CHARACTERIZATION OF DIAMOND-SEMICONDUCTOR INTERFACES

by

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A dissertation submitted to the Graduate Council of Texas State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy with a Major in Materials Science, Engineering, and Commercialization August 2020

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DEDICATION

In memory of my mother.

ACKNOWLEDGMENTS

I would like to express my deepest appreciation and gratitude to my advisor Dr. Edwin Piner for his guidance and allowing me the freedom to conduct this research as I saw fit. I am deeply grateful to my labmates Dr. Jeff Simpson, Dr. Raju Ahmed, and Dr. Anwar Siddique as well as the many collaborators that I have had the pleasure of working with for providing me with such interesting samples to analyze.

I also wish to thank Dr. Mark Holtz, Dr. Logan Hancock and Dr. Mohammed Nazari for our collaboration which greatly helped with interpreting the results obtained in this work.

Special thanks must also be extended to the Kleberg Advanced Microscopy Center at the University of Texas at San Antonio and especially Dr. Arturo Ponce-Pedraza and Dr. Josefina Arellano-Jiménez for their guidance through the world of transmission electron microscopy.

Finally, none of this would have been possible without the funding that supported this research that was provided by the Defense Advanced Research Projects Agency, the Army Research Laboratory, and the Shared Research Operations team here at Texas State under Dr. Casey Smith.

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ABSTRACT

The extremely high thermal conductivity of diamond thin films makes them an ideal candidate for heat spreaders that can be integrated with electronic devices. By more effectively dissipating the heat generated during operation device dimensions can be shrunk increasing yield, performance losses due to self-heating can be mitigated, and the need for external cooling systems can be reduced or even eliminated. However, the extreme conditions required for diamond deposition can unintentionally impact the substrate the diamond is being deposited on.

This work focuses on characterizing the changes occurring near the diamond-substrate interface using transmission electron microscopy and chemical analysis by electron energy loss spectroscopy and energy dispersive X-ray spectroscopy. Variations in the changes occurring are studied both as a function of the method of diamond deposition (microwave plasma versus hot filament chemical vapor deposition) as well as substrate material (Si versus SiN_x adhesion layers used to produce GaN-on-diamond structures). Finally, a detailed analysis of a GaN-diamond interface formed without the use of an adhesion layer created by a combination of selected area diamond seeding and epitaxial lateral overgrowth of the GaN is presented. An understanding of these changes is necessary for process optimization to protect the substrate as well as to accurately model the thermal transport through the structure.

1. INTRODUCTION

Novel thermal management techniques are required to deal with the large heat fluxes generated during operation of modern semiconductor power devices in order to maximize their efficiency. This is particularly true in GaN high electron mobility transistors (HEMTs) operating at high power densities. In devices operating at 7.8 W/mm temperature rises of up to 350 °C caused by self-heating have been reported.¹ The temperature rises in these regions has been studied extensively using infrared thermography and micro-Raman spectroscopy.^{2,3} This self-heating causes the channel current to droop leading to reduced output power and thus lower power added efficiency.^{4,5} This in turn results in increased device sizes and the need for external cooling systems increasing the total cost of the system.

In a study comparing the performance of HEMTs fabricated on different substrates it was found that there was less current droop for the devices on SiC substrates compared to sapphire.⁶ This was attributed to the higher thermal conductivity of the SiC being able to better dissipate the heat generated during operation. This naturally leads to the conclusion that if a substrate material with even higher thermal conductivity was used then the device performance should continue to improve as well.

Based on this argument, diamond, with the highest known thermal conductivity of any material, would be the ideal choice for a substrate. Practically, this can be achieved by using polycrystalline diamond thin films deposited by chemical vapor deposition (CVD). These films films show reduced thermal conductivity compared to single crystal diamond (23.2 W/cm K for type IIA diamond) with exact values varying significantly but are typically reported to be around 18 W/cm K for good quality material.^{7–9} These values are compared to the thermal conductivity of other materials in Figure 1.1.



Figure 1.1: Comparison of the thermal conductivity of different materials.

The drawback to this approach is that in order to grow the diamond the substrate is subjected to a harsh environment where it is exposed to H, C, and O radicals at temperatures of 700 °C or greater for several hours. This work focuses on studying the changes that occur at the diamond-substrate interface as a function of diamond deposition method and substrate material.

1.1 Gallium Nitride

The first device quality GaN was produced in the mid-1980s¹⁰ and the first GaN HEMT was demonstrated in 1993.¹¹ GaN HEMTs differed from HEMTs that had been implemented using GaAs technology¹² in that the GaN HEMTs did not require any extrinsic doping. Instead, they rely on the strong spontaneous and piezoelectric fields to cause the conduction band to dip below the Fermi level resulting in the formation of a two-dimensional electron gas (2DEG).^{13,14} In addition to its polarization properties GaN is particularly attractive for high-power and high-frequency applications due to its wide band gap, high carrier mobility,

Material	$E_g (eV)$	$\mu \; (\mathrm{cm}^2 \mathrm{V}^{-1} \mathrm{s}^{-1})$	$v_{sat} (10^7 cm/s)$	V_{BR} (V/mm)
Si	1.1	1,300	1.0	0.3
GaAs	1.42	8,500	1.3	0.4
SiC	3.26	700	2.0	3.0
GaN	3.39	2,000	2.5	3.3

 Table 1.1: Material Parameters

high saturation velocity, and large breakdown voltage. A comparison of these properties for different materials is summarized in Table 1.1.¹⁵

Despite its less than ideal thermal conductivity, Si remains a popular substrate choice for GaN power devices due to large substrates¹⁶ being readily available at low cost and the numerous processes developed for Si technology that can be leveraged. GaN is deposited on Si by starting with a <111> oriented substrate and depositing an AlN layer followed by a series of transition layers.¹⁷ The purpose of these layers is to prevent cracking of the GaN that can occur during cool down from the deposition temperature of 1,000-1,100 °C due to differences in lattice constants and coefficients of thermal expansion between the GaN and Si. On top of the transition layers a thick GaN buffer layer followed by a ~ 20 nm thick AlGaN layer is deposited. The thin AlGaN is pseudomorphically strained to the underlying GaN causing a piezoelectric field to form leading to the band bending that produces the 2DEG. The materials are grown by either metal organic chemical vapor deposition (MOCVD) or molecular beam expitaxy (MBE) with MOCVD having the advantage of higher growth rates compared to MBE. In MOCVD a mixture of trimethylaluminum, trimethylgallium, and ammonia is introduced into a reaction chamber and is then thermally decomposed to form the desired film. The details of how MOCVD systems work are discussed at length in other works.¹⁸



Figure 1.2: Precursor ratios used for diamond deposition.

1.2 CVD Diamond

Growth of diamond films using low pressure conditions first began in the early 1980s when it was realized that by mixing in hydrogen with a carbon source graphitic carbon would be removed leaving only diamond.¹⁹ Two reactor designs emerged using different methods to decompose the precursors. In the first, and simplest design, a tungsten wire is heated to 2,000+ °C causing the precursors to thermally decompose. In the second design a plasma is generated using a RF source which causes the break down of the precursors.

Generally, the diamond growth process is done by first coating the substrate with diamond seed particles that act as nucleation sites for the diamond growth. The substrate is then heated to ~ 700 °C and a mixture of methane, hydrogen and oxygen is introduced into the reaction chamber.¹⁹ The ratio of the precursors is important because there is a narrow range of compositions that result in diamond growth as is seen in Figure 1.2.²⁰ form diamond. Typically diamond growth uses a methane concentration in the range of 1-3% balanced with hydrogen and only a



Figure 1.3: Current process of producing GaN-on-diamond structures.

trace amount of oxygen. A lower methane concentration results in a final film with less non-diamond carbon and higher thermal conductivity at the cost of lower growth rates, whereas diamond grown with a higher methane concentration has a higher growth rate but also more non-diamond carbon and lower thermal conductivity.²¹

1.3 GaN-on-Diamond

The standard process for producing GaN-on-diamond structures is illustrated in Figure 1.3.²² In this process a AlGaN/GaN HEMT structure is first grown using the methods described previously. Next, the structure is temporarily bonded to a carrier wafer and the original substrate is etched away along with any transition layers and a portion of the GaN buffer to locate the diamond as close as possible to the 2DEG. An adhesion layer is then deposited on the freshly exposed GaN surface followed by diamond deposition. After the diamond growth, the temporary carrier wafer is removed leaving a free standing GaN-on-diamond structure that is ready for device processing.

Recent studies of GaN-on-diamond structures have shown the properties of the adhesion layer are critical to optimizing the thermal transport within the structure.²³ In addition to the thermal conductivity of the materials used, the thicknesses of the layers and the thermal boundary resistance (TBR) between the layers must be taken into consideration. The TBR is a temperature differential that develops across the interface of two dissimilar materials, and can be a major factor in determining the thermal transport properties of a system.^{24,25}

1.4 Dissertation Overview

In chapter 2 the principles of transmission electron microscopy are discussed in detail with emphasis placed on techniques used to characterize the interfaces discussed in later chapters.

