and practical limits. Currently most devices use complementary metal-oxide semiconductors (CMOS) technology. Downscaling of data storage has been enabled by advances in fabrication methods; the transition from linear to rotary actuation, the use of magneto-resistive heads, and then tunneling magneto-resistive heads. Magneto-resistive heads currently use atomically thin layers of MgO between CoFeB or Fe that obtain ~100% magnetoresistance ratio, but further reduction of the thickness of these layers will result in defects that affect the performance of such devices.

There are a variety of proposed ways to continue the down-scaling of technology, including integration of 2D materials such as graphene and/or hexagonal boron nitride (h-BN) with existing silicon based technology, or as novel beyond-CMOS electronic or spintronic devices. Spintronic devices are devices that combine the spin of the electron with the charge as a degree of freedom or use the spin degree of freedom alone for novel device applications. h-BN acts as a spin filter with or without graphene, making atomic layer control of its thickness and rigorous alignment important for integration into spintronic devices.

Graphene has been a topic of interest since few layer graphene was demonstrated for field effect devices, where charge carrier mobility much larger than Si was demonstrated using mechanically exfoliated layers from graphite. Since then there have been many reports of device fabrication using physical exfoliation and transfer of 2D materials (BN and/or graphene). These are not practical for the industrial manufacturing scale and introduce
contamination and defects into the device. Use of 2D materials for devices requires direct nucleation and growth of h-BN and graphene by industrially scalable methods. Spintronic device applications relying on spin filtration are critically dependent on the number of rigorously azimuthally alignment layers of h-BN and graphene on the substrate. h-BN is isoelectronic to graphene and has a close lattice match with both Ni(111) and graphene, making it a flat, low lattice strain substrate for direct graphene growth.

The ability to grow large area h-BN(0001) films epitaxially on oxidized transition metal substrates significantly increases the types of suitable substrates for h-BN and h-BN/graphene applications. The effect of an interfacial oxide layer—however thin—on BN/metal interactions, including interfacial orbital hybridization, would also be of significant interest due to the strong orbital hybridization demonstrated between h-BN and Ni or Ru. Oxygen intercalates at elevated temperatures between Ru(0001) and BN, which can modify or eliminate the strong interfacial orbital hybridization observed between a BN monolayer and clean Ru(0001) substrate. h-BN becomes catalytic to O₂ dissociation when supported by Ni or Au substrates, whereas it is inert to O₂ when freestanding, demonstrating the importance of understanding the substrate/h-BN effects.

Current battery technology must also continue to improve to yield faster, smaller, lighter, safer devices. Use of an inorganic solid-state electrolytes (SSEs) in an all-solid-state lithium battery (ASSLB) could satisfy these needs. Major issues must be addressed before the effective operation of ASSLB can become feasible. One of these issues is SSE reactivity with moisture and CO₂ to produce a lithium carbonate (Li₂CO₃) passivation barrier on the surface which inhibits mobility of Li⁺ ions. Carbonate removal reverses the degradation of ion mobility. Upon removal of carbonate, BN might serve as a suitable passivation layer,
depending on surface cleanliness. It has been theorized that passivation barriers such as h-BN could negate the interface impedance of Li\(^+\) ion conduction, increase the wetting of electrodes to the passivation barrier/Li garnet structure.\(^{30,31}\) It has also been shown that BN grown by CVD increases the stability of the Li garnet with respect to a Li metal electrode, therefore improving the lifetime of high energy density SSE.\(^{31}\) Therefore, Li Garnet surface cleaning is described in this dissertation.

Direct growth of h-BN on various substrates is vital for the above applications. Thus growth of h-BN on RuO\(_2\)/Ru and Ni(111) were pursued. Additionally, in situ cleaning of Li garnet substrates was investigated as a preparation for BN ALD. The work presented here demonstrates growth, by ALD, of h-BN(0001) on a monolayer of RuO\(_2\)(110) grown on Ru(0001); as well as h-BN(0001) grown epitaxially on Ni(111) substrate and subsequent graphene deposition. Atomic layer deposition (ALD) provided atomic layer control of the h-BN layers and azimuthal alignment of the resulting thin films. Epitaxial graphene growth was accomplished by chemical vapor deposition (CVD) on the h-BN/Ni substrate. Low energy electron diffraction (LEED) was used to determine the registry of the overlayers. This work also presents two ultra-high vacuum (UHV)-compatible methods of Li\(_2\)CO\(_3\) removal from an air exposed SSE; annealing in UHV, and sputtering at elevated temperatures, in order to prepare such surfaces for the deposition of BN passivation layers. The surface chemistry of the above was monitored by in situ X-ray photoelectron spectroscopy (XPS).

1.2 Hexagonal Boron Nitride

Hexagonal Boron Nitride (h-BN) is isoelectronic to graphene and is sp\(^2\) hybridized\(^{32}\) with a variety of useful properties for applications including microelectronics and spintronics. h-BN has a large bandgap of ~5.9 eV.\(^{33,34}\) Figure 1.1 shows the optimized geometry.\(^{34}\) h-BN and the
magnetic substrates Ni (111) and Co(0001) have a close in-plane lattice match making them good substrates for direct growth of h-BN.\textsuperscript{35,36} h-BN and graphene also have a very close lattice match (~1.7% mismatch)\textsuperscript{13,37} which provides a dielectric substrate for the growth of high quality graphene and integration of graphene into devices.\textsuperscript{38}

Figure 1.1: Optimized electronic geometry of h-BN, showing AB stacking. (Green spheres = B, Grey spheres = N). From reference 34.

Industrially scalable growth of h-BN is problematic because physical exfoliation is not a viable option for large scale manufacturing. CVD of h-BN has been accomplished using borazine decomposition, but is largely self-limiting to 1 monolayer (ML) or is amorphous after the first monolayer.\textsuperscript{17,18,39} Since the spin filtering or spin transport is predicted to rely on azimuthal alignment and number of layers of h-BN(0001), multilayer h-BN(0001) has significant advantages.\textsuperscript{8,10,40} Several techniques have been proposed for direct growth of multilayer h-BN(0001); molecular beam epitaxy (MBE), pulsed laser deposition, and atomic layer deposition (ALD).\textsuperscript{41–45} The precise number of monolayers is difficult to control with MBE, and MBE
results in island-like growth indicating heterogeneous nucleation.\textsuperscript{41,45} Pulsed laser deposition results in h-BN(0001) formation on HOPG substrates, but yields amorphous BN on oxidized substrates, and the resulting thickness can be difficult to control.\textsuperscript{46}

ALD was chosen for the work presented herein. ALD is a specific type of CVD where sequential self-limiting gas-solid reactions with the surface saturate at each step to produce conformal layers.\textsuperscript{47} There are several ALD methods that have been developed for the deposition of BN. The reaction between BCl\textsubscript{3}/NH\textsubscript{3} at elevated temperature was selected for the work presented here. This reaction sequence was first presented by Ferguson et. al.\textsuperscript{43} BCl\textsubscript{3}/NH\textsubscript{3} was chosen over BBBr\textsubscript{3}/NH\textsubscript{3} because most reports of BN by BBBr\textsubscript{3}/NH\textsubscript{3} resulted in amorphous, turbostratic, or wurtzite type growth.\textsuperscript{7,44,48,49}

Applications of BN grown by ALD in literature include; B\textsubscript{2}O\textsubscript{3} capped with BN for Si doping,\textsuperscript{50,51} BN grown using PEALD for capacitors,\textsuperscript{52} BN nanotubes for water purification,\textsuperscript{44} tuning the bandgap of graphene for field effect transistors,\textsuperscript{53} and spin-transfer torque magnetoresistive random-access memory,\textsuperscript{8} metal-insulator varisistor,\textsuperscript{54} spintronic applications (magnetic tunnel junction, nonlocal spin valves, spin injection and nonvolatile memory).\textsuperscript{4,8,10,40,42,55,56}

1.3 \hspace{1em} Graphene

Graphene, single layer graphite, has been attracting much attention in recent years, since its isolation and demonstration of its interesting and unique properties.\textsuperscript{11} Graphene is sp\textsuperscript{2} hybridized carbon, which forms a single atom thick, benzene-like matrix. Single/few layer graphene was initially isolated from graphite by physical exfoliation methods, (the “Scotch tape” method), where increasingly thin layers of sp\textsuperscript{2} carbon were obtained from each peel of the tape. Graphene is a zero-bandgap conductor, with high carrier mobility and long carrier lifetimes,
making it a very attractive option for integration into spintronic devices at temperatures for device operation. Theoretical work shows that these attributes should make graphene an ideal component of spintronic devices. The charge carriers in graphene have an effective mass of \( \sim 0.04 \, m_e (m_e = \text{electron rest mass}) \), and the mean free path of the electron in graphene can be up to 1 μm. Defects in the graphene layer such as contamination in the film, or ripples can decrease performance from these theoretical maxima. Therefore deposition on a flat surface with relatively low lattice strain (such as on h-BN) could help maximize the favorable properties of graphene.

Physical exfoliation methods are impractical on an industrial scale partly because the domain size of graphene from physical exfoliation methods are dependent upon the domain size of the graphene in the original graphite from which it was exfoliated. Physical exfoliation could also introduce defects and is time-consuming. Many other methods to obtain highly ordered pure graphene have emerged, such as MBE, CVD, thermal decomposition of SiC to form an order graphene shell around a SiC core, etc. Thermal decomposition of SiC is not practical for any substrates other than SiC, and MBE can be used to epitaxially deposit graphene on h-BN, however the actual thickness of the resulting films can be difficult to control.

CVD of graphene is carried out by exposing a heated substrate (\( \sim 1000 \, \text{K} \)) to a hydrocarbon such as methane or ethylene. The precursor decomposes on the surface at high temperatures and the thickness is dependent on the time and pressure of hydrocarbon used and the substrate on which it is being deposited. On some metal substrates, such as Cu, the graphene layer growth is largely self-limiting to one monolayer for most hydrocarbon species, whereas for other metals such as Ni the growth can be monolayer or multilayer. On h-BN ordered, multilayer graphene growth has been obtained using ethylene at 1000 K.
1.4 RuO$_2$(110)/Ru(0001) Surface

Transition metal substrates for direct growth of h-BN and graphene are of interest.\textsuperscript{18,42,61,64,65} Ruthenium has been proposed for integration of h-BN and graphene in existing electronic devices as well as a template for direct growth of 2D materials such as h-BN and graphene.\textsuperscript{20,66,67} Interactions between BN and transition metal substrates are of interest because they have been shown to change the properties of BN, for example BN behaves as a catalysis of O$_2$ when supported on Ni or Au, whereas freestanding BN is inert to O$_2$.\textsuperscript{21,22} BN grown on metal oxides have been reported in the literature, including BN ALD on crystalline ZrO$_2$ particles with diameter of $\sim$ 50 nm, which resulted in amorphous BN deposited uniformly on the particles.\textsuperscript{43}

Significant orbital hybridization between h-BN(0001) and Ru(0001) has been reported.\textsuperscript{15,65,68} In a study, one monolayer of h-BN(0001) was deposited on substrates with significant lattice mismatch [Ru(0001), Rh(111), Pt(111), and Ir(111)]; it was shown that Ru(0001) had the highest degree of orbital hybridization.\textsuperscript{65} This is consistent with reports of 2 distinct bonding environments in N 1s spectra for monolayer h-BN(0001) grown by CVD on Ru(0001).\textsuperscript{20,65,68} Evidence for orbital hybridization for h-BN grown by ALD has also been reported as a decreased band gap by STM.\textsuperscript{15} There are 13x13 unit cells h-BN for each 12x12 unit cells Ru, with h-BN having a lattice constant of $\sim$2.5 Å and Ru(0001) $\sim$2.7 Å.\textsuperscript{65,69,70} Thus, this gives areas of strong interaction between the h-BN(0001) and Ru(0001), (chemisorption) and areas of low interaction (physisorption).\textsuperscript{65} In a study on the stability of these h-BN(0001)/Ru(0001) interfaces the B 1s and N 1s initially exhibited the two distinct bonding environments, but upon heated exposure to O$_2$, oxygen intercalated between the h-BN(0001) and Ru(0001), disrupting this orbital hybridization and shifting the spectra to lower binding energy.\textsuperscript{20}
Thus, nucleation of h-BN directly on a Ru(0001) surface covered by a single monolayer of RuO₂ is interesting to demonstrate what effect this interfacial layer has on the interactions at the surface.

For this work Ru(0001) was deposited on Al₂O₃ single crystals by magnetron sputter deposition (ex situ). The film was thick enough that Al signal could not be seen through the Ru by XPS, estimated <200 nm. Atomic force microscopy ex situ confirmed that the Ru(0001) film was smooth (<1 nm roughness). The sample was annealed for several hours 1000 K in O₂ to remove carbon from the surface. These anneals in O₂ oxidized the surface of the thick Ru(0001) film, and after annealing in UHV a ~1 monolayer thick film of RuO₂(110) had ordered on the surface rotated approximately 30° from the metallic surface. This allowed what effect that a very thin, well ordered layer of RuO₂ between a thick Ru(0001) and h-BN(0001) to be assessed.

1.5 Ni(111) Surface

Nickel metal is a 3-fold face centered cubic (111) surface with a lattice constant of 2.49 Å. The close lattice match and the dominance of minority spin states at the Fermi level, and the shared K point of Ni(111), h-BN and graphene make Ni(111) a good candidate for the deposition of h-BN or graphene for spintronic devices.

In the work presented here a Ni(111) single crystal was obtained from commercial vendors. The sample was determined to be clean when XPS indicated minimal contamination and 3-fold LEED pattern was observed. This single crystal was cleaned in situ through annealing in O₂, Ar⁺ ion sputtering, and UHV annealing.

1.6 Predictions of Graphene/h-BN/Ni(111) Spin Tunneling

Magnetic tunnel junctions (MTJ) are structures formed by an insulator sandwiched between two ferromagnetic materials. Ferromagnets’ conduction bands are populated with
minority spin carriers, thus they exhibit high spin polarized tunneling.\textsuperscript{4,72} These structures control that amount of current flowing through them, where a large amount of current is the “ON” state and a small amount of current is the “OFF” state. Current MTJs use thin MgO as the insulating barrier, but further reduction in the thickness will introduce defects, so another material/system must be found.\textsuperscript{3} Spin polarization depends on the ratio of spin up ($n_{\uparrow}$) to total electrons ($n_{\uparrow} + n_{\downarrow}$) when an external field ($a$) is applied to a structure:\textsuperscript{72}

$$a = \frac{n_{\uparrow}}{n_{\uparrow} + n_{\downarrow}}$$ \hspace{1cm} \text{EQ 1.1}

The spin tunneling through media depends on the magnetoresistance ratio and the resistance-area (RA) products. The tunneling magnetoresistance (TMR) is defined as:

$$\text{TMR \%} = \frac{(C_{P} - C_{AP})}{C_{AP}} \times 100$$ \hspace{1cm} \text{EQ 1.2}

where $C_{AP}$ and $C_{A}$ are the conductances with the two electrodes in the antiparallel and parallel states of magnetization.\textsuperscript{4,73} High magnetoresistance values are desired to have a large ON/OFF ratio. This is shown in Figure 1.2.

![Figure 1.2: Schematic of a magnetic tunnel junction showing an insulator sandwiched between two ferromagnetic electrodes, with high transmission when the magnetization of the electrode is parallel, and low transmission when it is antiparallel.](image)

TMR is not the only property that needs to be considered in device applications, the resistive area (RA) must also be suitable to the application.\textsuperscript{74} Despite the achievability of higher
TMR values, if the RA is not sufficiently low, the device is not useful. RA is the product of resistance of the magnetic head, and the area.

Graphene sandwiched between Ni electrodes has a predicted TMR of ~100%. When h-BN(0001) is inserted between the Ni(111) and graphene layers the RA can be tuned arbitrarily without loss of TMR. Some of MgO’s success as an insulator for MTJ has been attributed to its crystallinity. This demonstrates the need for atomically flat, precise, and thin insulating barriers for advanced device applications. ALD of h-BN(0001) provides atomic layer control of an insulating barrier. Ni(111) is a ferromagnetic substrate, with a good lattice match with h-BN, graphene’s lattice constant is close to h-BN, which provides a theoretically flat, crystalline, low lattice strain system. Figure 1.3 (from ref 4) shows that ~2 ML h-BN on a Ni(111) FM will optimize the TMR and in conjunction with graphene give a tunable RA.

Figure 1.3: Magnetoresistance and spin polarization prediction from Karpan et al. showing atomic level control of atomically thin BN films for optimization of device performance. From reference 4.
Karpan et al. predicted that the use of h-BN in magnetic tunnel junctions in conjunction with Ni(111) and Co(0001) in conjunction with graphene would create “ideal” spin injectors.\textsuperscript{4} Their predictions show that the spin polarization can be enhanced by 2-5 monolayer h-BN between Ni and graphene [Fig. 1.3].

