



MASTERARBEIT | MASTER'S THESIS

Titel | Title

Selective defect creation in 2D hexagonal boron nitride via low-energy Ar⁺ irradiation

verfasst von | submitted by
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angestrebter akademischer Grad | in partial fulfilment of the requirements for the degree of
Master of Science (MSc)

Wien | Vienna, 2025

Studienkennzahl lt. Studienblatt | Degree
programme code as it appears on the
student record sheet:

UA 066 876

Studienrichtung lt. Studienblatt | Degree
programme as it appears on the student
record sheet:

Masterstudium Physics

Betreut von | Supervisor:

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Abstract

Point defects in hexagonal boron nitride (hBN) have received increasing attention for being an excellent host for single photon emitters (SPE). SPEs are a growing research area that have potential applications in quantum communications, quantum information and quantum simulations, as well as photonics. This raises the question of whether defect creation in hBN can be controlled. Here, we explore the possibility of selectively creating one type of vacancy, either single boron or nitrogen, double or more complex vacancies, in two-dimensional monolayer hBN.

We successfully prepare monolayer hBN samples using an electrochemical delamination method for transfer from copper foil to electron microscopy grids, and then subject them to low-energy Ar^+ irradiation. The resulting defect structures are imaged via scanning transmission electron microscopy (STEM). Low-energy argon ions with different energy profiles were used for the irradiations. Using an interconnected ultra-high vacuum system, the irradiation effects could be directly imaged via STEM without exposing the samples to ambient conditions. Semi-autonomous STEM image acquisition was performed to acquire hundreds of images of hBN before and after irradiation. Pre-irradiation data was used to assess the intrinsic defect concentration and post-irradiation data was used to analyse the irradiation induced vacancy types and concentration for each of the energies. The intrinsic defect concentration was found to be $0.0601 \pm 0.0094 \text{ nm}^{-2}$ with $43.54 \pm 9.40 \%$ single vacancies ($55.01 \pm 4.93 \%$ V_B and $44.99 \pm 4.93 \%$ V_N), $37.40 \pm 8.93 \%$ double vacancies and the rest being more complex vacancy structures. The ion-induced defect concentration was found to be $0.2401 \pm 0.0478 \text{ nm}^{-2}$. Since the results from the different energy profiles were similar, a weighted mean was calculated for all the valid data points and shows $65.10 \pm 6.57 \%$ single vacancies with $89.87 \pm 4.57 \%$ V_B and $10.13 \pm 4.57 \%$ V_N , $26.52 \pm 4.73 \%$ double vacancies with the rest being more complex structures.

Overall, this work showcases the possibility of selectively creating one type of vacancy, primarily boron single vacancies, in hBN via Ar^+ irradiation. However, the underlying mechanism behind the vacancy creation is yet to be understood, since the experimental results contradict predictions based on atomistic simulations.

Zusammenfassung

Punktdefekte in hexagonalem Bornitrid (hBN) haben zunehmend Aufmerksamkeit auf sich gezogen, da sie als Quellen für die Emission einzelner Photonen dienen. Diese sind relevant für potenzielle Anwendungen in den Bereichen Quantenkommunikation, Quanteninformation und Quantensimulationen sowie in der Photonik. Dadurch kommt die Frage auf, ob die Defektbildung in hBN kontrolliert werden kann. In dieser Arbeit untersuchen wir die Möglichkeit, selektiv eine Art von Defekten zu erzeugen, konkret einzelne Bor oder Stickstoff Leerstellen, doppelte, mehrfache oder komplexe Leerstellen.

Dafür transferieren wir einschichtige hBN-Proben mit Hilfe einer elektrochemischen Delaminierungsmethode von Kupferfolien auf Elektronenmikroskopie-Gitter, und unterziehen sie dann niederenergetischer Ar^+ Bestrahlung. Die resultierenden Defektstrukturen werden mittels Rastertransmissionselektronenmikroskopie (RTEM) abgebildet. Die Bestrahlung wurde mithilfe niedrigerenergetischer Argon-Ionen mit unterschiedlichen Energieverteilungen durchgeführt. Unter Verwendung eines Ultrahochvakuumsystems, konnten die Bestrahlungseffekte direkt mittels RTEM abgebildet werden, ohne die Proben Luft auszusetzen. Die RTEM-Bildaufnahme wurde halbautonom durchgeführt, um hunderte von Bildern von hBN vor und nach der Bestrahlung aufzunehmen. Die Daten vor der Bestrahlung wurden verwendet, um die intrinsische Defektkonzentration zu ermitteln und die Daten nach der Bestrahlung wurden zur Analyse der durch die Bestrahlung verursachten Defekttypen und -konzentrationen für die jeweilige Energie verwendet. Die intrinsische Defektkonzentration lag bei $0,0601 \pm 0,0094 \text{ nm}^{-2}$ mit $43,54 \pm 9,40 \%$ einfache Leerstellen ($55,01 \pm 4,93 \%$ V_B und $44,99 \pm 4,93 \%$ V_N), $37,40 \pm 8,93 \%$ doppelte Leerstellen und der Rest sind komplexere Leerstellenstrukturen. Die ioneninduzierte Defektkonzentration betrug $0,2401 \pm 0,0478 \text{ nm}^{-2}$. Da die Ergebnisse für verschiedene Energieprofile ähnlich waren, wurde ein gewichteter Mittelwert für alle gültigen Datenpunkte berechnet, welcher $65,10 \pm 6,57 \%$ für einzelne Leerstellen mit $89,87 \pm 4,57 \%$ V_B und für $10,13 \pm 4,57 \%$ V_N , $26,52 \pm 4,73 \%$ für doppelte Leerstellen beträgt, der Rest sind komplexere Strukturen.

Insgesamt zeigt diese Arbeit die Möglichkeit der selektiven Erzeugung bestimmter Leerstellen in hBN durch Ar^+ Bestrahlung, in erster Linie Bor-Einfachleerstellen. Allerdings muss der genaue Leerstellenbildungsmechanismus noch verstanden werden, da die experimentellen Ergebnisse den Vorhersagen aus atomistischen Simulationen widersprechen.

Acknowledgements

Firstly, I would like to thank my supervisor Jani Kotakoski for accepting me into his research group and providing me with a research contract by the Vienna Doctoral School of Physics (VDSP) for the duration of my master's program. The project that I had the opportunity of working on was an extremely exciting and fun journey from start to finish, and wouldn't have been possible without his constant guidance and insightful feedback. His expertise in the field is unmatched and I am extremely grateful to be working as part of the group now and in the future as well.

I would like to thank my mentor and co-supervisor Manuel Längle for all the training sessions with the electron microscope and the plasma source. I am super glad that I was able to learn, problem solve, and work on projects with him because his wisdom always provided a grounded reality of experimental research, making it a much more enjoyable and fulfilling process.

I cannot thank Clemens Mangler enough for all of his contributions throughout my entire time in the research group. He is truly an unsung hero who is always around to help when something is not working. His love for teaching and helping others is an incredible support system for our research group and I am very grateful for all of his help with the electron microscope, vacuum equipment, Linux & IT things, and for helping me build the deceleration setup that we installed together as part of the work done for this thesis. I would also like to thank Kimmo Mustonen for all of his help and guidance with the electron microscope and CVD furnace, and also for the general research discussion that we had.

And now to all the group members for making my time in the group very memorable. Thanks to my master's buddies Milan and Barbara for hanging out and studying with me during the last year as we painfully took exams and completed courses. Thanks to Philipp and Thuy An for helping me with the sample preparation process and the time you spent helping me look at samples at the microscope. Thanks to Wael, Clara, and Jana for being fun and lovely people both in and out of work, and for all the chats and laughs that we had together. Special thanks to David for making my time outside of work really fun with all the sports events, movies, and walks. Thanks to all the remaining people that I would have loved to individually write about but didn't have the time to show my

appreciation. And also a special thanks to Wael, Carsten, and Clara for introducing me to Magic!

A special shout-out and thanks goes to Tamara Beltrán, whom I had the pleasure of mentoring during her summer internship at the group. Without her help, the sample preparation method for hBN transfer onto TEM grids would not be what it is now, and I am very thankful for all the tweaks and suggestions that she made to the method for making it more user-friendly and efficient.

And finally but most importantly, thanks to my parents and family for providing me with the opportunity of studying abroad and pursuing a career many thousands of km away from them. I will forever be grateful and I hope that I can keep making them proud.

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Chapter 1

Introduction

The field of 2D materials emerged when the first experimental isolation and electronic characterisation of graphene, a one-atom layer of carbon atoms, was made in 2004 [1]. Graphene was synthesised using mechanical exfoliation consisting of repeated peeling of graphite flakes with scotch tape. Soon after this, a monolayer of hexagonal boron nitride (hBN), so-called white graphene [2], was also synthesised using a similar mechanical exfoliation method [3, 4] and also via other methods involving chemical solvents and reactions [5].

Defect creation in 2D materials and the understanding of the underlying mechanism are of utmost importance due to our reliance on materials that make up the devices used in our modern semiconductor world. Particle irradiation, and more specifically ion-irradiation, has been proven to be one of the most important tools for the modification of 2D materials at the atomic scale [6]. Point defects in hexagonal boron nitride (hBN) have received increasing attention for being an excellent host for single photon emitters (SPE) at room temperature [7, 8]. It has been predicted that carbon atom substitutions in a boron site beside a nitrogen vacancy ($C_B V_N$) in hBN are the most likely emission source [9]. SPE are a growing research area for their potential applications in quantum communications, information, and simulations [10, 11]. The ideal SPE emits exactly one photon at a time at a given spatio-temporal mode and that each photon is identical (signature of indistinguishability) [12]. Since there has been no solid experimental confirmation about which type of point defect is responsible for the emission, it would be beneficial to explore the selective creation of defect types in hBN so that future research on quantum applications can have a fundamental understanding of the material.

1.1 Selective defect creation

Experimental evidence for defect type selectivity in hBN has not yet been shown using ion irradiation, but a couple theoretical studies have been conducted showing some degree of selectivity. A 2010 study using molecular dynamics (MD) simulation study and analytical potentials (AP) investigated the effects of noble gas ion irradiation on monolayer hBN [13]. They found that depending on the energy of the noble gas ion, the probability of creating particular defect types differed. For argon (Ar), at lower energies of up to 0.1 keV, single boron and single nitrogen vacancies dominate with both having roughly the same probability of creation. At medium energies ranging from 0.1 keV to 10 keV, apart from single vacancies, the ions tend to displace a boron-nitrogen pair creating double vacancies as well. And at high energies greater than 10 keV, due to collision cascades and the recoil of target atoms in-plane, complex vacancies dominate. A more recent study used analytical potential molecular dynamics with more accurate inter-atomic potentials for the interaction between boron and nitrogen, as well as the interaction between the noble gas atoms and the target atoms [14]. They found that, with an Ar ion fluence of 5×10^{14} ions/cm², the vacancy concentration (per nm²) of nitrogen single vacancies always dominate in the ion energy range of 50-200 eV. This is followed by double vacancies, boron single vacancies and then complex vacancies. The vacancy concentration of nitrogen single vacancies is approx double that of boron single vacancies.

This degree of vacancy selectivity in hBN raised the question of whether this could be reproduced experimentally. Work done by colleagues at the research unit Physics of Nanostructured Materials [15], experimentally showed that irradiation with Ar⁺ energies ranging between 90 and 250 eV on monolayer hBN produced ca. 55% boron single vacancies, followed by ca. 18% complex vacancies, 14% complex vacancies and then 12% nitrogen single vacancies. This defect-engineering study showed a high selectivity for boron single vacancies and was a direct contrast to the above computational studies that showed selectivity for nitrogen single vacancies.

Another colleague performed Ehrenfest time dependent density functional theory (TDDFT) molecular dynamics (MD) simulations of Ar irradiation on monolayer hBN and the results can be seen in Table 1.1. These simulations are more accurate as they use Ar⁺¹ ions as the projectile in comparison to the above theoretical studies that use neutral Ar as the projectile. The electrons here are propagated with the time-dependent Kohn-Sham

Schrodinger equation and molecular dynamics allow for the nuclei to move simultaneously.

	Ar - N	Ar⁺¹ - N	Ar⁺² - N	Ar - B	Ar⁺¹ - B	Ar⁺² - B
Ar⁺ energy	34.5 eV	34.5 eV	31.5 eV	39.5 eV	45.5 eV	42.5 eV

Table 1.1: Ehrenfest time dependent density functional theory (TDDFT) molecular dynamics (MD) simulation results. The Ar⁺ energy above is the energy required by the ion to successfully displace the target atom from its lattice position.

Since we are interested only on the effects of singly charged argon ions, the results here show that Ar⁺¹ requires 34.5 eV to displace a nitrogen atom and requires 45.5 eV to displace a boron atom, in a head-on collision, in hBN. This 11 eV difference is the motivation for this experimental study on selective defect creation in hBN where we explore the possibility of creating primarily nitrogen single vacancies using Ar⁺¹ with energy below ca. 45 eV and also reproducing results from reference [15] to create primarily boron single vacancies with Ar⁺¹ energies of ca. 150 eV.

With the use of an atomic resolution scanning transmission electron microscope (STEM) equipped with a semi-autonomous image acquisition software tool [16], the resulting defect structures in hBN were assessed. This correlation study was made possible because of an interconnected ultra-high vacuum system, called CANVAS [17], as the hBN samples could be transported between the electron microscope and the irradiation chamber without exposing it to ambient conditions. This is essential so that we can make accurate claims about our findings after irradiation without introducing external factors.

Chapter 2

Materials

2.1 Hexagonal boron nitride (hBN)

Boron nitride (BN) is a chemical compound made up of boron and nitrogen, with atomic numbers $Z = 5$ and $Z = 7$ respectively. Depending on the arrangement of the boron and nitrogen atoms in the material, it exists in different forms. The non-crystalline form is called amorphous boron nitride (a-BN) where there is no long range order in the arrangement of the atoms. The crystalline ones exist in three different forms: hexagonal boron nitride (hBN), cubic boron nitride (c-BN), and wurtzite boron nitride (w-BN) [18].

hBN, the most stable crystalline form, consists of a layered structure, similar to that of graphite, where the atoms form a honeycomb structure with alternating boron and nitrogen atoms. c-BN has a crystal structure that is similar to that of diamond, and is less stable than hBN. w-BN is a metastable material with a hexagonal polymorph-like structure [19], where the boron and nitrogen atoms form a honeycomb-like structure that is interlocked within different layers of the material. In the context of this thesis, only hBN is discussed.

2.1.1 Structure

The bulk structure of hBN has layers that are stacked on top of each other and are held together by weak van der Waals (vdW) forces that arise from instantaneously induced dipole interactions between the atoms in each of the layers. The interlayer bonding also has a small electrostatic contribution due to the partially charged atomic centres in hBN

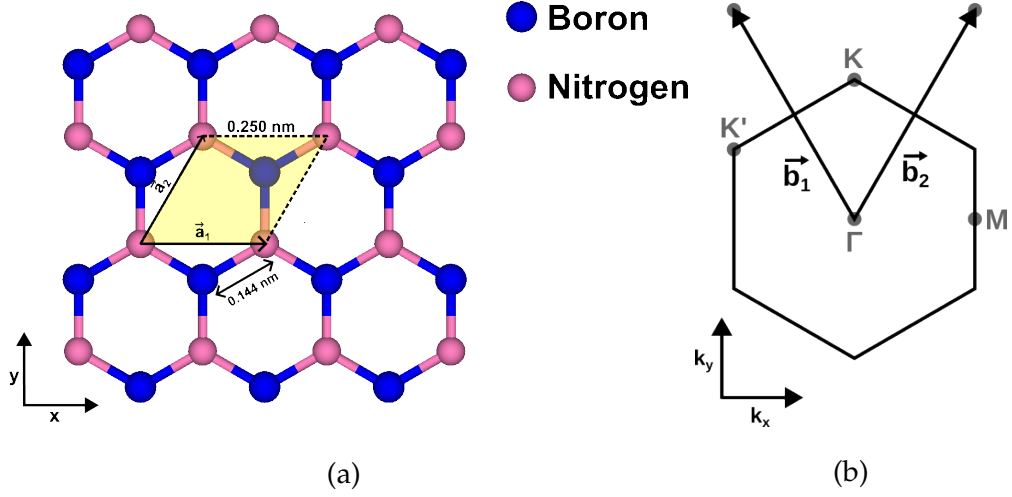


Figure 2.1: **Illustration of the real and reciprocal space structure of monolayer hBN.** (a) Honeycomb structure with alternating boron and nitrogen atoms. The unit cell is highlighted in yellow with the lattice vectors $\vec{a}_1$ and $\vec{a}_2$. (b) The first Brillouin zone with high-symmetry points Γ , K , K' , and M . The reciprocal lattice vectors are $\vec{b}_1$ and $\vec{b}_2$. (Figure credits: Philipp Irschik)

[20]. A single layer in this material, with a thickness of one atom, is known as monolayer hBN and is shown in Fig. 2.1 (a). The honeycomb-like structure in monolayer hBN consists of alternating boron and nitrogen atoms that form a two-dimensional (2D) lattice in the x and y planes. The unit cell is defined by the lattice vectors $\vec{a}_1$ and $\vec{a}_2$ with a lattice constant of $a = 0.250$ nm. The boron-nitrogen bond has a length of 0.144 nm. Fig. 2.1 (b) shows the first Brillouin zone, a hexagon with four symmetry points Γ , K , K' , and M marked, which is the Wigner-Seitz cell of the reciprocal lattice defined by vectors $\vec{b}_1$ and $\vec{b}_2$ [21].

The forces between the individually stacked layers can be easily overcome by exfoliation methods where the layers are peeled apart until there is only one layer remaining. Fig. 2.2 shows bilayer hBN in the AA' configuration [22], where boron atoms in the bottom layer are directly below the nitrogen atoms in the top layer (and vice versa) with an inter-layer separation of 0.333 nm.

The ground state electronic configuration of boron is $1s^2 2s^2 2p^1$ and that of nitrogen is $1s^2 2s^2 2p^3$. In hBN, boron's $2s$ and two $2p$ (p_x, p_y) orbitals undergo hybridisation to form three sp^2 hybrid orbitals and similarly, nitrogen does the same. Each boron and nitrogen atom form three σ -bonds, that are in-plane, with its neighbouring three nitrogen and boron atoms, respectively with the hybrid sp^2 orbitals forming the hexagonal lattice struc-

ture. The remaining unhybridised $2p_z$ orbitals on both boron and nitrogen, that are out-of-plane, participate in weak π -bonding. Since boron's electronegativity is 2.04 (Pauling units) and nitrogen's electronegativity is 3.04 (Pauling units) [23], the boron-nitrogen σ -bond has a polar covalent nature where the electron cloud density in the σ -bonds are slightly pulled towards the nitrogen atom [24].

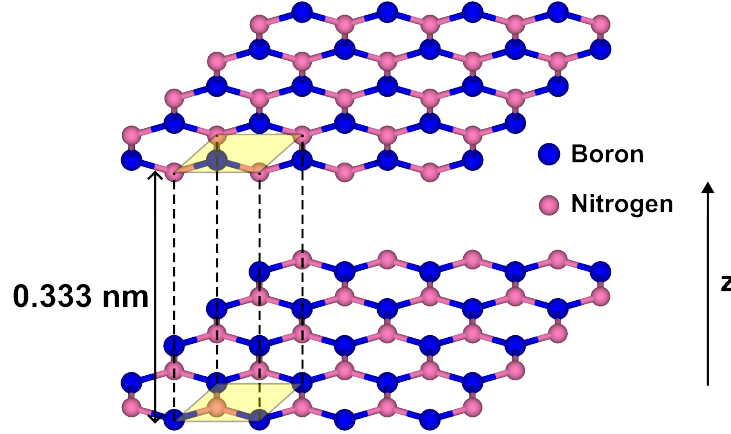


Figure 2.2: **Two layers of hBN stacked in the AA' configuration.** (Figure credits: Philipp Irschik)

In 2D materials and crystallography, point defects are a type of crystallographic defect of zero dimensionality that occur only at a single lattice point [25]. The two types of point defects that are of interest in this study are vacancies and substitutions. A vacancy is a type of point defect where an atom in a lattice is missing from its original lattice position and results in a vacant spot. A substitution is when this vacant spot gets filled by an atom of a different element, sometimes called an impurity atom [26]. In hBN, boron and nitrogen vacancies appear to be triangular in shape and can be distinguished by the direction of the triangle. Fig. 2.3 shows a MAADF STEM image of boron and nitrogen vacancies in hBN.

Point defects in hBN have been receiving increasing attention for being excellent hosts for single photon emitters (SPEs) at room temperature [7, 8]. It has been predicted that carbon substitutions in a boron site beside a nitrogen vacancy ($C_B V_N$) in hBN are the most likely emission source [9].

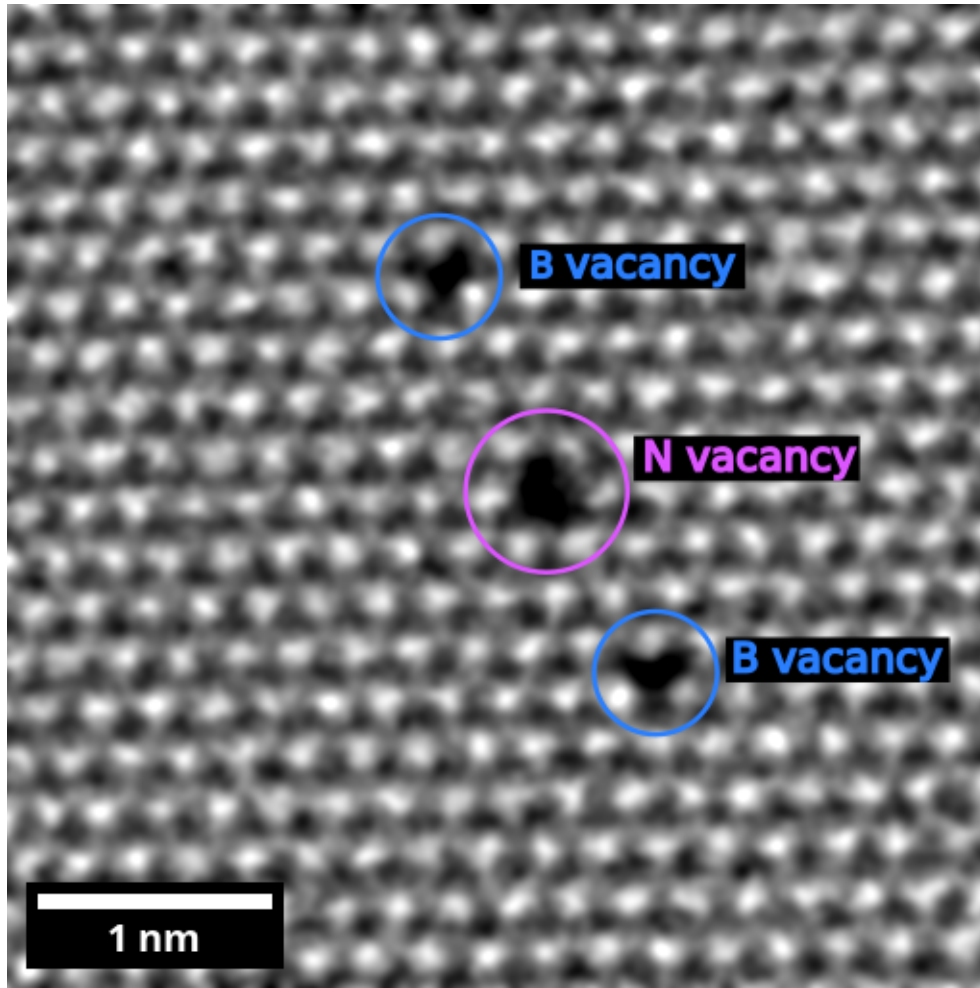


Figure 2.3: **MAADF STEM image of B and N vacancies in hBN.** The boron vacancy sites (circled in blue) have a missing boron atom each and the nitrogen vacancy site (circled in pink) has a missing nitrogen atom. (The image has been processed with a gaussian blur filter with $\sigma = 3.00$).

