Characterising the Fundamental Properties of Boron Doped Diamond Single Crystals

by

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List of Abbreviations

AFM	Atomic force microscopy	
BDD	Boron doped diamond	
C-AFM	Conductive atomic force microscopy	
CE	Counter electrode	
CV	Cyclic voltammetry	
CVD	Chemical vapour deposition	
E1/2	Half wave potential	
ΔE_p	Peak-to-peak potential	
EBSD	Electron backscatter diffraction	
ET	Electron transfer	
FCC	Face-centred cubic	
FWHM	Full width at half maximum	
HOPG	Highly oriented pyrolytic graphite	
НРНТ	High pressure, high temperature	
HRXRD	High resolution X-ray diffraction	
IMFP	Inelastic mean free path	
LEED	Low energy electron diffraction	
p-BDD	Polycrystalline boron doped diamond	
QRCE	Quasi-reference counter electrode	
RE	Reference electrode	
RHEED	Reflection high-energy electron diffraction	
SC	Single crystal	
SC-BDD	Single crystal boron doped diamond	
SECCM	Scanning electrochemical cell microscopy	
SECM	Scanning electrochemical microscopy	
SEM	Scanning electron microscopy	
SIMS	Secondary ion mass spectrometry	
Sq	Root mean square height	
UHV	Ultra-high vacuum	

- WE Working electrode
- XPS X-ray photoelectron spectroscopy
- XRD X-ray diffraction

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Declaration

This thesis is submitted to the University of Warwick in support of my application for the degree of Master of Chemistry by Research. It has been composed myself and has not been submitted in any previous application for any degree.

The work presented (including data generated and data analysis) was carried out by the author except in the cases outlined below:

- Boron doped diamond samples were grown by Element Six Ltd.
- Single crystal samples were polished by Adam Rathmill.
- The (111)-oriented single crystal sample was cut by Joshua Tully.
- Raman spectroscopy data was acquired by Ben Breeze.
- Low energy electron diffraction and X-ray photoelectron spectroscopy data was acquired by Marc Walker.
- Scanning electron microscope images were taken by Daniel Houghton.
- Bulk electrochemical measurements were made by Katherine Levey.

Abstract

Boron doped diamond (BDD) has many favourable properties that lend themselves to electrochemical applications: it is chemically inert, has low background currents, a wide solvent window, resistance to corrosion and fouling, and metal-like behaviour upon doping above $\sim 10^{20}$ B atoms cm⁻³. As a result, BDD has found applications in areas such as electroanalysis, advanced oxidation of pollutants and electroorganic synthesis. Typically, research revolves around the use of polycrystalline BDD since it can be readily grown in large wafers, with wavers ~ 150 mm in diameter being commercially available. However, polycrystalline BDD is inherently inhomogeneous; the presence of grains, with varying amounts of boron doping, hinder the study of BDD's fundamental properties on a macroscale. Grain boundaries may also contain sp² carbon, which is more electrocatalytically active that sp³ carbon increasing the background currents, decreasing the solvent window, and further adds to the surface's heterogeneity. Therefore, to study the fundamental behaviour of BDD, one approach is to use homogeneous single crystal (SC) surfaces.

Growing appropriately doped SC-BDD of the correct orientation and post processing it such that the surface is smooth and free from defects and surface damage is challenging, and very few studies have achieved this. This thesis outlines the growth, processing, and characterisation of three freestanding homoepitaxially chemical vapour deposition grown BDD SC samples of (111), (110) and (100) orientation that have metallic level doping and were polished to sub-nanometre roughness. First, the orientation of each sample was confirmed using X-ray diffraction and any off-angle orientation corrected by further polishing of the crystal. The samples were further characterised using low energy electron diffraction, Raman spectroscopy, atomic force microscopy and X-ray photoelectron spectroscopy to confirm crystal quality, surface finish and chemical functionality. Finally, scanning electrochemical cell microscopy was used to spatially map the electron transfer (ET) kinetics across the surface using an outer-sphere redox couple.

1. Introduction

1.1 Diamond

Diamond is a useful material possessing an array of remarkable properties which have led to its use in a variety of applications. Notably, diamond is highly chemically inert and is the hardest known naturally occurring material (85-100 GPa)¹, resulting from its strong tetrahedrally arranged sp³ bonds. It also has a high room temperature thermal conductivity (2200 Wm⁻¹K⁻¹), high electrical resistivity as a wide band gap semiconductor (5.47 eV at 300 K). ^{1,2} These unique characteristics have paved the way for numerous uses of diamond, for example, diamond's high thermal conductivity combined with its hardness allows it to survive harsher conditions than many other materials, and has resulted in it use in cutting tools, heat sinks and diamond anvil cells.³ Furthermore, the potential applications of diamond can be further expanded by introducing dopants such as boron or nitrogen, unlocking possibilities in electrochemical and quantum applications.¹

The structure of diamond is based upon the face-centred cubic (FCC) Bravais lattice (**Figure 1.1**). In an FCC lattice, atoms are situated in each corner of the cubic lattice, in addition to one atom in the centre of each of the 6 faces – making 14 lattice points in total. In the diamond structure, however, four additional atoms are present. These atoms are situated in the (χ , χ , χ), (χ , χ , χ), (χ , χ , χ), and (χ , χ , χ) positions. Diamond's cubic structure can also be considered analogous to that of zinc blende, where all atoms are instead carbon atoms.^{4,5} Pure diamond has a lattice parameter *a* of 0.357 nm (see **Figure 1.1**), with each C–C bond being 0.154 nm in length.⁵



Figure 1.1: Diamond's crystal lattice structure (taken from J. Honstra)⁶ with the positions of the atoms which are not present in a standard FCC lattice indicated in red, and the lattice parameter indicated in blue.

There are three low-index planes of interest: the (100), (110) and the (111). As per the Bravais rule for crystal growth, a plane **(hkl)** with a higher reticular density – more lattice points per unit surface – will grow slower than a plane with a lower reticular density.^{7,8} This holds true for diamond, with the (111) plane being the one that grows the slowest and has the highest reticular density.⁸

1.2 Diamond Growth

Diamond is a metastable allotrope of carbon. In terms of thermodynamics, graphite is a slightly more stable allotrope at room temperature (see **Figure 1.2**), however the graphitisation of diamond is unfavourable, owing to the high energy barrier to rearrangement of atoms from diamond's tetrahedral sp^3 structure to graphite's sp^2 structure. Natural diamond synthesis occurs under the conditions where diamond is more thermodynamically stable – at temperatures and pressures of around 70-80 kbar and 1400-1600 °C.¹



Figure 1.2: Diamond phase diagram, including regions denoting where high pressure, high temperature synthesis and chemical vapour deposition takes place. (Taken from E.Burkel and F.Zhang). ⁹

1.2.1 High Pressure High Temperature

High pressure, high temperature (HPHT) synthesis is a method of diamond growth using conditions where diamond formation is thermodynamically favourable, emulating the conditions of natural diamond formation. Typically, these are pressures >5 GPa and temperatures >1400 °C.¹⁰ Under these conditions, a highly pure source of carbon, often graphite, is dissolved in a molten metal, alloy, or organic salt such as iron, nickel, or cobalt, in the presence of a piece of seeding diamond.^{1,11} The dissolved carbon is precipitated onto the diamond seed and recrystallises out as diamond. The composition and purity of the diamond–namely the presence of inclusions of non-carbon atoms within the crystal can depend upon factors such as the growth rate and melt used.^{10,12} Typically, diamonds grown via HPHT are small grains, suitable for abrasive applications.¹ HPHT-grown diamonds are prone to incorporating nitrogen impurities, which give the crystal a yellow-brown colouring.¹¹ This is particularly problematic when growing BDD, as it results in N-B charge compensation, reducing the number of available charge carriers and thus making the resulting BDD less suitable for electrochemical applications.^{13,14} Nitrogen impurities can also cause increased dislocations and dislocation bundles, creating internal strain.¹⁵

1.2.2 Chemical Vapour Deposition

Unlike HPHT, which occurs in diamond's thermodynamically stable region, chemical vapour deposition (CVD) diamond synthesis occurs in the metastable region and is driven by kinetics as opposed to thermodynamics. The CVD process still requires a high temperature but sub-atmospheric pressures – typically below 300 Torr.^{1,16}

CVD uses a ratio of carbon to hydrogen where hydrogen is in excess, and the amount of carbon (often in the form of methane) is small – typically less than 5%. Hydrogen is activated by heating it to temperatures in excess of 2000 K via the use of hot filaments or plasmas, where it dissociates into an atomic form.^{1,12} These atomic hydrogen atoms react with the hydrocarbon gas to create radical carbon species. The diamond is grown by the deposition of carbon radicals onto the substrate. Excess hydrogen in the vessel serves to stabilise diamond growth and attach itself to dangling bonds, preventing the surface from reconstructing into graphitic carbon.¹²

The crystallinity of the resulting diamond is highly dependent upon the substrate it is grown on. This is due to factors such as the substrate's crystallographic orientation, strain, and lattice parameter, where any mismatches may lead to the formation and propagation of defects. Homoepitaxial substrates are often the ideal for CVD growth of diamond. This is important especially when trying to grow single crystal (SC) diamonds, where mismatches in lattice parameter, and high amounts of strain can result in defects and polycrystallinity.¹ As a result, SCs are usually homoepitaxially grown on substrates that are

of the desired crystallographic orientation. (100)-oriented diamond substrates have been found to yield lower densities of structural defects in the resulting SC,¹⁷ however, homoepitaxial growth on (111)¹⁸ and (113)¹⁹ substrates have also been reported. As large area, high-quality diamond is more expensive in comparison to non-diamond substrates,¹² heteroepitaxial SC diamond growth on non-diamond substrates such as sapphire or silicon are also being invesitgated.^{20,21}

Unintentional incorporation of non-carbon atoms in CVD grown diamond lattice can occur due to impurities in the gases used in the reaction vessel, and their presence will also affect growth rate.^{5,8} The availability of high-purity source gases means that the purity of CVD-grown diamonds is often much higher than that of HPHT-grown diamonds.¹ The intentional incorporation of p- and n- type dopants such as boron or phosphorous is possible by mixing gases such as diborane or phosphine into the reaction chamber.²²

