Investigating the Properties of h-BN on Sapphire Substrate for Rare Gas Intercalation

Thesis

Presented in Partial Fulfillment of the Requirements for the Degree Master of Science in
the Graduate School of The Ohio State University

By

Shrivatch Sankar

Graduate Program in Electrical and Computer Engineering

The Ohio State University

2023

Thesis Committee

Prof. Shamsul Arafin, Advisor

Prof. Sanjay Krishna

Abstract

Hexagonal boron nitride (h-BN) has emerged as a promising 2D material for various applications due to its exceptional properties, including high thermal and chemical stability, wide bandgap, and excellent insulating properties. One potential application of h-BN is in intercalation processes, where foreign atoms or molecules are inserted between the h-BN layers to modify their properties. In this study, we present a comprehensive characterization of h-BN for intercalation purposes using a range of techniques, including Scanning electron microscopy (SEM), Atomic Force Microscopy (AFM), Raman spectroscopy, Cathodoluminescence (CL), Photoluminescence (PL).

The Raman spectra of h-BN exhibit the characteristic E_{2g} phonon mode peak at ~1368.1 cm^{-1}, confirming the presence of h-BN. Furthermore, the cathodoluminescence spectroscopy analysis showed that h-BN has strong near-band emission around 402 nm, which indicates higher crystal quality and low defect density. Our findings suggest that h-BN is a suitable material for intercalation processes, and the characterization techniques employed in this study provide valuable insights into the properties of h-BN that can be modified through intercalation. The results indicate that h-BN's properties can be tailored for various applications, including electronics, optoelectronics, and energy storage. This study serves as a foundation for further research into the intercalation of h-BN and expands our understanding of the unique properties of this 2D material.

Dedication

I dedicate this thesis to my family members

Acknowledgments

I would like to express my sincere gratitude to my advisor, Prof. Shamsul Arafin, for providing me with the opportunity to join his exceptional research group. His unwavering dedication, enthusiastic energy, and never-give-up attitude have been a great source of inspiration for me, and his guidance and support have been invaluable in shaping my research work. I would also like to express my heartfelt gratitude to Prof. Sanjay Krishna for generously devoting his valuable time from his busy schedule to serve as a member of my thesis committee.

I would like to take a moment to express my deep appreciation to my wonderful colleagues who have provided invaluable support in various ways throughout my master's program. Working with Dr. Saha, Fatih, Najib, Weicheng, Riazul, Saiful, Arnob, Ismail, Dongsu, Shafaat, and Yongkang has been a truly enriching experience. Additionally, I extend my thanks to the staff at Nanotech West, Dan from CEMAS, and Barbara from the Chemistry department for their support and guidance in training me to use various tools.

My achievements would not have been possible without the unwavering support of my parents and sister, and for that, I am incredibly grateful to them.

Vita

Bachelor of Engineering	Electrical and Electronics Engineering
	Anna University, India (2019)
Graduate Engineering Trainee	Lucas TVS Ltd Chennai, India (2021)
Master of Science	The Ohio State University (2021 - present)

Publications

1. M. S. I. Sumon, **S. Sankar**, W. You, I. I. Faruque, S. Dwivedi, and S. Arafin, “Modeling of GaSb-based Monolithically Integrated Passive Photonic Devices at $\lambda > 2$ µm above 2 µm”*, MIOMD Conference* (Under Review)

2. M. S. I. Sumon, **S. Sankar**, W. You, I. I. Faruque, S. Dwivedi, and S. Arafin, “Design of GaSb-based monolithic passive photonic devices at wavelengths above 2 µm”, *JPhys Photonics* (Under Review)

3. S. Saha**, S. Sankar**, Sk S. S. Nikor, and S. Arafin, “A review of intercalation of rare gas solids on graphene and hexagonal boron nitride”, *PSS-RRL* (Invited), (Under Review)

4. M. M. Rahaman, S. Saha, S. M N Hasan, W. You, A. Ghosh, SK S. S. Nikor, M. S. I. Sumon, B. Freeman, **S. Sankar**, H. Colijn, S. M. Sadaf, J. Garg, and S. Arafin, “Luminescence and Raman spectroscopic properties of cubic boron nitride by drop-casting technique”, *J. Cryst. Growth,* vol. 593, pp. 126781 (1-6), June 2022.

Fields of Study

Major Field: Electrical and Computer Engineering

Table of Contents

List of Tables

List of Figures

Chapter 1. Introduction

1.1 Motivation

The field of quantum technologies is rapidly advancing, with the potential to revolutionize areas such as sensing, information science, and computing. However, to fully realize the potential of quantum technologies, it is essential to develop materials that can meet the unique demands of these applications. Two-dimensional (2D) materials, such as graphene, and hexagonal boron nitride (h-BN), have emerged as promising candidates for quantum technologies due to their exceptional electronic, mechanical, and optical properties [1-3]. Intercalation is a process of inserting foreign atoms or molecules between the layers of a 2D material to modify its properties. 2D materials have garnered significant attention in recent years due to their unique properties such as high thermal and chemical stability, excellent mechanical flexibility, and high surface-to-volume ratio [4-6]. These properties make them ideal candidates for various applications, including quantum technologies [2]. The field of quantum technology has garnered significant interest in recent years due to its potential for revolutionizing a wide range of fields such as computing, sensing, and communication. Quantum technology harnesses the properties of quantum systems, which exhibit behavior that is fundamentally different from classical systems [7].

Intercalation tailors electronic and magnetic properties of 2D materials for use in quantum technologies [1-3]. For example, intercalated graphene has potential for magnetic field sensors and quantum dots [8]. Intercalation of h-BN can enhance single-photon detectors for quantum communication and is a promising candidate for spin qubits [9, 10]. These materials have already shown promising results in various quantum applications, exhibiting tunable properties for high sensitivity and accuracy.

1.2 Thesis Outline

The primary objective of this thesis is to develop and characterize hexagonal boron nitride (h-BN) as a host two-dimensional host material for intercalation. The thesis provides comprehensive characterization results of h-BN grown on a sapphire substrate, and identifies the optimal, less defective material for intercalation.

Chapter 2 offers a comprehensive review of the intercalation process, including the selection of host materials, growth techniques for host 2D materials, and intercalation methods for the intercalants in 2D materials.

Chapter 3 is dedicated to the h-BN, with a detailed growth and characterization process that includes SEM, AFM, Raman, CL, and PL. The data illustrates the less defective nature of the material used for the study which can be used for the intercalation process.

Lastly, Chapter 4 outlines the future plans for intercalating the less defective h-BN with Ne rare gas solids for the development of single photon emitters and spin-related devices. The thesis provides a valuable contribution to the field of intercalation in terms of material selection and offers potential avenues for future research.

Chapter 2. Literature Review of Intercalation

2.1 Intercalation

Intercalation is a process that involves the insertion of foreign species into a host material, leading to changes in its structural, optical, thermal, electrical, magnetic, and mechanical properties. The ability to modify the properties of materials in a controlled manner makes intercalation a popular process in various fields of research and technology [11, 12]. One of the primary properties that can be modified through intercalation is the electrical conductivity of materials. Intercalation can increase the charge carrier density by changing the density of energy states in the material, thus enhancing the electrical conductivity [13]. This property is crucial in developing materials for electronic applications such as sensors, batteries, and electrochromic displays [2]. The highest possible doping in host materials can be achieved through intercalation, which is necessary for achieving high conductivity in materials [14]. In addition to electrical properties, intercalation can also modify the magnetic properties of materials. By introducing magnetic species into the host material, the magnetic properties of the material can be enhanced. This makes intercalation useful for developing materials for magnetic storage applications. Intercalation can also be used to tailor the magnetic properties of materials for specific applications such as spintronics [15-21].

Thermal properties can also be modified through intercalation. By introducing foreign species into the host material, intercalation can induce structural changes that affect the thermal conductivity of the material [22]. This property is essential in developing materials for thermal management applications such as heat sinks. Intercalation can modify the surface properties of materials, leading to enhanced catalytic activity [23, 24]. By introducing foreign species into the host material, intercalation can enhance the catalytic activity of the material. This property is important in developing materials for catalytic applications such as in fuel cells and catalytic converters.

Intercalation can also modify the electronic structure of materials, leading to changes in their optical properties [24]. By introducing foreign species into the host material, intercalation can modify the electronic structure of the material, leading to changes in its optical absorption and transmission properties. This property is important in developing materials for optoelectronic applications such as solar cells and light-emitting devices. Finally, intercalation can modify the mechanical properties of materials. By introducing foreign species into the host material, intercalation can induce structural changes that affect the mechanical properties of the material. This property is important in developing materials for structural applications such as in aerospace and automotive industries.

In general, intercalation is a powerful process that can modify various properties of materials. Its ability to modify properties in a controlled manner makes it a popular process in various fields of research and technology. The properties that can be modified through intercalation include electrical conductivity, magnetic properties, thermal properties, surface properties, electronic structure, and mechanical properties. Intercalation has the potential to create new materials with superior properties, leading to advances in various technological fields.

