I, Maeve Helen Sorcha McLaughlin, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the work.
Abstract

Heavily boron doped diamond (BDD), which displays quasi-metallic properties, is the ultimate electrode material for high sensitivity detection in extreme environments. BDD has a unique combination of chemical, mechanical, and electrical properties. These are manipulated in this thesis to optimise the sensing capabilities of the BDD electrodes used.

One exceptional property of BDD is its electrochemical window, which is the widest of any known material. This means that with a BDD sensor it is possible to detect the broadest range of chemical reactions. This parameter is well understood at room temperature. However, until the work presented in this thesis there was no systematic study investigating how it changes as the temperature of the electrochemical reaction is increased above 100 °C. Through comparison of polished and unpolished BDD electrodes (with hydrogen and oxygen surface terminations) it is determined that the electrochemical window of BDD electrodes narrows as temperatures increase. The corresponding activation energies are reported. Three methods of determining the precise size of the electrochemical window from experimental results are critically compared.

The addition of catalytically active gold nanoparticles (AuNPs) have previously been shown to improve the sensitivity of BDD electrodes for mercury detection in aqueous environments. In this work, two AuNP sizes were deposited onto as grown and mechanically polished BDD electrodes, in pursuit of defining the optimum combination of these parameters to achieve the highest sensitivity for mercury detection. A novel method of producing small AuNPs (10 nm diameter) on the BDD surfaces was developed, using a TEM grid as a shadow mask. Exceptional sensitivity (pM) is achieved with the AuNP decorated polished BDD electrodes.

Electrochemical impedance spectroscopy (EIS) is used to investigate the mechanism by which the AuNPs improve the sensitivity of the BDD electrodes. AuNP decorated BDD electrodes are directly compared to bare BDD electrodes (as grown and mechanically polished) under the same conditions as in the first electrochemi-
Abstract

cal study. The performance of each electrode is assessed by their electron transfer rate ($k_0$), alongside the capacitance and electron transfer resistance at their surface, recorded during mercury detection measurements.
Impact Statement

The results presented in this thesis highlight how BDD electrodes can be optimised for sensing with high sensitivity in extreme environments.

Academically, this research has extended the knowledge in this field through two published papers, with a third recently submitted. This work has produced the first published study investigating the influence of temperature on the performance of a series of BDD electrodes. BDD substrates with two surface terminations (oxygen and hydrogen) and two surface types (as grown and mechanically polished) are analysed. The results from this work are the first to quantify the electrochemical window of a BDD electrode above 100 °C. This brings the development of commercial BDD sensors for high temperature environments one step closer, as it is now possible to identify the potential range in which chemical reactions can be detected at elevated temperatures.

A highlight from this thesis is the high sensitivity achieved with a polished BDD electrode decorated with gold nanoparticles (AuNPs) for mercury detection, which is good when compared to recent reports of alternative electrode materials in the literature. It is a promising result for the possibility of high sensitivity detection in the field. The outcome of this research is that BDD based sensors could be developed for commercial use in sensing mercury in real water samples. Although, this will require significant modification from the work in this thesis, which has focused on improving the sensitivity of electrodes for mercury detection but has not addressed the issue of selectivity for mercury ions. This is an important factor when designing a sensor to be used to analyse real water samples because many other ions and molecules will be present in the solution which may impede or block the signal for mercury detection. High sensitivity mercury detection in water is important to environmental studies and for industries which have mercury in their waste streams. Mercury accumulates in the food chain, ultimately poisoning humans. Detecting this heavy metal at lower concentrations means that interventions can be made sooner to prevent further spread of the mercury. Areas where a ‘clean
up’ is required can also be identified, cutting off contaminated sections of the food chain.

The results from the electrochemical impedance spectroscopy (EIS) study are unexpected. EIS was used to analyse the mechanism of mercury detection at the surface of BDD electrodes decorated with AuNPs. Previously, it was understood that during these measurements mercury ions are pre-concentrated onto the AuNPs, resulting in improved sensitivity of the BDD electrode compared to when AuNPs were not present. However, it was found that mercury also pre-concentrated onto the sp² carbon regions of the BDD electrode surfaces, at higher concentrations of mercury. This presents a new area of study for mercury detection with diamond electrodes.
Acknowledgements

Like any PhD, almost none of this work would have been possible without a whole community of people who have supported, taught, supervised, collaborated, travelled, and laughed with me over the last few years.

The first thanks must go to Richard Jackman, who has never wavered in his encouragement and faith in my abilities. His enthusiasm for new ideas and trust in his students to tackle them has made a wonderful culture in the DEG, of collaboration and independent work led by students. Thank you to all the DEG members, past and present; these years of exciting research and science tourism wouldn’t have been nearly as fun without you all!

To Alex, thank you for asking the questions that have pushed me to be a better scientist. To Ralph and Steven, thank you for helping me build our DIY science equipment. To Joe, thank you for keeping everything running. To Marie, Max, Safe, Laurie, Daniel and Troy thank you for all the lunches and the debates. You’ve even got me drinking coffee now!

My PhD would not have been possible without the sponsorship from Schlumberger, who generously let me use their facilities for some experiments beyond the possibilities of our university lab. Particular thanks go to Débora and Emma for their support during my time with them.

Thank you to everyone at ULU. Canoe polo is a weird sport and I sometimes regret deciding to play when matches are at 7am and the BAs are frozen, but you all make it worth getting on the pitch every time.

To my friends, thank you for reminding me that there is a whole world outside my little corner of academia. I can’t wait for our adventures once the new dreaded c-word is finally under control!

Thank you to my family for your love, support, and encouragement. I hope you know how much I appreciate you.

Finally to Ben, thank you for everything.
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List of Abbreviations

AFM  Atomic Force Microscopy
ASV  Atomic Stripping Voltammetry
AuNP Gold Nanoparticle
BDD  Boron Doped Diamond
BDDH Hydrogen Terminated Boron Doped Diamond
BDDO Oxygen Terminated Boron Doped Diamond
CE   Counter Electrode
CPE  Constant Phase Element
CV   Cyclic Voltammetry
CVD  Chemical Vapour Deposition
EIS  Electrochemical Impedance Spectroscopy
FAAS Flame Atomic Absorption Spectrometry
GC-AFS Gas Chromatography - Atomic Fluorescence Spectroscopy
HF   Hot Filament
HFCVD Hot Filament - Chemical Vapour Deposition
HPHT High Pressure High Temperature
ICP-MS Inductively Coupled Plasma - Mass Spectrometry
IHP  Inner Helmholtz Plane
$J_{cut-off}$ Current Density Cut Off
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>LSV</td>
<td>Linear Sweep Voltammetry</td>
</tr>
<tr>
<td>MWP</td>
<td>Microwave Plasma</td>
</tr>
<tr>
<td>MWPECVD</td>
<td>Microwave Plasma Enhanced Chemical Vapour Deposition</td>
</tr>
<tr>
<td>ND</td>
<td>Nanodiamond</td>
</tr>
<tr>
<td>NDC</td>
<td>Non-Diamond Carbon</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>OHP</td>
<td>Outer Helmholtz Plane</td>
</tr>
<tr>
<td>pBDD</td>
<td>Polished Boron Doped Diamond</td>
</tr>
<tr>
<td>PEEK</td>
<td>Polyether Ether Ketone</td>
</tr>
<tr>
<td>RE</td>
<td>Reference Electrode</td>
</tr>
<tr>
<td>RTA</td>
<td>Rapid Thermal Annealing</td>
</tr>
<tr>
<td>RTP</td>
<td>Rapid Thermal Processing</td>
</tr>
<tr>
<td>SCR</td>
<td>Schlumberger Cambridge Research Ltd.</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SWASV</td>
<td>Square Wave Atomic Stripping Voltammetry</td>
</tr>
<tr>
<td>WE</td>
<td>Working Electrode</td>
</tr>
</tbody>
</table>
There is an ever increasing demand for sensing capabilities in extreme environments; from down-well sensors in the oil industry, to remote applications in outer space and at the bottom of the planets oceans. Diamond electrodes present one of the best options for addressing many of these challenges. They can be left in remote locations for extended time periods without fouling and are stable at extreme temperatures, pressures, and pHs, whilst also being radiation hard. The exceptional properties of heavily-boron doped diamond (BDD) electrodes, displaying quasi-metallic characteristics, make them the ideal material for the development of sensors for new discoveries not possible with other electrodes. The influence of altering BDD surfaces by polishing, changing the surface termination, and the addition of gold nanoparticles (AuNPs) on the electrochemical performance of BDD sensors have been directly compared throughout this work.

Research into using BDD electrodes for electrochemical detection has been well established since the 20th century and more recently investigations into this material have extended to using BDD electrodes in extreme environments. However, despite the multitude of published literature focused on using BDD electrodes for high sensitivity detection, some assumptions are made. This thesis aims to extend the current understanding of the physical changes that happen at the surface of BDD electrodes during high temperature electrochemical measurements and high sensitivity detection under standard laboratory conditions.

BDD has the widest electrochemical window of any known electrode material, at \( >3 \) V in aqueous solution at room temperature. This is the potential range that can be applied across the electrode before the onset of oxidation or reduction of the electrolyte at its surface. Chemical reactions can only be detected electrochemically within this range. This means that BDD electrodes can be used to detect the broadest range of chemical reactions and sense the largest number of analytes, compared to any other electrode material. The electrochemical window of BDD is a
well understood parameter at room temperature. However, until the work presented in Chapter 6 of this thesis (published in Scientific Reports) there was no systematic investigation into how this parameter changes at higher temperatures. This is vital information to have when designing a BDD sensor to be used above room temperature, as it defines the limit in the potentials where it will be possible to observe any chemical reactions.

Gold based electrodes are commonly used as the basis for sensing systems aiming to detect mercury. This is due to the often quoted ‘high affinity’ between mercury and gold. BDD electrodes are commonly decorated with AuNPs for this purpose. In this thesis, a set of BDD substrates (both as grown and mechanically polished) were decorated with AuNPs of varying sizes, in pursuit of defining the optimum configuration of these parameters for mercury detection with the highest sensitivity. This work is followed by a detailed EIS study, used to investigate the interaction between gold and mercury at the surface of the BDD electrodes, to gain a better understanding of the physical and chemical reasons for the ‘high affinity’ between them.

Chapter 2 introduces diamond as a material and outlines its exceptional physical properties. The historical development of diamond synthesis by laboratory processes is reviewed, followed by a discussion of the methods of doping synthetic diamond substrates. Chapters 3 and 4 review the theory behind the electrochemical techniques used throughout this thesis, from the electrochemical detection of analytes to electrochemical impedance spectroscopy for the analysis of electrochemical systems. Chapter 5 reviews the experimental methods used throughout this thesis.

In Chapter 6, the electrochemical window of BDD electrodes, with different levels of surface polishing and terminations, are measured over a wide temperature range, from 21 °C to 125 °C. This is the first study investigating this fundamental property of BDD electrodes at elevated temperatures.

In Chapters 7 and 8, the influence of modification of BDD electrode surfaces with gold nanoparticles (AuNPs) on the sensitivity of these electrodes for mercury detection is investigated. In Chapter 7, the focus is optimising the size of the AuNPs on two BDD substrate types (as grown and mechanically polished) to obtain the lowest limit of detection for mercury sensing. In Chapter 8, the same conditions are analysed using electrochemical impedance spectroscopy (EIS) to gain further insight into the exact influence that the AuNPs have on the electrode performance.

Chapter 9 summarises the results presented in Chapters 6, 7, and 8 of this thesis. Chapter 10 presents the future work that will follow on from the conclusions drawn in this thesis.
Publications

Diamond electrodes for high sensitivity mercury detection in the aquatic environment: influence of surface preparation and gold nanoparticle activity.

Influence of temperature on the electrochemical window of boron doped diamond: a comparison of commercially available electrodes.

A detailed EIS study of boron doped diamond electrodes decorated with gold nanoparticles for high sensitivity mercury detection.
Conference papers

Poster presentations
Trace detection of mercury with a boron doped diamond electrode:
*SBDD XXIII, Hasselt Diamond Workshop, Belgium, 2018*
*De Beers Diamond Conference, Warwick, UK, 2018*

A comparison of gold nanoparticle dispersions on boron doped diamond electrodes for trace mercury detection:
*ICDCM, Dubrovnik, Croatia, 2018*

Oral presentations
Modified boron doped diamond electrodes for the trace detection of mercury:
*INASCON, Trondheim, Norway, 2018*

Diamond electrodes for high sensitivity mercury detection in the aquatic environment: influence of surface preparation and gold nanoparticle activity:
*De Beers Diamond Conference, Warwick, UK, 2019*
*ICDCM, Seville, Spain, 2019*
Diamond

Diamond is an exceptional material that has been sought after for centuries. Perhaps best known as a rare gemstone, diamond has extreme properties that make it highly desirable for many scientific applications. It is the hardest known material, an excellent thermal conductor, chemically inert, and transparent from deep UV to far IR, as well as being semiconducting and biocompatible. These extraordinary properties are a result of the lattice of carbon bonds that make up the diamond structure.

2.1 Carbon bond

Carbon, atomic number 6, has the electronic configuration 1s², 2s², 2p². Valence bond theory would therefore suggest that carbon is divalent, as it should only form two covalent bonds via the half-filled 2p orbital. Divalent carbon does exist in the form of transient intermediates such as the carbenes. However, stable carbon compounds are tetravalent, meaning that four valence electrons must be present [146].

![Bohr model of carbon electron shells.](image)

Within the filled k shell of carbon there is one s-orbital, which contains two electrons of opposite spins. The electrons in the k shell do not participate in bonding due to their high stability, as a result of being in a filled shell and their proximity to the nucleus. Carbon bonds are made with the remaining four electrons in the
half-filled L shell through molecular orbital hybridisation, which Linus Pauling first proposed in 1931 to explain the bonding structure of methane [142]. Pauling’s theory describes the formation of hybrid 2sp\(^n\) atomic orbitals (where n = 1, 2 or 3), in which the respective wavefunctions of the 2s and 2p orbitals mix via promotion of the 2s orbital electrons to higher energy and demotion of the 2p electrons to lower energy.

An sp hybrid orbital (with half s and half p orbital character) is found in linear molecules that contain triple bonds between some atoms, such as alkynes. In each alkyne carbon atom the 2s and 2p\(_x\) orbitals are hybridised, which leaves the 2p\(_y\) and 2p\(_z\) orbitals to form two \(\pi\) molecular orbitals with the 2p orbitals on the adjacent carbon atom [30].

The sp\(^2\) hybrid orbital has one third s and two thirds p orbital character. It is found in trigonal planar molecules that contain double (\(\pi\)) bonds, such as alkenes. On each carbon atom in an alke the 2s, 2p\(_x\) and 2p\(_y\) orbitals are hybridised, leaving the 2p\(_z\) orbital available to form a \(\pi\) molecular orbital with the 2p\(_z\) orbital on the adjacent carbon atom. Although, in the case of graphite the two electrons in the 2p\(_z\) orbital are delocalised and free to move between sheets of covalently bonded carbon atoms, resulting in the electrically conductive and soft properties associated with the material [200].

The sp\(^3\) hybrid orbital has one quarter s and three quarters p orbital character. Sp\(^3\) hybridisation is found in tetrahedral molecules that contain single bonds
2.2 Diamond properties

The exceptional properties of diamond are a result of its molecular geometry. Within the diamond lattice, except at surfaces, each carbon atom is covalently bonded in a tetrahedral arrangement to four neighbouring carbon atoms with a bond strength of 370 kJmol\(^{-1}\), length 1.54 Å [146]. The bond strength between adjacent...
2.2. Diamond properties

carbon atoms in diamond is weaker than those in graphite (680 kJmol\(^{-1}\), length 1.42 Å). However, although the covalent bonds within each graphite sheet are very strong, the London dispersion forces between the sheets are the weakest known intermolecular forces. Therefore the layers are easily separated, resulting in the soft properties of graphite.

![Figure 2.5: a) The face centred cubic structure of diamond, modified from [34] and b) the [100], [110] and [111] Miller planes of diamond.](image)

The lattice structure of diamond is face centred cubic, with eight atoms per unit cell, usually described with the Miller indices: [100], [110] and [111] (Figure 2.5). In the unit cell there are atoms on the faces of the cube and at the corners of the cube. The additional carbon atoms are located at \(a_0\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)\), \(a_0\left(\frac{3}{4}, \frac{3}{4}, \frac{1}{4}\right)\), \(a_0\left(\frac{1}{4}, \frac{3}{4}, \frac{3}{4}\right)\) and \(a_0\left(\frac{3}{4}, \frac{1}{4}, \frac{3}{4}\right)\), where \(a_0\) is the lattice constant at room temperature (3.567 Å ± 2.6x10\(^{-6}\)) [71][72]. The C-C bond length, \(d\), is equal to one quarter of the cubic body diagonal, so that \(d = \sqrt{3a_0/4} = 1.54\) Å [176].

The atomic density of diamond is 1.76x10\(^{23}\) atoms/cm\(^3\), which is the highest of any known solid [61][170][131]. This explains why diamond is the hardest, stiffest and least compressible of all known materials. Additionally, although the precise tensile strength of diamond is unknown it could theoretically have a magnitude of 90 - 225 GPa depending on the crystal direction, as the tensile strength is highest in the [100] direction [200]. The most interesting property of diamond to this thesis is that diamond can be doped for electronic applications, which paired with the chemical inertness and radiation hardness of the material makes diamond well suited for use as an electrode in extreme environments [26].
Diamond growth

Graphite is the thermodynamically stable allotrope of carbon at room temperature and pressure. Diamond is a metastable allotrope of carbon because the large activation barrier means that carbon cannot undergo a phase change between graphite and diamond. This is due to the large kinetic barrier between the sp² (graphitic carbon) and sp³ (diamond carbon) phases. Diamond can be synthesised when the growth conditions overcome this large kinetic barrier, see carbon phase diagram Figure 2.6. Once formed, diamond is kinetically stable under standard conditions.

Diamond forms naturally in the Earth’s mantle at depths of over 150 km as a result of the high temperatures (greater than 1000 °C) and pressures (GPa) present [44]. Natural diamond may be transported to the Earth’s surface during kimberlite eruptions. These mainly occur at continental cratons, for example in Russia, Canada and South Africa, which contain sites of the largest natural diamond mines [166]. Some limitations of natural diamond include inhomogeneity across the structure, variable impurity inclusions and high cost. However, these limitations can be overcome by the generation of artificial diamonds through the high pressure high temperature (HPHT) and chemical vapour deposition (CVD) techniques described below.

2.3.1 High pressure high temperature synthesis

HPHT growth employs conditions where the formation of diamond is more thermodynamically stable than the formation of graphite. As seen in the carbon phase

<table>
<thead>
<tr>
<th>Diamond property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical Hardness</td>
<td>90 GPa</td>
</tr>
<tr>
<td>Compressibility</td>
<td>$8.3 \times 10^{-13}$ m²/N</td>
</tr>
<tr>
<td>Thermal Conductivity at 25 °C</td>
<td>$3.15 \times 10^3$ W/mK</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient at 25 °C</td>
<td>$0.8 \times 10^{-6}$ K⁻¹</td>
</tr>
<tr>
<td>Transparency</td>
<td>from deep UV to far IR</td>
</tr>
<tr>
<td>Room Temperature Resistivity</td>
<td>$10^{16}$ Ωcm</td>
</tr>
<tr>
<td>Band Gap</td>
<td>5.47 eV</td>
</tr>
<tr>
<td>Dielectric Strength</td>
<td>$1 \times 10^7$ Vcm⁻¹</td>
</tr>
<tr>
<td>Electron Mobility</td>
<td>2.2 cm²/Vs</td>
</tr>
<tr>
<td>Hole Mobility</td>
<td>1.6 cm²/Vs</td>
</tr>
</tbody>
</table>
2.3. Diamond growth

2.3.1. HPHT growth

Diagram (Figure 2.6), which was first proposed by Leipunsky in 1939, diamond is unstable with respect to graphite at temperatures below 1300 °C and pressures below 40 kbar [100][172]. Although, even when these conditions are met the kinetics of the reaction must be considered, as the activation energy for conversion from graphite to diamond is very high. Transition metals such as nickel are commonly used as catalysts to exceed the activation energy at lower temperatures and pressures, therefore reducing the cost and energy requirement of HPHT diamond synthesis.

There are limitations to this technique, most significantly the incorporation of both strain and impurities (particularly nitrogen, boron and metals) within the diamonds produced. However, boron inclusions can be desirable as these produce blue diamonds and conductive diamonds at higher boron concentrations. The concentration of nitrogen can be reduced by the addition of getters, Ti, Zr or Al, to the nickel catalyst [133].

2.3.2. Chemical vapour deposition

Diamond growth by CVD was first investigated in the 1950s as a low pressure alternative to the HPHT method, however, it did not become an established technique until the mid 1980s. CVD is primarily used for the production of polycrystalline...
diamond, but growth of homoepitaxial single crystal diamond is now also possible (although with size limitations). Single crystal diamonds are grown homoepitaxially on a single crystal substrate, which is either a natural diamond or a diamond produced by HPHT synthesis [78][182]. The crystal plane orientation ([100], [110] or [111]) of the initial substrate dictates the resultant orientation of the grown diamond [177]. Polycrystalline diamond, which is the focus of this work, is produced from heteroepitaxial growth on a variety of different substrates [153].

During the CVD process a gas mixture of methane (generally <1%) and hydrogen are introduced into a vacuum chamber at a pressure between 10 - 50 torr, which is then activated with a hot filament (HF) (2200 °C) or by a microwave plasma (MWP) near the substrate (700 - 10000 °C) [133]. The small proportion of methane gas is the source of carbon in the system. Hydrogen radicals generated by the dissociation of hydrogen gas dimers react with methane molecules via the mechanism shown in Figure 2.7 to produce synthetic diamond [114]. During the CVD growth

![Figure 2.7: Mechanism of CVD diamond growth process, taken from [114].](image)
process the majority of carbon-carbon bonds formed are graphitic $sp^2$ bonds rather than the $sp^3$ bonds of diamond. The hydrogen radicals preferentially attack the $sp^2$ bonds, therefore favouring the production of $sp^3$ bonds at the surface of the synthesised diamond [146][133].

Figure 2.8: Schematic of the HFCVD reactor developed at NIRIM, taken from [112].

In HFCVD the hydrogen/methane gas mixture, at 10 - 100 torr, flows past a metal filament (tungsten, tantalum, molybdenum or rhenium) which is electrically heated to 2000 - 2400 °C (Figure 2.8) [105][112]. Under these conditions the molecules of the gas mixture are thermally activated as they flow past the filament. Diamond is deposited on a substrate (normally silicon or molybdenum) that is mounted a few millimetres below the filament. The substrate is kept at a temperature between 700 - 1000 °C by radiation from the heated filament or via a separate heater [105][114]. The filament is made from a metal that will not significantly react with the process gas. Tungsten and tantalum are most commonly used, although, they will eventually react with carbon in the process gas and form a metal
2.3. Diamond growth

carbide. This limits the deposition time possible in a single HFCVD run because the carbide formation causes the filament to become brittle, reducing its lifetime [114]. In addition, tungsten and tantalum can absorb large quantities of hydrogen from the process gas, forming a brittle metallic hydride, which can cause the filament to become brittle even when no methane is present [27]. Another major limitation of HFCVD is unwanted contamination of the diamond with metal impurities from the filament, which makes the diamond produced unacceptable for electrical applications for which a high level of purity is required. Although, this method is suitable for three dimensional coating, which has led to its wide spread use for producing protective coatings and tool applications [134].