Figure 1.4: From reference 8, showing the tunneling current from Co through 6 (d) and 8 (e) ML h-BN and the resulting TMR (f). $I_{↑↑}$ is the current from the majority channel and $I_{↓↓}$ is from the minority channel for the parallel magnetization. $I_{↑↓}$ is the transmission current for the antiparallel magnetization.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1_4.png}
\caption{From reference 8, showing the tunneling current from Co through 6 (d) and 8 (e) ML h-BN and the resulting TMR (f). $I_{↑↑}$ is the current from the majority channel and $I_{↓↓}$ is from the minority channel for the parallel magnetization. $I_{↑↓}$ is the transmission current for the antiparallel magnetization.}
\end{figure}
However theoretical predictions from Faleev et. al. showed that h-BN can act as a minority spin filter due to Brillouin Zone filtering, without a graphene layer to act as the spin filter.\textsuperscript{8} Figure 1.4 shows that a small change in bias voltage is predicted to yield a significant increase in the current due to minority spin carriers in the parallel direction (as opposed to majority spin carriers in the parallel direction or total transmission in the antiparallel direction). The predicted TMR at room temperature is \~250\% at low bias voltages, making this appealing for spintronic devices.\textsuperscript{8}

Experimentally a single layer of h-BN and single layer/bilayer graphene have been physically transferred, which showed spin filtration through the BN layer into the graphene.\textsuperscript{56,77} It has also been experimentally shown that multilayer h-BN has is superior to monolayer h-BN for spin filtering and injection applications into graphene.\textsuperscript{55} However in previous experiments on spin transport through BN, it was physically exfoliated and transferred, which creates defects in the transferred films. This is why the TMR measured at room temperature for exfoliated and transferred h-BN flakes on to Co electrodes was \~0.3\%-0.5\%, much less than the theoretically predicted \~250\% for the Co/h-BN/Co system.\textsuperscript{8,77} These results demonstrate that physical transfer methods are not scalable to industrial scale or for high quality, epitaxially aligned films. Also, these results demonstrate that atomic layer control of multilayer h-BN is important because multilayers are superior to monolayers for spin filtering applications.

1.7 Li Garnet

Current lithium ion batteries use liquid lithium electrolytes. These devices have problems with lifetime and safety because of the reactivity of the liquid electrolyte.\textsuperscript{23} One alternative to this is the use of inorganic solid-state electrolytes (SSEs) in an all-solid-state lithium battery (ASSLB).\textsuperscript{23,24}
ASSLBs, however, have a high reactivity with moisture and CO₂ which results in the spontaneous formation of a thick layer of lithium carbonate (Li₂CO₃) upon exposure to atmosphere.⁷⁸ This lithium carbonate layer inhibits mobility of Li⁺ ions.²⁵–²⁹ Removal of this layer reverses the degradation of ion mobility²⁷–²⁹ and removal of the Li₂CO₃ surface layer has been reported by polishing in inert atmosphere,²⁸ annealing in inert atmospheres²⁸,²⁹ and sputtering at room temperature⁷⁹ as well as inhibited by treating the garnet with carbon.⁷⁸ However, to prevent degradation of the films, a passivation barrier must be put in the place of the removed Li₂CO₃ layer in order to keep the carbonate from reforming. Many of the methods for Li₂CO₃ removal, such as mechanical polishing and annealing in inert atmosphere, are not conducted in vacuum and could not have a subsequent passivation barrier deposited on them without some reformation of the Li₂CO₃ barrier, due to ambient exposure.

The methods presented here were conducted in UHV, with the ability to deposit subsequent passivation barriers in this environment without intermediate ambient exposure. Cubic garnet-type solid-state electrolyte (SSE) with nominal composition LLZTaO (Li₆.₅La₃Zr₁.₅Ta₀.₅O₁₂) was prepared by solid-state synthesis by a collaborator at Wayne State University (Prof. Leela Arava and students). This sample was introduced into the UHV multi chamber deposition and analysis chamber and was cleaned and analyzed in situ. This removal of the Li carbonate layer will allow for the deposition of subsequent passivation barriers such as BN, because it has been shown that BN grown by CVD increases the stability of the Li garnet with respect to a Li metal electrode, therefore improving the lifetime of high energy density SSE.³¹

1.8 Conclusions

In considering the efforts for the advancement of existing technology involving BN and
graphene-based devices, the scalability of such efforts must be considered. Physical transfer of BN and graphene flakes are not feasible methods for industrial applications. Similarly, mechanical polishing of Li garnet materials to remove the layer of Li$_2$CO$_3$ that spontaneously forms upon exposure to atmosphere is not compatible with many integration efforts unless subsequent ambient exposure is entirely avoided.

Multilayer h-BN can be grown on technologically promising substrates such as RuO$_2$, and Ni(111) by ALD. The alignment of the atoms is predicted to have significant impact on the electrical properties of resulting devices, which is why epitaxial alignment of films with the substrates is important. Many devices are processed at high temperatures, which is why thermal stability and quality after high temperature processing is considered. High quality graphene deposition in azimuthal registry with the substrate is also of significant concern for many applications.

LLTaZO thermal stability is of interest if it will be integrated into future chips, which as stated before can be processed at high temperatures. Removal of the Li$_2$CO$_3$ passivation barrier that spontaneously forms upon exposure to atmospheric conditions can reverse the degradation in Li ion conduction that these films experience when covered with lithium carbonate.

A fundamental understanding of the deposition processes of BN and graphene and the removal of spontaneously formed passivation barriers from ASSLB to allow deposition of more favorable passivation barriers, is important for the advancement of the semiconductor industry to advanced-CMOS devices, and beyond CMOS spintronic devices.

1.9 Chapter References


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CHAPTER 2

EXPERIMENTAL METHODS

2.1 Surface Science System for Film Growth, Deposition, and Characterization

A major component of the research presented deals with the deposition of hexagonal boron nitride (h-BN) on industrially important substrates, subsequent deposition of graphene on h-BN. Cleaning of solid-state electrolyte materials is also addressed. In order to accomplish these endeavors a key feature is the ability to deposit and characterize materials in situ, without ambient exposure. Conditions must be controlled from room temperature to > 1000 K, and from ambient conditions to UHV. Figure 2.1 is a schematic of the system that was used for this work.

![Schematic of UHV/ALD deposition and analysis chamber.]

Figure 2.1: Schematic of UHV/ALD deposition and analysis chamber. Due to the corrosive nature of BCl₃ the ALD chamber is equipped with a butterfly valve to protect the turbo pump from corrosion, and a dedicated mechanical pump is used corrosive gas exhaust to ~10⁻³ Torr before the chamber is opened to the turbo pump.

This multi-chamber system has 3 chambers separated by mechanically operated gate valves; one for atomic layer deposition (ALD), for molecular beam epitaxy (MBE) and for UHV analysis including x-ray photoelectron spectroscopy (XPS) and low energy electron diffraction.
Transfer between the chambers is accomplished by a magnetically coupled feedthrough arm.

The ALD growth chamber is also used for sample introduction. The ALD chamber is equipped with multiple leak valves for gas and liquid precursor introduction into the chamber. This chamber is pumped by a turbomolecular (turbo) pump backed by an oil filled rotary vane mechanical pump. The turbo pump can be closed off from the chamber with a manually operated butterfly. This allows a different rotary vane roughing pump filled with corrosion-resistant oil to create a flow-through for corrosive gases, such as BCl₃, without damaging the turbo pump. This allows for pressures up to 1 Torr to be used during deposition. This chamber is also equipped with a resistive ceramic heater capable of heating to 1000 K in corrosive environments, and temperatures are monitored by a K type thermocouple mounted near the sample. The pressures in this chamber are monitored by a nude ion gauge and a Baratron millitorr gauge. The base pressure of the ALD chamber is \(~1*10^{-7}\) Torr, but deposition pressures are 200-600 mTorr. This combination of gauges allows pressures to be monitored in both high vacuum and rough vacuum regimes.

The UHV analysis chamber consists of a 100 mm mean radius hemispherical analyzer with a multichannel plate detector, a dual anode (Al and Mg) x-ray source, \(\text{Ar}^+\) ion sputter gun, and a reverse view LEED system. The stage in UHV is capable of temperatures up to \(~1470\) K, and of rotation and linear motion in the x, y and z direction. This allows for the stage to be aligned and rotated for use of all the instruments in this chamber. The base pressure of this chamber is \(~1*10^{-10}\) Torr.

Sample stages in all chambers were calibrated using a K type thermocouple mounted directly to the surface of a sample, while heating up to 1000 K and referencing to the K type
thermocouple mounted near the sample. All temperatures reported are corrected for the
temperature of the surface of the sample based on these calibrations. Pressures in all chambers
were monitored using nude ion gauges calibrated for N₂ without further correction.

2.2 Characterization Methods

2.2.1 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a powerful technique for the characterization
of thin films, chemical bonding environments, and elemental composition of the top ~10-100 Å
of a sample.¹ XPS studies reported here used non-monochromated x-rays produced by a dual
anode x-ray source. Data presented herein were gathered using the AlKα source operated at 15
keV and at 300 W. This illuminated the surface with 1486.6 eV photons. Excitation of surfaces
with soft x-rays, such as the ones produced by Al or Mg anodes causes the emission of
photoelectrons from core electron orbitals. This effect is illustrated in Figure 2.2, showing that
the X-rays penetrate core orbitals of atoms and eject electrons from those orbitals. The emission
of a photoelectron results in a hole as shown in Figure 2.2. A decay of a less tightly bound
electron to fill the core hole can result in the ejection of an additional electron, as also shown in
Fig. 2.2. These are called Auger electrons which are also detected during XPS scans. While
Auger electron spectroscopy is often used for assays of surface composition and cleanliness, the
work reported here used XPS, due to the greater sensitivity of this method to surface chemical
bonding environments.¹

Electrons from the core orbitals of each element have characteristic binding energies.¹,²
From these characteristic binding energies a specific element can be identified based on the
presence of peaks a specific binding energies. Shifts in these characteristic binding energies can
be indicative of the environment an element is in, such as oxidation state and bonding.¹,²
Figure 2.2: Photoemission: X-Ray penetrates the core orbitals of an atom and excites an electron out of the atom, leaving a hole. Auger: An electron from a less tightly bound orbital falls into the hole, and another electron is emitted taking the excess energy. The binding energy of electrons increases with lower orbitals.
The binding energy (BE) of ejected electrons can be calculated using:

\[ \text{BE} = h\nu - KE - \Phi \quad \text{EQ 2.1} \]

where the original binding energy of an electron from a core orbital can be calculated using the energy of the incoming photon \((h\nu)\), 1486.6 eV from Al K\(\alpha\), minus the kinetic energy \((KE)\) that the electron came into the detector with, minus the work function of the spectrometer \((\Phi)\). The work function of the spectrometer is needed as the sample transition is from the vacuum to the spectrometer detector.\(^1\) Despite being grounded this emission of electrons from the surface causes a net buildup of charge, especially on insulting substrates, which must be accounted for by charge referencing the resulting spectra. This is accomplished by choosing a reference peak of known oxidation state or from the bulk of the sample and fixing it to a specific binding energy based on literature/known binding energy of that peak. All other peaks in the spectra are then shifted by the same amount to negate the surface charging effects.

The intensity of peaks relative to each other is representative of the concentration of their corresponding elements. Due to this, XPS is useful for determination of the thickness of overlayers using the ratio of peaks characteristic to the substrate and the overlayer. This is accomplished using the following equations where O is the overlayer and S is the substrate:\(^1\)

\[ I_O = A_S F_O (1 - e^{-t/\lambda_{O,O} \cos\Theta}) \quad \text{EQ 2.2} \]
\[ I_S = A_S F_S (e^{-t/\lambda_{S,O} \cos\Theta}) \quad \text{EQ 2.3} \]

where \(I_S\) and \(I_O\) are the intensities of the overlayer and substrate respectively. \(A_S F_S\) and \(A_S F_O\) are the atomic sensitivity factors of the substrate and overlayer respectively. \(t\) is the thickness of the overlayer in Å. \(\lambda_{O,O}\) and \(\lambda_{S,O}\) are the inelastic mean free paths (IMFP) of the overlayer through the overlayer and of the substrate through the overlayer. \(\Theta\) is the angle between the analyzer slit and the sample normal. IMFP values were calculated using the TPP-2M equation.\(^3\)
The thickness of the overlayer can be found by plotting EQ 2.2 and 2.3 using the experimentally derived values for $I_O$ and $I_S$ and where the two lines intersect is $t$, the thickness of the overlayer.

XPS can be used to determine the relative atomic concentrations in a film. This method can be used to determine the composition of the top $\sim 100$ Å. This determines the level of contaminants present as well as allows elemental ratios to be determined:

$n = I/\text{ASF}$ (where $\text{ASF} = F\sigma\Theta AT\lambda y$)

EQ 2.4

where $n$ is the number of atoms per cm$^2$ on the surface, $I$ is the intensity in counts per second (CPS) from the detector, and ASF is the atomic sensitivity factor for a given element for the given system. The ASF depends on $F$ (flux of photons in photon/cm$^2$/sec), $\sigma$ (photoelectric cross-section in cm$^2$ for the specific atomic orbital), $\Theta$ (angular efficiency factor for the instrument and the electron), $y$ (efficiency of the photoelectric process of the specific instrument), $\lambda$ (IMGS of the electrons in the sample), $A$ (area of the sample from which photoelectrons are being emitted/detected from), $T$ (detection efficiency for the specific instrument).\textsuperscript{4,5}

Using EQ 2.4 a relation can be derived to determine the atomic percentage of the elements that make up the top $\sim 100$ Å of the surface, shown in EQ 2.5. Atomic percentage ($A_\%$) is calculated using the following equation, where it is the intensity ($I_v$) of a specific element divided by the ASF ($\text{ASF}_v$) for that element, divided by the sum of all of the intensities ($\Sigma I_i$) for all the elements present in the sampling depth of the XPS divided by their respective ASF values ($\text{ASF}_i$):

$$A_\% = \frac{I_v/\text{ASF}_v}{\Sigma(I_i/\text{ASF}_i)}$$

EQ 2.5

2.2.2 Low Energy Electron Diffraction

LEED is a surface sensitive technique used to study the top few layers of a surface. It can be used to determine the crystallinity of surface. This technique is particularly useful for 2D
thin films to determine the alignment, orientation and relative spacing of the deposited crystalline films. The intensity of the spots as well as the pattern generated is quantitatively useful for the crystallinity of the film. A schematic of a typical LEED setup is shown in Figure 2.3.

![Figure 2.3: Schematic of how typical LEED equipment is set up.](image)

An electron gun using a LaB$_6$ filament produces a collimated beam of electrons, typically at energies from 60 – 300 eV. This electron gun is held at a negative potential to the substrate that is being investigated (which is grounded). This accelerates electrons away from the gun, toward the surface. These electrons are focused using a series of electrodes that act as electron lenses. These low energy electrons interact strongly with the first few layers of the surface and are backscattered. Detectors contain 3-4 metal grids and the fluorescent screen. The grids filter out the electrons that did not interact significantly with the surface. The screen is held at a positive potential to attract and accelerate electrons. As electrons hit the screen, they form bright spots which allow for the visualization (and capture via photography) of the diffraction pattern of the electrons from a crystalline surface.

Electrons in this case are treated as waves due to De Broglie’s principle. Electrons are repelled by regions of high electron density (the electron clouds around atoms). The wavelength of a 60 eV electron can be calculated using De Broglie’s equation, EQ 2.6:
\[ \lambda = \frac{h}{mv} \quad \text{EQ 2.6} \]

\[ KE = \frac{1}{2}mv^2 \text{ thus } v = (2KE/m)^{1/2} \quad \text{EQ 2.7} \]

\[ \lambda = \frac{h}{mv} = \frac{h}{(2mKE)^{1/2}} \quad \text{EQ 2.8} \]

\[ \lambda = 6.63 \times 10^{-34} \text{ Js} / (2 \times (9.11 \times 10^{-31} \text{ kg}) \times (9.61 \times 10^{-18} \text{ J}))^{1/2} = 1.58 \text{ Å} \quad \text{EQ 2.9} \]

1.58 Å is on the scale of interatomic distance. Figure 2.4 shows a schematic of these electrons impinging on the surface and creating constructive interference.

\[ \lambda \]

Constructive Interference

\[ a = dsin\Theta \]

\[ d = n\lambda \quad \text{EQ 2.10} \]

\[ n\lambda = a \times sin\Theta \quad \text{EQ 2.11} \]

This shows that the backscattering of these electrons is partially governed by Bragg's law, which can be expressed as:

To obtain constructive interference the path difference (d) of the backscattered electrons must be an integer number (n) of the wavelength (\(\lambda\)) of the scattered electron. The wavelength of the backscattered electron is a function of the interatomic distance (a) and the angle at which it is being scattered (\(\Theta\)).
LEED can determine the size and rotational alignment of adsorbates with respect to underlying substrate or deposited thin films. Low energy electrons can only penetrate 10-50 Å into a surface, making this an extremely surface sensitive technique. A typical LEED pattern of h-BN on Ni(111) at 60 eV is shown in Figure 2.5.