1.3 Boron Doping of Diamond

Intrinsic diamond is an electrically insulating material, with a wide bandgap of about 5.47 eV at 300 K.¹ The introduction of acceptor-type charge carriers (holes) into the valence band by p-doping diamond with boron during growth reduces its resistivity, changing its electrical properties. This decrease in resistivity scales linearly with boron concentration.²³

Below 10¹⁹ B atoms per cm⁻³, BDD will behave as a semiconductor with valence band conduction (see **Figure 1.3**). Here, the number of free carriers will be dependent upon the concentration and ionisation energy of the boron acceptors and the temperature. As any of these three factors increase, the Fermi level will decrease.³ For dopant densities above 10¹⁹ B atoms per cm⁻³, there is a steeper decrease in resistivity with boron concentration. Conduction via nearest-neighbour hopping becomes possible at room temperature.²³

As dopant densities rise to be greater than $\sim 10^{20}$ B atoms per cm⁻³, the behaviour of BDD can be described as 'metal-like'— it is at these boron concentrations that BDD is considered useful electrochemically. It is from here that conductivity begins to decrease as temperature increases, as is observed in true metals. In this regime, hole propagation is possible without thermal activation into the valence band. ²³ However, unlike a true metal, the density of states – the states accessible to electrons at a particular energy level – for highly doped BDD is orders of magnitude lower.²⁴



Figure 1.3: Resistivity of BDD as a function of boron concentration. (Taken from J.-P.Larange, A.Deneuville and E.Gheeraert)²³

Upon removal from the growth chamber, CVD BDD will be hydrogen terminated, owing to the high concentrations of hydrogen that were present during growth.¹ The surface will be hydrophobic, with a positive electron affinity, but will gradually oxidise in air, converting it to an oxygen terminated surface. Oxygen terminated BDD has a lower electron affinity, and is hydrophilic, resulting in increased wetting of the surface.²⁵ Whether a BDD surface is hydrogen or oxygen terminated can often be checked for by observing the contact angle of a droplet of water. The hydrophobic hydrogen terminated surface will result in large contact angles close to 90 °C, however an oxygen terminated surface will have lower contact angles, ranging from 0.6-20.5 °C depending upon the surface roughness and the functional groups involved in the oxygen termination.^{26,27}

Depending upon the application of the BDD, different terminations may be preferred, and so a number of methods have been developed to convert hydrogen to oxygen termination. This includes e.g. acid treatment,²⁸ thermal oxidation,²⁹ UV-ozone treatment³⁰ and electrochemical oxidation.^{31,32}. Though hydrogen and oxygen terminations are the most common, they are not the only possible terminations. Szunerits *et al.* described the amination of hydrogen terminated surfaces using ammonia plasma treatment.³³ Similarly, Senisenko *et al.* detailed the properties of fluorine-terminated BDD, prepared using a CF_4 -plasma.³⁴

There are a number of properties that make BDD an attractive material for electrodes. It has a wide solvent window, with low background currents in both aqueous³⁵ and non-aqueous³⁶ media and low electrocatalytic activity which makes it particularly useful for electroanalysis.^{1,2} Recently reported applications include the detection of vitamin B12 by a Co(I/II) redox pair by Pereira *et al.*³⁷, simultaneous detection of dopamine and melatonin by Yang *et al.*³⁸, and the detection of cadmium and lead ions using BDD of different surface morphologies by Štenclová *et al.*³⁹ Much like intrinsic diamond, BDD is highly inert and resistant to attack by acids–including hydrofluoric acid.³⁶ This makes BDD electrodes suitable for use in the treatment of acidic wastewater,⁴⁰ and also allows the surface to undergo harsh oxidising acid cleaning without deterioration of the surface.⁴¹ BDD has also seen applications in bioelectrochemistry, advanced electrochemical oxidation and sensor development.⁴²

1.4 Polycrystalline Boron Doped Diamond

The relative ease of growth of polycrystalline BDD (p-BDD) compared to single crystals makes it popular for use in electrodes – especially since it can be grown heteroepitaxially via CVD, eliminating the need for large diamond substrates.^{1,2} p-BDD is easily distinguishable from SC-BDD by the presence of grains, which are visible even under an optical microscope. They become more noticeable under a scanning electron microscope (SEM), where grains containing a higher boron content appear darker (see **Figure 1.4a**).⁴³ This also corresponds to the crystallographic orientation of the grain. Under otherwise identical conditions, boron uptake rate has been shown to be highest for the (111) and then decrease in the order: (111) > (110) > (100).⁴⁴ The less frequently studied (113) orientation has been found to have boron incorporation rates similar to that of the (100) orientation.¹¹



Figure 1.4: SEM image of a p-BDD surface taken at 5 kV using an InLens detector and b) a schematic showing a cross section of the grain structure of p-BDD (taken from N.R.Wilson et al.)⁴⁵

The grain structure of p-BDD is non-uniform, and differences in grain size can be seen between wafers, typically dependant on growth conditions.¹ Typically, the (110)-oriented facets grow at a faster rate compared to those of (100) and (111) orientation. As a result, the polished surface of a p-BDD crystal will be predominantly (110)-oriented, as shown using electron backscatter diffraction (EBSD)⁴⁶ and scanning transmission electron microscope.⁴⁷

Given that electrochemistry is highly surface sensitive, it is no surprise that the inhomogeneity of p-BDD has a measurable effect on electrochemical response. Wilson *et al.* showed that individual grains of p-BDD have different conductivities by using conductive atomic force microscopy (C-AFM) to simultaneously record height and conductivity across the p-BDD surface.⁴⁸ Differences in the current associated with the oxidation of ferrocenylmethyltrimethylammonium (FcTMA⁺) – an outer-sphere, therefore non-surface-sensitive, redox mediator – were measured by Patten *et al.* using scanning electrochemical cell microscopy (SECCM).²⁴ The current variations were found to correspond directly to the variations in boron dopant density. In addition to variations in boron uptake across the surface, p-BDD may also contain non-diamond carbon impurities at grain boundaries. The presence of sp² carbon can alter the electrochemical response of BDD electrodes, increasing background currents and decreasing the solvent window because the sp² carbon is more electrocatalytic.^{21,26} Hence in order to study the fundamental properties of BDD, we should move away from p-BDD to an inherently more uniform form of BDD – single crystals.

1.5 Single Crystal Boron Doped Diamond

For fundamental studies on BDD, it is not so straightforward as to simply study the electrochemical response of SC-BDD instead of p-BDD. Even once the significant contributor to inhomogeneity – the grains – are taken away, there are still other factors to consider that may affect its behaviour as an electrode. One major factor is the surface orientation. The orientations considered in this thesis are the low-index (100), (110) and (111) planes (see **Figure 1.5a**). These differ in the number of dangling bonds – 2 for (100) and (110) orientations and 1 for (111) – and therefore also the terminating groups on the surface (see **Figure 1.5b**). Here we consider only oxygen terminated BDD.



Figure 1.5: a) Unit cells of (100), (110) and (111)-oriented diamond and b) their typical functional group terminations when oxygen-terminated

Even when grown on top of SC substrates, the resulting diamond is not guaranteed to be a perfect single crystal and may inherit defects from its growth substrate, ^{49,50} with (111) SC's being particularly prone to twinning⁴⁹ – the intergrowth of separate crystals originating from shared lattice points – which makes diffraction experiments such as X-ray diffraction (XRD) and low energy electron diffraction (LEED) vital to assessing the surface quality. When it comes to growing BDD SCs suitable for electrochemical studies, there are further challenges to contend with. The microwave power density that is known to give good crystalline quality (low defect) intrinsic diamond cannot produce high levels of boron doping.⁵¹

Furthermore, addition of boron to the diamond lattice leads to the formation of (110) growth sectors around the sample edges,⁵¹ can induce stress into the crystal and higher amounts of B_2H_6 encourages soot formation.⁵² Therefore, it is crucial that single crystals are thoroughly characterised, to understand the crystal structure and quality before performing electrochemical studies.

One of the most comprehensive studies on SC-BDD electrodes to date was undertaken by Liu et al. on three heteroepitaxially-grown (100)-oriented SC-BDD samples, grown by microwave plasma-enhanced CVD and each doped to $>10^{21}$ B atoms cm⁻³.²¹ Two of these samples were grown off-axis such that the (100) plane had a 4° tilt, and the third was grown on-axis. 2D X-ray diffraction (2D XRD), SEM and Raman spectra were performed to ensure that the samples were indeed single crystals, (100)-and had a low sp² carbon content. Atomic force microscopy (AFM) was also used to determine surface roughness S_a. Though these samples were polished, their surfaces were still quite rough, with their Sa ranging from 3.4 - 8.8 nm. An inner sphere redox couple, $Fe(CN)_6^{3-/4-}$, was used to investigate cyclic voltametric responses of the SC-BDD compared to p-BDD electrodes in terms of their peak to peak potentials (ΔE_p). Inner sphere redox couples undergo ET by binding to the surface, therefore are sensitive to the electrode surface. Only the SC-BDD electrodes with Sa values smaller than that of the p-BDD electrode resulted in smaller ΔE_p values – 232 and 276 mV for the SC electrodes compared to 371 mV for the p-BDD electrode – highlighting the importance of surface roughness in electrochemical measurements. Finally, scanning electrochemical microscopy (SECM) was used to clearly distinguish the differences in surface homogeneity of SC electrodes compared to p-BDD electrodes. The SC electrodes had nearuniform current outputs across the surface, unlike the p-BDD electrode which showed a larger distribution of current values which appeared to match the size and distribution of grains in the sample.