Microwave plasma enhanced CVD (MWPECVD) provides a growth environment with fewer contaminants and the possibility of longer growth runs than HFCVD. The specific chamber design of MWPECVD reactors varies (see Figures 2.9 and 2.10).

![Figure 2.9: Schematic of the microwave plasma reactor developed at NIRIM, taken from [158].](image)

A schematic of the first microwave plasma reactor is illustrated in Figure 2.9 [84][158]. In this reactor the 2.45 GHz waveguide is modified by the insertion of a silica glass tube (inner diameter 18 mm), which causes the electric field maxima to occur at the centre of the silica glass tube. The resulting plasma ball (referred to as the afterglow by the authors) is held just above the silicon substrate [158]. It
2.3. Diamond growth

was found that when the silicon substrate was placed in the centre of the plasma silicon etching became the predominant reaction, which led to 3 µm ‘spire like’ silicon on the surface of the grown diamond where the etched silicon was re-deposited. This design is widely used in research due to the low construction cost and simple design, compared to other MWPECVD reactors. However, there are several limitations to this design, particularly in the size of the diamond that it is possible to produce which is limited by the internal diameter of the reactor tube and the reported growth rate of 1 µm h\(^{-1}\) [158]. In addition to this, many of the growth parameters are linked which prevents independent investigation of the parameters such as temperature, which varies with changes in pressure and microwave power. Also, the proximity of the silica glass tube walls to the plasma increases the likelihood of silica contamination of the diamond due to silica being etched from the inner walls [141].

![Schematic of the ASTeX-type bell jar microwave plasma CVD reactor](image)

**Figure 2.10:** Schematic of the ASTeX-type bell jar microwave plasma CVD reactor, taken from [104].

A schematic of the ASTeX-type bell jar microwave plasma reactor is illustrated in Figure 2.10. The process gases are contained within the bell jar, which is continuously pumped with a vacuum pump to below atmospheric pressure. The bell jar sits inside a cylindrical 2.45 GHz microwave resonance cavity, with the electric field maxima occurring at the centre of the bell jar. The growth plasma results from
coupling between the electric field maxima and microwave power into the process gases [159]. The moveable sample holder is used to control the substrate position so that it sits just below the ball shaped plasma. Lower temperature diamond growth (\(\sim 400^\circ\text{C}\)) has been demonstrated with this reactor design [104]. This was achieved by reducing the microwave power and process gas pressure, which resulted in a slower deposition rate. Although, higher deposition rates are possible when the substrate is actively cooled, which allows more standard growth conditions to be used. A growth rate of 1.25 \(\mu\text{m h}^{-1}\) has been reported, which was maintained over a 24 h growth run [159]. The main advantage of this reactor design compared to the microwave plasma reactor developed at NIRIM is that the microwave power can be tuned whilst the equipment is running, which enables adjustment of the position of the maximum electric field to the optimum position for growth [159][158].

2.4 Polycrystalline diamond

Polycrystalline diamond is produced from hetero-growth on a variety of different substrates[153]. Individual crystals emerge from nucleation sites on the substrate surface since there is no available non-diamond substrate with a lattice match close enough to diamond to enforce high quality epitaxy. These crystals grow outwards in three dimensions until they meet and a polycrystalline film is formed, which then continues to grow vertically (Figure 2.11). The properties of polycrystalline diamond are defined by the size of the individual crystals (grain size) and by the grain boundaries between the individual crystals, which may contain graphitic carbon and therefore degrade the properties of the diamond. High quality polycrystalline growth is possible, particularly over large areas, on the microcrystalline (grain size > 0.1 \(\mu\text{m}\)), nanocrystalline (grain size 5-100 nm) and ultrananocrystalline (grain size < 5 nm) scales [156].

Controlling the nucleation of CVD diamond growth allows the optimisation of the resulting diamond properties including the grain size, orientation, transparency, and roughness [98]. During the early development of the CVD process the majority of diamonds produced were single crystal, using a natural diamond as the initial substrate. Although, there was also some use of diamond seeds for polycrystalline growth. The first CVD diamond growth without a diamond substrate or diamond seed was achieved by Matsumoto in 1982 [112]. However, the non-diamond substrates had low nucleation densities and it was not possible to grow a continuous film. In 1987 Mitsuda et al. found that scratching the substrate surface with a diamond powder greatly improved the nucleation density [124]. For silicon substrates, with a nucleation density of \(10^4 \text{ cm}^{-2}\), scratching with diamond powder has
consistently been shown to increase the nucleation density to $10^7 - 10^8$ cm$^{-2}$ [98]. Substrate scratching is now commonly used in CVD growth of polycrystalline diamond to produce fine, uniform grain sizes with a high nucleation density. Coating the substrate surface with amorphous carbon, diamond like carbon or graphite has also been shown to improve the nucleation density [98].

2.4.1 Nanodiamonds

Nanodiamonds (NDs) are commonly used as seeds for the growth of polycrystalline diamond by CVD. These are particles with a diameter of 1 - 100 nm and generally consist of an sp$^2$ carbon shell coating an sp$^3$ carbon core. NDs are found in crude oil at concentrations up to 1000 ppm in certain sediment layers on Earth and in meteorites, interstellar dust and protoplanetary nebulae [86]. They can also be produced either by grinding bulk diamond, which usually leads to larger NDs of around 50 nm in diameter, or by detonation of TNT and Octogen (HMX) or Hexogen (RDX) in a chamber with a controlled atmosphere [66][37].

The ‘top down’ approach of grinding bulk diamond to produce NDs allows a higher level of control of the impurities in the material and therefore the properties of the NDs can be tailored. For example, conductive boron doped NDs are produced from bulk BDD and NDs with high proportions of nitrogen impurities are used extensively in the biosciences as fluorescent markers [66][126][86]. Modification of the surface termination of NDs further expands their variety of applications to include drug delivery, quantum engineering, luminescence imaging and for surface
2.5. Doping

The detonation of carbonaceous explosives (TNT, HMX, RDX) in a cooled, low oxygen chamber produces detonation nanodiamonds at the point where the Chapman/Jouguet point of the shockwave passes, which allows the crystallisation of sp$^3$ carbon for a few microseconds [37]. Once the temperature and pressure in the chamber fall below the energy requirement of diamond growth (see carbon phase diagram, Figure 2.6) graphite forms, coating the NDs in soot. The soot that is collected following the explosion contains strongly aggregated clusters of NDs, with a primary particle size of 5 nm [165]. This technique was developed by Russian scientists during the 1960s. However, it was not until the end of the Cold War that research into detonation nanodiamonds expanded internationally and processes were developed to de-aggregate the ND clusters into mono dispersed ND colloids [37][74]. The colloids are produced through a combination of milling with micron-sized ceramic beads and ultrasonic treatments [201].

2.5 Doping

The sp$^3$ carbon bonds in the diamond lattice are responsible for the many exceptional properties of the material, but they also hinder the incorporation of dopant atoms needed to enhance the electrical characteristics of diamond. The dopants act as donors or acceptors within the diamond bandgap, leading to semiconducting or metallic behaviour. Most doping processes are restricted to substitutional doping during diamond growth because the metastable nature of diamond limits the temperatures to which it can be heated to for interstitial diffusion doping [81].

During CVD growth dopant gases can be introduced, enabling the substitutional incorporation of dopants into the diamond lattice. Doping can also be achieved during HPHT growth by using a metal catalyst that contains the desired dopant. Alternatively, ion-implantation can be used. However, this technique results in lattice strain, therefore reducing the quality of the diamond for electronic applications [82].

2.5.1 N-type doping

The relatively short length of the sp$^3$ carbon bond, at 1.54 Å, makes substitutional doping in diamond difficult, leading to dopants with large activation energies [146]. Suitable n-dopants include nitrogen and phosphorus which both have one more electron in their outer L shell than carbon. Substitutional nitrogen doping creates a donor state 1.7 eV from the conduction band, which results in an activation energy that is too high for conduction at room temperature [32][83]. More success has
been achieved with phosphorous, which is a shallower n-type dopant than nitrogen and has an activation energy of 0.6 eV [143]. However, the high positive formation energy and large atomic radius of phosphorus presents additional challenges as this results in lattice distortions throughout the diamond when it is substitutionally included in its structure [196]. Currently, the properties of n-type doped diamond are not of a quality to make this an attractive option for electronic technologies.

### 2.5.2 P-type doping

In contrast to n-type doping, p-type doping with boron is relatively trivial and is widely employed. Boron has one fewer electron in its L shell than carbon, so creates an acceptor level of 0.37 eV above the valence band [32]. Electrons are promoted to the acceptor level from the valence band, leaving behind a hole which carries a positive charge. Metal-like conductivity can be achieved through boron dopant concentrations greater than $1 \times 10^{20}$ cm$^{-3}$ (Figure 2.12), at which point an impurity band forms at the 2p states [146][75].

![Figure 2.12: Room temperature resistivity as a function of boron doping concentration, taken from [95].](image)

The large activation energy of boron means than only 1% of the dopant atoms
are activated at room temperature. Although, this energy barrier is reduced with increasing boron doping concentration (down to a few tens of meV at a boron concentration of $3 \times 10^{20}$ cm$^{-3}$) due to the formation of a metallic impurity band [19]. As the boron concentration in the diamond lattice increases the hole mobility decreases and the type of conduction changes (Figure 2.12). At boron concentrations between $10^{16}$ cm$^{-3}$ and $10^{19}$ cm$^{-3}$ valence band conduction is observed, in which the dominant carrier transport mechanism is the movement of free holes in the valence band. As the boron concentration is increased to $10^{20}$ cm$^{-3}$ the main carrier transport mechanism changes to hopping conduction, in which there is overlap of the impurity wavefunctions, allowing carriers to tunnel between the nearest ionised and neutral acceptors [76]. At boron concentrations $>10^{20}$ cm$^{-3}$ the overlap of the impurity wavefunctions allows the carriers to pass the metal-insulator transition to become metallically conductive at room temperature.

![Figure 2.13](image)

**Figure 2.13:** Conductivity of boron doped diamond homoepitaxial layers, with a series of boron doping concentrations ($3 \times 10^{20}$, $2 \times 10^{16}$, $4 \times 10^{15}$) as a function of temperature, taken from [20].

The conduction regimes in BDD were investigated by Borst and Weiss in a comprehensive study that analysed the conductivity of boron doped samples as a function of temperature (Figure 2.13) [20]. They found that the conductivity of the heavily boron doped substrates ([B] $3 \times 10^{20}$ cm$^{-3}$) was independent of tempera-
2.5. Doping

ture, corroborating the theory that at boron concentrations \( >10^{20} \text{ cm}^{-3} \) diamond is metallically conductive. The main conduction pathway through the substrates with lower concentrations of boron dopants (\([B] \ 2\times10^{16} \text{ and } 4\times10^{15} \text{ cm}^{-3} \)) is valence band conduction, so the conductivity of these substrates increased as the temperature increased (Figure 2.13).

![Figure 2.14: Hole mobility in boron doped diamond as a function of the number of impurities at 300 K (black) and 500 K (grey), taken from [193].](image)

Increasing the boron doping concentration and therefore the number of impurities in BDD substrates leads to a decrease in hole mobility (Figure 2.14). The hole mobility (\( \mu \)) varies with temperature (\( T \)) by the function \( \mu = T^\alpha \), where \( \alpha \) corresponds to the ratio between boron and carbon [127]. At high boron concentrations (\([B] >10^{20} \text{ cm}^{-3} \)) the hole mobility drops due to increased scattering from acceptor impurities and the low mobility nature of hopping conduction, which is the main conduction pathway at this point [127]. Scattering from the greater donor impurity contribution also results in lower mobility in highly compensated materials [21]. In polycrystalline diamond there may be additional transport losses at grain boundaries, although this effect may be more significant in lightly doped BDD films [136]. The metallic impurity band forms at boron concentrations above \( 3\times10^{20} \), where the hole mobility reduces to <3 cm²/Vs (with reported values as low as 0.28 cm²/Vs) [21][136].
2.5.2.1 P-type doping by hydrogen termination

The p-type behaviour of a hydrogen terminated diamond surface was first observed by Landstrass and Ravi in 1989 [96]. The hydrogen termination induces surface conductivity as a result of surface transfer doping of electrons from the diamond valence band to an adsorbed electrolyte (most commonly water) [110]. The charge transfer occurs because of the misalignment of the Fermi levels at the interface between the diamond surface and adsorbate. This potential difference causes electrons from the diamond valence band to be driven into the unoccupied electronic acceptor levels of the adsorbate species, causing band bending [54]. The adsorbates at the diamond surface then have a negative charge, which is compensated by the accumulation of holes in the diamond valence band. The redistribution of surface charge leads to the hole accumulation (p-type) layer as described above.

Diamond is highly resistant to corrosion, so does not undergo oxidative dissolution under normal laboratory conditions. This means that the surface transfer doping reaches a thermal equilibrium in which there is a sub-surface conductive hole channel in the diamond [28]. However, the hydrogen termination of diamond undergoes oxidation after prolonged use and is unstable at high temperatures, meaning that this method of doping diamond is not suitable for commercial use.

### 2.6 Metal contacts on diamond

The metallisation of diamond to form electrical contacts is crucial when fabricating diamond devices. The type of metal-semiconductor contact that is made is dictated by the difference in the workfunctions of the two materials because the Fermi levels of materials in contact tend to align, either producing an ohmic or a Schottky contact.

#### 2.6.1 Ohmic contact

A perfect ohmic contact has no energy barrier to charge carrier flow between the semiconductor and metal in either direction. Therefore, current will increase linearly through the semiconductor-metal junction with applied potential, following Ohm’s law ($V = IR$, voltage = current × resistance).

Ohmic contacts can easily be made on heavily doped diamond. This is because metallic or near-metallic doping of diamond means that whilst there is a barrier at the surface statistically a large number of charge carriers can be injected through a few nm of the depletion region into the device, without non-linear phenomena being observed [191]. As the boron doping concentration decreases ohmic contact formation becomes more difficult. A tunnel contact is formed at any dopant concentration
where the depletion region that results from the work function differences between the metal and semiconductor can be measured in nm- or quantum-like dimension. In this case, the wave property of the electronics supersedes the classical particle picture of an electron. Under such circumstances the electron wave will penetrate the barrier and begin to decay. Provided the barrier is sufficiently thin, the wave will not have decayed to zero before emerging onto the other side. Thus, electrons forbidden in classical physics will have ‘quantum mechanically tunnelled’ through the barrier [33]. This is most easily achieved by using very high doping levels since depletion layer width directly relates to doping level.

Ohmic contacts are commonly made on diamond with titanium/platinum/gold or titanium/gold. Once the metal stack is deposited the sample is annealed between 400 - 700 °C to form a carbide at the interface with the diamond, which reduces the contact resistance [130]. The platinum is added to form a diffusion barrier that prevents poisoning of the titanium by gold. Ohmic contacts have been also achieved on diamond when some damage or graphitisation has been created at the diamond-metal interface. However, this process is destructive and is reported to result in fragile, noisy contacts [181].

### 2.6.2 Schottky contact

In a Schottky contact there is an energy barrier to charge flow between the semiconductor and metal in one direction. Therefore, when a potential is applied across the semiconductor-metal junction the barrier height will either reduce or increase [43]. For example, in a p-type semiconductor when a positive bias is applied to the metal, the energy barrier will increase and the current will be reduced towards zero. If a negative bias is applied to the same sample the energy barrier would be reduced and the current would increase with larger applied bias. The barrier height of different metals on the semiconductor will be dependent on processing, temperature requirements and the desired application for the device. Common metals used to make Schottky contacts on diamond are molybdenum, zirconium and aluminium [181][188][186]. However, it has been shown that for aluminium contacts the barrier heights will decrease and the contact will become ohmic-like after annealing above 700 K [46].
Electrochemical detection

Traditionally, the analytical methods used for the trace detection of heavy metal ions include gas chromatography-atomic fluorescence spectroscopy (GC-AFS), inductively coupled plasma mass spectrometry (ICP-MS) and flame atomic absorption spectrometry (FAAS) \[5\]\[23\]. These techniques are associated with complex instrumentation, high costs and require skilled personnel for their operation \[5\]. In contrast, electrochemical detection is relatively low cost, with simple instrumentation and it is well suited to in situ analysis.

Electrochemical detection uses the charge transfer between an electrode and electrolyte during the oxidation or reduction of one or more species in the electrolyte to determine the concentration of those species. For each electrode material the charge transfer will occur at a characteristic potential for each species that is oxidised or reduced. When both processes occur, the potential difference between the oxidation and reduction of the species gives insight into the kinetics of the reaction.

3.1 Electrodes

During electrochemical measurements the concentration of the species of interest is probed with a working electrode (WE), conventionally made from a material that is chemically inert and a good conductor, such as gold, platinum or carbon. The potential of the WE is measured against a non-polarisable reference electrode (RE). The RE contains a stable redox couple in which the concentration of each soluble component is saturated, so remains constant \[194\]. This means that any changes in the electrochemical cell can be ascribed to the WE. Commonly used REs include the saturated calomel electrode and the Ag|AgCl electrode \[9\].

In a two electrode system (WE and RE) current flows through the RE. In the case of the Ag|AgCl RE, current flowing through the electrode will cause the chloride ions to be oxidised and Ag will rapidly convert to AgCl, until eventually all of the Ag and Cl\(^{-}\) will have reacted and the reaction will stop (Equation 3.1).
3.1. Electrodes

\[ \text{Ag} (s) + \text{Cl}^- (aq) = \text{AgCl} (s) + e^- \] (3.1)

In a three electrode system (WE, RE and counter electrode (CE)) the addition of the CE enables the flow of current between the WE and CE, without compromising the RE, which allows current and potential to be applied and measured independently. The surface area of the CE should be much larger than the surface area of the WE, as this prevents the reaction at the WE from being limited [9]. A supporting electrolyte, which contains a non-electroactive species such as potassium chloride (KCl), is used to prevent ohmic drop (solution resistance) between the electrodes [194].

Each electrode is connected in a circuit with a potentiostat, shown in Figure 3.1. The current at the WE can be measured independently due to the inclusion of a low impedance ammeter at the CE and a high impedance voltmeter, which prevents the flow of current at the RE [9].

**Figure 3.1:** Diagram of a three electrode cell, modified from [9].

A pseudo-RE can be used in place of a traditional RE, when the conditions inside the electrochemical cell are known. Platinum and silver wires are commonly used as pseudo-REs [77]. Most standard REs work over a limited range of conditions (for example pH and/or temperature), outside of which the behaviour of the electrode is unpredictable so cannot be used as a reference. Whereas, a pseudo-RE will not maintain a constant potential, but will vary predictably with changing temperature or pH inside the electrochemical cell [9]. This means that by taking account of the variation in potential of the pseudo-RE it can be used to accurately study systems over a much wider range of experimental conditions. Another advantage of using a pseudo-RE is that there is no contamination of the electrolyte by solvent molecules or ions, which could occur with a traditional RE [77].
3.1. Electrodes

Pseudo references can also be used for electrochemical measurements in non-aqueous electrolytes. The International Union of Pure and Applied Chemistry (IUPAC) first recommended using the ferrocene/ferrocenium (Fc/Fc\[^{+}\]) redox couple for this purpose in 1984 [58]. When a redox couple is used as a pseudo reference it is added to the electrolyte after the positions of the peaks corresponding to the electrochemical reaction in its absence have been established. This ensures that there will be no peak overlap once the redox couple is added. The peaks in subsequent plots are then aligned so that the position of the reference redox couple is constant, with the central point between the oxidative and reductive peak at 0 V (Figure 3.2) [50]. Conventionally a one electron redox process, such as Fc/Fc\[^{+}\], is chosen because the separation between the oxidation and reduction peaks of the pseudo reference will remain constant at 59 mV [24].

![Figure 3.2: Demonstration of how a) raw data from two electrochemical measurements using a pseudo reference system are re-scaled in b) by taking account of the variation in potential of the pseudo reference redox couple (in the red-dashed box) and adjusting the CV sweeps so that the potential at which the pseudo reference redox couple occurs is consistent.](image)

3.1.1 Diamond electrodes

BDD has the widest electrochemical window of any known electrode material. This is the potential range that can be applied across the electrode before the onset of either oxidation or reduction of water at its surface, in an aqueous environment [109][179]. Diamond electrodes also offer reduced fouling during use compared with other electrodes. This is due to the chemically inert and physical nature of diamond which make it difficult for organic species to ‘stick’ to diamond surfaces. When allied to the low background and capacitive currents associated with the material these properties make BDD electrodes ideally suited to the trace detection of analytes [109]. Further, the ability of BDD to withstand extreme temperatures and
pressures and being radiation hard makes BDD an exceptional electrode material for use in extreme environments. However, these properties can be affected by the conditions of BDD growth. For example, it has been shown that in CVD growth the rate at which boron is included affects the electrochemical response of a BDD WE [190].

Arguably, an ideal BDD electrode would solely consist of sp\(^3\) carbon bonds as the inclusion of non-diamond sp\(^2\) carbon (NDC) can alter the catalytic activity at the electrode surface. Although, the presence of some NDC on the surface of a BDD electrode can be advantageous for some applications [68][180][197]. In general, an optimum BDD electrode will have a low NDC content so that the excellent properties of diamond for electrochemistry can be exploited and a boron dopant concentration of at least 10\(^{20}\) B atoms cm\(^{-3}\) in order to produce degenerate doping and semi-metallic properties.

The surface termination of BDD can have a great impact on the electrochemical response, as this influences the electron transfer kinetics at the WE and alters the wetting properties of the BDD. Oxygen terminated BDD is electrochemically stable over a longer period of time than hydrogen, so it is often recommended that electrochemical measurements are performed with oxygen terminated BDD [109]. Also, it has been reported that the BDD electrochemical window is wider when oxygen terminated than when hydrogen terminated, which allows a wider range of analytes to be detected [187]. However, for applications where gold nanoparticles (AuNPs) are deposited onto the BDD surface (where they can act as a catalytic centre assisting the electrochemical process, see later) a hydrogen terminated surface may be more appropriate. AuNPs have been shown to have stronger adherence to hydrophobic surfaces and specifically to BDD surfaces when they are hydrogen terminated, compared to oxygen terminated BDD [2][178]. This is due to a combination of the electrostatic and hydrophobic interactions between the AuNPs and the diamond surface when it is hydrogen terminated, which result in the formation of a non-covalent bond [80][106].

3.2 Principles of electrochemistry

3.2.1 Electrode/solution interface

When a three electrode system is used for electrochemical analysis the chemistry of interest occurs at the interface between the electrolyte and the surface of the WE.

Helmholtz proposed a simple model to describe the electrode/electrolyte interface in 1853, which assumes that no Faradaic processes occur between a metal
3.2. Principles of electrochemistry

In the Helmholtz model charge neutrality is maintained because the charge density at the metal electrode surfaces, which is a result of an excess or deficiency of electrodes, is counteracted by an opposite charge in the solution at the interface. The charge in the electrolyte is a result of the redistribution of ions at the electrode/solution interface or reorientation of the dipoles in the solvent molecules. Ions in the electrolyte are assumed to have a solvation shell. When water is the solvent a hydration shell forms, in which H$_2$O molecules surround the ions as a result of charge–dipole interaction. The solvation or hydration cell surrounding the ions limits how close the ions can get to the electrode surface [56]. The minimum distance between the electrolyte ions and the electrode is known as the outer Helmholtz plane (OHP), see Figure 3.3a. There is a potential difference across region between the electrode ($\Phi_m$) and the OHP ($\Phi_{OHP}$), known as the charge double layer. The potential drops linearly across the charge double layer from the electrode to the OHP, where the potential of the bulk electrolyte is reached ($\Phi_s$) (Figure 3.3b) [48].