2.2 2D Host Materials

The use of two-dimensional (2D) materials as host materials for intercalation has gained significant interest in recent years due to their excellent electronic, optical, mechanical, and thermal properties [25, 26]. 2D materials, such as h-BN and graphene, are ideal platforms for intercalation due to their atomically thin and high aspect ratio nature, which provides large interlayer gaps for the insertion of foreign species without breaking the in-plane covalent bonds which can be inferred from Figure 2.1. In contrast to 3D materials, which trigger chemical reactions with foreign species and form covalent bonds that disrupt structural properties and create defects, 2D materials allow guest species to reside on the atomic surface and ions to easily migrate to interlayer sites, without disturbing the structural bonding [27]. 2D materials exhibit a greater surface area-to-volume ratio in contrast to their three-dimensional (3D) counterparts, making them ideal for intercalation as a host material. These materials consist of a single layer or a few layers of atoms arranged in a 2D lattice structure, resulting in a large surface area for intercalation and facilitating the diffusion of intercalants between the layers, leading to a high degree of intercalation [1, 28]. On the other hand, intercalation in 3D materials is more challenging due to their lower surface area-to-volume ratio. The limited surface area available for intercalation can hinder the penetration of intercalants into the bulk material, resulting in a lower degree of intercalation and limited control over the properties of the host material.

In addition to their surface area, another advantage of 2D materials as host materials for intercalation is their flexibility and mechanical properties. Due to their thin and flexible nature, 2D materials can undergo changes in geometry and deformation upon intercalation, which can induce structural changes in the host material and lead to changes in its mechanical properties [29, 30]. This property is essential in developing materials for applications that require flexibility and mechanical stability. Moreover, 2D materials have unique electronic and optical properties that can be further enhanced by intercalation. Graphene, a 2D carbon material, for instance, has high electrical conductivity and optical transparency [8]. The intercalation of foreign species into the graphene lattice can further enhance its electronic and optical properties, making it a suitable material for various applications. Additionally, 2D materials have high thermal conductivity, which can be further enhanced by intercalation [31]. The intercalation of foreign species can induce structural changes in the 2D material, leading to an enhancement of its phonon transport properties [32, 33]. This property is essential in developing materials for thermal management applications, such as heat sinks.

Another advantage of 2D materials as host materials for intercalation is their tunable electronic properties [34]. Depending on the nature and arrangement of the constituent atoms, 2D materials exhibit a range of electronic properties, including semiconducting, metallic, and insulating behavior. The intercalation of foreign species can alter the electronic properties of the host material, providing a means to tune its electronic behavior. This property is useful in developing materials for electronic and optoelectronic applications, such as transistors, and UV light-emitting diodes [35]. Additionally, 2D materials have high surface reactivity, making them suitable for chemical functionalization [36]. The functionalization of 2D materials with various chemical groups can alter their surface chemistry, leading to changes in their electronic, optical, and mechanical properties. This property is useful in developing materials for applications such as catalysis, sensing, and energy storage.

Furthermore, 2D materials are easy to grow using various techniques, such as mechanical exfoliation, chemical vapor deposition, molecular beam epitaxy, and drop casting. These techniques enable the production of high-quality 2D materials in large quantities and at low cost. The scalability and cost-effectiveness of 2D material production make them a promising candidate for various applications. Finally, 2D materials have exceptional environmental stability, making them resistant to oxidation and degradation [37]. The intercalation of foreign species can further enhance their stability, providing a means to develop materials with superior stability in harsh environments. This property is useful in developing materials for a wide range of applications that require long-term stability, such as protective coatings, environmental sensors, and electronic devices.

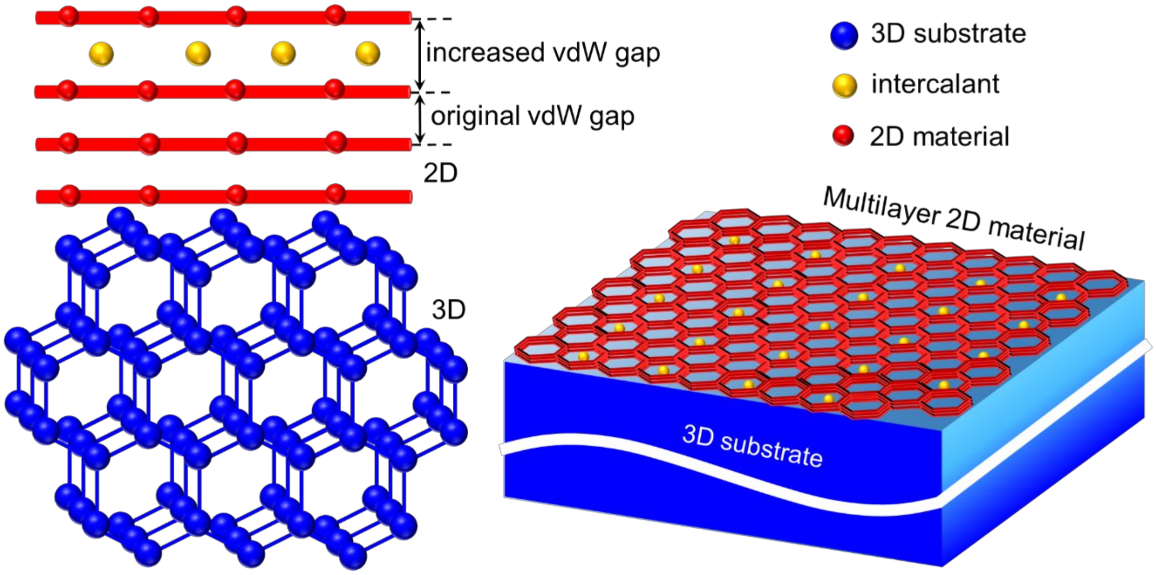


Figure 2.1 Atomic geometry of intercalants/multilayer 2D material/3D substrate (left), and schematic view of a structure with multilayer 2D material/3D substrate where foreign particles are intercalated (right).

2.3 2D material Growth Techniques

Various techniques have been developed for the synthesis or epitaxial growth of 2D materials, including liquid or mechanical exfoliation under ambient conditions, the low-vacuum technique CVD or MOCVD, and the high vacuum technique MBE. **Figure 2.2** illustrates all the possible technologies used for the growth of 2D materials. This section will discuss different exfoliation techniques employed for the synthesis of two 2D materials, followed by the vacuum growth tools utilized for the same purpose.

Mechanical exfoliation: This is one of the earliest and simplest techniques for producing 2D materials. In this technique, a bulk material is cleaved using adhesive tape or a similar material to produce a thin layer [38]. The resulting layer is then transferred to a substrate to obtain the desired 2D material. Graphene, the first discovered 2D material, was obtained using this technique.

Drop casting: This is a simple and low-cost technique for producing 2D materials. In this technique, a solution containing the desired 2D material is dropped onto a substrate [39]. The solvent evaporates, leaving behind a thin layer of the material on the substrate. Drop casting can produce large-area, high-quality 2D materials, and it has been used to produce graphene, black phosphorus, and other 2D materials.

Chemical vapor deposition (CVD): CVD is a widely used technique for producing high-quality 2D materials [40]. In this technique, a precursor gas is introduced into a reaction chamber containing a substrate. The gas decomposes on the substrate, forming the desired 2D material. The growth parameters such as temperature, pressure, and gas flow rate can be controlled to obtain high-quality 2D materials. CVD is a scalable technique, and it has been used to produce graphene, hexagonal boron nitride (h-BN), and other 2D materials.

Metal-organic chemical vapor deposition (MOCVD): MOCVD is a technique similar to CVD, but it uses metal-organic precursors instead of inorganic precursors. In this technique, a metal-organic precursor and a carbon source are introduced into a reaction chamber containing a substrate. The precursor decomposes on the substrate, forming the desired 2D material. MOCVD has been used to produce high-quality graphene and h-BN [41-43].

Molecular beam epitaxy (MBE): MBE is a high vacuum technique that involves the deposition of atoms or molecules on a substrate. In this technique, a solid source of the material is heated, and the evaporated atoms or molecules are directed onto a substrate. The deposited material grows layer by layer, resulting in high-quality and uniform films. MBE is a precise and well-controlled technique, and it has been used to produce high-quality h-BN [44].