Kondo *et al.* compared the electrochemical behaviour of semiconducting homoepitaxial (100) and (111)-oriented SC-BDD to a p-BDD sample.⁵³ These samples were first characterised using reflection high-energy electron diffraction (RHEED) and Raman spectroscopy to assess the crystal orientation, quality and sp² carbon content, and secondary ion mass spectrometry (SIMS) to determine boron concentration to be 2×10^{18} and 2×10^{19} cm⁻³ for the (100) and (111) samples respectively. Capacitance measurements in 0.1 M H2SO₄ showed the lowest background currents for the (111) electrode, which was suggested to make them more suitable for electroanalysis than p-BDD. ΔE_p for the (111)-oriented electrode was found to be 213 mV in Ru(NH₃)6^{2+/3+} and 337 mV in Fe(CN)6^{3-/4-}. However, for both outer and inner sphere redox mediators, the peak-to-peak separations were lower for the p-BDD electrode, at 93 mV for Ru(NH₃)6^{2+/3+} and 113 mV for Fe(CN)6^{3-/4-}. For both electrodes and redox mediators, the responses were indicative of quasi-reversible ET.

Differences between (100) and (111)-oriented single crystals were also studied by Ivandini et al. ⁵⁴ Unlike the Kondo study,⁵³ these samples contained very similar levels of boron doping, as measured by SIMS and were found to be 4.2×10^{20} cm⁻³ for the (100) sample and 3.8×10^{20} cm⁻³ for the (111) sample. The orientation of the SC sample's surface was confirmed via low energy electron diffraction (LEED). The absence of a sp² carbon peak in Raman spectroscopy indicated that the samples were of high quality, however comparison of X-ray photoelectron spectra (XPS) showed both samples contained ~5% of sp² carbon. For the (111) surface, the XPS spectra showed no C=O peak present, unlike that for the (100 surface) which was justified as the (111) surface should only have one dangling bond. Electrochemically, the (111) surfaces were found to have smaller ΔE_p values compared to the (100) sample regardless of surface termination but were not at all close to reversible. For the oxygen-terminated (111) electrode ΔE_p was 870 mV with Ru(NH₃)₆^{2+/3+} and 1470 mV with Fe(CN)₆^{3-/4-}. In comparison, the p-BDD electrode had much smaller ΔE_p values, and showed good reversibility in Ru(NH₃)₆^{2+/3+}, with a ΔE_p of 60 mV and 150 mV in Fe(CN)₆^{3-/4-}. This study lacked analysis of surface roughness which could have been achieved via AFM. It is possible that there were disparities in surface roughness between the SC and p-BDD electrodes, which resulted in the large differences in ΔE_p , similar to the results of the previously discussed paper by Kondo et al. 53

These works have shown the amount of characterisation that is needed to understand the properties of a SC-BDD sample. In some cases, different characterisation techniques have been used to determine the same information – for example XRD, RHEED and LEED were all used in the above studies to determine the crystallographic orientation of the SC samples. As a result, it is also important to know the strengths and limitations of each technique, so the most appropriate ones can be selected.

1.6 X-ray Diffraction

X-ray diffraction is a non-destructive technique that facilitates the analysis of crystal structures by providing information about the distance between atoms in terms of the d spacing or interplanar distance d_{hkl} which can then be used to calculate the lattice parameter. High resolution XRD (HRXRD) can determine sample tilt up to the nearest 0.0001° depending upon the instrument.⁵⁵

When monochromatic X-rays are directed at a crystalline lattice, atoms within the lattice will both absorb and diffract the incoming radiation. Since the wavelength of X-ray radiation is comparable to the distance between atoms, diffraction of the X-ray radiation will result in regions of constructive and destructive interference at angles characteristic to the sample.⁵⁶ X-rays that scatter from atoms below the surface of the crystal lattice will have to travel further than those scattered from surface atoms. This path difference is equal to $d_{hkl}sin(\theta)$, where θ is the angle at which constructive interference is

strongest, known as the Bragg angle. When the path difference is an integer number of wavelengths, then this is described by Bragg's law (**Equation 1.1**), where *n* is the diffraction order and λ is the wavelength. Constructive interference only occurs when *n* is an integer value:⁵⁶

$$2d_{hkl}\sin\theta = n\lambda \tag{1.1}$$

The interatomic spacing can be related to the Miller indices **(hkl)** and the lattice parameter by the following equation:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$
 1.2

Which can be combined with Bragg's law (Equation 1.1) to give:

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)$$
 1.3

Intensities detected also depends upon how well the material absorbs x-ray radiation. Given by:

$$\frac{I}{I_0} = \exp{-\alpha x}$$
 1.4

Where *I* is the transmitted intensity, I_0 is the incident intensity, α is the absorption coefficient and x is the material thickness.⁵⁶

A goniometer measures four angles to define the relative positions and orientation of the sample, X-ray beam and detector: the angle between the incident beam and the detector (2ϑ) and three rotational degrees of freedom of the sample χ , ω , and φ . The XRD instrument can be configured to be in double or triple-axis modes (see **Figure 1.6**). Double-axis setup involves only a monochromator to provide a conditioned beam, and the detector. This can be used to measure rocking curves. Rocking curves (or omega scans) involve the tilting of the sample with the detector at a specific Bragg angle ($\theta = \omega$) and measuring the intensity. Samples with a spread of lattice parameters will give peaks at a wider range of ω values, and therefore a broader peak (a larger full width at half maximum (FWHM)). As a result, this can be used to evaluate the misorientation and/or the strain of the sample but cannot distinguish between the two.^{3,57}



Figure 1.6: XRD instrument set-up, with both double axis and triple axis detectors, used in this thesis.

Triple-axis diffractometry introduces an analyser crystal, which is used to limit the angular acceptance of the detector. This allows for more high-resolution imaging, and the ability to differentiate between tilted and strained lattices.⁵⁶ Triple axis is typically used for coupled scans. A coupled $2\vartheta - \omega$ scan, which is used here, involves the rotation of the sample about the omega axis, whilst the detector rotates at twice the rate, so that $2\vartheta = 2\omega$. This can be used to obtain information about the d-spacing of the sample, and therefore any changes in the lattice parameter caused by strain or change in composition – in this case, changes in boron content. Since 2ϑ is the angle between the detector and the incident x-ray beam, this is unaffected by the sample orientation, therefore removing any error that may result from the sample plane being uneven or tilted.

1.7 Low Energy Electron Diffraction

LEED is another diffraction technique useful for studying the arrangement of atoms in a crystal lattice. Unlike XRD, which provides information about the bulk of the material's crystal structure, LEED is highly surface-sensitive.⁵⁸ This comes from the shallower penetration depth electrons used in LEED compared to photons used in XRD. Another significant difference between LEED and XRD is the strength of the electron vs photon scattering. In XRD, single scattering of photons is dominant, which makes determining atomic positions and structure analysis easier than with LEED. In comparison, the quantitative analysis of LEED spectra is complicated by the occurrence of multiple scattering events from two or more atoms in succession. However, much useful information can be gleamed simply from qualitative interpretation of the diffraction pattern, such as the surface unit cell shape, degree of ordering and defects, and surface adsorbate coverage. As a result, the use of both techniques in combination can be useful for getting a more complete understanding of a crystal structure.¹

LEED is performed in an ultra-high vacuum (UHV) chamber for the operation of the electron gun, whilst also keeping the sample surface clean. The electron gun fires a stream of low-energy electrons at the grounded sample (**Figure 1.7**). Since the de Broglie wavelength of these low-energy electrons is comparable to atomic spacing, scattering events occur. Electrons are backscattered onto a fluorescent screen where they are detected. The resulting image displays the reciprocal lattice of the surface.



Figure 1.7: Schematic of LEED setup. (Taken from W.Moritz and M.A. Van Hove)⁵⁹

1.8 Raman Spectroscopy

Raman Spectroscopy is another non-destructive technique that can be used to assess the sp² carbon content in a BDD sample and determine the concentration of boron present. This technique is based on the scattering of photons at the surface of the sample. When an incident photon from laser light, typically in the visible region, activates the sample, the activated state relaxes by releasing another photon. The photon that is released may be scattered either elastically, where the photon energy is unchanged (Reyleigh scattering) or inelastically where there is a change in energy and therefore wavelength of the photon (Raman scattering).⁶⁰ If energy is transferred to the sample, a red shift (shift to larger wavelengths) occurs which is known as Stokes scattering. If energy is transferred from the sample into the scattered photon, blue shift occurs (shift to higher wavelengths), which is known as anti-Stokes scattering. The shift in wavelength between ingoing and outgoing photons is associated with different vibrational modes in the sample.⁶⁰ Raman scattering requires incident photons to be higher in energy than the molecular vibrations, usually in the visible region, which allows it to be coupled with optical microscopes.

The Raman spectra of undoped diamond are characterised by an intense diamond Raman line located at 1332.2 cm⁻¹ at room temperature.⁶¹ However, the introduction of boron dopants results in additional complexities, which alter the spectra. For the diamond Raman line, this can be seen through a peak shift (red shift), decrease in intensity and a Fano line shape, the latter of which occurs when the boron doping levels exceed ~10²⁰ boron atoms per cm³ and the BDD is metallically doped. This is due to quantum interference between the discrete zone-centre Raman transition and a continuum of electronic Raman scattering.^{62–64} Besides the diamond Raman line, there are other characteristic features of metallically doped BDD, namely: an asymmetric band at ~1200 cm⁻¹ attributed to the maximum of the phonon density of states, and a wide asymmetric band at ~500 cm⁻¹.⁶⁵ A wide band at ~1300-1600 cm⁻¹ may also be observed if graphitic carbon is present.³¹

The expansion of the diamond lattice upon Introduction of boron also causes of downshift of the diamond Raman line in BDD.⁶² Mortet *et al.* observed that the wavenumber of the asymmetric bands at ~500 cm⁻¹ and ~1200 cm cm⁻¹ were linearly related to the wavenumber of the diamond Raman line.⁶⁶ This trend is independent of the sample orientation and laser excitation wavelength. Similarly, there was a downwards trend when comparing the boron concentration as measured by SIMS with the position of the ~500 cm⁻¹ band, with lower concentrations of boron resulting in higher wavenumbers. Interestingly, the study found that epitaxial (111)-oriented BDD layers doped to a B/C ratio of 2000 ppm (approximately 2.6 × 10^{20} B atoms per cm⁻³) – above the metallic threshold – did not exhibit the

asymmetric band at ~500 cm⁻¹.⁶² This has also been observed in (100)-oriented BDD doped to B/C ratio of 4000 ppm (approximately 7×10^{20} B atoms per cm⁻³).³¹

1.9 Atomic Force Microscopy

AFM is a technique used for acquiring topographical information about a surface. Here, it was used to measure the change in height across the sample surface and thus calculate the surface roughness of each sample. This was reported in terms of their root mean square height (S_q).