The Helmholtz model was refined by Gouy and Chapman, who independently proposed that the excess charge density in the electrolyte is not solely located at the OHP. They hypothesised that the ions in the OHP would disperse by Brownian
3.2. Principles of electrochemistry

Figure 3.4: a) The Gouy–Chapman model and b) the corresponding potential drop with increasing distance from the electrode surface, modified from [48].

Figure 3.5: a) The Stern model and b) the corresponding potential drop with increasing distance from the electrode surface, modified from [48].
motion in the electrolyte [48]. The Gouy—Chapman model therefore includes a diffuse layer, instead of a single plane (Figure 3.4a). The charge in the diffuse layer is most concentrated at the minimum distance to the electrode that the ions can occupy, which corresponds to the location of the OHP in the Helmholtz model.

In 1924 Stern combined the Helmholtz and Gouy-Chapman models. The Stern model proposes that there is a layer of ions at the OHP, with a linear drop in potential from the electrode to the OHP, then a diffuse layer from the OHP further into the solution ($\Phi_s$) that has a gradual drop in potential (Figure 3.5) [56].

In 1947 Grahame made an addition to the Stern model, to propose that although the region closest to the electrode surface will mostly contain solvent molecules it is possible for some ions to lose their solvation shells and directly contact the electrode surface through ‘specific adsorption’. The adsorption is ‘specific’ because only certain ions are adsorbed and the adsorption is often unrelated to the charge of the ion [48]. The ions closest to the electrode surface are defined as sitting in the inner Helmholtz plane (IHP), see Figure 3.6.

Figure 3.6: a) The Grahame model and b) the corresponding potential drop with increasing distance from the electrode surface, modified from [48].
3.2. Principles of electrochemistry

3.2.2 Mass transport

The rate at which reactants and products move toward or away from the WE surface is controlled by mass transport, which has three modes: diffusion, migration and convection [63].

Diffusion occurs when there is a concentration gradient between the bulk electrolyte and the electrode surface, which is induced by redox processes at the surface of the electrode. The rate of diffusion is dependent on the magnitude of this concentration gradient.

Migration is the movement of charged particles in response to a local electric field. An example of a local electric field is the potential drop between the electrode surface and bulk electrolyte discussed in section 3.2.1. When a charge-transfer process occurs at the electrode surface this can affect the local electric field, leading to a change in the mass transport of charged particles by migration. This makes migration difficult to model and causes the electrochemical reaction to be difficult to interpret. Therefore, migration is suppressed during electrochemical measurements by the use of a chemically and electrochemically inert, highly conducting supporting electrolyte at a concentration of 0.1 M, or roughly $100 \times$ the concentration of the analyte of interest. The ions in the supporting electrolyte allow electroneutrality to be maintained and prevent the buildup of electric fields in the solution [48].

Convection can be natural or forced. Natural convection occurs due to thermal gradients or a variation of densities in the solution, which can be difficult to predict. Therefore, natural convection is normally reduced during electrochemical measurements by using a stagnant solution without any gradients, controlling the environment to reduce mechanical vibrations and limiting the experiment time [24]. Forced conduction is commonly achieved by mechanical stirring of the solution, bubbling gas through the solution or pumping the solution through a flow loop. Forced convection is used to overwhelm any natural convection, therefore, ensuring that the experiment is reproducible over longer experiment times $>20s$ [48].

The movement of reactants and products toward and away from the WE is a complex function of the three modes of mass transport. However, in the majority of experiments the migration of particles is suppressed by inclusion of a supporting electrolyte and convection of particles is suppressed by taking measurements in a static system. This means that the sole mode of mass transport of ions in solution is diffusion, which allows the current in the cell (i) to be described by Equation 3.2, in which $n$ is the number of electrons in the redox reaction, $F$ is the Faraday constant, $D$ is the diffusion coefficient for the species reacting at the WE, $C_{bulk}$ is
3.3. Electrochemical methods

3.3.1 Linear sweep voltammetry

Linear sweep voltammetry (LSV) is the simplest electrochemical method. In LSV the potential sweep starts at a potential where no electrolysis occurs and is then increased or decreased at a constant rate (Figure 3.7a). Therefore, the potential at any time during the experiment is given by addition of the initial potential applied and the product of scan rate and time (Equation 3.3). Where \( E_0 \) is the initial potential, \( \nu \) is the scan rate and \( t \) is time.

\[
E(t) = E_0 + \nu t
\]  
(3.3)

A typical voltammogram that results from an LSV experiment is shown in Figure 3.7b. The Faradaic current starts to flow once the potential reaches the value at which electrolysis begins. The potential continues to increase or decrease and the electroactive species at the WE surface is oxidised or reduced, which lowers the concentration of the electroactive species until its concentration at the WE surface reaches zero. At this point the observed current reaches a maximum point \( (I_p \text{ in Figure 3.7b}) \), as the mass transfer of the reactant from the bulk electrolyte to the WE reaches a maximum. As the potential is increased or decreased past this point the depletion of the reactant species causes the diffusion layer at the WE surface to become thicker and the observed current decreases [9].

Electrochemical reactions are classed as reversible with fast kinetics, or quasi-reversible/irreversible when the kinetics of the reaction are slow. As seen in Figure 3.8a, when the reaction kinetics are fast compared to all of the scan rates used then increasing the scan rate results in the peak current increasing, at a consistent potential. When the scan rate is higher the LSV scans take less time to perform. This means that the diffusion layer at the surface of the WE develops for a shorter time (so is thinner than it would be if a slower scan rate was used) which leads to a higher current being recorded. For a reversible redox reaction the height of the current peak(s) increases with increasing scan rate in the relationship: \( I_p \propto \nu^{1/2} \)
3.3. Electrochemical methods

Figure 3.7: a) A typical waveform from a LSV experiment and b) an example of the voltammogram that results from a LSV experiment.

where \( v \) is the scan rate and \( I_p \) is the peak current [9].

This relationship is not true for quasi-reversible or irreversible reactions, in which the kinetics of the reaction are slow compared to the scan rate used. As seen in Figure 3.8b, when the rate constant decreases the peak current position shifts. This shift occurs because no current flows until the applied potential is large enough to induce electron transfer, causing a delay in the establishment of equilibrium at the potentials swept [48]. Whereas, when the electrode kinetics are reversible the reaction will take place as soon as it is thermodynamically viable. For a quasi-reversible or irreversible reaction the electron transfer rate constants can be estimated by analysing the variation of the peak position with each scan rate when multiple scan rates are used.

Figure 3.8: Example LSV plot showing the effect of a) increasing the scan rate used during a LSV sweep of a reversible reaction and b) when the rate constant of a quasi-reversible or irreversible reaction decreases.
3.3. Electrochemical methods

3.3.2 Cyclic voltammetry

Cyclic voltammetry (CV) is one of the most commonly used electrochemical techniques, in which a potential is applied and the resultant current is measured. The applied potential can be used to drive an electrochemical reaction, such as the one electron redox in Equation 3.4.

\[
A_{(aq)} + e^{-} \overset{k_{\text{red}}}{\underset{k_{\text{oxd.}}}{\rightleftharpoons}} B_{(aq)} \quad (3.4)
\]

CV is conducted in a stationary solution, so relies on diffusion for the transport of material to the electrode surface due to concentration gradients [48]. The potential of the WE is swept linearly in one direction from potential \(E_1\) where no reaction occurs to \(E_2\) where the electron transfer is driven rapidly. The direction of the potential sweep is then reversed so that it returns to the original potential \(E_1\), this gives the triangular potential cycle, shown in Figure 3.9a.

![Figure 3.9: a) A typical waveform from a CV experiment and b) an example of the cyclic voltammogram that results from a CV experiment for a reversible system.](image)

The resulting current at the WE is measured by the potentiostat and a cyclic voltammogram (an example of which is shown in figure 3.9b) is generated by plotting the measured current against the applied potential. As shown, for B to be oxidised back to A (from Equation 3.4) an overpotential is required, as the oxidation potential \(E_{p \text{ oxd.}}\) occurs at a lower potential than the reduction potential \(E_{p \text{ red.}}\). For a one electron redox couple (such as Fc/Fc\(^+\), see section 3.1) at 298 K the offset between the oxidation and reduction potentials \((\Delta E_p)\) is 59/n mV, where \(n\) is the number of electrons transferred, as described by the Nernst equation (Equation 3.5) [24]. The components of the Nernst equation are the electrochemical cell potential \(E\) (at the temperature of interest), the standard cell potential \(E^0\), the universal
gas constant R, temperature T, number of electrons n, the Faraday constant F and the activities of the oxidised (Oxd.) and reduced (Red.) species in the system at equilibrium [42].

\[
E = E^0 + \frac{RT}{nF} \ln \left( \frac{\text{Oxd.}}{\text{Red.}} \right)
\]  
(3.5)

The shape of the cyclic voltammogram is diffusion controlled. During the forward sweep from \(E_1\) to \(E_2\) the current initially increases as there is a high concentration of B present in the diffusion layer between the WE and the bulk electrolyte that is available to be reduced (Figure 3.9b). The kinetics of the conversion from A to B becomes more favourable as the potential increases, until the point at which all of the B species in the diffusion layer has been reduced to A and therefore the current drops [48]. The height of the current peaks increase with increasing scan rate in the relationship: \(I_p \propto \nu^{1/2}\) where \(\nu\) is the scan rate, whereas the potential of the peaks are independent of scan rate [9]. The relationship between the scan rate and height of the current peak is the same as for a LSV experiment, which is discussed fully in section 3.3.1.

3.3.3 Square wave anodic stripping voltammetry

Although CV is a commonly used analytical tool, other electrochemical techniques such as stripping voltammetry are more suited to the trace detection of analytes due to their sensitivity, which can be up to three orders of magnitude higher [36][11]. In addition, when this technique is used with a BDD electrode (which has higher sensitivity and longevity than conventional glassy carbon electrodes) a wider range of analytes can be detected due to the wide band gap and electrochemical window of BDD [116].

Unlike CV, with stripping voltammetry the metal of interest is electroplated onto the WE, by applying a sufficiently reducing potential. The applied potential is then scanned in a positive direction, which causes the deposited metal to be oxidised and stripped from the electrode surface, generating a peak in the measured current [11]. The position and magnitude of this peak can be used to identify the metal and determine its concentration in the solution.

Anodic stripping voltammetry (ASV) is the most common technique for the trace detection of heavy metals. In this work square wave-ASV (SWASV) has been used because this technique allows for rapid potential sweeping without interference from double layer currents on the surface of the WE, therefore, improving the
Figure 3.10: Simplified schematic of a SWASV measurement, showing a) the electrodeposition of the metal of interest onto the WE (mercury in this example) and b) stripping voltammetry, where the solid metal is stripped from the surface of the WE due to the application of a suitably oxidising potential, resulting in the characteristic stripping peak for that metal.

signal to noise ratio [90]. There are four steps to SWASV measurements. In step one the metal of interest is pre-concentrated onto the surface of the WE by applying a sufficiently reducing potential. The potential, time, stirring, temperature and electrode area variables in this step are carefully controlled to ensure reproducible results are possible. In the second step the electrochemical cell is held at the initial potential for a period of time, with no stirring, to allow the diffusion layer to recover and the electroplated metal to homogenise on the WE surface [11]. Following this, an oxidising potential is applied and the metal of interest is stripped from the electrode surface. Finally, in the fourth step the WE surface is cleaned in preparation for a repeat SWASV run by holding the electrochemical cell at a sufficiently oxidising potential to remove any remaining metal at the WE.
Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a powerful technique that can detect small changes that occur at the electrode-solution interface in an electrochemical system. In an electrochemical process different reaction steps will dominate at certain frequencies and by using EIS measurements across a broad frequency range the response can be used to identify any rate limiting steps. This technique is relatively low cost and combines rapid measurements, low detection limits and the ability to perform real-time monitoring of samples. These factors make EIS a valuable tool in many scientific fields, including corrosion, battery, fuel cell and coatings analysis. EIS can be used to identify degradation of an electrode over time, as the charge transfer characteristics will change as the electrode surface degrades.

4.1 Impedance

For a direct current (DC) voltage only a resistor will obstruct the current, following Ohm’s Law (Equation 4.1), where $E$ is the applied potential, $I$ is the resulting current and $R$ is the resistance.

$$E = IR \quad (4.1)$$

For an alternating current (AC) voltage there are additional elements such as capacitors and inductors that influence the electron flow. These elements will affect the magnitude and phase of the AC waveform. For an AC current with a frequency greater than zero Ohm’s law is represented by Equation 4.2, where $E$ is the potential, $I$ is the current, and $Z$ is the impedance.

$$E = IZ \quad (4.2)$$
Like resistance, impedance obstructs current flow and has a magnitude, but impedance also has a phase, due to any capacitive (reactance) elements present. Impedance can be thought of as being made up of two components: resistance ($Z'$) and reactance ($Z''$). The resistance is the opposition to electrical current of the materials that the electrons travel through and is independent of frequency. The reactance is an imaginary component that opposes a change in current and is frequency dependent [154]. As the total impedance has both a real and imaginary component it must be expressed as a complex number. There are of course additional elements used in EIS, which relate to the diffusion (Warburg impedance) in electrochemical systems and the non-ideal characteristics of electrode surfaces (constant phase element). These are discussed in section 4.4.

### 4.2 Electrochemical impedance spectroscopy (EIS)

![Figure 4.1](image)

**Figure 4.1:** a) The incident sinusoidal AC potential and b) the measured current response in a linear system. The phase difference (phase angle) and amplitude of the measured current oscillation have been highlighted.

EIS measurements are normally made in a three electrode electrochemical cell, with a working electrode, reference electrode and counter electrode. The three electrode system compensates for the solution resistance between the reference and counter electrodes [9]. In a potentiostatic EIS experiment, an AC potential is applied as a sinusoidal wave between the working and reference electrodes. The current is carried through the electrolyte, which is measured between the working and counter
4.2. Electrochemical impedance spectroscopy (EIS)

Electrodes. The phase shift, amplitude and real and imaginary parts of the current response are recorded (Figure 4.1) [132]. The measured current is linearly proportional to the applied potential (Equation 4.2) and the value of impedance depends on the frequency at which the potential oscillates.

The oscillating wave can be expressed as (Equation 4.3), where \( E_t \) is the potential at time \( t \), \( E_0 \) is the amplitude and \( \omega \) is the angular frequency, which is \( 2\pi \) times the conventional frequency in Hz [9].

\[
E_t = E_0 \sin(\omega t) \tag{4.3}
\]

In a linear system, the current response will be shifted in phase and have a different amplitude than the incident potential (Figure 4.1), which is expressed as:

\[
I_t = I_0 \sin(\omega t + \phi) \tag{4.4}
\]

where \( I_t \) is the current at time \( t \), \( I_0 \) is the amplitude of the signal, \( \omega \) is the angular frequency and \( \phi \) is the phase angle [9]. By combining Equations 4.3 and 4.4 using Ohm’s law, the total impedance of the system can be measured, with the expression:

\[
Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = \frac{Z_0 \sin(\omega t)}{\sin(\omega t + \phi)} \tag{4.5}
\]

Therefore, the impedance is expressed in terms of a magnitude (\( Z_0 \)) and a phase angle (\( \phi \)) [51]. However, as the impedance has both a real and imaginary component it must be expressed as a complex number. This is done using Euler’s relationship (\( \exp(j\phi) = (\cos\phi) + j\sin(\phi) \)), which makes the expressions for the applied potential and measured current complex functions:

\[
E_t = E_0 \exp(j\omega t) \quad \text{and} \quad I_t = I_0 \exp(j\omega t + \phi) \tag{4.6}
\]

When the complex functions for the applied potential and measured current are then combined using Ohm’s law this is the resultant complex impedance expression:

\[
Z(\omega) = \frac{E}{I} = Z_0 \exp(j\phi) = Z_0(\cos\phi + j\sin\phi) \tag{4.7}
\]
This follows the standard expression for a complex number \( Z = a + jb \), which can be represented in a right hand orthogonal system of axes. Time is no longer part of the expression, as the impedance is independent of time (provided that the system is stable with time) [12]. The imaginary number \( j = \sqrt{-1} = \exp(j\pi/2) \), which on a set of axes corresponds to a \( 2\pi \) anticlockwise rotation from the x-axis. Typically, the real part of the impedance (\( Z' \) or \( a \)) is plotted along the x-axis and the imaginary part of the impedance (\( Z'' \) or \( b \)) is plotted along the y-axis [12]. The complex impedance (\( Z = Z' + jZ'' \)) can therefore be plotted on a graph of \( Z' \) versus \( Z'' \) (Figure 4.2). The phase angle of the total impedance is represented by \( \theta \) and the magnitude of the complex impedance is \( |Z| \).

**Figure 4.2:** The complex impedance (\( Z \)) plotted as a planar vector, modified from [12].

From Figure 4.2 we see that the rectangular coordinates for the real impedance (\( \text{Re}(Z) \)) and imaginary impedance (\( \text{Im}(Z) \)) components of the complex impedance are:

\[
\text{Re}(Z) = Z' = |Z| \cos(\theta) \quad \text{and} \quad \text{Im}(Z) = Z'' = |Z| \sin(\theta) \quad (4.8)
\]

The magnitude of the impedance is given by \( |Z| = \sqrt{(Z')^2 + (Z'')^2} \) and the phase angle of the impedance (\( \theta \)) is expressed as Equation 4.9 [12].
4.3 Analysing EIS data

Before EIS data is analysed with Bode plots, Nyquist plots and equivalent circuit modelling, the suitability of the raw data for analysis by these methods must be assessed with a Lissajous plot and a Kronig-Kramers test.

4.3.1 Lissajous plot

A Lissajous plot can be used to monitor the progress of an EIS experiment in real time and to identify potentially erroneous data. This is important because the Bode and Nyquist plots used to analyse EIS data are representations of processed data, so if a system does not respond as expected it can be difficult to use them to determine the cause, such as due to a non-linear response or noisy data [121]. A Lissajous plot combines the input and output signals on a single current vs potential plot (Figure 4.3). The shape of this plot will vary depending on the system studied, the applied frequency and the amplitude. These plots are helpful in identifying noise in electrochemical systems, which are susceptible to external noise pick up, as the Lissajous plot will appear noisy in this case [12].

\[
\theta = \tan^{-1} \left( \frac{Z''}{Z'} \right)
\]  

(4.9)

**Figure 4.3**: A typical Lissajous plot for a stable electrochemical system, modified from [12].

For a stable, linear electrochemical system there will be either a tilted oval or straight diagonal line on the Lissajous plot, that is repeatedly traced over with
each new frequency measured. For standard EIS measurements, the system must be linear (or pseudo-linear) to ensure that the response to the applied sinusoidal potential is at the same frequency, but shifted in phase [51]. In the case of a non-linear system the Lissajous plot would not be symmetrical.

4.3.2 Kronig-Kramers test

In addition to a Lissajous plot, a Kronig-Kramers (KK) test can be used to identify potentially erroneous data. A KK test is used to determine if the electrochemical system satisfies the conditions of being linear, causal and stable [140]. In a linear system the response is first order, so does not change with larger applied potentials. In many electrochemical systems the current varies non-linearly with the applied potential, however, if the amplitude of the applied potential is kept as low as possible (<10 mV) the response can be kept as linear as possible [93][22]. The system must be causal, meaning that the response is only a result of the applied potential. The system must be stable, so that the response does not change with time or continue to change once the applied perturbation has been removed. If the electrochemical system does not satisfy these conditions then it will not be possible to fit the raw data to an appropriate equivalent circuit for analysis.

The KK relations are integral equations which connect the real and imaginary parts of a complex function. The interdependence of the real and imaginary parts of the impedance are presented in the KK transform integrals (Equations 4.10 and 4.11) [22]. In these, $Z_{re}$ is the real impedance, $Z_{im}$ is the imaginary impedance, $R_\infty$ is the resistance of the electrolyte, and $\omega$ is the angular frequency.

\[
Z_{re}(\omega) = R_\infty + \frac{2}{\pi} \int_0^\infty \frac{xZ_{im}(x) - \omega Z_{im}(\omega)}{x^2 - \omega^2} dx \tag{4.10}
\]

\[
Z_{im}(\omega) = \frac{2\omega}{\pi} \int_0^\infty \frac{Z_{re}(x) - \omega Z_{re}(\omega)}{x^2 - \omega^2} dx \tag{4.11}
\]

The data from a stable system must adhere to these transformation rules. If the real and imaginary parts of the impedance in both integrals do not match up then the data set must be considered to be non-linear or to vary with time, and therefore be unsuitable for EIS analysis using equivalent circuit modelling.

The main problem with using the KK transformation is the need to integrate over the frequency range 0 - $\infty$. To address this issue, the measured impedance data is modelled with a chain of series connected, parallel RC circuits (a Voigt circuit,
see Figure 4.4) [22]. The number of data points is equal to the number of RC parallel sub-circuits in the chain. When very noisy data is suspected, a reduced number of RC sub-circuits can be used to avoid over-fitting of the data, which would include the noise into the model [123]. Each RC circuit is KK transformable, so the entire circuit must also be KK transformable [22]. Therefore, if the experimental data can be modelled with the Voigt circuit (with a certain allowable error limit) then the data must obey the KK test conditions of being stable, causal and linear.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{equivalent_circuit.png}
\caption{The equivalent circuit model for the Kronig-Kramers test of experimental impedance spectroscopy data, modified from [22].}
\end{figure}

### 4.3.3 Bode plot

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{bode_plot.png}
\caption{Example of a Bode plot, depicting the magnitude and phase angle of the complex impedance of an electrochemical cell as a function of frequency, modified from [60].}
\end{figure}

The Bode plot is a plot of the magnitude of the total impedance of the system
4.3. Analysing EIS data

and the phase angle shift of the observed current against the frequencies at which the EIS measurements were made (Figure 4.5). These plots enable identification of the total impedance behaviour as a function of frequency and are commonly used in corrosion analysis. The total impedance can indicate corrosion formation on a sample surface and for this purpose it is not necessary for the individual components of the impedance to be de-convoluted [154]. An advantage of Bode plots is that impedance at high frequencies is presented with equal weight to low frequency impedance, whereas, in a Nyquist plot the high frequency information tends to bunch together towards the high frequency intercept on the Z’ axis (real impedance contribution, see Figure 4.6a) [12]. However, Bode plots are limited because it is not possible to extract information about the individual impedance components from them, so they are less commonly used to present data for electrochemical sensors.

When a Bode plot is used to represent data from EIS measurements the general trends in each frequency region can be used to identify some characteristics of the electrochemical system analysed. For example, in the exemplar provided in Figure 4.5: at high frequencies (right hand side) the impedance curve reaches a horizontal amplitude, meaning that at this point the impedance is independent of frequency, and the phase angle tends to 0°. This is the classic response of uncompensated resistance, which will predominantly correspond to the solution resistance through the electrolyte (R_s, series resistance) [60]. In the low frequency region of this example plot (left hand side) the characteristics of the two curves correspond to the total impedance of the system, with a horizontal, linear amplitude in the impedance and a phase angle of 0° [144]. In the centre of the example Bode plot, in the middle frequency region, the impedance is linear (slope close to -1) and the phase angle tends towards -90°. This is the characteristic response of a capacitor [60]. In the case of an EIS experiment this corresponds to the double laye capacitance at the surface of the working electrode.