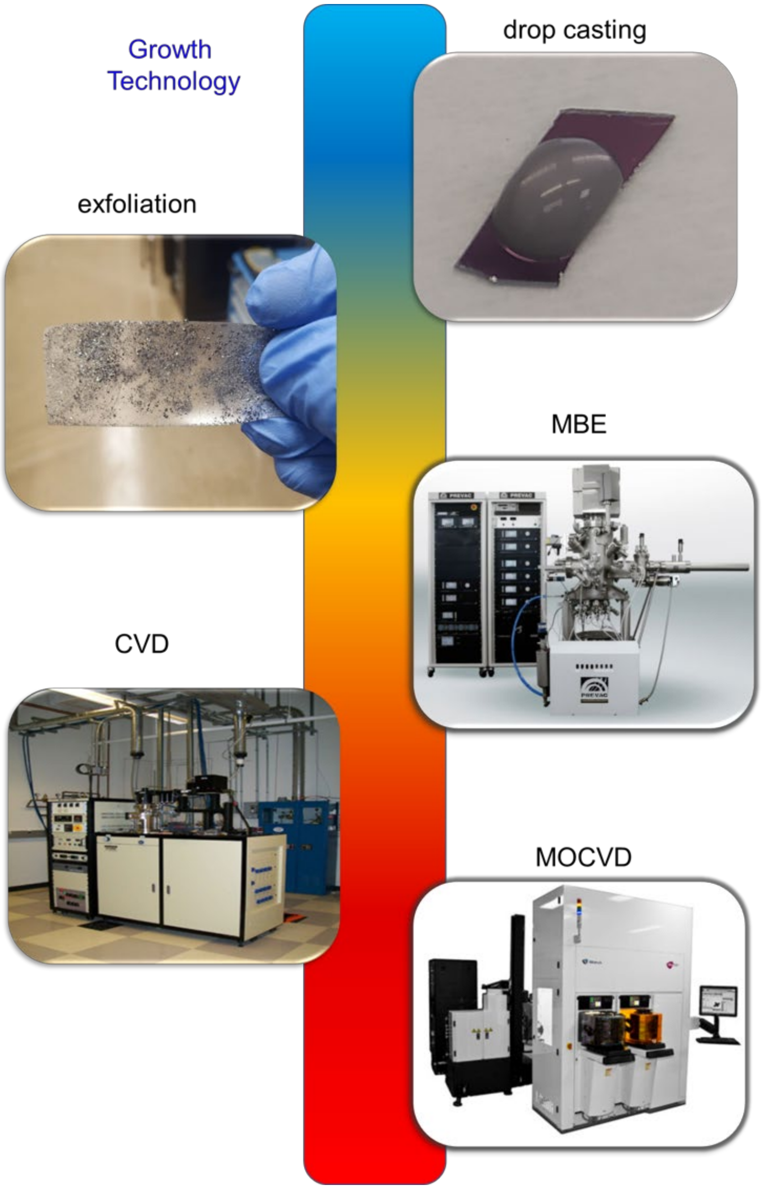


Figure 2.2 Various synthesis or growth techniques of 2D materials.

2.4 Rare Gas Solids as Intercalant

The rare gas elements, also known as noble or inert gases, including helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), radon (Rn), and the recently discovered oganesson (Og), possess noteworthy characteristics as intercalants. These elements are present in trace amounts in the atmosphere and form rare gas solids at very low temperatures under atmospheric pressure (around 100 K). These solids have the highest electronic bandgaps of any material, with the bandgap of solid Ne being four times that of diamond, making them particularly attractive for quantum information science (QIS) applications. In addition, rare gas solids offer a matrix that is completely devoid of electronic or nuclear spins, such as solid Ar. These unique properties make them potential candidates for QIS and other advanced technological applications [10, 45, 46]. To harness the potential of rare gas solids for QIS applications, it is essential to stabilize them at room temperature. A possible solution to this challenge is to utilize the van der Waals pressure by sandwiching the rare gas solids between two-dimensional (2D) materials like graphene and h-BN. This technique would enable the operation of quantum devices and systems at room temperature. Although van der Waals forces between 2D materials are weaker than covalent bonds, they can still generate high pressures, estimated to reach up to 10,000 atmospheres for encapsulated species [47].

The ability of rare gas solids to intercalate into host lattices depends on their atomic radii and diffusion rates during the process, which are illustrated in 2D schematics in Figure 2.3. Helium, for example, has a small atomic radius and high diffusion rate, making it capable of filling all available sites in the host material. However, its kinetic instability limits its suitability for intercalation and it cannot be trapped easily in the 2D/substrate interface. Argon, due to its larger atomic radius, is not an optimal choice for intercalation as it can cause vacancy defects in the crystal structure. Most 2D materials have smaller atomic sizes than Ar, but if intercalation occurs, the gas atoms can be trapped in the 2D/substrate interface. This is because the collision with 2D materials atoms reduces their kinetic energy, preventing them from reflecting back. Neon, on the other hand, has an intermediate atomic radius and moderate diffusion rate, taking a few hours to diffuse into the lattice. The diffusion rate can be increased by higher pressure, but this also leads to a reduction in the size of interstitials and channels, which has little impact on the diffusion rate. Kr has shown high intercalation occupancy at high temperatures, but Xe's size makes it unsuitable for intercalation.

Certain rare gases, such as ^{3}He and ^{129}Xe, possess a non-zero nuclear spin that is optically inaccessible and well-shielded from the external environment, allowing for long coherence times [15]. Ensembles of these gas spins can maintain coherence for several hundred hours at room temperature, making them useful for applications in medical imaging [48], quantum information science, sensing technology, and entanglement generation [10, 45, 46]. However, achieving and sustaining such entanglement requires precise control and isolation, which has been accomplished with trapped atoms and ions [49, 50], alkali-metal spins [49, 51, 52], high-quality mechanical oscillators, and quantum defects in crystals [53]. Recent experiments have also demonstrated strong coherent coupling between optically-accessible spins of rare gas ^{3}He by incorporating multiple rare gas solids into 2D host materials, introducing a range of atomic and molecular spin defects [15].

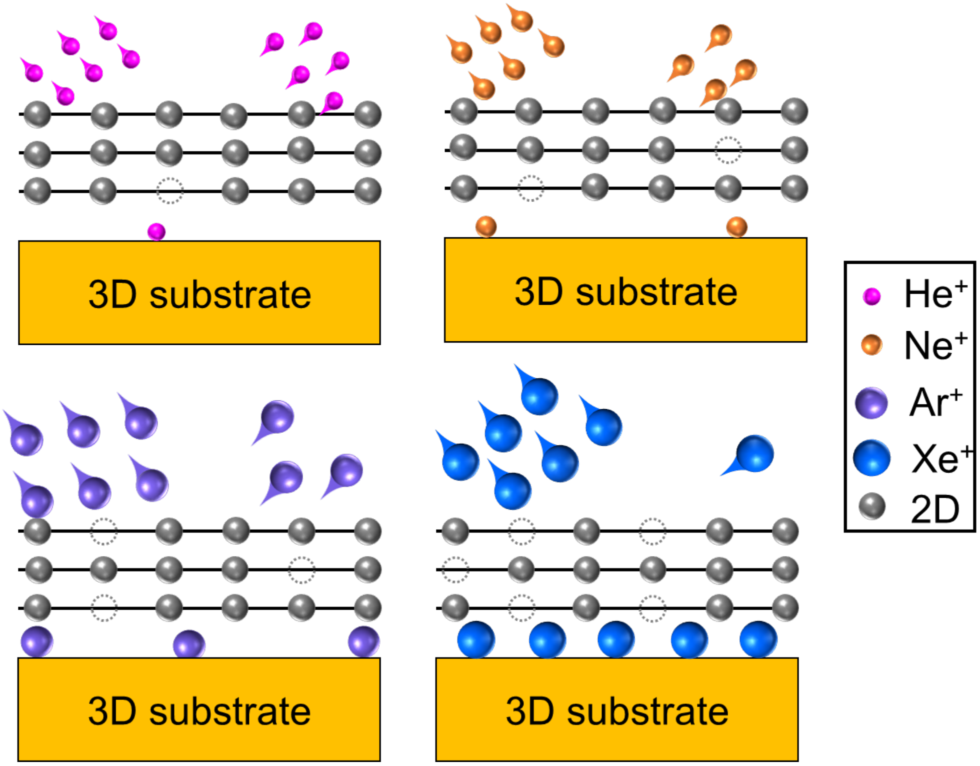


Figure 2.3 Schematic representation of intercalation of **(e)** He, **(f)** Ne, **(g)** Ar, and **(h)** Xe atoms, respectively.

2.5 Intercalation Process

Intercalation of rare gas solids has been a subject of interest for decades. In this regard, different techniques including sputtering, ion-beam implantation and, irradiation have been extensively used. **Figure 2.4** depicts these methods.

Sputtering is a physical vapor deposition (PVD) technique commonly used for thin film deposition in various fields, including materials science and nanotechnology. In rare gas intercalation, sputtering is used to introduce rare gas atoms into the interstitial sites of a material's lattice structure. The sputtering process involves bombarding a target material with high-energy ions, typically argon, in a low-pressure gas environment. This causes the atoms of the target material to be ejected and deposit on a substrate to form a thin film. In rare gas intercalation, the ejected target atoms are replaced by rare gas atoms, such as helium or neon, which are introduced into the interstitial sites of the lattice structure. This process can modify the physical and electronic properties of the material, leading to interesting and potentially useful properties.

The rare gas intercalation process can also be performed using ion implantation and ion irradiation, where the rare gas ions are directly implanted into the material's lattice structure.[54] In both techniques, ions are accelerated to high energies and directed towards the 2D material, causing damage and creating vacancies in the lattice. The rare gas atoms can then intercalate into these vacancies and form a solid within the 2D material.