2.1.2 Properties

Mechanical properties

Monolayer hBN exhibits a large specific surface area compared to bulk hBN, which gives it a high surface-to-volume ratio. This enhances monolayer hBN's mechanical as well as chemical properties [27]. The Young's modulus, a measure of mechanical stiffness has been measured to be 0.865 ± 0.073 TPa and the fracture strength to be 70.5 ± 5.5 GPa. Surprisingly, the strength of hBN remained roughly the same when scaling from monolayer to few-layer (up to nine layers) which is in contrast to graphene that exhibits more than a 30% drop in strength at eight layers when compared to that of monolayer [28]. In comparison, the Young's modulus of steel is approx 200 GPa [29], which shows

just how robust a single atomic layer of hBN is.

Thermal properties

The thermal conductivity (κ) has been measured to be 751 ± 340 W/mK close to room temperature. Two- and three-layer hBN were also measured and κ were found to be 646 ± 242 and 602 ± 247 W/mK, respectively. This indicates that κ decreases with increasing thickness in hBN. For comparison, the κ of monolayer graphene was measured to be 2102 ± 221 W/mK, being the best thermal conductor ever measured. Also, a counter-intuitive but interesting property that hBN shares with graphene is a negative thermal expansion coefficient (TEC). This means that it contracts when heat is supplied to it. Experimentally measured TEC for monolayer hBN is $(-3.58 \pm 0.18) \times 10^{-6}$ /K close to room temperature [30]. This is due to the negative contribution from the dominant transverse out-of-plane phonon modes (ZA modes) compared to the planar phonon modes in hBN. In other words, due to the dimensionality of hBN, it 'flexes' out-of-plane resulting in an effective 'shrinking' in the in-plane direction when heated [31, 32]. In addition to this, hBN exhibits a high thermal stability of up to 1000 °C in air and 1400 °C in vacuum [33, 34]. Hence it is often used as a substrate for other 2D materials as it allows for high stability and oxidation resistance in high-temperature applications [35].

Electronic properties

hBN is a wide bandgap material, an electrical insulator. A 2004 study showed a direct-gap bandgap of 5.971 eV [36] and a more recent study reported an indirect bandgap of 5.955 eV [37]. This makes hBN a suitable dielectric owing to its superior insulating properties and chemical inertness.

2.1.3 Synthesis

Synthesis of monolayer hBN can be done via two approaches: top-down and bottom-up. Top-down synthesis methods start with a 3D bulk material and work downwards by breaking it into smaller and smaller pieces until a 2D monolayer is achieved. Here, exfoliation techniques have proven to be the best way to synthesise monolayer materials [3]. An older [5, 34] top-down method involves the use of high temperature solvents and high pressures to grow the hBN crystals. On the other hand, bottom-up synthesis methods start with precursor compounds that are brought together to chemically react and

form the desired monolayers. The most common and widely used bottom-up synthesis method is chemical vapour deposition (CVD).

Out of the different top-down synthesis methods, mechanical exfoliation via the scotch tape method [1], famously demonstrated in the discovery of graphene, uses the adhesive force of tape to overcome the vdW inter-layer bonding in graphite. A similar method termed micro-mechanical cleavage [3] uses the layered crystal and is rubbed against another surface where flakes of the material get stuck. Out of these cleaved flakes, single layers can be found and transferred readily. Similarly, BN powder can also be exfoliated to produce monolayer hBN. Since then, many different types of exfoliation methods have been designed that are more time-efficient and can be scaled up to give large quantities of exfoliated monolayer material. One such method is Liquid Exfoliation [38] of 2D materials where the bulk material is dispersed into a solvent with surface tension values that minimise the energy of exfoliation. Another method is Electrochemical exfoliation [39] where the bulk material is made up into an electrode that participates in an electrochemical cell reaction. The ions & radicals in the electrolyte are able to intercalate into the layers of the bulk material and exfoliate it on applied voltage resulting in flakes of varying thickness in the electrolyte.

CVD growth is the most promising bottom-up route for monolayer synthesis because of its flexible controllability during the growth process. The domain size, growth orientation, morphology, layer number and even stacking-order can be controlled [10]. The CVD growth mechanism for monolayer hBN follows three steps [40]: (1) the precursors (ammonia, borane, borazine, etc) decompose into boron and nitrogen containing species under high temperature, (2) the boron and nitrogen containing species deposit onto a metal substrate and combine into clusters, (3) the clusters grow into larger and larger islands until they form a continuous film of monolayer hBN [10, 41]. Each of these steps can be tuned accordingly for different applications.

The hBN samples used in this study are commercial CVD grown on copper foil purchased from Sigma-Aldrich [42].

2.2 Noble gases

Noble gases are the chemical elements that occupy Group 18 of the periodic table, namely helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), radon (Rn) and oganesson (Og). They are unique as they have completely filled valence electron shells and therefore do not participate in forming chemical bonds. Hence, they exist as mono-atomic gases at room temperature and are chemically inert, colourless, and odourless. Noble gases are used extensively in applications that require inert atmospheres. They are also commonly used as a filler gas in incandescent light bulbs and halogen lamps where they glow with distinctive colours when heated up and ionised [43].

2.2.1 Argon

Argon in particular is used during the synthesis of air-sensitive materials and compounds in fabrication units and glove boxes. Since the Earth's atmosphere is made up of 0.934 % Ar by volume, it is readily available for use cases and air is used as the primary industrial source for making purified Ar [44]. In this study, we use argon as our ion source for defect-engineering 2D materials. It was chosen because we require an inert atom that does not chemically react with the sample.

Chapter 3

Methods and Equipment

3.1 Scanning Transmission Electron Microscopy (STEM)

The following sections on transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) are adapted from references [45, 46, 47].

3.1.1 Electron microscopy overview

Electron microscopy is an imaging technique that uses a beam of electrons as the illumination source. Advanced microscopy techniques have transitioned to use electrons instead of visible light because of the wavelength related resolution limit given by the Abbe relation [48]

$$\Delta d = 0.61 \frac{\lambda}{n \sin \beta} = 0.61 \frac{\lambda}{NA}, \quad (3.1)$$

where Δd is smallest resolvable distance, λ is the wavelength of the radiation used as the probe, n is the refractive index of the medium that the radiation travels through, and β is the convergence semi-angle. The numerical aperture (NA) is defined as $n \sin \beta$. Therefore it is easy to see using equation 3.1 that with the use of visible light (wavelengths between 380 and 750 nm), one cannot resolve distances Δd smaller than approx 200 nm. Since the size of atoms and inter-atomic distances are in the order of ångströms (10^{-10} m or Å) and lower, visible light microscopy (VLM) cannot resolve atomic positions and

lattices. Electron microscopes have a wavelength that is expressed using the de Broglie wavelength of matter waves [49] in the relativistic limit (due to the high velocities of electrons in an electron microscope) as

$$\lambda = \frac{h}{\sqrt{2m_0eU}} \frac{1}{\sqrt{1 + \frac{eU}{2m_0c^2}}}, \quad (3.2)$$

where h is the Planck constant, m_0 is rest mass of an electron, e is the elementary charge, U is the acceleration voltage (electron energy) and c is the speed of light. Typical transmission electron microscopes (TEMs) have acceleration voltages in the range of 30 - 300 kV [50]. For example with a 60 kV acceleration voltage and using equation 3.2, we get a wavelength $\lambda \approx 4.9$ pm. Hence, electron microscopy can be used to resolve atomic lattices and individual atoms themselves. In practice however, resolution is not only limited by the wavelength but by aberrations as well, and correcting for them can immensely improve resolution allowing it to reach close to the theoretical values [51].

3.1.2 Electron sources

There are two kinds of electron sources used in TEMs and STEMs, namely a thermionic source and a field-emission source. In this study, we have a field-emission electron source, usually called a field-emission gun (FEG). It uses a fine needle point of tungsten wire across which a high voltage is applied, which lowers the work-function barrier, allowing the electrons to tunnel out of the tungsten tip. This method requires a contamination free environment and pristine surfaces, and is operated in ultra-high vacuum (UHV) conditions of $< 10^{-9}$ mbar. The tungsten tip is also kept at ambient temperatures and the electron source is commonly called 'cold'-FEG. This type of electron gun is preferred in modern TEMs and STEMs because of high current density, high brightness and a coherent source [45].

Once the electrons tunnel out, they are then accelerated through a potential difference, with a chosen acceleration voltage (e.g. 100 kV), and acquire an energy of 100 keV. The electrons are then focused using electromagnetic lenses that can have their strength changed by altering the current, and hence the magnetic field, through a coil of wire around an iron core. More information about electron lenses is given in Section 3.1.4.

3.1.3 Electron scattering

Broadly speaking, in a two-body scattering event, interactions of either elastic or inelastic type can take place. Similarly, in an electron microscope, electrons undergo elastic and inelastic scattering when they interact with the atoms of the sample. Fig. 3.1 shows the different ways an electron can interact with an atom, and how its trajectory can change accordingly.

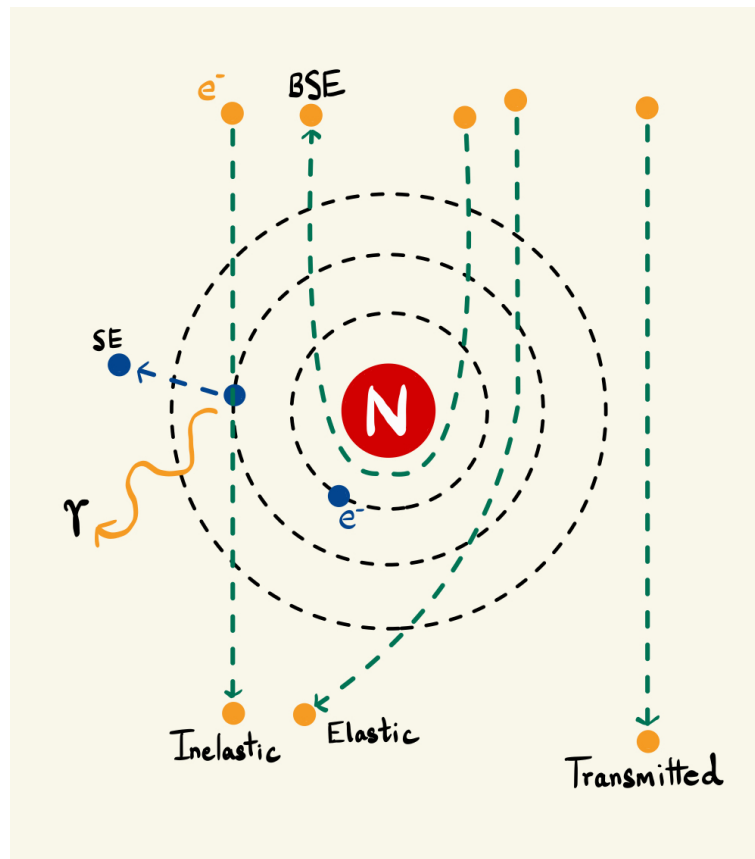


Figure 3.1: **Illustration of the different electron-nucleus scattering events.** The primary electrons (yellow), the bound electrons (blue) and the nucleus (red) are depicted along with elastic, inelastic, BSE, SE (along with the emission of an X-ray photon γ), and transmitted trajectories.

Elastic scattering is the process where the total kinetic energy of the system is conserved. In the case of an electron interacting with an atom in the sample, when the negatively charged electron approaches the positively charged nucleus of an atom, they experience an attractive Coulombic force (electrostatic force) between them. Depending on the distance of approach (the closer, the stronger the force), the electron can either be slightly deflected from its initial trajectory, or heavily deflected to the point where it's backscattered in the opposite direction of approach. Since the mass of an electron is about 1/2000

the mass of a proton or neutron, the nucleus of the atom experiences a negligible change in its velocity. The deflected electrons and their altered trajectory is the key concept in STEM imaging, and is explained in more detail in Section 3.1.5.

Inelastic scattering is the process where the kinetic energy of the system is not conserved after the interaction. Here, the kinetic energy of the ion is (partially) lost to other energy forms. There are a few ways this can take place when an electron interacts with an atom in the sample. The primary electron can interact with a bound electron (in the electron shells) of the atom and possibly knock it out, emitting a secondary electron. This process is usually accompanied with the relaxation of an electron from a higher energy shell to the now empty shell resulting in the emission of characteristic X-rays. The primary electron can also interact with quasiparticles such as phonons, plasmons, or excitons in the sample also resulting in inelastic scattering processes. The inelastically scattered electrons and their energy loss or gain is the basis for spectroscopy techniques like electron energy loss spectroscopy (EELS), and the emitted X-rays can be used in energy dispersive X-ray (EDX) spectroscopy. These two spectroscopy techniques are often implemented in STEM and are used to get elemental information from the atoms in the sample.

Cross-section

The angular distribution of scattered electrons is given by the differential cross-section $d\sigma$

$$\frac{d\sigma}{d\Omega} = \frac{1}{2\pi \sin \theta} \frac{d\sigma}{d\theta}, \quad (3.3)$$

where σ is the cross-section, θ is the scattering angle, and Ω is the total solid angle of scattering. An incremental increase in the scattering angle $d\theta$ gives an incremental increase in a solid angle $d\Omega$. Integrating over the angular space gives the likelihood that scattered electrons deflect within this angular range.

The Rutherford model approximates the elastic scattering from the atomic nucleus in relativistic terms [45]

$$\sigma_R(\theta) = \frac{Z^2 \lambda_R^4}{64\pi^4 a_0^2} \frac{d\Omega}{\left[\sin^2\left(\frac{\theta}{2}\right) + \frac{\theta_0^2}{4} \right]^2}, \quad (3.4)$$

where Z is the atomic number of the atom that the electron interacts with, λ_R is the rel-

ativistic de Broglie wavelength of the primary electron, a_0 is the Bohr radius, and θ_0 is a screening parameter that describes the screening effect of electrons around the nucleus of an atom. Hence, from equation 3.4 it can be seen that the Rutherford scattering cross-section angle-dependency is proportional to Z^2 . Experimental measurements of the angle dependency shows that it increases with about $Z^{1.7}$ instead of the theoretically calculated Z^2 [52, 53, 54]. In STEM, the use of Z -contrast imaging is central to its concept and is explained in more detail in Section 3.2.5.

3.1.4 Aberrations and their correction

As mentioned in section 3.1.1, the resolution in STEM is aberration-limited. Aberrations are intrinsic physical properties in optical systems with lenses that translate to blurs or distortions in the image. Since electromagnetic lenses are complicated, non-aberration corrected electron microscopes often suffer from significant spherical and chromatic aberration, astigmatism, and coma.

Electron lenses

Electron lenses are electromagnets that use electrostatic fields to focus the electrons. An electron lens is made up a coil of copper wire that surrounds a soft iron core, called the polepiece, with a hole drilled though it to accommodate the electron beam path. A current is passed through the coil, and a magnetic field is created in the region of the hole. The force felt by the electron in a magnetic field is given by the Lorentz force

$$F = q(E + v \times B) = -e(E + v \times B), \quad (3.5)$$

where $q = -e$ is the charge of an electron, B is the magnetic field strength, and v is the velocity of the electron. As the electrons travel through the lens, it spirals and follows a helical trajectory. Electron lenses can be explained reasonably well by being approximated to convex glass lenses. The following are explained using this approximation and the theory of refraction.

Spherical aberration

Spherical aberrations arise due to the shape of the lens. As the electron beam-paths pass through the lens, they get refracted and are focused to a point. Spherical aberration (pos-

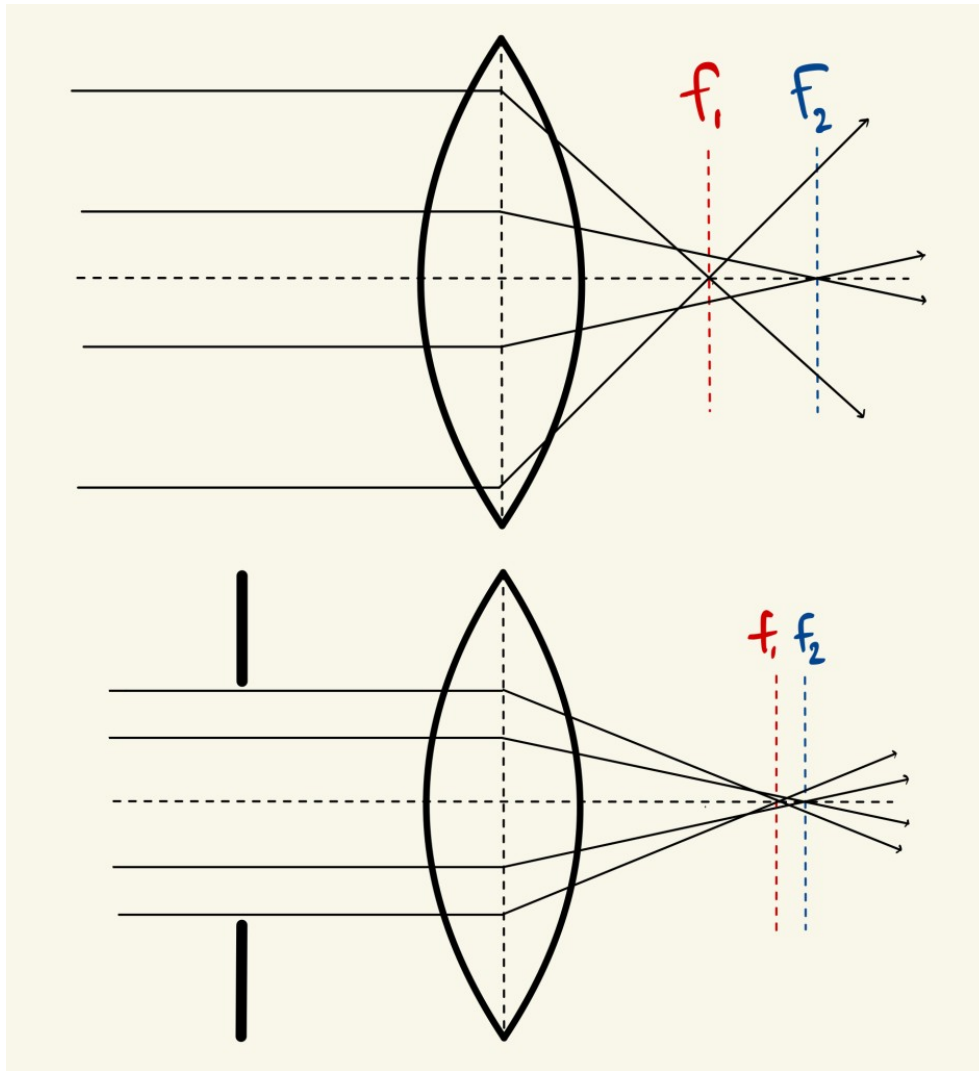


Figure 3.2: **Illustration of spherical aberration resulting in two focal points f_1 and f_2 .** The use of an aperture results in the two focal points being much closer together.

itive) causes the beam-paths that are further away from the optical axis to be refracted stronger, thereby over-focusing the beam. Hence, the further away from the optical axis, the stronger the refraction and this results in an infinite number of focal points. The resulting image looks sharp in the centre and becomes increasing blurred towards the edges [45]. Fig. 3.2 illustrates spherical aberrations and its correction.

Chromatic aberration

Chromatic aberrations arise not due to the lens, but because of the electron probe. All electron sources, emit electrons with a finite energy spread. Due to the slightly different energies of the electrons (and slightly different velocities), they refract differently as the strength of the refraction is velocity dependent. This translates to a larger electron probe size and also blurs the resulting image. However, it is often insignificant in modern STEM

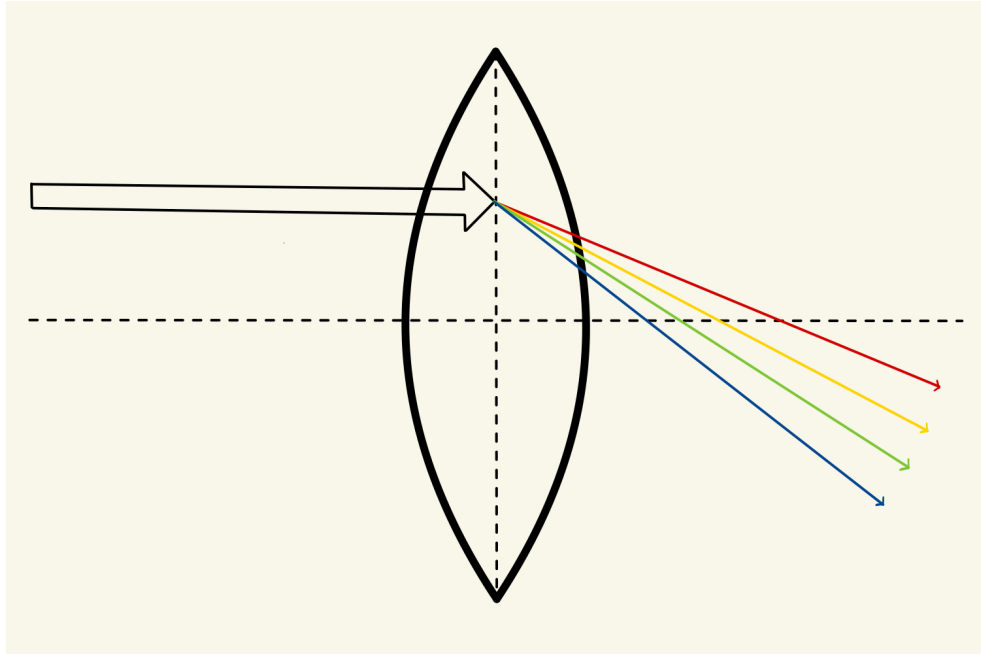


Figure 3.3: **Illustration of chromatic aberration.** The incoming electron beam path represented with the white arrow refracts into the different colours that represent the different energies of the electron beam.

instruments due to advancements in electron sources and the use of monochromators [45, 55]. Fig. 3.3 illustrates chromatic aberration.

Astigmatism

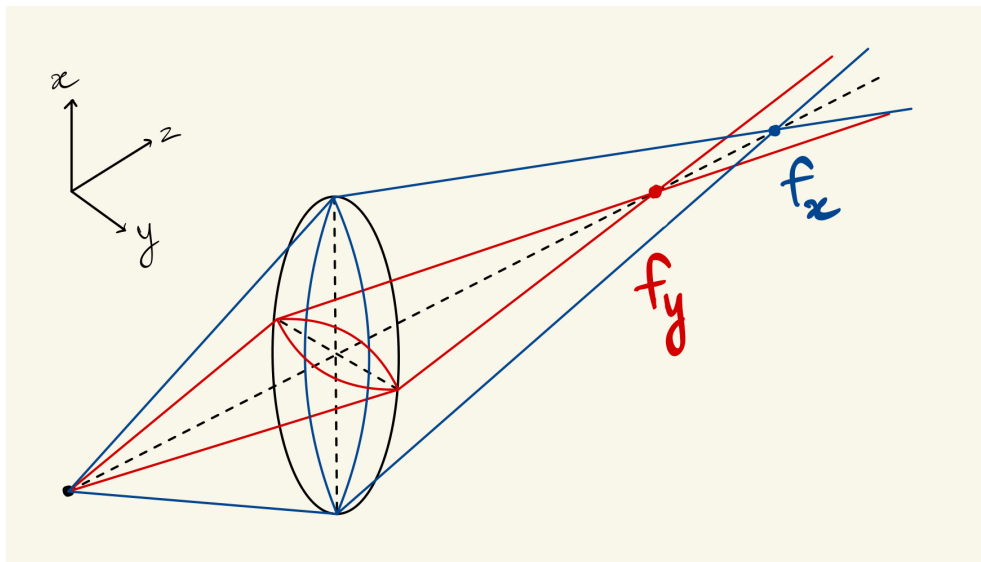


Figure 3.4: **Illustration of astigmatism.** Due to the different refractive strengths along the perpendicular axes (x and y), the two focal points f_x and f_y differ.