When the sharp AFM probe approaches a surface, the force interaction between the AFM probe and the surface results in deflection of the probe's cantilever, which is controlled by the spring constant of the lever. The amount of deflection is determined using a laser focused on the back of the cantilever which reflects into a position sensitive detector. As the tip moves along different positions across the surface, changes in deflection can be used to acquire topographical information about the surface.

1.10 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive analytical technique that enables the identification and quantification of elements (barring H and He) and the elucidation of their chemical states and environment.⁶⁷ This is done by measuring the energy of electrons emitted via the photoelectric effect.

Electrons are bound to atomic nuclei with a binding energy E_B – the minimum energy required to excite the electron and remove it from the atom or ion. This binding energy is dependent upon the type of element and the chemical environment that it came from. Since binding energy cannot be measured directly, XPS measures the kinetic energy E_K of detected electrons, then use this to calculate a binding energy. To do this, X-rays of known energy hv, where h is Planck's constant, and v is frequency are directed at the sample surface. When an X-ray photon interacts with an electron in the sample, it transfers its energy to the electron. This results in the ejection of a photoelectron with an amount of kinetic energy – the energy remaining after the binding energy has been overcome. Along with the work function of the spectrometer (ϕ_s) which has been calibrated to the binding energies of electrons from standard orbitals of elements (for example gold and copper). These quantities are related by the following equation:^{67,68}

$$E_K = h\nu - E_B - \phi_s \qquad 1.5$$

Given that the spectrometer work function is constant, changing the X-ray source will result in a shifting of the kinetic energy intensities caused by photoelectrons. However, not all intensities may experience a shift since photoelectrons are not the only types of electrons capable of being detected. The vacancy left upon photoelectron emission may be filled by an electron in a higher energy level, which stimulates the emission of a secondary electron—this is known as an Auger emission.⁶⁷ Since this process does not involve any X-ray photons, the kinetic energy position of Auger peaks will be the same, regardless of the excitation wavelength used, and thus, equation 5 does not apply in this case. In carbon materials, the first derivative of the carbon Auger spectrum (C KLL) has been shown to provide information about the type of carbon present, notably being able to differentiate between sp² and sp³ carbon based upon the D parameter — the separation between the most positive maximum and the most negative minimum points on the differentiated Auger spectrum.^{69,70} Pure diamond will have D-parameter of ~13.7 eV⁷¹ and as the degree of sp² bonding in the carbon material increases, there will be a linear increase ⁷² in the D-parameter until it reaches a value of ~21.2 eV for highly oriented pyrolytic graphite (HOPG).⁷⁰

The relative probability of a photoelectron being ejected by a photon in a given atom is known as the photoionization cross section (σ). The inability to detect H and He results from the small photoionization cross sections of the 1s level. Similarly to LEED, XPS has a well-defined, short, penetration depth. This depends upon the take-off-angle of the incident X-rays, but also the escape depth of electrons in the solid. Electrons may undergo collisions with atoms in the solid as they escape which can result in a decrease in the kinetic energy. If energy loss does occur, it will contribute to the background signal, as it will no longer be characteristic of its environment. ^{67,73} At increasing depths, electrons will be more likely to undergo energy loss. The proportion of electrons emitted at a depth **d** can be described by the Beer-Lambert relationship (**Equation 1.6**):⁷⁴

$$\frac{I}{I_0} = \exp{-\frac{d\cos\theta}{\lambda}}$$
 1.6

Where *I* is the intensity of electrons emitted from the sample at depths greater than *d*, I_0 is the intensity emitted from an infinitely thick, uniform substrate, ϑ is the angle of electron emission and λ is the inelastic mean free path (IMFP). The IMFP is the average distance an electron of a given energy will travel through a solid before undergoing inelastic collision and is dependent upon the material the electron is passing through.^{74,75} It can therefore be shown that, for example, 95% of electrons emitted at 90° to the sample surface will come from a depth of 3 λ or less.

Spectra are typically plotted as binding energy against intensity since binding energy is not dependent upon the energy of the incoming X-rays. Differences in chemical environment, lattice sites and oxidation states will cause variations in the binding energy of a core electron. This difference is known as the chemical shift. When the chemical shift is small, this may result in the overlap of peaks in the spectrum if the instrument resolution is low. In such cases, curve-fitting is necessary.

"Shake-up" features result when valence electrons are able to be excited into higher unoccupied valence levels. When these electrons relax back down, a photoelectron is emitted which appears at a higher binding energy than the main peak and is lower in intensity. The detection of this photoelectron is what results in shake-up or satellite peaks. In carbon materials, a possible source of shake-up peaks is due to $\pi \rightarrow \pi^*$ transitions in graphitic carbon, which causes peaks in the C 1s spectra.⁷⁶

1.11 Cyclic Voltammetry

Cyclic voltammetry (CV) is a common technique used for studying electrochemical systems. Typically, it is conducted in a solution that contains both a redox active species and a supporting electrolyte. The redox active species is the one that undergoes faradaic ET, resulting in a current output when the potential is cycled. The role of the supporting electrolyte is to increase the conductivity of the solution and reduce ion migration caused by the electric field.

CV involves the application of a starting potential at the working electrode (WE) with respect to the reference electrode (RE) using a potentiostat. This potential is then swept to a switching potential, and then back to the starting potential. The rate of change of potential is kept constant throughout and is referred to as the scan rate (v). The current at the WE is recorded as a function of the applied potential difference. For macroscale electrodes, a third electrode, the counter electrode (CE), is used to complete the current flow circuit and avoid passing through the reference electrode as this will disrupt the constant potential.

Electrochemical reversibility refers to how facile ET is at a WE with respect to the timescale of the experiment. An electrochemically reversible redox reaction will readily undergo ET at the electrode. For a diffusion limited system this is characterised by a CV with a peak-to-peak separation of 57/n mV at 25 °C, where n is the number of electrons transferred.⁷⁷ Larger peak separations indicate quasi-reversibility or even irreversibility, and that the process is no longer mass transport limited, and instead is electron transfer limited. In such processes, larger potentials must be applied to drive ET.

For a reversible ET system, the concentrations as a function of potential can be predicted using the Nernst equation:

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}}$$
 1.7

Where the potential E is related to the standard potential of the redox species E^0 , temperature T, ideal gas constant R and Faraday's constant F. a is the activity of the oxidating (ox) and reducing (red) species. The peak current i_p is recorded in the CV given by the Randles–Ševčík equation, which at 25°C is:

$$i_p = (2.69 \times 10^5) n^{\frac{3}{2}} A D_i^{\frac{1}{2}} c_i^* v^{\frac{1}{2}}$$
 1.8

Where A is the electrode area and D_i is the diffusion coefficient of the species *i*.

1.12 Scanning Electrochemical Cell Microscopy

Scanning electrochemical cell microscopy (SECCM) is a technique that is able to provide spatially resolved electrochemical measurements on a WE surface. In SECCM the probe, a glass capillary filled with the electrolyte solution and redox solution confines the electrochemical reaction to the droplet (meniscus) that forms at the end of an electrolyte-containing nanopipette.⁷⁸The diameter of the droplet footprint on the surface is controlled by the diameter of the pipette (typically micrometre and smaller) and the hydrophilicity of the surface.⁷⁹

In a single-barrel setup, a pipette tip is produced using a pulled glass capillary that is filled with electrolyte and wire quasi-reference counter electrode (QRCE) inserted into it.⁷⁸ A unlike a RE, a QRCE is not under thermodynamic equilibrium with its oxidised ion, as a result, the potential it measures may change, for example due to dissolution of the oxidised ion, reaction with impurities or polarisation.⁸⁰ However, they are easy to prepare, small and are suitable for the low volumes used in SECCM pipette tips. The current at the WE surface (*isurf*) is measured when a potential (*Eapp*) is applied between the QRCE and the WE. A CV is recorded when *isurf* reaches a threshold value.⁸¹ For this reason, single-barrel setups are only suitable for conductive WE materials.⁸² The use of a hopping scanning regime, in which the meniscus is detached fully from the surface after each measurement and then 'hopped' to an adjacent position via piezoelectric positioners without overlapping previously probed areas (see **Figure 1.8**), means that the activity measured in each spot can be attributed to that specific position on the surface.^{82,83} This can be used to map out surface features such as grain boundaries on a polycrystalline surface.^{24,43,84}



Figure 1.8: Schematic of SECCM setup and hopping mode process.

The footprint left by the meniscus can be separately imaged via scanning electron microscopy to determine the contact radius – and from this the area of the working electrode that is active for each measurement. Though this area is largely determined by the size of the pipette tip, it will also be influenced by the wetting properties of the WE. For BDD, wetting is independent of boron concentration,²⁵ however it is strongly affected by surface termination, with O-terminated BDD having larger footprint areas due to its hydrophilicity causing lower contact angles.^{26,79}

The limiting current i_{lim} in a mass transport-controlled regime can be described by the following equation:

$$i_{lim} = nFAk_T c^* 1.9$$

The active area of the electrode **A** is equal to the footprint of the droplet and k_T is the mass transport coefficient.⁸⁵ Furthermore, the standard electron transfer rate constant k^0 can be related to the half wave potential (E_{\varkappa}) via a Butler-Volmer relation:

$$k_{1/2}' = \frac{\pi dk^0}{8D_{ox}} \exp[-\alpha nF(E_{1/2} - E^{0'})]$$
 1.10

Where $\mathbf{k'}_{\mathbf{k}}$ is the reaction rate constant at the half wave potential, d is the diameter of the droplet, $\boldsymbol{\alpha}$ is the transfer coefficient and is $\mathbf{E}^{\mathbf{0'}}$ standard potential of the redox couple.