4.3.4 Nyquist plot

A common presentation of EIS data is the Nyquist plot (known as a Cole-Cole plot in solid state systems) which shows the relationship between the real (Z’) and imaginary (Z”) components of the total impedance (Figure 4.6a). The real component of the impedance is the opposition to electrical current of the materials that the electrons travel through and is independent of frequency. The imaginary component of the impedance opposes a change in current and is frequency dependent. When imaginary impedance is present it causes a 90° phase shift between the voltage and current, with the direction of the shift dependent on whether the component is an
4.3. Analysing EIS data

inductor or a capacitor [154].

![Nyquist plot diagram](image)

**Figure 4.6:** a) Example of a Nyquist plot, depicting the real and imaginary components of the total impedance of an electrochemical cell and b) the corresponding simple Randles equivalent circuit, modified from [154].

Each point on a Nyquist plot corresponds to a measurement at a different frequency, with higher frequencies on the left hand side of the graph close to the origin and lower frequencies on the right hand side. A major shortcoming of the Nyquist plot representation of EIS data is that it is not possible to determine the exact frequency at which each plotted impedance was measured. The semi-circle on the example Nyquist plot (Figure 4.6a) represents the complex impedance of a diffusionless electrochemical system, with solely kinetic control, that can be modelled by the simple Randles circuit (Figure 4.6b) [154]. The dominating components of the total impedance in this example are \( R_s \), the solution resistance of the electrolyte, \( R_{ct} \), the charge transfer resistance due to a Faradaic process and \( C_{dl} \), the double layer capacitance at the surface of the working electrode. The limiting cases of the Nyquist plot (Equation 4.12) and the condition at the peak of the curve (\( \omega R_{ct} C_{dl} = 1 \)) allow the values of the capacitance, effective series and parallel resistances of the working electrode material to be obtained by numerical fitting of the semi-circle(s) on the Nyquist plot to the measured data.

\[
Z(\omega \to 0) = R_s + R_{ct} \quad \text{and} \quad Z(\omega \to \infty) = R_s
\]  

(4.12)

At intermediate frequencies between these limiting cases the impedance will
have a value between $R_s$ and $R_s + R_{ct}$, so will have both real and imaginary components. This produces the semi-circle shape of the plot. When there is more than one electrode process that results in an impedance change, on different timescales, multiple concurrent semi-circles (with different diameters and heights) will be displayed on the Nyquist plot [154].

When a system with combined kinetic and diffusion control is analysed with a Nyquist plot the diffusional impedance is represented by an additional diagonal line (slope 45°) that corresponds to the Warburg impedance (see Figure 4.11). The Warburg impedance is discussed in section 4.4.2.

### 4.4 Equivalent circuit modelling

Fitting experimental EIS data to an equivalent circuit enables precise determination of the kinetic and electrical parameters within the electrochemical cell. EIS is most useful when measuring parameters in well understood systems that can be fit to a single fully understood equivalent circuit. EIS analysis is limited for more complex or poorly understood electrochemical systems, for which more than one equivalent circuit gives an equally good fit to the data. Designing an equivalent circuit in which each component corresponds directly to the electrochemical system is crucial, as stated by IUPAC in 1994 it is “definitely wrong to analyze experimental impedance data by just fitting to an equivalent circuit corresponding to a network chosen by trial and error” [168]. This is because the impedance response of several different equivalent circuits can follow the same frequency, with different interpretations of the corresponding elements. With an unlimited number of parameters a random circuit can be made to fit almost any data set, however, without having an a priori model the meaning of the parameters in the circuit will be undefined and give no useful information about the electrochemical system [12].

#### 4.4.1 Common circuit elements for equivalent circuit modelling

The standard circuit elements used to build up an equivalent circuit model for EIS experimental data are resistors, capacitors, and inductors. A constant phase element (CPE) or Warburg impedance (W) can be added to aid the modelling of non-ideal capacitive or diffusion characteristics in the measured data respectively [29].

##### 4.4.1.1 Resistor

A resistor is a basic circuit element that models resistance and follows Ohm’s law ($E = IR$). It has no frequency dependence. The impedance of a resistor has only a real value and no imaginary component ($Z = R$) [140]. Therefore, the imaginary value of the impedance will always be zero and on a Nyquist plot resistance will
4.4. Equivalent circuit modelling

appear as a single point on the $Z'$ (real impedance) axis (Figure 4.7a). On a Bode plot the phase angle will be zero at all frequencies (as the resistor is independent of frequency) and the impedance will be a linear horizontal line at the value of the resistance (Figure 4.7b) [10].

![Figure 4.7: a) The impedance spectrum of an ideal resistor on a Nyquist plot and b) the impedance spectrum of an ideal resistor on a Bode plot, modified from [10].](image)

4.4.1.2 Capacitor

A capacitor is commonly used to represent the double layer capacitance at the surface of the working electrode in an EIS experiment (see Section 3.2.1). The electrode/solution interface acts as a capacitor, as the electrode surface has a charge and the ions in the electrolyte solution immediately adjacent to the surface will have the opposite charge, forming the double layer. Half of the capacitor is made up of ions in solution, which means that it will take time for the double layer to form whilst the ions diffuse through the solution to the electrode surface (at a speed determined by their diffusion coefficient) [48]. This means that there is a time dependence, so impedance must be used in place of resistance in Ohm’s Law ($E = IZ$) [10].

The impedance of a capacitor has only an imaginary component ($Z = 1/j\omega C$) [140]. This means that the real impedance value will be zero at every frequency and so, capacitance on a Nyquist plot will appear as a linear vertical line on the imaginary impedance axis (Figure 4.8a). On a Bode plot, the phase angle will be $-90^\circ$ at all frequencies and the magnitude of the impedance will be represented by a linear line, slope -1, on logarithmic axes (Figure 4.8b) [57].

4.4.1.3 Inductor

An inductor is a circuit element that stores energy in a magnetic field, which is induced when an electric current flows through it. When the electric current is
4.4. Equivalent circuit modelling

Figure 4.8: a) The impedance spectrum of an ideal capacitor on a Nyquist plot and b) the impedance spectrum of an ideal capacitor on a Bode plot, modified from [10].

removed the stored energy is released, as the magnetic field breaks down. The impedance of an inductor has only an imaginary component \((Z = j\omega L)\) and has the inverse response to a capacitor, so the impedance will increase as the frequency increases [140]. The current response will be shifted by +90° at all frequencies and in a Bode plot the inductance will be represented as a slope of +1 [60].

4.4.1.4 Constant phase element

In practice the electrode/solution interface often cannot be represented fully by an ideal capacitor, particularly if the electrode surface is rough or non-homogeneous (such as a polycrystalline material or an electrode coated with nanoparticles) [10]. In this case, a constant phase element (CPE, also represented as Q) is used in place of a capacitor to model the double layer capacitance at the surface of the electrode. A pseudo-capacitive constant is added to the circuit when a CPE replaces an ideal capacitor. This causes a reduction in the imaginary component of the impedance, resulting in the characteristic depression of the semi-circle(s) in the Nyquist plot when a CPE is used [55]. In a Bode plot the presence of a CPE rather than an ideal capacitor is indicated by phase angles of less than 90° at all frequencies [57].

The impedance of a CPE is expressed in Equation 4.13, where \(Y_0\) is a constant that is used to calculate the effective capacitance (see Equation 4.14) and \(N\) is the exponent, which will be in the range 0 - 1 [140].

\[
Z_{CPE} = \frac{1}{Y_0(j\omega)^N} \quad (4.13)
\]

When \(N = 1\), the CPE is equal to an ideal capacitor at the same impedance.
4.4. Equivalent circuit modelling

Figure 4.9: The simple Randles circuit modified by the replacement of the ideal capacitor with a constant circuit element (CPE).

When a CPE is used in place of a capacitor N will have a value between 0.85 and 1. When N = 0.5 the CPE will be the Warburg impedance, which corresponds to the impedance due to the diffusion of electrons between the bulk electrolyte and electrode surface (see section 4.4.2) [121].

The effective capacitance can be calculated from the impedance of the CPE, on the assumption that the effective capacitance is uniform across the surface of the electrode. When the equivalent circuit model is a simple Randles circuit, modified by replacing the ideal capacitor with a CPE (0.85 < N < 1) as in Figure 4.9, the effective capacitance is given by Equation 4.14 [121].

\[
C_{\text{eff}} = Y_0^{\frac{1}{N}} \cdot \left[ \frac{1}{R_s} + \frac{1}{R_{\text{ct}}} \right]^{\frac{N-1}{N}} \tag{4.14}
\]

4.4.2 Randles equivalent circuit

A Randles equivalent circuit is typically used as the basis for equivalent circuit models of electrochemical systems (Figure 4.10) [108]. Without modification, it is suitable for a single step charge transfer process that includes the diffusion of reactants and/or products to the working electrode interface with the electrolyte. The Randles equivalent circuit includes a series resistor (R_s) which corresponds to the series solution resistance through the electrolyte and a parallel resistor (R_{ct}) which represents the charge transfer resistance due to a Faradaic process [60]. The parallel capacitor (C_{dl}) corresponds to the double layer capacitance at the electrode surface. The parallel inductor (Z_W) is a constant phase element that relates to the impedance of electrons due to the diffusion interface between the bulk electrolyte and the electrode surface. The incorporation of the Warburg impedance (Z_W), for
diffusional impedance, makes the Randles equivalent circuit suitable for systems with combined kinetic and diffusion control [154].

![Figure 4.10: The Randles equivalent circuit, modified from [193].](image)

In an infinite medium the Warburg impedance, $Z_W$, takes the form of Equation 4.15, where $Z$ is the impedance, $j$ is the imaginary number $\sqrt{-1}$, $\omega$ is the angular frequency and $\tau$ is the time constant [140].

$$Z = 1/\sqrt{j\omega \tau}$$

(4.15)

As the Warburg impedance scales with the inverse of frequency, the $Z_W$ value will generally be small at higher frequencies and will only be noticeable at lower frequencies (from approximately 10 Hz) as the reactants have to diffuse further at lower frequencies [140]. At high frequencies the timescale is so short that diffusion is not a factor that influences the current and so, the charge transfer kinetics solely dictate the current [9]. On a Nyquist plot the Warburg impedance appears as a diagonal line with slope 45° (see Figure 4.11) and on a Bode plot the Warburg impedance is seen as a phase shift of 45° [154]. The Warburg impedance is visible at low frequencies on a Nyquist plot, when diffusion effects completely dominate the electrochemical reaction mechanism (4.11) [12].

The Warburg impedance element is used in EIS to model semi-infinite linear diffusion, that occurs when the diffusion layer has infinite thickness [129]. In an electrochemical cell this corresponds to the unrestricted diffusion of species in the solution to a large, planar electrode [140]. This is the simplest diffusion situation because only the linear distance from the electrode is considered.
4.5 Further analysis

The ‘performance’ of an electrode can be defined in terms of its electron transfer rate ($k_0$), given in Equation 8.3 [155].

$$k_0 = \left(\frac{RT}{nF}\right) \frac{1}{nSFR_{ct}C_0}$$  \hspace{1cm} (4.16)

In this, R is the universal gas constant, T is the absolute temperature, n is the
number of electrons transferred during the redox reaction, \( F \) is Faraday’s constant, \( S \) is the surface area of the electrode exposed to the electrolyte, \( R_{ct} \) is the electron transfer resistance of the electrode and \( C_0 \) is the concentration of the redox couple in the electrolyte [12][155]. A higher \( K_0 \) value corresponds to higher reactivity of the electrode.
Experimental methods

5.1 Cleaning diamond substrates

The diamond samples were cleaned through the following processes before use. All processes were carried out in a fume hood, with the appropriate safety precautions.

5.1.1 Piranha etch cleaning

A highly oxidising Piranha clean was performed on each BDD substrate upon delivery to remove most organic contaminants such as bacteria and proteins from the diamond surfaces, which may have been deposited during handling or postage of the substrates. The exothermic Piranha solution (which can reach 120 °C) consists of sulphuric acid and hydrogen peroxide, in a 1:1 ratio [189]. The BDD substrates were soaked in the piranha solution for 10 min, before rinsing in five successive reverse osmosis water baths and drying under nitrogen. The Piranha cleaning solution is a strong oxidiser that removes the majority of organic matter, leaving the BDD surfaces predominantly terminated with hydroxyl (-OH) groups and therefore making the substrates hydrophilic.

5.1.2 Degrease

A degreasing process was used to remove non-organic contaminants from the diamond surfaces prior to the oxidising acid clean. In this procedure the substrates were sequentially submerged for 5 min in acetone, followed by isopropanol, then reverse osmosis water for rinsing. The samples were dried under nitrogen.

5.1.3 Oxidising acid clean

Following the degrease, a highly oxidising acid clean was used to remove adventitious carbon, hydrocarbons and graphitic carbon on the surface of the laser cut BDD substrates. The cleaning solution is a saturated solution of ammonium persulphate (20 g) in concentrated sulphuric acid (20 ml) [8]. The BDD substrates were placed into the solution, which was then heated to 200 °C, and held at this temperature
for 20 min. The cleaning solution was left to cool to room temperature before the BDD substrates were transferred to the ‘rinsing’ solution, consisting of ammonium hydroxide (10 ml) and hydrogen peroxide (10 ml), for 10 min. The substrates were then rinsed thoroughly in reverse osmosis water and dried under nitrogen.

5.2 Raman spectroscopy

Raman spectroscopy was used to qualitatively assess the non-diamond carbon (NDC) and boron content within the BDD substrate surfaces, using a Renishaw Raman spectrometer with a 532 nm green laser source. The Raman analysis was performed with 20× magnification, 10 s exposure and an average was taken over ten accumulations for each substrate. The microscope was calibrated using a silicon substrate. WiRE (v 2.0) software was used for data acquisition.

Raman scattering, the inelastic scattering of light, was first observed experimentally by Raman and Krishnan in 1928 as a signal of shifted frequency when monochromatic light was scattered by solid material [152]. However, it was not utilised as a spectroscopic technique to observe the vibrational and rotational frequency modes of a system until the development of lasers in the 1960s [160].

![Figure 5.1: Diagram of the Raman and Raleigh scattering processes, modified from [169]](image)

During Raman spectroscopy a substrate is exposed to a monochromatic light source (laser) which may be absorbed, scattered or pass straight through the material. If the incident photons from the light source have the same energy as the energy gap between the ground and excited states of the material then the photons may be absorbed and the molecule temporarily promoted to the virtual higher energy state. The photon will then be emitted either by Rayleigh scattering, where the molecule will return to the energy level it originated at or by Raman scattering where the photon is inelastically scattered [115]. When the photon is emitted by
5.3 Terminating diamond substrates

Inelastic scattering the molecule will either fall from the virtual energy state to an energy state higher than its origin (Stokes scattering) or to an energy level lower than its original state (Anti-Stokes scattering). As seen in Figure 5.1, during Raman spectroscopy there is an indirect transition between the vibrational energy levels of a material through a virtual energy level, whereas, when infrared absorption is used there is a direct transition between vibrational energy states. Therefore, the wavelength of the incident light is typically in the visible spectrum (close to the infrared region) so that the energy difference between the energy states of a molecule is given by the difference in wavelength of the incident light and the Raman scattered light [169].

In a Raman spectrum the wavelength (cm\(^{-2}\)) plotted corresponds to the shift from the incident photon energy. Vibrational frequencies are specific to the bonds and symmetry of a molecule, meaning that the Raman shift of each molecular bond is indicative of its structure. Raman spectroscopy can therefore be used to identify the molecules and bonding types within the surface of a substrate [115].

Raman spectroscopy is specifically used in this thesis for analysis of the ratio between sp\(^2\) and sp\(^3\) carbon at the surface of the diamond electrodes. This is done by comparison of the height of the characteristic sp\(^3\) diamond carbon peak at 1332 cm\(^{-1}\) and the sp\(^2\) non-diamond carbon G peak at 1575 cm\(^{-1}\), to qualitatively assess the relative proportions of these two carbon bond types. It is not possible to quantify this ratio because the relative intensities of the two peaks are dependent on the grain size, film stress, doping density, and excitation wavelength used [18]. When the wavelength of the light source is in the visible spectrum (380 - 740 nm) the resultant Raman spectrum will over emphasise the sp\(^2\) content because the size of the Raman cross section of graphitic carbon is approximately fifty times larger than for diamond carbon at this wavelength [173][99]. This is advantageous to this thesis, as Raman spectroscopy using an excitation wavelength of 532 nm is very sensitive to sp\(^2\) contamination in an sp\(^3\) lattice [88]. Whereas, if an excitation wavelength in the UV range (100 - 400 nm) was used, then the diamond sp\(^3\) carbon peak would be very prominent and so little information about other carbon bond types would be visible, as the sensitivity of the Raman technique to the sp\(^2\) graphitic G peak decreases with decreasing wavelength of the incident light [199][99].

5.3 Terminating diamond substrates

At the diamond surface one of the four sp\(^3\) bonds of each carbon atom is not part of the carbon lattice so it is left ‘dangling’ and the termination of this bond can be controlled to influence the surface electronic properties of the BDD.
5.3. Terminating diamond substrates

5.3.1 Hydrogen treatment
CVD grown diamond is naturally hydrogen terminated as the ‘dangling’ bonds at the diamond surface bond to hydrogen radicals present in the growth plasma. Hydrogen terminated BDD is reported to have a slightly narrower electrochemical window than when oxygen terminated. However, as hydrogen termination displays greater attachment and adherence to gold nanoparticles (AuNPs) it is more suited to some applications, such as the trace detection of mercury [187][178]. The acid cleaning steps performed on diamond substrates partially oxidise the diamond surface. Therefore, the hydrogen terminated surface may need to be refreshed.

Hydrogen termination was performed in a SEKI Technotron Corp AX5010 Plasma Reactor. The substrates were placed onto a heating stage inside the plasma reactor, under a vacuum of $10^{-5}$ mbar. The substrates were exposed to a hydrogen plasma at 700 °C platen temperature (Williamson Dual-Wavelength Pyrometer), 800 W power, 40 Torr pressure for 10 min. The substrates were then cooled to room temperature under a flow of hydrogen (99.1 sccm).

Similar conditions (hydrogen plasma, 40 mbar pressure, 900 kW microwave power, 10 min) have previously been utilised in an AX6500X Technotron Corp diamond growth reactor to de-wet metal films into nanoparticles [14]. This has the advantage that for nanoparticle production by a de-wetting method (described in section 5.7) the termination of the substrate and de-wetting of the gold layer into AuNPs can be achieved in a single step. However, there can be issues with the reproducibility of this method, with different parameters in the diamond growth reactor being required each time to achieve the same results [13][14]. For this reason the sputtered gold films used to produce AuNPs in this thesis were de-wet using a rapid thermal annealer, see section 5.7.

5.3.2 Ozone treatment
Oxygen termination is commonly used to suppress the hydrogen based surface conductivity of CVD grown diamond. Common routes to terminate diamond with oxygen moieties include anodic oxidation, acid cleaning, oxygen reactive ion etching and ozone treatment. Ozone treatment has been used throughout this thesis as it is a dry process that has a much slower etch rate than oxygen reactive ion etching.

Ozone is a powerful oxidising agent due to the delocalised electrons between the two equivalent O-O bonds, resulting in easy dissociation into O$_2$ and O· radicals ($O_3 \rightarrow O_2 + O^·$). During the ozone treatment the substrates were placed onto a heating stage inside a sealed chamber (ozone cleaner NL-UV253) under a vacuum of $10^{-6}$ mbar. The substrate was heated to 200 °C for 30 min, before the chamber
was filled with O₂ to a pressure of 50 mbar. The ozone radicals were generated inside the chamber with an ozone generator (10 g/h) for one hour. The substrates were left to cool to room temperature under ozone.

5.4 Contact angle measurements

The termination of the BDD substrates were qualitatively assessed with a Kruss DSA1 Contact Angle Goniometer, using reverse osmosis water (18 MΩ-cm resistivity). The Kruss DSA1 v 1.80 drop shape analysis software was used to determine the contact angle θ between the baseline (BDD surface) and the tangent of the water droplet at the three-phase contact point to the BDD surface [92].

\[ \gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \] (5.1)

Contact angle measurements are used to determine the wettability of a surface via the Young equation (Equation 5.1) i.e. how hydrophobic or hydrophilic the surface is. In the Young equation θ is the angle at the three-phase contact point between the tangent of the droplet and the solid baseline, where the interfacial free energy at the liquid-vapour (\( \gamma_{lv} \)), solid-vapour (\( \gamma_{sv} \)) and solid-liquid (\( \gamma_{sl} \)) interfaces are in equilibrium [125].

![Figure 5.2: Schematic of contact angles on hydrophobic and hydrophilic surfaces, modified from [125]](image)

When the contact angle is greater than 90° the surface is hydrophobic and so has poor wettability, whereas an angle <90° shows that a surface is hydrophilic (Figure 5.2). However, there are inaccuracies in the contact angles measured due to hysteresis, which is observed as a result of evaporation and is exacerbated by the small droplet sizes used (conventionally 1 - 10 µl). In addition, it has been shown that the contact angle can be affected by increasing the roughness of the substrate surface [17].
The change in the contact angle of a water droplet on a rough surface is explained by the Wenzel model, which defines the relationship between the roughness of a substrate and its wettability by Equation 5.2, in which $\theta_m$ is the measured contact angle, $\theta_Y$ is the Young contact angle (for a perfectly flat surface) and $r$ is the roughness ratio \[195][198].

$$\cos \theta_m = r \cos \theta_Y$$ \hspace{1cm} (5.2)

The roughness ratio, $r$, is the ratio between the actual substrate surface and the ideal (flat) surface, with $r=1$ for a smooth surface and $r>1$ for a rough surface. This means that on a hydrophobic ($\theta \geq 90^\circ$) rough surface the contact angle will be greater than for a smooth surface because $\theta_m > \theta_Y$. On a hydrophilic ($\theta \leq 90^\circ$) rough surface the contact angle will be smaller than for a smooth surface because $\theta_m < \theta_Y$. Therefore, it is expected that there will be a difference in the contact angles observed on the unpolished substrates (surface roughness $\sim$50 µm) compared to the polished substrates (surface roughness $\sim$50 nm), due to the different values of $r$.

The Wenzel model is an approximation that becomes more accurate when the radius of the water droplet is large compared to the scale of the roughness of the substrate measured \[17\]. In this thesis 4 µl water droplets were used. The radius of a water droplet of this volume is 1.24 mm, which is five orders of magnitude greater than the scale of the roughness of the unpolished substrates and eight orders of magnitude greater than the scale of roughness on the polished substrate surfaces. Therefore, the trends predicted by the Wenzel model are expected to be more accurately observed in the contact angles of the polished substrate surfaces.

### 5.5 Atomic force microscopy

Atomic Force Microscopy (AFM) is a high resolution scanning probe microscopy technique that overcomes the limitation of the scanning tunnelling microscope, which can only be used on conducting or semiconducting substrates. AFM was used in this thesis to measure the AuNPs produced by the gold deposition and dewetting process described in section 5.7.