Astigmatism occurs due to the electrons refracting differently due asymmetrical refractive

strengths (magnetic fields) in the lenses. The electron beam along one of the perpendicular axes gets refracted more strongly than along the other. This causes a shifted focal point on one axis compared to the focal point on the other. Hence, the image cannot be in focus along both axes at the same time. In practice in a STEM, the electron probe is elongated along one direction making the image appear elongated in one direction when trying to focus the image along one axis [45]. Fig. 3.4 illustrates astigmatism in lenses.

Coma

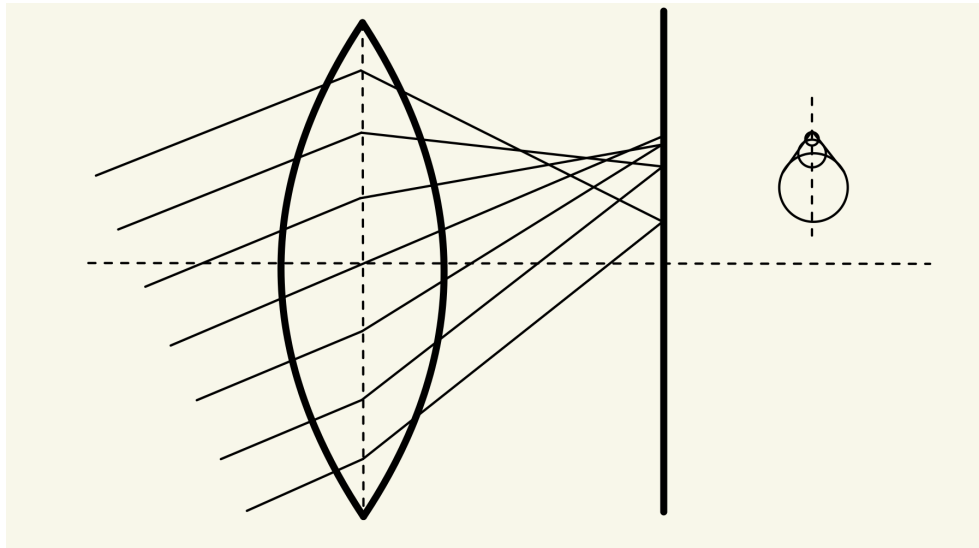


Figure 3.5: **Illustration of coma.** The incoming electron beam path at an angle with respect to the optical axis. This results in the comet-like distortion in the probe as seen on the right-hand side of the figure.

Coma occurs when the electrons refract differently due to the incident angle of the beam-path with respect to the optical axis. Different annular sections of the lens refract the electron beam differently and this causes the focal point in each of the annular sections to be slightly shifted in the direction that the beam is tilted. Fig. 3.5 illustrates coma and how the incident angle of the electron beam distorts it one direction on refraction resulting in the comet-like probe, hence the name coma.

Correctors

In electron optics, correcting for these aberrations is not as simple as correcting for them in glass lenses. In STEM, spherical aberration correctors (C_s) were the first to be corrected using a quadrupole-octupole corrector [56]. With just C_s correction, they were able to get a probe size of less than $1\text{\AA}$ at 100 kV. To improve resolution even further, chromatic aberration and higher order geometric aberrations (astigmatism and coma) needed to be

corrected [51]. More recently, STEM correctors are able to eliminate or greatly reduce all aberrations up to and including fifth order [57, 46].

3.1.5 Detectors and image formation

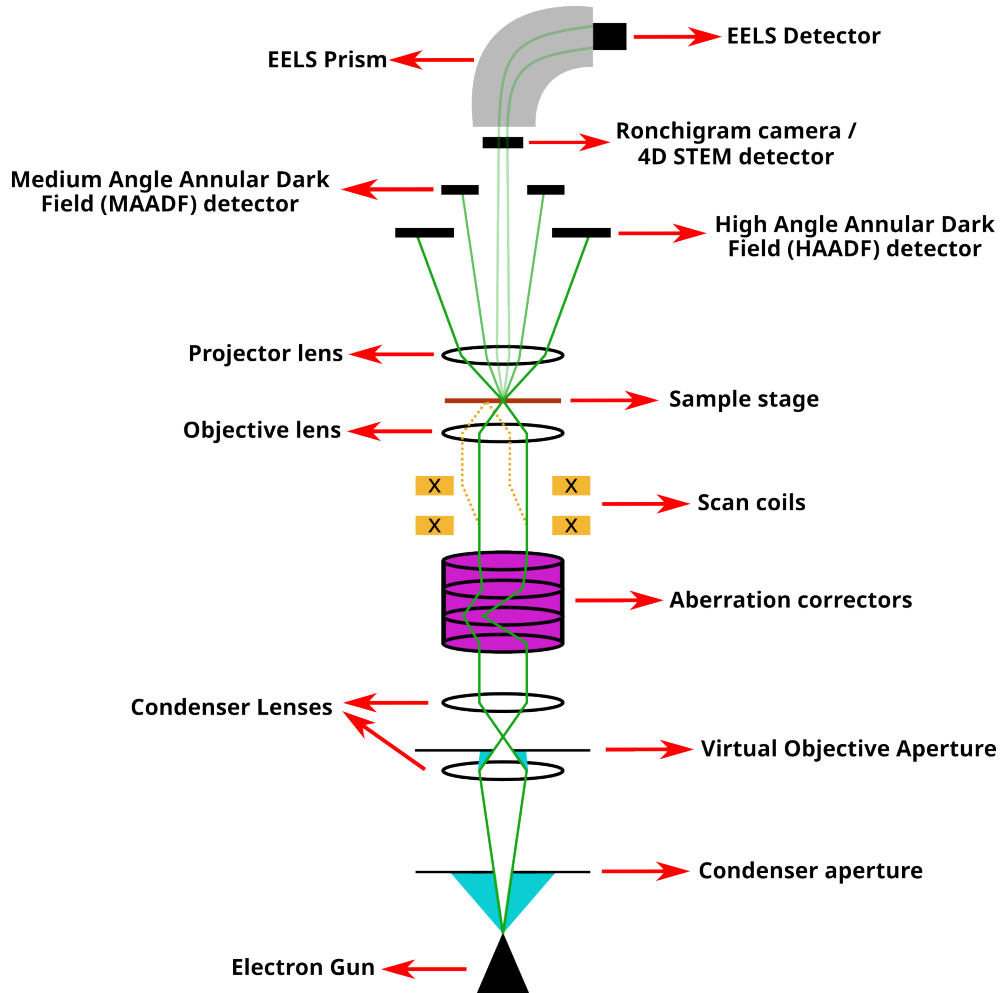


Figure 3.6: **Illustration of the Nion UltraSTEM 100 in Vienna.** The various components that make up the device are all labelled. (Designed from individual images provided by Carsten Speckmann and Umair Javed)

Scanning transmission electron microscopy (STEM) uses a beam of electrons that are focused, with the help of condenser lenses, apertures and aberration correctors, to a probe of size of approx 1 Å [51]. Fig. 3.6 shows a schematic illustration of the Nion UltraSTEM electron microscope used in this study. The electron probe is scanned over the sample with the help of scan-coils in a raster-scanning fashion. The scan-coils are also a kind of magnetic lens that deflect the Å-sized probe back and forth to perform the scanning in a STEM. Multiple parameters such as the pixel dwell time (how long the probe is posi-

tioned at one pixel, in μs), the pixel count (total frame size in px), and the field-of-view (FOV in nm) can be chosen. At each pixel position, the electrons from the probe scatter from the atoms in the sample and have their trajectories either altered or unchanged as explained in Section 3.1.3. With the help of a projector lens, the forward scattered (transmitted) electrons are collected via various detectors positioned at different spots as seen in Fig. 3.6.

The transmitted electrons can be collected by a Ronchigram camera that is positioned along the optical axis. This camera is used to record ronchigrams and the projected electron beam can be de-focused to allow sample navigation using bright field (BF) imaging.

The scattered electrons can be collected by ring-like detectors called annular detectors which are positioned off-axis at the scattering angles described by their Z -dependency $Z^{1.7}$ [52, 53, 54]. STEM usually uses two annular detectors, namely a medium angle annular dark field (MAADF) detector and a high angle annular dark field (HAADF) detector. The name dark field arises from the fact that the resulting images acquired using these detectors have dark contrast which represents areas of little to no scattering (dark background) and bright areas which represent areas of scattering. The detectors and the electronics correlate the position of the probe (the pixel which is being scanned) with the integrated intensities at that pixel. Hence in Z -contrast ADF imaging, higher the number of electrons scattered at a particular pixel, brighter the pixel in the image. And because of the $Z^{1.7}$ dependency, atoms that have a higher atomic number (Z) scatter electrons more intensely which results in brighter contrast in the image.

The choice of using MAADF or HAADF is up to the user but does depend on the samples that are being studied. As the scattering angle depends on the atomic number, MAADF imaging is better to use on lighter atoms (e.g., boron, carbon, nitrogen, or oxygen) as it would provide better signal-to-noise ratio and better contrast. HAADF imaging is better suited for heavy atoms (transition metal elements, sulfur, or selenium) as they scatter to higher angles allowing the HAADF detector to perform better. Z -contrast imaging can become less straightforward to interpret when the thickness of the sample is increased. The increased number of atoms in a thick sample, causes the electrons to scatter to higher angles as the number of scattering centres increase resulting in brighter contrast throughout the image making features hard to distinguish. Contaminated samples would also result in the same effect of brighter contrast and need to be dealt with careful understanding of

the scattering processes [46].

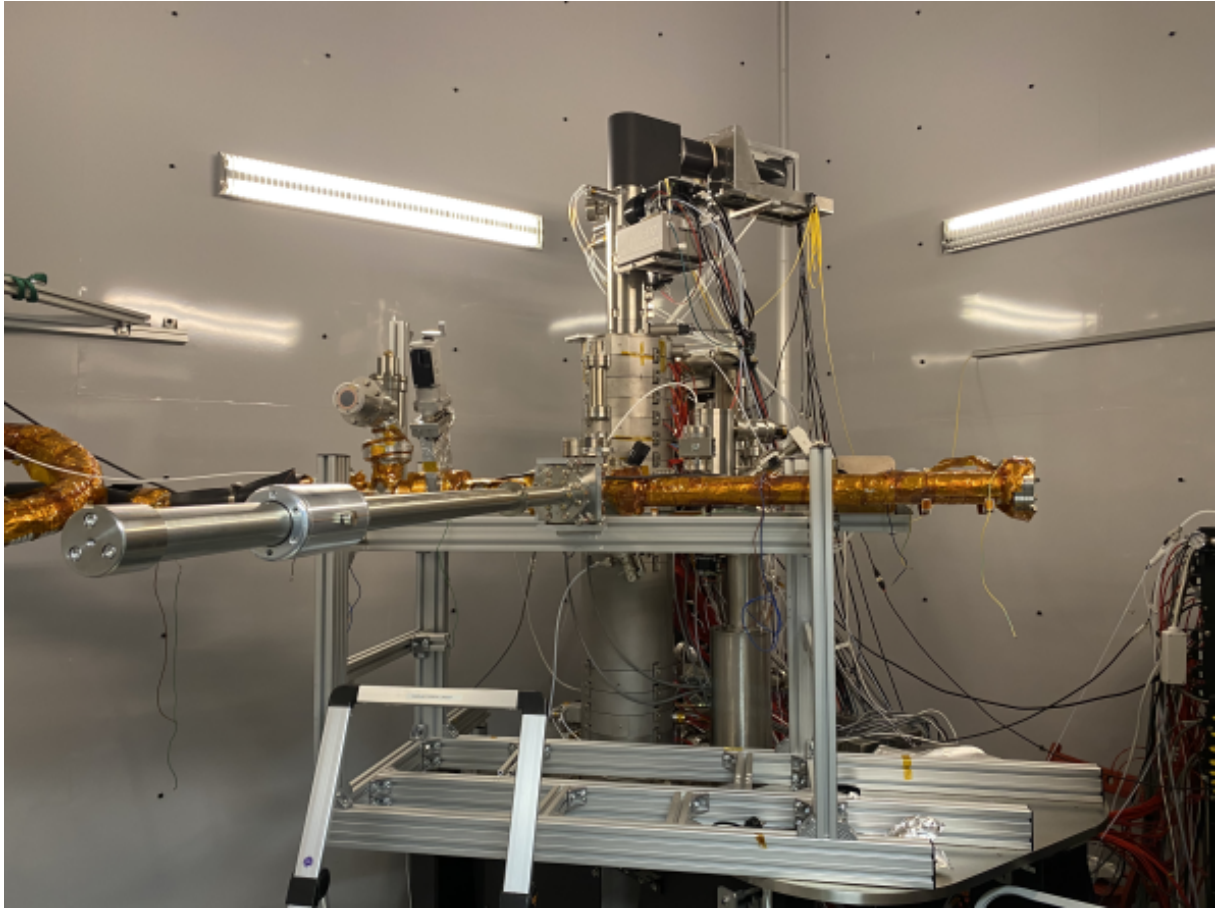


Figure 3.7: A photograph of the Nion UltraSTEM 100 in Vienna.

The microscope used in this study is the Nion UltraSTEM 100 at the University of Vienna. Fig. 3.7 shows a picture of the device with additional modifications that are explained in more detail in Section 3.3. The electron source positioned at the bottom is a 100 kV cold-FEG. It can be operated with acceleration voltages from 40 - 100 kV. The MAADF detector is positioned at a semi-angle range of 60 - 200 mrad, and the HAADF detector at a semi-angle range of 80 - 300 mrad. The base pressure at the sample stage is in the order of 10^{-10} mbar. It also has 3rd generation C3/C5 aberration correctors that focus the probe to a minimum size of 1 - 1.3 Å at 60 - 100 kV [58, 59].

As explained in Section 3.1.3, the electron beam scatters from the atoms in the sample in different ways. In some instances, the electron beam can also damage the material that we are imaging in STEM. One example of damage is via knock-on damage that can happen during elastic scattering where energy from the electron can be transferred to the atom that it scatters from, causing the displacement of that atom from its lattice position. The maximum energy that can be transferred from the electron to the atom is in the case

of a backscattered electron (BSE) where the electron is scattered opposite to the direction of approach. The displacement threshold energy T_d is the minimum amount of energy required for an atom to be successfully displaced from its lattice position.

According to density functional theory (DFT) molecular dynamics (MD) simulations [60], $T_d = 19.36$ eV for boron and $T_d = 23.06$ eV for nitrogen. Electron knock-on damage alone cannot be the reason for electron beam damage in hBN because the maximum energy that can be transferred, for 60 kV electrons, is lower than the displacement threshold energy for both boron and nitrogen. Therefore, other beam damage mechanisms must be responsible for the effects seen [61].

For graphene, a conductive material, the knock-on damage has been extensively studied and understood [62, 63, 64]. But for semiconducting or insulating materials such as MoS₂ and hBN, the mechanisms are not fully understood. Inelastic scattering can also cause damage where the electron beam can interact with the bound electrons, phonons, plasmons, or excitons causing charging, ionization or electronic excitations [65]. Recently, the role of valence ionization has been studied in hBN [61]. Since only ground-state dynamics had been previously considered, the beam damage at 60 kV could not be explained. So it was found that beam-induced excitations in hBN may reduce the bond energies between boron and nitrogen, and reduce the displacement threshold energy which could explain the beam damage observed at 60 kV.

3.2 Ion irradiation

Ion irradiation is a versatile tool that is widely used in the manufacturing of devices. In more recent years, ion irradiation has grown to become the first choice for defect-engineering of 2D materials where a wide range of defect types can be created with high precision [6]. In this study we use singly-charged noble gas ions that are accelerated to < 1 keV energy, as our projectile for defect creation. Their potential energy is insignificant compared to their kinetic energy, so it can be assumed that their interaction with the sample are purely due to their kinetic energy. The interaction between the positively charged ion and the positively charged nucleus can be described using the Coulomb potential

$$V(r) = \frac{Z_1 Z_2 e^2}{r} \chi(r), \quad (3.6)$$

where Z_1 is the atomic number of the ion and Z_2 is the atomic number of the target atom, e is the elementary charge of an electron and r is the distance between them. The screening function $\chi(r)$ is used to represent the screening of the nucleus by the electrons around it.

In ion irradiation, ions also interact with the atoms of the sample via elastic and inelastic processes. The elastic processes are categorised into nuclear stopping and the inelastic processes into electronic stopping. In nuclear stopping the ions scatter from the nucleus of the atoms and tend to have sudden changes in their trajectory along with large energy losses. This type of scattering dominates at low energy of ions and high Z of the atoms in the sample. In electronic stopping, the ions scatter inelastically with the electronic structure of the material (accompanied with electron excitations and ejections). Here there is a negligible change in the ions trajectories, and have comparatively smaller losses in energy. This type of scattering dominates at high energy of ions and low Z of the atoms in the sample [66]. Since we use low energy ions in our experiments, we need to consider the elastic nuclear stopping process.

The energy of the ion is transferred to the atom in the sample can be approximated via a ballistic knock-on scattering process, that is elastic as the kinetic energy of the system (interacting ions and atoms) is conserved. In the simplest picture, we can assume that there are only two-atom collisions, where classical dynamics explain the interaction, and that the target atom is stationary. The maximum energy that can be transferred T_M , from the ion to the atom, in a head-on collision, is given by [66]

$$T_M = \frac{4M_1 M_2 E_0}{(M_1 + M_2)^2}, \quad (3.7)$$

where M_1 is the mass of the projectile ion, M_2 is the mass of the atom in the sample, and E_0 is the kinetic energy of the projectile ion. Since the ion irradiation effects are probabilistic in nature, the energy-transfer scattering cross section needs to be defined. This is given by

$$\sigma(E) = \frac{\pi}{4} (2Z_1 Z_2 e^2)^2 \frac{M_1}{M_2 E_0} \left[\frac{1}{T_{min}} - \frac{1}{T_M} \right], \quad (3.8)$$

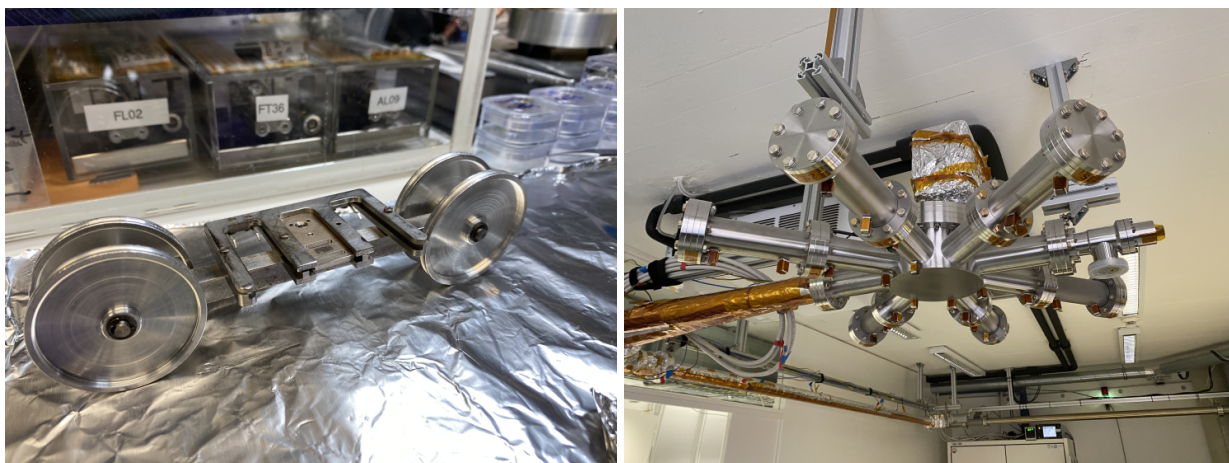
which is a general expression for the total cross-section where T_{min} is the minimum energy transferred. In practice, the distance between the ion trajectory and the atom plays a huge role and a head-on collision has an incredibly small scattering cross-section. From equation 3.8 it can be seen that as the energy of the ion is increased, the scattering cross-section decreases. This is because the duration of the ion-atom interaction is reduced and requires an ion trajectory that is very close to the atom for the energy transfer and successful displacement to take place [66].

Since equations 3.7 and 3.8 are dependent on the mass of the interacting species as well as the energy of the projectile ion, it can be seen that by keeping the energy of the projectile ion constant, different amounts of energy can be transferred to boron and nitrogen in hBN. And since T_d for boron and nitrogen are different, it opens the possibility of displacing one type of atom and not the other. Hence, this study explores that possibility of selectively creating one type of vacancy in hBN via Ar^+ irradiation.

3.3 Experimental setup

The Nion UltraSTEM 100 is connected to a custom-built interconnected UHV system. The controlled alteration of nanomaterials in vacuum down to the atomic scale (CANVAS) system is a two-story UHV system designed for the transport of samples between various devices. The entire CANVAS system consists of the Nion UltraSTEM 100, an atomic force microscope (AFM) GETec AFSEM, a glove box, a target chamber consisting of a plasma source for ion irradiation, a thermal evaporation source, multiple electron beam evaporators, a laser for cleaning samples, and a heating stage. A load-lock is also connected where the samples enter and exit the system, and there are two large sample storage units (garages) one on each story capable of storing up to 72 samples in UHV. The entire system is kept at pressures of low 10^{-9} to 10^{-10} mbar [17]. The different devices are connected via stainless steel pipes within which transport vehicles (referred to as cars) are driven through the pipes with the help of magnets on the car and on the outside of the pipes.

The pipes seen attached to the microscope on the front of Fig. 3.7 are part of the CANVAS system and a gripper arm is used to take sample pucks out the cars and insert them into the stage of the microscope. Fig. 3.8 and 3.9 show photographs of the CANVAS



(a)

(b)

Figure 3.8: **Photographs of a car and a garage in which they are stored.** (a) The car has 3 slots in which sample ‘pucks’ can be inserted. The pucks have a hole where the TEM grids are clamped onto. The front and back wheel of the car have magnets via which they can be maneuvered through the CANVAS system. (b) A garage storage unit where the samples are stored in UHV. The two magnets on the outside of the pipe are used to move a car between the various devices in the system.

system, a garage and a car that are used to transport samples between the devices. This system is central to this work, because it allows the transportation of the samples from the microscope to the plasma source, for ion-irradiation, and back to the microscope without having to expose the samples to ambient conditions in between. This ensures that the samples do not get contaminated from the exposure and allows us to directly measure the ion-induced effects via STEM.

3.3.1 SPECS plasma source and deceleration setup

The target chamber, which is a part of the CANVAS system, is where the ion irradiation is performed. It is home to the SPECS plasma source as well as the deceleration setup used to decelerate ions that are emitted from the plasma source. Fig. 3.10 is an illustration of the SPECS plasma source and the deceleration setup installed at the target chamber.