1.13 Aims

The aim of this thesis is to characterise SC samples with orientations (100), (110) and (111) which have been grown via CVD. First, the material properties of these of single crystal samples will be characterised to narrow the pool of samples down to those which have the highest crystalline quality (X-ray diffraction), are of the correct orientation, contain minimal sp² carbon and have the appropriate boron doping levels (Raman) for further electrochemical characterisation. The most promising samples will be processed further using high-grade polishing and then used to undergo further characterisation – LEED, AFM and XPS. This is in order to gain better understanding of the surface properties and how defect-free the samples are. Finally, a series of microscale electrochemical measurements will be made using SECCM to assess the variation in ET kinetics across each single crystal surface, and thus the surface homogeneity.

2. Experimental

2.1 Chemicals

All solutions were prepared using \geq 18.2 M Ω cm resistivity, 25 °C deionized water (Milli-Q, Millipore Corp.). Chemicals were used as received from the supplier.

Chemical	Formula	Purity	Supplier
Sulfuric acid	H ₂ SO ₄	>= 95%	Fisher Chemical
Potassium nitrate	KNO3	>99%	Sigma Aldrich
Rutheniumhexaamine chloride	$Ru(NH_3)_6Cl_3$	>99%	Strem Chemicals
(Ferrocenylmethyl)trimethylammonium	FcTMA ⁺ PF ₆ ⁻		Made in house according to the procedure described by Lemay <i>et</i> <i>al</i> . ⁸⁶
Iron(II)perchlorate,	Fe(ClO ₄) ₂	98%	Sigma Aldrich
Potassium chloride	KCI	>= 99%	Fisher Chemical
Silver wire, temper annealed, 0.125 mm diameter		99.99%,	Advent
Silicone oil		Pure	Sigma Aldrich

 Table 2.1: List of chemicals used in this thesis.

2.2 Sample Growth and Processing

SC samples were grown by Element Six Ltd, Oxford, via microwave plasma CVD on homoepitaxial substrates of the respective orientation ((100), (110) or (111)) which were obtained by cutting and polishing ~4 × 4 × 4 mm CVD diamond crystals grown in the (100) direction. The growth chamber was comprised of ~5% methane in hydrogen gas atmosphere and varying proportions of boron-containing gases. The (110) and (111) were grown using the same proportion of boron gases in the growth chamber, however the (100) was grown with a higher amount to increase the amount of boron doping. This was done at 700-950 °C and 100-200 Torr, with microwave powers of 1-3 kW at 2.45 GHz. A p-BDD sample also grown by Element Six was used for comparison during electrochemical studies in **Section 3.6** and **3.7**. The sample is from an Electroanalytical Grade wafer with the same specifications of this p-BDD wafer type described by Hutton *et al* (sample E).⁸⁷

An Oxford Lasers E Series laser micromachining system with a Nd:Yag Laser (332 nm) with 32 ns pulse time and 7 W power was used where cutting of samples was necessary. Samples were lapped mechanically using a resin bonded wheel then scaife cast iron polished to reduce the surface roughness. After processing, their final dimensions are as follows: 4.69×4.71 mm (100), 3.25×3.25 (110) and 2.51 \times 2.52 (111). The samples were free standing and 0.2 - 0.5 mm in thickness.

Samples were acid cleaned before AFM and SECCM measurements by boiling in H_2SO_4 supersaturated with KNO₃ to remove any loosely bound sp² carbon.⁸⁷ For bulk electrochemical measurements, a Ti/Pt/Au electrical contact of 50/50/200 nm thickness was made on the backside of the sample, which was then annealed in a rapid thermal annealer (RTP Solaris 100, SSI Inc., USA) at 600 °C for 5 minutes under argon atmosphere.

2.3 X-Ray Diffraction

For the data reported in this thesis, a PANalytical X'Pert Pro MRD (Malvern Panalytical Ltd, UK), instrument with a 4-bounce germanium (220) hybrid monochromator emitting pure copper K α 1 radiation and a Pixcel detector (Malvern Panalytical Ltd, UK) was used for high resolution XRD measurements. First, pole figures were run at an $\boldsymbol{\omega}$ angle of 59.9°, 37.7° and 22.1° for the (100), (110) and (111) samples respectively using an open detector, rotating the azimuthal angle ($\boldsymbol{\varphi}$) by 360° and the angle around the y axis ($\boldsymbol{\chi}$) by up to 30°. $\boldsymbol{\omega}$ rocking curves and 2 $\boldsymbol{\theta}$ - $\boldsymbol{\omega}$ triple axis curves were recorded with the detector positioned at the chi and azimuthal angles of highest intensity, as determined by the pole figures.

2.4 Low Energy Electron Diffraction

In this thesis, LEED was undertaken using SPECTALEED optics (Scienta Omicron, Sweden) under ultrahigh vacuum. Diffraction patterns were recorded after annealing to 400, 500 and 600 °C and letting the sample cool back to < 100 °C.

2.5 Raman Spectroscopy

All Raman spectra were recorded using a InVia Raman Microscope (Renishaw, UK), using a 514.5 nm 35 mW laser, 1800 l/mm grating and X50 objective. The acquisition time was 25 seconds.

2.6 Atomic Force Microscopy

Measurements were made using a Bruker Dimension Icon microscope (Bruker, UK) operating in ScanAsyst Air mode. This uses active feedback control to maintain a constant force between the tip and the surface at each pixel point along the surface. A ScanAsyst Air probe was used, with a spring constant $k \sim 0.4 \text{ Nm}^{-1}$ and tip radius < 12 nm. 5 measurements, each covering a 5 × 5 μ m² area, were taken across different areas of the BDD surface. The AFM data was processed using Gwyddion (Version 2.55), which was used to calculate the mean S_q value for each measurement. The reported S_q value is an average over all 5 measurements.

2.7 X-Ray Photoelectron Spectroscopy

For our studies, XPS data was acquired using an Omicron Multiprobe. The sample was mounted onto stainless steel Omicron flag plates using tantalum foil and loaded into a fast-entry chamber. After reaching pressures below 1×10^{-6} mbar, the sample was stored at pressures below 2×10^{-10} mbar.

The XPS measurements were made under illumination by a XM1000 monochromatic aluminium K α Xray source (Omicron NanoTechnology) with a photon energy of 1486.7 eV. The pressure in the main analysis chamber had a base pressure of 2 × 10⁻¹¹ mbar. A Sphera electron analyzer was used for detection of photoelectrons. The spectrometer work function was calibrated using polycrystalline silver, and the analyser transmission function was calibrated using silver, gold, and copper foils. Survey scans were acquired using a 50 eV pass energy and 1.51 eV step size. Core-level spectra were recorded with a 10 eV pass energy and 0.47 eV step size. Auger spectra were recorded with a 20 eV pass energy and 0.69 eV step size.

Measurements were taken of the BDD samples, first non-annealed and after annealing to a series of temperatures. First, XPS measurements were taken on the non-annealed sample. For successive measurements, a resistive heater and K-type thermocouple attached to the manipulator head were used to anneal the sample 400, 500 and 600 °C. Between each annealing, the sample was allowed to cool to below 100 °C before the next measurement was made.

2.8 Cyclic Voltammetry

CV was carried out using a Metrohm VIONIC (Metrohm AG, Switzerland) potentiostat and threeelectrode system, using a coiled platinum wire CE and a saturated calomel (SCE) RE. All potentials are stated with respect to the SCE RE.

Capacitance and solvent window measurements were run in 0.1 M KNO₃ at 0.1 Vs⁻¹. The limit for insignificant electrochemical activity was defined as the current density being within \pm 0.4 mAcm⁻².

Redox activity was investigated using the following redox couples: $Ru(NH_3)_6^{3+/2+}$ in a solution of 1 mM $Ru(NH_3)_6Cl_3$ in 0.1 M KNO₃; FcTMA^{+/2+} in a solution of 1 mM FcTMA⁺PF₆⁻ in 0.1 M KNO₃ at a scan rate of 0.1 Vs⁻¹ and finally Fe^{2+/3+} in a solution of 1 mM Fe(ClO₄)₂ in 0.1 M KNO₃.

2.9 Scanning Electrochemical Cell Microscopy

Nanopipettes used for SECCM measurements were fabricated by pulling glass capillaries (1.2 mm outer diameter \times 0.69 mm inner diameter \times 100 mm length, Harvard Apparatus 30-0044) to give a sharp tip using a CO₂ laser puller. (P-2000 Sutter Instruments, U.S.A.). The following two-line pulling program was used to produce a tip \sim 280 nm in diameter:

For fabrication of the Ag/AgCl QRCE, annealed silver wire was anodized in saturated KCl solution for ~5 minutes. The QRCE was then left in saturated KCl solution to age for approximately 12 hours. The open circuit potential (OCP) was then measured over 10 minutes against a Leak-free Ag/AgCl Reference electrode (Alvatek, UK) in a solution of 1 mM Ru(NH₃)₆Cl₃ and 30 mM KCl using a Metrohm VIONIC (Metrohm AG, Switzerland) potentiostat to ensure that the OCP remained stable. The QRCE was inserted into a single-barrelled nanopipette filled with 1 mM Ru(NH₃)₆Cl₃ and 30 mM KCl, such that it was positioned ~2 cm away from the nanopipette's tip. A droplet of silicone oil was then added to minimize solvent evaporation during scanning.

The probe was mounted on the z-piezoelectric positioner and moved to the area of interest. It then approached the surface in the z-direction at a rate of 2 μ m s⁻¹ with an applied potential of 0.5 V (-0.5 V at the BDD WE) vs QRCE until the current feedback at the surface reached a threshold value of 0.6 pA. From there, the potential was held for 40 ms before switching to -0.1 V where it was swept linearly to 0.6 V and back. The tip was retracted 5 μ m in the z direction after each measurement then moved 1 μ m laterally for the next measurement.