Ion implantation involves the use of a focused ion beam to implant rare gas ions into the 2D material. Ion irradiation, on the other hand, involves bombarding the 2D material with a broad beam of ions. The ions penetrate the surface and create a cascade of collisions that causes lattice damage and creates vacancies. The rare gas atoms can then diffuse into these vacancies and intercalate into the lattice. However, sputtering has an advantage in the sense that it can deposit thin films over a larger area with less damage, making it more appropriate for intercalation applications.

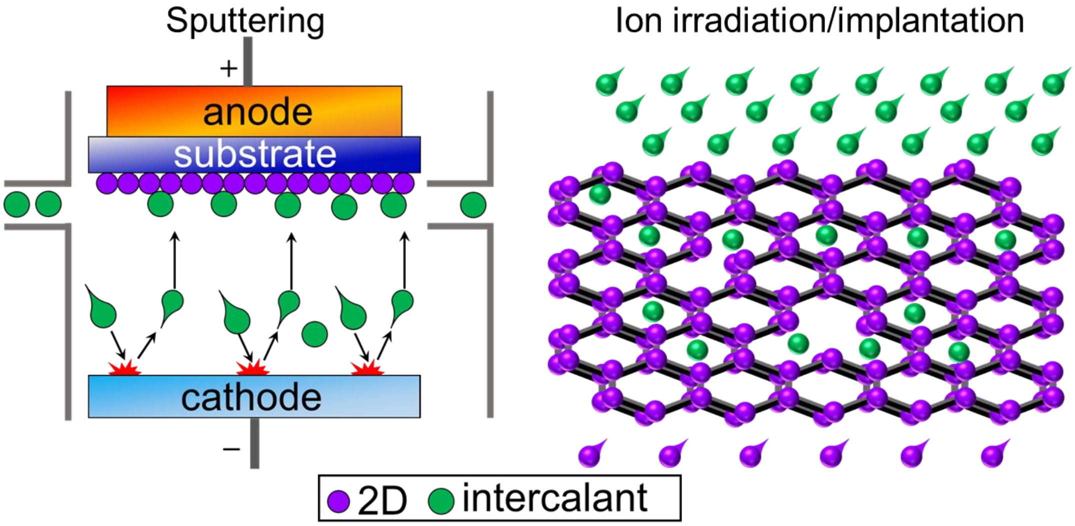


Figure 2.4 Various intercalation techniques of rare gas solids: (a) sputtering and (b) ion irradiation/implantation.

Chapter 3. h-BN – Host material

3.1 Why h-BN?

Hexagonal Boron Nitride (h-BN) is a unique two-dimensional (2D) material that has gained significant attention in the scientific community in recent years due to its exceptional properties and potential applications in various fields. One of the most notable features of h-BN is its hexagonal lattice structure, which is similar to that of graphene. This hexagonal lattice structure results in a highly ordered crystal structure, making it an excellent material for use in high-precision applications. However, unlike graphene, h-BN is an insulator due to the presence of a wide bandgap approximately 6 eV [55]. Due to its insulating properties, h-BN does not conduct electricity, which makes it a desirable material for use in electronic and optoelectronic devices that require high insulation. In addition to its insulating properties, h-BN also has high mechanical strength, making it resistant to mechanical stress and deformation. This property makes it an excellent material for use in applications where mechanical stability is crucial, such as intercalation [56, 57].

The another most notable properties of h-BN is that it does not have any dangling bonds, making it an ideal material for various applications such as electronic devices, optoelectronics, and catalysis [58]. The absence of dangling bonds in h-BN is due to the strong covalent bonds between the boron and nitrogen atoms. This results in a highly stable and robust material that can withstand high temperatures and harsh chemical environments. The lack of dangling bonds also makes h-BN an excellent insulator, with a high dielectric constant and low loss tangent, which is important for its use in electronic devices [58].

h-BN has excellent thermal stability and can withstand high temperatures without undergoing any significant structural changes. It can resist temperatures of up to 900°C, making it an ideal material for high-temperature applications [57]. Another unique property of h-BN is its optical properties, such as a high transmittance in the visible and ultraviolet regions of the electromagnetic spectrum. This property makes h-BN an ideal material for optical applications, such as UV LEDs [59]. The h-BN is highly chemically inert, which means it does not react with other chemicals or substances easily and this property makes h-BN a desirable material for use in harsh chemical environments [60].

3.2 Substrate Selection and Growth of h-BN

The substrate for h-BN growth was selected based on several properties related to the substrate material and their impact on h-BN. Four different popular substrate materials were selected, including Highly Oriented Pyrolytic Graphite (HOPG), Silicon carbide (SiC), Nickel (Ni), and Sapphire (Al_2O_3). The first and foremost criterion for the substrate selection was the lattice matching between h-BN and the substrate materials. SiC and Sapphire showed a high degree of matching with h-BN. The second criterion was thermal stability, which plays a major role during the growth process of h-BN. Since the 2D material is grown at a high temperature, it is necessary for the substrate material to be thermally stable. Most of our selected materials excelled in this property except for Nickel. As CVD was selected as the growth technique, the third criterion was compatibility with CVD, and all of the materials selected were compatible with CVD growth.

To ensure optimal performance of h-BN, the substrate material's bandgap and absorption coefficient are two critical criteria that must be considered. This is particularly important when creating single photon emitters by identifying color centers in h-BN, which are produced by point defects. During spectroscopy measurements, the emitted light from color centers should not be absorbed by the substrate, requiring a substrate with high electronic bandgap and low absorption coefficient. Based on these properties, sapphire was identified as an excellent substrate material for growing h-BN. The properties of substrate materials can be inferred from Table 3.2.

Criteria	HOPG	SiC	Ni	Sapphire
Lattice matching h-BN	1.8%	11.7%	0.8%	9.38%
Thermal stability	High	High	Intermediate	High
Bandgap(eV)	-	2.3-3.3	-	10
absorption coefficient (cm^{-1})	2.2×10^{5}	Moderate	High	NA
CVD compatibility	✓	✓	✓	✓

Table 3.2 Substrate selection for h-BN

As discussed in Chapter 2.3, there are various methods available for growing 2D materials, including CVD, MOCVD, and MBE. Although there are other methods available for growing 2D materials, CVD was chosen as it is a well-established and versatile technique for synthesizing high-quality h-BN films with large areas. The growth of h-BN on a sapphire substrate using the CVD process was conducted by Michael Snure from Air Force Research Lab (AFRL) in Dayton, as part of our project collaboration. Borazine was utilized as our precursor and grew h-BN on a sapphire substrate at a temperature of 1500 ºC for 3 hours. Our growth resulted in six monolayers of h-BN, each with a thickness of 0.33 nm. Six monolayers were selected as a starting point to study the properties of h-BN on sapphire, considering that anything exceeding 10 monolayers is considered to be bulk in the field of 2D materials. Our plan for the next growth process is to grow monolayer h-BN on a sapphire substrate for intercalation purposes.

3.3 Morphological Characterization

3.3.1 Optical Microscopy

The CVD grown h-BN sample underwent a comprehensive optical microscopy analysis using the HRM-300 Series microscope, and no major deformities or debris were detected. Additionally, the h-BN film appeared to be uniform throughout the sample, as shown in Figure 3.1.

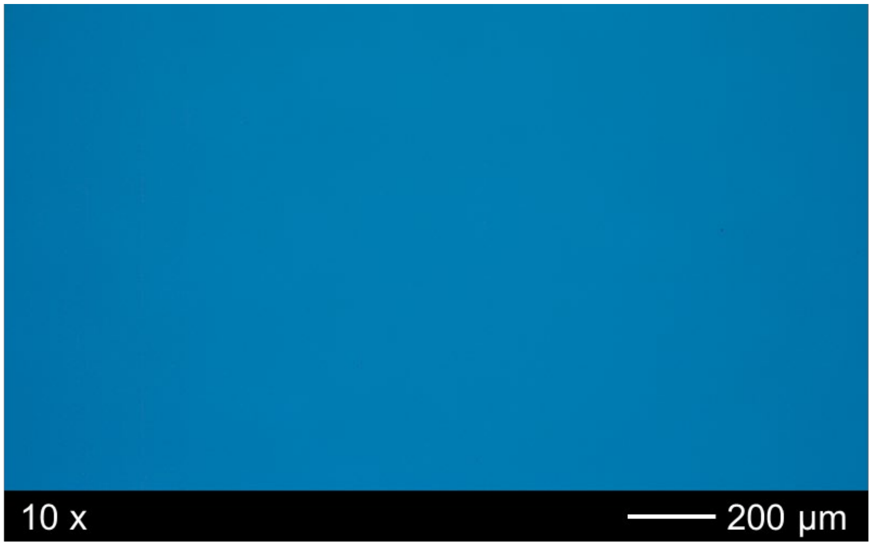


Figure 3.1 Optical microscopy image of the h-BN film

3.3.2 Scanning Electron Microscopy (SEM)

To examine the morphology and topology of the h-BN sample, SEM was conducted using the Zeiss Ultra 55 Plus FE-SEM tool. The SEM image in Figure 3.2 depicted that the h-BN film exhibited a smooth surface without any visible hillocks or wrinkles. This indicates that the film had a homogeneous texture and was devoid of any irregularities or deformities. The lack of significant roughness suggests that there is minimal or no thermal stress between the h-BN film and the underlying substrate. This finding is of great significance as it indicates that the h-BN film was grown under optimal conditions, resulting in a high-quality and uniform film.