The plasma source device is a microwave plasma source (MPS) that uses electron cyclotron resonance (ECR) to generate the plasma. A microwave with frequency of 2.45 GHz is generated by a magnetron source that is coupled into the plasma chamber that

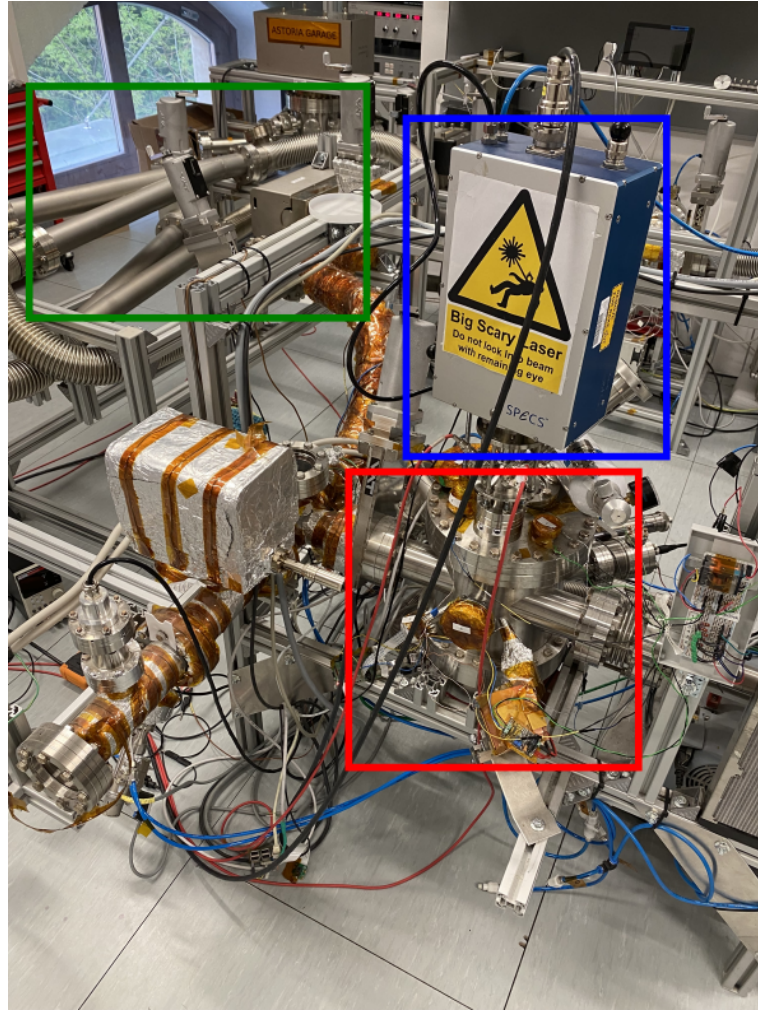


Figure 3.9: **A photograph of the CANVAS system.** The target chamber (marked in red) is where the ion irradiation is performed with the use of the SPECS plasma source (marked in blue). The samples are transported through the stainless steel pipes (marked in green) that connect the entire system.

discharges electrons. A 86 mT surface of a multi-polar magnetic array cause the electrons to rotate in an electron cyclotron motion that is in resonance with the microwaves. A leak valve is located at the plasma chamber that is connected to a gas bottle (in our case, an argon bottle). As gas is leaked into the plasma chamber, the electrons that are in cyclotron motion ionize the gas atoms on impact. The positively charged ions also rotate in cyclotron motion but in the opposite direction of the electrons and results in the visible plasma in the plasma chamber. The SPECS plasma source is operated in a hybrid mode that utilises anode and extractor electrodes for the extraction of the ion beam. In our experiments, the anode voltage was set to 0 V (resulting in no further acceleration of the ions) and the extractor voltage was set to its default value of -60 V which is sufficient for extracting the positive ions from the plasma and directing it downwards into the target

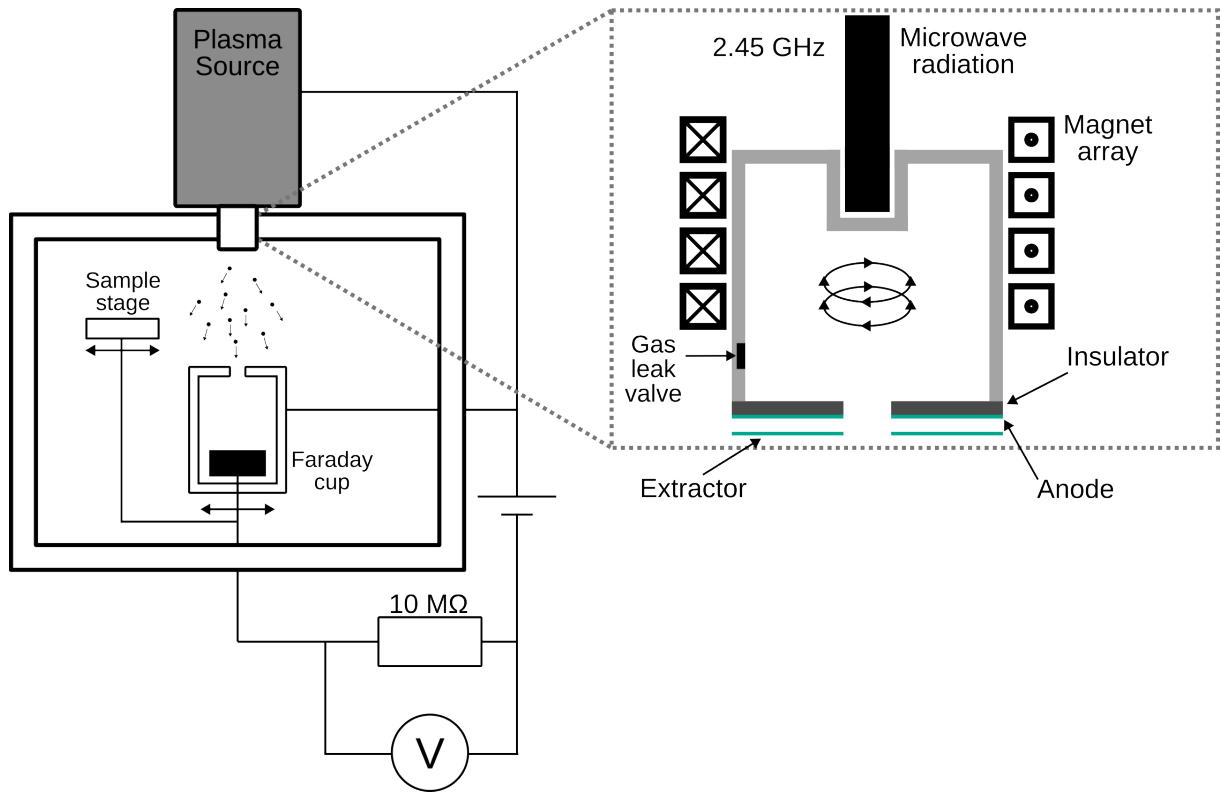


Figure 3.10: **Illustration of the plasma source and deceleration setup.** (Figure credits: Manuel Längle [59])

chamber.

The deceleration setup consists of a Faraday cup and a puck stage for the sample, as seen in Fig. 3.11. A Faraday cup is essentially a metal cup that is designed to catch charged particles, and is used to measure the resulting current produced by those charged particles [67]. In our system, it is designed to measure the positive ion beam current produced from the plasma source by positioning it directly under the beam. It has an aperture diameter of 6.35 mm and has a magnet at the aperture that deflects electrons, preventing it from entering the cup. The ion beam current (as a function of voltage) is read out using a multi-meter that is connected to the control unit of the deceleration setup that can be seen in Fig. 3.12. The puck stage is designed to hold a single sample puck and can be positioned directly under the beam to irradiate the sample. Both the Faraday cup and the puck stage are connected to a power supply which makes it possible to positively bias one or the other. By applying a positive bias, the positive ions coming from the plasma source feel an electrostatic repulsive force and are decelerated, hence reducing their kinetic energy. Hence, the energy of the ion beam can be tailored by adjusting the bias voltage. In this study, five different hBN samples were irradiated with mean energies of 0, 20, 40,

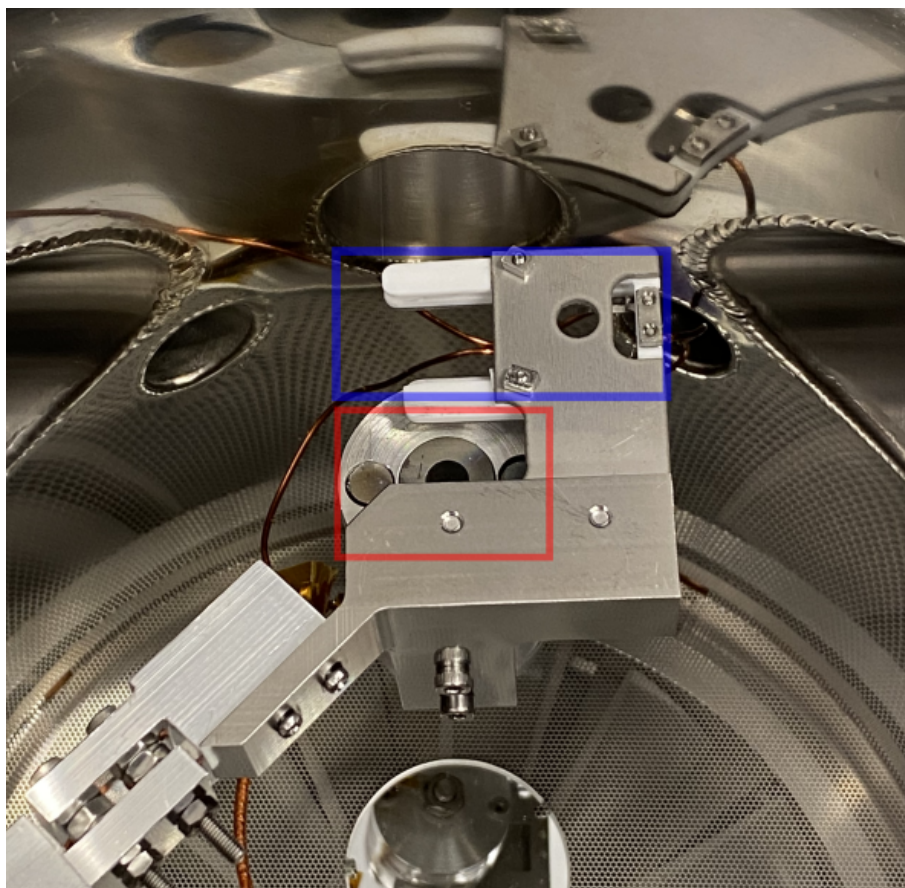


Figure 3.11: A **top-view photograph of the deceleration setup**. The Faraday cup (marked in red) and the puck stage (marked in blue) can be moved into position under the ion beam using a rotary dial attached to a flex-bellow.

60 and 150 eV using the deceleration of the ions with the positive bias to achieve these energies. See section 4.3 for more information regarding the deceleration and irradiation of the samples. The control unit for the deceleration setup was designed as part of this thesis for the easier, safer and stress-free handling of the biasing using the power supply, as seen in Fig. 3.12.

3.4 Data acquisition and analysis

3.4.1 Acquisition

This study requires atomic resolution images of hBN in order to be able to identify point defects (vacancies) in the lattice. Since STEM acquisition can typically only image areas that are at most a few tens of nm in FOV at atomic resolution, to get an idea of the vacancy



Figure 3.12: A photograph of the deceleration setup control unit. The front panel has switches to turn on the power supply, put the multimeter in the loop, and switch between the Faraday cup or the sample puck. An analog voltmeter that is used to readout the voltage supplied and a multimeter that is used to measure the beam current, are placed above the power supply unit.

density and distribution for statistical relevance, one would have to manually capture 100s of images in representative areas of the sample. This is a time consuming task and is not feasible in defect-engineering studies such as this. In the case of hBN, electron beam damage also becomes a concern while acquiring a large number of images because of the high electron dose that can be supplied to it during imaging. If the user is not quick enough to capture images and move to different locations, a bias would be introduced because of the vacancies created while imaging, which doesn't capture the true vacancy density being measured [61].

To solve this issue, a semi-autonomous large area image acquisition tool was implemented in the Nionswift microscope control software [16]. This tool allows the user to define an area of interest by setting four corners of a quadrangle where you want to acquire a large number of images. The tool is then able to divide the selected area into evenly spaced squares with coordinates. Parameters such as FOV (defines the size of the square), pixel dwell time (μs), framesize (px), image offset (how many squares to skip between captured frames), and sleep time (how long to wait for the stage to settle before

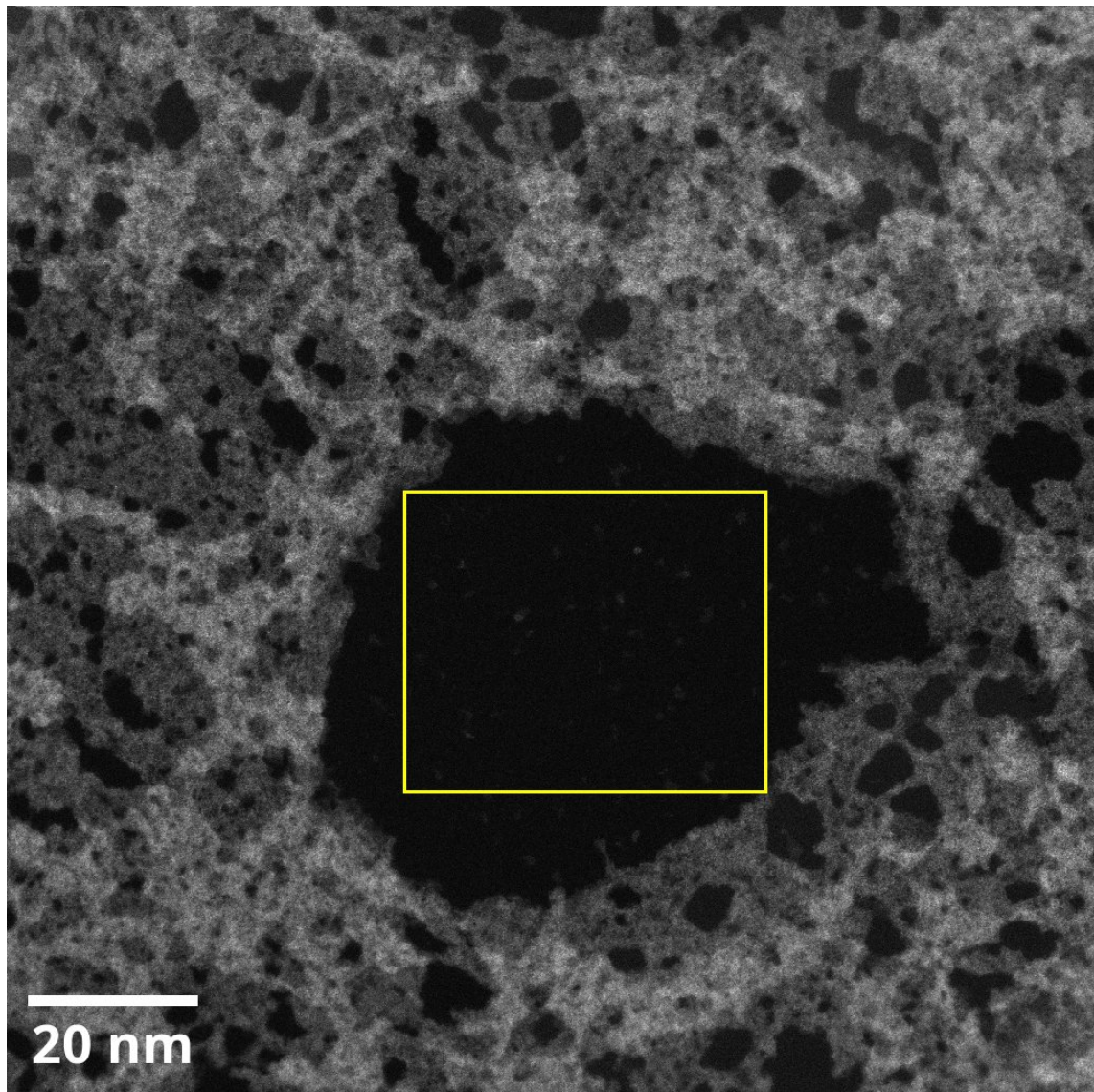


Figure 3.13: **Example MAADF overview image of an area of interest.** The yellow quadrangle marks the area selected for semi-autonomous imaging. The area in dark contrast is monolayer hBN.

capturing the next frame) can be chosen by the user. Using these parameters, the tool gives an output in the command line with how many frames would be captured, the total area (in nm^2) that is being imaged and how long the entire acquisition would take. The tool utilises the precise movement of the sample stage to get to the defined coordinates and the algorithm uses a bilinear interpolation function to calculate the focus offset between each stage position coordinate. The focus needs to be accurately set at the four corners before starting the acquisition algorithm to get good results and minimal manual intervention. Fig. 3.13 is an example of a MAADF overview image of a region that was selected for imaging marked with the yellow quadrangle.

Using this tool, we are able to acquire 100s of atomic resolution images of hBN before and after irradiation with argon ions. Along with the acquisition of a large number of images, electron beam damage is minimised as electron dose per image is reduced. Table 3.1 shows the parameters that were used for all the image acquisition datasets in this study.

Table 3.1: Image Acquisition Parameters

FOV (nm)	Frame Size (px)	Dwell Time (μ s)	Offset (images)	Sleep Time (s)
4	512	16	2	3

3.4.2 Analysis

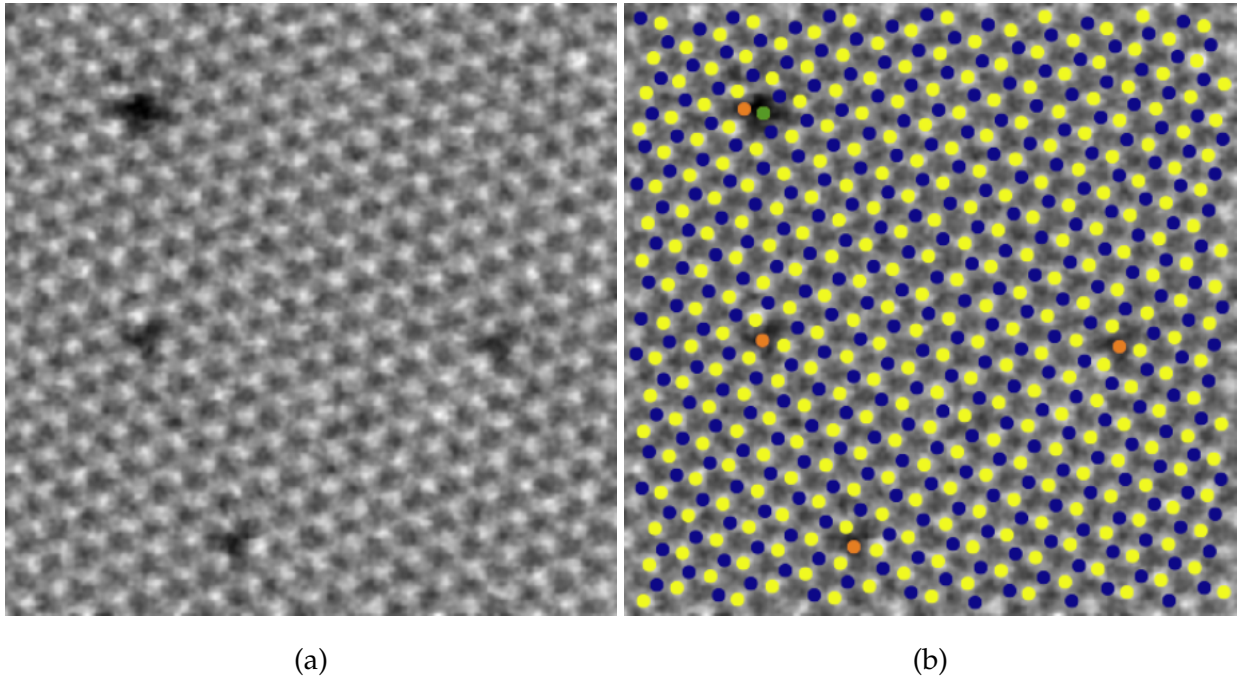


Figure 3.14: **Identification of the lattice and defects in hBN by the CNN.** (a) An example MAADF image of hBN with visible vacancies in the lattice. (b) The output from the neural network showing the atomic positions (yellow is a nitrogen atom and blue is a boron atom), and the defects (green is a missing nitrogen atom and blue is a missing boron atom) identified by the neural network analysis tool.

Once the semi-autonomous image acquisition tool has acquired the large number of images, they need to be analysed for the different defects and their concentrations. Since analysing all these images by hand would be time consuming and might introduce hu-

man error, we employ a convolution neural network (CNN), which is a data analysis tool developed at our research unit [65] for the automated image analysis of large datasets. Before running a dataset of images through the neural network, a non-contaminated frame is chosen and filtered with a double Gaussian filter [53]. A threshold of 1.1 times the maximum intensity of the histogram spread is chosen, above which is classified as contamination and not part of the hBN lattice. The images in the dataset are thereby preprocessed by masking out contamination regions using this threshold to help the identification of atomic positions by the analysis tool. The model in the CNN is trained on simulated STEM-ADF images of hBN generated using *ab*TEM [68]. The dataset is then fed into the neural network and it outputs a map of atomic positions for each image in the dataset. For hBN, the network does not directly classify defects in the structure and outputs atomic positions for a perfect lattice even when there are no underlying atoms in the image. With the help of defect classifiers, which requires manually thresholding the histogram for each image in the dataset, we can classify whether an atomic position is a lattice point or a defect [69]. Since this step involves manual input, human error in the classification of defects is possible and is acknowledged in the results when significant. The output from the neural network can then be represented through plots or tables for understanding the type and concentration of defects for each dataset. Fig. 3.14 shows an example MAADF input image and the overlay of the atomic positions and defects recognised by the neural network.

Chapter 4

Results

4.1 Sample preparation

In this study, we use scanning transmission electron microscopy (STEM) to image and analyse the material at the various steps. For this, we require free-standing hBN so that the electrons can transmit through and be collected by detectors on the other end (for a more detailed explanation of STEM and imaging, see Section 3.2). So, hBN is transferred onto TEM grids, that have holes through which the electrons can be transmitted. Since the starting material is CVD-grown hBN on copper foil, we need to be able to transfer the hBN from the copper (Cu) foil onto TEM grids of our choosing. Therefore, the following sample preparation process was developed for this purpose.

For this study, the electrochemical delamination method [70, 41] for hBN sample preparation was implemented at the research unit Physics of Nanostructured Materials. This was explored for the goals of maximising sample coverage while minimising contamination in those areas that are covered. The method starts with CVD-grown monolayer hBN on a copper (Cu) foil substrate that was purchased from the commercial supplier Sigma-Aldrich (Merck Group) [42]. The following methodology was developed and implemented over the course of several months. Parameters in each of the sections had to be fine-tuned to achieve the required goals of the preparation process. An illustration of the whole sample preparation procedure can be seen in Fig. 4.1.

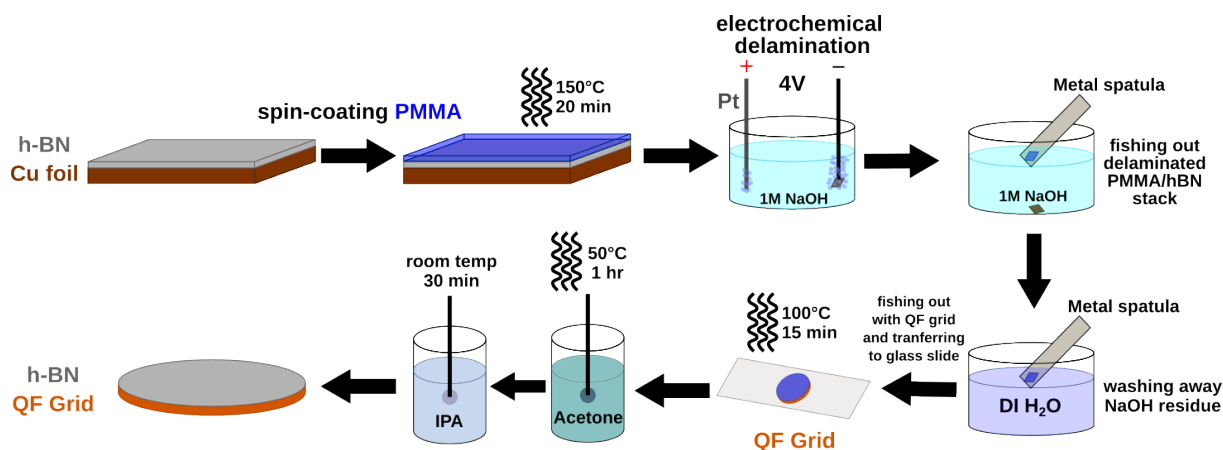


Figure 4.1: Illustration of the hBN sample preparation method via electrochemical delamination. (Designed from individual images provided by Philipp Irschik).

4.1.1 Cutting and spin-coating

The starting material is shown in Fig. 4.2(a). Since it is a large piece of foil and TEM grids are small, a section is chosen and cut into smaller pieces, using a razor blade, that are slightly larger than the size of a standard TEM grid (3 mm in diameter).