SEM was used to image the pipette and the sample after SECCM measurements and determine the sizes of the pipette end and droplet footprint. Images were taken using a GeminiSEM- Field Emission Scanning Electron Microscope (ZEISS, Germany) at an accelerating voltage of 5 kV using an InLens detector.

3. Results and Discussion

3.1 X-Ray Diffraction

The first step towards selecting the best SC-BDD samples for detailed study was to confirm the crystallographic orientation of each of the possible candidates. Pole figures were recorded, and only samples with one single region of intensity were further studied, as multiple intensities are indicative of more than one grain being present.

Given that these samples were grown homoepitaxially upon single crystal substrates, it was expected that the resulting BDD crystals would also be single crystals of the same orientation as the substrate. However, from microscopy and XRD studies we found that growth on top of a single crystal didn't guarantee perfect SC growth. For example, on a sample thought to be a (111)-oriented SC, multiple grains were found to be visible under an optical microscope, situated along the edges of the sample (**Figure 3.1a**). XRD pole figures showed that these grains were all (111)-oriented, however had varying degrees of offcut (tilt) relative to the (111) direction. As a result, scans run in double and triple-axis modes were broad, noisy, and low intensity. Only after these defected edges were physically removed *via* laser micromachining did the signal become more intense and more symmetric (**Figure 3.1b**).



Figure 9.1: Optical images a) before and b) after laser micromachining of a (111) sample.

However, for this signal to be detected the sample had to be tilted to an angle of $\chi = 16.6^{\circ}$ indicating that the sample was "offcut" – the surface was not parallel to the (111) plane. The challenges of growing free-standing SC-BDD have been previously documented in the literature,¹² this is exacerbated in (111) -oriented samples, which are particularly prone to twinning – especially on edges and corners.¹⁹ As a result, further processing was required. In this case, one of the misoriented crystals was polished so that its surface was parallel to the (111) plane. **Figure 3.2** shows the pole figures of this sample before and after polishing. After polishing, the position of the intensity on the radial axis is centred around $\chi = 0^{\circ}$, indicating that the offcut has been removed and the sample surface is now parallel to the (111) plane.



Figure 3.2: Pole figures a) before and b) after polishing the (111) -oriented sample. The ϑ axis plots the ϕ (rotation) angle and the radial axis plots the χ (tilt) angle.

Following pole figure measurements which were used to confirm sample orientation, further highresolution scans were performed to better assess promising samples. Triple axis $2\vartheta - \omega$ scans were used to confirm that the samples were indeed single crystals and of the expected crystallographic orientation; ω scans (rocking curves) were used to assess the quality of the crystals in terms of their strain and/or misorientation.

Figure 3.3 shows the $2\vartheta - \omega$ diffraction profiles for the three single crystals chosen for more extensive characterisation after the initial pole measurements. The resulting Bragg diffraction peaks could each be assigned unambiguously to the (004), (022) and (111) reflections located at approximately 119°, 75° and 43° respectively, corresponding to the (100), (110) and (111) crystal planes. The intensity of the response decreases as the density of surface atoms decreases, as there are fewer atoms for X-rays to diffract from. The (110) and (111) crystals gave single peaks in the $2\vartheta - \omega$ scan. However, for the (100), crystal, a second, lower intensity peak which did not result from K-alpha2 radiation was observed alongside the main peak (Figure 3.3b). This peak can still be attributed to (100)-oriented diamond, but the displacement of its position suggests that there could be high strain in this sample, possibly resulting from high boron dopant concentrations in the bulk of the sample.⁵⁰



Figure 3.3: a) Diffraction profiles from triple axis $2\vartheta - \omega$ scans on three samples (111), (110) and (100) in orientation, b) expanded view of (100) $2\vartheta - \omega$ scan.

The lattice parameters of all three of these boron doped samples (see **Table 3.1**) were larger than that of pure diamond, measured in the literature to be 3.567095 Å.⁸⁸ This is due to the inclusion of boron, which has a larger atomic radius compared to carbon, thus increasing the lattice parameter. The boron concentration of the samples was estimated via Vergard's Law (**Equation 3.1**):⁸⁹

$$a_{A_{(1-x)}B_x} = (1-x)a_A + xa_B$$
 3.1

Where $a_{A(1-x)Bx}$ is the measured lattice parameter of the boron doped diamond samples, x is the proportion of the sample that is boron doped, a_A is the lattice parameter of pure diamond and a_B is the lattice parameter of boron atoms arranged in the diamond FFC structure. The lattice parameter for the boron structure was calculated to be 4.081 Å, using a B-B bond length of 1.767 Å.⁹⁰

The (100) sample had a higher concentration of boron present compared to the (110) and (111) samples (see **Table 3.1**). The (100) orientation is known to uptake boron less efficiently during growth compared to the (110) and (111) orientations,^{44,91} however this (100) sample was grown with a different recipe

which resulted in higher doping densities compared to the (110) and (111) samples. This higher boron concentration may explain the peak splitting that was observed. The position of the second, lower intensity peak corresponds to a lattice parameter of 3.567 Å - closer to that of pure diamond – which could indicate that there is a region of lower doping or relaxation of the crystal lattice. XRD measurements do not give positional information, so we cannot know where in the sample these regions are situated.

Sample	hkl	$d_{hkl}\left(\mathrm{\AA} ight)$	$\alpha(\text{\AA})$	Est. [B]
				(B atoms cm ⁻³)
(100)	(004)	0.892	3.569	7×10^{20}
(110)	(022)	1.261	3.568	2×10^{20}
(111)	(111)	2.060	3.568	2×10^{20}

Table 3.2: *d* spacing, lattice parameters and estimated boron concentrations for the three samples (100), (110) and (111). The values for the (100) sample are based upon the main peak.

In XRD rocking curves (double-axis measurements), a narrow FWHM is indicative of higher levels of crystal quality due to less strain and/or misorientation. For the rocking curves on the (100), (110) and (111)—oriented samples (**Figure 3.4**), FHWM values, were found to be 0.0742° (~267 "), 0.0092° (~33") and 0.0219° (~79") respectively, reported in degrees and then arcseconds (where 1° = 3600"). All peaks displayed some level of asymmetry, but the (110)-oriented crystal gave the most symmetrical peak and the lowest FWHM, indicating that it had the least strain and/or misorientation of the three.



Figure 3.4: XRD rocking curves (double axis ω scans) for a) (100) b) (110) c) (111)-oriented samples. FWHM = 0.0742° (~267 "), 0.0092° (~33″) and 0.0219° (~79″) respectively.

The FWHM of the (100)-oriented sample only accounts for the width of the main (most intense) peak and is comparable to the value reported for heteroepitaxially grown, semiconducting (100)-oriented BDD reported by Kwak et.al.²⁰ As discussed earlier, the second peak in the triple axis measurement corresponds to smaller lattice parameters. The presence of the second peak in the rocking curve measurements may suggest that macro stresses are present throughout the crystal. This could be due to the high levels of boron doping in the bulk crystal.⁹²

A small amount of peak splitting was also observed for the (111) sample (see **Figure 3.4c**), which may be due to faceting – the SC surface not being uniformly flat. Interestingly, peak splitting in the rocking curve was not observed before mechanical polishing was undertaken to remove the sample offcut (see **Figure 3.5**), showing that the faceting was caused by the polishing. Despite this, polishing resulted in a decrease in FWHM for this sample. This suggests that unlike the (100) sample, the stresses present in the (111) are micro-stresses on the scale of approximately tens of microns.⁹² Faceting of the (111) surface will be further discussed in **Section 3.2**.



Figure 3.5: Rocking curve for the (111)-oriented sample before the offcut was removed by polishing. FWHM = 0.03566° (~128″)

XRD is an effective initial technique for investigating SC-BDD sample. In addition to providing basic information about the crystallographic orientation, interplanar spacing and lattice parameter, XRD can also be used to evaluate the crystal quality and even estimate the boron concentration in BDD samples. It is important to note that the estimation of boron concentration is approximate, and the limitations of this estimation will be discussed in **Section 3.3**. The data acquired from the (111) in particular, highlights the importance of taking XRD measurements both before and after any processing that will induce surface changes such as polishing, as it may result in unintended changes to the crystallographic structure.

3.2 Low-Energy Electron Diffraction

LEED patterns provide a visual representation of the size and shape of the sample's unit cell in reciprocal space. **Figure 3.6** shows that each of the three samples display unambiguously the square, rectangular, and diamond geometries of (100), (110) and (111) unit cells respectively (refer to **Figure 1.5a**), in agreement with the data collected via XRD.



Figure 3.6: LEED patterns after annealing to 600°C on a) (100) surface at 115 eV, b) (110) surface at 112 eV, c) (111) surface at 100 eV. Colours have been inverted for clarity.

The peak splitting observed in the XRD measurements for the (100)-oriented sample suggested that there would be two regions with different lattice parameters (**Section 3.1**). However, the LEED patterns exhibit distinct spots which do not split or broaden even upon changes in temperature and energy, with the only other spots appearing being the second order spots as energy is increased due to higher-order diffraction or multiple scattering events.⁹³ This may suggest that the region of diamond responsible for the second XRD intensity is sub-surface, originating from deeper within the sample in a region inaccessible by LEED. Since electrochemistry is surface sensitive, the impact of this region of the diamond may be minimal – SECCM measurements may be able to confirm whether this is true.



Figure 3.7: LEED patterns for the (100)-oriented sample at 400 and 600°C

Figure 3.8 shows the LEED patterns for the (110)-oriented sample which at 75 eV, only two first order spots are visible. The missing spots correspond to those of type (0, (2n+1)) (where n is an integer) along the [110] direction. This is an example of glide mirror symmetry present in (110)-oriented diamond planes, where the unit cell is reflected then translated by half a unit vector in the [110] direction. This has been previously observed by Maier *et al.* in (110)-oriented intrinsic diamond.⁹⁴ As the temperature is increased, there is an increase in intensity of spots, and a slight increase in streaking along the [001] direction. This was also observed in the study by Maier *et al.*⁹⁴ and was attributed to monatomic steps on the surface of the sample. Steps on the SC surface could result from either a tilt of the sample surface or from surface roughness (to be discussed in **Section 3.4**).