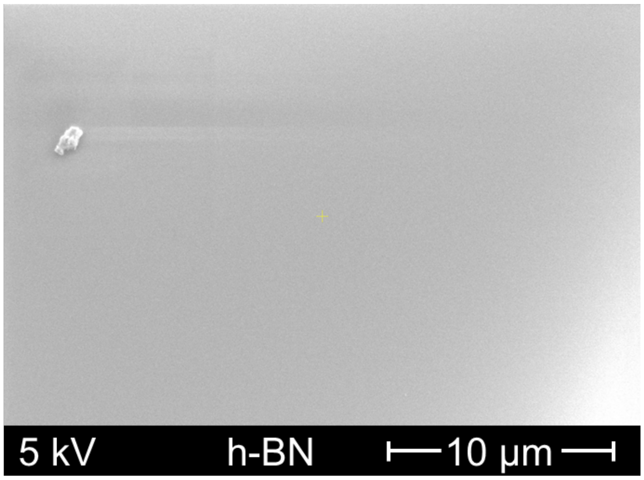


Figure 3.2 SEM image of the h-BN film

3.3.3 Atomic Force Microscopy (AFM)

The AFM analysis was carefully performed using the highly precise Bruker Icon 3 AFM tool to confirm the SEM results. The results of the analysis were truly remarkable as they revealed that the h-BN film was incredibly smooth, exhibiting an RMS surface roughness of merely 1.72 Å. This exceptional level of smoothness is highly desirable for various optical characterizations such as cathodoluminescence and photoluminescence, as it significantly reduces light scattering on the h-BN film. Moreover, a smoother surface will substantially enhance the mechanical strength and durability of the material. The mapped AFM data can be inferred from Figure 3.3.

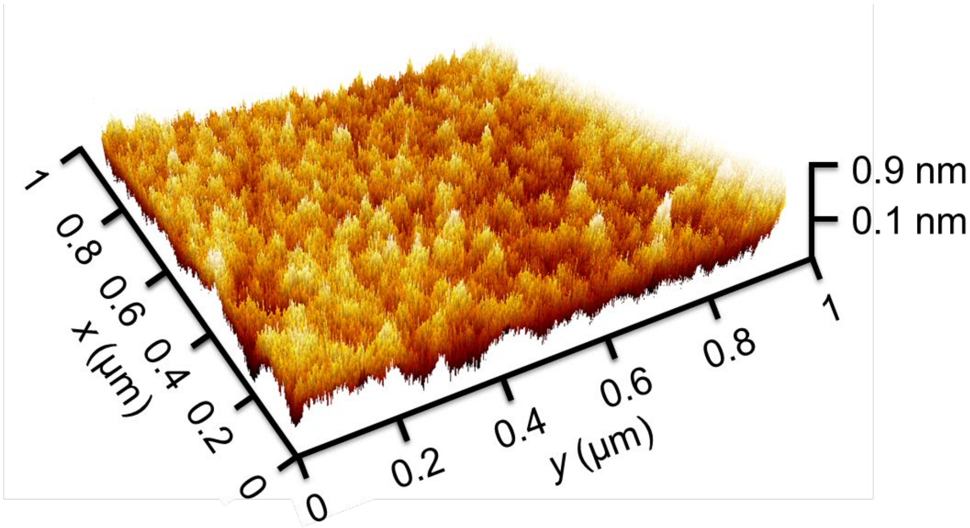


Figure 3.3 AFM image of the h-BN film

3.4 Spectroscopic Characterization

3.4.1 Raman Spectroscopy

Raman spectroscopy is a powerful tool to study the vibrational properties of a material so it was utilized to verify the presence of the h-BN film by evaluating h-BN's vibrational properties. The Renishaw Raman and FTIR microprobe tool was used to conduct the Raman measurements at room temperature using a laser with an excitation wavelength of 458 nm and an optical power of 2 mW. The collected data was plotted as a graph in Figure 3.4. Five Stokes shifted peaks of the sapphire substrate were identified in the spectral range of 400 cm^{-1} to 800 cm^{-1}, indicating the existence of defects in the sapphire substrate. The peak at 750.3 cm^{-1} had a high intensity, whereas the peak at 431 cm^{-1} was low in intensity.

Moreover, a prominent E_{2g} phonon peak was observed at 1368.1 cm^{-1}, which corresponds to the h-BN film and confirms the existence of h-BN polymorphism. The E_{2g} phonon peak is attributed to the in-plane vibrations of boron and nitrogen atoms in the hexagonal lattice structure of the h-BN and they are considered as a characteristic peak of h-BN. The E_{2g} phonon peak's full-width at half-maximum (FWHM) was measured to be 42.87 cm^{-1}, which is comparable to the bulk h-BN's FWHM value. The presence of the h-BN peak at 1368.1 cm^{-1} confirms the successful growth of the h-BN film and its high crystalline quality.

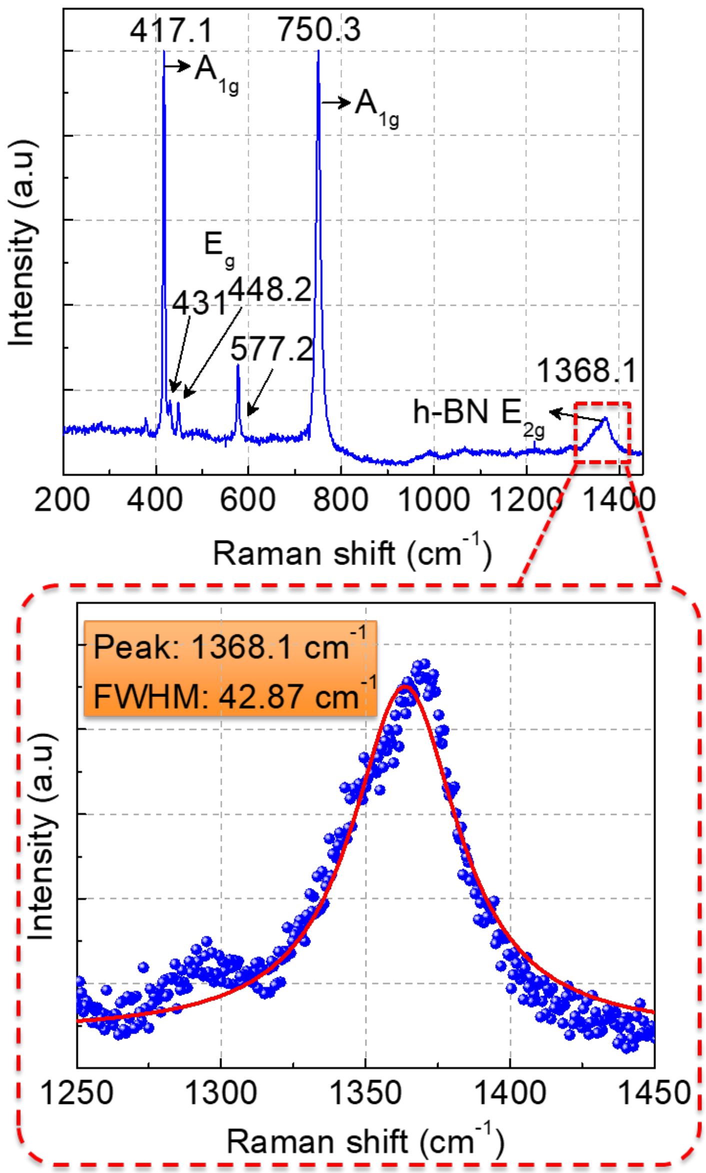


Figure 3.4 Room temperature Raman measurement of h-BN

Temperature-dependent Raman measurements were performed to observe the changes in the h-BN film's vibration properties at low and high temperatures. The measurements were performed from -180 ºC to 370 ºC, and the E_{2g} phonon peak of the h-BN film was recorded and plotted in Figure 3.5. At -180 ºC, the E_{2g} peak center of h-BN was found to be at 1374 cm^{-1}, and it underwent a small red shift with an increase in temperature. However, after 90 ºC, there was a moderate red shift can be observed, and finally, at 370 ºC, the peak was found to be shifted to 1355 cm^{-1}. During the temperature measurements from -180 ºC to 370 ºC, a 19 cm^{-1} red shift was observed.

The observance of this red shift in h-BN with temperature indicates that as the temperature increases, the h-BN lattice is subjected to thermal expansion. The lattice expansion leads to an increase in the bond stiffness of the material and reduces the vibrational frequency of the material. This makes sense since at high temperatures, the kinetic energy of phonons within the lattice will increase, resulting in collisions between multiple phonons and a decrease in energy and frequency. This increase in lattice vibrations can have significant effects on the physical and electronic properties of the material, such as changes in thermal conductivity, electrical conductivity, and mechanical strength.