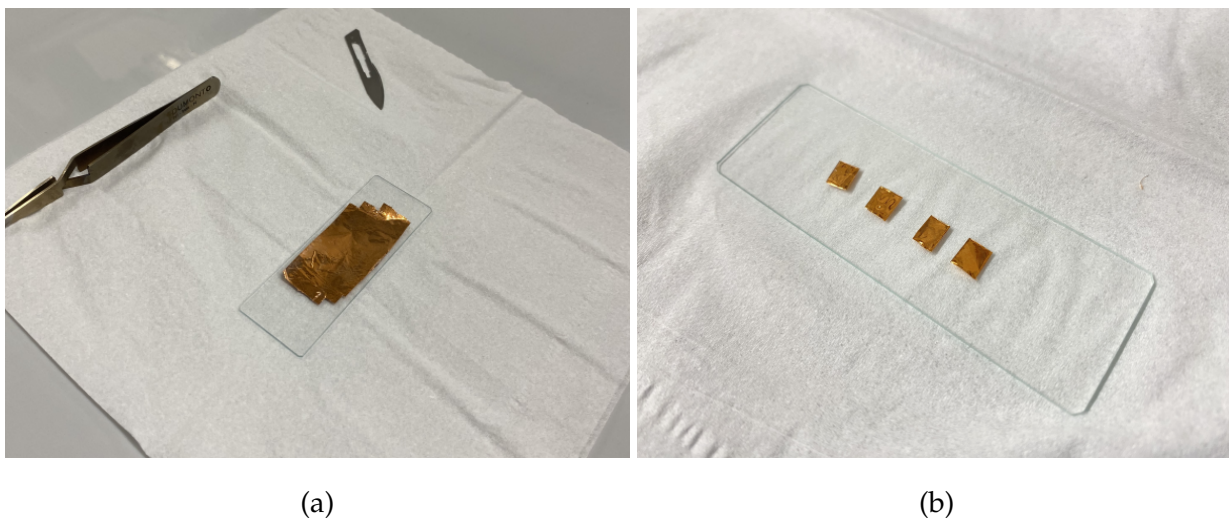


Figure 4.2: Photographs of CVD-grown hBN on copper foil. (a) The large piece of foil is placed on top of a glass slide and the razor blade is used for cutting it into (b) smaller pieces for the subsequent steps.

While cutting, it is essential that only downward force is applied to the foil as any lateral motion while cutting could easily damage the hBN as well as possibly tear the Cu foil. Once the smaller pieces are cut, they are transferred onto a glass slide as shown in Fig. 4.2 (b). By placing another glass slide on top of them and applying gentle and even force,

the pieces are flattened to remove wrinkles and slight bumps in the foil. This is done carefully, because the glass slide can slip and damage the hBN if it moves in the lateral directions while applying force downwards.

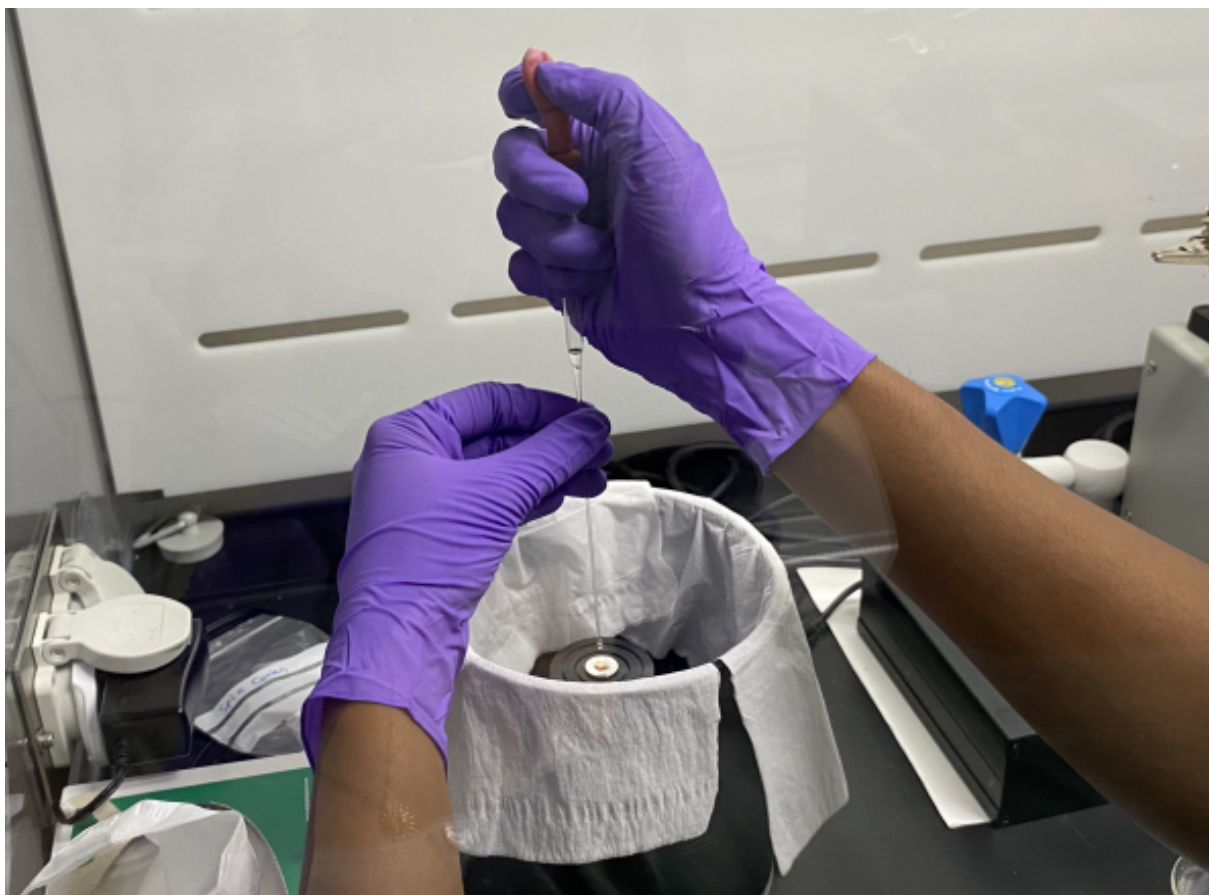
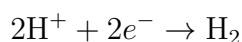


Figure 4.3: **A photograph of the spin-coating process.** Two drops of PMMA are released using a glass dropper onto the Cu foil, while the spin coater is spinning at 500 rpm. (Picture credits: Tamara Beltrán)

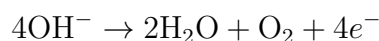
The foils are now ready to be spin-coated. The synthetic polymer polymethyl methacrylate (PMMA) is used to act as a protective support film on top of the hBN preventing unnecessary damage during the transfer process [71]. The foil is placed on the stage of the NiLo Spin Coater [72], where a vacuum suction holds it in place. Two drops of PMMA (E-beam Resist AR-P 642.04 [73]) are carefully dropped onto the foil as it is spinning at 500 rpm as shown in Fig. 4.3. The spin coater then ramps up to 1000 rpm (steps of 100 rpm) and sustains it for 15 s, and then ramps up to 2000 rpm (steps of 100 rpm) and sustains it for a total of 60 s. This spreads the PMMA into a uniform film on top of the foil. The foil is then transferred back onto a glass slide and put on a hot plate at ca. 150 °C for 10 - 15 min to allow the PMMA to dry out and cure.

4.1.2 Electrochemical delamination

The electrochemical delamination method is often referred to as the 'bubbling' method because of the generation of H_2 gas, which is the driving force for the delamination of hBN from the Cu foil. The mechanism behind the electrochemical delamination is a simple electrochemical cell and the water reduction reaction [74, 75]. A 1M NaOH solution is used as the electrolyte with a platinum (Pt) wire as the anode and the Cu foil (PMMA/hBN/Cu stack) as the cathode. The Pt wire is inert and does not take part in the reaction, and the Cu foil is where the H_2 bubbling takes place. The reduction reaction taking place at the cathode is given by



The most likely oxidation reaction taking place at the Pt wire is



The NaOH readily dissociates into Na^+ and OH^- when dissolved in water, and only acts to increase the conductivity of ions and electrons in the electrolyte helping the bubbling reaction to take place more efficiently [75].

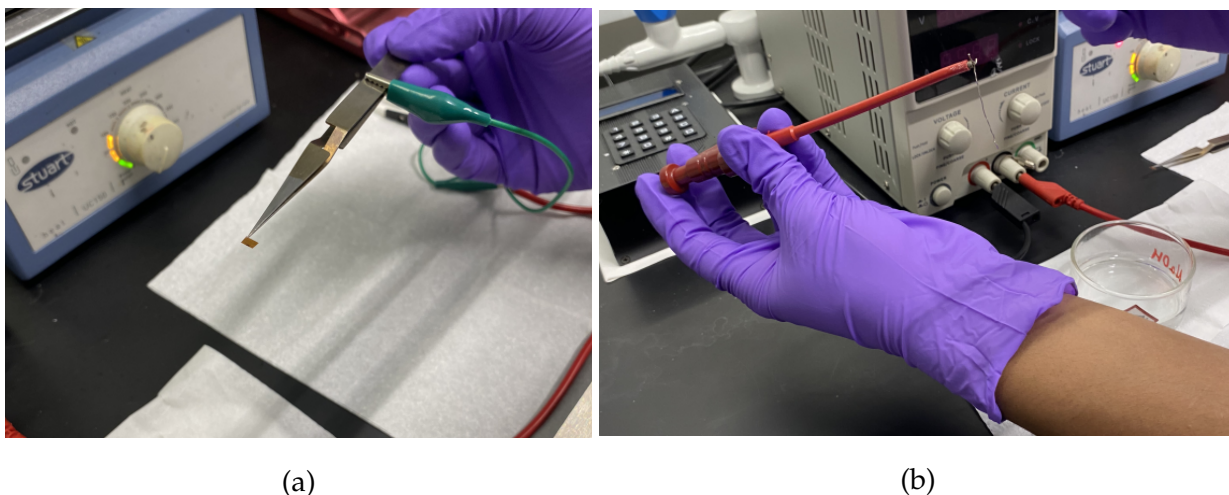


Figure 4.4: **Photographs of the electrochemical delamination setup.** (a) The cathode is connected to the inverted tweezers that are holding the Cu foil. (b) The anode is the Pt wire. (Picture credits: Tamara Beltrán)

Before performing the electrochemical delamination, the spin-coated Cu foils are pre-treated. Using a razor blade once again, less than 1 mm is cut off from all the edges of the foil. This is done because during the spin-coating process, PMMA tends to spill over the edges of the foil and prevents the PMMA/hBN stack from delaminating. Once the edges are freshly cut, the Cu foil is held via inverted tweezers (Fig. 4.4 (a)), and connected to the negative terminal (cathode) of the power supply via a clip-cable. On the other side, the Pt wire (Fig. 4.4 (b)) is connected to the positive terminal (anode) of the power supply also via a clip-cable and then placed in the NaOH solution.

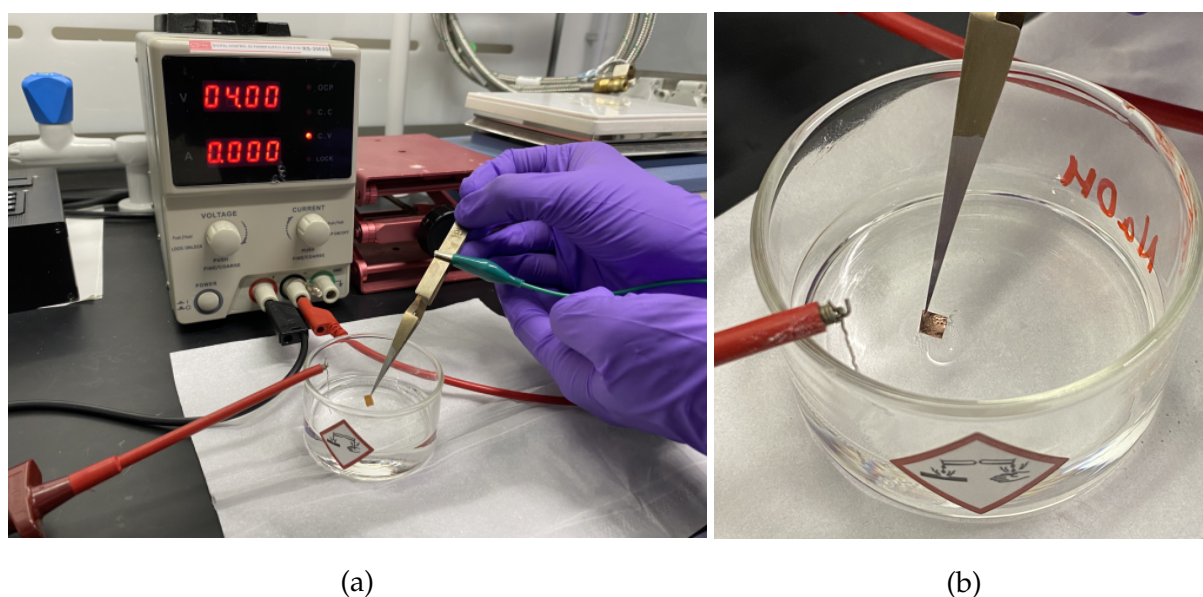


Figure 4.5: **Photographs of formation of bubbles at the cathode with an applied potential of 4V.** (a) The entire electrochemical delamination setup with the power supply set to 4V. (b) The bubbles can be seen forming at the Cu foil resulting in the delamination of hBN. (Picture credits: Tamara Beltrán)

The power supply is turned on and set to 4V. The Cu foil is then gently immersed at an angle of approx 30° to 45° into the NaOH solution, and the H_2 gas bubbles form from the reaction and slowly trickle into the gap between the hBN and the Cu foil, and delaminate the PMMA/hBN stack. Fig. 4.5 shows the formation of bubbles at the Cu foil when a potential of 4V was applied. Once the entire foil has been delaminated, the power supply is turned off and the foil is released from the inverted tweezers. Using a metal spatula, the delaminated PMMA/hBN stack is scooped-out ('fished out') from the NaOH solution and transferred to a deionised (DI) water bath to wash off the solution residue.

4.1.3 Microscopy grids and transfer

In this study, we primarily use Quantifoil (QF) gold grids (total size is 3 mm in diameter) with an amorphous carbon (AC) membrane with hole diameters of 1.2 μm and 2 μm . Another TEM grid made of silicon nitride (Silson SiN) on Si with 3 μm hole diameter was also experimented with, but consistent transfer results were not achieved. Fig. 4.6 (a) & (d) show examples of the two kinds of grids. After making dozens of samples, it appears that hBN prefers to stick to the flexible AC membrane of the QF grids rather than sticking to the flat SiN grid surface. Hence, the QF grids are chosen for this project.

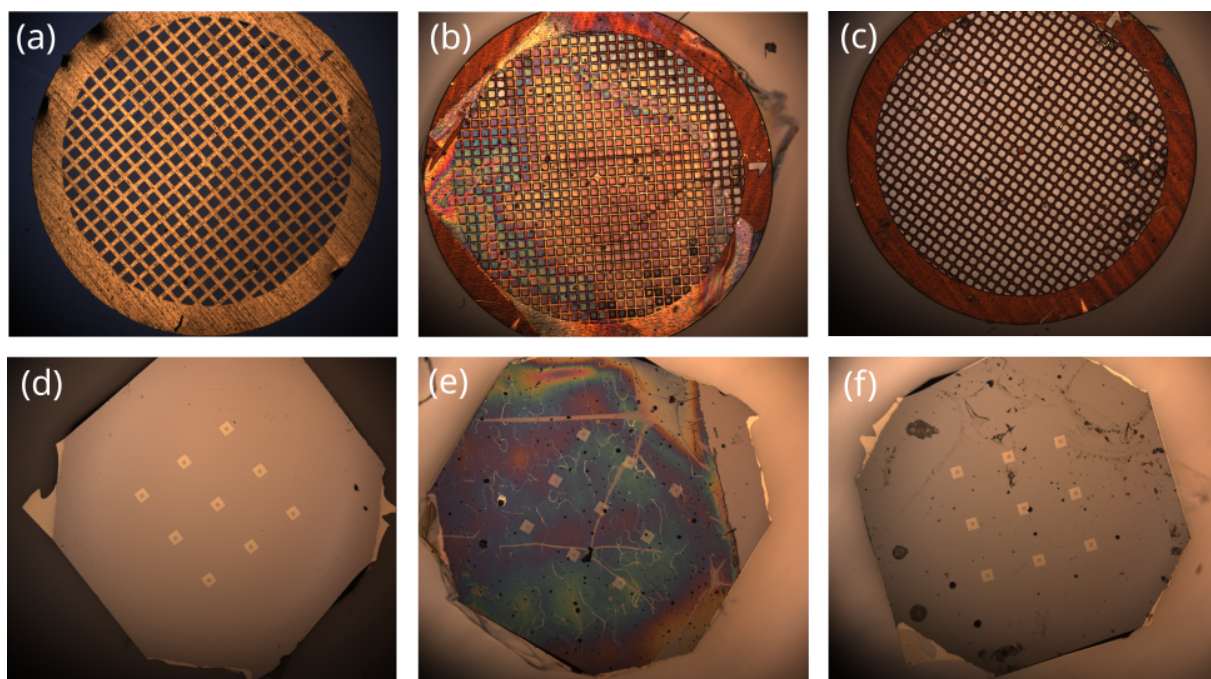
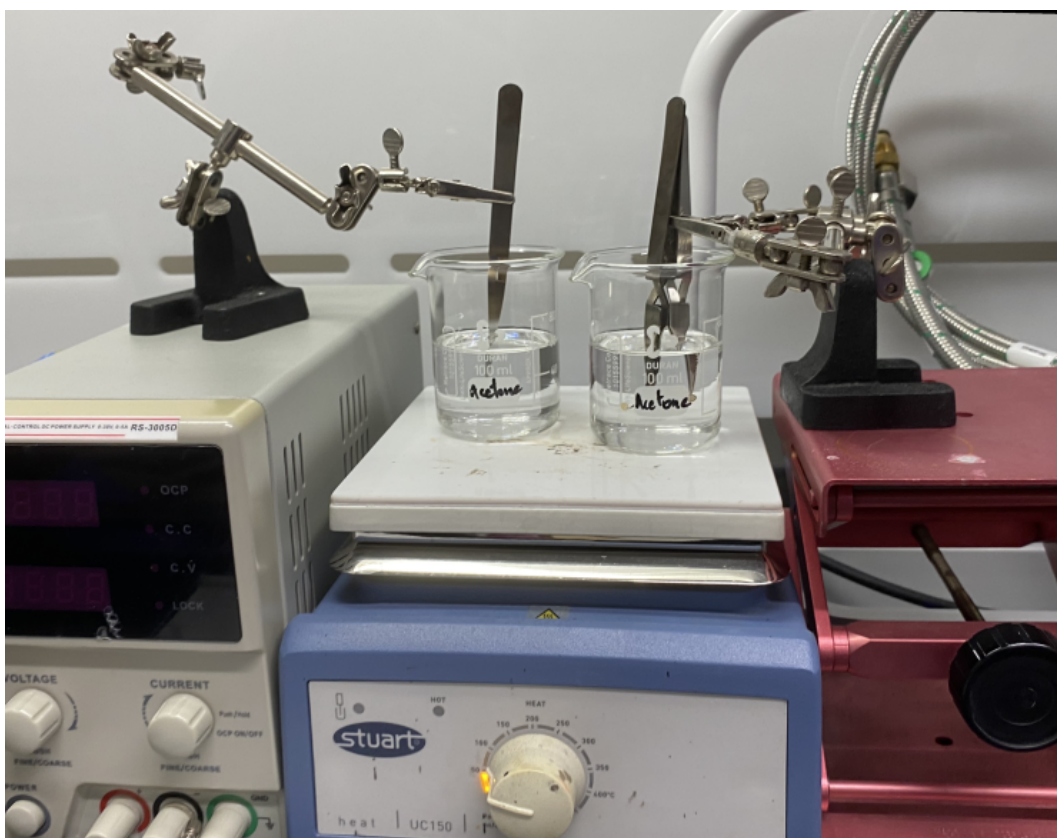
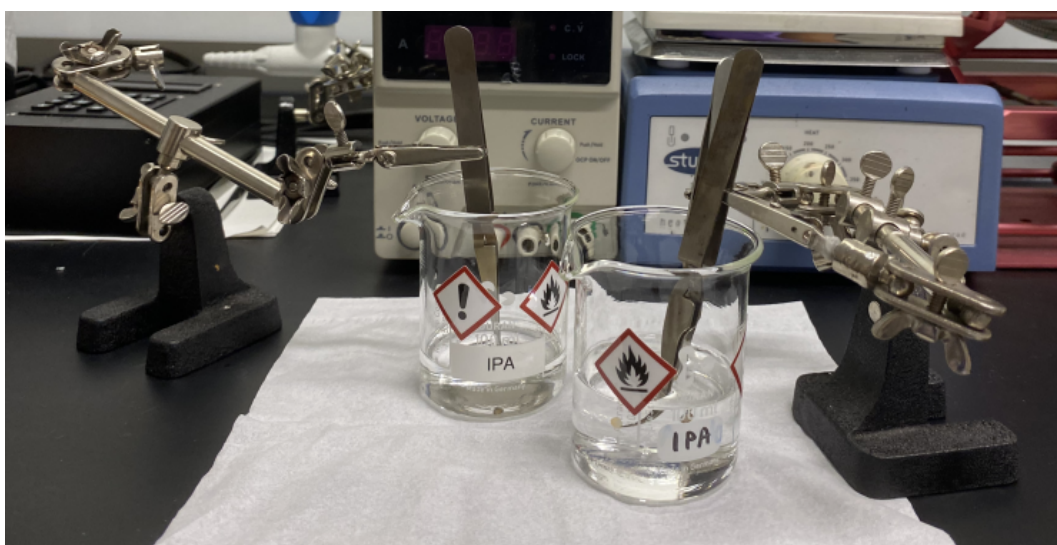


Figure 4.6: **Visible light microscope images of QF and SiN grids used to fish out the PMMA/hBN stack in the sample preparation process.** (a) & (d) are example QF and SiN grids, respectively. (b) & (e) are QF and SiN grids that have just been used to fish the PMMA/hBN stack, respectively. The colourful patterns are indicative of PMMA on the top. (c) & (f) are QF and SiN grids that have had PMMA dissolved with the acetone and IPA baths, respectively.

After the preparation of the PMMA/hBN stack, as described above, it is fished out of the DI water using a QF grid, with its AC membrane side facing upwards, so that the hBN can stick to that surface. The grid is then placed on a glass slide, with the PMMA/hBN stack facing up, and on a hot plate at ca. 100 $^{\circ}\text{C}$ for 10 - 15 min to dry out. It is then transferred to a CVD furnace tube that is evacuated to ca. $1 - 3 \times 10^{-2}$ mbar and is left in vacuum overnight to evaporate residue solvents and promote adhesion to the QF grid.



(a)



(b)

Figure 4.7: **Photographs of the acetone and IPA baths used for the removal of PMMA.** (a) The hot acetone bath at 50 °C with 'helping hands' holding the inverted tweezers that are holding the grids, immersing them in the solvent on the hot plate. (b) The IPA bath at room temperature. The same 'helping hands' are used to submerge the grids via the inverted tweezers. (Picture credits: Tamara Beltrán)

4.1.4 Polymer removal and heat treatment

After fishing out the PMMA/hBN with a grid of choice, the sacrificial PMMA film has to be removed. For this, the QF is held with an inverted tweezer and immersed in a beaker containing acetone that is at 50 °C as seen in Fig. 4.7 (a). Special care is taken when immersing the QF grid into the acetone bath as the high vapour pressure could easily damage the hBN. The QF grid is immersed perpendicular to the surface of the solvent to avoid unnecessary surface tension damage. Acetone is an effective solvent for dissolving PMMA and by warming it up, the process is sped up. The QF grid sits in the hot acetone bath for approx 1 h. After this, it is quickly transferred to an isopropyl alcohol (IPA) bath (Fig. 4.7 (b)) at room temperature for 30 min following the same steps of care during immersion. This is done to wash away the residual acetone that may be sticking to the surfaces of the QF grid, and also because acetone's high vapour pressure could potentially burst the transferred hBN when it quickly evaporates. Fig. 4.6 showcase the different steps in the sample preparation process up until and including the PMMA removal in the hot acetone bath.