![LEED pattern](image)

**Figure 2.5: Typical LEED pattern, h-BN on Ni(111) at 60 eV.**

2.2.3 Atomic Force Microscopy

Thick Ru(0001) films were deposited on Al₂O₃(0001) single crystal substrates using magnetron sputter deposition. The surface roughness was characterized by atomic force microscopy (AFM). AFM uses a piezoelectric motor to move a SiN tip on a cantilever across the surface of a sample. As the tips moves across the surface, changes in the Z-height are detected by a laser reflecting into a photodiode. This translates into an image that gives information about the smoothness of the ex situ deposited films. Figure 2.6 shows the AFM image of the Ru(0001) sample that was used in this study.

The image is the standard deviation of the changes in the surface height. Smooth surfaces are important for further deposition on the sample, the maximum resolution of the
instrument is 10 nm RMS. AFM measurements were performed ex situ in ambient conditions before samples were placed in the UHV system described above.

Figure 2.6: AFM of Ru(0001) deposited by magnetron sputter deposition. RMS 0.8 ±0.2 nm.

2.3 Deposition Methods

2.3.1 Atomic Layer Deposition

Atomic layer deposition (ALD) allows conformal, monolayer control of thickness layers of deposited films. ALD refers to a specific type of chemical vapor deposition (CVD), where ALD is sequential self-limiting, solid-gas reactions used to accomplish conformal atomic-layer thickness control. The self-limiting reactions are saturation coverages of one precursor, followed by pump down of the chamber. Another precursor is introduced for a saturation coverage, followed by another pump down. This reaction forms a thin film of the solid products of the chemical reaction (for example BN). This produces thin conformal films, epitaxially on
surfaces that are capable of long-range order and large domain sizes. This method is industrially scalable and yields monolayer control over the thickness of the deposited films. In this work the precursors used are BCl₃ and NH₃, shown schematically on a Ni substrate in Figure 2.7.

Figure 2.7: Reaction scheme for ALD of BN. Substrate is heated to 600 K. A) BCl₃ adsorption b) pump down of BCl₃ c) Adsorption/reactions of NH₃ d) pump down of NH₃.

This ALD process was demonstrated by Ferguson et al.,⁷ and optimized on Co(0001).⁸ This reaction was adapted for Ni(111) and RuO₂ substrates, showing it can be adapted for both metallic and oxidized substrates. Highly ordered films with atomic layer control were achieved. Excess contamination was easily removed by annealing in UHV.

2.3.2 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a gas-solid reaction where the thickness is not inherently self-limiting. The thickness of films deposited by CVD is dependent on the time and pressure of the precursor(s) and the temperature of the substrate, among other factors such as
chemical interactions.\(^9\) Graphene can be grown by CVD using a hydrocarbon precursors such as methane or ethylene at high temperatures (~1000 K). This causes the precursor to decompose on the surface to provide a source of C where the thickness is dependent on the time and pressure of hydrocarbon used and its interactions with the substrate.\(^9\) On certain substrates the thickness of a graphene layer can be self-limiting, such as Cu where it is limited to 1 monolayer.\(^10\) On other substrates the same process can result in multilayer graphene.\(^9\) In the case of CVD of graphene on BN multilayer growth can be accomplished using ethylene at 1000 K.\(^11\) A schematic of graphene grown by CVD is presented in Figure 2.8.

**Figure 2.8:** Schematic of a substrate being exposed to hydrocarbons, those hydrocarbons decomposing on the surface to give H\(_2\) gas and the carbon left of the surface forming the honeycomb matrix of graphene.

Electron mobilities of CVD grown graphene were not initially as high as those reported for transferred graphene, however when graphene was grown on h-BN it had electron mobilities comparable to physically exfoliated graphene, which was attributed to favorable lattice match of h-BN and graphene.\(^9\) Physical exfoliation of graphene is time-consuming and not scalable to an industrial scale. Whereas it has been demonstrated that CVD can produce high quality, graphene with properties comparable if not better than physically transferred graphene.

### 2.3.3 Magnetron-Sputter Deposition

In magnetron sputter deposition a plasma creates energetic ions such as Ar\(^+\) using an
alternating magnetic field within the chamber. Other gases can be used other than Ar\(^+\) but other gases will react with the target or substrate material if possible. These Ar\(^+\) ions are accelerated toward a target of the material to be deposited by holding the target at a negative potential. Behind the target there is a strong permanent or electromagnet that keeps electrons near the magnet, creating a higher plasma density near the target. This dense plasma can either ionize more Ar\(^+\) atoms or sputter material from the target. To prevent charge build up the polarity of the target is reversed at a high enough frequency so that the ions are not repelled, usually in the MHz range. This is “radio frequency” or RF.

Most magnetron sputtered films are polycrystalline, but smooth, epitaxial deposition of metallic films by magnetron sputter deposition broadens the scope of useful applications. The quality of the films deposited has to do with the pressure of the Ar\(^+\) gas, the distance from the sample to the target, the temperature of the substrate, power of the plasma, etc. This process is shown in Figure 2.9

![Figure 2.9: Magnetron sputter deposition](image)

Sputter deposition of these materials was not accomplished in the UHV chamber described above, but was done in a dedicated deposition system. This chamber was pumped by a
The film thickness was estimated to be > 200 nm, based on the deposition rate of previous samples, and the absence of detectable Al in the XPS spectra of the film. Thick films were annealed in vacuum before being characterized by AFM \textit{ex situ} before introduction into the UHV system described in Section 2.1.

2.4 Cleaning Methods

2.4.1 Ar$^+$ Ion Sputtering

When samples are introduced into the UHV chamber there is some amount of atmospheric contamination on the surface, usually in the form or carbon or oxygen. Depending on the reactivity of the surface this layer of contamination can be very difficult to remove in order to get an acceptably clean surface. Ar$^+$ sputtering is one method to remove this top layer of contamination. The chamber is backfilled with Ar (g) before a filament is energized. This filament emits electrons that are accelerated into an anode. Between the filament and anode these electrons strike Ar atoms, removing some of the valence electrons to create Ar$^+$. Since the anode and filament are biased positively the ions created by these collisions are accelerated out of the gun, and focused by a series of optics. A schematic of this process is shown in Figure 2.10.

The amount of the surface that is removed is dependent on the pressure of the Ar gas (how many Ar$^+$ ions are formed), emission current, and beam voltage. Sputtering was conducted at the theoretical optimum operating parameters for the sputter gun installed, 25 mA emission current and 5 keV beam voltage unless otherwise specified. The damage done to the substrate by sputtering was recovered by heating in UHV, and the crystallinity of the surface was confirmed by LEED before samples were used.
2.5 Chapter References


3.1 Introduction

The direct growth of multilayer h-BN(0001) films without exfoliation or physical transfer is critical for industrial scale development of 2D-based devices. This includes a range of beyond-CMOS electronic or spintronic applications, both as a spin filter\(^1\textsuperscript{-4}\) and as substrate for graphene epitaxy.\(^5\textsuperscript{,}\textsuperscript{6}\) Atomic layer deposition (ALD), with precise control of epitaxial BN film thickness, has obvious advantages for some of these applications.\(^4\textsuperscript{,}\textsuperscript{5}\) To date, however, most investigations of single or few-layer BN growth, whether by ALD, chemical vapor deposition, or magnetron sputter deposition have involved BN growth on clean transition metal surfaces,\(^5\textsuperscript{--}\textsuperscript{10}\) although polycrystalline BN growth on Si(100) has recently been reported.\(^11\) The ability to grow large area h-BN(0001) films epitaxially on oxide substrates would significantly increase the types of suitable substrates for direct growth of h-BN and h-BN/graphene heterostructures for device applications. Of additional interest are the possible effects of an interfacial oxide layer—however thin—on BN/metal interactions, including interfacial orbital hybridization.\(^8\textsuperscript{,}\textsuperscript{12}\textsuperscript{--}\textsuperscript{14}\) Yang et. al.\(^15\) showed that oxygen intercalation at elevated temperatures between Ru(0001) and BN can modify or eliminate the strong interfacial orbital hybridization observed between a BN monolayer and clean Ru(0001) substrate, although effects on the relative orientations of the BN and Ru lattices were not discussed. The results reported here demonstrate for the first time the direct epitaxial growth of h-BN(0001) on a RuO\(_2\)(110) substrate, using an ALD process. The results further demonstrate that a monolayer of RuO\(_2\) disrupts the strong orbital hybridization...
that occurs at the BN/Ru metal interface.

The ALD process employed here involves alternate BCl$_3$ and NH$_3$ exposures at 600 K, similar to that employed for multilayer h-BN(0001) growth on Co(0001). The chemistry has been shown capable of producing polycrystalline films on non-crystalline oxides. The relatively mild temperatures involved and the precise control over film thickness inherent in the ALD process make this method attractive for device fabrication. Since multilayers of BN, even if physically transferred, are superior to monolayers for spin injection, the advantages of ALD over the often-used but monolayer self-limiting borazine pyrolysis method are evident. ALD also has inherent advantages over MBE or sputter magnetron deposition, particularly for proposed spin filter applications, where precise, atomic level control of film thickness—and azimuthal alignment between layers is important for device performance.

In this paper, x-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) data are presented demonstrating layer-by-layer epitaxy of h-BN(0001) on a monolayer of RuO$_2$(110) formed on Ru(0001). The data indicate that the BN lattice is aligned with that of the Ru(0001) substrate, with an absence of the strong BN 2p/Ru(3d) orbital hybridization observed at the BN interface with metallic Ru(0001). XPS and LEED also indicate that the ALD process itself leaves intact the RuO$_2$(110) monolayer, demonstrating that this ALD process is suitable for preserving the surface structures and thicknesses of ultrathin oxide films during deposition.

3.2 Experimental

The Ru(0001) film used was deposited on sapphire (Al$_2$O$_3$(0001)) by magnetron sputter deposition at 700 K in an Ar plasma. Film roughness was evaluated \textit{ex situ} by AFM after magnetron sputter deposition, and after further annealing (to 1000 K) in UHV. The final rms
roughness of the film used was $< 1$ nm.

The system used for BN ALD growth and characterization has been described previously\textsuperscript{5}. Briefly, the system included a chamber for ALD (base pressure $3 \times 10^{-6}$ Torr) and a chamber for XPS and LEED analysis in UHV (base pressure $3 \times 10^{-10}$ Torr). Pressures in the ALD chamber were recorded by a combination of nude ion and baratron gauges, while pressures in UHV were recorded with a nude ion gauge calibrated for N$_2$. Sample temperatures were varied by resistive heating and measured by a K type thermocouple mounted on the sample stage near the sample. Samples were transported between the chambers without exposure to ambient conditions by use of a magnetically coupled feedthrough.

XPS data were acquired with a 100 mm mean radius hemispherical analyzer operating at a constant pass energy mode (44 eV), with non-monochromatic Al K$_\alpha$ x-ray source operated at 15 keV, 300 W. XPS spectra were analyzed with commercially available software. Relative atomic concentrations, and thicknesses were calculated by standard methods\textsuperscript{20} using inelastic mean free paths through BN; 30.42 Å and 27.15 Å for Ru 3d and O 1s photoelectrons, respectively\textsuperscript{21}. The XPS-derived thickness of a BN monolayer was taken to be 3.3 Å, in agreement with previous STM studies of multilayer BN on Ru(0001)\textsuperscript{22} and of multilayer graphene.\textsuperscript{23} Ru 3d$_{5/2}$ was decomposed into metallic and oxidized peaks, the metallic Ru peak was charge corrected to 280.1 eV.\textsuperscript{24}

LEED images were obtained using a commercial three grid reverse-view LEED apparatus. LEED images were captured from 300 eV to 60 eV before significant charging of the sample (due to $\sim 5$ ML insulating BN) obscured the lower energies, then LEED images were captured 400 eV to 220 eV.

Prior to BN ALD, Ru was annealed at 1000 K in UHV for 2 hours, and then cooled to
room temperature. The sample was subsequently annealed at 1000 K in oxygen (1 x 10^{-7} Torr) for 30 minutes to remove contamination resulting from ambient exposure, and further annealed at 1000 K for 4.5 hours more in UHV to order the surface region of the film. Resulting XPS showed that after the extensive annealing in UHV, ~2 Å average thickness of O remained, and LEED data indicated an ordered overlayer similar to that reported for RuO_{2}(110).^{25} Thus, the surface of the substrate is most accurately described as an adsorbed O layer with the lattice structure of RuO_{2}(110).

BCl_{3} and NH_{3} gases were electronic grade, obtained from commercial vendors and used without further purification. The turbo pump to the deposition chamber was closed off during each exposure, and a dedicated roughing pump was used to create a flow through system during exposures. BCl_{3} pressure during an exposure was 250 mTorr for 5 minutes, and NH_{3} pressure was 350 mTorr for 2 minutes, all at 600K. Between BCl_{3} and NH_{3} exposures the rough pump was closed off and the turbo pump reopened for 2 minutes to the system to allow any excess gas to be pumped away.

Space filling models of the coincident BN(0001) and RuO_{2}(110) direct space lattices were generated using commercially available software^{26} using literature values for atomic diameters and bond lengths.^{27}

3.3 Results

3.3.1 BN Deposition on RuO_{2}(110)

XPS Ru 3d and O 1s spectra of the sample prior to ALD are shown in Figure 3.1(a, b) respectively. Corresponding LEED data are shown in Figure 3.2(a). The Ru 3d_{5/2} spectrum can be decomposed into a main feature at 280.1 eV characteristic of metallic Ru^{24}, and a smaller feature near 281 eV Figure 3.3. XPS data for the Ru 3d spectrum are displayed in Fig. 3.3 both
before (Fig. 3.3a) and after (Fig. 3.3b) 20 ALD cycles of BCl$_3$/NH$_3$ and annealing. The smaller feature near 281 eV corresponds to the feature for the RuO$_2$ surface layer.

Figure 3.1: XPS spectra of Ru and O core levels. (a) Ru 3d and (b) O1s: (black trace) before h-BN(0001) deposition, (red trace) after 20 BCl$_3$/NH$_3$ exposures, (blue trace) after 800 K anneal in UHV.

These binding energies are in excellent agreement with those of clean and oxidized Ru(0001) respectively$^{15,24,28}$. The LEED data before ALD [Fig 3.2(a)] is consistent with RuO$_2$(110)$^{25}$ although a smearing of some oxide-related LEED spots suggests a certain amount of disorder in the oxide layer. Such disorder is also suggested by the breadth of the O 1s spectrum of the surface prior to ALD [Fig. 3.1(b)], possibly due to the presence of adsorbed OH and/or H$_2$O species on the RuO$_2$ monolayer$^{28-30}$.

ALD induces only a small shift in the Ru 3d feature to higher binding energy [Fig.
3.1(a)], although the intensity is reduced, as expected, by the presence of the BN overlayer. The small shift to higher binding energy is consistent with a slight additional oxidation, or chlorination, of the surface during the ALD process, but this small shift is largely reversed upon annealing the BN/Ru surface to 800 K in UHV [Fig. 3.1(a)].

ALD induces significant change in the O 1s feature [Fig. 3.1(b)], including the attenuation of the low binding energy feature below 530 eV, and the broadening of the O 1s feature to higher binding energies at ~ 533.5-530 eV, centered near 532.5 eV. That the total O 1s intensity—unlike the Ru 3d intensity—is not reduced upon formation of the BN overlayer, and indeed increases after 20 BCl₃/NH₃ cycles [Fig. 3.1(b)], indicates that a portion of the total O 1s signal originates from the BN overlayer, rather than at the BN/RuO₂ interface. The observed O 1s binding energies are consistent with the formation of B suboxide or hydroxide. Annealing of the BN/Ru sample to 800 K in UHV significantly reduces the width and intensity of the O 1s feature. After annealing, the O 1s peak maximum is observed to shift back towards 532 eV. However, the overall O 1s intensity remains greater than observed prior to ALD. These observations demonstrate that the BN ALD process, under these experimental conditions, results in some oxygen content within the growing BN film, and this is significantly but not completely reversed by annealing in UHV.

A comparison of the surface sensitive (80 eV beam energy) LEED spectrum before and after the deposition of 1 monolayer of BN(0001) (4 BCl₃/NH₃ cycles) is given in Fig. 3.2(a and b), respectively. The unit cells of the BN(0001) and RuO₂(110) reciprocal lattices are outlined. The persistence of the Ru oxide layer in the LEED spectrum upon deposition of the first BN monolayer is evident. Also evident is the coincidence between the BN(0001) and RuO₂(110) reciprocal lattices. Extra spots are apparent in the 1 ML BN/RuO₂/Ru(0001) spectrum, which
are attributable to double layer scattering\textsuperscript{8}. These spots are not observed after the deposition of the second BN layer [Fig. 3.2(c)], consistent with the extra spots in Fig. 3.2b being due to double layer scattering. The data in Figs. 3.2(b and c) indicate that the BN lattice is rotated 30\degree with respect to the oxide substrate, and is azimuthally aligned with the lattice of the Ru(0001) metallic substrate. The data in Figs 3.1 and 3.2 therefore indicate that ALD of BN on a monolayer of RuO$_2$(110)/Ru(0001) preserves the structure of the oxide substrate lattice while yielding highly ordered h-BN(0001) overlayers.