Chapter 3 discusses results obtained from diamond grown on a Si substrate by microwave plasma CVD, and also discusses a novel TEM sample preparation technique developed to remove surface damage created by focused ion beam milling that causes inaccurate measurements of the non-diamond carbon content by electron energy loss spectroscopy. The material in this chapter has been published as reference 26.

Chapter 4 again focuses on a diamond-Si interface, however this time the diamond was deposited by HFCVD. A substantial amount of filament material and contamination on the filament are found in the diamond, at the interface, and diffused into the substrate. A portion of this chapter has been published in reference 27.

In chapter 5 the focus shifts to a GaN-on-diamond structure formed using a SiN_x adhesion layer where it is found that the SiN_x undergoes significant chemical and structural changes when exposed to the diamond growth environment.

Finally, in chapter 6 a GaN-diamond interface produced without an adhesion

layer via lateral overgrowth is analyzed in detail.

2. ELECTRON MICROSCOPY

2.1 Introduction

This chapter discusses the major principles of transmission electron microscopy (TEM) starting with an overview of the history of the development of the instrument. Conventional transmission electron microscopy (CTEM) is discussed in detail followed by its relationship to scanning transmission electron microscopy (STEM) via the principle of reciprocity as well as annular dark-field imaging (ADF). Finally, chemical analysis through the use of inelastically scattered electrons by energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) is discussed. The published literature on all of these topics is quite extensive, and several well regarded textbooks are available for CTEM,^{28,29} STEM,³⁰ EDS,³¹ and EELS.³²

2.2 History

The development of the electron microscope began with the development of magnetic lenses. The first designs for magnetic lenses for electrons were proposed in 1927, but were not implemented until 1929 by Ernst Ruska and were used to produce the first electron-optical images.³³ This early design was extended to produce magnified images in 1931 making it the first transmission electron microscope (TEM), however, it was limited to a less than impressive magnification of 14.4X before even robust samples were damaged due to heating as the image contrast was primarily generated by absorbtion of the electrons. Two years later in 1933 after making improvements to the lens design, a much more respectable magnification of 12,000X was obtained for images generated using diffraction contrast which now allowed for the use of thin samples. For his work in electron

microscopy Ruska was awarded the Nobel prize in physics in 1986.³³

While Ruska was focused on developing the TEM, Manfred von Ardenne was working to develop the scanning electron microscope (SEM). The first SEM was produced in 1937 and evolved into the scanning transmission electron microscope (STEM) in 1938.³⁴ Further development of the STEM was hampered by the quality of the electron sources available at the time, and by the unfortunate destruction of von Ardenne's STEM in an air raid in 1944. Development of the STEM was resumed mid-1960s by Crewe once field emission electron sources and suitable vacuum systems became available.³⁰ This period also saw the implementation of electron energy loss spectroscopy (EELS) that had first been proposed in 1943.³³

The next major advances came in the late 1990s with the introduction of aberration correction systems for both TEMs and STEMs. Aberration corrected systems not only enable higher resolution to be obtained but also (and perhaps more importantly) allow for resolution to be maintained under non-ideal conditions. Examples of this would include using high beam currents (1+ nA) when performing chemical analysis using EDS or EELS, and when using lower accelerating voltages to prevent damage to beam sensitive materials.³⁰ Current state-of-the-art systems can produce atomic resolution images with accelerating voltages as low as 30 kV and, when equipped with a monochromator to reduce the energy spread of the electrons emitted from the source, achieve an energy resolution of 10 meV allowing for the mapping of phonons.³⁵

2.3 Transmission Electron Microscopy

The major components that make up a TEM are illustrated in the diagram shown in Figure 2.1.²⁹ Starting at the top, the electrons are generated by the electron gun and accelerated towards the specimen. The specific design of the gun will vary significantly depending on if the electrons are generated by thermionic or



Figure 2.1: Diagram showing the major components of a conventional TEM.

field emission, however in both cases the emitted electrons form a cross-over point. An image from the cross-over region is formed with the first condenser lens. The setting of this lens determines the size of the probe that can be formed. The second condenser lens either spreads the beam to form a parallel beam of electrons to illuminate of the sample or focuses it into a probe that can be used for diffraction or chemical analysis. The condenser aperture provides a means for limiting the beam current and determines the beam convergence angle which plays an important role in certain diffraction measurements and EELS analysis.²⁸

After the electrons pass through the sample they are focused by the objective lens, which also provides most of the magnification of the image, and then operating in diffraction mode the objective aperture is positioned to select the desired beams



Figure 2.2: Formation of bright- and dark-field images.

to form an image. The details of how different types of images are formed using this process are discussed below.

Similar to how the objective aperture selects part of the diffraction pattern to form an image, the selected area aperture can be used to select a region of the image to generate a diffraction pattern. With this technique it is possible to generate diffraction patterns from regions of the as small as ~ 100 nm in diameter.²⁸ Diffraction patterns from even more localized regions, even less than 1 nm in diameter, can be generated by using a technique known as nanobeam diffraction.³⁶ This is done by inserting a small condenser aperture and adjusting the condenser lenses to form a narrow beam of parallel illumination. The intermediate lens is used to select between displaying an image or diffraction pattern. While a single intermediate lens is shown in Figure 2.1 in practice several lenses are used Finally, the projector lens is used as a final magnification step and to set the camera length which determines the separation of the spots in a diffraction pattern. It also plays an important role in STEM imaging where it can be used to vary the collection conditions for ADF and EELS. The type of image formed depends on the placement of the objective aperture. In practice this is accomplished by generating a diffraction pattern on the viewing screen and inserting the objective aperture to select the desired portion of the pattern. If only the direct beam (the most intense beam) is selected a bright-field image is formed, alternatively a diffracted beam can be selected to form a dark-field image as is illustrated in Figure 2.2(a) and Figure. 2.2(b) respectively. This approach is not considered the optimal way of forming a dark-field image because it involves forming an image with electrons off the optical axis of the microscope leading to distortions due to spherical aberration.²⁸ The solution to this is to tilt the electron beam using deflection coils near the gun (not shown in Figure 2.1) causing the diffraction pattern to shift and positioning the desired diffracted beam on the optical axis for imaging as shown in Figure 2.2(c) thus avoiding the issues with spherical aberration.

So far the imaging methods discussed have all been based on diffraction contrast using a single beam. In contrast, high resolution TEM (HRTEM) images are formed by orienting the sample to a high symmetry zone axis and selecting multiple beams with the objective aperture. This results in images formed by the relative phase differences of the beams that are related to the crystal structure of the sample. An example of this process is illustrated in Figure 2.3. Figure 2.3(a) shows an experimentally recorded HRTEM image and Figure 2.3(b) shows the fast Fourier transform (FFT) of Figure 2.3(a). The FFT can be thought of as a diffraction pattern calculated from the image rather than being experimentally recorded. The position of the objective aperture used to form the images is illustrated by the red circle in Figure 2.3(b). By filtering the image to only include specific spots and then taking the inverse FFT it is possible to see how the individual components contribute to the final image. Figure 2.3(c) shows an image formed only from the spots marked by yellow squares in Figure 2.3(b), and similarly the image in Figure



Figure 2.3: HRTEM image formation. The red circle in (b) marks the position of the objective aperture. Images (c) and (d) are made by selecting sets of spots from (b).

2.3(d) was formed by using only the spots marked by blue triangles. The result in both cases is a series of fringes that run perpendicular to a line drawn between the two spots. Images such as these can be particularly useful in identifying dislocations such as the one marked in Figure 2.3(c).

When an image is formed using both sets of spots the fringes interfere to produce what appear to be atomic columns as is seen in Figure 2.4(a). As more spots are included, the resolution of the image increases, and when all of the spots



Figure 2.4: Images formed using multiple diffraction spots.

are included the result is shown in Figure 2.4(b).

It must be emphasized that HRTEM images such as the one shown in Figure 2.3(a) are not direct images of the crystal lattice, only related to it. An example of this is the question: are the atomic columns are represented by the bright or dark spots in the image? To answer this we look at the objective lens transfer function²⁸ $T(\mathbf{u})$ which can be written as

$$T(\mathbf{u}) = A(\mathbf{u}) \exp\left(-i\chi(\mathbf{u})\right) \tag{2.1}$$

In this expression A describes the objective aperture and is 1 for $0 < \mathbf{u} < \mathbf{u}_{\max}$ and 0 for $\mathbf{u} > \mathbf{u}_{\max}$. The phase shift χ of a reciprocal lattice vector \mathbf{u} can be written as a function of the defocus Δf , spherical aberration C_s , and electron wavelength λ as

$$\chi(\mathbf{u}) = \pi \Delta f |\mathbf{u}|^2 + \frac{1}{2} \pi C_s \lambda^3 |\mathbf{u}|^4$$
(2.2)

When T is negative the atomic columns appear as the darker areas and when it is positive the columns appear as the lighter areas. However, note the oscillatory dependence of T in Equation 2.1 on χ , and note that χ depends on the focus setting Δf in Equation 2.2. Thus by simply adjusting the focus setting the contrast in the



Figure 2.5: Simulated images of Si_3N_4 with different thicknesses and focus conditions.

image will reverse making the final result dependent on both the specimen and the microscope. An excellent example of the dependence on the focus conditions as well as sample thickness can be seen in Figure 2.5 which shows an array of simulated images of Si_3N_4 at different thicknesses/focus conditions.³⁷



Figure 2.6: Comparison of CTEM and STEM illustrating the principle of reciprocity.