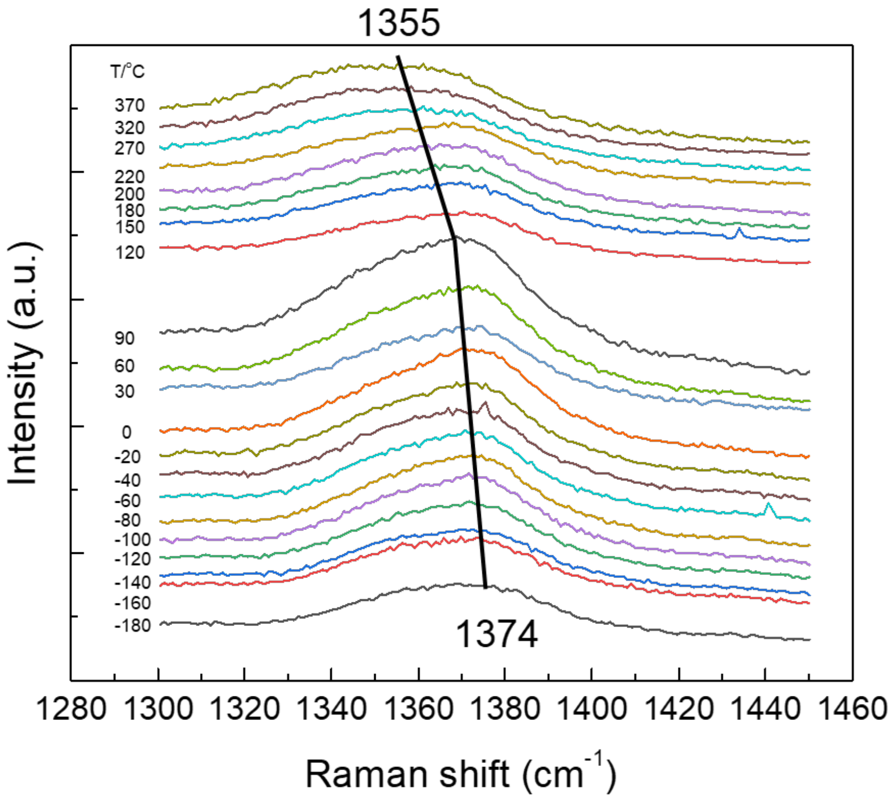


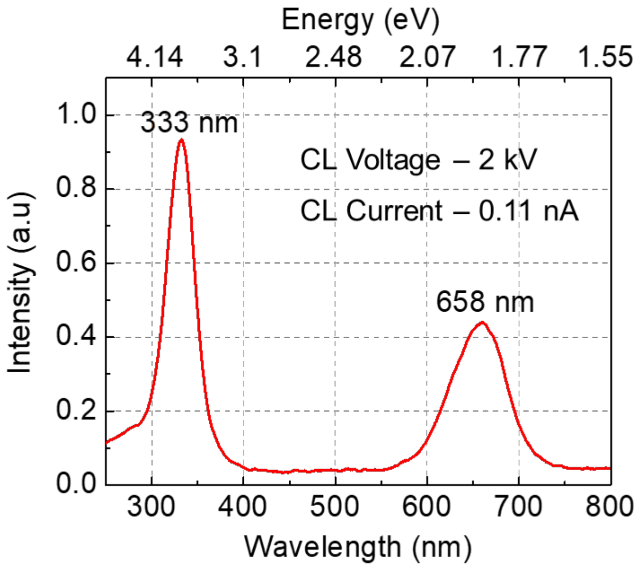
Figure 3.5 Temperature-dependent Raman measurement for the h-BN film

3.4.2 Cathodoluminescence (CL)

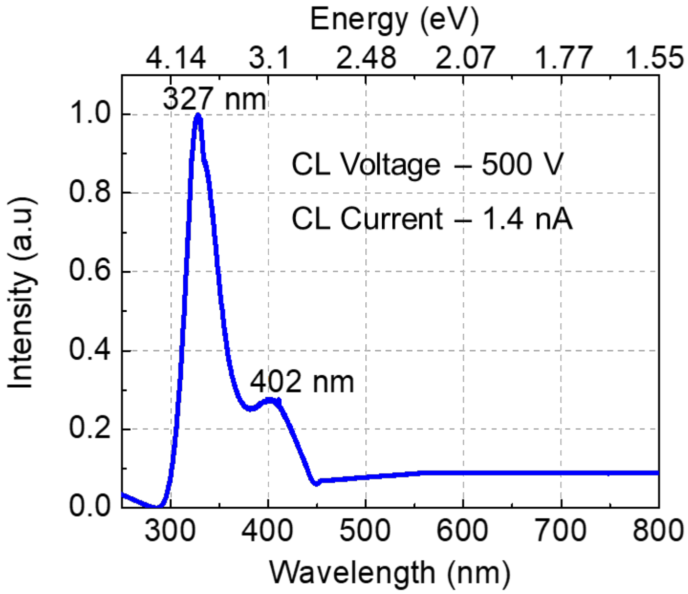
CL is a powerful characterization technique used to study the luminescence properties of materials. It involves exciting a material with a focused beam of electrons, typically in a SEM, and collecting the resulting emitted photons. The energy and wavelength of the emitted photons can provide information about the electronic and optical properties of the material being studied. In the case of h-BN, luminescence measurement is crucial as it helps to identify color centers which are of interest, without the need for additional analysis. So, CL was performed using Thermo Scientific Quattro ESEM tool.

During the initial measurements, a CL excitation voltage of 5 kV and a current of 0.11 nA were used. Although 5 kV is a commonly used low excitation voltage in CL studies, the results were unexpected since no h-BN peaks were observed as shown in Figure 3.6 A. Instead, peaks were identified in the sapphire substrate at 333 nm and 658 nm. Further investigation revealed that the choice of CL excitation voltage could have been the cause of the discrepancy. The 5 kV voltage appeared to penetrate the substrate and collect data from it instead of the h-BN thin film. To address this issue, a lower CL voltage of 500 V was selected for the measurements. This voltage was chosen based on a simulation check with Casino software, which indicated that the penetration depth of electrons at 500 V was around 4 nm. This voltage was deemed suitable for the h-BN thin film since it could prevent interference from the substrate and enable accurate measurement of the h-BN’s properties.

After adjusting the CL excitation voltage to 500 V, two peaks were observed in the h-BN thin film at 327 nm and 402 nm shown in Figure 3.6 B. Interestingly, the peak at 402 nm was not observed in previous measurements and could indicate a point defect in the h-BN film that may have created a color center. However, the origin of the 327 nm peak remains unclear as a shift of 6 nm was observed from the 333 nm peak at high CL voltage. This shift suggests that the 327 nm peak could potentially be attributed to the substrate, although further investigation is required to confirm this hypothesis. Overall, the results indicate that adjusting the CL excitation voltage to 500 V was an effective strategy for improving the accuracy and reliability of the measurements on the h-BN thin film.



A



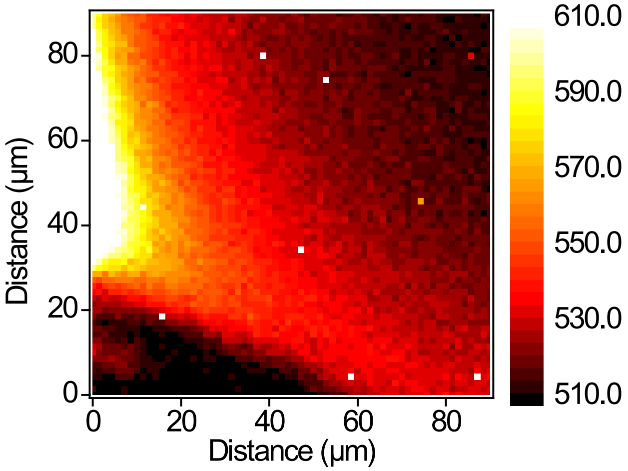
B

Figure 3.6 A – High CL excitation voltage, B – Low CL excitation voltage of h-BN

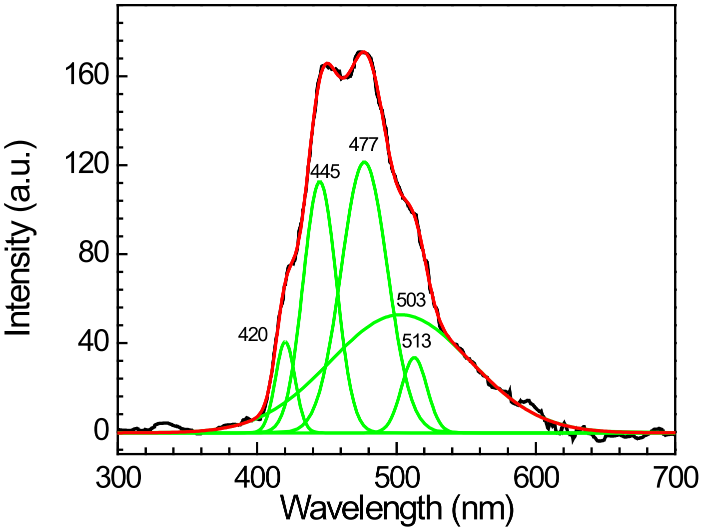
3.4.2 Photoluminescence

To further confirm our previous statement regarding the point defect in the h-BN thin film, photoluminescence (PL) measurements were conducted on the h-BN sample by our collaborators at National Taiwan Normal University (NTNU). PL is a non-destructive optical spectroscopy technique that allows us to measure the emission of photons from excited states in the material. The PL measurements were performed using a 480 nm laser excitation with a power of 0.169 mW. The results showed that there was a peak at 420 nm in the PL spectrum which may be the closest to the peak at 402 nm in the CL spectrum. Although the exact match between the two peaks could not be established, this finding still suggests that the peak at 402 nm observed in the CL measurement could indeed be attributed to a point defect in the h-BN thin film that created a color center.