![Figure 3.2: LEED of evolution of ALD BN on RuO$_2$(110)/Ru(0001). (a) RuO$_2$(110)/Ru(0001); (b) One monolayer BN (4 BCl$_3$/NH$_3$ cycles) on RuO$_2$(110)/Ru(0001); (c) Two monolayers BN (8 BCl$_3$/NH$_3$ cycles) on RuO$_2$(110)/Ru(0001). All LEED acquired at 80 eV beam energy.](image)

3.3.2 Multilayer h-BN(0001)

XPS B 1s and N 1s spectra are shown in Fig 3.3 after 4 and 20 BCl$_3$/NH$_3$ ALD cycles, and after 800 K UHV anneal, corresponding to the formation BN films (before anneal) with XPS-derived average thicknesses of ~1ML, and 5ML. Corresponding B 1s and N 1s peak binding energies are also listed in Table 3.1 and compared to relevant binding energies from the literature. The data in Fig. 3.3a and Table 3.1 demonstrate that upon formation of the first ALD monolayer, a B 1s binding energy of 191.8 eV is observed, but that this value relaxes toward 191.1 eV as the BN film thickens. In contrast, no such change is observed in the N 1s peak binding energy with increasing film thickness. (Fig. 3.3b, Table 3.1).
Upon annealing in UHV, however, both B 1s and N 1s peak binding energies shift toward larger binding energies—191.6 eV and 398.7 eV, respectively—coincident with loss of Cl and some O (Figs 3.3b and 3.1a, respectively) and a visible narrowing of the B 1s feature. The observed B 1s and N 1s binding energies after the anneal are close in value to those reported\textsuperscript{5} for an annealed BN film of comparable thickness on Co(0001). The energy difference between the N 1s and B
1s features ($\Delta$, Table 3.1) is, however, $\sim 0.6$ eV smaller than that reported for borazine-derived BN monolayer on Pt(111)\textsuperscript{32} or for the borazine-derived BN monolayer on Ru with an intercalated oxide layer\textsuperscript{15}.

Table 3.1: The binding energies of B 1s, N 1s, and $\Delta$ after 4 BCl$_3$/NH$_3$ exposures, after 8 BCl$_3$/NH$_3$ exposures, after 20 BCl$_3$/NH$_3$ exposures, after a 30 min 800 K anneal, and relevant data from literature.

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>N</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 BCl$_3$/NH$_3$ cycles</td>
<td>191.8</td>
<td>398.1</td>
<td>206.3</td>
</tr>
<tr>
<td>8 BCl$_3$/NH$_3$ cycles</td>
<td>191.5</td>
<td>398.1</td>
<td>206.6</td>
</tr>
<tr>
<td>20 BCl$_3$/NH$_3$ cycles</td>
<td>191.1</td>
<td>398.0</td>
<td>206.9</td>
</tr>
<tr>
<td>After 30 800 K</td>
<td>191.6</td>
<td>398.7</td>
<td>207.1</td>
</tr>
<tr>
<td>6 ML BN on Co(0001)\textsuperscript{5}</td>
<td>191.2</td>
<td>398.3</td>
<td>206.8</td>
</tr>
<tr>
<td>1 ML BN on Ru(0001)\textsuperscript{15}</td>
<td>190.94</td>
<td>398.99, 398.02</td>
<td>208.05, 207.26</td>
</tr>
<tr>
<td>1 ML BN + Oxygen intercalation, 100 C\textsuperscript{15}</td>
<td>190.66</td>
<td>398.46</td>
<td>207.8</td>
</tr>
<tr>
<td>Monolayer h-BN on Pt foil\textsuperscript{32}</td>
<td>189.9</td>
<td>397.6</td>
<td>207.7</td>
</tr>
</tbody>
</table>

The Cl 2p intensity (Fig. 3.4a, arrow) indicate a Cl atomic concentration of $\sim 5$ at\% after 20 BCl$_3$/NH$_3$ cycles, but after a brief 800 K anneal in UHV, the Cl concentration in the BN layer decreased to $< 1$ at. %, in line with previous ALD BN results on Co(0001)\textsuperscript{5}. These data also indicate a somewhat broad B 1s feature, prior to anneal, which is not inconsistent with a small amount of oxidized or chlorinated B near $\sim 193$ eV\textsuperscript{31,33}. The narrowing of the B 1s feature after the anneal suggests the removal/reduction of such species. However, the proximity of the Cl 2p feature prevents a firm conclusion on this point.

The evolution of XPS-derived BN average film thickness and the corresponding XPS-derived B:N atomic ratio with the number of BCl$_3$/NH$_3$ cycles are displayed in Fig. 3.5. The increase in average thickness is linear with the number of BCl$_3$/NH$_3$ cycles, as expected for an ALD process. The y-intercept of the linear regression of the average thickness of BN does not go through 0, indicating that the initial sticking coefficient of BN on RuO$_2$ was higher than the
sticking coefficient on BN, consistent with what was observed for BN grown by magnetron sputtering on clean Ru(0001)\(^6\). The data in Fig. 3.5 also show that during the ALD process, the B:N atomic ratio is consistently 1.1:1(±0.1), with the estimated uncertainty related to the measurement of the XPS intensities. After annealing in UHV, however, the B:N atomic ratio exhibits a slight reduction to the expected value of 1.0:1 (±0.1). This is consistent with the annealing-induced removal of a small B impurity, either B-O or B-Cl. In summary, the data in Figs. 3.2-5 demonstrate the deposition of an epitaxial BN(0001) layer on Ru(0001), with an average BN film thickness that is linearly proportional to the number of BCl\(_3\)/NH\(_3\) cycles.

![Figure 3.4: XPS spectra of (a) B 1s and (b) N 1s for h-BN(0001) film on RuO\(_2\)(110)/Ru(0001): (black trace) after 4 BCl\(_3\)/NH\(_3\) cycles; (red trace) after 20 BCl\(_3\)/NH\(_3\) cycles; (blue trace) after 800K UHV anneal. Cl 2p feature is marked by arrow in (a)](image-url)
Figure 3.5: (■) thickness after each deposition and after 800 K anneal as a function of the number of BCl$_3$/NH$_3$ exposures (■): B:N atomic ratio after each deposition and after 800 K anneal as a function of the number of BCl$_3$/NH$_3$ exposures., Straight lines are least-square fits to data.

3.4 Discussion

The data in Figs. 3.1 and 3.2 indicate that ALD BN on monolayer RuO$_2$(110) on Ru(0001) yields an epitaxial BN layer rotated 30$^\circ$ with respect to the oxide substrate and azimuthally aligned with the lattice of the metallic Ru(0001) underlayer. Data in Fig. 3.1b, however, demonstrate that the ALD process under these conditions is accompanied by inclusion of an oxygen impurity. The degree of impurity can be estimated by calculating the total O 1s intensity due to the interfacial oxide layer, attenuated by ~ 5 ML of BN, and subtracting this amount from the total O 1s intensity observed after ALD of BN but prior to annealing in UHV (Fig. 3.1b). The O 1s intensity after this subtraction is then the approximate intensity due to non-interfacial O—i.e., to impurities incurred during ALD. Using an estimated O 1s photoelectron inelastic mean free path of 27.20 Å thru BN, the O 1s “impurity intensity” is then the total O 1s intensity less the corrected intensity due to interfacial oxygen. This results in an estimated B:O atomic impurity ratio of 8:1 prior to annealing and 10:1 B:O after annealing in UHV.

The data in Fig. 3.4a and Fig. 3.5 also indicate that the ALD process at the temperatures
reported here yields an observable Cl impurity, which is greatly reduced upon annealing in UHV. The reduced width of the B 1s spectrum after annealing (Fig. 3.4a) and the corresponding change in observed B:N stoichiometry from 1.1:1 to 1.0:1 (Fig. 3.5) suggests that this Cl impurity is associated with volatile BClₓ species, which are desorbed during the annealing step.

The decrease in impurity O, Cl and excess B upon annealing demonstrate that while the growth temperature chosen allows the ALD reaction to proceed, the inclusion of impurities is observable by XPS. As a practical matter, therefore, the production of device-worthy BN multilayers by this process requires some further optimization—possibly alteration of exposure conditions, substrate temperatures, or more frequent annealing steps, in order to produce films with levels of impurities too small to be observed by XPS.

The LEED and XPS data (Figs. 3.2 and 3.4 and Table 3.1) provide further insight into how a monolayer of oxide alters BN/Ru electronic interactions. STM and XPS data demonstrate that a BN monolayer produced by either borazine pyrolysis¹⁰,¹⁵ or by ALD with BCl₃ and NH₃⁸ results in strong Ru/BN orbital hybridization. This correlates with the observation of two N 1s bonding environments at the BN/Ru interface produced by borazine pyrolysis¹⁰,¹⁵ shifting to one broad peak at lower binding energy upon oxygen intercalation at elevated temperatures¹⁵ (Table 3.1). In contrast, the N 1s feature in the growth process reported here exhibits a constant binding energy (prior to anneal in UHV) of ~ 398.1 eV at all BN film thicknesses. In contrast, the B 1s binding energy (Fig. 3.4a, Table 3.1) exhibits a monotonic decrease in binding energy with film thickness prior to annealing. Given that the N 1s binding energy remains constant as the B 1s binding energy decreases, this shift cannot be ascribed to band bending at the interface, but instead reflects an interfacial B-substrate interaction that is attenuated as additional BN layers are formed. We suggest that the increased B 1s binding energy observed in the first BN layer on Ru
(Table 3.1) reflects some B interaction with the surface oxide. Thus, the XPS data for BN/RuO$_2$(110) suggests a weak but observable B-surface oxide interaction, and negligible N-RuO$_2$(110) interaction. This is in contrast to BN interactions with clean Ru, where strong N/Ru orbital hybridization is apparent$^{8,15}$.

The shift of both B 1s and N 1s binding energies to higher energy upon annealing in UHV (Fig. 3.4, Table 3.1) coincides with removal of Cl impurity, and therefore suggests some band bending due to the potential of Cl$^-$ impurities at or near the interface. After the anneal, the B 1s and N 1s binding energies are in good agreement with those previously reported for multilayer BN(0001) film of comparable thickness on Co(0001)$^5$.

The difference in N1s and B1s binding energies ($\Delta$, Table 3.1) is independent of band bending or energy scale calibration, and allows comparison of values for both multilayer and single layer BN films. The $\Delta$ value observed here, $\sim 207$ eV (Table 3.1) is in very good agreement with that reported for an ALD 6 ML BN(0001) film on Co(0001) formed under similar reaction conditions$^5$. This value, however, is $\sim 0.6$ eV – 0.8 eV smaller than those generally reported for monolayer BN films derived by borazine pyrolysis on transition metal substrates$^{10,13,15,32}$. Whether this reflects on some fundamental differences between films produced by borazine pyrolysis vs. BCl$_3$/NH$_3$ ALD, or points to some difference in electronic structures for epitaxial multilayer or single layer films, requires further study.

Finally, the monolayer of interfacial oxide alters the orientation of the BN lattice relative to the substrate. Previous ALD of BN on Ru(0001) produced a monolayer of BN rotated 30° with respect to the Ru lattice$^8$. In contrast, the data in Fig. 3.2 demonstrate that the BN lattice is rotated 30° with respect to the oxide lattice, and aligned with the metal Ru(0001) lattice beneath the surface oxide. The data in Fig. 3.2b, demonstrate that this rotation produces a close
coincidence between the BN(0001) and RuO$_2$(110) lattices. The growth of epitaxial BN(0001) on RuO$_2$(110)/Ru(0001) is therefore an example of BN growth on a coincident substrate. This is illustrated in Fig. 3.6, which shows the overlay and unit cells of the BN(0001) and RuO$_2$(110) direct space in-plane lattices. Since graphene, Co(0001) and Ni(111) in-plane lattice constants are all similar to BN, this suggests multiple schemes for the epitaxial integration of graphene and BN with Co and Ni on RuO$_2$(110) for spintronic applications$^{2,4}$. Indeed, the ability to grow smooth RuO$_2$(110) on oxide films such as MgO(100)$^{30}$, which can in turn be grown epitaxially on Si(100)$^{34}$ suggests a route towards the integration of 2D-based nanoelectronics or spintronics devices with Si(100).

![Image]

Figure 3.6: Simulated space filling model of h-BN(0001) deposited on RuO$_2$ (110). The substrate is RuO$_2$ (110) (black = Ru, red = O). The overlayer is BN (green = N, blue = B). Unit cells shown overlaid in bottom left corner.

As a final note of caution, the data reported here provide no definitive conclusion regarding the continuity of the BN layer with respect to the presence/absence of pinholes or islands, etc. Transport/tunneling measurements on fabricated structures are therefore of obvious significance. However, the quenching of Ru metal-related LEED spots and spots related to double layer scattering after the deposition of only a second BN monolayer (Fig. 3.2b,c); as well as the linearity of XPS-derived film thicknesses with ALD precursor cycles (Fig. 3.5) strongly
suggest that this process produces uniform, macroscopically continuous BN films suitable for device applications, consistent with previous applications of this process on Co(0001)\textsuperscript{5} and on Ru(0001)\textsuperscript{8}.

3.5 Summary and Conclusions

XPS and LEED data demonstrate the epitaxial growth of stoichiometric h-BN(0001) layers on RuO\textsubscript{2}(110)/Ru(0001) using a BCl\textsubscript{3}/NH\textsubscript{3} ALD process at a growth temperature of 600 K, followed by annealing in UHV at 800 K. The oxide monolayer remains intact during the deposition process, and the interfacial oxide inhibits the strong interfacial interactions observed for BN on clean Ru(0001). The BN average film thickness is linearly proportional to the number of BCl\textsubscript{3}/NH\textsubscript{3} cycles. The BN layers are also in azimuthal alignment with each other, and coincident with the RuO\textsubscript{2}(110) lattice. The data demonstrate that this ALD BCl\textsubscript{3}/NH\textsubscript{3} process has potential for the formation of multilayer epitaxial BN films for a variety of beyond-CMOS applications.

3.6 Acknowledgments

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3.7 Chapter References


CHAPTER 4

ATOMIC LAYER DEPOSITION OF h-BN(0001) MULTILAYERS ON Ni(111) AND
CHEMICAL VAPOR DEPOSITION OF GRAPHENE ON h-BN(0001)/Ni(111)*

4.1 Introduction

Direct, epitaxial growth of hexagonal boron nitride (h-BN(0001)) and graphene by industrially scalable methods is of critical interest for a variety of device applications.1–4 This includes tunneling spin filters, in which the predicted tunneling magnetoresistance depends directly on rigorous azimuthal alignment between Ni or Co electrodes and BN and/or graphene layers, as well as the number of aligned BN and graphene monolayers (ML).3–5 h-BN and Ni (111) have a close in-plane lattice match (2.50 and 2.49 Å respectively)6,7 making Ni(111) a good magnetic substrate for direct growth of h-BN. h-BN and graphene also have a very close lattice match (~1.7% mismatch)8,9 which allows for a theoretically flat surface and low lattice strain for graphene. Atomic layer deposition (ALD) of h-BN allows for ML control over the thickness of the epitaxial layers, which offers clear advantages for some applications.3,10 ALD is a very specific type of chemical vapor deposition (CVD) where ALD is defined as sequential self-limiting, solid-gas reactions used to accomplish conformal atomic-layer thickness control.11 This is in contrast to CVD, where the thickness is not inherently self-limiting but dependent on the time and pressure of the precursor(s) exposure and the temperature of the substrate, among other factors such as chemical interactions.12–15 For example, CVD of graphene is normally accomplished by exposing a substrate to a hydrocarbon such as methane or ethylene at high temperatures (~1000 K) where the precursor decomposes on the surface to provide a source of C

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where the thickness is dependent on the time and pressure of hydrocarbon used.\textsuperscript{12,13}

Applications for ALD in the literature include membranes,\textsuperscript{16} photovoltaics,\textsuperscript{17} water purification,\textsuperscript{18} biosensors,\textsuperscript{19} microelectronics,\textsuperscript{20} and spintronics.\textsuperscript{2,5} ALD applications for BN have been widely reported in the literature; B\textsubscript{2}O\textsubscript{3} capped with BN for Si doping,\textsuperscript{21,22} BN grown using PEALD for capacitors,\textsuperscript{20} BN nanotubes for water purification,\textsuperscript{18} and possible spintronic devices.\textsuperscript{2,5,23,24} BN has been proposed for a variety of applications within spintronics, including minority spin filtering for spin injection for magnetic tunnel junctions,\textsuperscript{2,5,23,24} and as the dielectric for a nonlocal spin valve.\textsuperscript{23} ALD gives the atomic-layer control needed for fabrication of spintronic devices such as magnetic tunnel junctions using Al\textsubscript{2}O\textsubscript{3}\textsuperscript{25} or h-BN\textsuperscript{2,5} because spin devices rely heavily on atomically thin films.\textsuperscript{25} The precise control over film thickness inherent to ALD, as well as the resulting azimuthal alignment between layers, make this method attractive for device fabrication, especially since multilayers of h-BN are superior to monolayers for certain spin injection applications.\textsuperscript{24,25}

Previously, several attempts were made to deposit multilayer, epitaxial h-BN on Ni(111) (in addition to exfoliation methods). h-BN deposition has been achieved by borazine pyrolysis at substrate temperatures ranging from 973-1073 K.\textsuperscript{26,27} Growth by this method was found to be polycrystalline after the first ML as indicated by the absence of LEED spots.\textsuperscript{27} Significant orbital hybridization between the Ni and h-BN \(\pi\) bands on monolayer h-BN grown by CVD of borazine has previously been demonstrated.\textsuperscript{27,28} Multilayer growth of h-BN was achieved using molecular beam epitaxy (MBE), but precise control over the thickness using MBE is difficult.\textsuperscript{29,30} Other deposition methods like magnetron sputtering\textsuperscript{31} and pulsed laser deposition\textsuperscript{32} do not provide atomic-layer control of h-BN growth. ALD of h-BN allows for epitaxial, multilayer growth, unlike growth by borazine CVD, which is largely self-limiting to 1 ML, for epitaxial h-
Here we report (for the first time) epitaxial, multilayer h-BN deposited on Ni(111) by ALD and the subsequent growth of azimuthally-aligned graphene by CVD.