2.4 Scanning Transmission Electron Microscopy

The configuration of a STEM is very similar to that of a CTEM. However now instead of illuminating the sample with a broad parallel beam, the electrons are now focused into a small probe that is scanned across the sample. As the probe is scanned, various detectors record the measured intensity which is then combined with the position of the probe to form an image. The main hardware differences between a STEM and CTEM are the addition of a set of scan coils to control the position of the beam and the placement of the objective lens between the source and sample rather than between the sample and detector as in a CTEM. The similarities between the two designs are illustrated in Figure 2.6.³⁸

Electrons that are used to form bright field images only experience elastic scattering and thus their energy is conserved which in turns implies the path of the electrons is time reversible. This is known as the principle of reciprocity. This argument shows that the pre-specimen optics of the STEM are equivalent to the post-specimen optics of the CTEM but now points in the CTEM detector plane are now replaced with electron sources and the STEM source is replaced with a detector. This powerful argument allows many results that had been obtained for CTEM to be directly applied to STEM.³⁸

Unfortunately, this also means the same issues that plague HRTEM will also be encountered in bright-field STEM images. If instead of forming an image using these electrons that have stayed close to the optical axis, an annular detector can be used to detect only electrons that have been scattered to larger angles than can be achieved by diffraction by either thermal diffuse scattering arising from interactions with phonons or by Rutherford scattering. This approach is known as annular dark-field (ADF) imaging and provides an incoherent imaging technique that can avoid the issues of bright field images. The requirements for incoherent imaging are satisfied if the inner collection angle is three times the convergence angle (defined by the condenser aperture) and covering an angular width of at least 50 mrad. In practice the inner and outer collection angles can be varied by adjusting the projector lens. These conditions are called high-angle annular dark-field (HAADF) imaging, in which the observe intensity scales as $\sim Z^{\nu}$, where Z is the atomic number and ν is in the range of 1.6–1.9 depending on the specific configuration of the microscope.³⁹ The relationship to the atomic number of the elements present makes HAADF images particularly useful as it allows chemical as well as structural information to be obtained.



Figure 2.7: Illustration of inelastic scattering in carbon.

2.5 Energy Dispersive X-ray Spectroscopy

When the electron beam interacts with the atoms in the sample there is a chance that the electrons scatter inelastically causing a core shell electron to be ejected as is illustrated in Figure 2.7.³¹ X-rays can be created when a valence shell electron fills the hole created by the electron beam. These X-rays are then collected by a silicon detector. When the X-ray hits the detector it produces a number of electron-hole pairs that depends on the energy of the incident X-ray. The detector is biased to separate the electrons and holes and collect the electrons at an amplifier creating electrical pulses. Pulse processing electronics then bin by energy and count the detected pulses.³¹

In practice, EDS tends to be relatively simple to use for qualitative analysis with there being minimal restrictions on sample thickness (thicker samples can generate a stronger X-ray signal at the cost of spatial resolution) and prior knowledge of the elements present. The main drawback to this technique is the low collection efficiency of the detector. This is due to the X-rays being emitted isotropically and the active area of the detector only being able to cover a limited solid angle meaning the majority of the X-rays go uncollected. There are also issues with where exactly the X-rays are coming from as they can be generated by electrons as they scatter around the microscope after they have hit the sample. It is very common to see a strong Cu signal from the support grid and even signals from other components within the microscope can be detected. Furthermore, X-rays generated within the sample can cause the fluorescence of other X-rays of lower energy from different parts of the sample. Additional spectral artifacts can occur including sum peaks when two X-rays hit the detector in a short enough time interval that they cannot be discriminated and escape peaks that occur when an X-ray causes the creation of a Si X-ray from the detector causing the incident X-ray to appear to have an energy 1.7 keV (the energy of a Si K shell X-ray) less than it actually does. EDS also suffers from a relatively poor energy resolution, typically around 125 eV at best.³¹

2.6 Electron Energy Loss Spectroscopy

An alternative to measuring the energy of the X-rays is to measure the energy of the electrons in the beam after they have undergone inelastic scattering and then knowing their initial energy from the accelerating voltage calculate the amount of energy lost in the collision. This is the basis for EELS. An example of an EELS spectrometer setup is shown in Figure 2.8.⁴⁰ After passing the specimen, the electrons pass through an entrance aperture and into the EELS spectrometer. The spectrometer works by creating a magnetic field of strength B perpendicular to the beam which by the Lorentz force causes the electrons to deflect with a radius of curvature of

$$R = (\gamma m_0 / eB)v \tag{2.3}$$



Figure 2.8: Diagram of a STEM equipped with an EELS spectrometer.

where γ is the relativistic factor $1/\sqrt{1-v^2/c^2}$, m_0 the rest mass of the electron, e the charge of the electron, and v the electron's velocity. Electrons that have undergone inelastic scattering will have a different v and thus a different R by Equation 2.3. The separated electrons are focused on to a CCD screen where they are recorded and converted to an energy spectrum. This configuration where all the electrons are collected simultaneously is sometimes referred to as parallel EELS or PEELS in contrast to older spectrometers that were based on sweeping a photomultiplier tube to record each energy loss channel serially. Since the the electrons remain close to the optical axis the collection efficiency is much higher than EDS and the signal comes from a more localized area as there is no signal from scattered electrons or fluorescence issues.³²



Figure 2.9: Different regions of an EELS spectrum.

An EELS spectrum can broadly be divided into three distinct regions which are illustrated in Figure 2.9.⁴⁰ In sufficiently thin samples, the most intense peak occurs at 0 eV and is the so called zero-loss peak and represents the electrons that have passed through the sample only experiencing elastic scattering. The width of this peak is determined by the emission characteristics of the electron source, and provides information about the energy resolution and limits the lower bound of energy losses that can be observed. The energy resolution can be improved by filtering the electrons from the source through a monochromator at the cost of reduced beam intensity and thus lower count rates and longer collection times.

The next region of the spectrum extending from the zero-loss peak out to about 100 eV is referred to as the low-loss region and is the result of plasmons, which are collective oscillations of the valence electrons. The relative intensities of the low-loss and zero-loss peaks can be used to measure the thickness of a region of the sample relative to the mean free path of electrons in the material. This is important



Figure 2.10: EELS spectra obtained from different forms of carbon.

because having a very thin sample is critical for accurate analysis by EELS and this provides a quick check to see if a region is suitable for analysis.

Finally, at higher energies core-loss features are observed. These transitions are caused by the inelastic scattering from the core shell electrons similar to EDS. However, in EELS the significantly higher energy resolutions allows for much more information to be extracted from the first ~30 eV, which is referred to as the energy loss near edge structure (ELNES), and is determined by the density of unoccupied states. This relationship to the electronic structure of the material makes the technique highly sensitive to the local bonding environment and shifts in peak position or intensity can indicate differences in chemical bonding.⁴¹ An example of ELNES is seen in Figure 2.10 where three spectra obtained from diamond, amorphous carbon, and a mixture of diamond and non-diamond carbon are shown. The top spectrum in blue was obtained from a sample of amorphous carbon deposited by thermal evaporation. The left most peak at 285 eV is characteristic of sp² bonds from a 1s to π^* transition, while the broader peak between 290 and 315

eV is attributed to 1s to σ^* transitions.⁴² The diamond spectrum, collected from a CVD diamond film (bottom, black), shows no peak at 285 eV indicating the material is completely sp³ bonded. It is also observed that the single peak between 290-315 eV in the amorphous carbon sample has now separated into three peaks. Finally, the middle spectrum in red is from a region of diamond like carbon where the sp² peak at 285 eV indicates non-diamond carbon, but the region between 290-315 eV can be seen to have separated into three peaks, similar to the diamond spectrum.

From this discussion it is clear that EELS has several advantages over EDS, however it also has some significant drawbacks. Samples must be extremely thin as to avoid issues from multiple scattering. The different regions (zero-loss, low-loss, and core-loss) have significantly different intensities as is shown in Figure 2.9 which makes it difficult to record signals from different regions simultaneously without damaging the detector by exposing it to an intense electron beam for too long. It is also difficult to collect a spectrum over a large energy range due to the limited number of channels of the detector and the aperture to the spectrometer must be adjusted to maximize the signal to noise ratio for different regions.