Moreover, the PL measurements also revealed additional peaks in the spectrum. Specifically, a broad peak and few shoulder peaks from 420-512 nm were observed. The shoulder peaks from 420-512 nm shown in Figure 3.7 B could be due to the recombination of excitons with defects in the material. The presence of these peaks in the PL spectrum further supports the hypothesis that the h-BN thin film contains point defects that contribute to its optical properties.



A



B

Figure 3.7 A **-** PL data mapping, B - PL spectrum plot

Chapter 4. Future Works

The characterization of the h-BN thin film has shown promising results in terms of its optical properties and point defects. Through the use of cathodoluminescence and photoluminescence measurements, it was possible to identify the presence of point defects in the h-BN thin film which contribute to its optical properties. Specifically, a peak at 402 nm in the CL spectrum was observed which may be attributed to a point defect that creates a color center. Additionally, the PL measurements showed a peak at 420 nm which supports this hypothesis.

In the pursuit of further understanding the unique properties of h-BN, future work will focus on the intercalation of Ne rare gas into the material. The intercalation process has been demonstrated to introduce new physical properties, such as magnetism and photoluminescence, which are highly desirable for a range of applications, including spintronics and quantum information processing. The introduction of Ne rare gas into the h-BN thin film is expected to enhance its optical and magnetic properties, and enable the creation of new spin-based devices.

The process of intercalation involves the insertion of Ne atoms into the interlayer spaces between h-BN layers by either sputtering or ion irradiation process. Once the intercalation process is complete, a series of measurements will be performed to characterize the optical and magnetic properties of the intercalated h-BN thin film. Cathodoluminescence and photoluminescence measurements will be used to evaluate the optical properties of the material. The use of luminescence measurements is a powerful technique for characterizing the luminescence properties of materials, and it is particularly useful for investigating the electronic structure of semiconductors. The resulting luminescence spectrum can provide valuable information on the energy band structure and optical properties of the material.

In addition to the luminescence measurements, several other techniques will be employed to study the material's properties in more detail. Transmission electron microscopy (TEM) will be used to investigate the microstructure and crystallography of the intercalated h-BN thin film. This will enable the visualization of the intercalated Ne atoms and their distribution within the h-BN lattice, providing important information about the structural changes induced by intercalation. Scanning tunneling microscopy (STM) will also be used to study the electronic and surface properties of the intercalated h-BN thin film. STM is a powerful technique that can provide atomic-resolution images of the surface and reveal information about the trapping of Ne atoms in the h-BN/substrate interface including the vacancies created during the intercalation process.

X-ray photoelectron spectroscopy (XPS) will be used to investigate the chemical composition of the intercalated h-BN thin film. This technique can provide information about the chemical bonding states of the elements present in the material, and can be used to investigate the presence of impurities or defects that may affect the material's properties. X-ray diffraction (XRD) will be employed to investigate the crystal structure of the intercalated h-BN thin film. XRD can provide detailed information about the crystallographic orientation of the material and the lattice parameters, which can be used to investigate the structural changes induced by intercalation.

Collectively, these techniques will provide a comprehensive characterization of the intercalated h-BN thin film, allowing for a detailed understanding of its electronic, optical, magnetic, and structural properties. By combining these results with the luminescence measurements, it will be possible to gain insights into the potential for using intercalated h-BN in spin-based devices for quantum information processing. Spin-based devices have the potential to revolutionize the field of quantum information processing, enabling faster and more efficient data processing compared to classical computers.

Overall, the intercalation of Ne rare gas on h-BN represents an exciting avenue of research that has the potential to unlock new physical properties of the material. The insights gained from this research may ultimately lead to the development of new spin-based devices for quantum information processing, and could have important implications for a range of other applications, including magnetism and photovoltaics. With careful experimental design and measurement techniques, it is hoped that this research will contribute significantly to our understanding of h-BN and its potential for use in future technologies.

Bibliography

[1] Y. Jung, Y. Zhou, and J. J. Cha, "Intercalation in two-dimensional transition metal chalcogenides," *Inorg. Chem. Front.,* vol. 3, no. 4, pp. 452-463, 2016.

[2] J. Wan, S. D. Lacey, J. Dai, W. Bao, M. S. Fuhrer, and L. Hu, "Tuning two-dimensional nanomaterials by intercalation: materials, properties and applications," *Chem. Soc. Rev.,* vol. 45, no. 24, pp. 6742-6765, 2016.

[3] Q. Cao, F. Grote, M. Huβmann, and S. Eigler, "Emerging field of few-layered intercalated 2D materials," *Nanoscale Adv.,* vol. 3, no. 4, pp. 963-982, 2021.

[4] K. S. Novoselov *et al.*, "Two-dimensional atomic crystals," *Proc. Natl. Acad. Sci. U. S. A.,* vol. 102, no. 30, pp. 10451-10453, 2005.

[5] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, and A. Kis, "2D transition metal dichalcogenides," *Nat. Rev. Mater.,* vol. 2, no. 8, pp. 1-15, 2017.

[6] K. Novoselov, o. A. Mishchenko, o. A. Carvalho, and A. Castro Neto, "2D materials and van der Waals heterostructures," *Science,* vol. 353, no. 6298, p. aac9439, 2016.

[7] A. S. Holevo, (Quantum Systems, Channels, Information). Berlin, Boston: De Gruyter, 2019.

[8] P. Ares and K. S. Novoselov, "Recent advances in graphene and other 2D materials," *Nano Mater. Sci.,* vol. 4, no. 1, pp. 3-9, 2022.

[9] T. Vuong *et al.*, "Deep ultraviolet emission in hexagonal boron nitride grown by high-temperature molecular beam epitaxy," *2D Mater.,* vol. 4, no. 2, p. 021023, 2017.

[10] C. Gemmel *et al.*, "Ultra-sensitive magnetometry based on free precession of nuclear spins," *Eur. Phys. J. D,* vol. 57, no. 3, pp. 303-320, 2010.

[11] M. Chhowalla, Z. Liu, and H. Zhang, "Two-dimensional transition metal dichalcogenide (TMD) nanosheets," *Chem. Soc. Rev,* vol. 44, no. 9, pp. 2584-2586, 2015.

[12] H. Yuan, H. Wang, and Y. Cui, "Two-dimensional layered chalcogenides: from rational synthesis to property control via orbital occupation and electron filling," *Acc. Chem. Res.,* vol. 48, no. 1, pp. 81-90, 2015.

[13] M. Inagaki, "Applications of graphite intercalation compounds," *Journal of Materials Research,* vol. 4, no. 6, pp. 1560-1568, 1989.

[14] H. Yoo, K. Heo, M. H. R. Ansari, and S. Cho, "Recent advances in electrical doping of 2D semiconductor materials: Methods, analyses, and applications," *Nanomater.,* vol. 11, no. 4, p. 832, 2021.

[15] R. Shaham, O. Katz, and O. Firstenberg, "Strong coupling of alkali-metal spins to noble-gas spins with an hour-long coherence time," *Nat. Phys.,* vol. 18, no. 5, pp. 506-510, 2022.

[16] O. Katz, R. Shaham, and O. Firstenberg, "Quantum Interface for Noble-Gas Spins Based on Spin-Exchange Collisions," *PRX Quantum,* vol. 3, no. 1, p. 010305, 01/10/ 2022, doi: 10.1103/PRXQuantum.3.010305.

[17] O. Katz, R. Shaham, and O. Firstenberg, "Coupling light to a nuclear spin gas with a two-photon linewidth of five millihertz," *Sci. Adv.,* vol. 7, no. 14, p. eabe9164, 2021.

[18] O. Katz, R. Shaham, E. S. Polzik, and O. Firstenberg, "Long-Lived Entanglement Generation of Nuclear Spins Using Coherent Light," *Phys. Rev. Lett.,* vol. 124, no. 4, p. 043602, 01/29/ 2020, doi: 10.1103/PhysRevLett.124.043602.