A number of precursors have been used for the ALD of BN on various substrates, such as Al₂O₃, Si, and SiO₂. The use of BBr₃ and NH₃ as precursors has been reported at substrate temperatures ranging from 673 – 1023 K, which resulted in turbostratic growth. This was followed by other reports using the same precursors for laser-assisted ALD of BN on SiO₂, also resulting in turbostratic growth of BN. Thermal and plasma-assisted ALD of BN using non-corrosive precursors have also been established. Triethylborane and NH₃ were used to deposit BN on Si and Al₂O₃ between 770-1170 K, which at lower temperatures resulted in amorphous BN, but at higher temperatures resulted in sp² BN, but the process was no longer self-limiting above 873 K. Triethylborate and N₂/H₂ plasma were used in plasma-assisted ALD to grow h-BN between 470 – 620 K.

The ALD process reported here uses alternating exposures of BCl₃ and NH₃ at 600 K, similar to that employed for multilayer h-BN(0001) growth on Co(0001), RuO₂(110)/Ru(0001), ZrO₂ and on B₂O₃/Si(100). A schematic of this reaction is presented in Section 2.3.1. This chemistry is robust for h-BN deposition on transition metals, oxides of main group elements, and transition metal oxides. Here, x-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) data are presented, demonstrating layer-by-layer, epitaxy of h-BN(0001) on a Ni(111) single crystal. The data indicate that the BN lattice is aligned with the Ni substrate, and that graphene subsequently deposited by CVD is epitaxially deposited on and azimuthally aligned with the h-BN.

4.2 Experimental

A 5 mm x 5 mm Ni(111) single crystal was obtained from commercial vendors and was
introduced into a multi-chamber vacuum system described elsewhere.\textsuperscript{10,21} Briefly, the system included a turbomolecularly pumped chamber for ALD (base pressure 3x10\textsuperscript{-6} Torr), and a turbomolecularly pumped chamber for XPS, reverse-view LEED, and Ar\textsuperscript{+} ion sputter gun for sample cleaning in UHV (base pressure 1x10\textsuperscript{-10} Torr) separated by manually operated gate valves. The ALD chamber is equipped with a manually operated butterfly valve that allows the chamber to be closed to the turbo pump, and a dedicated rough pump that creates a flow through of the gasses during exposures, allowing pressurization of the chamber to hundreds of militorr. Pressures in the ALD chamber were recorded by a combination of nude ion gauge to measure pressures in the high vacuum regime and baratron gauge to measure pressures at higher pressures between 1 mTorr and 1 Torr. Pressures in UHV were recorded with a nude ion gauge calibrated for N\textsubscript{2}. Sample temperatures in each chamber were varied by resistive heating and measured by a K type thermocouple mounted on the sample stage near the sample. Heating in UHV occurred with the use of a ceramic-encapsulated heater designed for use in reactive environments. Samples were transported between the chambers without exposure to ambient conditions via a magnetically coupled feedthrough. A detailed schematic of this multi-chamber system can be found elsewhere.\textsuperscript{21}

XPS data were acquired with a 100 mm mean radius hemispherical analyzer operating at a constant pass energy (50 eV), with non-monochromatic Al K\alpha x-ray source operated at 15 keV, 300 W. XPS spectra were analyzed with commercially available software and all spectral binding energies were calibrated to that of metallic Ni 2p\textsubscript{3/2} at 852.7 eV. Relative atomic concentrations and thicknesses were calculated by standard methods\textsuperscript{43} using inelastic mean free paths (IMFP) of Ni through BN, B through BN, and N through BN of 19.98 Å, 29.48 Å, and 30.05 Å respectively. The thickness of graphene was determined by the IMFP of B, N, and C
through graphene 32.63 Å, 28.49 Å, and 30.79 Å respectively. The XPS-derived thickness of BN and graphene monolayers were taken to be 3.3 Å and 3.35 Å respectively, in agreement with previous STM studies of multilayer BN on Ru(0001) and of multilayer graphene. A commercial three grid reverse-view LEED apparatus was used to collect LEED images which were captured from 300 eV to 60 eV on all samples.

The 5 mm x 5 mm x 0.5 mm Ni(111) single crystal was cleaned in situ by annealing in O₂ (10⁻⁷ Torr, 1000 K; AirGas, 99.999% purity, CAS# 7752-44-7) to remove adventitious C. Ni substrates were subsequently exposed to a flux of Ar ions (Scott Specialty Gases, 99.9999% purity, CAS# 7440-37-1) at a pressure of 5 x 10⁻⁵ Torr at a beam energy 3 keV, and beam current of 25 mA to remove the surface oxygen. The crystal was then annealed repeatedly to 1000 K in UHV to remove any residual contamination as determined by XPS, and to order the surface until a well-defined hexagonal LEED pattern was obtained. The relatively small size of the sample, combined with an analyzer source area of ~ 1 mm x 5 mm, resulted in some Ta 4p intensity present in N 1s spectra. This did not, however, impact any of the conclusions presented here.

Electronic grade BCl₃ (IGX Group, CAS # 10294-34-5, 99.999% purity) and NH₃ (Praxair, CAS# 7664-41-7, >99.999% purity) gases were used as precursors without further purification. The turbo pump to the deposition chamber was closed off during each exposure, and a dedicated roughing pump was used to create a flow-through system during exposures. BCl₃ exposures were at 250 mTorr for 5 minutes, and NH₃ exposures were at 350 mTorr for 2 minutes, all at 600 K. Between BCl₃ and NH₃ exposures the rough pump was closed off and the turbo pump was reopened for 2 minutes to the system to allow any excess gas to be pumped away.

Graphene growth was accomplished by heating the substrate to 1000 K and then
exposing the sample to 100 mTorr CH₂CH₂ (Matheson, CAS# 74-85-1, 99.999% purity) for 23 min. In this case, the substrate consisted of Ni(111) with 2 ML of h-BN(0001) deposited by ALD, as this BN thickness has been suggested as optimal for certain spin filter applications.⁵

4.3 Results and Discussion

4.3.1 ALD of h-BN(0001) on Ni(111)

XPS spectra of B 1s and Cl 2p, N 1s, Ta 4p₃/₂, and Ni 2p₃/₂ regions are shown in Figs. 1(a-c) respectively after 0, 2, and 4 cycles of BCl₃/ NH₃ at 600 K and subsequent UHV anneals to 1000 K to remove chlorine contamination. Fig. 4.1(a) shows an increase in the intensity of B 1s at ~ 191 eV with increasing number of BCl₃/NH₃ reaction cycles. This binding energy is consistent with BN formation.²²,⁴¹,⁴⁷,⁴⁸ UHV anneals to 1000 K reduced Cl impurities to < 3 at.%. Fig. 1(b) shows N 1s growth at ~398 eV, also consistent with BN formation.²²,⁴¹,⁴⁷,⁴⁸ Ta is also observed in this sample [near 401 eV, Fig. 4.1(b)] The breadth of the Ta 4p₃/₂ feature indicates both metallic and oxidized Ta. The attenuation in the Ni 2p₃/₂ signal [Fig. 4.1(c)] was used to calculate the thickness of the h-BN film through both B 1s and N 1s.

Chlorine removal at 1000 K in UHV after 2 cycles BCl₃/NH₃ at 600 K is shown in Fig 4.2(a). The intensity of the B 1s peak slightly decreases and shifts to a lower binding energy after a 3 hour 1000 K UHV anneal, indicating some desorption of undissociated or partially dissociated BClₓ from the surface. After this anneal, the N 1s peak [Fig. 4.2(b)] narrows significantly at ~ 398 eV, consistent with h-BN formation.¹⁰,⁴⁰,⁴¹ The full width at half maximum (FWHM) of the N 1s component of the region narrows from 4.2 eV after deposition to 3.2 eV after 3 hours of 1000 K anneals in UHV. These data indicate a reduction in the number of bonding environments, possibly due to desorption of some partially dissociated NHₓ or the conversion of some partially reacted BClₓ and NHₓ to h-BN and HCl gas.
Figure 4.1: XPS spectra of (a) B 1s and Cl 2p (i) before BCl3/NH3 cycles (black dot trace), (ii) after 2 BCl3/NH3 cycles + 1000 K UHV anneal; fit of B 1s (red dash trace) and raw data (thin red line), and (iii) after 4 BCl3/NH3 + 1000 K UHV anneal; fit of B 1s (blue solid trace) and raw data (thin blue line), (b) N 1s and Ta 4p3/2 before BCl3/NH3 cycles (black dot trace), after 2 BCl3/NH3 cycles + 1000 K UHV anneal (red dash trace), and after 4 BCl3/NH3 + 1000 K UHV anneal (blue solid trace), (c) Ni 2p3/2 before BCl3/NH3 cycles (black dot trace), after 2 BCl3/NH3 cycles + 1000 K UHV anneal (red dash trace), and after 4 BCl3/NH3 + 1000 K UHV anneal (blue solid trace).
Annealing in UHV resulting in removal of Cl from the film is necessary to ensure a high quality, pure h-BN film with minimal contamination, in rigorously azimuthal alignment with the substrate, which would be necessary for device applications.2,5,23,24 Fig. 4.2(b) shows that the intensities of both N 1s and Ta 4p3/2 features increased upon annealing. This is likely due to Ta metal’s relative chemical inertness, indicating that after 1000 K UHV anneal any adsorbed BCl3 or NH3 on the Ta desorbed from the Ta straps holding the sample to the holder.

Figure 4.2: XPS spectra of a) B 1s and Cl 2p regions, and b) N 1s and Ta 4p3/2 regions after 2 cycles BCl3/NH3 at 600 K; sum of components (black dot trace), raw data (thin black trace), and subsequent UHV 3 hour anneal to 1000K sum of components (red dash trace), raw data (thin red trace).

Fig. 4.3(a) shows the average XPS-derived thicknesses of h-BN deposited on Ni(111) by BCl3/NH3 at 600 K on three different, identically prepared sample surfaces. In each case, the
single crystal was cleaned by Ar + ion sputtering and annealing in O2 and in UHV, before exposures to BCl3/NH3 at 600 K. For one sample (designated Sample 1) the single crystal was exposed to 2 cycles BCl3/NH3 at 600 K. For the second ALD process, the clean single crystal was exposed to 2, then to and additional 2 cycles BCl3/NH3 at 600 K (designated Sample 2). For the third study, the clean surface was exposed to 4, then to a total of 8 cycles BCl3/NH3 at 600 K (designated Sample 3).

Figure 4.3: (a) Plot of XPS-derived average thickness of BN and (b) B:N atomic ratios after 2, 2, 4, 4, and 8 BCl3/NH3 exposures at 600 K followed by UHV anneals vs. number of BCl3/NH3 cycles at 600 K. The solid line in (a) is a least-squares fit to the data.

The average thickness of h-BN was found by the attenuation of Ni 2p3/2 through both B 1s and N 1s, and error was determined from the standard deviation of this average. There is a
high level of consistency between samples, reflected by the nearly identical thicknesses determined for identical reaction cycles carried out on different surfaces (Fig. 4.3a). The linear fit of the data in Fig 3(a) is consistent with an ALD process, but has a y-intercept of $3.07 \pm 0.24$ Å with an indicated growth rate of $1.65 \pm 0.07$ Å/cycle. This growth rate is consistent with other reports of BN deposition on B$_2$O$_3$/Si,$^{22}$ Co(0001)$^{40}$ and ZrO$_2$. This non-zero y-intercept of the linear regression of thickness vs. cycle [Fig. 3(a)], indicates that BCl$_3$/NH$_3$ has a higher sticking coefficient on the bare Ni(111) surface than on h-BN, consistent with previous reports of BN growth by ALD of h-BN on RuO$_2$/Ru,$^{41}$ and Co (0001)$^{40}$ and by magnetron sputter deposition on Ru.$^{31}$ Fig. 3(b) shows the B:N atomic ratio corresponding to each of the thickness calculations. The atomic ratio stays very close to 1:1 indicating linear, stoichiometric growth of h-BN.

**Table 4.1: Summary of B 1s and N 1s binding energies during depositions.**

<table>
<thead>
<tr>
<th>BCl$_3$/NH$_3$ Cycle</th>
<th>B 1s</th>
<th>N 1s</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Cycles</td>
<td>191.4</td>
<td>398.7</td>
<td>207.4</td>
</tr>
<tr>
<td>Sample 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Cycles</td>
<td>191.4</td>
<td>399.0</td>
<td>207.6</td>
</tr>
<tr>
<td>4 Cycles</td>
<td>191.8</td>
<td>399.0</td>
<td>207.2</td>
</tr>
<tr>
<td>Sample 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 Cycles</td>
<td>192.0</td>
<td>399.0</td>
<td>206.9</td>
</tr>
<tr>
<td>8 Cycles</td>
<td>192.0</td>
<td>399.0</td>
<td>206.9</td>
</tr>
</tbody>
</table>

Table 4.1 shows the binding energies of the B 1s and N 1s with an average uncertainty of ± 0.3 eV, and the difference (Δ) between those binding energies after completion of different numbers of BCl$_3$/NH$_3$ cycles. The B 1s binding energy shifts to higher binding energy with increasing numbers of cycles, while the N 1s remains essentially constant. The Δ values between B 1s and N 1s are generally consistent with other reports of h-BN ALD by BCl$_3$/NH$_3$, but are somewhat smaller than those reported for BN grown by CVD methods. $^{49,50}$ Δ shifts to lower
values because the binding energy of B 1s increases from 2 to 4 cycles. The different behaviors of the B 1s and N 1s binding energies with film thickness demonstrates that this is not a result of the p-type band bending theorized for h-BN on Ni. The B 1s shift to higher binding energies with increasing BN thickness is instead consistent with some Ni→B charge transfer at the interface that does not extend to subsequently grown layers.

4.3.2 CVD of Graphene on h-BN(0001)/Ni(111)

Figure 4.4 shows XPS spectra of C 1s, B 1s, Cl 2p, and the N 1s/ Ta 4p3/2 regions before and after graphene CVD with no subsequent UHV anneals, on a 2 ML thick h-BN film on Ni(111) (Sample 1). Fig. 4.4(a, ii) shows the increase in carbon at a peak binding energy of ~284.5 eV corresponding to sp2 carbon. The FHWM of the C 1s region after CVD (~3.5 eV) is somewhat broad, consistent with the persistence of adventitious C (~ 285.6 eV) present before CVD as shown in Figure 4.4(a, i). Using this deconvolution, the average thickness of the graphene layer calculated using the ratio of the intensities of B 1s and N 1s through the C 1s was 10.9 ± 0.7 Å (~3 ML).