3. STRUCTURE OF DIAMOND-SILICON INTERFACES

3.1 Introduction

This chapter discusses the structure and composition of the interface of diamond thin films deposited on Si substrates by chemical vapor deposition using atomic resolution electron microscopy, and EELS. The latter technique allows the analysis of the relative Si to C composition as well as the nature of the bonding to determine the relative sp^2/sp^3 content of the diamond film. Results show considerable intermixing of silicon and carbon across an interfacial region 3 nm thick, which corresponds with an amorphous region. This region also contains the highest concentration of sp^2 bonded C. To perform this analysis a novel method of producing diamond TEM samples was developed which combines standard FIB techniques and removal of surface damage by thermal decomposition at 350 °C.

3.2 TEM Sample Preparation

To perform an accurate analysis using STEM techniques, it is imperative to have a high-quality sample. Specifically, EELS analysis requires the sample to be very thin; even thinner than what is necessary for electron transparency. The thickness of the sample can be estimated using spectra from the low-loss region. For accurate measurements, the sample thickness should be less than 1 and more ideally between 0.2 and 0.5 times the mean free path of electrons in the material.

For carbon, a sample with electron transparent areas of approximately 5 μ m wide by 3 μ m deep meet these requirements and can be produced using standard focused ion beam (FIB) milling techniques, with a Ga ion beam. Several studies have been conducted on diamond using EELS, but all have relied on standard mechanical polishing methods that are highly destructive.⁴³ Preparation by FIB



Figure 3.1: Sample damage caused by low energy ion milling during final polishing. The red box marks the transition from smooth to roughened diamond.

minimizes the damage caused during the sample preparation and allows the sample to be taken from a specific region. To our knowledge this is the first report of preparing diamond samples by FIB that meet the requirements for study by EELS.

The process for preparing samples is based off methods that have been described elsewhere.⁴⁴ In brief, the process involves first depositing a protective layer of platinum in situ using a gas injection system. The first 100 nm of Pt is deposited using the electron beam to protect the sample's surface. An additional 1.5-2 μ m is then deposited using the ion beam to protect the sample through the thinning process. After the protective layer is deposited, trenches are milled on both sides of the region of interest. The bottom and sides of the sample are then milled and the sample is attached to a tungsten needle for extraction. The sample is then attached to a grid for final thinning. Final thinning involves milling the sample at an angle relative to the top of the sample starting at a higher angle and then gradually reducing it as the sample becomes thinner. For diamond, it has been experimentally found that it is best to start at 4 degrees and finish at 1 degree.
It is well known that sample preparation by FIB can leave a damaged surface layer.⁴⁵ This layer would appear as non-diamond carbon in EELS analysis, which would have a substantial impact on the interpretation of the results. Typically, this layer is removed by performing final polishing steps using lower accelerating voltages at a high angle of incidence. However, with diamond the strong interatomic bonds result in a low sputtering yield at these lower accelerating voltages which can lead to uneven milling of the sample surface. An extreme example of this is seen in Figure 3.1, which shows a high-angle annular darkfield STEM image collected during sample preparation using a FEI Helios Nanolab 400 operating at 30 kV. The sample has undergone several minutes of polishing at 5 kV, much longer than is typically used, and incomplete removal of the material has roughened the sample's surface. In the region marked by the red box, the upper half of the diamond appears smooth. Around the middle of box vertical striations begin to appear parallel to the direction of the ion milling, and indicated incomplete removal of the material during the milling. These strictions become more pronounced moving towards the bottom of the marked region, and can be seen to extend laterally across the sample.

Even with careful sample preparation, using the standard techniques a residual amount of sp² carbon can be detected in the sample as shown in Figure 3.2. The data presented in Figure 3.2 shows the percentage of sp² bonded C calculated by the method described by Bruley⁴² (a sample of amorphous C prepared by thermal evaporation was used as the sp² reference) through a 1 μ m thick diamond film beginning at the Si substrate interface. There is elevated sp² content in the first 50 nm of the film, then the sp² content drops to a near constant value around 20% through the rest of the film thickness. If this is truly representative of the material, then this would have substantial implications on the thermal conductivity and TBR. However, from this data alone we cannot determine if the elevated sp² content away from the interface is representative of the as grown material or an



Figure 3.2: sp^2 content measured from a sample prepared by focused ion beam milling. artifact caused by the damage to the sample's milled surfaces during preparation.

The thickness of the damage layer was estimated by using the implantation depth of the Ga in the diamond obtained from Monte Carlo simulations performed using SRIM 2013.⁴⁶ For 30 kV Ga ions at an angle of 1 degree relative to the top of the sample, conditions typically employed in the preparation of the sample, results in an implantation depth of 7 nm. For a sample 60 nm thick, and recognizing that the ion beam damage occurs on both sides of the sample, this means the damaged region accounts for approximately 23% of the volume probed. Assuming a mean free path of 112 nm for 200 kV electrons in diamond,⁴⁷ 60 nm is consistent with the measured thickness of the studied samples, including the sample shown in Figure 3.2. It would therefore be useful to find a means to remove this damage layer that does not rely on ion milling. Two such techniques have been investigated: exposing the sample to an oxygen plasma and a thermal cleaning method.

In the oxygen plasma method, samples were prepared using the method



Figure 3.3: BF TEM image of sample after exposure to oxygen plasma.

described above and then placed into a Plasma Etch PE 50 Series plasma system. The pressure in the chamber was maintained at 150 mTorr with the time and RF power employed as experimental variables. The bottom two spectra in Figure 2.10 show the results of EELS measurements before and after the cleaning taken at identical locations on the sample, i.e. the same distance from the diamond/silicon interface. In the post treatment spectrum, the sp² peak at 285 eV is no longer detected confirming that damage from the ion milling was responsible for the elevated sp² content seen in Figure 3.2. However, this sample was also observed to have thinned significantly, which suggests that this is an aggressive method of polishing. Thus, the drawback is that it significantly degrades the surface of the sample thereby roughening the surface. Exposing a sample to an oxygen plasma for 30 s per side with the RF power set to 5 W (the gentlest conditions that could be employed) resulted in nanoscale roughening of the sample. Figure 3.3 shows a bright field TEM image collected using a JEOL 1200EX-II operating at 120 kV.

The speckled contrast throughout the diamond thin film indicates roughening of the ion milled surfaces. This sample roughening is unacceptable as it obscures crystallographic features of interest thereby making EELS measurements difficult to correlate to crystal defects and thin film regions of interest. To avoid such damage to the sample we have developed a thermal cleaning method. This method was adapted from a process that had been developed to reduce the sp^2 content of nanodiamond powder.⁴⁸ Following thinning to electron transparency, the sample is heated to 350 °C for 30 minutes on a hot plate in air. This temperature is not sufficient to decompose diamond but will cause nondiamond carbon to react with oxygen. As observed in Figure 3.4 there is no visible speckling, in contrast to the sample cleaned using the oxygen plasma seen in Figure 3.3. The process employed to produce the sample for Figure 3.4 utilized a 60 minute anneal and indicates that there is no diamond degradation, even under prolonged subjection to the annealing environment. Further studies indicated heating for 30 minutes was sufficient to remove the damage layer but not so aggressive as to completely remove all sp^2 bonded carbon so that we can accurately study the composition of these materials.

3.3 Interface Study

Figure 3.5 shows a high resolution bright field STEM image of the diamond silicon interface collected using a JEOL ARM 200F operating at 200 kV. EELS spectra were collected using a Gatan GIF Tridiem spectrometer. The silicon substrate, at the bottom of the image, is aligned to the [110] zone axis. The crystalline silicon transitions into an amorphous region 1-3 nm thick. Above this transition region the polycrystalline diamond film is observed. On the right-hand side, and within the diamond film, additional lattice planes are observed. The spacing of these planes is consistent with diamond (111). From the diffraction pattern calculated from the image using a Fourier transform, all crystal orientations



Figure 3.4: BF TEM image after sample was heated to 350 °C for 1 hour.

can be attributed to either Si or diamond with no evidence of SiC phases in this sample.

To study the composition of the interface EELS spectrum images were analyzed. With this technique, a full EELS spectrum is collected at each pixel in the image. Then for each pixel the background is subtracted and the signal integrated under each peak to create an elemental map. Maps of Si and C obtained from the Figure 3.5 sample are shown in Figure 3.6 with lighter regions indicating a higher concentration of the element mapped. These images show a 50 nm by 50 nm area that was scanned in 1 nm steps using an electron beam nominally ~ 1.5 Å in diameter. From these EELS spectrum images, an abrupt transition from the silicon substrate to the deposited diamond is identified. Since a full spectrum was collected at each pixel, it is possible to gain further insight into the chemistry of the interface. Figure 3.7(a) shows a series of spectra extracted from across the diamond-silicon interface region with the background signal removed by power law subtraction.



Figure 3.5: High resolution BF STEM image of the diamond-Si interface showing Si (bottom), interfacial layer, and diamond (top).



Figure 3.6: 50 nm x 50 nm EELS spectrum images mapping Si (a) and C (b) across the interface. Lighter regions indicate a higher concentration of the element.