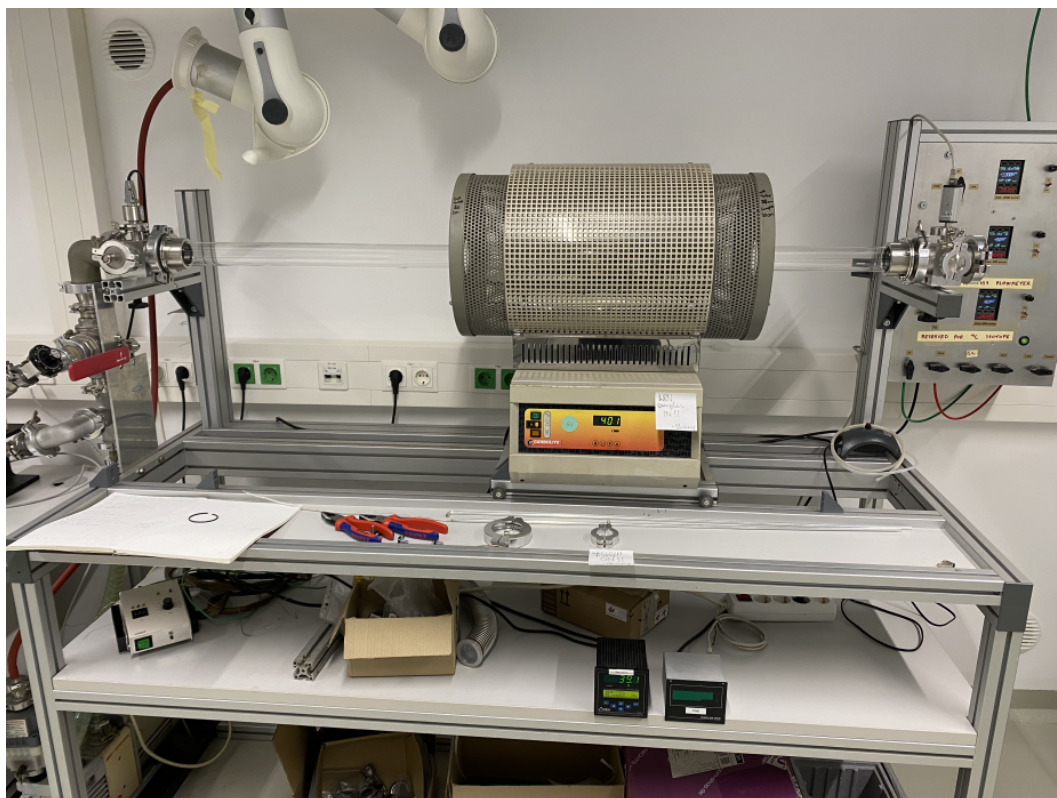


Figure 4.8: **Photograph of the CVD furnace used for the heat treatment.** The main heating cylinder can be seen positioned around the hBN samples in the CVD tube and set to a temperature of 400 °C.

As an additional step to the acetone bath for PMMA removal, CVD furnace heating is also employed to further help remove any residual PMMA. The QF grids are placed in the CVD furnace tube and heated to 400 °C under a constant flow of argon for approx 1 h, at a pressure of approx 40 mbar. Fig. 4.8 shows an image of the CVD furnace. Once the grids are taken out after the heating, the hBN samples are ready. Fig. 4.7 (c) & (f) showcase examples of successfully made hBN samples, on QF and SiN grids, respectively.

4.1.5 Challenges

The method development and fine tuning of parameters during the hBN sample preparation was a tricky process. At the beginning, with the use of the PMMA available at the lab [73], the number of drops required to sufficiently coat the copper foil was unclear. When using four to five drops, it was found that the spin coater stage and the foil would get flooded with the PMMA that appeared to form a non-uniform film on top of the foil. This also made the delamination fail because of the excess PMMA on top and bottom of the foil, from the spillage during the spin-coating process. As the delamination kept failing, it was initially thought that the voltage might not be enough to release the PMMA/hBN stack from the copper foil, and it was increased up to 10 V but with no success. Once we found that two drops was sufficient to coat the copper foil properly, using 4 V [41] during the delamination was found to work consistently.

Another problem that was encountered was the poor, ripped-looking and multi-layered coverage of hBN on the QF grids. After several attempts to prepare samples more carefully, ensuring no folds when fishing out the hBN during the multiple steps in the process, and also experimenting with the size of foil that was being used, it was decided that the problem must be with the starting material that we were working with. Once we moved to using the CVD-grown monolayer hBN from Sigma-Aldrich [42], and allowing the samples to sit in vacuum in the CVD furnace tube overnight after fishing out with the QF grids, we found much better monolayer and total coverage. But it was quickly found that the coverage we had, did not have large enough clean areas of monolayer hBN on which good data acquisition could be performed. The duration and temperature of the acetone bath were experimented with to better dissolve the PMMA, that was most likely contaminating our samples, but this didn't seem to help much. So, the heat treatment in the CVD furnace was the last step added to the process and at 400 °C, was found to help

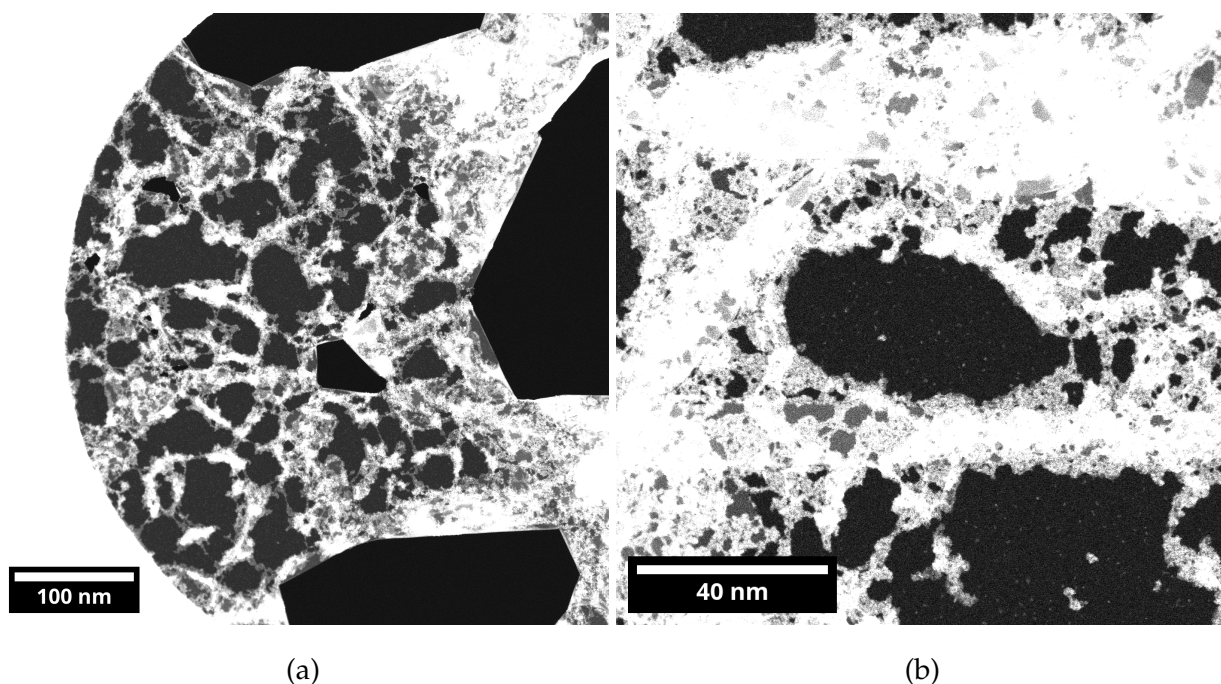


Figure 4.9: **MAADF STEM overview images of clean monolayer hBN areas.** Free-standing monolayer hBN over a hole of a QF grid with a few rips and folds in the coverage. In (a), the darkest contrast corresponds to vacuum.

remove more of the residue PMMA and other hydrocarbon contamination resulting in clean areas of monolayer hBN in the range of up to 50 - 70 nm² as seen in example images in Fig. 4.9.

Transfer of hBN onto SiN grids was found to be very inconsistent even though the same procedure was followed. It appeared that the SiN grid surface was not 'sticky' enough for the hBN and it was perhaps getting washed away with the acetone during the PMMA dissolving step. In a couple random successful transfers onto SiN grids, another problem was found when imaging with the Nion STEM. As we focused the electron probe on the free-standing hBN, up to higher magnifications, we observed that it would get destroyed leaving folded hBN on the rim of the hole. Fig. 4.10 shows an example of this destruction through a zoom series of images captured when focusing the electron beam and magnifying the image. Since hBN and the SiN grid are both insulating in nature, this destruction of hBN is assumed to be because of a Coulomb explosion-type mechanism, as the higher dose from focusing the electron beam could cause charge build-up and eventual destruction of the free-standing hBN.

We tried to solve this by using SiN grids that are coated with a conductive material such as a metal so that the charge could dissipate when imaging. We used grids with 5 nm

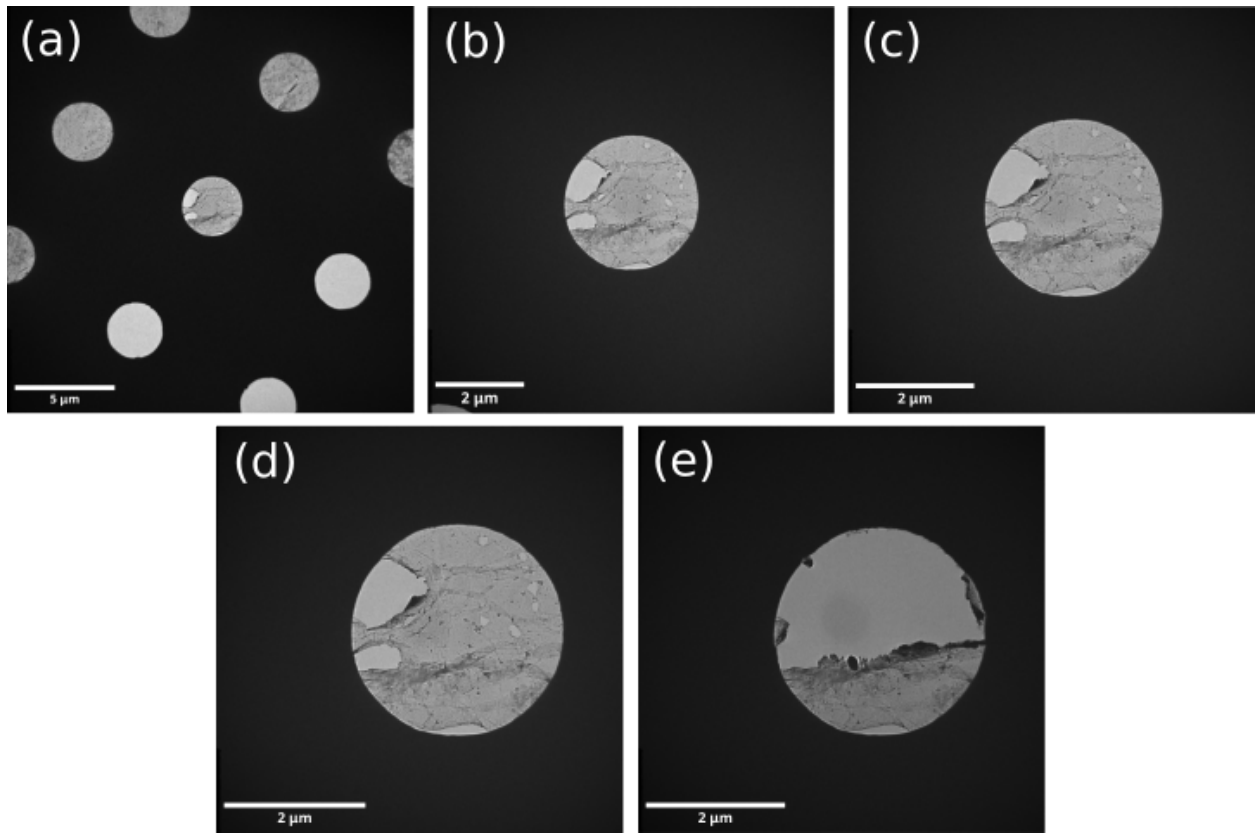


Figure 4.10: **Bright-field ronchigram zoom series.** (a) Free-standing hBN over the holes of a SiN grid. The beam is focused and magnification is increased from (a) to (e). In (e) the hBN is destroyed by the electron beam.

of gold and also grids with 5 nm of platinum evaporated onto them but unfortunately from the limited testing, we were unable to achieve any hBN coverage on the grids and were unable to confirm whether the metal coating helped with the charging damage. In the end, QF grids were chosen as they produced hBN samples with good coverage and quality, and with high consistency. In addition to that, QF grids do not suffer from charging damage because the amorphous carbon supporting film allows for the charge to dissipate.

4.2 Atomic structure of as-prepared samples

Five hBN samples are used in this study and are irradiated with Ar^+ ions of mean energy 0 eV, 20 eV, 40 eV, 60 eV, and 150 eV, respectively. The naming scheme for the different data points follow this ascending energy. For example, the data acquired from the 0 eV irradiation sample is called DP0, from the 20 eV irradiation sample is called DP20, from

the 40 eV irradiation sample is called DP40, and so on.

Once the samples are loaded into the CANVAS system at the load-lock (where the samples enter and exit the system) they are baked at 170 °C bake for ca. 12 h. This is done to remove surface contaminants from the sample, pucks and the car since they are exposed to ambient conditions during sample loading and preparation, and we want to avoid contaminating the rest of the CANVAS system.

4.2.1 Intrinsic defect concentration

The as-prepared hBN samples are first imaged with the Nion UltraSTEM 100 at 60 kV. Monolayer regions similar in size to that shown in Fig. 4.9 are chosen for the semi-autonomous image acquisition. This step is used to measure the intrinsic defect concentration in hBN across the samples studied here so that we can use it as a base line for the defect concentration measured after irradiation to estimate the ion-induced defect concentration in hBN for the different ion energies.

It should be noted that the 20 eV irradiation sample was completely contaminated after the irradiation and therefore post-irradiation data acquisition was not performed. Hence, data analysis for this data point (DP20) was also not performed and will not be presented in this thesis. Also, it should be noted that the 150 eV sample was hBN transferred onto a SiN grid. This was the first sample prepared out of the five, and was primarily used for training purposes with the electron microscope and with the plasma source. It was also used to replicate the results from reference [15] to showcase the ability of creating defects in hBN with Ar⁺ ions. Table 4.1 shows the defect types and their respective occurrence identified from the various samples prepared prior to irradiation. DP60 and DP150 contain two datasets acquired from different regions of the sample to keep the total number of images acquired roughly equal across the different samples. This was also done for the post-irradiation results in section 4.4, done in order to acquire a consistent number of images from representative areas of the sample for statistical significance.

The intrinsic defect concentration (mean and standard deviation weighted with the area imaged) was found to be $0.0601 \pm 0.0094 \text{ nm}^{-2}$ with $43.54 \pm 9.40 \%$ single vacancies ($55.01 \pm 4.93 \%$ V_B and $44.99 \pm 4.93 \%$ V_N), $37.40 \pm 8.93 \%$ double vacancies and the rest being more complex vacancy structures. This defect concentration was found to be about twice

Table 4.1: Pre-irradiation defect types and their percentages.

DP No.	Dataset	Single Vacancies (%)	V_B (%)	V_N (%)	Double Vacancies (%)
DP0	1	33.33	52.50	47.50	49.17
DP40	1	58.09	62.03	37.97	28.68
DP60	1	35.85	50.00	50.00	44.34
DP60	2	43.59	58.82	41.18	29.49
DP150	1	47.06	56.25	43.75	44.12
DP150	2	45.65	50.00	50.00	29.35
Weighted Mean	–	43.54	55.01	44.99	37.40
Weighted Std. Dev.	–	9.40	4.93	4.93	8.93

than what was previously measured experimentally [15], but could be attributed to the different manufacturer of the starting material, i.e., the CVD-grown hBN on copper foil. Focusing on the single vacancies, the roughly 50/50 mixture of boron and nitrogen vacancies is what is expected from the CVD-growth process where there is no preference of the type of defect occurring in the structure of hBN. A small percentage of these defects could have been created from the imaging process with the electron beam [61].

Fig. 4.11 shows a visual representation of the data-points in the form of plots of defect concentration against the different defect sizes measured. Defect size one corresponds to single vacancies, size two corresponds to double vacancies, size three to triple vacancies, and so on. Single and double vacancies are the primary defect structure observed among intrinsic defects with a non-negligible defect concentration of triple vacancies also being present. The more complex vacancy structures (defect size 4 and above) are seen to rarely occur in the as-prepared hBN samples and can be considered to be negligible compared to the rest. Above each of the individual plots, the total number and type of defect identified are displayed in a box.

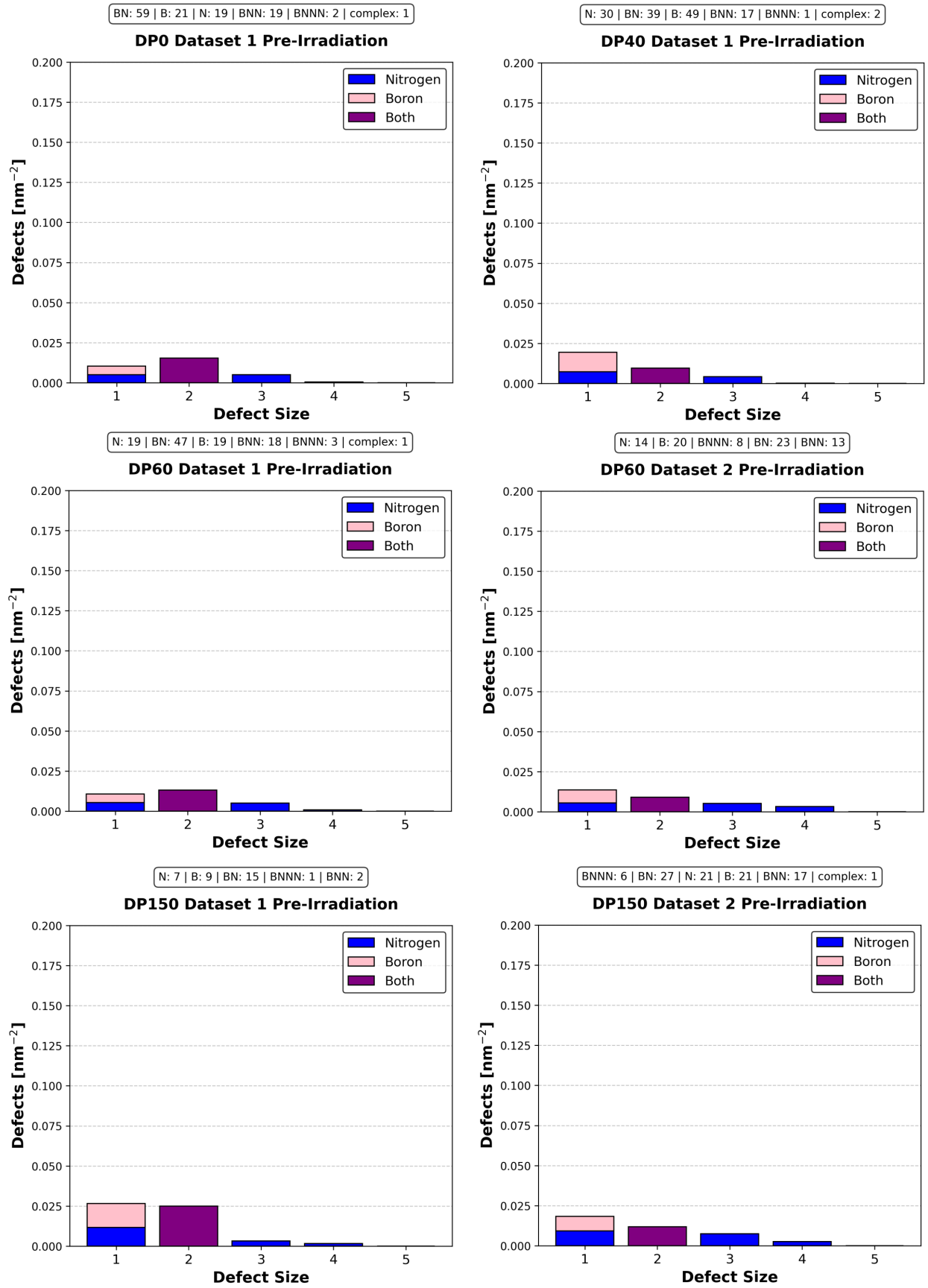


Figure 4.11: Defect concentration (nm^{-2}) vs defect type before irradiation.

4.3 Argon irradiation

Once the hBN samples had been analysed structurally pre-irradiation, the samples are then transported to the target chamber through the CANVAS system for the ion irradiation. The sample puck is placed into the deceleration setup stage with the help of a gripper arm. A method of achieving a stable pressure in the target chamber with the use of the leak valve for leaking in argon gas was employed [59]. For all the irradiations performed in this thesis, the pressure was stabilised in the range of $6 - 8 \times 10^{-6}$ mbar, and the parameters shown in Table 4.2 were set using the SPECS plasma source control unit. In order to get a stable beam current, the plasma source was allowed to warm up for 15-20 min after the plasma was first ignited.

Table 4.2: SPECS plasma source irradiation parameters.