Fig. 4.4(b) shows a narrowing of B 1s region and a further reduction in the area of the Cl 2p region after CVD. This could be from a reaction of H from the ethylene with any remaining Cl when the graphene was deposited on the surface, or simply Cl removal by heating to 1000 K during the CVD process, similar to the effect demonstrated in Fig 2(a). Fig 4.4(c) shows the N 1s and Ta 4p3/2 region before and after CVD. The N 1s region also narrowed and shifted downward in binding energy upon CVD, which could be due to the removal of H incorporated in the film (BNH2 or B2NH) from the high temperature used for CVD or a reaction with desorbed Cl species to produce HCl. The Ta 4p3/2 regions also shifted lower in binding energy, possibly as a result of H from ethylene reducing the oxidation of the Ta straps used in mounting the sample.
Figure 4.4: XPS spectra of (a) C 1s after (i) ALD of h-BN showing adventitious carbon (black dot-dashed trace), (ii) C 1s after CVD showing sp² C 1s (red dot trace), adventitious carbon (red dashed trace), and sum of components (solid red trace); (b) B 1s and Cl 2p, (i) sum of components after ALD (black solid trace), raw data (thin black trace) and (ii) sum of components after CVD (red dash trace), raw data (thin red trace); (c) N 1s and Ta 4p₃/₂ (i) after ALD showing N 1s (solid black trace), Ta 4p₃/₂ metallic (black dash trace), Ta 4p₃/₂ oxidized (black dot trace), raw data (thin black trace) and (ii) after CVD showing N 1s (red dash-dot trace), Ta 4p₃/₂ metallic (red small-dot trace), Ta 4p₃/₂ oxidized (red dash-dot-dot trace), raw data (thin red trace).
Overall, the data in Fig. 4.4 demonstrate that the 2ML thick h-BN was intact after graphene CVD. Fig. 4.5 displays in detail the C 1s spectrum after ethylene CVD and UHV anneals to order the surface. This data is shown to highlight the $\pi \rightarrow \pi^*$ shake up at 291 eV, corroborating the $sp^2$ nature of the deposited C layer.

![C 1s spectrum](image)

**Figure 4.5:** XPS of C 1s after CVD (100mTorr, 23 min CH$_2$CH$_2$ exposure at 1000 K) and subsequent UHV anneals to 1000 K.

![LEED images](image)

**Figure 4.6:** LEED images at 80 eV of (a) clean Ni(111) single crystal, (b) of h-BN after 2 cycles BCl$_3$/NH$_3$ cycles at 600 K and UHV anneals, and (c) graphene after CVD and UHV anneals at 1000 K.

LEED data of the Ni(111) surface before and after h-BN deposition, and after graphene CVD, are displayed in Fig. 4.6(a-c), respectively. These data, all acquired at the same beam
energy of 80 eV, demonstrate that the surface lattice remains hexagonal with approximately constant lattice spacing, as expected for a graphene/BN/Ni(111) heterostructure. These data, however, also demonstrate that the h-BN lattice [Fig. 4.6(b)] and graphene lattice [Fig. 4.6(c)] remain in close azimuthal alignment with the lattice of the Ni(111) surface. Such azimuthal alignment is critical for the “Brillouin zone spin-filtering mechanism” proposed for Ni(111) (or Co(0001)/BN/graphene spin filters).

4.3.3 Ambient Exposure of Graphene/BN/Ni Heterostructure

Figure 4.7(a-b) shows the XPS spectra of the N 1s and B 1s features after CVD and after ambient exposure. Ambient exposure was accomplished by moving the sample into the chamber for ALD, isolating that chamber with the manually operated leak valves, and turning the pumps off (turbo pump and mechanical pump). This allowed the chamber to vent, filling with the ambient air from the lab, through the vent valve on the turbo pump. The sample was left in the chamber at atmospheric pressure, filled with ambient air for a minimum of 5 minutes before the pumps were turned back on, and the chamber was allowed to pump down to 10⁻⁶ Torr before being transferred back to the UHV chamber for XPS and LEED. Fig 4.7(a) shows a slight attenuation of N 1s intensity and the shift to lower binding energy. Both the B 1s and N 1s features exhibit shifts to lower binding energies [Fig. 4.7(a, b)]. Ni 2p feature [Fig. 4.7(c)] attenuates due to the adsorption of C and O species on the surface [Fig 4.7(d-e)].

The C 1s feature [Fig. 7(d)], however, exhibits a small increase in intensity and notable broadening, as well as a diminution of the \( \pi \rightarrow \pi^* \) shakeup feature. There is also a substantial increase in O 1s intensity [Fig. 4.7(e)]. The data in Fig. 4.7(a-c) show no evidence of direct oxidation of Ni, B or N sites. The general shift towards lower binding energy observed in these spectra also suggests a band bending effect induced, perhaps, by the absorption of oxygen-
containing species at the graphene surface. Oxygen adsorption might lead to electron charge transfer from the substrate (graphene/h-BN/Ni(111)) resulting in the formation of an electron-depleted surface, leading to upward band bending.\textsuperscript{53,54} Such a band bending causes binding energy shifts of both core levels and valence band towards the Fermi level ($E_F$). Hence, the binding energy of B 1s and N 1s shift to lower binding energies [Fig 4.7(a-b)]. Nitrogen is also an electron acceptor in BN, and therefore, the shift in the N 1s core level is higher than those observed in Ni 2p or B 1s regions.

Figure 4.7: XPS spectra of (a) N 1s, Ta 4p 3/2, (b) B 1s, Cl 2p, (c) Ni 2p, (d) C 1s, (e) O 1s before ambient exposure (black trace), and after ambient exposure (red trace).

Figure 4.8: LEED image, acquired at 80 eV beam energy, of graphene/h-BN/Ni heterostructure after ambient exposure and brief (<5 min) UHV anneal to 1000 K.
Fig. 4.8 shows the LEED image at 80 eV after ambient exposure and a brief (<5 min) 1000K anneal. These data are consistent with Fig. 4.6(c) demonstrating that the graphene overlayer remained intact and was ordered after a brief UHV anneal. The data in Fig. 4.8 also indicate that the partial oxidation observed in Fig. 4.7 is reversible upon annealing in UHV.

4.4 Summary and Conclusions

Multilayer h-BN(0001) was grown epitaxially on Ni(111) by ALD, using sequential BCl$_3$/NH$_3$ reactions at 600 K and annealing to 1000 K in UHV. Multilayer graphene was subsequently grown on h-BN(0001) by CVD of ethylene at 1000 K. LEED shows that all three components of the graphene/BN/Ni heterostructure are in azimuthal registry. Exposure of the Ni/2 ML h-BN/3 ML graphene heterostructure to ambient resulted in some oxidation of the graphene surface, but without oxidation of Ni, B or N sites. A brief anneal of the exposed heterostructure to 1000 K in UHV yielded the same well-defined LEED image as observed prior to exposure. The well-aligned Ni, BN and graphene layers indicate that such heterostructures, fabricated in this manner, are suitable for various spin filters and related spintronics applications. Further, the ability to grow such heterostructures, with controlled BN and graphene thicknesses—and the resilience of these heterostructures upon exposure to ambient—indicate that devices based on these heterostructures can be produced by industrially scalable and practical methods. This provides a scalable frame-work for the fabrication of theoretically ideal spin filters for beyond-CMOS spintronic devices.

4.5 Acknowledgments

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CHAPTER 5

IN-SITU X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF LITHIUM CARBONATE REMOVAL FROM GARNET-TYPE SOLID-STATE ELECTROLYTE USING ULTRA HIGH VACUUM TECHNIQUES*

5.1 Introduction

Lithium ion batteries have attracted much attention for the application of rechargeable energy storage devices, but currently used electrolytes will not be able to meet the demands of the next generation of lithium ion battery needs due to persistent issues with stored energy density, service life, and safety.¹ An attractive candidate for the next generation of battery technology is an all-solid-state lithium battery (ASSLB) utilizing inorganic solid-state electrolytes (SSEs).² Various SSEs have been investigated, of which garnet-type SSE has several advantages, including a wide electrochemical stability window (~6 V vs Li⁺/Li), high chemical stability with metallic Li, high lithium ion conductivity, etc.³ The high chemical stability of garnets with respect to Li enables the use of a lithium metal anode, which has the highest theoretical specific capacity of 3860 mAh g⁻¹.⁴ There are, however, major issues that need to be addressed for the effective operation of ASSLBs.

The lithium rich LLZTaO (Li₆.5La₃Zr₁.₅Ta₀.₅O₁₂) reacts with moisture present in atmosphere to form lithium hydroxide (LiOH), which further reacts with carbon dioxide (CO₂) to form lithium carbonate (Li₂CO₃) on the surface.⁵ This formation occurs spontaneously on the SSE surface when it is processed in atmosphere, and is a significant issue that needs to be addressed for the development of next generation batteries.⁶,⁷ Li₂CO₃ formation decreases the

mobility of Li ions, but this can be reversed by removal of carbonate species from the surface.\textsuperscript{7–9} Carbonate removal has been reported by polishing in inert atmosphere,\textsuperscript{8} annealing in inert atmospheres\textsuperscript{8,9} and sputtering at room temperature.\textsuperscript{10} \( \text{Li}_2\text{CO}_3 \) formation has been inhibited by treating Li garnet with carbon.\textsuperscript{11} The ability to remove surface carbonate and other impurities from the Li garnet surface with UHV-compatible techniques is an important step both in fundamental studies of relevant surface/interface chemistry, and in applications such as the deposition of passivation barriers, for dendrite prevention.\textsuperscript{12,13}

XPS is an important and widely used method to monitor changes in chemical composition of SSE surfaces, but there is significant controversy as to how XPS binding energies should be referenced. SSE surfaces are electronic insulators, and therefore experience sample charging—a net accumulation of positive or negative charge—during XPS data acquisition. This causes shifts in the apparent binding energies of elements, which can impact interpretation of the corresponding surface chemistry. There are many reports of calibration to the C 1s feature for adventitious carbon at 284.5 – 285 eV.\textsuperscript{7–10,12,14–25} Others have calibrated to core level binding energies of Au\textsuperscript{15,26,27} Ag,\textsuperscript{28} F (in LiF),\textsuperscript{17,29,30} or implanted Ar\textsuperscript{10,31} when available. It has recently been proposed to use the Li 1s BE for \( \text{Li}_2\text{O} \) (\( \sim \) 55-56 eV) from the deconvoluted Li 1s spectrum, on the assumption that \( \text{Li}_2\text{O} \) will almost always be present in a film containing Li.\textsuperscript{6} Additionally, the surface effects of \( \text{Ar}^+ \) ion sputtering are of significant interest, as depth-profiling of these films has been used in studies probing the composition and stability of similar Li-containing SSEs. \( \text{Ar}^+ \) ion sputtering rapidly removes the carbon at lower BE which is used to calibrate most spectra, but enhances the \( \text{Li}_2\text{O} \) component.\textsuperscript{10,17,19,27,29,30,32–35}

Herein, we report UHV techniques to remove the surface carbonate species from the SSE surface, while studying the removal using \textit{in situ} XPS. Our results demonstrate that annealing in
UHV has similar effects to annealing in inert gas environments,\textsuperscript{8,9} while \textsuperscript{Ar} sputtering at mild temperatures removes all carbon from the surface. After the initial sputtering, La 3d, Zr 3d, and Ta 4f are present and well-resolved from baseline and interfering peaks. These elements’ presence in XPS spectra have been used as markers for the absence of surface impurities formed during ambient exposure.\textsuperscript{8} O 1s intensity decreases and shifts to lower BE, consistent with other cleaning methods.\textsuperscript{8,9} Calibrating with respect to the Li 1s/Li\textsubscript{2}O standard should give similar results to calibrating to underlying metals such as Au,\textsuperscript{15} because there should be Li\textsubscript{2}O in the bulk of the sample, with Li\textsubscript{2}CO\textsubscript{3} and LiOH formed on the surface.\textsuperscript{17,27,30,34} XPS spectra were calibrated with respect to Li\textsubscript{2}O (Li 1s at 56.4 eV).\textsuperscript{6} This method results in elimination of some discrepancies induced by calibration with respect to C 1s-as previously suggested,\textsuperscript{6} and is also more practical for sputtered surfaces with little or no C present.

5.2 Experimental

5.2.1 Li Garnet Preparation

Cubic garnet-type solid-state electrolyte (SSE) with nominal composition LLZTaO was prepared by solid-state synthesis.\textsuperscript{36} Stoichiometric amounts of lithium carbonate (15 wt.\% excess to compensate for the lithium loss during sintering), lanthanum oxide, zirconium oxide and tantalum oxide were added to a Teflon container and were ball-milled for 6 hours with a small amount of isopropanol. The obtained slurry was dried and calcined at 1173 K for 6 hours. The calcined powder was again ball-milled for 12 hours and later pressed into pellets using a uniaxial press at 300 MPa pressure. Then, the pellets were covered with more calcined powder and annealed at 1433 K for 16 hours with a heating and cooling rate of 1 K/min to prevent any significant lithium loss. The obtained pellets were polished with a polishing machine using a 1200 grit SiC emery paper to ensure a smooth and uniform surface. The crystalline nature of the
synthesized LLZTaO was analyzed with an X-ray diffractometer (Bruker D2 Phaser, PXRD) using Cu–Kα radiation (1.5418 Å). The as-synthesized LLZTaO samples were examined using a field-emission scanning electron microscope (SEM, JSM 7600 FE SEM), and a confocal Raman microscope with a laser excitation wavelength of 532 nm (Nanonics Imaging Ltd.).

5.2.2 UHV Studies

A LLZTaO pellet of 1 cm in diameter and 200 µm thickness was introduced into a multi-chamber vacuum system described elsewhere. Briefly, the system included a chamber for atomic layer deposition (ALD--base pressure 3x10⁻⁶ Torr), and a UHV chamber for XPS and for sample cleaning (base pressure 1x10⁻¹⁰ Torr). The UHV chamber was equipped with an Ar⁺ ion sputter gun for sample cleaning, a 100 mm mean radius hemispherical analyzer with multichanneltron detector, and a dual anode unmonochromatized X-ray source for XPS acquisition. The Ar⁺ sputter gun (PHI Ion Gun 04-191) has an approximate sputter rate of 24 Å/hour at 500 K, based on the rate of removal of SiO₂ from Si under the sputter conditions used. The sample stage permitted sample heating between 300 K and 1200 K. Pressures in UHV were recorded with a nude ion gauge calibrated for N₂. Sample temperatures were varied by resistive heating and measured by a K type thermocouple mounted on the sample stage near the sample. Samples were transported between the chambers without exposure to atmospheric conditions by a magnetically coupled feedthrough.

XPS data were acquired with the analyzer operating at a constant pass energy (50 eV), with a non-monochromatic Al Kα x-ray source operated at 15 keV, 300 W. XPS spectra were analyzed with commercially available software and all spectral binding energies were calibrated to Li₂O at 56.4 eV as described by Wood et. al. In this calibration the FWHM was constrained to be less than 2 eV for all spectral components as suggested by Wood et. al. The Li 1s feature
was fit with Li₂O, Li₂CO₃, LiOH, and Li⁰ peaks with fixed distance between the binding energies. The spectra, for comparison, were also calibrated using the more common method of placing the binding energy (BE) of the non-carbonate C 1s feature at 284.8 eV. This was accomplished by fitting the C 1s region with 3 components (adventitious C, C-O/C=O, and CO₃²⁻) all with equal FWHM 2.3 eV, based on previous experiments.

As shown below, calibration using the Li 1s reference proved more consistent regarding the interpretation of surface chemical processes. Relative atomic concentrations were calculated by standard methods. Sputtering was done by back-filling the UHV chamber to 5 x 10⁻⁵ Torr Ar⁺ (Scott Specialty Gases, 99.9999% purity, CAS# 7440-37-1) at 3 kV, 25 mA sputter conditions at 500 K to remove carbon from the surface. Heating to 500 K began simultaneously with the Ar⁺ ion sputter. Samples were heated to temperature at approximately 1K/min to prevent Li loss or sample cracking during sputtering and UHV annealing.

5.3 Results and Discussion

5.3.1 LLZTaO Characterization

Figure 5.1(a) shows that the X-ray diffraction (XRD) pattern of the synthesized garnet-type SSE matches well with the cubic phase of Li₅La₃Nb₂O₁₂ (PDF 80-0457), as reported elsewhere, validating the cubic structure of LLZTaO, that has a better lithium ion conductivity when compared to tetragonal LLZTaO. A digital image of the translucent polished LLZTaO pellet of about 1 cm in diameter and 200 µm is shown in Figure 5.1(b). Figure 5.1(c) shows the field-emission scanning electron microscopy (FE-SEM) image that reveals the highly dense structure of the garnet-type SSE, with an average grain size of 10 µm. The Raman spectrum further confirms the cubic phase of the garnet-type SSE, in Figure 5.1(d). In the Raman spectrum, the peak at 120 cm⁻¹ (E₉) corresponds to the vibrational bands of heavy La cations.
whereas the peaks at 218 (T\textsubscript{2g}) and 255 (A1g) cm\textsuperscript{-1} are due to the oxygen bending mode. The peaks at 361 (T\textsubscript{2g}), 410 (E\textsubscript{g}/T\textsubscript{2g}) and 514 (T\textsubscript{2g}/E\textsubscript{g}) cm\textsuperscript{-1} correspond to the Li-ion bonding region.\textsuperscript{43} These Raman peaks indicate the cubic phase purity of the LLZTaO with I\overline{3}4d space group. The results shown in Figure 1 are comparable to those reported in the literature.\textsuperscript{43}

Figure 5.1: (a) XRD pattern of the as-prepared LLZTaO. (b) Digital image of the polished LLZTaO pellet. (c) FE-SEM image of the as-prepared LLZTaO. (d) Raman scan of the as-prepared LLZTaO.