Figure 3.8: LEED patterns for the (110)-oriented sample at 75 and 135 eV after annealing to 400 and 600°C.

In the LEED patterns for the (111)-oriented sample, the (0,0) spot is located directly above the electron gun (see **Figure 3.9**), caused by the bottom side of the sample not being completely parallel to the top when the offcut was removed, preventing the sample from lying flat. Due to the thinness of the sample, it was difficult to remove more material to make the sample lie perfectly flat. This may have had an impact upon the SECCM measurements, where it was required for the sample to be mounted flat (see **Section 3.7**).

A diffuse background intensity was observed which decreased as the annealing temperature was increased. There are multiple possible reasons why a diffuse background may be present, including point defects, surface reorganisation and thermal vibration of atoms.^{58,93} However, given that the background intensity reduces upon annealing, this is most likely due to a contaminant layer of adsorbed species at the surface, which are removed upon annealing. The aforementioned study by Maier *et al.* on an (110)-oriented, as-polished intrinsic diamond surface also found that this diffuse background was reduced by annealing, however beyond 1000 °C, an intense background reappeared which was suggested to be due to graphitization.⁹⁴ This behaviour has also been observed for (100) and (111)-oriented samples.^{95,96}

At 130 eV, spots appear to be individual and distinct, however changing the energy results in spot splitting. This splitting, most easily noticed at 100 eV, is caused by faceting of the SC surface.⁹³ Each facet will scatter electrons in a different direction, resulting in their own independent LEED pattern, both of

which are visible simultaneously. Spot splitting as opposed to broadening indicates that the facets are larger than the coherence length of the electron beam in the LEED instrument⁹³ which is typically on the order of \sim 10 nm.⁵⁸ As discussed in **Section 3.1**, this is likely to have arisen during polishing.



Figure 3.9: LEED patterns over a 1.8 mm area for the (111)-oriented sample after annealing to 400, 500 and 600 °C, at 100, 130 and 150 eV.

The data acquired from LEED acts to compliment the initial XRD measurements, allowing us to infer more about the crystal quality at the surface of the sample. This is especially relevant for BDD as an electrode material, where the surface properties have a significant influence upon its electrochemical response.

3.3 Raman Spectroscopy

Raman spectroscopy was used to qualitatively assess the boron concentration present in each of the three SC-BDD samples and assess for non-diamond carbon presence. Spectra were recorded at three different arbitrary points on the sample surface to compare the uniformity across the sample (Figure 3.10). All three SC samples showed Fano resonances indicative of boring doping above the metallic threshold.⁹⁷ Asymmetric bands centred around ~500 cm⁻¹ and ~1200 cm⁻¹, also typically attributed to metallic levels of boron doping,^{63,66} were present on all three samples, and were especially prominent on the (100)-oriented sample. Furthermore, for each of the three measurements taken on an individual sample, the diamond Raman line always appeared at the same wavenumber. Between samples, the intensity of the diamond Raman line was noticeably different, being most intense for the (110)-oriented sample and least intense for the (100)-oriented sample, whose diamond Raman line intensity was comparable to that of its asymmetric bands at \sim 500 cm⁻¹ and \sim 1200 cm⁻¹. This suggests that the boron concentration for this set of samples decreased in the order: (100) > (111) > (110). This is further supported by the position of the diamond Raman lines. All three samples show a downwards shift in wavenumber from the expected ~1332.2 cm⁻¹ value for the diamond Raman line (Table 3.2), which is too large to be explained by fluctuations in temperature.^{61,98} The amount of shift experienced by the (100)-oriented sample was the largest, followed by the (111) and then finally the (110) which had the least shift in position.



Figure 3.10: Raman spectra at three different sampling positions on a) (100)-oriented b) (110)-oriented and c) (111)-oriented single crystals. Note that the complete overlap of two of the lines in b) and partially in a) result in one of the lines not being visible.

	Diamond Raman line position
	(cm)
(100)	1319.19
(110)	1328.55
(111)	1325.37

Table 3.3: Diamond Raman line position for a) 100)-oriented b) (110)-oriented and c) (111)-oriented single crystals.

The comparatively lower levels of doping of the (110)-oriented sample makes the lack of G-band attributed to sp² carbon in the 1300-1600 cm⁻¹ region easily noticeable. However, for the (111) and (100) samples, the broad asymmetric background caused by electronic Raman scattering makes it difficult to confirm definitively that graphitic sp² carbon is not present in these samples. Fitting of the spectra to deconvolute any possible unresolved peaks would be necessary⁹⁹ and is something we would have liked to try were there more time for the MRes project.

The Raman data supports the XRD boron dopant density analysis that the (100)-oriented sample has the highest amounts of doping. However, the Raman data suggests that the (111) sample is more highly doped than the (110) sample. In contrast, XRD analysis suggests that doping for both the (110) and (111) samples are the same. As discussed in **Section 3.1**, boron concentration estimates from XRD data come from the calculated lattice parameter for a sample. Though the inclusion of boron increases the lattice parameter, lattice strain or relaxation also factor into the lattice parameter that is measured which may increase or decrease the calculated concentration. As a result, using Raman spectra to assess boron concentration likely gives a more reliable estimate, providing that there are other samples to compare the spectra with. For example, comparing the intensities of the diamond Raman line and asymmetry peaks at ~500 cm⁻¹ and ~1200 cm⁻¹ of the (100)-oriented sample with spectra in the literature, broad asymmetric peaks of higher intensity than the diamond Raman line are typically characteristic of BDD doped to 10^{21} boron atoms cm⁻³.^{21,99}

3.4 Atomic Force Microscopy

As discussed in **Section 1.5**, high surface roughness can have a significant impact upon the electrochemical reversibility of ET processes, so the samples were polished to be as smooth as possible, so that surface roughness did not have a major effect upon the following electrochemical measurements. AFM measurements were used to determine the surface roughness of each of the samples in terms of the average S_q value (Figure 3.11). The reported values are an average over 5 different areas, each covering a 5 × 5 μ m² area on the surface.



Figure 3.11: AFM image of a) (100), b) (110) and c) (111) -oriented single crystal surfaces.

The S_q of the (100) and (111) surfaces were 0.3 nm (± 0.2 nm) and 0.24 nm (± 0.05 nm) respectively. This (110)-oriented sample had an S_q value of 0.5 nm (± 0.1 nm). Prior to AFM, this sample was the only one of the three to have undergone electrochemistry in solutions of both FcTMA⁺ and [Ru(NH₃)₆]³⁻ (to be discussed in **Section 3.6**). It is possible that either solvent or some of these species were still adsorbed on the surface, even after acid cleaning, resulting in the features seen in **Figure 3.11b**.

3.5 X-Ray Photoelectron Spectroscopy

During this project, XPS data was only able to be collected for the (111) sample. Spectra were recorded alongside LEED measurements and were measured as loaded (at room temperature) and after annealing to 300, 400, 500 and 600 °C at take-off angles of both 90° and 30°. The purpose of annealing is to remove volatile adsorbed contaminants from the sample surface. The data discussed here is all reported after annealing to 500 °C as this was the temperature at which there were no further changes to the XPS spectrum, indicating that 500 °C annealing was enough to remove the volatile contaminants. As discussed in **Section 1.10**, probing at two different angles, changes the analysis depth which is useful in assessing the sample properties sub-surface.¹⁰⁰

Analysis of the Auger spectra confirmed that the surface of the (111)-oriented sample is sp³ carbon. The D parameter was found to be 12.6 eV at a take-off angle (TOA) of 90°, and 12.8 eV at a 30° TOA (**Figures 3.12a and b**. Previous studies have reported D parameters for diamond in the range of 13.7-14 eV, with increasing sp² carbon content resulting in a linear increase in the D parameter.⁶⁹ However, the D parameter has been found to vary by as much as 1.5 eV depending on the method of calculation and software used.⁷² The Auger spectrum is surface sensitive, with around 95% of the signal originating from a depth of around one C1s IMFP ~12 Å at a 90° TOA. This is further decreased at a 30° TOA, in which 95% of the signal originates from half of the C1s IMFP or approximately the upper 6 Å of the sample surface.^{74,101}



Figure 3.12: Differentiated Auger spectra for the (111) sample at TOA of a) 90° and b) 30° after annealing to 500°C.

The C1s spectra (**Figures 3.13 a and b**) were fit using a Gaussian-Lorentzian line shape (GL(30)) for all peaks, with the exception of the sp² carbon peak, which should be fit with an asymmetric line shape due to final-state effects which occur after photoelectron ejection.⁷² This was fit as an asymmetric Gaussian-Lorentzian – (A(0.4,0.38,20)GL(20)).^{72,102} At 90° TOA, C1s peaks were observed at 284.2 (sp² carbon), 284.5 (sp³ carbon), 285.3 (C-O) and 286.2 eV (C=O). At 30°, peaks were observed at 284.6 (sp³ carbon), 285.7 (C-O) and 286.6 (C=O) eV. Given the confidence we had that the surface was sp³ diamond, it was somewhat unexpected to find that at the 90° TOA, there was an sp² carbon peak present, contributing to 17.9 % of the total signal. At 30° TOA, the spectrum fit without an sp² carbon component, suggesting that the sp² carbon is sub-surface. The polishing of SC diamond is known to induce sub-surface damage.¹⁰³ This damage may be exacerbated in (111) oriented samples, where the large interplanar distance (refer to **Table 3.1**) results in weaker bond strength, and thus are more able to break.¹⁰⁴

At 90° TOA, 5.5% of the C1s signal was attributed to bonding with oxygen. The ratio of O1s:C1s intensities suggests that at this TOA, 3.2 % should result from oxygen bonding. For a (111)-oriented surface, DFT calculations have shown that hydroxyl termination (C-OH) is more stable than carbonyl terminations, providing that atomic hydrogen is present.¹⁰⁵ However, discrepancies in amounts of C-O present may arise if there is ether termination present, as a single oxygen atom will bond to two different carbon atoms, thus artificially increasing the C1s C-O signal. At 30°, 6.5% of the C1s signal was from bonding to oxygen. This should indicate that the fit is good, as the ratio of the O1s:C1s areas gives a similar value of 7.3 % oxygen.⁷²



Figure 3.13: Fitted C1s spectra for the (111) sample at TOA of a) 90° and b) 30° after annealing to 500°C.