Magnetron current (mA)	Anode voltage (V)	Extractor voltage (V)
16	0	-60

4.3.1 Deceleration and irradiation

Using the power supply connected to the deceleration setup, the Faraday cup and the puck stage can be biased as explained in the methods. By sweeping the bias supplied to the cup and measuring the resulting beam current on the multimeter, a beam shape measurement can be performed to identify the energy of the ion beam. Taking the beam shape measurement of Fig. 4.12 as an example, the bias voltage is swept from 0 V to 300 V. It can be seen that as the bias voltage is increased, the beam current drops, and at a particular range of bias voltages, the beam current drops more steeply. The derivative of this measurement is the beam shape of the ion beam. Using this drop as the centre, an error function plus a polynomial for the background is fit over the curve assuming a Gaussian shape of the energy spread of the ion beam. The resulting fit provides the ion beam energy and the energy spread as seen in Fig. 4.12 (b). As the bias voltage is increased, electrons coming from the plasma source (along with the ions) are attracted to the Faraday cup. At a particular range of bias voltages that match the energy range of the ions, they are effectively stopped by the deceleration potential which results in the sharp drop in the beam current. Therefore, the centre of this drop is taken as the centre of the

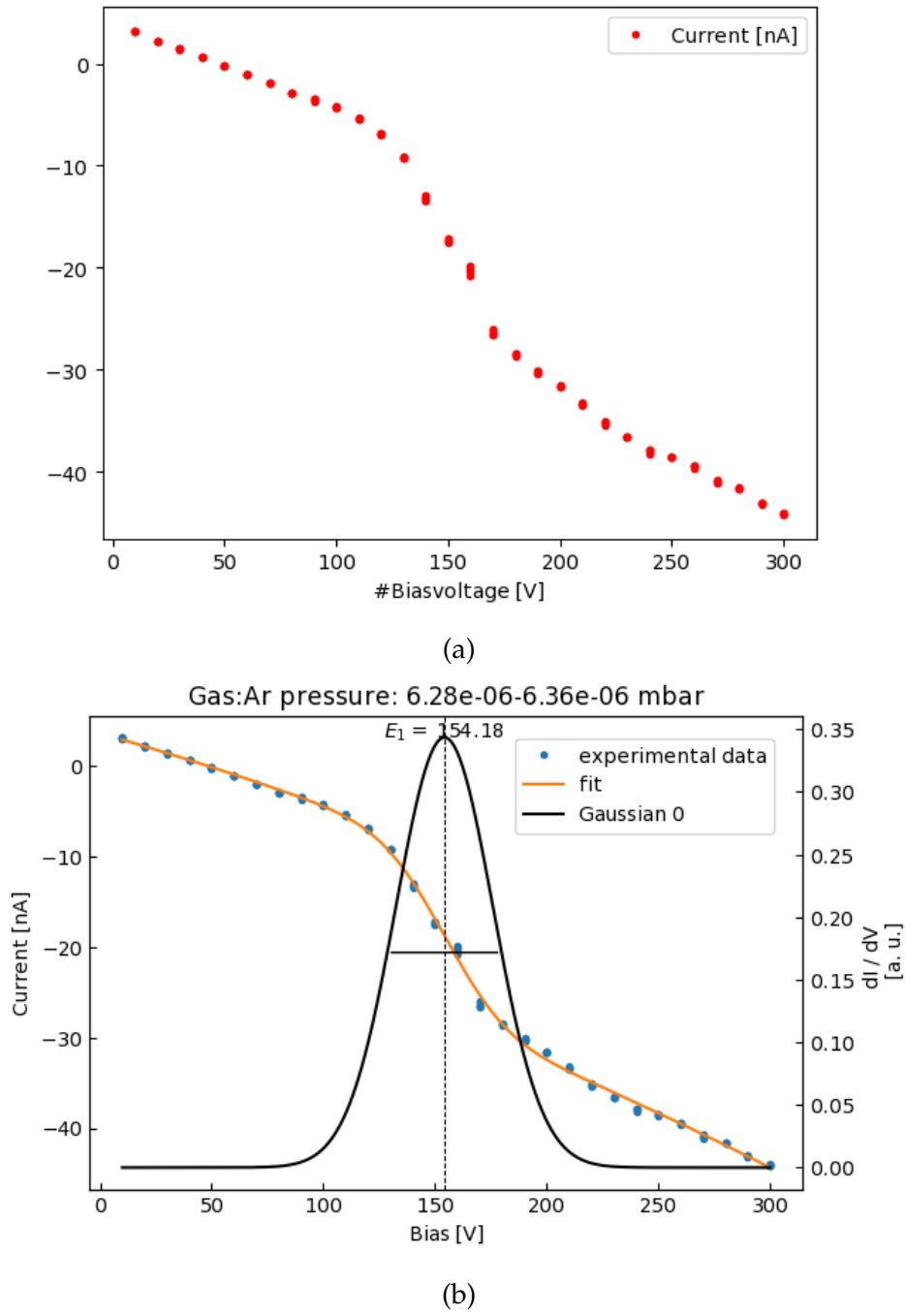


Figure 4.12: **Beam shape measurement performed prior to the 0 eV irradiation.** (a) Raw output measured when biasing the Faraday cup from 0 V to 300 V. (b) Energy of the ion beam identified by fitting the curve.

energy spread of the ions that are emitted from the plasma source.

After the identification of the energy and spread of the beam, the ions could be decelerated accordingly by biasing the puck stage where the sample is. For the beam shape measurement acquired prior to the 0 eV irradiation (DP0), the ion beam energy and spread were identified to be $154 \text{ eV} \pm 22 \text{ eV}$. Since we wanted to irradiate the sample with 0

eV ions, the sample was biased to 154 V to effectively allow only $0 \text{ eV} \pm 22 \text{ eV}$ ions to reach the sample. For clarification, the 0 eV irradiation is physically an irradiation with the higher (positive) energy spread of the beam shape when biased to exactly the beam energy identified.

Since the position of deceleration setup is controlled by a rotary dial on the outside of the target chamber, the puck stage was biased to 500 V to time the irradiations correctly. This allowed the movement of the stage directly below the ion beam preventing all the ions from reaching the sample. The bias was then set according to the energy required for the duration of the irradiation, and was then set back to 500 V to halt the irradiation and move it out the beam path. The duration of the irradiation was adjusted depending on the ion beam current measured prior to the irradiation so that all samples would be irradiated with the same ion dose. In all experiments in this thesis, the beam current used to calculate the irradiation duration was measured with a 5 V bias applied to the Faraday cup. Since the aperture of the Faraday cup has a diameter of 6.35 mm and the irradiations were aimed to match a dose corresponding to a 5 nA beam current and 5 min irradiation duration, the ion beam dose rate and fluence can be calculated as follows. With a 5 nA beam current, the ion dose rate is

$$\phi = 9.85 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}. \quad (4.1)$$

With the irradiation duration of 5 min, the fluence that is matched for all the irradiations is

$$D = 2.96 \times 10^{13} \text{ cm}^{-2}. \quad (4.2)$$

Since this was the fluence measured at the Faraday cup and not at the sample, the resulting dose that the sample would be subjected to during the irradiation is assumed to be in the same order of magnitude. For easier comparison with post-irradiation defect concentrations, the ion dose can be written as $0.296 \pm 0.018 \text{ nm}^{-2}$ (uncertainty calculated from the fluctuation in the beam current measured by the multimeter).

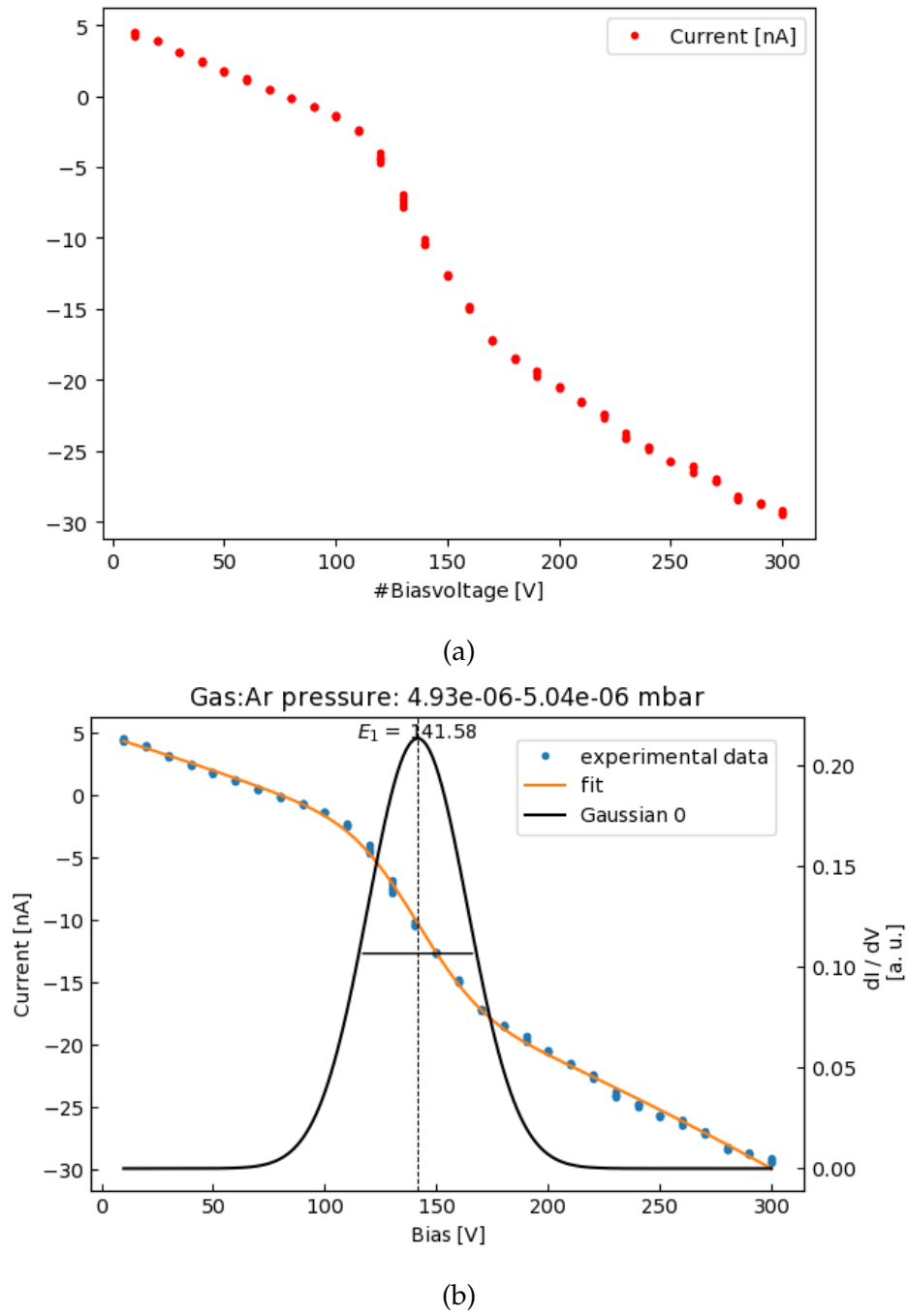


Figure 4.13: **Beam shape measurement performed prior to the 40 eV irradiation.** (a) Raw output measured when biasing the Faraday cup from 0 V to 300 V. (b) Energy of the ion beam identified by fitting the curve.

It was found that the energy of the beam was a function of the pressure at the target chamber. If the same pressure was achieved and stabilised, the resulting energy of the ion beam would be within the uncertainty first measured. Even though this was tried and tested, a beam shape measurement was performed before and after each irradiation to make sure of the energy and spread of the ion beam. It was found that the subsequent measurement of the beam shape was roughly the same as the one before the irradiation.

In the case of DP0 (Fig. 4.12), the beam shape fit gave $154 \text{ eV} \pm 22 \text{ eV}$ as the ion energy and spread. The beam current measured prior to the irradiation was ca. 4.2 nA. Hence with a 154 V bias, the sample was irradiated for a total of 6 min to achieve the desired dose.

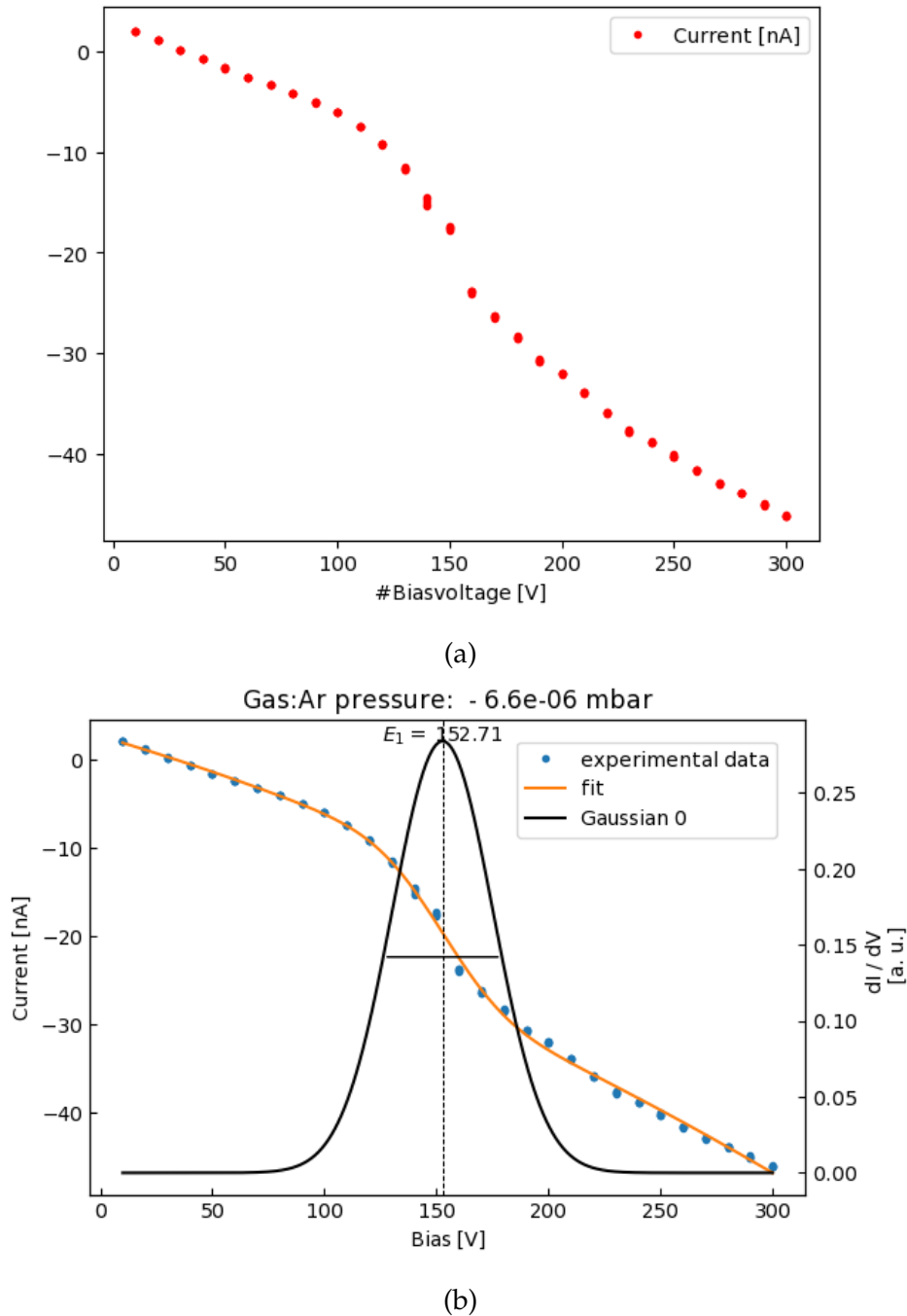


Figure 4.14: **Beam shape measurement performed prior to the 60 eV irradiation.** (a) Raw output measured when biasing the Faraday cup from 0 V to 300 V. (b) Energy of the ion beam identified by fitting the curve.

In the case of DP40 (Fig. 4.13), the beam shape fit gave $142 \text{ eV} \pm 22 \text{ eV}$ as the ion energy and spread. To achieve an irradiation with 40 eV ions, the bias voltage was set to 102 V

to effectively allow $40 \text{ eV} \pm 22 \text{ eV}$ ions to reach the sample. The beam current measured prior to the irradiation was ca. 5.1 nA. Hence with a 102 V bias, the sample was irradiated for a total of 5 min to achieve the desired dose.

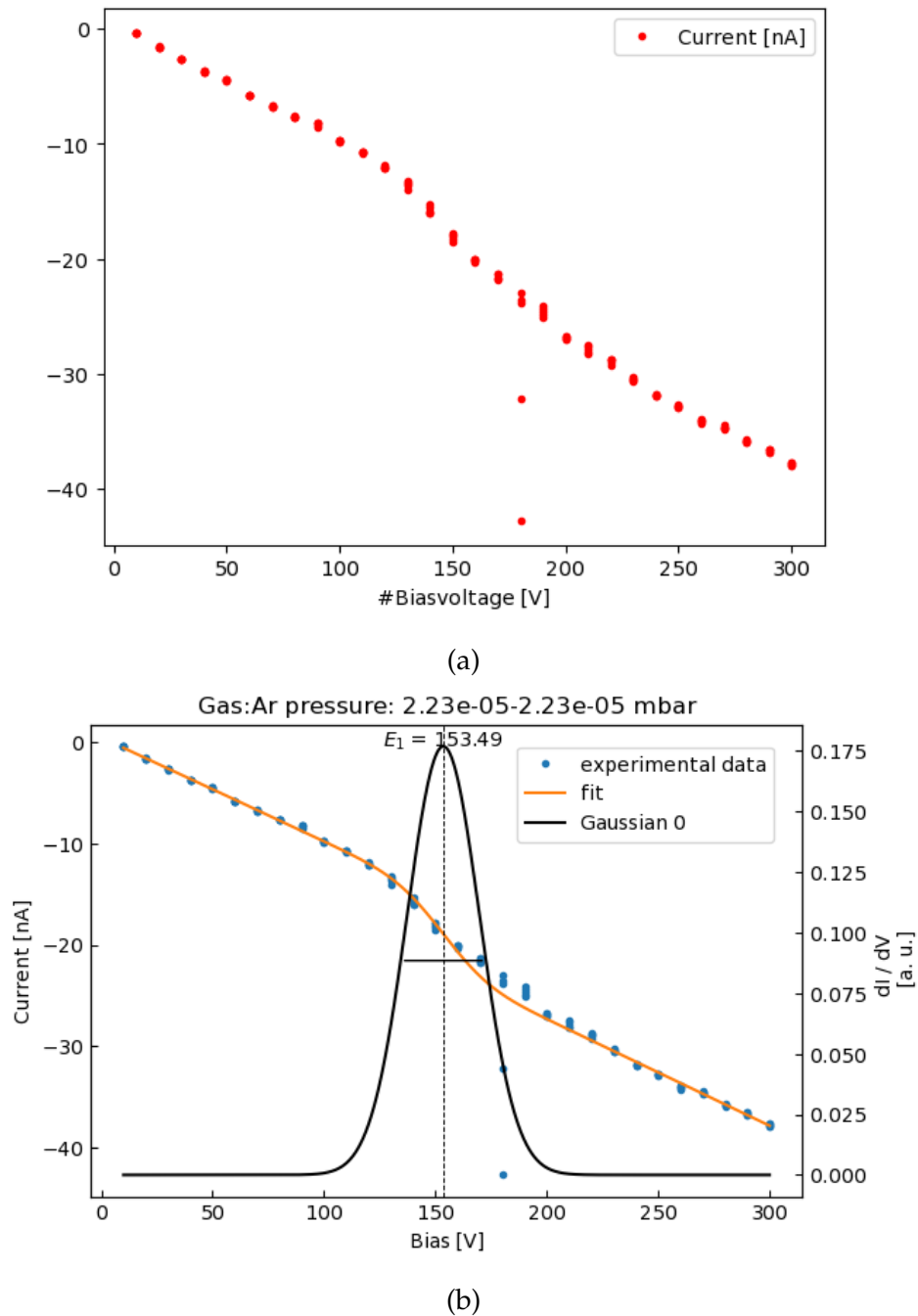


Figure 4.15: **Beam shape measurement performed prior to the 150 eV irradiation.** (a) Raw output measured when biasing the Faraday cup from 0 V to 300 V. (b) Energy of the ion beam identified by fitting the curve.

In the case of DP60 (Fig. 4.14), the beam shape fit gave $153 \text{ eV} \pm 23 \text{ eV}$ as the ion energy and spread. To achieve an irradiation with 60 eV ions, the bias voltage was set to 93 V to effectively allow $60 \text{ eV} \pm 23 \text{ eV}$ ions to reach the sample. The beam current measured

prior to the irradiation was ca. 3.3 nA. Hence with a 93 V bias, the sample was irradiated for a total of 8 min to achieve the desired dose.

And lastly, in the case of DP150 (Fig. 4.14), the beam shape fit gave $153 \text{ eV} \pm 16 \text{ eV}$ as the ion energy and spread. Since the sample is being irradiated with no deceleration at the 'natural' energy of the ion beam emitted from the plasma source, the sample was irradiated with the sample puck being held in the gripper arm under the plasma source. The beam current measured prior to irradiation was ca. 0.2 nA. The sample was irradiated for a total of 3 min. This particular irradiation was conducted when the deceleration setup was positioned differently with respect to the plasma source in the target chamber, hence the completely different irradiation parameters. It can also be seen that the drop in the beam current around the expected energy of the ion beam is not as evident as the other measurements above. In addition to this, there appears to be a couple stray measurements at beam currents much lower than the trend. The resulting fit seems to do a decent job of identifying the energy and spread but does appear to under estimate it a little bit.

4.4 Post-irradiation

Once the samples had been irradiated, they were transported back to the microscope through the CANVAS system for imaging. Since leaving the samples in UHV for a long time could result in the build-up of contamination on the surface of the samples and possibly cover some of the vacancies created with the ions, post-irradiation data was acquired no later than a couple days after the irradiation was performed.

4.4.1 Ion-induced defects

As before, monolayer regions of large enough size were chosen for the image acquisition but this time from multiple areas across the sample to get an understanding of the distribution of vacancies. Out of the regions chosen, the same area imaged in the pre-irradiation was chosen again, to get a direct look at the defects formed due to the ion irradiation. The other regions are chosen to acquire data from representative areas of the sample. The ion-induced defect concentration was found to be $0.2032 \pm 0.0769 \text{ nm}^{-2}$ and was calculated by subtracting the base line intrinsic defect concentration from the post-

irradiation defect concentration. Table 4.3 shows the tabulated defect types and their respective percentages post irradiation.

Table 4.3: Post-irradiation defect types and their percentages.

DP No.	Dataset	Single Vacancies (%)	V _B (%)	V _N (%)	Double Vacancies (%)
DP0	1.0	67.19	92.49	7.51	24.61
DP0	2.0	53.06	89.83	10.17	34.35
DP0	3.0	60.00	94.25	5.75	30.69
DP40	1.0	70.37	85.53	14.47	25.31
DP40	2.0	74.00	76.58	23.42	18.00
DP60	1.0	67.92	93.19	6.81	24.86
DP60	2.0	67.56	91.81	8.19	25.57
DP60	3.0	69.91	88.74	11.26	20.83
DP150	1.0	51.59	53.85	46.15	29.37
DP150	2.0	55.56	61.05	38.95	23.39
DP150	3.0	75.00	70.59	29.41	23.53
Weighted Mean	–	63.79	83.33	16.67	26.27
Weighted Std. Dev.	–	7.73	13.06	13.06	4.39

By taking the mean and standard deviation weighted with the area imaged, the statistics for the defect types and their percentages are calculated. For DP0, we found 58.70 ± 5.94 % single vacancies (91.68 ± 1.86 % V_B and 8.32 ± 1.86 % V_N), for DP40 we found 71.95 ± 1.79 % single vacancies (81.62 ± 4.44 % V_B and 18.38 ± 4.44 % V_N), for DP60 we found 68.09 ± 0.86 % single vacancies (91.70 ± 1.51 % V_B and 8.29 ± 1.51 % V_N), and for DP150 we found 59.35 ± 9.49 % single vacancies (61.16 ± 6.42 % V_B and 38.84 ± 6.42 % V_N). The total weighted mean calculated across all the data points gave 63.79 ± 7.73 % single vacancies (83.33 ± 13.06 % V_B and 16.67 ± 13.06 % V_N).

From this, it can be seen that there is a high selectivity for boron single vacancies across all the ion energies. The 150 eV irradiation is an outlier to this trend having a much closer balance between the boron and nitrogen single vacancies. These results were not expected from the irradiations since predominance of nitrogen single vacancies was expected at ion energies lower than ca. 45 eV according to the Ehrenfest TDDFT simulation results.