Each spectrum is the average of 10 lateral pixels to reduce noise and each are separated vertically by 1 nm. The bottom, black spectrum of Figure 3.7(a) is representative of the Si $L_{2,3}$ edge (taken in the Si, away from the interface), with the vertical line marking its onset. In the next spectrum, shown in red, the sharp peak

near the onset has vanished and there is distortion around 285 eV where the C K edge begins. In the next two spectra, shown in blue and green, the onset of the edge has clearly shifted to a higher energy. Shifts such as this are caused by changes in chemical bonding. In the blue spectra, there is a C edge, and in the green, there is a significant reduction in the intensity of the Si edge relative to the C edge. These spectra indicate the high sensitivity of EELS to spatial variation in the chemical characteristics of the diamond-silicon interface region. Finally, in the purple spectrum of Figure 3.7(a), a new peak is observed. The onset of this peak has shifted from 100 eV to 80 eV. This is too large of a shift in the position of the peak to be the result of a chemical shift, and furthermore this peak is narrower than the Si peak (black spectrum) indicating that it is not the Si peak. We attribute this peak to a third order plasmon. Plasmon peaks are the result of energy losses from interactions with valance electrons, rather than the core electrons that are the source of the other peaks that have been discussed. Plasmon peaks occur at integer multiples of an energy that is characteristic to a material. For diamond this peak occurs at 34 eV so a peak at approximately 100 eV would be consistent with three times this value.

In Figure 3.7(b), we see a detailed view of the carbon edges seen in Figure 3.7(a). The graphs have been offset vertically for clarity, and the horizontal region at the left of each graph marks the zero-intensity reference point after background subtraction. There is an increase in the maximum intensity of the C edge from the bottom spectrum to the top. The concentration of an element is related to the integrated intensity of its peak, so this increase in intensity indicates increasing carbon content. The bottom spectrum shows sp² content but the full spectrum (Figure 3.7(a)) shows there is still a significant Si content. This spectrum is likely from the transition region seen in Figure 3.5 since the transition from Si to diamond occurs over 3 nm which is consistent with the thickness of this amorphous region.



Figure 3.7: EELS spectra across interface showing both Si and C (a) and detailed view of the C edges (b). Each spectrum is separated spatially by 1 nm.

This suggests what the sp^2 content is due to an interaction with the substrate rather than poor quality diamond being deposited at the beginning of the growth. In the middle spectrum, the features of the C edge show no evidence of sp^2 bonded carbon despite there still being a detectable amount of Si. This indicates the quality of the diamond is quite good even near the interface.

The overlap of the diamond plasmon peak and Si $L_{2,3}$ edge limits the ability to detect Si in the diamond. EDS measurements (not shown) also show a 2-3 nm transition region, confirming the EELS results, with no further mixing of Si in the diamond or C in the Si. This indicates any further diffusion that may be occurring is below the detection limits of these techniques. In other samples, this transition region has not been observed, even after heating to 350 °C for 75 minutes, indicating its presence is a result of the diamond growth and not an artifact of sample preparation. Analysis is ongoing and future publications are anticipated. Since there is no detectable mixing in the Si or diamond and the thermal polishing is not responsible for the amorphous interface, we conclude that the thermal polishing does not significantly alter the sample.

3.4 Summary and Conclusions

We have shown that high quality TEM samples of CVD diamond films for analysis by EELS can be prepared using FIB milling. Additional sample preparation steps are required to remove the damage layer formed on the surface of the sample during milling to accurately measure the sp² content of the diamond. We have investigated two techniques: (1) using an oxygen plasma and (2) using thermal decomposition to remove this damage layer. The oxygen plasma damages the surface of the sample, but heating the sample to 350 °C is effective at removing the damaged layer with minimal to no degradation of the sample. With the artifacts of the sample preparation removed, we observe minimal sp² content, even near the diamond nucleation region. There is a region approximately 3 nm wide near the interface that shows elevated sp² content, however Si is also present in this region indicating that it is the result of an interaction with the substrate rather than due to poor quality diamond in the initial growth.

4. FILAMENT CONTAMINATION IN HFCVD DIAMOND

4.1 Introduction

Hot filament CVD (HFCVD) is a particularly attractive approach for growing diamond films because of the lower equipment costs compared to microwave plasma systems. However, the design of HFCVD reactors creates the possibility that material from the filaments can be incorporated into the films. The work presented in this chapter explores the results of this contamination in the diamond and Si substrate and provides an interesting contrast to the results obtained in the previous chapter where the diamond films were deposited in a microwave plasma reactor.

Previous work has detected filament material in diamond films using SIMS⁴⁹ and RBS^{50,51} but these techniques lack the spatial resolution to understand the distribution of the material in the diamond. A detailed evaluation of any contamination in the diamond is vital to understanding its thermal transport properties because even parts-per-million levels of impurities have been shown to significantly reduce the thermal conductivity.⁵²

4.2 Experimental Methods

Diamond films ~1.5 μ m thick diamond films were deposited on 100 mm [100] Si wafers seeded with diamond nanoparticles using a mixture of 1.5 % and 3% methane balanced with hydrogen. The heater assembly consists of an array of 9 commercial grade W filaments measuring 0.25 mm in diameter spaced ~1 cm apart and heated using a DC power supply set to 6 kW. The wafer was placed on a rotating, water-cooled stage 6 mm below the heater wires. Lamellas were prepared by focused ion beam milling using a FEI Helios Nanolab 400 operated at 5-30 kV and then heated in air to remove surface damage on the diamond.²⁶ High-angle annular



Figure 4.1: HAADF image of filament contamination in diamond (a) and EDS spectrum collected from the region (b).

dark-field scanning transmission electron microscopy (HAADF-STEM) images and energy dispersive x-ray spectroscopy (EDS) spectra were collected using a JEOL ARM 200F operating at 200 kV. Additional EDS spectra were collected from an unused filament wire by SEM using a JEOL 6010 PLUS/LA operating at 8 kV.

4.3 Results and Discussion

Figure 4.1(a) is a HAADF-STEM image collected from the diamond. In this image we can see bright dots measuring ~ 1.5 nm in diameter distributed throughout the field of view. In addition to these dots, on a larger scale, more diffuse regions of lower intensity are also observed. An EDS spectrum collected from the diamond is shown in Figure 4.1(b), and identifies Al, Cr, Fe, and W (the Ga and Cu peaks are attributed to the sample preparation and the support grid, respectively) in the diamond.

A larger concentration of the deposited material is found to accumulate at the diamond-Si interface as shown in the HAADF-STEM image in Figure 4.2(a) where



Figure 4.2: HAADF images of the diamond-Si interface grown at 1.5% methane (a) and EDS spectrum collected from the region (b).

the filament material appears as a bright region 10 nm thick layer between the two. Analysis of this region by EDS in Figure 4.2(b) shows a distinct composition compared to the diamond. The Fe and W signals have increased while the Cr has decreased. Al can still be detected but now overlaps with a W peak, but a distinct splitting can be seen upon close inspection. EDS scans from the filament wire confirm the origin of the impurities observed in the film. Scanning individual points indicated that the wires were mostly free from impurities, however, localized regions showed high impurity concentrations. The spectrum from one such region is shown in Figure 4.3. We see clear peaks for Al and Ca which were identified in the interfacial region and a Fe peak could also be detected. Na was also identified as being present on the wire but was not observed in the film. No Cr was identified in these scans. However, due to the sporadic distribution of the impurities it is possible that none was present in any of the regions scanned.

The distribution of the filament material at the interface was observed to change significantly when the methane percentage was increased to 3%. In contrast to the



Figure 4.3: EDS spectrum collected from an unused filament wire.

continuous layer of material accumulated at the interface of the sample grown at 1.5%, the filament material at the interface of the 3% sample shown in Figure 4.4 is more dispersed with the largest concentration of the material is confined to a ~ 4 nm region near the interface with individual particles being seen to extend into the diamond layer.

The difference in the accumulation of material at the interface is attributed to the difference in growth rates of the diamond. As the overall growth rate of the 1.5% sample was much slower than the 3% sample, it is reasonable that the initiation of growth on the diamond seeds was slower as well giving the filament material more time to form as a distinct layer whereas with the 3% sample the faster initiation of diamond growth leads to a situation where the diamond and filament material are being co-deposited resulting in the material being more



Figure 4.4: HAADF images of the diamond-Si interface grown at 3% methane

dispersed. Despite the differences in the accumulation of material at the interface, in both samples bright regions can be seen to extend into the Si indicating that the metal species from the filament have diffused into the substrate. This is most clearly seen in the region marked by the arrow in Figure 4.4.

In both images shown in Figure 4.2 and Figure 4.4 the Si surface is mostly smooth. However, in other regions significant roughening of the Si has occured such as the region from the 1.5% sample shown in Figure 4.5. In addition to the roughening of the Si in Figure 4.5, a large inclusion is seen to have been incorporated and completely surrounded by the substrate. High resolution HAADF images of the substrate and inclusion shown in Figures 4.6(a) and (b). These images show that the inclusion has a completely different crystal structure compared to the substrate as is highlighted by the difference in the Fourier transforms of the images shown as insets in the bottom right corner of the images.