AFM was developed by Binnig, Quate and Gerber in 1986 \[16\]. In this technique a cantilever with a sharp tip (1-5 nm wide) on a piezo-scanner head is scanned across the substrate surface, resulting in tip deflections when the atoms at the tip of the cantilever experience distance dependent atomic forces from the substrate surface atoms \[64\]. The deflections of the cantilever during a scan are measured by
laser deflection and can be operated with different feedback loops, normally categorised as contact or tapping mode.

In contact mode the tip is rastered across the sample surface at a distance on the order of angstroms from the surface, at which there is a very strong repulsive force between the cantilever tip and the sample. This strong repulsion is a result of the overlap of electronic orbitals which occurs at these sub-atomic distances and is the dominant force in contact AFM. In tapping mode the cantilever vibrates near its fundamental resonance frequency and a time averaged interaction is determined. As the tip is scanned across the sample surface electrostatic forces between the tip and the substrate surface cause the amplitude of the tip to change. The height of the tip is then adjusted to maintain a consistent amplitude. Tapping mode is commonly used for soft samples or when the sample is not well adhered (for example nanodiamonds seeded on silicon) that could be displaced during contact imaging or stick to the AFM tip, causing a tip artefact. Tip artefacts are recurring, anomalous shapes that appear across an AFM image and convey the distorted shape of the AFM tip, not the geometry of the sample surface [157]. Tapping mode is also useful when analysing very hard samples, such as diamond, which will quickly blunt the sharp AFM tip and cause the image quality to degrade. In this thesis PeakForce Tapping mode has been used, in which the cantilever oscillates below its resonance frequency, which avoids the lateral forces of other techniques by intermittently contacting the substrate surface in addition to avoiding the filtering effect and dynamics of a resonating system [25].

![Schematic of AFM technique](image)

**Figure 5.3:** Schematic of AFM technique, modified from [64]

A major disadvantage of using AFM for this thesis is the 13 µm z-range limitation of the piezo-scanner head on the Bruker Dimension Icon AFM, which makes this technique inappropriate for the BDD substrates used, which have a surface roughness of $R_A \sim 50$ µm. Therefore, AFM was only employed to measure the
AuNPs produced during the process optimisation of the AuNP production process on silicon substrates, alongside scanning electron microscopy measurements that could be compared to the AuNPs produced on the BDD substrates.

### 5.6 Scanning electron microscopy

Scanning electron microscopy (SEM) is a high vacuum microscopy technique that offers magnification up to 50,000 times greater than microscopy using light rather than electrons. Although, the substrate must be conductive (as in the case of BDD) or coated with a conductive film to achieve high resolution images and minimise charging effects [101]. SEM was used in this thesis to image the AuNPs produced by the processes described in section 5.7. The SEM images, made with consistent working distance and magnification, were then analysed with ImageJ software to assess changes in the size, shape and surface coverage of the AuNPs during the optimisation of their production, as described in Chapter 7.

![Diagram of SEM](image)

**Figure 5.4:** The sampling volume of secondary and backscattered electron signals in SEM, modified from [65]

In SEM a beam of primary electrons is rastered across a substrate surface under high vacuum. The electron beam interacts with the atoms at the surface of the sample and the reflected electrons are detected. The count of secondary or backscattered electrons are measured for each pixel, generating an image in which the contrast is a result of the material and topographical properties of the surface. The
5.7. Gold nanoparticle production

The deposition of gold nanoparticles (AuNPs) on the BDD surface, which act catalytically during the electrochemical measurements, has been shown to improve the sensitivity of BDD for mercury detection [170]. The AuNPs used in this thesis were produced on the electrode surfaces and characterised by the following techniques.

5.7.1 Gold sputter treatment

[Figure 5.5: Schematic of gold sputter coater process]
This gold coating technique was originally designed to enable non-conducting materials to be viewed by SEM, as the gold coating lessens charging effects that reduce the image quality [151]. Sputter coating has advantages over thermal evaporation techniques because the energetically high impact of the gold atoms gives them greater adherence to the substrate surface [150]. In the Emscope SC500 model a magnetic deflection assembly surrounds the gold target, which enables ionisation to occur at very low voltages, therefore removing the requirement to heat the sample [150].

As seen in Figure 5.5, inside the coating chamber the substrate is held at a positive potential and a negatively ionising potential is applied to the cathode target (in this case gold), producing a plasma discharge. An inert gas (in this case argon) is slowly released into the coating chamber which is under a vacuum of 0.1 - 0.05 torr. The ionised argon gas molecules collide with the positively charged gold target, dislodging some gold atoms which are then attracted to the anode substrate holder. As the gold atoms travel towards the substrate they collide with the argon molecules and become deflected in all directions, resulting in omnidirectional coating of the substrate [150].

The thickness of the gold layer deposited on the substrate surface can be controlled by changing the amount of time for which the potential is applied between the gold target (cathode) and the substrate holder (anode).

5.7.2 Rapid thermal annealing

A thin (~nm) homogeniously deposited gold film can be used to form AuNPs, following an annealing process. Provided the gold film is sufficiently thin, heating leads to surface tension reduction through the film, causing segregation into spherical-like nanoparticles. This process is often referred to as ‘de-wetting’ due to the role of surface tension.

Rapid Thermal Annealing (RTA) is a subset of the Rapid Thermal Processing (RTP) techniques used in semiconductor device fabrication [163]. RTA was used to de-wet the gold films produced in the gold sputter treatment (5.7.1) into AuNPs on the electrode surfaces, for use in Chapters 7 and 8. In comparison to annealing in a furnace, RTA allows for shorter processing times (10 ns - 5 min), whilst providing higher electrical activation of ion implanted dopants and accurate control of dopant redistribution [62]. In this process the substrate is loaded onto a silicon wafer that sits on the quartz sample tray, which is connected to the control thermocouple. The chamber is purged with nitrogen gas and the temperature of the sample is rapidly increased from ambient temperature up to 1100 °C, typically over less than one
minute. A homogeneous temperature is achieved across the sample through the use of separately controlled heating lamps (Figure 5.6). The sample is held at the upper temperature for up to 5 min before being left to cool naturally under nitrogen. The slow cooling prevents sample breakage or dislocations caused by thermal shock [175].

### 5.7.3 Ellipsometry

Knowledge of the thickness of the gold layers deposited with the gold sputter treatment (5.7.1) was critical for optimisation of the annealing process described in 5.7.2. Ellipsometry is a non-destructive optical technique that can give information about the composition, thickness and porosity of thin films [162]. Ellipsometry data is not useful in itself, but must be applied to computer models to obtain the required information, therefore, the accuracy of this technique is limited by the quality of the model used.
5.8. Electrochemical methods

In an ellipsometer a linear white light source passes through a polarizer and compensator to prepare a known polarization state of light, which is incident to the planar sample (at angle $\theta$) as seen in Figure 5.7. The light is reflected by the sample and passes through a compensator and analyser to the detector [185]. The compensators act as monochromators which select specific wavelengths of light. Upon reflection by the sample the amplitude and the phase of the polarized light may change, depending on the material and thickness of the sample. The characteristics of the light reflected from or transmitted through the sample can be used with known material specific models to infer the thicknesses of the film(s) present [103].

5.7.4 Ultrasonication

Ultrasonication is the process by which a liquid sample or sample placed in a liquid is agitated by sound waves at ultrasonic frequencies (>20 kHz). Ultrasonication is used in this thesis for extended lifetime testing to measure the physical stability of AuNPs on BDD substrate surfaces. The AuNP decorated substrates were placed in reverse osmosis water in a Guyson KC2 Ultrasonic Bath at 38 kHz ± 10% for 10 min [59].

5.8 Electrochemical methods

5.8.1 BDD electrode characterisation

The BDD electrodes were characterised with CV scans to determine their electrochemical window in Chapter 6. A stainless steel counter electrode (4 mm diameter) and a silver wire reference electrode (1.5 mm diameter) were used in addition to a Fc/Fc$^+$ pseudo reference system. The stainless steel counter and silver wire reference electrodes were used as these metals are stable at the temperature (up to 125 °C) and pressure (5 barr) used in these measurements. The pseudo reference system, which uses a Fc/Fc$^+$ redox couple as an internal reference, was selected as a conventional reference electrode such as Ag|AgCl, with an operating temperature range of 0 - 80 °C, is not suitable for these high temperature experiments [122]. This is explained in more detail in section 6.2.2. The BDD working electrode was metallised with Ti-Pt-Au and soldered to a Be-Cu pin, in house at Schlumberger Cambridge Research Ltd. (SCR), to form the required carbide to create an ohmic electrical contact to the potentiostat. In this setup 0.07 cm$^2$ of the BDD electrode was exposed to the electrolyte.
5.8.2 SWASV scans for mercury detection
The square wave anodic stripping voltammetry (SWASV) measurements for mer-
cury detection were performed with a three electrode setup, controlled by a
Metrohm Autolab PGSTAT204 potentiostat, using NOVA 2.1 software. A Metrohm
Ag/AgCl reference electrode with double junction and Metrohm platinum sheet
counter electrode with approximate surface area 1 cm$^2$ were used in addition to the
BDD working electrode, with a surface area of 0.14 cm$^2$ exposed to the electrolyte.

5.8.3 Electrochemical Impedance spectroscopy (EIS)
The EIS measurements were controlled by a Metrohm Autolab PGSTAT204, us-
ing the FRA32M module and NOVA 2.1 software for the impedance analysis. A
Metrohm Ag/AgCl reference electrode with double junction and Metrohm platinum
sheet counter electrode with approximate surface area 1 cm$^2$ were used in addition
to the BDD working electrode, with a surface area of 0.14 cm$^2$ exposed to the elec-
trolyte.
6

Influence of temperature on the electrochemical window of boron doped diamond: A comparison of commercially available electrodes

Published as: M. H. S. McLaughlin, E. Corcoran, A. C. Pakpour–Tabrizi, D. Campos de Faria and R. B. Jackman. Scientific Reports (10) 15707, 2020 [117].

6.1 Introduction

Boron doped diamond (BDD) can act as an exceptional electrode material, with the widest electrochemical window of any known material — that is the potential range that can be applied across a working electrode before the onset of either oxidation or reduction of the electrolyte at its surface [109][179]. To date, there has not been a systematic study reported on how the electrochemical window of BDD is affected by temperature. This has particular relevance to the use of BDD electrodes that are employed in extreme environments, such as down oil wells, where the electrode can be exposed to temperatures exceeding 150 °C [164]. This work aims to give an initial insight into how temperature impacts the electrochemical window of BDD electrodes.

Experimentally, the electrochemical window of an electrode is determined by measuring a polarisation curve over a potential range wide enough to observe the anodic and cathodic decompositions of the electrolyte at the working electrode; the electrochemical window is the region between these two points [128]. There are several methods that can be employed to define the electrochemical window of an electrode from experimental data. The most commonly used method is to plot the current density (J) in mA/cm² against the applied potential, then to read off the po-
6.1. Introduction

The potential at a defined current density cut off ($J_{\text{cut-off}}$). The arbitrary choice of the $J_{\text{cut-off}}$ value, reported in the range $0.01 - 5.0$ mA/cm$^2$, can result in electrochemical windows for the same electrode being quoted to differ by as much as 0.9 V \[128][139][203][35]. This method is heavily influenced by mass transport of the electrolyte, meaning that changing the concentration of the electrolyte will affect the electrochemical window recorded \[128]. Therefore, it is not possible to accurately compare electrochemical windows that have been determined using different $J_{\text{cut-off}}$ values.

The second method of defining the electrochemical window that is investigated here is taking the first derivative of the current vs potential data obtained by the cyclic voltammetry (CV) measurements \[203][45]. This method allows clearer identification of the potentials at which the anodic and cathodic decompositions of the electrolyte begin than when the $J_{\text{cut-off}}$ method is used. Taking the first derivative of the data also has the advantage of removing the error introduced by the choice of the $J_{\text{cut-off}}$ value.

Finally, an approach introduced by Olson and Bühlmann has been considered, which was designed to address the inconsistencies that occur when defining the electrochemical window of an electrode by using $J_{\text{cut-off}}$ values \[138]. In this method, linear fits are made of the three sections of the CV curve, before and after the oxidation and reduction of the electrolyte at the working electrode. The intersections of the linear fits are taken to define the electrochemical window \[128][138]. The benefit of this technique is that the defined electrochemical window is less sensitive to the concentration of the electrolyte than when the $J_{\text{cut-off}}$ method is used. Also, this method more closely resembles the method of defining the limits of detection of ion-selective electrodes recommended by the IUPAC \[138][102]. Here, these methods are compared and contrasted with the aim of setting a standard approach for the determination of electrochemical windows from experimental data.

To facilitate investigation of the methods described and to define an electrochemical window from experimental results, heavily boron doped diamond electrodes ([B]$>10^{20}$ cm$^{-3}$) have been used here with two roughnesses: $R_A \sim 50$ nm and $R_A \sim 50$ µm. Half of the substrates were hydrogen terminated (BDDH) and half were oxygen terminated (BDDO). BDDH has been shown to have a slightly narrower electrochemical window than BDDO at room temperature, however, there are some sensing applications for which BDDH is more suitable \[187][118]. The CV measurements were repeated with each electrode over the temperature range $21 - 125$ °C, to identify how the electrochemical window of BDD is affected by temperature. The experiment was run at 5 bar pressure to avoid complications due
to bubble formation. Although pH will also influence the electrochemical window of BDD this is outside the scope of this work. The pH of the electrolyte was fixed at pH 7 throughout the experiments through use of a buffer system.

6.2 Experimental

Electrochemical grade BDD (\([B] > 10^{20} \text{ cm}^{-3}\), 10 × 10 × 0.5 mm) substrates were purchased from Element Six Ltd. (e6cvd.com). Half of the substrates were unpolished polycrystalline BDD, with surface roughness \(R_A \sim 50 \mu\text{m}\). The remaining substrates were polished polycrystalline BDD (pBDD), with surface roughness \(R_A \sim 50 \text{ nm}\). The substrates were laser cut into 3 mm diameter pieces at Laser Micromachining Ltd. (lasermicromachining.com). All chemicals, unless otherwise stated, were purchased from Sigma-Aldrich. Milli-pure water, resistivity 18 MΩ-cm was used throughout (0.22 µm membrane filter).

It is not possible to give more information on the exact nature of the polishing process as this was performed by Element Six Ltd. under proprietary conditions and the substrates procured on a commercial basis. The substrates are specified to have a boron doping concentration in the range 2 to 6 × 10^{20} \text{ atoms/cm}^3 (typically \sim 3 \times 10^{20} \text{ atoms/cm}^3, averaged over 0.4 \text{ mm}^2) which is sufficiently high to overcome the Mott transition, therefore making these substrates metallically conductive (Figure 2.13) [20][41]. However, the doping concentration was not checked experimentally by probing the conductivity through the substrates as a function of temperature, as in Figure 2.13. This measurement could have been used to confirm that the doping concentration was sufficient for the substrates to be metallically conducting (see sample #1 in Figure 2.13). Instead, it was assumed that the specification of the BDD material was accurate [41]. The substrates were visually assessed and have the characteristic very dark blue colour of heavily doped BDD [85][137]. Further, the presence of the Fano resonance and boron peaks in the Raman spectra of the BDD and pBDD substrates (Figure 6.3) indicates that the boron doping concentration within these substrates is at least 1 \times 10^{20} \text{ atoms/cm}^3 [1][148]. This is discussed in more detail in section 6.3.1.

6.2.1 BDD surface preparation and characterisation

Prior to processing, the 3 mm diameter BDD and pBDD substrates were cleaned with a highly oxidising acid clean to remove adventitious carbon, hydrocarbons, and graphitic carbon on the surface of the diamonds. During the acid clean, the substrates were heated to 200 °C for 10 min in a cleaning solution (ammonium persulfate (20 g) and concentrated sulfuric acid (20 g)) before being placed in the
6.2. Experimental rinsing solution (ammonium hydroxide (10 ml) and hydrogen peroxide (10 ml)) for 10 min [13]. The substrates were rinsed thoroughly with water and dried under N\textsubscript{2} gas.

The graphitic carbon content at the surface of the electrodes was assessed with a Renishaw micro-Raman spectrometer (532 nm laser source). The microscope was calibrated using a silicon substrate and the Raman analysis was performed with 20\times magnification, 10 s exposure and an average was taken over ten accumulations. WiRE (v 2.0) software was used for data acquisition.

One each of the BDD and pBDD substrates were hydrogen terminated in an AX5010 Seki Technotron Inc. reactor with H-plasma for 10 min, at 400 °C platen temperature (Williamson Dual Wavelength pyrometer), 700 W power, 35 Torr pressure. One BDD and one pBDD substrate were oxygen terminated via ozone treatment in an Ozone Cleaner NL-UV253, under 10^{-6} mbar vacuum, at ozone generation of 10 g/h for one hour.

The extent of the hydrogen and oxygen terminations at the substrate surfaces was assessed with contact angle measurements, conducted with a Kruss DSA1 contact angle goniometer, using 4 µl water droplets. Kruss DSA1 v1.80 drop shape analysis software was used to determine the contact angle at the three-phase contact point between the water droplet and the electrode surfaces. The contact angles of the water droplets were measured immediately. The errors in the contact angles obtained using the image fitting in the Kruss DSA1 v1.80 drop shape analysis software were determined from three repeats of each measurement.

6.2.2 Electrode preparations

The back-face of the 3 mm diameter BDD pieces were metallised with Ti-Pt-Au and soldered to Be-Cu pins to form the working electrode in-house at Schlumberger Cambridge Research Ltd. (SCR). The electrode construction process involved temperatures sufficient for the formation of the required carbide within the diamond-ohmic contact stack given the duration of the process. The bulkhead into which the electrode was placed was machined from PEEK (polyether ether ketone) in-house at SCR. A steel counter electrode (4 mm diameter) and a silver wire reference electrode (1.5 mm diameter) were used. The three electrodes were sealed into the bulkhead body using Loctite Hysol 9483 epoxy (rated to 150 °C), which was injected into the channels from behind the pins whilst constant pressure was applied to the front face to avoid leakage of the epoxy to the BDD surface (which would require vigorous polishing to remove, thus destroying the terminations).

The bulkhead did require some polishing before the electrochemical measure-
ments, both to activate the surface of the electrodes and to remove dust and other residues left on its surface following the sealing of the electrodes with epoxy. At room temperature, hydrogen and oxygen terminated diamonds have slightly different electrochemical windows [109]. For this reason, the impact of changing temperature on the electrochemical window of BDD was measured for both terminations. Therefore, it was important that the terminations of the BDD working electrodes were disturbed as little as possible during the polishing of the bulkhead surface, to ensure that both hydrogen and oxygen terminated BDD electrochemical windows could be analysed.

Different bulkhead polishing options were tested to determine what would cause the least disturbance to the BDD terminations whilst still preparing the electrodes for the optimum electrochemical response. The three polishing methods tested were: polishing with a non-woven polyester/cellulose wipe (FG Clean Wipes, 7-C30-45L-00), polishing with water on a PSU-M polishing pad (Kemet International Ltd.) and polishing with 3 µm diamond slurry (Kemet International Ltd.) on a PSU-M polishing pad (Kemet International Ltd.). Contact angle measurements were performed on each BDD substrate (unpolished BDDH, polished BDDH, unpolished BDDO, polished BDDO), after the hydrogen or oxygen termination and following each of these polishing processes, using a Kruss DSA1 contact angle goniometer and 4 µl water droplets. A CV staircase sweep with upper vertex potential 0.6 V, lower vertex potential 0 V, 0.0085 V step potential and 0.1 Vs\(^{-1}\) scan rate was performed for the polished, oxygen terminated BDD electrode as a guide to the performance of the electrodes following each of the polishing processes tested. The electrolyte for the CV sweeps was a 1 M phosphate buffer (pH 7), (0.025 M \(K_2HPO_4\), 0.025 M \(KH_2PO_4\), 0.1 M KCl) doped with 0.5 mM 3-ferrocenophane sulfonate (prepared in-house at SCR) as a pseudo reference system.

### 6.2.3 Electrochemical measurements

Cyclic voltammetry (CV) measurements were used to determine the electrochemical window of each BDD working electrode in a 1 M phosphate buffer (pH 7) electrolyte (0.025 M \(K_2HPO_4\), 0.025 M \(KH_2PO_4\), 0.1 M KCl) doped with 0.5 mM 3-ferrocenophane sulfonate (prepared in-house at SCR) as a pseudo reference system. A conventional reference electrode such as Ag/AgCl, with an operating temperature range of 0 - 80 °C, is not suitable for these experiments, which use temperatures up to 125 °C [122]. The pseudo reference system, which uses a Fc/Fc\(^+\) redox couple as an internal reference, enables high temperature electrochemical measurements to be made as the response of the diamond working is calibrated to the Fc/Fc\(^+\) couple,
which although not at constant potential, will vary predictably with the changing temperature of the system [9]. The potential of the Fc/Fc⁺ redox couple is subtracted from the response of the diamond working electrode, causing the whole CV sweep to shift so that the halfway point between the oxidative and reductive peaks of the Fc/Fc⁺ redox occurs at 0 V [50]. This enables the CV sweeps to be plotted against the Fc/Fc⁺ internal reference over a significantly wider range of experimental conditions than possible with a Ag|AgCl reference electrode [122]. The use of the Fc/Fc⁺ internal reference is well established for ionic electrolytes, but it can also be used in aqueous systems and has been shown to be effective up to 145 °C [139][3][167]. Before the CV measurements, the electrodes were polished with a 3 µm diamond slurry (Kemet International Ltd.) on a PSU-M polishing pad (Kemet International Ltd.) and rinsed thoroughly with water.

The bulkhead was placed in a PEEK flow cell using viton o-rings to seal it in place, then the cell was placed in a steel box (to aid heat transfer). A thermocouple was inserted into the bottom of the cell to measure the temperature. The cell was connected to a two-channel syringe pump system (Syrris Asia pump) via Hastelloy® fittings inside an oven. The flow-line to the electrode was held at 5 bar pressure, to prevent the electrolyte from boiling at the elevated temperatures measured. The solution was injected into the cell, via a heating coil inside the oven, to fill the sensing chamber above the electrode (approx. 1 mm high). Measurements were made after the temperature in the cell was stable for 10 min. The flow was diverted to waste just before measurement, so that static conditions were achieved at the electrode surface whilst taking a scan, and reopened after measurement to flush the sensing chamber. CV staircase scans with upper vertex potential 1.5 V, lower vertex potential -1.9 V and 0.0085 V step potential were used to determine the electrochemical windows. The CV scans were repeated at the scan rates 0.1, 0.5, and 1.0 Vs⁻¹ for each temperature measured (21, 50, 75, 100, and 125 °C) with each electrode. As the electrochemical window is independent of the scan rate the data at each scan rate was combined with the repeats made using each electrode to determine the error in the observed current.
Figure 6.1: Schematic of the experimental setup for CV measurements over the temperature range 21 - 125 °C, detailed in section 5.2.3.
6.3. Results and discussion

6.2.4 Electrochemical window determination

Three methods for determining the electrochemical window from the experimental data have been explored, as illustrated in Figure 6.2, in which the vertical dotted lines represent where the electrochemical window is defined for each method. Figure 6.2a shows the current/potential curve obtained experimentally, to which three linear fits have been applied. The electrochemical window is defined as the potential window between the two intersections of the linear fits. In Figure 6.2b the first derivative of the observed current has been plotted against the applied potential. This allows the potentials at which the hydrogen evolution and oxygen reduction reactions begin to be more easily seen than in the original current/potential curve. The potential window is taken as the linear horizontal region of the plot. Figure 6.2c illustrates the $J_{\text{cut-off}}$ method for the $J_{\text{cut-off}}$ values 1.0 mA/cm$^2$ and 5.0 mA/cm$^2$. Here the electrochemical window is defined as the potential window between the points where the $J_{\text{cut-off}}$ value intersects with the current density/potential curve.