[19] B. C. Rose *et al.*, "Observation of an environmentally insensitive solid-state spin defect in diamond," *Science,* vol. 361, no. 6397, pp. 60-63, 2018, doi: doi:10.1126/science.aao0290.

[20] E. D. Herbschleb *et al.*, "Ultra-long coherence times amongst room-temperature solid-state spins," *Nat Commun,* vol. 10, no. 1, p. 3766, 2019/08/28 2019, doi: 10.1038/s41467-019-11776-8.

[21] B. Naydenov *et al.*, "Increasing the coherence time of single electron spins in diamond by high temperature annealing," *Appl. Phys. Lett.,* vol. 97, no. 24, p. 242511, 2010.

[22] M. Rajapakse *et al.*, "Intercalation as a versatile tool for fabrication, property tuning, and phase transitions in 2D materials," *npj 2D Mater. Appl.,* vol. 5, no. 1, pp. 1-21, 2021.

[23] G. Alberti and U. Costantino, "Recent progress in the intercalation chemistry of layered α-zirconium phosphate and its derivatives, and future perspectives for their use in catalysis," *Journal of molecular catalysis,* vol. 27, no. 1-2, pp. 235-250, 1984.

[24] J. Wan, S. D. Lacey, J. Dai, W. Bao, M. S. Fuhrer, and L. Hu, "Tuning two-dimensional nanomaterials by intercalation: materials, properties and applications," *Chemical Society Reviews,* vol. 45, no. 24, pp. 6742-6765, 2016.

[25] M. S. Stark, K. L. Kuntz, S. J. Martens, and S. C. Warren, "Intercalation of layered materials from bulk to 2D," *Advanced Materials,* vol. 31, no. 27, p. 1808213, 2019.

[26] Z. Li *et al.*, "Intercalation strategy in 2D materials for electronics and optoelectronics," *Small Methods,* vol. 5, no. 9, p. 2100567, 2021.

[27] Y. Wu, D. Li, C.-L. Wu, H. Y. Hwang, and Y. Cui, "Electrostatic gating and intercalation in 2D materials," *Nat. Rev. Mater.,* pp. 1-13, 2022.

[28] A. J. Jacobson and L. F. Nazar, "Intercalation chemistry," *Encycl. Inorg. Chem.,* 2006.

[29] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, "The electronic properties of graphene," *Reviews of Modern Physics,* vol. 81, no. 1, pp. 109-162, 01/14/ 2009, doi: 10.1103/RevModPhys.81.109.

[30] A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nature Materials,* vol. 6, no. 3, pp. 183-191, 2007/03/01 2007, doi: 10.1038/nmat1849.

[31] X. Xu, J. Chen, and B. Li, "Phonon thermal conduction in novel 2D materials," *Journal of Physics: Condensed Matter,* vol. 28, no. 48, p. 483001, 2016.

[32] H. W. Kim *et al.*, "Nanoscale control of phonon excitations in graphene," *Nat. Commun.,* vol. 6, no. 1, p. 7528, 2015.

[33] X. Gu and R. Yang, "Phonon transport and thermal conductivity in two-dimensional materials," *Annual review of heat transfer,* vol. 19, 2016.

[34] Y. Qi *et al.*, "Recent Progress in Strain Engineering on Van der Waals 2D Materials: Tunable Electrical, Electrochemical, Magnetic, and Optical Properties," *Advanced Materials,* vol. 35, no. 12, p. 2205714, 2023.

[35] Q. Ma, G. Ren, K. Xu, and J. Z. Ou, "Tunable optical properties of 2D materials and their applications," *Advanced Optical Materials,* vol. 9, no. 2, p. 2001313, 2021.

[36] B. Ma, C. Martín, R. Kurapati, and A. Bianco, "Degradation-by-design: how chemical functionalization enhances the biodegradability and safety of 2D materials," *Chemical Society Reviews,* vol. 49, no. 17, pp. 6224-6247, 2020.

[37] D. Tyagi *et al.*, "Recent advances in two-dimensional-material-based sensing technology toward health and environmental monitoring applications," *Nanoscale,* vol. 12, no. 6, pp. 3535-3559, 2020.

[38] Y. Alaskar *et al.*, "Towards van der Waals epitaxial growth of GaAs on Si using a graphene buffer layer," *Adv. Funct. Mater.,* vol. 24, no. 42, pp. 6629-6638, 2014.

[39] R. Wang *et al.*, "A peeling approach for integrated manufacturing of large monolayer h-BN crystals," *ACS nano,* vol. 13, no. 2, pp. 2114-2126, 2019.

[40] S. M. Kim *et al.*, "Synthesis of large-area multilayer hexagonal boron nitride for high material performance," *Nat. Commun.,* vol. 6, no. 1, pp. 1-11, 2015.

[41] T. Nasir *et al.*, "Wafer-Scale Growth of 3D Graphene on SiO2 by Remote Metal Catalyst-Assisted MOCVD and Its Application as a NO2 Gas Sensor," *Cryst. Growth Des.,* 2022.

[42] S. Saha *et al.*, "Comprehensive characterization and analysis of hexagonal boron nitride on sapphire," *AIP Adv.,* vol. 11, no. 5, p. 055008, 2021.

[43] S. Saha *et al.*, "Sub-bandgap photoluminescence properties of multilayer h-BN-on-sapphire," *Nanotechnology,* vol. 33, no. 21, p. 215702, 2022.

[44] T. S. Cheng *et al.*, "High-temperature molecular beam epitaxy of hexagonal boron nitride layers," *J. Vac. Sci. Technol. B:Nanotechnol. Microelectron.,* vol. 36, no. 2, p. 02D103, 2018.

[45] T. Kornack, R. Ghosh, and M. V. Romalis, "Nuclear spin gyroscope based on an atomic comagnetometer," *Phys. Rev. Lett.,* vol. 95, no. 23, p. 230801, 2005.

[46] D. A. Thrasher *et al.*, "Continuous comagnetometry using transversely polarized Xe isotopes," *Phys. Rev. A,* vol. 100, no. 6, p. 061403, 2019.

[47] K. Vasu *et al.*, "Van der Waals pressure and its effect on trapped interlayer molecules," *Nat. Commun.,* vol. 7, no. 1, pp. 1-6, 2016.

[48] T. Chupp and S. Swanson, *Medical imaging with laser-polarized noble gases* (Advances in Atomic, Molecular, and Optical Physics). Elsevier, 2001, pp. 41-98.

[49] H. Häffner *et al.*, "Scalable multiparticle entanglement of trapped ions," *Nature,* vol. 438, no. 7068, pp. 643-646, 2005.

[50] I. Bloch, "Quantum coherence and entanglement with ultracold atoms in optical lattices," *Nature,* vol. 453, no. 7198, pp. 1016-1022, 2008.

[51] K. Hammerer, A. S. Sørensen, and E. S. Polzik, "Quantum interface between light and atomic ensembles," *Rev. Mod. Phys.,* vol. 82, no. 2, p. 1041, 2010.

[52] J. Kong, R. Jiménez-Martínez, C. Troullinou, V. G. Lucivero, G. Tóth, and M. W. Mitchell, "Measurement-induced, spatially-extended entanglement in a hot, strongly-interacting atomic system," *Nat. Commun.,* vol. 11, no. 1, pp. 1-9, 2020.

[53] P. Neumann *et al.*, "Multipartite entanglement among single spins in diamond," *Science,* vol. 320, no. 5881, pp. 1326-1329, 2008.

[54] J. Q. Zhong *et al.*, "Ionization-facilitated formation of 2d (alumino) silicate–noble gas clathrate compounds," *Adv. Funct. Mater.,* vol. 29, no. 20, p. 1806583, 2019.

[55] P. Li *et al.*, "Infrared hyperbolic metasurface based on nanostructured van der Waals materials," *Science,* vol. 359, no. 6378, pp. 892-896, 2018.

[56] H. Cun, M. Iannuzzi, A. Hemmi, S. Roth, J. r. Osterwalder, and T. Greber, "Immobilizing individual atoms beneath a corrugated single layer of boron nitride," *Nano Lett.,* vol. 13, no. 5, pp. 2098-2103, 2013.

[57] H. Cun, M. Iannuzzi, A. Hemmi, J. r. Osterwalder, and T. Greber, "Two-nanometer voids in single-layer hexagonal boron nitride: formation via the "can-opener" effect and annihilation by self-healing," *ACS nano,* vol. 8, no. 7, pp. 7423-7431, 2014.

[58] J. Zhang *et al.*, "Atomically thin hexagonal boron nitride and its heterostructures," *Advanced Materials,* vol. 33, no. 6, p. 2000769, 2021.

[59] D. A. Laleyan *et al.*, "AlN/h-BN heterostructures for Mg dopant-free deep ultraviolet photonics," *Nano letters,* vol. 17, no. 6, pp. 3738-3743, 2017.

[60] S. Angizi, S. A. A. Alem, and A. Pakdel, "Towards integration of two-dimensional hexagonal boron nitride (2D h-BN) in energy conversion and storage devices," *Energies,* vol. 15, no. 3, p. 1162, 2022.