5.3.2 UHV Cleaning and Binding Energy Calibration

XPS core level spectra were obtained after annealing the Li Garnet surface in UHV. Section 5.3.2.1 discusses calibration of XPS core binding energies relative to the adventitious C 1s standard (284.8 eV), which is the most commonly reported method.\textsuperscript{7–10,12,14–25} Section 5.3.2.2 discusses calibration of the same XPS spectra according to the Li 1s/Li\textsubscript{2}O standard of 56.4 eV, recently proposed by Wood et al.\textsuperscript{6} Section 5.3.2.3 compares the results obtained using the two
calibration methods. Section 5.3.2.4 describes other effects of UHV annealing, including appearance of La 3d, Zr 3d core levels, and the atomic percentages (at. %) of all elements.

The evolution of C 1s, Li 1s and O 1s core level spectra upon annealing in UHV are shown respectively, in Fig. 5.2(a-c), calibrated according the C 1s adventitious C spectrum and in Fig. 5.2(d-f) calibrated according to the Li 1s/Li$_2$O standard.

Figure 5.2: XPS spectra of (a) C 1s calibrated to adventitious C standard at 284.8 eV; (b) Li 1s calibrated to adventitious C; (c) O 1s calibrated to adventitious C 1s; (d) C 1s calibrated to Li 1s/Li$_2$O standard at 56.4 eV; (e) Li 1s calibrated to Li 1s/Li$_2$O; (f) O 1s calibrated to Li 1s/Li$_2$O; after atmospheric exposure (black square trace), after 900 K UHV anneal (red circle trace), and after 1050 K UHV anneal (blue triangle trace).
Calibration to the adventitious C 1s standard required the deconvolution of the carbon spectrum into 3 components. The lowest binding energy component, designated sp²/adventitious carbon, was set at 284.8 eV; the highest binding energy was assigned to be carbonate; and another peak between the two was attributed to C-O/C=O at 286-287 eV.

The calibration to the Li 1s/Li₂O standard was accomplished by deconvolution of the Li spectrum into components associated with Li₂O, Li₂CO₃, LiOH, and Li⁰ peaks. As suggested by Wood et al. the Li₂O component was fixed at 56.4 eV, with LiOH set 1.0 eV higher than Li₂O, and Li₂CO₃ at 1.65 eV higher than Li₂O and the metallic/suboxidized Li⁰ peak 1.43 eV below the binding energy of Li₂O. These binding energies correspond to those shown by Wood et al when discussing their results referenced to Li 1s/Li₂O standard. FWHM of the components used to fit the spectrum were constrained to be less than 2 eV, using the calibration method proposed by Wood et. al.

In order to determine the sensitivity of our results to the constraints on FWHM of the fitting components used, fits to the data were also preformed constraining the FWHM < 1.75 eV, and < 1.5 eV Figure 5.3. Change in Li 1s FWHM fitting constraints changed the amounts of Li₂O relative to LiOH, Li₂CO₃, LiOH, and Li⁰ as well as the relative goodness of fit, as measured by the residual standard deviation (RSD) [Fig. 5.3]. As shown in Figure 5.3, FWHM of <1.75 eV gave overall the lower RSD values, with smaller FWHM constraints the apparent amount of Li₂O (as opposed to LiOH and Li₂CO₃) present after ambient exposure increased. In contrast, reports in the literature which indicate that the major species present after ambient exposure should be Li₂CO₃ and LiOH, as observed for using the FWHM constraint of < 2.0 eV. Therefore calibration to Li₂O with components of the Li 1s spectra constrained to less than 2 eV will be used. It should also be pointed out, however, that fitting the Li 1s spectra using
different FWHM fitting constraints did not significantly affect the interpretation of the corresponding C 1s and O 1s data obtained, and calibrated according to the Li 1s/Li₂O standard.

Figure 5.4.

Li Constrained to 2 eV max- as in Figure 5.2

Li Constrained to 1.75 eV max

Li Constrained to 1.5 eV max

Figure 5.3: Li 1s with FWHM of components constrained to be < 2 eV (same as Figure 5.2d-f), constrained to be < 1.75 eV, and < 1.5 eV. Residual standard deviation (RSD) is the standard deviation of the residual, where residual is the distance between the data and the fitted curve.
Calibrated to Li fit to 2 eV max - as in Figure 5.2

Calibrated to Li fit to 1.75 eV max

Calibrated to Li fit to 1.5 eV max

Figure 5.4: Carbon 1s and Oxygen 1s spectra after ambient exposure (red trace), after 900 K UHV anneal (green trace), and after 1050 K UHV anneal (blue trace) calibrated to the Li 1s spectra displayed in Figure 5.3.
5.3.2.1 Calibration to Adventitious Carbon

Results in Figure 5.2(a) show that when the spectra are calibrated to the C 1s adventitious C standard at 284.8 eV, annealing step-wise in UHV causes the carbonate C 1s feature to increase in binding energy, outside the original FWHM. The intensity of adventitious carbon peak increases as the intensity of the carbonate peak decreases. This increase in adventitious carbon intensity can be somewhat suppressed using a quicker heating schedule (going from ambient exposure to 1100 K in larger increments, Figure 5.5).

Figure 5.5: Carbon 1s spectra after ambient exposure (black square trace), after 660 K UHV anneal (red circle trace), and after 1100 K UHV anneal (blue triangle trace). Spectra were calibrated with respect to the Li 1s/Li2O standard at 56.4 eV.

This apparent shift to higher BE [Fig. 5.2(a)] is outside of the original FWHM [Fig. 5.2(a), Fig. 5.5], which would suggest that a higher BE carbon environment (than was originally present on the surface) is being formed upon UHV annealing, which is a reducing environment. Carbonate is the most oxidized form of carbon present on the surface, and Li2CO3 has been reported to have a slightly higher BE for carbon (~290-292 eV)\textsuperscript{6,10,11,46} than other metal carbonates (TaCO3, LaCO3, ZrCOO\textsuperscript{-} \textasciitilde288.5-290 eV).\textsuperscript{47-50}
The Li 1s intensity increases and FWHM broadens (2.0 to 2.7 eV) between the atmospheric exposure and the 900 K anneal [Fig. 5.2(b)]. This is indicative of an increase in the number of Li bonding environments. When the spectra are calibrated to adventitious C [Fig. 5.2(b)], the broadening of the Li 1s spectra occurs toward both higher and lower binding energy regions, but more towards the former. A primary intensity increase at higher binding energies would be more consistent with an increase in the lithium carbonate species, which is contrary to the removal of carbonate observed in the C 1s data [Fig. 5.2(a)]. After annealing to 1050 K, the Li 1s feature overall decreases in intensity and remains on the high binding energy side of the spectrum. The decrease in Li intensity is consistent with the melting point of Li2CO3 at ~1000 K. However, removal of lower binding energy Li is not consistent with the removal of Li2CO3 [Fig. 5.2(b)].

Figure 5.2(c) shows that the O 1s spectrum shifts to higher BE and most of the reduction in intensity occurs at the lower BE side of the region, which would be more consistent with forming hydroxides or carbonates, not removing them. Upon annealing to 900 K, the overall intensity decreases and a low binding energy shoulder forms which is consistent with formation of metal oxides. Upon annealing to 1050 K the low binding energy shoulder is reduced, which would indicate a loss of Li2O/metal oxides, which is contrary to other reports of lithium carbonate removal from the literature.

5.3.2.2 Calibration to Li2O in Li 1s

Figure 5.2(d), which shows the C 1s spectra calibrated to the Li 1s/Li2O standard, indicates that the C at low binding energy after ambient exposure is not, as previously suggested, entirely elemental or graphitic C. Instead, this calibration method indicates that the lower BE carbon is initially at least partly C-O or C=O in nature. As carbonate and
oxygen are removed during UHV anneals, carbon’s bonding environment is reduced to sp$^3$ carbon, with a significant amount of oxidized species still present.$^{52,53}$

Figure 5.2(e) shows that when the Li 1s spectra are calibrated to Li 1s/Li$_2$O, after the 900 K UHV anneal when the intensity and breadth of the feature increases, the increase mainly takes place on the lower BE side of the Li spectrum. This is consistent with the Li$_2$O component being enhanced as carbonate and hydroxide components are diminished at the surface. A shoulder begins to form in the Li 1s spectra after the 900 K anneal and becomes more pronounced after the 1050 K anneal, revealing a small amount of Li$^0$ (metallic/suboxide). This would be consistent with the stoichiometry indicated by XRD and Raman [Figure 5.1(a, c)], where Li$_{6.5}$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ does not have enough O to account for Li$_2$O, Ta$_2$O$_5$, La(OH)$_3$, and ZrO$_2$. This has been previously explained in similar systems as Li-O having a weak bond.$^7$ After annealing to 1050 K, the intensity of the Li 1s feature decreases, consistent with other reports of Li$_2$CO$_3$ removal and with the melting point of Li$_2$CO$_3$ being $\sim$1000 K.$^9$

Figure 5.2(f) shows that when the O 1s spectra are calibrated to the Li$_2$O component, the O 1s diminishes primarily at higher binding energy, consistent with the removal of -OH and -CO$_3^{2-}$ species.$^6,51$ The shoulder that forms as the oxygen is removed shifts to lower binding energy, which could indicate the formation or enhancement of metal oxide species such as Li$_2$O, Ta$_2$O$_5$, and ZrO$_2$ [Fig. 5.2(f)].$^9,51$

Calibration to the Li$_2$O component of the Li 1s spectra has been addressed in more detail in Figure 5.6. Figure 5.6 shows the deconvolution of the Li 1s feature displayed in Figure 5.2(e) into four components corresponding to Li$^0$, Li$_2$O, LiOH, and Li$_2$CO$_3$. 

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Figure 5.6: XPS spectra of the Li 1s spectra calibrated to Li$_2$O (a) after ambient exposure (b) 900 K anneal and (c) 1050 K anneal decomposed into Li$_2$O (red solid trace), LiOH (black dotted line trace), Li$_2$CO$_3$ (black dash-dot trace), metallic/suboxide Li (black dash-dot-dot trace in b and c only), sum of components (blue open triangle trace), raw data (black square scatter).
Figure 5.6(a) shows the Li 1s spectra after exposure to atmosphere with a small component corresponding to Li$_2$O at 56.4 eV and two major components corresponding to LiOH and Li$_2$CO$_3$ at 57.40 eV and 58.05 eV respectively. This would be consistent with a significant amount of carbonate and hydroxide on top of the oxidized lithium, which has been previously reported.\cite{17,27,30,34}

Figure 5.6(b) shows an increase in the Li$_2$O component and a decrease in the LiOH component. This is consistent with removal of O at higher binding energy because the O 1s binding energy is slightly higher for \(-\text{OH}\) than for \(-\text{CO}_3^{2-}\). Therefore, the removal of higher binding energy O [Fig. 5.6(f)] is consistent with removal of LiOH [Fig 5.6(b)].\cite{51} Figure 5.6(b) also shows the appearance of a small shoulder at 55 eV, which becomes more pronounced after 1050 K anneal [Fig. 5.6(c)] corresponding to Li$^0$ (metal/suboxidized Li).\cite{6} The overall height of the Li 1s peak decreases between the 900 K to 1050 K anneals but broadens significantly.

5.3.2.3 Comparing Calibration to C 1s vs Li 1s

The distance between the two major peaks in C 1s gets larger with UHV annealing [Fig. 5.2(a, d)]. If the spectra are referenced to the lower binding energy C 1s/adventitious C standard [Fig 5.2(a)] the carbonate peak shifts to higher binding energies. This shift cannot be accounted for by carbonate forming or migrating to any other element present in LLZTaO.\cite{6,10,11,46–50} When the spectra is referenced to Li 1s/Li$_2$O standard [Fig 5.2(d)], the C 1s carbonate feature stays essentially fixed, and the lower binding energy carbon shifts from a somewhat oxidized state (C-O and C=O) to a less oxidized state, (sp$^3$).\cite{44,45}

These data and increase in intensity of carbon at lower BE after annealing in UHV [Fig. 5.2(a, d)] indicate that the proposed mechanism\cite{54} for carbonate decomposition is not the dominant reaction that occurs on LLZTaO under these conditions, in agreement with recovery
studies conducted in inert atmosphere. Rather, at least some carbonate is decomposed to form reduced carbon, and lower oxidation state lithium species (metallic/suboxide lithium). These results, are in agreement with studies of annealing in inert environments:  

\[ \text{Li}_2\text{CO}_3 \rightarrow \text{Li}_2\text{O} + \text{CO}_2 \]  

The initial x-ray excited valence band spectrum is consistent with the presence of Li₂CO₃, when the spectrum is calibrated to the Li₂O/Li 1s standard [Fig. 5.7]. The shift in valence band maximum (VBM) with annealing temperature is shown in Table 5.1 and Figure 5.8. When the spectra in Figure 5.8 are calibrated to Li 1s/Li₂O standard, the VBM are consistent with the values reported by Wood et al for a spectra dominated by Li₂CO₃ shifting to a spectra dominated by Li₂O. In contrast, when the VBM are calibrated to the C 1s standard, the VBM is more consistent with Li₂O₂, which is not supported by the Li data [Fig. 5.2(e) and Fig. 5.6].

![Figure 5.7: X-ray excited valence band spectrum after ambient exposure of LLTaZO.](image)
Figure 5.8: XPS spectra of the X-ray excited valence band, red lines are the linear regression used to determine the valence band maxima for (a, c, e) VB calibrated to Li2O after ambient exposure, 900 K anneal, and 1050 K anneal respectively; (b, d, f) VB calibrated to C 1s after ambient exposure, 900 K anneal, and 1050 K anneal respectively.

Table 5.1: VBM calibrated using Li 1s/Li2O and C 1s/adventitious C schemes

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>VBM Calibrated to Li2O</th>
<th>VBM Calibrated to C</th>
</tr>
</thead>
<tbody>
<tr>
<td>~300 K</td>
<td>5.33 ± 0.38</td>
<td>3.07 ± 0.12</td>
</tr>
<tr>
<td>900 K</td>
<td>4.39 ± 0.11</td>
<td>3.01 ± 0.12</td>
</tr>
<tr>
<td>1050 K</td>
<td>4.24 ± 0.08</td>
<td>3.28 ± 0.10</td>
</tr>
</tbody>
</table>
5.3.2.4 Additional Effects of UHV Annealing

XPS spectra of Zr 3d, La 3d, and Ta 4f core levels as a function of annealing temperature, and calibrated to the Li 1s/Li$_2$O standard, are shown in Figure 5.9(a-c) respectively. La and Zr begin to appear after 1000 K anneals [Fig. 5.9(a, b)]. The Ta 4f feature [Fig. 5.9(c)] has a significant amount of interference from O 2s, La 2s, and Li$_2$CO$_3$ valence spectra.$^{18,51}$ La 3d peaks are resolved into the expected distinct multiplet splitting, consistent with other reports of SSE cleaning.$^8,9$ The appearance/resolution of the La 3d and Zr 3d have been reported to be markers of the surface being clean for cleaning in inert atomospheres.$^8$ The binding energy of the La and the intensity of the satellite peak for La 3d in Figure 5.9(b) are consistent with La(OH)$_3$.\textsuperscript{55,56}

Figure 5.10(a) shows the atomic percentages (at. %) of the total C 1s, O 1s, Li 1s, Ta 4f, Zr 3d, and La 3d regions with respect to the annealing temperature. Figure 5.10(b) shows the amount of carbonate relative to the total C 1s area (C$_{CO3}$/C$_{total}$). The data in Figure 5.10 demonstrate that although the total C 1s at. % increases with annealing temperature in UHV [Fig 5.10(a)], the portion due to carbonate consistently decreases [Fig 5.10(b)]. The increase in total C 1s upon annealing at above 1000 K [Fig. 5.10(a)] is consistent with the significant conversion of CO$_3$ to C with a C 1s binding energy at 285.5 eV, possibly sp$^3$ hybridized (significantly reduced from CO$_3$ or CO$_2$).\textsuperscript{51,57}

Changes in at. % during the low temperature anneals (400 K-600 K) in UHV were negligible. Oxygen content consistently decreases during UHV anneals above 600 K. Some removal of O and C from the substrate above 600 K corresponds to enhancement of Li at. %.
Figure 5.9: XPS spectra of (a) Zr 3d, (b) La 3d (c) Ta 4f, O 2s, La 2s calibrated to Li₂O after ambient exposure (black square trace), 900 K anneal (red circle trace), and 1050 K anneal (blue triangle trace)
Figure 5.10: (a) Atomic percentages of C 1s (pink triangle trace), O 1s (black circle trace), Li 1s (green inverted triangle trace), Ta 4f (red square trace), Zr 3d (blue diamond trace), and La 3d (purple star trace) regions relative to the annealing temperature in K. (b) Percentage of the C 1s signal attributed to carbonate (BE ~292 eV) relative to annealing temperature in K.