For the O1s spectrum at 90° (Figure 3.14a), it is difficult to distinguish the components of the signal and so has been fit as one broad component centred around 531.5 eV. At 30° (Figure 3.14b) it was possible to split the signal into two components at 532.6 and 531.2 eV, comprising 23.8% and 76.2% of the total signal respectively. C=O signal is typically attributed to carbonyl (C=O) groups but may also result from chains of ether-terminated carbons.²⁹



Figure 3.14: Fitted O1s spectra at TOA of a) 90° and b) 30° take-off angle after annealing to 500°C.

3.6 Bulk Electrochemistry

Figure 3.15 shows CV's measuring the bulk response of the (110) SC-BDD electrode compared to a polycrystalline BDD electrode for both an outer sphere FcTMA⁺ (**Figure 3.15a**) and inner sphere Fe(ClO₄)₂ (**Figure 3.15b**) redox couple in background electrolyte. The (110) BDD electrode showed slightly better reversibility in FcTMA⁺, with peak-to-peak potentials of 62 mV and 69 mV for the (110) and polycrystalline electrodes respectively. The behaviour in Fe(ClO₄)₂ was quasi-reversible, and ΔE_p values were 846 mV for the (110) and 887 mV for the polycrystalline electrode. However, whilst interesting, bulk CVs provide an electrochemical response that averages over the entire electrode area and does not provide any meaningful information about surface heterogeneities. Heterogeneities are present in polycrystalline BDD due to different boron concentrations present in different grains,²⁵ but may be present in the single crystal due to such defects.¹⁰⁶ Given the limited time available for this MRes project, we decided to forgo bulk electrochemical measurements on the other two single crystal samples in favour of focusing on SECCM, where the electrochemistry on the SC-BDD surfaces could be spatially resolved.



Figure 3.15: CVs in a) 1 mM FcTMA⁺ in 0.1 M KNO₃, b) 1 mM Fe(ClO₄)₂ in 0.1 M HClO₄ at a scan rate of 0.1 V s⁻¹.

3.7 Scanning Electrochemical Cell Microscopy

Different growth directions of BDD are known to take up different amounts of boron even when grown under identical conditions.^{45,107} In p-BDD, this can result in different grains on the same sample having different resistivities depending upon which grain is being studied (refer to **Figure 1.3**). Single-barrel SECCM was used to probe the electrochemical behaviour of three BDD samples. First, a p-BDD sample was measured to observe how the electrochemical behaviour changes over an inhomogeneous surface before moving onto the (110) and (111) SC samples, both of which were grown under the same conditions.

Electron back scatter diffraction (EBSD) has shown that p-BDD is primarily (110)-oriented, with grains of other orientations also present.²⁵ Though a single-barrel setup has been shown to work for hydrogenterminated BDD,⁸⁴ studying BDD using a dual-barrel setups is more common.^{25,32,43} Single-barrel SECCM measurements require a conductive substrate, unlike double barrel measurements that are suitable for both conductive and non-conductive surfaces.⁸² The BDD surfaces studied here were all highly doped enough to be sufficiently conductive for single-barrel SECCM. For all three samples, a pipette containing 1 mM of the redox mediator Ru(NH₃)₆³⁺ and 30 mM KCl was used. SECCM measurements were taken using a scanning hopping regime, where the tip approaches the surface, measures a CV, retracts and then moves to an adjacent spot 1 μ m away from the last. Following the measurement, SEM images were taken of the sample surface to determine the size of the spots in each array and whether any surface features such as grains were present.

The pipette used for the polycrystalline sample was approximately 300 nm in diameter, resulting in droplet footprints (therefore electroactive areas) of approximately 580-770 nm in diameter (estimated using SEM scale bar). The view of the p-BDD grains is somewhat unclear in the SEM image due to the presence of solvent residue, possibly caused by inadequate storage and drying; however, it is possible to distinguish droplet footprints and where the regions of high and low boron doping are. In SEM, darker grains correspond to more highly boron doped regions of the surface.⁴⁵ Comparing the resulting SECCM maps with the SEM image of the same area showed there was grain-dependence in the electrochemical behaviour across the polycrystalline surface (**Figure 3.16b** and **c**). Higher doped regions appear to have higher limiting current and half wave potential values. The half wave potential can relate back to the heterogenous electron transfer rate constant, showing that higher doped regions had faster ET kinetics (refer to **Equation 1.10**). Similar maps on p-BDD have been previously reported by Patten et.al using a dual barrelled setup with better spatial resolution than is reported here,⁴³ where in addition to mapping grain-dependent surface heterogeneities, differences within individual grains were also clearly observed.



Figure 3.16: a) An SEM image taken at 5 kV using an InLens detector, b) Plot of limiting current in pA c) Plot of E_{2}^{\prime} in V on the same area of a polycrystalline BDD surface.

The (110) sample was measured using a pipette about 340 nm in diameter, resulting in footprints of in the range of 460-730 nm in diameter (**Figure 3.17**). The limiting current and E½ maps of this surface are highly uniform, especially in comparison to the polycrystalline surface. Excluding the $y = 20 \ \mu m$ row, where the current began to drift, the limiting currents sat within a 0.5 pA range of 5.25-5.75 pA. Given that the background noise of the SECCM system was 0.3 pA, the variation in limiting current is almost negligible. The reason for the current drift in $y = 20 \ \mu m$ is still unknown, and further investigation is necessary to determine the cause, however no drift was observed in the map of the half wave potential (Figure 3.17c).



Figure 3.17: a) SEM image and the corresponding b) Plot of limiting current and c) Plot of E½ on the on the (110)-oriented SC

A pipette of about 350 nm was used for imaging the (111)-oriented sample, resulting in droplet footprints ranging from 460-560 nm in size. Compared to the p-BDD and (110) samples, the droplets on the (111) sample appeared to be more uniform in size and shape (**Figure 3.18a**). This could indicate that the (111) surface is less prone to wetting, however more data is needed to ensure that this didn't result from a systematic error.

a)



Figure 3.18: a) SEM image b) Plot of limiting current and c) Plot of E½ on the on the (111)-oriented single crystal sample.

The limiting current across the (111) sample is less uniform compared to the (110) sample. A streak of higher current can be seen which appears to match up to a surface feature present in the SEM image (**Figure 3.18b**). Furthermore, as the scan progresses, starting at (0,0) moving from right to left up to (51,51), there is a shift in limiting current starting from the $y = 17 \mu m$ row. This is easier to distinguish on the half wave potential plot. One potential explanation for the limiting current shift observed for the (111) sample is that, as discussed in **Section 3.2**, the sample does not lie completely flat. It is possible that the pipette did not retract enough between individual CV's, affecting subsequent approaches. Another explanation could be that there was drift in the QRCE reference potential during the (multiple

hours long) scan duration. The half wave potential for the (111) at the start of the scan (before the shift) was ~0.18 V – the same as for the (110) sample. However, the half wave potential range for the p-BDD sample is higher in comparison. This suggests that QRCE stability must be monitored more closely. Finally, (111) sample not lying completely flat may have also caused slight sample movement, which resulted in the array not being evenly spaced throughout the scan (see **Figure 3.18a**).

4. Conclusions and Future Work

The aim of this thesis was to prepare a set of three well-characterised SC-BDD samples of the low index orientations (100), (110) and (111), grown by CVD that were free-standing and metallically doped. From a large number (~80) of BDD samples, it was possible to narrow these down to select one sample of each orientation for comparison which has not been seen in the literature to date. We were able to build up a picture of each of the three samples in terms of their crystalline quality, boron dopant concentration, surface finish, surface chemistry and electrochemical behaviour. Furthermore, by using multiple techniques in conjunction, it was possible to infer more about these samples than would have been possible if only a handful of techniques were carried out. Notably, we realised the need for further processing of SC-BDD samples after growth, as they often have surfaces with tilts, defects and roughness which may affect their performance as electrode materials. The three resulting samples had surfaces with minimal tilt, sub-nanometre roughness and displayed limited kinetic variability during SECCM measurements, especially when compared to a p-BDD sample. Though there is still much work to complete with these samples, we now have a set of unique samples for future work, for example investigating the mechanisms for surface modification on each of the three orientations.

Due to the limited time scale available for the MRes project, there were some aspects of the project that were unfinished or not fully explored. Fitting of Raman spectra would allow for a more quantitative comparison of boron concentration between samples. There have been multiple possible ways to acquire the boron concentration from fitted Raman spectra, including the position and width of the diamond Raman line,^{66,99} integrated area of the diamond Raman line²⁴ and the position of the ~500 cm⁻¹ asymmetric band.¹⁰⁸ Another next step would be to examine the variation of boron concentration across the single crystal surface via Raman mapping, rather than choosing three arbitrary points on the surface.

We were unable to run XPS on all three samples, which would have allowed us to compare the surface chemistry between the three orientations. Given the possible sub-surface changes in the (100) sample's crystal structure (Section 3.2), the ability to probe the surface at different depths by changing the TOA would allow us to see whether there were changes in chemistry as a result. XPS data would also be useful if we were to compare the results of bulk electrochemical measurements on each of the three SC samples – particularly using inner sphere redox mediators, as differences in surface termination (identified *via* XPS) may result in different ET kinetics.

Further refinement of the method used in SECCM, including pipette fabrication, sample preparation (cleaning) and attachment of the sample to the holder, may help to produce better resolved SECCM

images. Measuring the size of the droplet footprints could be done more accurately if measured in the SEM software rather than by using the scale bar in the image. The effect of sample tilt on the (111)oriented SC could be investigated by running the same measurement before and after rotating the sample by 90° to see if the limiting current gradient also rotates 90°. Lastly, the open circuit potential of the QRCE should be measured both before and after SECCM measurements to ensure that drift in the reference potential is minimal.

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