Further analysis of the interfacial region by EDS offers further insight into the



Figure 4.5: Substrate surface roughening and metal inclusion in the Si.

mechanism of the impurity incorporation. EDS scans comparing the material at the interface, diffused into the substrate, and the substrate below where the diffusion was observed are shown in Figure 4.7(a) and a detail view of the lower energies is



Figure 4.6: High resolution HAADF images comparing Si and inclusion.



Figure 4.7: EDS spectra collected from different regions near the interface (a) and detailed views of the lower energy portion of the spectra (b).

shown in Figure 4.7(b). From Figure 4.7(a) it is clear that the material at the interface is primarily composed of W while the inclusion is mostly composed of Fe and Cr. Again, the Cu signal is attributed to the support grid the lamella is attached to. From Figure 4.7(b) it is clear that there is a significant amount of Al in all three regions. The presence of Al offers a potential mechanism for the impurity incorporation into the Si. Due to the similarity in atomic number of Al (Z=13) and Si (Z=14) it would be difficult to identify where Al has diffused into Si using HAADF images. But if the other elements were incorporating purely by diffusion, the brighter region would extend to the surface indicating another mechanism for incorporating the impurities is at play.

From the Al-Si phase diagram, incorporation of Al can significantly lower the melting temperature of Si by forming a eutectic and melting at 570 °C, a temperature well below the substrate temperature of 700 °C measured by pyrometer during growth. The molten Al-Si would allow impurities with higher melting temperatures to sink into the substrate. As the Al continues to diffuse into the substrate, the concentration decreases increasing the melting point of the Si

allowing it to re-crystalize. This process would also explain the roughening of the Si surface. Fe and Cr have melting points of 1,538 °C and 1,907 °C, 53 both of which are substantially lower than the ~2,400 °C of the C-W eutectic that is responsible of the W incorporation.⁵⁴ This suggests the Fe and Cr melt on the wire before diamond deposition begins and by the time the C-W eutectic begins to form, diamond deposition has begun and the seeds have coalesced preventing the material from reaching the substrate. The presence of Al in the diamond is also problematic because it is an effective dopant for diamond, which may alter the electronic properties of the diamond in undesirable ways depending on the application.⁵⁵

4.4 Summary and Conclusions

An understanding of the impurities in the diamond is critical to understanding the thermal and electrical properties of these films, especially when integrated with high-frequency, high-power devices. HAADF-STEM imaging provides an effective means to observe the incorporation of contamination from the filaments into both the diamond and substrate. EDS analysis identifies the contamination as a mixture of W from the filament wires and a variety of other elements identified on the surface of the filaments. Several of these elements, particularly Al and Na, are especially problematic for Si based electronic devices.

5. COMPOSITIONAL CHANGES OCCURING IN GAN-ON-DIAMOND ADHESION LAYERS

5.1 Introduction

This chapter focuses on structural changes occurring in SiN_x adhesion layers used to produce GaN-on-diamond devices have been observed using HAADF imaging combined with EELS. These changes in the adhesion layer can be attributed to the conditions present during diamond deposition and include the formation of carbon rich regions, both in the form of diamond and non-diamond carbon, along with etching of the SiN_x that can result in formation of voids in the underlying GaN. These features are difficult to observe in bright-field images that have previously been used to study the interfacial region of these structures and offer additional insight into the results obtained with Raman spectroscopy.

5.2 Experimental Methods

In this work a detailed analysis was conducted on the interfacial region of a structure consisting of a 100 μ m thick layer of polycrystalline diamond deposited by microwave-enhanced CVD on an AlGaN/GaN HEMT structure with a 40 nm SiN_x adhesion layer provided by provided by Element Six, Ltd. Previously, we have reported on differences in the stress in the GaN measured on both sides of the full 75 mm wafer^{56,57} and on the spatial variation of the non-diamond carbon (NDC) content by micro-Raman spectroscopy.⁵⁸

A lamella was prepared for cross-sectional analysis by focused ion beam (FIB) milling with a final polishing done at an accelerating voltage of 2 kV using a FEI Helios Nanolab 400. After FIB milling the sample was heated to 350 °C for 1 hour to remove any surface damage on the diamond caused by the milling.²⁶

Finally, bright-field and high-angle annular dark-field (HAADF) images collected by scanning transmission electron microscopy (STEM). Chemical analysis of the region was performed using electron energy loss spectroscopy (EELS). Both imaging and EELS analysis were done using a JEOL ARM 200F microscope operating at 200 kV equipped with a Gatan Tridiem EELS spectrometer.

5.3 Results and Discussion

A bright-field image of the interfacial region is shown in Figure 5.1(a). In this image there is very low contrast between the adhesion layer, marked by the dashed lines, and the diamond.

In this image the GaN appears clearly as the dark region at the top of the image but there is very low contrast between the adhesion layer, marked by the dashed lines, and the diamond. However, with careful inspection subtle contrast variations can be distinguished within the adhesion layer. This image is very similar to bright-field images that can be found in other works that have studied the thermal transport properties between GaN and diamond that also show similar features.^{59–62} Figure 5.1(b) is a HAADF image of the same region that was collected simultaneously with Figure 5.1(a). Here, there is much better contrast between the GaN, adhesion layer, and diamond. Figure 5.1(b) also shows that there is a more complicated structure within the adhesion layer than is readily apparent in the corresponding bright-field image. Inclusions similar to these were observed to be present across the entire electron transparent region of the sample indicating that they are not a localized phenomenon. In addition to the features in the SiN_x, a distinct interlayer region is observed between the inclusions and the diamond.

To better understand the changes occurring in the adhesion layer an EELS spectrum image was collected from the region shown in Figure 1. The EELS spectra were collected in 2 nm steps, and elemental maps formed by analyzing the C K, N



(b) HAADF

Figure 5.1: EELS elemental maps of the adhesion layer.

K, and Si $L_{2,3}$ edges are shown in Figure 5.2(a)-(c) respectively. While the EELS spectra were being collected, a HAADF image was being collected simultaneously and is shown in Figure 5.2(d). These spectra show that the inclusions on the left and right sides of the adhesion layer, marked as locations 1 and 2 in Figure 5.2(d), are composed entirely of carbon. The interlayer region can also be clearly distinguished in the elemental mapping images as having a reduced C content compared to the diamond and inclusion on the right and having a higher Si concentration compared to the SiN_x. It is also observed that there is little to no N content in this region. In the Si map shown in Figure 5.2(c), a region of lower intensity is seen at the top of







Figure 5.2: EELS elemental maps of the adhesion layer.

the image corresponding to the GaN that is clearly shown as the brightest region in the HAADF image. This is attributed to the overlap of the Ga $M_{4,5}$ and Si $L_{2,3}$ edges, rather than indicating incorporation of the Si into the GaN region.

Since a full EELS spectrum is collected at each pixel in the spectrum image, this information can be extracted to provide additional insight into what is occurring in the adhesion layer. The energy loss near edge structure (ELNES), which is the specific shape of the peak corresponding to an element in an EELS spectrum, can act as a fingerprint to provide information on the bonding configuration of that element. These features have been studied extensively in the investigation of different allotropes of carbon^{42,63} Spectra extracted from the spectrum image at

positions marked 1, 2, and 3 in Figure 5.2(d) are shown in Figure 5.3 along with spectra taken from the diamond and SiN_x regions for comparison. Here we see that there is no significant difference in the carbon ELNES from the inclusion on the left at region 1 and the bulk diamond indicating diamond has formed in the SiN_x . However, the C ELNES for the inclusion on the right at region 2 shows a structure that more closely resembles amorphous C, and the peaks at 100 eV and 400 eV indicate the presence of Si and N respectively. This shows the region is composed of a mixture of C, N, and Si. The C ELNES in the interlayer at region 3 is significantly different than that of the bulk diamond and more closely resembles that of region 2, except that the distinct peak at 285 eV that occurs due to sp^2 carbon bonding, clearly seen in the spectrum from region 2, is no longer visible. This is potentially due to a significant amount of hydrogen being present in this region. Previous studies have shown the C-H bonding leads to the appearance of a peak at 287 eV which could cause the peak at 285 eV and the peak from diamond at 290 eV to become indistinguishable.⁶⁴ The presence of Si and NDC in this region is significant because it is the result of changes to the SiNx adhesion layer, rather than the result of a large quantity of NDC being deposited along with the diamond. This NDC in the adhesion layer could also skew measurements by Raman spectroscopy, typically used to measure the NDC content of diamond films, making it appear as if the diamond has a larger NDC content than it actually does. This in turn would impact assumptions about the thermal conductivity of the diamond leading to inaccurate results in any further thermal transport modeling of the system.

A possible explanation for the cause of the deterioration of the adhesion layer comes from studies of reactive ion etching of SiN_x . Fluorocarbon plasmas have been seen to effectively etch silicon nitride, and it has been shown that introducing hydrogen can increase the etch rate.⁶⁵ These conditions, except for the presence of fluorine, are consistent with those encountered in the reaction chamber during



Figure 5.3: EELS spectra extracted from the location marked in Figure 5.2(d).

diamond deposition. In the etching process, the role of fluorine is to volatilize the Si, and its absence in the diamond growth process could lead to Si remaining, while the N is being removed, forming the Si-C interlayer. It could further interact with pinholes in the SiN_x to form cavities that allow diamond to grow in the SiN_x such as was seen in the inclusions in Figure 5.1.