6.3 Results and discussion

6.3.1 BDD surface preparation and characterisation

The proportion of sp$^2$ non-diamond carbon and sp$^3$ diamond carbon on the BDD surfaces was assessed with Raman spectroscopy before and after the acid cleaning process described in section 5.2.1 (Figure 6.3).

Before the substrates were acid cleaned (inset Figure 6.3) the characteristic 1332 cm$^{-1}$ diamond carbon peak is clearly seen in the centre of the BDD disks. However, at the edge of the disks the 1332 cm$^{-1}$ peak is broad and has a lower intensity than the non-diamond carbon G peak at 1575 cm$^{-1}$. This indicates that when the BDD disks were laser cut from the 10×10 cm$^2$ squares non-diamond carbon was most likely sputtered onto the edge of the diamond surface as a result of the laser ablating the diamond [8]. The acid cleaning procedure removed a significant proportion of this non-diamond carbon from the BDD surfaces, as indicated by the presence of the characteristic 1332 cm$^{-1}$ diamond carbon peak at both the centre and edge of each substrate, at a significantly greater intensity than the 1575 cm$^{-1}$ peak. The shape of the 1332 cm$^{-1}$ peak after the acid clean is indicative of the crystalline quality of the BDD substrates, as a lower quality diamond that contains more defects would have a shorter phonon lifetime and a broader line width than seen in Figure 6.3 [109].

Comparison of the 1332 cm$^{-1}$ and 1575 cm$^{-1}$ peaks can be used to assess the relative proportions of diamond and non-diamond carbon at the substrate surfaces.
Figure 6.2: Comparison of the three methods identified for determining the electrochemical window of an electrode from experimental data. The methods are: a) taking the intersection of the linear fits of the CV curve [128][138], b) taking the horizontal, linear section of the plot of the first derivative of the current/potential data [203][45] and c) the well-established $J_{cut-off}$ method that characterises the electrochemical window by a predefined current density (J) value, for example 1.0 or 5.0 mA/cm$^2$ [139][35].
6.3. Results and discussion

Figure 6.3: a) Raman spectrum of unpolished BDD substrate revealing the distinctive 1332 cm\(^{-1}\) peak of the diamond carbon phase, and (inset) Raman spectrum before the substrate was acid cleaned, and (b) similar measurements for the polished pBDD substrate materials.
Although, as the relative intensities of the two peaks are dependent on the grain size, film stress, doping density, and excitation wavelength used, one can only qualitatively compare the two peaks; in the visible region the sensitivity to $sp^2$ carbon is typically $100\times$ that of $sp^3$ carbon [18]. Following the acid clean the proportion of $sp^2$ carbon at the centre of the substrates is very low when compared to literature values where Raman spectroscopy is supported by other techniques [31][73]. The intensity of the $1575\, \text{cm}^{-1}$ peak remains high in relation to the $1332\, \text{cm}^{-1}$ diamond peak at the edge of the polished BDD substrate, even after the acid clean. This is likely due to the polishing process introducing damage to the diamond surface, which has not been completely removed during the acid clean.

The broad peaks between $500\, \text{cm}^{-1}$ and $1030\, \text{cm}^{-1}$ in the Raman spectra for both the polished and unpolished BDD substrates indicate a high boron doping concentration ($>10^{20}$ boron atoms cm$^{-3}$) within the diamond structures (Figure 6.3) [148]. The Fano resonance (asymmetry at the base of the $1332\, \text{cm}^{-1}$ peak) further confirms the high concentration of boron in the diamond lattices ($>10^{20}$ boron atoms cm$^{-3}$), as this corresponds to the onset of metallic conductivity in the diamond, which is a result of the boron impurity band transitioning into a continuum state [1][149]. Therefore, it can confidently be stated that both the BDD and pBDD substrates have metallic conductivity, as specified by their supplier, meaning that their conductivity is independent of temperature (Figure 2.13) [41]. This is important because this means that any change in the electrochemical windows due to increasing temperature reported during this work is not due to increased conductivity of the diamond substrates at higher temperature, which would be the case if they were more lightly boron doped and therefore not metallically conductive (Figure 2.12) [20].

The method of polishing the bulkhead following the electrode preparations detailed in section 5.2.2 was chosen after three different methods were tested on each of the BDD electrodes (unpolished BDDH, polished BDDH, unpolished BDDO, polished BDDO). Each test followed the same polishing procedure in which the surface of the electrode was placed onto the polishing material and moved with gentle pressure in three figure of eight motions, first clockwise, then anti-clockwise. This procedure is open to error due to unavoidable small variations in the amount of pressure applied each time. However, the contact angle measurements were primarily used to check if a significant difference in the hydrophobic/hydrophilic nature of the BDDH and BDDO electrodes was maintained following surface polishing and to give an insight into the disturbance of the surface terminations. The contact angle measurements were supported by CV sweeps following each polishing test to deter-
mine the level of polishing that would be required before the CV experiments. The impact of each polishing method on the surface terminations of the BDD electrodes was assessed with contact angle measurements (Table 6.1). The contact angle of the water droplets were measured immediately and obtained using the image fitting function in the Kruss DSA1 v1.80 drop shape analysis software. The errors in the contact angles provided in Table 6.1 were determined from three repeats of each measurement. The magnitude of the errors in these contact angles are comparable to those obtained by Taylor et al. using the same methodology [183].

Table 6.1: Three-phase contact angle on each substrate surface from contact angle measurements with 4 µl water droplets after the electrode surface was polished with the three material options (non-woven polyester/cellulose wipe, polishing with water on a PSU-M polishing pad and polishing with 3 µm diamond slurry on a PSU-M polishing pad.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Non-woven polyester/cellulose wipe</th>
<th>Water on a PSU-M polishing pad</th>
<th>3 µm diamond slurry on a PSU-M polishing pad</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unpolished BDDH</td>
<td>84 ± 0.5</td>
<td>93 ± 1.0</td>
<td>78 ± 0.5</td>
</tr>
<tr>
<td>Polished BDDH</td>
<td>41 ± 2.0</td>
<td>60 ± 1.5</td>
<td>55 ± 1.0</td>
</tr>
<tr>
<td>Unpolished BDDO</td>
<td>40 ± 1.0</td>
<td>39 ± 1.0</td>
<td>31 ± 0.5</td>
</tr>
<tr>
<td>Polished BDDO</td>
<td>21 ± 1.0</td>
<td>20 ± 0.5</td>
<td>29 ± 1.0</td>
</tr>
</tbody>
</table>

The initial contact angles measured on each BDD electrode surface immediately following the termination of their surfaces as described in section 5.2.1 are displayed in the second column of Table 6.2. Contact angle measurements are heavily influenced by the environment of the measurement, not just the electrode itself, especially in the case of small electrode sizes. This means that absolute contact angle measurements contain too much error for direct interpretation. However, relative measurements can still be informative. Here, BDDO contact angles were smaller than for BDDH, as expected. The terminations of the unpolished electrodes were less disturbed by the surface polishing because a smaller proportion of the unpolished electrode surfaces were exposed to the abrasion that the polished electrodes. There was a significant reduction in the contact angles recorded for the polished electrodes (both BDDH and BDDO) which were 98° and 36° respectively immediately after the electrodes were terminated, but decreased to 41° and 21° respectively.
6.3. **Results and discussion**

after they were polished with a non-woven polyester/cellulose wipe. The polished BDDH electrode was most affected by each method of polishing. Existing simulation and XPS research show that oxygen termination on diamond is more robust than hydrogen termination, meaning that surface polishing would be expected to disturb the hydrogen termination to a greater extent than the oxygen terminations [6][145].

For consistency, to allow comparison between the results of the CV measurements it was important that the same bulkhead polishing was performed with each electrode. Therefore, although there was less variation in the contact angle measured for the polished BDDO electrode when polished with the diamond slurry to the as terminated surface, for the majority of the electrodes their surface termination was closest to their as terminated states when they were polished with water on a PSU-M polishing pad. However, the electrochemical response of the electrodes following each of the polishing methods also had to be taken into consideration when determining how to polish the bulkhead before use for the CV experiments (Figure 6.4).

![Figure 6.4: CV sweeps investigating the Fc/Fc⁺ redox couple with polished BDDO working electrode after its surface was polished with a) non-woven polyester/cellulose wipe, b) water on a PSU-M polishing pad and c) 3 µm diamond slurry on a PSU-M polishing pad.](image)

CV sweeps investigating the Fc/Fc⁺ redox couple using the polished BDDO electrode after each proposed method for polishing the bulkhead surface were used as a guide to determine the minimum level of polishing that would be required to produce high quality experimental data. In Figure 6.4 the peaks corresponding to the redox reaction of the 3-ferrocenophane sulfonate in the electrolyte are only seen clearly in Figure 6.4c. Before this CV sweep the surface of the polished BDDO electrode was polished with a 3 µm diamond slurry on a PSU-M polishing pad. The CV sweeps made following the two other polishing methods (Figure 6.4a and b) show that these methods did not completely activate the electrode surface and
remove the residues left by the process of sealing the electrode into the bulkhead, as the reduction and oxidation peaks of the Fc/Fc\textsuperscript{+} reaction are not significant. Therefore, although polishing with water on a PSU-M polishing pad was shown to cause less disturbance to the surface termination of the BDD electrodes all of the experiments used bulkheads which had been polished with a 3 µm diamond slurry on a PSU-M polishing pad to ensure a good electrochemical response.

The extent of the hydrogen and oxygen terminations imparted by the processes described in section 5.2.1 were qualitatively assessed with contact angle measurements after the high temperature CV measurements. For comparison, the contact angle measurements were performed following the termination of the BDD electrodes, after the electrodes were polished with a 3 µm diamond slurry on a PSU-M polishing pad and after the high temperature measurements (Table 6.2).

Table 6.2: Three-phase contact angle on each substrate surface from contact angle measurements with 4 µl water droplets.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>After substrate termination</th>
<th>After polishing with 3 µm diamond slurry</th>
<th>After high temperature measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unpolished BDDH</td>
<td>92 ± 1.0</td>
<td>78 ± 1.0</td>
<td>78 ± 2.0</td>
</tr>
<tr>
<td>Polished BDDH</td>
<td>98 ± 0.5</td>
<td>55 ± 1.5</td>
<td>78 ± 1.0</td>
</tr>
<tr>
<td>Unpolished BDDO</td>
<td>55 ± 1.0</td>
<td>31 ± 1.0</td>
<td>30 ± 1.5</td>
</tr>
<tr>
<td>Polished BDDO</td>
<td>36 ± 0.5</td>
<td>29 ± 1.0</td>
<td>32 ± 0.5</td>
</tr>
</tbody>
</table>

Determination of the exact wetting angle from inspection of contact angle measurements is open to error, however, in Table 6.2 the values for the contact angle on the polished and unpolished BDDH electrodes after termination are consistent with a strongly hydrophobic and therefore hydrogen terminated surface, when compared to literature [205]. After polishing with 3 µm diamond slurry the contact angles on the unpolished and polished BDDH were reduced to 78° and 55° respectively, which corresponds to the hydrogen termination being damaged and the surfaces therefore becoming more hydrophilic. Both sets of contact angles for the unpolished and polished BDDO electrodes are indicative of a hydrophilic and therefore predominantly oxygen terminated surface [120]. The contact angle for a fully oxidised diamond surface would be expected to be <30°, but diamond is considered
to be predominantly oxygen terminated when the contact angle is between $0 - 60^\circ$ [109][202]. Although the contact angles of the electrodes were affected by the bulkhead polishing, the values reported for the hydrogen terminated and oxygen terminated surfaces remained different enough, with sufficient contact angles to be given the labels used throughout this work. The high temperature measurement did not, at least for the duration of the experiments carried out here, lead to any significant change in either. BDDH with a contact angle of $78^\circ \pm 1.0^\circ$ after polishing was subsequently measured at $78^\circ \pm 2.0^\circ$ after the high temperature measurements; BDDO ($31^\circ \pm 1.0^\circ$ after polishing) was subsequently measured at $30^\circ \pm 1.5^\circ$.

### 6.3.2 Electrochemical measurements

![Graphs](image)

**Figure 6.5:** Average CV scans and standard deviation from four repeats of the measurement to determine the electrochemical window of each electrode across the full temperature range tested. a) unpolished BDDH, b) polished BDDH, c) unpolished BDDO and d) polished BDDO at a scan rate of 0.5 Vs$^{-1}$ (similar results obtained at scan rates 0.1 Vs$^{-1}$ and 1.0 Vs$^{-1}$ are in the Appendix (Figures A.1 and A.2)).

The CV measurements made with each electrode were repeated four times at each temperature measured (21, 50, 75, 100, and 125 °C). The average observed
current from these repeats with the standard deviation for these values is plotted in Figure 6.5. The peaks of the Fc/Fc\(^{+}\) redox couple, used as an internal reference, are not seen on the scale of the spectra in Figure 6.5. The onset of oxidation and reduction of the electrolyte at the working BDD electrodes occurred at smaller positive and negative potentials as the temperature of the CV measurements was increased from 21 – 125 °C. Therefore, the electrochemical window for each electrode narrowed as the temperature was increased. As established through the manufacturer specification, Raman spectroscopy measurements and visual assessment, the substrates used in this work are metallically conductive (see section 6.2) [20][41]. This means that the conductivity of the substrate material is consistent with temperature and thermal dopant activation is not a factor in this work [21]. Therefore, the change in the electrochemical windows with increasing temperature is a result of thermal activation for the electrolysis of the aqueous electrolyte. However, if the boron doping concentration was lower, below the threshold of metallic doping, then increasing the temperature during these experiments would cause the dopant boron atoms to be thermally activated, which would result in increased conductivity and so, narrower electrochemical windows as the temperature increased [76].

As the electrochemical window for each electrode narrowed when the temperature increased this means that when using these electrodes in high temperature environments the user will need to consider the range of ions that it will be possible to identify, as redox peaks outside the electrochemical window will not be detected. Each electrode used here will only be appropriate for use at high temperatures when analysing redox peaks within this range. The unpolished electrodes will offer the most versatility as these electrodes have the widest electrochemical windows, so allow the detection of the widest range of ions.

In the plots for both the polished BDDH and polished BDDO electrodes (Figure 6.5b and 6.5d) there are broad peaks between -1.0 to 0 V and 1.0 to 1.5 V, when the measurements were made at temperatures >100 °C. As the solution was changed between each of the four repeats and these peaks are present each time it is unlikely that this is due to external contamination. These peaks are not present in the CV spectra of either the unpolished BDDH or unpolished BDDO electrodes, meaning that the presence of these peaks are likely to be related the the higher sp\(^2\) content at the surface of the polished electrodes, which has been shown to have a significant effect on the electrode reaction kinetics of some redox systems [119][15]. This is the first reported study that measures this electrochemical system at high temperatures, which means that further investigation is required to understand what reaction is being observed during the measurements >100 °C at the polished BDDH and pol-
ished BDDO electrodes. The additional peaks observed in these conditions could potentially be due to some dissolution from the surface of the silver wire reference electrode being oxidised at the sp$^2$ regions of the polished surfaces [147][52].

The activation energy for the oxidation potential for each electrode (Table 6.3) was determined from the slopes of Arrhenius plots of ln(current density) against the inverse temperature in Kelvin at the applied potential -1.4 V (Figure 6.6), which is part way through the oxidative curve for the electrodes at each temperature measured. By plotting the current densities as a function of inverse temperature the activation energies of the hydrogen evolution reaction at each electrode can be determined with the Arrhenius equation (Equation 6.1), where J is the current density, A is the Arrhenius pre-exponential factor, $E_A$ is the activation energy, $k_b$ is the Boltzmann constant and T is the absolute temperature.

$$J = A \cdot \exp \left( \frac{E_A}{k_b \cdot T} \right)$$

(6.1)

The Arrhenius plots in Figure 6.6 show that the current densities of the hydrogen evolution reaction (reduction of the electrolyte) recorded at -1.4 V for each electrode are temperature dependent. The anomalous peaks (Figure 6.5) at -0.5 V, -0.2 V and 1.25 V lead to analogously high current densities for the hydrogen evolution peak at -1.4 V for both polished electrodes (BDDH and BDDO), so these points were omitted from the data used to make the Arrhenius plots.

**Table 6.3:** Activation energies and standard error for each electrode derived from the Arrhenius plots in Figure 6.6.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Activation energy (eV)</th>
<th>Error (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unpolished BDDH</td>
<td>$6.68 \times 10^7$</td>
<td>$\pm 0.25 \times 10^7$</td>
</tr>
<tr>
<td>Polished BDDH</td>
<td>$5.02 \times 10^7$</td>
<td>$\pm 0.68 \times 10^7$</td>
</tr>
<tr>
<td>Unpolished BDDO</td>
<td>$7.41 \times 10^7$</td>
<td>$\pm 0.23 \times 10^7$</td>
</tr>
<tr>
<td>Polished BDDO</td>
<td>$5.16 \times 10^7$</td>
<td>$\pm 0.46 \times 10^7$</td>
</tr>
</tbody>
</table>

The activation energies derived from the Arrhenius plots are shown with the standard error in these values in Table 6.3. The activation energies are higher and with smaller errors for the unpolished electrodes compared to the polished electrodes. This corresponds to the wider electrochemical windows reported for the unpolished electrodes in Figure 6.7, for every method of determining the electrochemical windows. The surface roughness and therefore quality of the electrode surfaces (analysed with Raman spectroscopy as in Figure 6.3) had more influence.
Figure 6.6: Arrhenius plots of \( \ln[J] \) vs. inverse temperature at the potential -1.4 V, which is part of the way through the electrolyte oxidation at all temperatures from 21 – 125 °C for each electrode, for each scan rate: a) 0.1 Vs\(^{-1}\), b) 0.5 Vs\(^{-1}\) and c) 1.0 Vs\(^{-1}\).
on the activation of the electrodes than their surface termination. It has previously been shown that when these polished and unpolished electrodes are used for detection their surface roughness has a greater impact on their sensitivity than the application of nanoparticles to the electrode surfaces [118].

The activation energies are slightly higher for the BDDO electrodes than the BDDH electrodes (both polished and unpolished), as has been reported previously [187]. However, the different terminations resulted in significantly smaller changes in the activation energy and electrochemical windows reported than the different surface roughness of the electrodes. This is likely because the polished electrodes have a greater proportion of sp² carbon at their surface than the unpolished electrodes. It has been noted that when the number of sp² carbon impurities in diamond increase the electrochemical window is reduced [52]. This is because a higher sp²/sp³ carbon ratio changes the oxidation mechanism at the diamond surface, leading to changes in the electrocatalytic properties through reduction of the activation barrier for electron transfer reactions [52][39].

6.3.3 Electrochemical window determination

The electrochemical window of each electrode was determined by the three methods described in section 6.2.4. A comparison of how the electrochemical windows of the electrodes were affected by temperature with each of these methods is shown in Figure 6.7.

As seen in Figure 6.7, the electrochemical windows are wider for the unpolished electrodes (BDDH and BDDO) regardless of the method of determination used. The unpolished electrodes have a lower proportion of sp² to sp³ carbon at their surface (Figure 6.3) than the polished electrodes, meaning that a wider electrochemical window is expected [39]. When the proportion of sp² carbon is higher, as with the polished electrodes, the oxidation mechanism at the BDD surfaces is affected, reducing the barrier activation to the evolution of hydrogen and reduction of oxygen at the electrode surface, therefore reducing the electrochemical window [52].

The reported widths of the electrochemical windows of each electrode are similar when either the $J_{cut-off}$ or derivative method was used, but the reduction in the width of the window as temperature increased is much smaller when the linear fit method was used (Figure 6.7). To directly compare the values for the electrochemical window determined by each of the methods introduced in section 5.2.4 the results obtained are plotted for each electrode with the three methods on the same axes (Figure 6.8).
Figure 6.7: Comparison of the electrochemical window, with standard error, for each electrode over the temperature range 21 – 125 °C. The electrochemical windows are determined by the methods a) $J_{\text{cut-off}}$ at 1.0 mA/cm$^2$, b) taking the first non-horizontal points of the first derivative of the current/potential data and c) taking the intersection of the liner fits of each part of the CV curves.
6.3. Results and discussion

Figure 6.8: Comparison of each method for determining the electrochemical window, $J_{cut-off}$ at 1 mA/cm$^2$, derivative and intersection of linear fits, across the temperature range 21 – 125 °C for each electrode: a) unpolished BDDH, b) polished BDDH, c) unpolished BDDO and d) polished BDDO.

In Figure 6.8, where a direct comparison is made between the electrochemical windows determined with each method it is clear that the method of using the intersections of linear fits of the polarisation curve results in narrower apparent electrochemical windows. These reported windows also appear to be less affected by increasing temperature than the $J_{cut-off}$ (1.0 mA/cm$^2$) or derivative methods. There is some agreement between the $J_{cut-off}$ and derivative methods, with similar electrochemical windows being determined at each temperature for all of the electrodes. This is expected, as the derivative method was designed to more clearly identify the potentials at which the hydrogen evolution and oxygen reduction processes begin than on a current density/potential plot (Figure 6.2) and if the minimum possible $J_{cut-off}$ value is chosen the results should be very similar.

The linear fit method resulted in electrochemical windows that were apparently narrower at room temperature and less impacted by increasing temperature,
although the electrochemical windows still narrowed as the temperature increased (Figure 6.8). As the temperature of the CV measurements increased and the electrochemical windows narrowed the linear fits of the curves remain similar. The significant change is that the curves at the beginning of oxidation and reduction of the electrolyte become shallower as the temperature increased (Figure 6.9). The change in curvature is more subtle to the linear fit method, meaning that for the same experimental results the electrochemical window will appear to undergo less change with increasing temperature than when the $J_{\text{cut-off}}$ method is used.

![Graph showing current vs potential for different temperatures](image)

**Figure 6.9:** Oxygen reduction reaction at the polished BDDO electrode with increasing temperature from 21 – 125°C.

The electrochemical windows determined with the $J_{\text{cut-off}}$ method are heavily influenced by the choice of $J_{\text{cut-off}}$ value. The extent to which the arbitrary choice of the $J_{\text{cut-off}}$ value affects the determined electrochemical window is demonstrated in Figure 6.10, where three $J_{\text{cut-off}}$ values: 0.5, 1.0 and 5.0 mA/cm² are compared with the linear fit method, in which the potential range between the intersections of linear fits of the polarisation curve defines the electrochemical window. In Figure 6.10c the electrochemical window determined with $J_{\text{cut-off}}$ 0.5 mA/cm² is 2.31 V, but when determined with $J_{\text{cut-off}}$ 5 mA/cm² it is 0.88 V lower, at 1.43 V. This is a significant difference. It is not possible to compare the electrochemical windows quoted across literature where different $J_{\text{cut-off}}$ values have been used.
As this method is heavily influenced by the mass transport of the electrolyte it is only accurate to compare electrochemical windows for electrodes that have been determined under the same experimental conditions.

**Figure 6.10:** Comparison across the temperature range 21 – 125 °C of the electrochemical window of each electrode a) unpolished BDDH, b) polished BDDH, c) unpolished BDDO and d) polished BDDO, as determined by the $J_{\text{cut-off}}$ method at 0.5 mA/cm$^2$, 1.0 mA/cm$^2$, 5.0 mA/cm$^2$ and the intersection of linear fits method described in section 5.2.4.