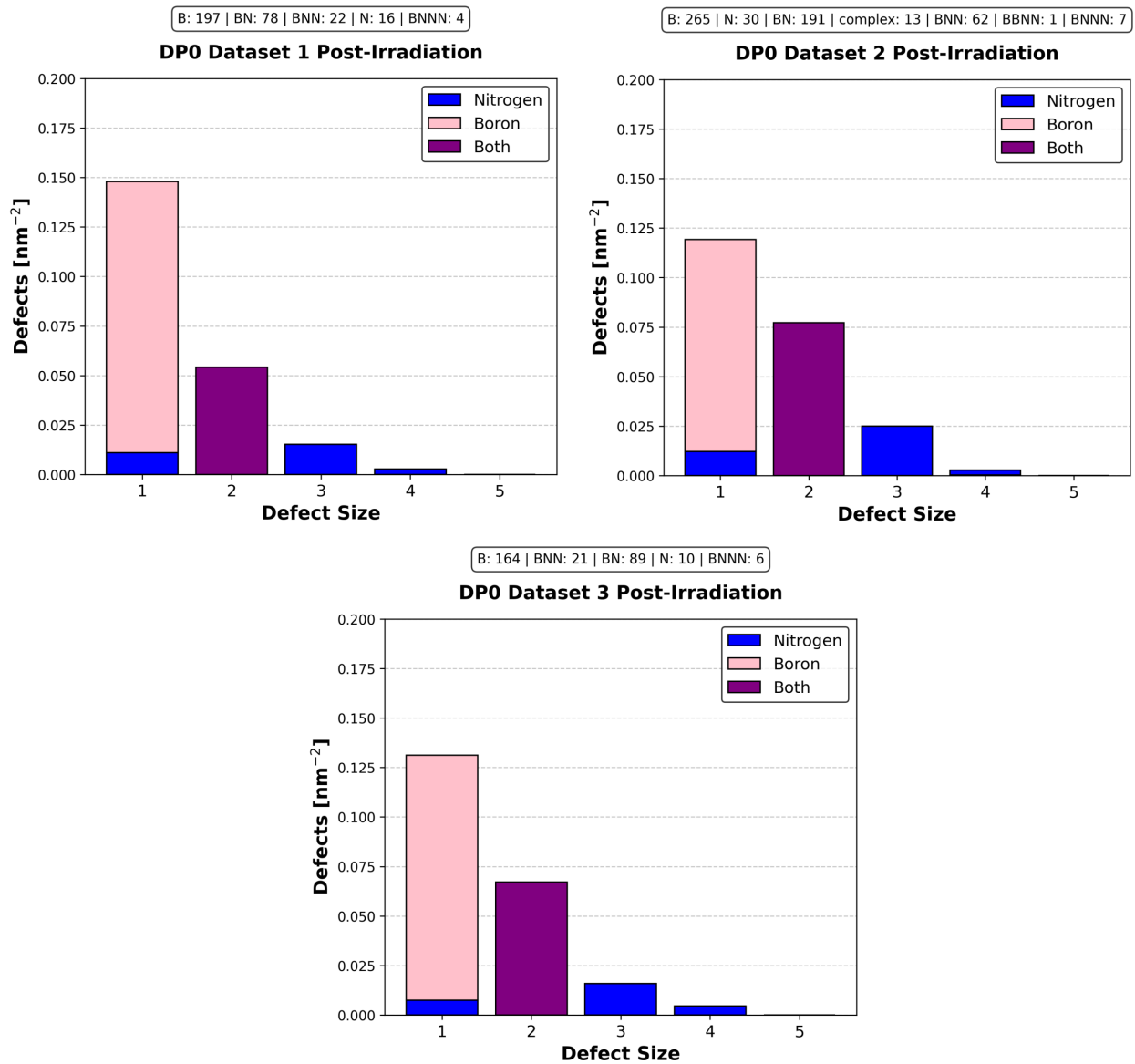


Figure 4.16: Defect concentration (nm⁻²) vs defect type for the 0 eV irradiation. The total imaged area for this data point is 5240 nm².

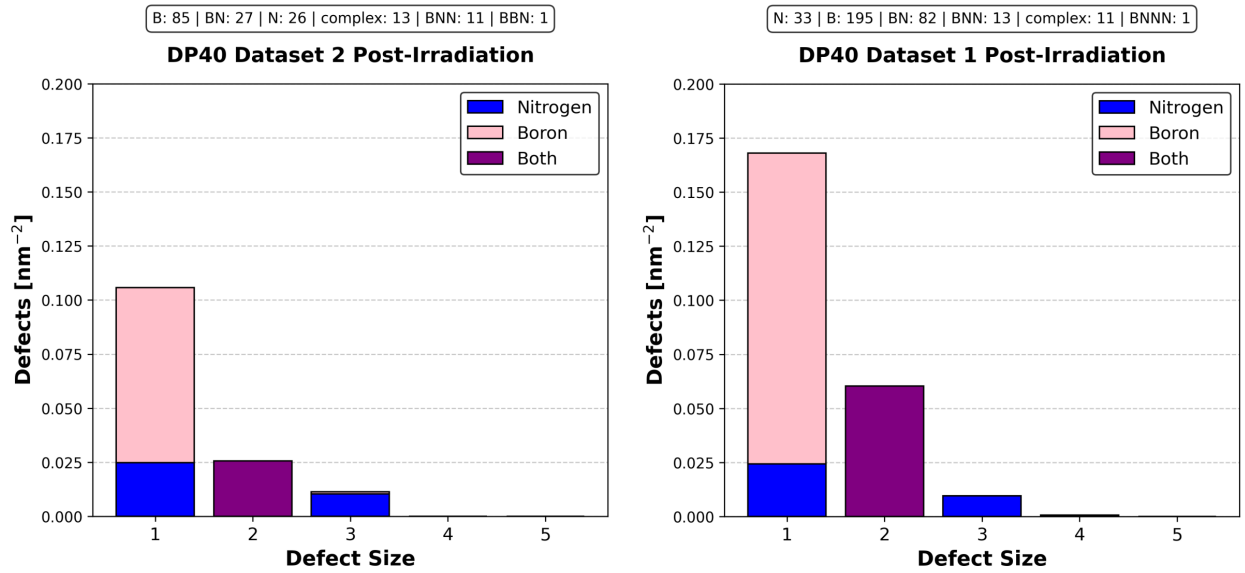


Figure 4.17: **Defect concentration (nm⁻²) vs defect type for the 40 eV irradiation.** The total imaged area for this data point is 2408 nm².

Fig. 4.16 to 4.19 show the post-irradiation data. Single and double vacancies dominate the defect types that are formed after the irradiation for all ion beam energies which is expected from the theory of binary collisions and is in line with results from theory [13, 14]. The results from DP0, DP40, and DP60 also align with the defect concentration distribution found from the experimental study [15]. If triple vacancies formed, they were found to be nitrogen dominated (meaning two nitrogen atoms and one boron atom missing beside each other) and hence the plots are coloured in blue to represent that for defect size 3. In Fig. 4.17, it can be seen that there is a significant difference between the defect concentration of the boron single vacancies and that of the double vacancies between the two plots. But when taking a weighted average of the two, they are found to be similar to the other data points. Perhaps there was a bias introduced depending on the region chosen for the automated image acquisition.

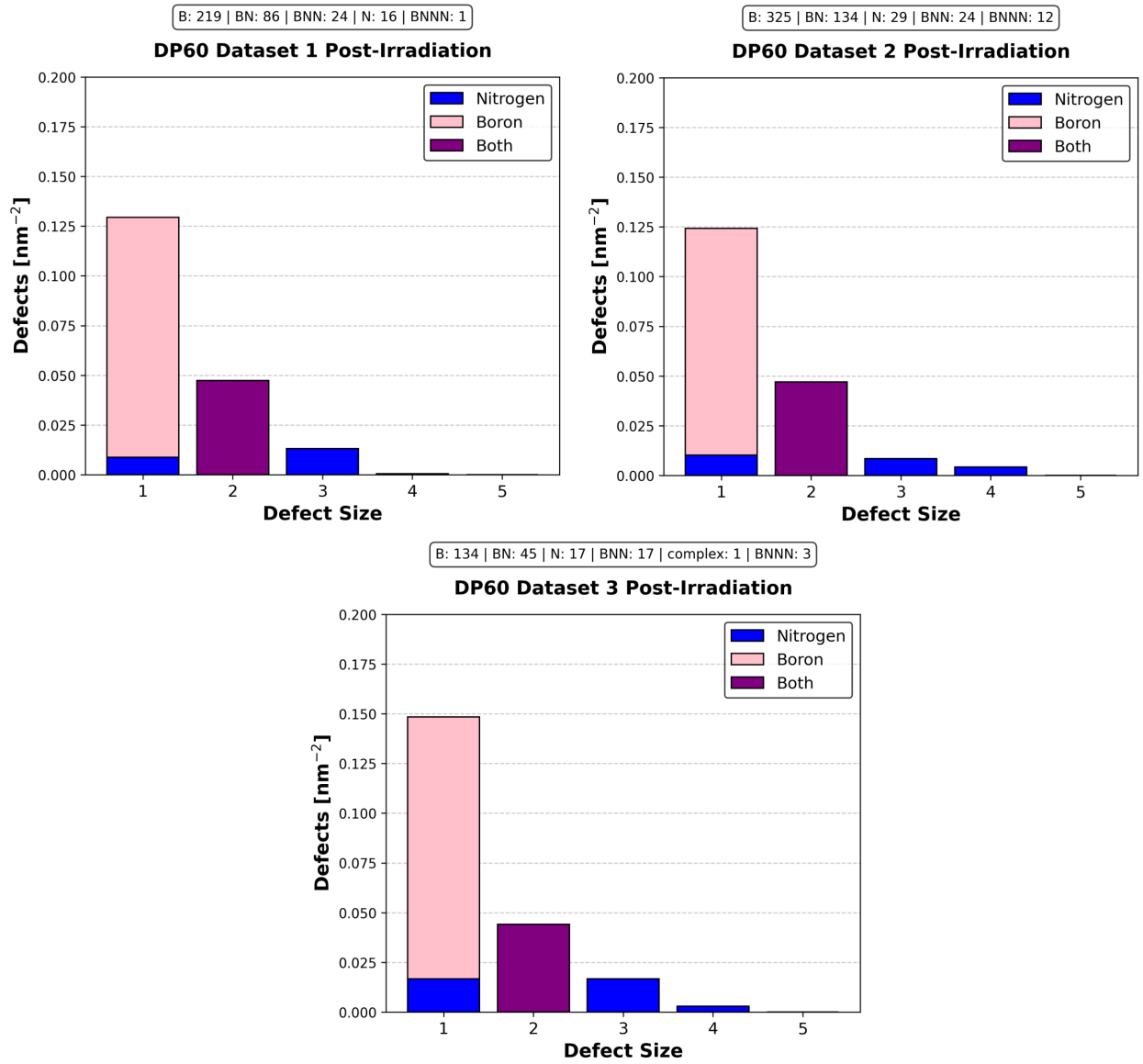


Figure 4.18: Defect concentration (nm⁻²) vs defect type for the 60 eV irradiation. The total imaged area for this data point is 5685 nm².

Fig. 4.19 for DP150 shows a comparatively lower defect concentration across the three datasets acquired and has a more balanced difference in the single vacancies formed showing lesser selectivity for boron vacancies. The image quality during acquisition, the classification of defects using the histogram classifiers and the statistics for this data point are also poor compared to the others and appears to skew the results calculated for the total mean and standard deviation weighted with the area imaged.

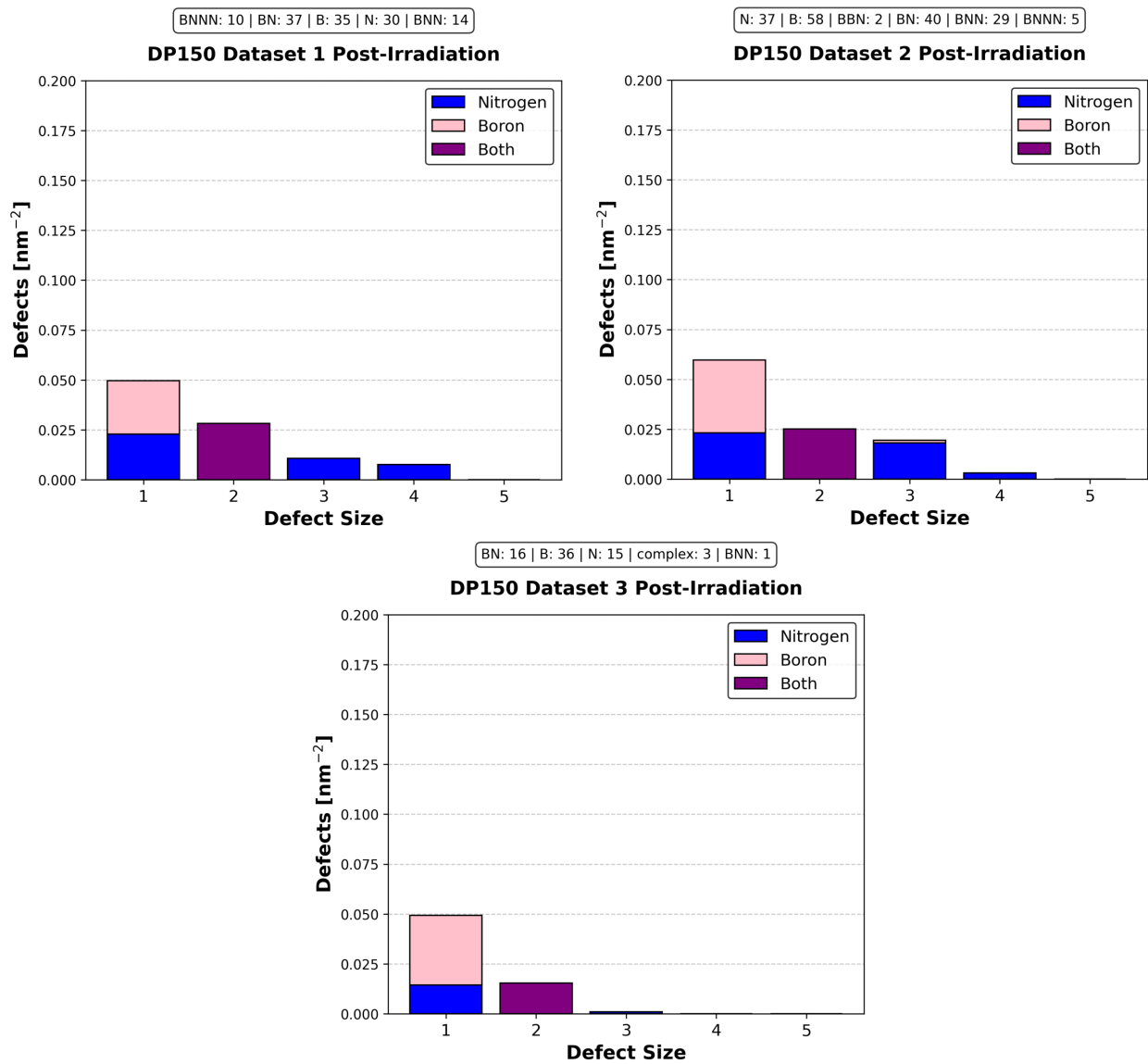


Figure 4.19: Defect concentration (nm^{-2}) vs defect type for the 150 eV irradiation. The total imaged area for this data point is 3931 nm^2 .

Chapter 5

Discussion

5.1 Sample preparation

The implementation of the electrochemical delamination method for hBN sample preparation was successful and resulted in samples with high coverage of monolayer hBN and large clean areas across the sample, showcasing the effectiveness of the vacuum heat treatment. The areas were large enough so that it was feasible to acquire a large number of images in one region using the semi-autonomous acquisition tool with minimal manual interference. This also makes defect-engineering studies in 2D materials, such as this one, more feasible as we can directly correlate the observed vacancies in the lattice with the ion irradiation. The CANVAS system has a newly installed UHV heater, which in theory should be able to clean the surface of contamination much better than the furnace used here due to the UHV conditions and higher, more localised temperature achievable. The electrochemical delamination method can also be expanded to other 2D materials that are grown on metal substrates because of the simple mechanism behind the transfer process. Recent experiments conducted to make samples using CVD-grown graphene on copper foil pre-coated with PMMA worked flawlessly, and the method should theoretically work just as well with any other material on X substrate.

The QF grids had to be chosen in this study because of the higher success rate in sample preparation even though the SiN grids were preferential. The QF grids are flexible and have out-of-plane variations in height. This makes large area imaging using the acquisition tool much more difficult because of the variation in the focus at the four corners

of the quadrangle chosen. There were times when the tool could not accurately interpolate the difference in focus where it necessitated constant manual intervention during the imaging process. This is not ideal as constant manual tuning of the beam defeats the purpose of the semi-autonomous tool. The SiN grids solve this issue because they have a flat, rigid surface with minimal variations in height. This makes the image acquisition more efficient with little to no manual intervention after setting up the area to be imaged. The SiN grids also allow for the possibility of using laser cleaning methods in the case of contamination build-up or mobile contamination issues while imaging, which would otherwise not be possible on QF grids as they can be easily destroyed from the intensity of the laser. Another reason for exploring the use of SiN grids is that mechanical studies using an AFM can be performed. The grids were initially designed by our research unit for this purpose alone, because it allows mechanical stiffness measurements of free-standing material, without itself being bent by the AFM probe in the process. We also believe that smaller hole diameters of the QF grids make the free-standing hBN more stable due to the size of the grains in CVD-grown hBN. Therefore, using SiN grids with smaller hole diameters than what was used here ($3\mu\text{m}$) could help with the stability of the transferred hBN. Hence, solving the coverage issue as well as the charging damage issue would be very beneficial for future experiments and collaborations.

5.2 Selective defect creation

The observed ion-induced defect concentration was found to be $0.2032 \pm 0.0769 \text{ nm}^{-2}$ with the approximate ion dose being ca. $0.296 \pm 0.018 \text{ nm}^{-2}$. This observation agrees with the fact that not every ion that interacts with the sample, creates a defect upon interaction. The energy transfer scattering cross-section determines the probability that the ion successfully displaces an atom and is a function of the ion trajectory. According to the TDDFT simulations, the type of vacancy formed in hBN is dependent on the energy of an argon ion used in the irradiation. We expected to see a difference in the defect type and distribution compared to the results of reference [15]. Instead, we found that boron single vacancies were preferentially created at all energies used here.

The immediate explanation for this could be due to a fault in the deceleration setup. It could be that the biasing of the puck stage was not connected, and the ions were not being

decelerated which means that we irradiated the four samples with the same energy of ca. $150 \text{ eV} \pm 25 \text{ eV}$ and found very similar results in all cases. However, the connections on the outside of the target chamber at the deceleration setup control unit were checked and no faulty connections could be found. Another possibility is that the electrons that are coming out of the plasma source and being attracted to the positive bias, could screen the decelerating bias. This could result in the unsuccessful or partial deceleration of the ions as they approach the sample. Hence across all the data points collected in this study, the sample could have been irradiated at similar, or at least unknown, energies resulting in a similar distribution of defects. Another unlikely possibility is the neutralisation of the ions as they can recombine with the electrons when they come out of the plasma source. Since they are neutral, the positive bias has no effect on them and interact with the sample as though there was no deceleration. Hence, future experiments and tests with the deceleration are required to prove whether the deceleration setup is performing as needed.

Table 5.1: Post-irradiation defect types and their percentages (excluding DP150).

DP No.	Dataset	Single Vacancies (%)	V_B (%)	V_N (%)	Double Vacancies (%)
DP0	1.0	67.19	92.49	7.51	24.61
DP0	2.0	53.06	89.83	10.17	34.35
DP0	3.0	60.00	94.25	5.75	30.69
DP40	1.0	70.37	85.53	14.47	25.31
DP40	2.0	74.00	76.58	23.42	18.00
DP60	1.0	67.92	93.19	6.81	24.86
DP60	2.0	67.56	91.81	8.19	25.57
DP60	3.0	69.91	88.74	11.26	20.83
Weighted Mean	–	65.10	89.87	10.13	26.52
Weighted Std. Dev.	–	6.57	4.57	4.57	4.73

DP150 broke away from the trend of exhibiting a high selectivity for boron single vacancies and had a more equal distribution between boron and nitrogen single vacancies. This contradicts theoretical results presented by reference [14] that shows single nitrogen vacancies dominating at 150 eV but the results do align with the older study [13] that shows an equal distribution of boron and nitrogen single vacancies at energies of a few 100s of eV. The observed defect concentration was also lower than that of other irradiation data-points. Both of these differences are most likely due to a different experimental setup that was later changed for the rest of the irradiations. The alignment of the Faraday cup with respect to the ion beam from the plasma source was slightly off, and this is known to have caused an incorrect readout of the beam current. Hence, irradiation duration for this sample was incorrectly decided and could explain the lower defect concentration observed. Another difference during this irradiation was that the sample puck was held in the gripper arm during the irradiation and was not inserted into the deceleration setup because it was irradiated with the 'natural' energy of the ions coming out of the plasma source, i.e., ca. $150 \text{ eV} \pm 20 \text{ eV}$ with no bias required. The gripper arm could have been incorrectly positioned and/or angled with respect to the centre of the ion beam during the irradiation causing oblique ion trajectories interacting with hBN. These differences could explain the outlier results observed with DP150. Therefore, for a better representation of the results acquired in this study, DP150 should be excluded from the statistics. If this is done, single vacancies are now calculated to be $65.10 \pm 6.57 \%$ with $89.87 \pm 4.57 \%$ V_B and $10.13 \pm 4.57 \%$ V_N , which show a stronger selectivity for boron single vacancies with lower uncertainty across the energies presented here. Also excluding DP150 from the calculation of the ion-induced defect concentration, we get $0.2401 \pm 0.0478 \text{ nm}^{-2}$.

Assuming a working experimental setup, this study shows that when monolayer hBN is irradiated with a range of argon ion energies, primarily boron single vacancies are selectively created. This is one of the first experimental studies on defect creation in hBN using Ar^+ ions in this energy range. The underlying mechanism of the defect creation is yet to be fully understood as from theory, it is expected that nitrogen single vacancies should be the dominating defect type observed at energies of 100 to 200 eV [14] (double than that of single boron vacancies) most likely because the energy transfer is more efficient as there is a closer mass difference between nitrogen and argon. There is also a very unlikely possibility that inelastic scattering effects taking place upon interaction between the ion and atoms in hBN could have an effect and explain the observations seen in this

work. Although experimentally found results point towards boron single vacancies dominating, as observed in this study and in reference [15], this research further expands and questions the fundamental mechanisms of selective defect creation in 2D materials using ion irradiation.

Chapter 6

Conclusions

In this work we sought out to develop and implement a new method for preparation of hBN samples. We have shown that the electrochemical delamination method for hBN, or in theory any other 2D material grown on a metal substrate, sample preparation is viable to prepare high quality samples with high coverage and minimal contamination. The additional heat treatment in the CVD furnace was proven to be very beneficial for cleaning and uncovering large areas of monolayer hBN across the sample, which could be improved further with the use of the UHV heater recently installed.

As boron and nitrogen have different displacement threshold energies, the selective defect creation of one type of vacancy in hBN was explored. TDDFT simulations suggested that with the use of Ar^+ ions with energies lower than ca. 45 eV only nitrogen single vacancies should be created. By experimentally irradiating hBN samples with Ar^+ energies of 0 eV, 40 eV, 60 eV, and 150 eV (with an energy spread of 20 to 25 eV), it was found that regardless of the ion energy, with the exception of the 150 eV irradiation, boron single vacancies dominate with ion-induced defect concentration found to be $0.2032 \pm 0.0769 \text{ nm}^{-2}$. For DP0, we found $58.70 \pm 5.94 \%$ single vacancies ($91.68 \pm 1.86 \%$ V_B and $8.32 \pm 1.86 \%$ V_N), for DP40 we found $71.95 \pm 1.79 \%$ single vacancies ($81.62 \pm 4.44 \%$ V_B and $18.38 \pm 4.44 \%$ V_N), for DP60 we found $68.09 \pm 0.86 \%$ single vacancies ($91.70 \pm 1.51 \%$ V_B and $8.29 \pm 1.51 \%$ V_N), and for DP150 we found $59.35 \pm 9.49 \%$ single vacancies ($61.16 \pm 6.42 \%$ V_B and $38.84 \pm 6.42 \%$ V_N). The total weighted mean calculations across all the data points gave $63.79 \pm 7.73 \%$ single vacancies ($83.33 \pm 13.06 \%$ V_B and $16.67 \pm 13.06 \%$ V_N). The 150 eV irradiation was regarded as an outlier to the trend due to different experimental parameters affecting the data-point. By excluding DP150 from the statistics, we

found 65.10 ± 6.57 % single vacancies with 89.87 ± 4.57 % V_B and 10.13 ± 4.57 % V_N .

In conclusion, future experiments where the irradiations are repeated to check for reproducibility and consistency should be performed to rule out the possibility of experimental setup flaws. In addition to this, more data-points of different ion energies should be explored to get a better understanding of the energy dependence in defect creation. If possible, narrower beam energy spreads would be favourable so that the irradiation energy and their effects do not overlap with one another causing confusion in the analysis. And finally, achieving the successful transfer and imaging of hBN on SiN grids would improve future experiments and open new possibilities for correlation studies.

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