In several samples, including samples taken from different regions of the original wafer, voids such as the one shown in Figure 5.4 were observed. The void is shown as the dark, triangular region in the center of the image. The void penetrates approximately 100 nm into the GaN, shown as the lighter region in the top half of the image, and is nearly a quarter of the total thickness of the layer. Additional dark regions seen as the line extending from the void to the left side of the image, and the darker region below the void extending in to the diamond in the bottom half of the image are attributed to the sample preparation. The remaining SiN_x has been outlined in red, and in the central region directly underneath the void the SiN_x is seen to have been completely removed. This suggests that the formation of voids such as this are another consequence of the etching process of the SiN_x . Studies have shown that GaN decomposes readily in high temperature, hydrogen rich



Figure 5.4: Void formed in the GaN as a result of adhesion layer etching.

environments such as the conditions used for diamond growth.^{[66} As the diamond begins to grow and coalesces it protects the GaN from further etching. Voids such as this would substantially reduce the conduction of heat from the device layers to the diamond and would compromise the structural integrity of the wafer making it prone to breakage during subsequent device processing. The voids also offer another possible explanation of the difference in stresses measured in the GaN on the free GaN surface and on the GaN/diamond interface side of the original wafer by Raman spectroscopy.^{56,57} This suggests that these measurements could potentially be used as a nondestructive way to check for damage of the GaN after diamond deposition.

5.4 Summary and Conclusions

In summary, we have observed significant changes throughout the SiN_x adhesion layer after diamond deposition as a result of exposure to the diamond growth environment. These changes include the formation of a Si-C interlayer between the adhesion layer and diamond as well as the formation of diamond and NDC regions within the adhesion layer. These features are clearly visible in HAADF images and in chemical analysis by EELS, but are not readily apparent in bright-field images typically shown in previous studies of the GaN-diamond interface. We have also observed the formation of large voids in the GaN in regions the SiN_x has been completely removed. These results highlight the importance of the adhesion layer as a protective layer of the underlying GaN as these voids would significantly compromise the mechanical stability and thermal transport properties of the material. An understanding of all of these features is critical to accurately understanding the thermal transport in these structures.

6. CHARACTERIZATION OF GAN OVERGROWTH OF DIAMOND

6.1 Introduction

As seen in the previous chapter, the random variations in the SiN_x can make it difficult to accurately predict the thermal transport properties from different regions of a single wafer, much less from regions on different wafers. This variation coupled with the intrinsically low thermal conductivity of SiN_x makes it highly desirable to remove or replace this layer. Recently, a novel method for creating GaN-on-diamond structures has been demonstrated that combines selected area diamond growth⁶⁷ and epitaxial lateral overgrowth of GaN.⁶⁸ This chapter presents a detailed analysis of the crystallographic relationship between the GaN and diamond as well as the chemical composition of the interfacial region.

6.2 Experimental Methods

The structure analyzed in this work was formed by growing GaN on a Si substrate by MOCVD using standard techniques.¹⁷ A layer of SiN_x was then deposited on the GaN and the wafer is then patterned to selectively seed areas with nanodiamonds suspended in photoresist to create openings in the diamond forming diamond stripes. After diamond deposition, the remaining SiN_x in the open regions was removed by reactive ion etching once again exposing the underlying GaN. Finally, a second GaN deposition step was performed to laterally overgrow GaN over the diamond stripes.⁶⁸ An illustration of the final structure is shown in Figure 6.1. The diamond was deposited using 3% methane and the overgrown GaN was grown with a V/III ratio of 1330 at 1020 °C and 40 torr for 25 minutes. The internal run numbers for the sample analyzed in this work are diamond growth: D171122A and MOCVD growth: 1180130C.



Figure 6.1: Illustration of the diamond overgrowth structure.

From this wafer a TEM sample was prepared from a set of diamond stripes running parallel to the GaN $<10\overline{1}0>$ direction using standard FIB techniques. Conventional TEM analysis and diffraction patterns were collected using a JEOL 2010F operating at 200 kV and STEM analysis including EELS was performed on a JEOL ARM200F operating at 200 kV equipped with a Gatan Tridiem spectrometer.

6.3 Results and Discussion

A cross sectional SEM image of the region investigated in Figure 6.2. The diamond stripe is seen as the dark region in the center of the image measures 4.4 μ m in width. The overgrown GaN is seen to have not completely coalesced over the diamond leaving a void over the center of the stripe. The vertical stripe directly below the void is the result of uneven milling of the material by the FIB. The GaN has grown laterally 1.9 μ m and and vertically 5.6 μ m. A bright-field STEM image of the right half of the stripe is shown in Figure 6.3. This image shows the dislocations in the GaN making 90° turns as well as a reduction in the number of dislocations above the diamond indicating that the material was formed from lateral overgrowth. The GaN is seen to closely follow the diamond, however there are voids present such as the white region seen on the right corner of the diamond. Smaller



Figure 6.2: SEM cross section of the studied region.

voids are also present in some of the valleys between the diamond peaks. The region marked by the arrow was selected for further investigation.

HRTEM images of the region are shown in Figure 6.4. In these images the diamond is seen as the lighter region in the top left and the GaN as the darker region in the bottom right. In Figure 6.4(a) an interfacial region ~ 20 nm wide separates the two materials. At higher magnifications, periodic fringes 1 nm apart can be seen in the interfacial region. These are marked by the parallel lines in Figure 6.4(b) and are attributed to a moiré pattern formed by the overlap of the diamond and GaN crystal structures. Nanobeam diffraction patterns were collected from the diamond near the interface, the GaN directly above the interface, and the interfacial region. These results are shown in Figures 6.5(a)-(c) respectively. From Figure 6.5(a) the diamond orientation is determined to be close to the [112] zone axis. The reflections from the (111) and ($\overline{2}20$) planes are labeled in the image.



Figure 6.3: Bright-field STEM image showing lateral overgrowth.

The diffraction pattern collected from the GaN shown in Figure 6.5(b) is what would be expected from single crystal GaN oriented along the $[10\bar{1}0]$ zone axis. The diffraction pattern collected from the interface in Figure 6.5(c) shows the two previous patterns superimposed on each other. From this data we can determine the relative orientations of the crystal structures and see that the diamond [$\bar{2}20$] is rotated 6.5° from the GaN [$1\bar{2}1\bar{2}$] and diamond [$11\bar{1}$] is rotated 24.5° from the GaN [0002]. The spacing D of the moiré fringes⁶⁹ formed by two overlapping crystal lattices with lattice spacings d_1 and d_2 rotated relative to each other by an angle ϕ can be calculated using the equation

$$D = \frac{d_1 d_2}{\sqrt{d_1^2 + d_2^2 - 2d_1 d_2 \cos \phi}} \tag{6.1}$$

Using values for d_1 , d_2 , and ϕ measured from Figure 6.5(c) for the GaN (1212) and diamond (220) reflections yields a D value of 1 nm, which is consistent with the



Figure 6.4: HRTEM images of the GaN-diamond interface. Moiré fringes are marked by the parallel lines in (b).

spacing measured in Figure 6.4(b). It should be noted that similar conclusions can be drawn if the GaN is oriented along the $[10\overline{1}2]$ zone axis. It should be noted that the $[10\overline{1}0]$ and $[10\overline{1}2]$ diffraction patterns can be difficult to differentiate and additional diffraction measurements are needed to confirm the exact orientation near the interface. Further analysis of this region was conducted using high resolution HAADF-STEM images. These images shown Figure 6.6 along with their



Figure 6.5: Nanobeam diffraction patterns collected from the diamond (a), the GaN (b), and the interface (c). Contrast has been inverted for clarity.



Figure 6.6: High resolution HAADF images showing rotation of the GaN c-plane.

FFTs and show a distinct rotation of the GaN c-plane on opposite sides of the peak. The spots corresponding to the GaN c-planes are marked in Figures 6.6(b) and (d). These results suggest that the GaN has nucleated and began to grow on the diamond and that the coverage of the diamond stripe is a combination of direct growth as well as lateral overgrowth.

An EELS line scan was performed across this region as shown as marked in



Figure 6.7: EELS line scan taken across the interface.



Figure 6.8: Region showing abrupt transition between the GaN and diamond.