From 900 K to 1050 K, the total atomic percentage of lithium and oxygen decreases, whereas carbon increased. A decrease in Li at or above 1000 K is consistent with the melting point of Li$_2$CO$_3$ being 1000 K. Li and C from carbonate are removed during each anneal at or above 1000 K; however O removal from the surface is only observed for the initial anneal at 1000 K, not for subsequent anneals at 1000 K. Only after the sample was annealed to 1050 K did the O 1s intensity decrease again. This could indicate that above 1000 K, when carbonate and lithium are reduced to less oxidized species, some O also remains on the surface, possibly as metal oxide.$^{51}$
The melting point of Li$_2$CO$_3$ is $\sim1000$ K, which accounts for the rapid decrease in both lithium and carbonate (from C 1s) features [Fig. 5.10(a, b)], but does not account for the persistence of a carbonate peak after annealing to 1050 K. The latter may indicate some non-uniformity in the sample temperature—with different areas of the sample above or below the lithium carbonate melting point. Although the Li at % decreases above 1000 K, it does not decrease significantly below its starting value ($\sim27$ % initially and $\sim28$ % after 1050 K anneal). Figure 5.9 shows that Zr, La, and Ta are well resolved after 1050 K anneal, and Figure 5.10 shows that their concentrations never exceed $\sim2$ at. % total.

5.3.3 Ar$^+$ Ion Sputtering

A second LLZTaO pellet was exposed to atmosphere, and initial XPS was acquired at room temperature ($\sim300$ K). These data are calibrated according to the Li 1s/Li$_2$O standard. The sample was sputtered at 5$\times$10$^{-5}$ Torr with 3 keV Ar$^+$ ions while heated to 500 K. Figure 5.11 shows XPS core spectra for C 1s, Li 1s, Zr 3d, La 3d, after 0 hours, 2 hours, and 17 hours of sputtering at 500 K. Figure 5.11(a) shows that all lower BE (non-carbonate) C is removed after 2 hours of Ar$^+$ ion sputtering at 500 K, and that the intensity of the carbonate feature decreased significantly. This has been demonstrated in other reports of Ar$^+$ ion sputtering, for depth profiling XPS, some of which reported calibration to the lower BE C 1s peak.$^{10,17,27}$ This demonstrates that calibration to lower binding energy C 1s is not feasible for some samples, especially ones subjected to sputtering.

The intensity of Li 1s core level is enhanced after the first 2-hour sputter, corresponding to the removal of the lower BE carbon [Fig. 5.11(b)]. This is consistent with removal of carbon species that do not contain lithium such as CO$_2$, CO, COH, methoxy, or hydrocarbons adsorbed to the oxide surface.$^{44,45,58}$ This would be consistent with a layer of oxidized and suboxidized
carbon being present on the top of the Li$_2$CO$_3$ layer. The removal of these, corresponding to an enhancement in the intensity (and FWHM) of the Li peak, is similar to what was observed in Figure 5.2(b, e).

Figure 5.11: XPS spectra of (a) C 1s, (b) Li 1s (c) Zr 3d and (d) La 4d calibrated to Li 1s/ Li$_2$O after ambient exposure (black square trace), 2 hour sputtering (red circle trace), and 17 hour sputtering (blue triangle trace) at 500 K.

Figure 5.11(c, d) show that the Zr 3d and La 3d core XPS spectra appear after the initial 2 hour sputter, and that they continue to be enhanced after subsequent sputters. Figure 5.11(c, d) shows that if the spectra are calibrated to the Li$_2$O/Li 1s standard, the binding energy of La 3d and Zr 3d do not shift during sputtering.
Figure 5.12 shows the total atomic percentages of the species present after Ar$^+$ sputtering. Carbon’s atomic percent decreases during all sputters, to $\sim 1 \pm 1$ at. % after $\sim 17$ hours. The Li 1s feature is initially enhanced ($\sim 30$ at.%) after the first 2 hour sputter, then Li at. % decreases but does not decrease below its initial values of $\sim 25$ at.% with subsequent sputtering. La 3d, Ta 4f and Zr 3d components are enhanced with each subsequent sputter.

![Graph of atomic percentages vs hours sputter](image)

Figure 5.12: Atomic percentages of C 1s (pink triangle trace), O 1s (black circle trace), Li 1s (green inverted triangle trace), Ta 4f (red square trace), Zr 3d (blue diamond trace), and La 3d (purple star trace) after each sputter.

5.4 Discussion

There are obvious risks to using the Li/Li$_2$O standard$^{6,10}$ since Li spectra, as here, are often complex, and determining the calibration standard by peak deconvolution can yield considerable uncertainty. However, calibration to C 1s is not applicable for samples cleaned by Ar$^+$ ion sputtering due to the facile removal of lower binding energy carbon. The increase in the difference between the binding energies of the two major components of the C 1s spectra is difficult to explain if the spectra are calibrated to C 1s at lower binding energy. Thus the Li/Li$_2$O standard calibration standard provide a more consistent chemical narrative.
Figure 5.13: XPS spectra of (a) C 1s calibrated to La(OH)$_3$, (b) Li 1s calibrated to La(OH)$_3$, (c) La 3d calibrated to La(OH)$_3$, (d) C 1s calibrated to Li 1s/Li$_2$O, (e) Li 1s calibrated to Li 1s/Li$_2$O, (f) La 3d calibrated to Li 1s/Li$_2$O after 2 hour sputtering (black square trace), 7 hour sputtering (red circle trace), and 17 hour sputtering (blue triangle trace) at 500 K.

There may be times that calibration to Li 1s/Li$_2$O standard is not practical. A possible alternative would be to reference to the carbonate C 1s. The carbonate peak, when calibrated
using the Li 1s/Li$_2$O standard, does not change binding energy, only decreases in intensity. It would be appropriate to calibrate to C 1s/CO$_3^{2-}$ at 292 eV when this feature is present, as has been reported previously.$^{14}$

If carbonate is not available, use of another core level spectrum present in the LLZTaO (Li$_{6.5}$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$) pellet, such as La 3d or Zr 3d could be feasible. From Figure 5.11(d) the BE of La did not change appreciably with increased sputtering. The ratio of the La 3d peaks to satellite peaks and difference in the binding energy ($\Delta$BE) is indicative of La(OH)$_3$, BE $\sim$ 834.7 eV.$^{55,56}$ A side by side comparison of C 1s, Li 1s and La 3d after sputtering 2, 7 and 17 hours, calibrated to Li$_2$O/Li 1s standard and to La 3d is given in Figure 5.11. The La region was fit according to Sunding et. al.$^{55}$ and Mullica et. al.$^{59}$ and upon calibrating to La(OH)$_3$ 3d$_{5/2}$, the binding energies of the carbonate and other components in the spectra do not shift, similar to when the spectra is calibrated to L 1s/Li$_2$O or to C 1s/carbonate.

There are reports of calibrating to implanted Ar$^{10,31}$ on sputter-cleaned samples. This is not feasible on samples that contain tantalum due to the interference between Ar 2p and Ta 4d spectra (Ar 2p$_{3/2}$ $\sim$241.9 eV, Ta 4d$_{5/2}$ $\sim$238 eV; data not shown).$^{51}$

Table 5.2: Atomic percentages of C 1s, O 1s and Li 1 from Figures 5, 7, for data after ambient exposure, 900 K anneal and 1000 K anneal and 0, 2, 17 hours Ar$^+$ ion sputtering. Uncertainty $\pm$ 1 at %

<table>
<thead>
<tr>
<th></th>
<th>C 1s</th>
<th>O 1s</th>
<th>Li 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>UHV Annealing</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300 K</td>
<td>21</td>
<td>51</td>
<td>27</td>
</tr>
<tr>
<td>900 K</td>
<td>18</td>
<td>44</td>
<td>37</td>
</tr>
<tr>
<td>1050 K</td>
<td>32</td>
<td>37</td>
<td>28</td>
</tr>
<tr>
<td><strong>Ar$^+$ Sputtering</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 hr.</td>
<td>20</td>
<td>54</td>
<td>25</td>
</tr>
<tr>
<td>2 hr.</td>
<td>10</td>
<td>53</td>
<td>30</td>
</tr>
<tr>
<td>17 hr.</td>
<td>1</td>
<td>35</td>
<td>24</td>
</tr>
</tbody>
</table>
The effects of the two cleaning methods—UHV annealing vs. Ar⁺ sputtering, are summarized in Table 5.2, which shows the numerical values for the atomic percentages of C, O and Li after exposure to ambient, UHV annealing to 900 K, 1050 K, and sputtering at 500 K after ambient, 2 and 17 hours (corresponding to the XPS spectra shown in Figure 5.2(d, e, f), 5.11(a, b)).

Li follows the same trend with both methods, where it is initially enhanced, but never significantly decreases below its initial value. Figure 5.2(b, e) and 5.11(b) also demonstrate this trend, that where when some C and O are removed from the surface, the Li 1s intensity is enhanced. This would be consistent with the top layer the surface exposed to ambient being a partly oxidized carbon layer that does not contain a significant amount of Li species. The Li 1s core level broadens to lower binding energy during both UHV annealing and Ar ion sputtering. This corresponds to some amount of metal/suboxidized Li forming or being revealed from the bulk pellet. This lower binding energy Li would be consistent with the stoichiometry indicated by XRD and Raman [Fig. 5.1(a, c)], and with previous reports of weak Li-O bonds in the bulk of these materials.⁷ These data demonstrate that although the Li 1s peak shifts and the overall intensity of the peak decreases during sputtering or UHV annealing, the actual amount of Li present within the XPS sampling depth is ultimately not significantly affected by either cleaning method.

The UHV anneals removed O during anneals above ~600 K, whereas there was essentially no change in O surface content after the initial 2 hour sputter 500 K sputter, so there is a much larger initial decrease in the O from UHV annealing than with Ar⁺ ion sputtering. With longer sputter times similar amounts of O are removed for both cleaning methods (~35 % after 17 hours sputtering and ~37% after 1050 K UHV anneal). This, in conjunction with the
XPS data presented in Figures 5.2 and 5.11 again suggests that there is a top layer of oxidized carbon (methoxy, C-OH, C-O, C=O) on top of the Li$_2$CO$_3$ passivation barrier. When the samples are sputtered, the lower binding energy carbon is rapidly removed. Both cleaning methods remove carbonate. However, a significant amount of carbonate is converted to partially oxidized or sp$^3$ hybridized carbon when the samples are annealed in UHV. In contrast, sputter cleaning removes all carbon species, which should make the surface more chemically similar to the originally generated films because the only source of C in the films is the atmospheric contamination. Other studies have found that these lower oxidation forms of carbon are not overly detrimental to the device performance; however the effect these reduced C films have on the passivation and nucleation of films deposited on these films has yet to be studied.

5.5 Summary and Conclusions

Calibration/charge correction of complex SSEs in XPS is a challenge that must be addressed and can significantly impact conclusions drawn from XPS data. The data reported here show that calibration to the Li 1s/Li$_2$O standard from deconvoluted Li 1s spectra provides an alternative to the widely accepted calibration to C 1s at ~285 eV, yielding a more reasonable interpretation of XPS data. This approach is necessary for samples that are sputtered because the lower binding energy C 1s is removed rapidly in Ar$^+$ sputtering and is unavailable for calibration of subsequent spectra. This, as well as the enhancement of the Li 1s intensity and breadth after some C and O removal suggests that there is a layer on top of the Li$_2$CO$_3$ that contains oxidized carbon that does not contain Li.

UHV annealing and Ar$^+$ ion sputtering produce similar effects in the Li and O concentrations within the surface region, where the Li abundance does not decrease below it’s initial at. %, and the at. % O is reduced after significant carbonate removal. However these two
methods produced very different effects for C and the transition metals. La, Ta and Zr spectra are observed after the initial Ar⁺ ion sputter and their intensities enhanced after each subsequent sputter. However, these core level spectra are not observed/resolved during UHV annealing at temperatures below 1000 K. The amount of reduced carbon was significantly enhanced after UHV annealing, but was completely removed after even initial sputtering. These different surface cleaning methods provide a way to examine the effects of this reduced carbon layer on subsequent deposition of passivating surface layers.

5.6 Acknowledgments

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5.7 Chapter References


CHAPTER 6

SUMMARY AND FUTURE WORK

Direct, epitaxially aligned multilayer 2D materials are important for use in novel CMOS devices and beyond-CMOS devices. Hexagonal boron nitride (h-BN) and graphene are two such materials that have garnered much interest recently. Physical transfer of h-BN and graphene have been reported, however physical transfer is not an industrially scalable method, and can introduce defects, and is limited by the grain size of the original substrate. There are many reports of h-BN growth by CVD processes, however these are generally limited to a single monolayer of h-BN. Atomic layer deposition (ALD) of h-BN was accomplished using cycles of BCl$_3$/NH$_3$ at 600 K substrate temperature and subsequent annealing in ultrahigh vacuum (UHV). In situ x-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) were used to monitor the thickness and orientation of as-deposited films.

XPS and LEED data demonstrate the epitaxial growth of stoichiometric h-BN(0001) layers on RuO$_2$(110)/Ru(0001) using a BCl$_3$/NH$_3$ ALD which was followed by annealing in UHV at 800 K. The oxide monolayer remains intact during the deposition process, and the interfacial oxide inhibits the strong interfacial interactions observed for BN on clean Ru(0001). The BN average film thickness is linearly proportional to the number of BCl$_3$/NH$_3$ cycles. The BN layers are also in azimuthal alignment with each other, and coincident with the RuO$_2$(110) lattice. The data demonstrate that this ALD BCl$_3$/NH$_3$ process has potential for the formation of multilayer epitaxial BN films for a variety of beyond-CMOS applications.

Multilayer h-BN(0001) was grown epitaxially on Ni(111) by ALD and annealing to 1000 K in UHV. Multilayer graphene was subsequently grown on h-BN(0001) by CVD of ethylene at 1000 K. LEED shows that all three components of the graphene/BN/Ni heterostructure are in
azimuthal registry. Exposure of the Ni/2 ML h-BN/3 ML graphene heterostructure to ambient resulted in some oxidation of the graphene surface, but without oxidation of Ni, B or N sites. A brief anneal of the exposed heterostructure to 1000 K in UHV yielded the same well-defined LEED image as observed prior to exposure. The well-aligned Ni, BN and graphene layers indicate that such heterostructures, fabricated in this manner, are suitable for various spin filters and related spintronics applications. Further, the ability to grow such heterostructures, with controlled BN and graphene thicknesses—and the resilience of these heterostructures upon exposure to ambient—indicate that devices based on these heterostructures can be produced by industrially scalable and practical methods. This provides a scalable frame-work for the fabrication of theoretically ideal spin filters for beyond-CMOS spintronic devices.

Current battery technology must also continue to improve to yield faster, smaller, lighter, safer devices. Use of an inorganic solid-state electrolytes (SSEs) in an all-solid-state lithium battery (ASSLB) could satisfy these needs. Calibration/charge correction of complex SSEs in XPS is a challenge that must be addressed and can significantly impact conclusions drawn from XPS data. The data reported here show that calibration to the Li 1s/Li2O standard from deconvoluted Li 1s spectra provides an alternative to the widely accepted calibration to C 1s at ~285 eV, yielding a more reasonable interpretation of XPS data. This approach is necessary for samples that are sputtered because the lower binding energy C 1s is removed rapidly in Ar+ sputtering and is unavailable for calibration of subsequent spectra. This, as well as the enhancement of the Li 1s intensity and breadth after some C and O removal suggests that there is a layer on top of the Li2CO3 that contains oxidized carbon that does not contain Li.

UHV annealing and Ar+ ion sputtering produce similar effects in the Li and O concentrations within the surface region, where the Li abundance does not decrease below it’s
initial at. %, and the at. % O is reduced after significant carbonate removal. However these two methods produced very different effects for C and the transition metals. La, Ta and Zr spectra are observed after the initial Ar$^+$ ion sputter and their intensities enhanced after each subsequent sputter. However, these core level spectra are not observed/resolved during UHV annealing at temperatures below 1000 K. The amount of reduced carbon was significantly enhanced after UHV annealing, but was completely removed after even initial sputtering. These different surface cleaning methods provide a way to examine the effects of this reduced carbon layer on subsequent deposition of passivating surface layers.

Deposition of BN on Li garnet SSE will need to be accomplished using an alternative ALD process due to the affinity Li$^+$ ions have for halides such as Cl. Therefore, a novel deposition method using non-halide precursors will need to be designed to achieve atomic layer control of BN on SSE surfaces. Deposition of a BN passivation barrier on Li garnet substrates, with and without a reduced carbon overlayer is the next step for the Li garnet SSE. The presence of reduced carbon on the surface affects the nucleation of precursors on a surface and may affect the quality and ordering of the resulting BN film. BN has been proposed as a passivation barrier for Li garnet SSE because it has been theorized to prevent Li dendrite formation between the Li metal electrode and the SSE. Dendrite formation at this interface has been linked to some of the safety hazards of existing Li ion batteries, therefore dendrite prevention is paramount for use of Li garnet SSE in battery applications. The stability of the SSE upon cycling and formation or prevention of Li dendrites will be assessed in the future in connection with the work presented here.
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