Particularly for the unpolished BDDH and BDDO electrodes (Figure 6.10a,c) the linear fit method has a similar trend to the $J_{\text{cut-off}}$ method using 5.0 mA/cm$^2$. This highlights the importance of choosing an appropriate $J_{\text{cut-off}}$ value because it is shown here that the linear fit method is less sensitive to changes in the curvature of the hydrogen evolution or oxygen reduction reactions (Figure 6.9), so is a less accurate method of determining the electrochemical window. This overshadows the aim of the linear fit method, to determine electrochemical windows by a method that is less influenced by the concentration of the electrolyte than the $J_{\text{cut-off}}$ method, meaning that comparison between literature is possible [128].
6.4 Conclusion

This work has been an investigation into how the electrochemical window of BDD electrodes is affected by temperature and how the method used to determine the electrochemical window from experimental data can affect the apparent result. The experiment was run at 5 bar pressure to avoid complications due to bubble formation. For every electrode, the electrochemical windows became narrower as the temperature increased from 21 °C to 125 °C, which is to be expected since the redox reaction is thermally activated. Although not explicitly measured, it is established through the manufacturer specification and Raman spectroscopy measurements that the diamond substrates used were heavily boron doped and metallically conductive. Therefore, thermal dopant activation is not a factor in the results of this work.

The widest electrochemical windows were reported for the unpolished electrodes, which have a lower proportion of sp\(^2\) carbon at their surfaces in comparison to the polished electrodes. The influence of the ratio between sp\(^2\) and sp\(^3\) carbon at the electrode surfaces was shown to have a much more significant impact on the electrochemical window value reported than the hydrogen or oxygen termination of the diamonds. Therefore, the unpolished electrodes would offer the most versatility for use in extreme environments because with their wider electrochemical windows they would enable the detection of the widest range of analytes.

A reliable standard procedure for determining electrochemical windows has been sought that could be used to make accurate comparisons across the published literature, unlike the commonly used J\(_{\text{cut-off}}\) method. The linear fit method proposed by Olson and Bühlmann is less affected by the assumptions required in the J\(_{\text{cut-off}}\) method. The application of this method to the results reported across the published literature would therefore enable a more accurate comparison of the variation in the value of the electrochemical window due to varying measurement conditions. This is valuable to selecting one type of electrode versus another. However, it is the electrochemical window determined when using the J\(_{\text{cut-off}}\) method, with a carefully selected J\(_{\text{cut-off}}\) value, that will give the effective electrochemical window that will be relevant for a given experimental arrangement where sensitivity to a given current level is required.
Diamond electrodes for high sensitivity mercury detection in the aquatic environment: Influence of surface preparation and gold nanoparticle activity

Published as: M. H. S. McLaughlin, A. C. Pakpour–Tabrizi, and R. B. Jackman. Electroanalysis, 31 (9) 1775–1782, 2019 [118].

7.1 Introduction

Mercury is a highly toxic heavy metal that exists in concentrations up to 100 mg/kg within the Earth’s mantle and may be released into the greater environment during the extraction and processing of crude oil [38]. Even in trace quantities mercury contamination poses a severe threat to human health because it tends to form complexes with ligands of biological matter, leading to an accumulation in the food chain [4]. The World Health Organisation guideline for the maximum safe quantity of mercury in potable water is 6 µg l\(^{-1}\), ca. 30 nM [97].

It is important that mercury can be detected in situ, where contamination may have occurred, rather than relying on post sample analysis in a remote laboratory. This is achievable through the use of an electrochemical detection procedure which can be built around portable equipment and rapidly deployed and used in a wide range of locations; unlike the traditionally used methods, such as inductively coupled plasma mass spectrometry or electrothermal atomic absorption spectrometry [5]. Moreover, with the emergence of the ‘internet of things’ there is significant interest in the use of networks of remote devices to give real-time monitoring over
large environmental areas. To date, the published literature indicates that concentrations of mercury detected electrochemically can be down to levels of around 0.42 nM, using a glassy carbon electrode modified with 36 nm diameter gold nanoparticles (AuNPs) [67]. The AuNPs improve the sensitivity of the electrode by acting catalytically during the pre-concentration step of the square wave anodic stripping voltammetry (SWASV) measurements, typically performed for electrochemical detection within an aqueous solution.

Boron doped diamond (BDD) has been gaining interest as an electrode for use in the trace detection of analytes [111]. In addition to the low background and capacitive currents associated with the wide-band gap material, it has the widest ‘electrochemical window’ of any known electrode — that is the widest voltage range that can be applied without the onset of either oxidation or reduction of the solvent at the working electrode [109][179]. The hardness and chemically inert nature of diamond also enables BDD electrodes to be used in environments where other electrodes would be damaged, which is particularly advantageous for the potential deployment of mercury sensors in the extreme conditions that can be encountered in various environmental locations.

Typical commercially available heavily boron doped diamond materials grown by chemical vapour deposition (CVD) methods are polycrystalline in nature; the presence of boron concentrations greater than $10^{20}\text{cm}^{-3}$ gives rise to quasi-metallic character, offering the conductivity required of the electrode due to the formation of an impurity band displaying so-called hopping conductivity [190]. The electronic properties of a BDD electrode are dependent on the boron concentration and the graphitic carbon content of the diamond (which affects film morphology) [190][197][187]. Surface electronic properties are strongly influenced by the nature of the surface termination species present. The hydrogen rich CVD growth produces diamond that is naturally hydrogen terminated and therefore hydrophobic. Hydrogen terminated BDD is reported to have a slightly narrower electrochemical window than when oxygen terminated, however, as AuNPs show greater electrical contact to hydrogen terminated BDD this has been used throughout this study [187][178].

Here, the influence of how the dispersion of AuNPs on the BDD surface affects the sensitivity of electrochemical measurements has been explored. This has been achieved through the novel approach of using a TEM grid to act as a shadow mask during gold deposition, producing a grid with 28 µm square patches of AuNPs separated by 23 µm gaps. Further, the influence of BDD surface roughness and nanoparticle (NP) size have been studied. Finally, information on the relative adhe-
sion properties of different NPs on the different surfaces has been assessed.

7.2 Experimental

Electrochemical grade BDD ([B] > 10^{20} \text{ cm}^{-3}, \ 10 \times 10 \times 0.5 \text{ mm}) substrates were purchased from Element Six Ltd (e6cvd.com). Initial experiments were performed with unpolished polycrystalline BDD, with a surface roughness R_A \sim 50 \mu m. Further investigations used polished polycrystalline diamond (pBDD), where the surface roughness was reduced to R_A values \sim 50 \text{ nm}. All chemicals unless otherwise stated were purchased from Sigma-Aldrich. Reverse osmosis derived water, resistivity 18 M\Omega-cm, was used throughout.

7.2.1 BDD surface preparation and characterisation

Prior to processing, organic contaminants were removed from the BDD and pBDD surfaces with a ‘Piranha’ etch clean (3:1 v/v of 98% HCl and 30% H_2O_2) for 10 min [189]. Between experiments, the electrodes were cleaned by application of 150 current pulses lasting 100 ms each, which alternated between 10 mA/cm^2 and -10 mA/cm^2, as has previously been shown to be effective [87].

The graphitic carbon content in the surface of each BDD and pBDD substrate was qualitatively assessed with a Renishaw micro-Raman spectrometer (532 nm laser source). The Raman analysis was performed with 20\times magnification, 10 s exposure and an average was taken over ten accumulations, the microscope was calibrated using a silicon substrate. WiRE (v 2.0) software was used for data acquisition.

The BDD and pBDD substrates were hydrogen terminated in an AX5010 Seki Technotron Inc. reactor with H-plasma for 10 min at 700 °C platen temperature (Williamson Dual wavelength pyrometer), 800 W power, 40 Torr pressure. The hydrophilic-hydrophobic nature of the termination on the diamond surfaces was assessed with a Kruss DSA1 contact angle goniometer, using 4 µl water droplets. Kruss DSA1 v1.80 drop shape analysis software was used to determine the contact angle at the three-phase contact point between the water droplet and the electrode surface. The contact angles of the water droplets were measured immediately. The errors in the contact angles obtained using the image fitting in the Kruss DSA1 v1.80 drop shape analysis software were determined from three repeats of each measurement.

7.2.2 Process optimisation of AuNP deposition

The process of depositing AuNPs onto the BDD electrode surfaces was first optimised on silicon substrates. A non-continuous gold film was sputtered onto each
silicon substrate with an Emscope SC500 gold sputter coater, in thicknesses: 5 nm, 10 nm, 15 nm, 20 nm, and 25 nm. The thickness of the sputtered gold film on each silicon substrate was verified with a Horiba MM16 spectroscopic ellipsometer. The non-continuous gold films were segregated into AuNPs by an annealing process (often referred to as ‘de-wetting’ due to the role of surface tension) in a Solaris 150 Rapid Thermal Processing System under nitrogen for 5 min, at both 400 °C and 600 °C for each thickness of gold deposited.

The AuNPs generated on the silicon substrates were measured with a Bruker Dimension Icon AFM in ScanAsyst PeakForce Tapping mode. Each scan was performed across a $2 \times 2 \mu m^2$ area, at 2 Hz and 512 samples/line. The average AuNP size was calculated from the mean of the nanoparticle diameters measured in five random locations across the sample surface. The AuNPs generated on the silicon substrates were also measured with a Zeiss XB1540 Crossbeam scanning electron microscope (10 kV operation voltage). Five scans from random locations across each sample were analysed with ImageJ software to calculate the average size and coverage of the AuNPs on the substrate surfaces. The scale bar from the SEM scans (performed at the same working distance and magnification) was used for scale calibration.

7.2.3 AuNP deposition and stability

A non-continuous 3 nm gold film was sputtered onto the BDD and pBDD electrodes with an Emscope SC500 gold sputter coater. On one BDD and one pBDD substrate the gold was sputtered through a copper TEM grid (dimensions: 23 µm bar, 28 µm hole), which acted as a shadow mask. This resulted in a grid pattern of gold on the diamond surfaces, with $28 \times 28 \mu m$ squares of gold separated by 23 µm channels of bare diamond. The use of the TEM grid shadow mask influenced the size distribution of the nanoparticles (discussed in section 7.3.3). The gold films were de-wet into nanoparticles by annealing in a Solaris 150 Rapid Thermal Processing System under nitrogen at 400 °C for 5 min.

AFM was not an appropriate technique to analyse the AuNPs produced on the BDD substrates, which have a surface roughness of $R_A \sim 50 \mu m$, as the piezo-scanner head of the Bruker Dimension Icon AFM has a z-range limit of 13 µm. To enable comparison of the AuNP production on the BDD and pBDD substrates SEM was used instead. A Zeiss XB1540 Crossbeam scanning electron microscope (10kV operation voltage) was used to quantify the size and dispersion of AuNPs on the electrode surfaces. Scans from five random locations across each substrate were analysed with ImageJ software to calculate the average size and surface coverage
7.2. Experimental

of AuNPs on each electrode. The scale bar from the SEM scans (performed at the same working distance and magnification) was used for scale calibration.

An extended lifetime test consisting of ultrasonication in water in a Guyson KC2 Ultrasonic Bath (75 W, 38 kHz ± 10%) for 10 min was performed on every diamond electrode after the surface was coated with AuNPs. SEM scans from five random locations across each substrate were analysed with ImageJ software before and after the extended lifetime test, to analyse the change in the size and distribution of the AuNPs. It will be seen in section 7.3.3 that the changes provoked by the extended lifetime testing were modest but measurable. Since the electrode surfaces are likely to be more representative of an electrode under use in the field, all subsequent sensing measurements were performed on electrodes following the described ultrasonication process.

The chemical stability of the AuNPs on the BDD and pBDD electrodes was determined by comparing SEM images taken before and after the mercury detection measurements. SEM scans from five random locations across each substrate were analysed with ImageJ software before and after the electrochemical measurements to analyse the change in the size and distribution of the AuNPs.

7.2.4 Mercury detection

SWASV measurements were used for Hg$^{2+}$ detection, with a AuNP decorated BDD or pBDD working electrode (0.14 cm$^2$ surface area exposed to the electrolyte), a Ag/AgCl KCl (3 M) reference electrode and a platinum counter electrode (surface area 1 cm$^2$). A standard 0.1 M HNO$_3$ electrolyte was used [13][178], being dosed with increasing concentrations of mercury nitrate (Hg(NO$_3$)$_2$) from 1 pM up to 1 mM to explore the lower detection limit available with each electrode. Control measurements were performed with a bare pBDD and bare BDD electrode over the same Hg(NO$_3$)$_2$ concentration range. Control measurements were also made using the four AuNP decorated electrodes, in the blank electrolyte before the addition of mercury nitrate.

In the bulk electrolyte, mercury was in the form Hg$^{2+}$, which was reduced to Hg$^0$ and pre-concentrated onto the working electrode surface by application of 0.35 V for 10 min, which is established in the literature as a sufficiently reducing potential to drive this process [94]. A SWASV scan from 0.35 to 1.1 V with a 0.005 V potential step, 0.01 V amplitude and 10 Hz frequency was then applied, as has been shown to be optimal [178]. During the SWASV scan, the Hg$^0$ was oxidised back to Hg$^{2+}$ in the bulk electrolyte. Between SWASV scans the working electrode surface was cleaned by application of 150× 100 ms current pulses, alternating between 10
mA/cm$^2$ and -10 mA/cm$^2$, as has been previously shown to be effective [87].

7.2.5 Custom design and construction of electrochemical cell

A custom cell was designed to ensure that only the face of the BDD electrodes coated with AuNPs was exposed to the electrolyte during the SWASV measurements. The glass funnel from a Cole-Palmer vacuum filtration system was repurposed for use as the electrochemical cell, using custom parts designed in Autodesk Fusion 360 (Figures 7.1, 7.2, 7.3). The custom parts, prepared by laser cutting with a Universal Laser System, were made from polypropylene, which is suitable for a wide range of electrochemical experiments due to its high chemical resistance. The cell structure was held together with M5 threaded steel rods, which also enabled simple assembly and disassembly of the cell when mounting the BDD electrodes. Threads were put into some of the polypropylene sheets with a tap set where required. Viton o-rings were placed between the glassware, BDD electrode and polypropylene sheets to seal the electrochemical cell. Electrical contact from the potentiostat to the BDD electrode was made through firm contact to copper tape which was clamped under the base of the BDD electrode, as has previously been shown to be effective [70].
Figure 7.1: The electrochemical cell designed for the mercury detection experiments, including copper tape which provides the back contact to the experimental electrode, and Viton O-rings which seal the various interfaces of the cell.
Figure 7.2: a) The full assembly of the electrochemical cell built for the mercury detection experiments and b) an exploded image to more clearly display each component.
Figure 7.3: Plan view of the laser cut parts for the custom electrochemical cell. Units in mm.
7.3 Results and discussion

7.3.1 BDD surface preparation and characterisation

The graphitic carbon content on the surface of the BDD and pBDD substrates was qualitatively assessed with Raman spectroscopy (Figure 7.4).

![Raman spectrum](image)

**Figure 7.4:** Raman spectrum of the unpolished BDD substrate, revealing the distinctive 1332 cm$^{-1}$ peak of the diamond carbon phase (black), and (inset) the second order Raman spectrum (black). Similar measurements for the polished pBDD substrate are displayed in red.

The shape of the characteristic 1332 cm$^{-1}$ diamond carbon peak is indicative of the crystalline quality of the substrate, as a lower quality diamond that contains more defects will have a shorter phonon lifetime and broader line width than seen in Figure 7.4 [109].

The intensity of various features in Raman spectra depend on several factors, which make the quantification of the sp$^2$ content of the film difficult. The relative intensities of the sp$^3$ and sp$^2$ features depend upon the grain size in the film, the film stress, doping density, and the excitation wavelength used; in the visible region the sensitivity to the sp$^2$ materials is typically 100× that of the sp$^3$ [18]. However, a comparison of the size of the non-diamond carbon (NDC) sp$^2$ G peak at 1575
cm\(^{-1}\) and the characteristic sp\(^3\) diamond carbon peak at 1332 cm\(^{-1}\) can be used to qualitatively assess the relative proportion of sp\(^2\) carbon within the diamond surface structure [47]. In Figure 7.4, for both BDD and pBDD, the intensity of the 1575 cm\(^{-1}\) peak is significantly smaller than the sp\(^3\) diamond carbon peak at 1332 cm\(^{-1}\). It can be stated that the sp\(^2\) content here is low, a few percent, when compared to literature examples where Raman spectroscopy measurements have been backed up by other techniques [31][73]. This is confirmed by the presence of the second order sp\(^2\) peak at 2920 cm\(^{-1}\), which is also of a significantly smaller magnitude than the 1332 cm\(^{-1}\) peak. A higher proportion of NDC on the pBDD surface, as a result of polishing damage, is indicated in Figure 7.4, due to the absence of the second order sp\(^2\) peak at 2920 cm\(^{-1}\). Increasing the proportion of sp\(^2\) carbon in a BDD electrode has been shown to favour electrochemical oxidation and have a significant effect on the electrode reaction kinetics of some redox systems [119][15].

The broad peaks between 500 cm\(^{-1}\) and 1200 cm\(^{-1}\) in the Raman spectra for both the BDD and pBDD substrates indicate a high boron doping concentration, greater than 10\(^{20}\) boron atoms cm\(^{-2}\), within the diamond structures [148]. The high boron concentration is further confirmed by the asymmetry at the base of the 1332 cm\(^{-1}\) peak - known as the Fano resonance, which corresponds to the onset of metal-like conductivity in the diamond as a result of the boron impurity band transitioning into a continuum state [1].

Each BDD and pBDD electrode was hydrogen terminated before the addition of AuNPs to the diamond surfaces because AuNPs have been shown to adhere more strongly to hydrogen terminated diamond than oxygen terminated diamond [13][178]. This is due to a combination of the electrostatic and hydrophobic interactions between the AuNPs and the diamond surface when it is hydrogen terminated, which result in the formation of a non-covalent bond [80][106]. The degree of hydrogen termination achieved following the processing of each electrode, including AuNP deposition, was explored using contact angle measurements, which gave an insight into the level of hydrophobicity imparted by the treatments (Figure 7.5, Table 7.1). The contact angle of the water droplets were measured immediately and obtained using the image fitting function in the Kruss DSA1 v1.80 drop shape analysis software. The errors in the contact angles provided in Table 7.1 were determined from three repeats of each measurement. The magnitude of the errors in these contact angles are comparable to those obtained by Taylor et al. using the same methodology [183].

Whilst absolute determination of the exact wetting angle from inspection of such images as those in Figure 7.5 is open to error, these values are consistent with
7.3. Results and discussion

Figure 7.5: Photographs of the 4 µl water droplet deposited on each electrode during contact angle measurements: a) BDD + 10 nm AuNPs, b) BDD + 22 nm AuNPs, c) pBDD + 13 nm AuNPs and d) pBDD + 23 nm AuNPs. Kruss DSA1 v1.80 drop shape analysis software was used to determine the contact angle between the water droplet and the electrode surfaces, to gain insight into the level of hydrophobicity at the surface of each AuNP decorated electrode.

Table 7.1: Three-phase contact angle on each substrate surface from contact angle measurements with 4 µl water droplets.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Contact angle °</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDD + 10 nm AuNPs</td>
<td>90 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>BDD + 22 nm AuNPs</td>
<td>88 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>pBDD + 13 nm AuNPs</td>
<td>95 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>pBDD + 23 nm AuNPs</td>
<td>93 ± 1.0</td>
<td></td>
</tr>
</tbody>
</table>

a strongly hydrophobic and hence H-terminated surface, as established in existing literature [205]. The results shown in Table 7.1 reflect that the hydrogen termination of the electrodes used here was preserved during the AuNP deposition process, which was ensured by annealing the gold films in an inert atmosphere during the de-wetting stage. There is evidence that the contact angle of a surface is reduced when the roughness of that surface is increased, which is why the BDD electrodes had smaller contact angles than the pBDD electrodes [17].

7.3.2 Process optimisation of AuNP deposition

The procedure for sputtering gold onto the substrates and segregating the gold into nanoparticles via de-wetting during an annealing step was optimised on silicon substrates before application to the BDD and pBDD electrodes. Silicon was used for
the process optimisation of the AuNP production as the cost of several samples was trivial, compared to the expense of the same number of diamond substrates. The depth of the gold films on each silicon substrate was controlled by adjusting the deposition time of the sputtering process. The thickness of the gold films sputtered onto the silicon substrates were verified through ellipsometry (Table 7.2).

**Table 7.2:** The thickness of gold sputtered onto each silicon substrate, as determined by ellipsometry.

<table>
<thead>
<tr>
<th>Expected Au thickness (nm)</th>
<th>Measured Au thickness (nm)</th>
<th>SiO$_2$ thickness (nm)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0</td>
<td>15.82</td>
<td>23.33</td>
</tr>
<tr>
<td>10</td>
<td>2.10</td>
<td>16.56</td>
<td>22.51</td>
</tr>
<tr>
<td>15</td>
<td>8.67</td>
<td>8.10</td>
<td>3.05</td>
</tr>
<tr>
<td>20</td>
<td>14.58</td>
<td>2.26</td>
<td>5.50</td>
</tr>
<tr>
<td>25</td>
<td>18.21</td>
<td>1.42</td>
<td>6.10</td>
</tr>
</tbody>
</table>

In Table 7.2 the $\chi^2$ values are particularly high for the thinner gold films, with expected thicknesses of 5 and 10 nm, because the gold had not formed a complete film (Figure 7.6a and 7.6b). This introduced a large error to the ellipsometry measurements, which are designed for the analysis of homogeneous films. As seen in Figure 7.6, the sputtered gold did not start to form a complete film until a thickness of 20 nm or more was deposited. Due to the inhomogeneous gold layers on the silicon substrates the standard model used for fitting the silicon oxide and gold layers did not provide accurate results for the measured thickness of each layer.

However, it was not necessary to record the exact thickness of gold deposited because the deposition time was controlled during the sputtering process, so the resulting gold films were repeatable, even if the thickness of gold was unknown. The de-wetting of the gold films into nanoparticles was also repeatable and the size and coverage of the AuNPs could be accurately calculated from a combination of AFM and SEM measurements. The average diameter and coverage of the AuNPs on each substrate were determined by analysing AFM and SEM scans taken over five random areas on each sample and are compared in Table 7.3.

No data is available for the AuNPs generated by a 400 °C anneal of either the 20 nm or 25 nm gold films because in these cases the films did not conventionally de-wet. Instead, incomplete gold layers formed, containing pits where the sputtered gold did not totally combine (Figure 7.7g and 7.7i). When the sputtered thickness of gold was greater than 20 nm no discrete nanoparticles formed when the substrates were annealed at 600 °C, instead the gold films were de-wet into ‘nano-islands’ (Figure 7.7h and 7.7j).
Figure 7.6: AFM spectra (2×2 μm²) of the extent of the gold films on each silicon substrate following the sputtering of gold, thicknesses estimated to be: a) 5 nm b) 10 nm c) 15 nm d) 20 nm and e) 25 nm.