Figure 6.7(a). The intensity of the C K and Ga $L_{2,3}$ edges are plotted along with the HAADF intensity in Figure 6.7(b). The results in the diamond and transition regions are as expected with no detectable amount of Ga being found in the diamond, followed by a linear increase in the Ga and HAADF signals as the C signal decreases. However, in the GaN the C signal does not drop to zero indicating a substantial amount of C has been incorporated into the GaN. Further EELS



(c) Non-diamond Carbon

(d) HAADF

Figure 6.9: Elemental maps of the GaN-diamond interface.

analysis was performed in a second region that showed a more abrupt transition between the GaN and diamond shown in Figure 6.8. This region was also near a gap between the GaN and diamond shown as the dark region on the left hand side of the image. An area mapping scan was taken from the region bound by the green box and the results are shown in Figure 6.9. In these images each pixel represents a 2 nm step. The angled region seen on the right hand side of the C and N maps shown in Figures 6.9(a) and (b) respectively indicates the thickness of the transition region is 2-6 nm, significantly smaller than the ~20 nm thickness of the transition seen in the region shown in Figure 6.4. The left hand side of Figure 6.9(a) (and the corresponding darker region in 6.9(b)) once again indicates a significant amount of C has been incorporated into the GaN. Interestingly, if the peak corresponding to sp² bonded C is mapped, a large concentration of non-diamond carbon(NDC) is seen to be present in the lower left just before the onset of the gap. This suggests that it may play a role in preventing the GaN from contacting the diamond. Spectra



Figure 6.10: EELS spectra taken from across the GaN-diamond interface.

from the locations marked in 6.9(d) are plotted in Figure 6.10. These spectra show a gradual transition from the N K edge (400 eV) starting at position 1 located in the GaN to the C K edge (290 eV) at position 5 in the diamond with a significant mixing of the two elements seen at position 3. No significant shifting of the C K or N K edges is observed. Finally, the ELNES of the C K edges from the region with a large NDC content and the diamond are compared in Figure 6.11. The first peak seen in the diamond (marked by the arrow) has shifted to a lower energy by $\sim 2 \text{ eV}$ relative to the sp² bonding peak (marked with the vertical line). This lower energy peak has been attributed to the presence of nitrogen-vacancy complexes⁷⁰ that may have formed as a result of exposure to the GaN growth environment.

The direct nucleation of GaN on the diamond stripe is not surprising as GaN islands were observed to have formed on regions completely covered by diamond as seen in Figure 6.12(a), which includes several large, hexagonal regions. The exact mechanism for the formation of these regions is not clear at this time. These oriented regions are very thick as seen in 6.12(b) where the structure is 10 μ m tall.



Figure 6.11: EELS spectrum showing N-V complexes in the diamond.



Figure 6.12: SEM images of GaN growing directly on the diamond surface.



Figure 6.13: Cross section of GaN grown directly on diamond.

A relatively small island showing distinct facets shown in Figure 6.13(a) was located in this region and cross sectioned for TEM analysis. A bright-field image of the island is shown in Figure 6.13(b). In this image the diamond appears as the light band in the top left separating the original GaN (top left) from the island (bottom right). The sample was oriented relative to the island and selected area diffraction patterns were collected from both the island and the underlying GaN. The pattern from the island shown in Figure 6.14(a) shows that it is oriented along the $[10\overline{1}0]$ zone axis where as the pattern collected from the underlying GaN shown in Figure 6.14(b) shows a completely different orientation indicating that there is no alignment of the crystal orientations of the island and the underlying GaN indicating the region was not formed by lateral overgrowth.

6.4 Summary and Conclusions

In summary the overgrowth of the diamond stripes is determined to be a combination of lateral overgrowth and direct nucleation. It will be important to take both modes into account when optimizing the process to maximize the lateral


Figure 6.14: Selected area diffraction patterns collected from the island (a) and underlying GaN (b).

growth to completely cover the diamond stripe while minimizing the vertical growth the keep the active region of the any device fabricated on these structures as close as possible to the diamond to maximize the heat dissipation. The orientation of the GaN relative to the diamond may also be problematic for very thin GaN layers because if the growth is along a non-polar orientation it will not be possible to take advantage of the piezoelectric properties of the GaN to form the 2DEG. From these results it is not clear what, if any, impact the roughness of the diamond has on the orientation of the GaN.

The direct growth of GaN on diamond raises an interesting question: why can GaN grow on diamond but diamond will not adhere to GaN? The answer likely lies in the formation of the carbon nitride layer formed at the interface when GaN is deposited on diamond. The formation of this layer is possibly related to the decomposition of the organometallic precursors, in this case trimethylgallium (TMG). The growth conditions for GaN are similar to those for diamond so it is likely that the methyl groups in the TMG can interact with the diamond surface in a similar way to the methane in diamond deposition.

The incorporation of C into GaN and N into the diamond can substantially alter the electrical properties of the materials. In GaN on Si, C doping has been used to increase the breakdown voltage but can also cause current collapse.⁷¹ Studies of the impact of C on have focused on doping levels of C, however the lower detection limit of EELS is on the order of 0.1% meaning the amount a C present here is several orders of magnitude higher than what has been previously studied. At these concentrations it is also possible that the thermal conductivity of the GaN is reduced similar to how it is seen to be reduced in AlGaN alloys compared to the binary compounds AlN and GaN.⁷² Finally, the incorporation of N in the grain boundaries of diamond thin films has been reported to make them conductive.⁷³ The consequences of these changes require further study to understand their potential impact on devices fabricated on these structures.

7. CONCLUSIONS AND FUTURE WORK

The unique capabilities now available at Texas State to grow both diamond and GaN creates several research opportunities to better integrate the two materials. This chapter discusses several potential avenues for future research based on the results that have been discussed.

7.1 GaN-on-Diamond

As was discussed in chapter 4, the current diamond deposition process introduces a substantial amount of impurities into the film that needs to be reduced, if not eliminated, to maximize the thermal conductivity of the diamond and eliminate questions about the growth process. Growth using low methane concentrations is necessary to minimize the non-diamond carbon content, but the thick accumulation of metal at the interface seen to occur raises questions about whether the diamond is nucleating on the diamond seeds or the evaporated metal, as diamond has been seen to grow directly on several metals including tungsten.

Reports have indicated that reducing the temperature or the filament wires can reduce the amount of filament material incorporated,⁷⁴ and from discussions with the equipment supplier many of the non-tungsten contaminants may be from surface contamination. Since W is fairly chemically inert, it may be possible to remove these contaminants by soaking the wires in hydrogen peroxide or similar metal etchant prior to deposition. Alternatively, preconditioning the wires prior to deposition may also help reduce impurities. This could be made more convenient by adding a retractable shutter to protect the substrate at the beginning of deposition. If these approaches do not work, there is also the option of switching to high purity tungsten wires to reduce contamination.

In order to better understand the direct growth of GaN on diamond it would be

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desirable to produce smooth diamond films with at least a preferred crystal orientation. Preliminary results have shown that diamond appears to grow epitaxially on cubic BN particles, thus depositing GaN on diamond grown on cubic BN may be a way to expedite this investigation. It may also be possible to vary the initial conditions of the GaN deposition to either promote or inhibit the deposition on diamond, which may be needed to achieve full coalescence of the laterally overgrown GaN over the diamond. This could also impact the incorporation of C in the GaN and N into the diamond– a topic that deserves its own investigation. The nucleation on the diamond may also be impacted by the organic groups used in the organometallics. Significant differences in GaN deposited on diamond may be seen if triethylgallium is used rather than trimethylgallium. It would also be beneficial to expand the studies of growth of nitrides on diamond to include AlN and high Al content AlGaN films to capitalize on the emerging interest in ultrawide band gap materials.

Finally, it remains to be seen that direct growth of GaN on diamond results in the best thermal transport. It is possible that a suitable material can be found that provides a better thermal coupling between the GaN and diamond exists. Thus, it is worth searching for potential alternatives beyond the SiN_x that has been used.

7.2 Advanced Microscopy Characterization

TEM and associated techniques will continue to play an important role in analyzing GaN-on-diamond structures by accurately measuring layer thicknesses needed for thermal simulations and evaluating the impact of diamond deposition on new adhesion layer materials. However recent developments in in-situ microscopy could significantly expand our understanding of these structures. Specialized sample holders for TEMs are now commercially available through companies such as Protochips and Hummingbird Scientific that allow experiments experiments, such as

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heating or electrically biasing samples, to be conducted within a TEM and to observe the results, even at the atomic scale, in real time. It has also been demonstrated with EELS that the plasmon peak position shifts with temperature allowing it to be used as a thermometer.⁷⁵ By combining in-situ techniques with a method of localized temperature measurement could offer an new way to measure thermal boundary resistances. Additionally, optical properties of materials can be extracted from EELS spectra through the use of Kramers-Konig relations,³² which could lead to a better understanding of time domain thermoreflectance measurements.

Due to the high cost of TEM experiments, both in money and time, it is prudent to consider a few key questions that will determine the likelihood of success of the project. First: can the desired information be acquired using other techniques? For example in the case of the thermal properties of materials, even if an interface between two materials was perfectly characterized in terms of structure and composition it is unlikely that simulations would be able to accurately model the thermal transport from first principles due to the complex nature of the system. TEM investigations will likely be most useful in cases where irregularities are seen in measurements by a different technique or there are discrepancies between different measurement techniques. This leads to the second question to ask which is: what do we expect to see? From personal experience, the results of TEM analysis are likely to be inconclusive if a concrete hypothesis has not been formulated beforehand that can be proved or disproved. Furthermore, this question will help the microscopist select the most appropriate techniques to answer the questions as accurately and efficiently as possible.

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