Table 7.3: Size and coverage of AuNPs generated on silicon substrate surfaces

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Sputtered Au thickness (nm)</th>
<th>Average AuNP diameter (nm)</th>
<th>Surface coverage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 °C</td>
<td>5</td>
<td>13</td>
<td>51</td>
</tr>
<tr>
<td>600 °C</td>
<td>5</td>
<td>22</td>
<td>63</td>
</tr>
<tr>
<td>400 °C</td>
<td>10</td>
<td>56</td>
<td>80</td>
</tr>
<tr>
<td>600 °C</td>
<td>10</td>
<td>70</td>
<td>78</td>
</tr>
<tr>
<td>400 °C</td>
<td>15</td>
<td>88</td>
<td>59</td>
</tr>
<tr>
<td>600 °C</td>
<td>15</td>
<td>97</td>
<td>80</td>
</tr>
<tr>
<td>400 °C</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>600 °C</td>
<td>20</td>
<td>280</td>
<td>53</td>
</tr>
<tr>
<td>400 °C</td>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>600 °C</td>
<td>25</td>
<td>206</td>
<td>50</td>
</tr>
</tbody>
</table>

Following the results from producing gold nanoparticles on silicon the same procedure of sputtering gold onto the substrate surfaces and annealing to de-wet the gold into nanoparticles was repeated on diamond substrates. The smallest AuNPs produced on the silicon substrates were made by annealing 5 nm of gold at 400 °C for five minutes. Therefore, on the diamond substrates the gold layer was also annealed at 400 °C for five minutes. The gold layers deposited on the BDD substrates were 3 nm in thickness, as the process optimisation on the silicon substrates showed that the thinnest layers of gold resulted in the smallest nanoparticles when annealed
7.3. Results and discussion

Figure 7.7: SEM spectra of AuNPs de-wet on silicon, under the conditions: a) 5 nm Au, 400 °C anneal b) 5 nm Au, 600 °C anneal c) 10 nm Au, 400 °C anneal d) 10 nm Au, 600 °C anneal e) 15 nm Au, 400 °C anneal f) 15 nm Au, 600 °C anneal g) 20 nm Au, 400 °C anneal h) 20 nm Au, 600 °C anneal i) 25 nm Au, 400 °C anneal j) 25 nm Au, 600 °C anneal.
and 3 nm was the thinnest layer of gold that it was possible to deposit with the Emscope SC500 gold sputter coater. It was expected that for mercury detection the greatest sensitivity would be obtained with electrodes decorated with the smallest AuNPs because these would have the largest surface area of gold, which acts catalytically during the preconcentration step of the SWASV measurements [67]. SEM spectra of the surface of each of the decorated BDD and pBDD electrodes are shown in Figure 7.8, which will be discussed in the following section.

![Figure 7.8: SEM spectra of the surfaces of each electrode, coated with AuNPs: a) BDD with 22 nm AuNPs, b) BDD with 10 nm AuNPs, c) pBDD with 23 nm AuNPs and d) pBDD with 13 nm AuNPs.](image)

### 7.3.3 AuNP characterisation

The average AuNP diameter and percentage coverage on the surface of each diamond electrode, along with the standard deviation of this value, was determined from an average of five SEM scans from random locations across each substrate, which were analysed using the ‘analyse particles’ function in ImageJ software (Table 7.4).

The AuNPs produced from gold films that were sputtered onto the electrode surfaces through a copper TEM grid (dimensions: 23 µm bar, 28 µm hole), which acted as a shadow mask, resulted in smaller AuNPs inside the gaps left by the TEM grid than those produced on the same electrode outside the area covered by the TEM grid.
7.3. Results and discussion

Table 7.4: Size and coverage of the AuNPs generated on the diamond substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Deposition type</th>
<th>Average AuNP diameter (nm)</th>
<th>Surface coverage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDD</td>
<td>No TEM grid</td>
<td>22 ± 9</td>
<td>56</td>
</tr>
<tr>
<td>BDD</td>
<td>With TEM grid</td>
<td>10 ± 3</td>
<td>51</td>
</tr>
<tr>
<td>pBDD</td>
<td>No TEM grid</td>
<td>23 ± 12</td>
<td>47</td>
</tr>
<tr>
<td>pBDD</td>
<td>With TEM grid</td>
<td>13 ± 5</td>
<td>44</td>
</tr>
</tbody>
</table>

grid (Figure 7.9).

![Image](image_url)

Figure 7.9: SEM spectra showing a) Average diameter 23 nm AuNPs on pBDD electrode, b) Patterned gold on pBDD surface after TEM grid was used as a shadow mask and c) Average diameter 13 nm AuNPs on pBDD electrode, inside the holes of the TEM grid shadow mask.

The AuNPs produced in 28 µm² squares through the TEM grid shadow mask had an average diameter ≥10 nm smaller than AuNPs produced without the use of a TEM grid shadow mask. During the gold deposition with the Emscope SC500, the substrate holder was held at a positive potential, which induced a charge in both the BDD and the TEM grid placed on its surface [150]. The positively charged copper TEM grid had a filtering effect on the gold, leading to smaller AuNPs inside the holes of the grid, most likely due to its electrostatic field affecting the sputtered gold ions in the chamber [184].
The physical stability of the AuNPs on the electrodes was tested by comparing each electrode surface with SEM scans taken on five random areas across each electrode before and after an accelerated lifetime test. This involved ultrasonication in water for 10 min; the results are shown in Figures 7.10 and 7.11.

![Figure 7.10: Comparison of AuNP average diameter and standard deviation on each electrode before and after ultrasonication in water (10 min), the AuNPs on the first two substrates were deposited through a TEM grid (copper, 23 µm bar, 28 µm hole).](image)

As seen in Figure 7.10 the ultrasonication of the electrodes resulted in a smaller standard deviation in AuNP diameter on every electrode. Where the gold was sputtered through a TEM grid the AuNP average diameter increased following the ultrasonication of the electrode, due to the agglomeration of a proportion of the smallest nanoparticles. In contrast, when the gold was sputtered onto the electrodes without a TEM grid shadow mask the AuNP average diameter decreased after sonication. This was a result of a proportion of the larger AuNPs being partially broken down into a mixture of smaller nanoparticle diameters. The discrepancy between these results can be explained by the filtering effect of the TEM grid on the gold during sputtering, which affected the bonding energy between the diamond surface and the AuNPs. This likely caused the smallest AuNPs (with the lowest surface area of
Figure 7.11: SEM spectra of (a) BDD electrode decorated with 22 nm AuNPs before ultrasonication in water and (b) afterwards, BDD electrode decorated with 10 nm AuNPs before (c) and after (d) ultrasonication in water, pBDD electrode decorated with 23 nm AuNPs before (e) and after (f) ultrasonication in water and pBDD electrode decorated with 13 nm AuNPs before (g) and after (h) ultrasonication in water.
contact with the diamond substrates) to have lower adhesion to the electrode surfaces, in comparison to the larger AuNPs produced from gold sputtered onto the electrodes in the absence of a TEM grid shadow mask [184].

The chemical stability of the AuNPs on each electrode was assessed by analysing SEM scans taken on five random areas across each electrode before and after the electrodes were used in SWASV measurements for mercury detection. An average AuNP diameter and the standard deviation of that value was calculated for each electrode before and after the SWASV measurements by using the ‘analyse particles’ function of ImageJ software; the results are shown in Figure 7.12.

![Figure 7.12](image)

**Figure 7.12:** Comparison of AuNP average diameter and standard deviation on each electrode before and after SWASV measurements, the AuNPs on the first two substrates were deposited through a TEM grid (copper, 23 µm bar, 28 µm hole).

The SEM images used to determine the chemical stability of the AuNPs are shown in Figure 7.13, where the persistence of the AuNPs can be clearly seen. The smallest AuNPs on the polished electrodes had the weakest adherence to the diamond surface and so were dislodged during the SWASV measurements (figure 7.13d).

Following the SWASV measurements there was a smaller average change in
Figure 7.13: SEM spectra of (a) BDD electrode decorated with 22 nm AuNPs before SWASV measurements and (b) afterwards, BDD electrode decorated with 10 nm AuNPs before (c) and after (d) SWASV measurements, pBDD electrode decorated with 23 nm AuNPs before (e) and after (f) SWASV measurements and pBDD electrode decorated with 13 nm AuNPs before (g) and after (h) SWASV measurements.
diameter of the AuNPs on each electrode after the chemical stability test, in comparison to the diameter change observed following the extended lifetime testing of ultrasonication in water for 10 min (Figure 7.11). However, the standard deviation in AuNP diameter increased during the SWASV measurements on every electrode, due to agglomeration of some of the smallest nanoparticles with the adjacent AuNPs of largest diameter (Figure 7.12). This produced larger maximum diameter AuNPs and reduced the overall surface coverage of the nanoparticles on the electrode surfaces. However, the majority of the AuNPs were unchanged following the SWASV measurements, resulting in only small changes in the average AuNP diameter on each electrode.

A greater increase in the standard deviation of the AuNP average diameter was observed on the pBDD electrodes than the unpolished BDD (Figure 7.12). This was a result of the lower adhesion of the AuNPs on the polished electrodes, which lead to a greater proportion of the AuNPs agglomerating, resulting in a lower coverage of nanoparticles after the SWASV measurements (Figure 7.13).

A lower adhesion of AuNPs on the diamond surface which were produced by annealing gold films deposited through a TEM grid was observed on both the polished and unpolished diamond electrodes. This is demonstrated by the loss of some AuNPs during SWASV measurements using the BDD electrode decorated with 10 nm AuNPs, depicted in the SEM images of Figure 7.13c before the SWASV measurements and 7.13d after the SWASV measurements. The weaker adhesion of the AuNPs deposited through a TEM grid is most likely due to the electrostatic effect of the TEM grid during the gold deposition, throughout which a bias was applied to the substrate and therefore also to the TEM grid placed on the diamond, causing them to become positively charged [150]. This resulted in smaller average diameter AuNPs inside the gaps left by the TEM grid, with reduced adhesion to the diamond surface in comparison to the AuNPs outside the TEM grid shadow mask.

### 7.3.4 Mercury detection

Before the mercury detection measurements, control CV measurements were made using bare pBDD and bare BDD electrodes over the same mercury concentration range as the standard experiment. No peaks were seen at any concentration of mercury nitrate in the electrolyte, for either of the bare electrodes. An example of the CV scans produced in these control measurements is shown in Figure 7.14a, which were produced when there was the highest concentration of mercury (1 mM) in the electrolyte. A second set of control measurements were made using the four AuNP decorated electrodes that are the focus of this work, in which SWASV measure-
ments were made in the blank electrolyte before the addition of mercury nitrate. Again, there are no peaks in the observed current of the resultant CV plot. An example of the results from these control measurements, are provided in Figure 7.14b.

![Figure 7.14: SWASV control measurements made with a) bare BDD and bare pBDD electrodes at 1 mM mercury concentration and b) the four AuNP decorated electrodes in the blank electrolyte, with no mercury present in the solution.](image)

As there are no peaks present in the CV spectra produced from either set of control measurements (Figure 7.14) this means that any peaks present in the CV spectra from the SWASV experiment will be a result of the addition of mercury nitrate to the 0.1 M HNO$_3$ electrolyte.

The SWASV measurements made with each diamond based working electrode were repeated four times at each concentration of mercury tested (1 pM, 1 nM, 1 µM, 5 µM, 10 µM, 50 µM, 0.1 mM, 0.5 mM, and 1 mM). The average observed currents from these repeats, with the standard deviation for these values is plotted in Figure 7.15.
Figure 7.15: Comparison of SWASV average scans and standard error with 0.005 V potential step, 0.01 V amplitude and 10 Hz frequency for each electrode at Hg$^{2+}$ concentrations (a) 1 pM, (b) 1 nM, (c) 1 µM, (d) 5 µM, (e) 10 µM, (f) 50 µM, (g) 0.1 mM, (h) 0.5 mM and (i) 1 mM.
7.3. Results and discussion

The reoxidation of Hg$^0$ at the working electrode surface to Hg$^{2+}$ during the SWASV measurements is observed at 0.45 V in Figure 7.15 [178]. This peak is first visible at 1 µM mercury concentration in sub-figure 7.15c with the pBDD electrode decorated with 13 nm AuNPs. This peak was not observed with the other pBDD-based electrode or either BDD-based electrode until a mercury concentration of 5 µM was added to the electrolyte.

The size of the AuNPs is an important factor in the sensitivity of these electrodes for mercury detection. The pBDD electrode decorated with 13 nm AuNPs showed greater sensitivity (higher observed current) than the pBDD electrode decorated with 23 nm AuNPs, due to the increased surface area of the catalytically active AuNPs. However, the same trend was not observed with the unpolished BDD electrodes for which the electrode with larger AuNPs had a lower detection limit for mercury. This is because a proportion of the average 10 nm diameter AuNPs on the BDD electrode were dislodged from the electrode surface during the SWASV measurements (Figure 7.13d), resulting in a reduction of the area of the electrode surface coated with catalytically active AuNPs.

At higher mercury concentrations (>10 µM) a competing oxidation reaction was observed around 0.8 V (Figure 7.15). As no peaks were present following the SWASV scans in either set of control measurements (Figure 7.14) this additional peak must be due to the addition of mercury nitrate to the bulk electrolyte. The peak at ~0.8 V has previously been observed in the literature and was hypothesised to be due to the formation of a mercuric dimer [89][178].

There is also an additional broad peak between 0.7 - 0.9 V at lower concentrations of mercury (1 pM - 1 µM) observed with both pBDD-based electrodes. Again, as no peaks were seen in either of the control measurements this peak must be a result of the addition of mercury nitrate to the electrolyte. It is possible that this is also due to the formation of a mercuric dimer, however, this is potentially a result of a species within the mercury nitrate stock solution being oxidised. The control measurements were made in the blank 0.1 M HNO$_3$ electrolyte before the addition of mercury to the system. Although no peaks were seen during these control measurements, the stock mercury nitrate had a different base solution. Therefore, it is possible that the additional broad peaks between 0.7 - 0.9 V are due to the oxidation of a contaminating species in the stock mercury nitrate solution. If these peaks are due to the detection of a mercuric dimer this would be an exceptional result, with pM sensitivity being achieved with the pBDD electrode decorated with 13 nm AuNPs. However, the origin of these peaks are currently unknown and require further investigation, meaning that only sensitivity to 1 µM can conclusively
be attributed to this electrode.

Although the size of the AuNPs affected the sensitivity of these electrodes, the $\text{sp}^2: \text{sp}^3$ carbon ratio in the two substrate types had a more significant impact. Greater sensitivity was achieved with the pBDD electrodes, with which lower concentrations of mercury in the electrolyte were detected than the unpolished BDD electrodes. The polishing process is known to encourage defect sites to propagate through the diamond lattice to a depth of several microns and creates surface-stable $\text{sp}^2$ carbon [161]. These effects, in addition to the size and distribution of the AuNPs on the pBDD electrode surface can explain the superior sensitivity achieved with these electrodes.

The sensitivity performance of the pBDD electrodes is good when compared to recent reports of alternative electrode materials for this purpose which are also in the $\mu$M range [40][189]. However, the sensitivity for the reoxidation of $\text{Hg}^0$ at the working electrode surface to $\text{Hg}^{2+}$ (1 $\mu$M, observed at 0.45 V) is lower than required by WHO, which recommends a maximum concentration of 6 $\mu$g$^{-1}$ (ca. 30 nM) mercury in potable water [97].

![Figure 7.16: SWASV average scans and standard error for mercury detection in the concentration range 0.5–100 $\mu$M with a BDD electrode decorated with 22 nm AuNPs, at 0.5 Hz frequency, 0.01 V amplitude and 0.005 V potential step.](image)

To determine if the mechanism of mercury detection was diffusion limited the SWASV measurements for the BDD electrode decorated with 22 nm AuNPs were repeated at a lower frequency of 0.5 Hz and therefore a $20 \times$ slower scan speed of 0.0025 $V_s^{-1}$ (Figure 7.16), in addition to the standard frequency of 10 Hz used
7.3. Results and discussion

throughout this study.

Mercury detection at the BDD electrodes was shown to be unaffected by the diffusion of ions to the electrode surface because when the SWASV measurements using the BDD electrode decorated with 22 nm AuNPs were repeated at a 20× slower scan speed the lower limit of detection was the same as for the previous SWASV measurements (5 µM, seen in Figure 7.15d).

The maximum current peak observed for the re-oxidation of mercury from Hg\(^0\) to Hg\(^{2+}\) at each detectable concentration with the BDD electrode decorated with 22 nm AuNPs was plotted against the mercury concentration in the electrolyte during that SWASV measurement at both 10 Hz and 0.5 Hz frequency (Figure 7.17).

![Figure 7.17](image)

**Figure 7.17:** a) Maximum current peak for each concentration of mercury in solution (range: 0.5—100 µM) detected with the BDD electrode decorated with 22 nm AuNPs upon application of SWASV scan with 0.005 V potential step, 0.01 V amplitude, 10 Hz frequency and b) with 0.5 Hz frequency.

A linear relationship between the peak observed current when mercury was detected and the concentration of mercury(II) in the electrolyte for that SWASV measurement was observed for the BDD electrode decorated with 22 nm AuNPs at 10 Hz scan frequency (Figure 7.17a). The same linear electrode response was also initially observed for the SWASV measurements at the lower scan frequency of 0.5 Hz, before the electrode became saturated at 100 µM mercury concentration. The saturation of the electrode resulted in no change in the maximum current of the mercury oxidation peak at concentrations greater than 100 µM (Figure 7.17b). This demonstrates that the BDD electrode becomes saturated at high concentrations of mercury when slow SWASV scan speeds are used. However, as the same sensitivity of 5 µM was recorded using the BDD electrode decorated with 22 nm AuNPs at both scan speeds, this highlights that it is not necessary to reach saturation of the sensor in order to achieve repeatable measurements.
7.4 Conclusion

This work presented has been an investigation into how the dispersion of AuNPs on BDD electrode surfaces and the roughness of the BDD surface affects the sensitivity of electrochemical measurements for mercury detection in aqueous solution. Although greater sensitivity was achieved with the pBDD electrode decorated with 13 nm AuNPs than the pBDD electrode decorated with 23 nm AuNPs, overall the size of the catalytically active AuNPs on the electrode surfaces was demonstrated to have a smaller effect on the sensitivity for mercury detection than the surface preparation of the BDD surface. A lower limit of detection was achieved with both polished BDD electrodes than with either unpolished BDD electrode. This was proven to not be caused by the diffusion of ions to the electrode surface by repetition of the SWASV measurements with the BDD electrode decorated with 22 nm AuNPs at a 20× slower scan speed. The same sensitivity was achieved as during the SWASV measurements using the same electrode at the higher scan rate. This demonstrates that the BDD electrodes are well suited to rapid in situ measurements for mercury detection in aqueous environments. The superior sensitivity of the pBDD electrodes can be explained by the higher graphitic carbon content on these electrodes, which was caused by polishing damage and characterised with Raman spectroscopy. The sensitivity (1 µM) achieved with the pBDD electrodes for the reoxidation of mercury from Hg$^0$ to Hg$^{2+}$ is good when compared to recent reports of alternative electrode materials in the literature. When allied to the demonstrated tenacious nature of the attached AuNPs during repeated measurement cycles and accelerated lifetime (ultrasonic) tests, this suggests a promising future for this approach for the realisation of robust, highly sensitive, mercury detectors for a wide range of aqueous environments.
A detailed EIS study of boron doped diamond electrodes decorated with gold nanoparticles for high sensitivity mercury detection

8.1 Introduction

Mercury is a highly toxic heavy metal that poses a severe threat to the environment and human health [97]. It is essential that mercury is detected in the environment with high sensitivity as it tends to form complexes with biological ligands, which leads to accumulation in the food chain [4]. The primary source of mercury exposure in humans is from food, predominantly fish, which have been exposed to mercury contaminated water [79]. Electrochemical techniques are ideal for mercury detection with sufficient sensitivity, as they can be performed using portable equipment for real-time monitoring at the site of suspected mercury contamination. The use of electrochemical impedance spectroscopy (EIS) offers some advantages over other electrochemical approaches. EIS is a steady-state technique, meaning that signal averaging can be used to achieve the required precision level within an individual experiment. With standard instrumentation, EIS measurements are conducted over a wide frequency range (< 1 MHz to > 1 MHz), which permits a broad range of electrochemical processes to be investigated in the same experiment [107]. These characteristics surpass those of equivalent techniques based on time domain experimentation and have led to EIS becoming one of the principal methods for investigating interfacial reaction mechanisms.

Whilst diamond is considered a wide band gap semiconductor, it can display quasi-metallic properties if boron is incorporated at concentrations in excess of $10^{20}$
8.1. Introduction

Such heavily boron doped diamond (BDD) as an electrode material is well suited to the high sensitivity detection of mercury and other species via electrochemical measurements. This material is associated with low background currents, a wide electrochemical window and chemical stability [111]. In addition, BDD electrodes are stable at extreme temperatures and pressures and are resistant to fouling, so are ideal for the application of portable sensors for in situ measurements over extended periods of time, even in harsh environments.

The EIS measurements in this chapter are an extension to the work in Chapter 7 where BDD electrodes, some decorated with gold nanoparticles, were used to detect mercury in a 0.1 M HNO$_3$ electrolyte via square wave anodic stripping voltammetry (SWASV) [118]. The gold nanoparticles act catalytically during the measurements, improving the sensitivity of the BDD electrodes. During the SWASV measurements the mercury in the electrolyte was pre-concentrated onto the working electrode surface by application of 0.35 V for 10 min. Mercury was detected in the potential range 0.5–0.8 V during these SWASV measurements [118].

![Figure 8.1: Average SWASV scan and standard error from four repeats of the measurement for mercury detection (mercury concentration 0.1 mM) from Chapter 7, showing why 1.0 V was chosen as the stripping potential for EIS measurements. At this potential there are no peaks on the SWASV plot and so no reaction taking place. All of the mercury has been stripped from the surface of each of the electrodes.](image_url)

In this study, EIS measurements are used to identify the change in the reactivity of BDD-based electrodes during the different stages of the SWASV measurements described above. The reactivity of the electrodes is indicated by the charge transfer
resistance at their surface and quantified by an electron transfer rate \( k_0 \), which is calculated from the raw EIS data. The EIS measurements were performed following the application of the potentials corresponding to the steps of the SWASV measurements in Chapter 7 [118]. The EIS measurements were performed at 0.35 V (at which the mercury ions in the solution were pre-concentrated onto the surface of the working electrode during the SWASV measurements), which is referred to as the deposition potential in this work. The EIS measurements were then performed at 1.0 V, which is referred to as the stripping potential. This potential was chosen because in the SWASV measurements of the previous work in Chapter 7 (see Figure 8.1) this is the potential at which there are no peaks on the resulting voltammogram for any electrode or mercury concentration configuration tested, meaning that all of the mercury ions had been stripped off and no further reactions were occurring at the electrode surface. EIS measurements were also made at open circuit potential to serve as a control for the behaviour of the system, following the methodology of Petovar et al. [144].

8.2 Experimental methods

Electrochemical grade BDD (\([B] > 10^{20}\) cm\(^{-3}\), 10×10×0.5 mm) substrates were purchased from Element Six Ltd (e6cvd.com). The experiments used unpolished polycrystalline BDD, with a surface roughness \( R_A \sim 50 \mu m \), and polished polycrystalline diamond (pBDD), where the surface roughness was reduced to \( R_A \sim 50 \text{ nm} \). All chemicals unless otherwise stated were purchased from Sigma-Aldrich. Reverse osmosis derived water, resistivity 18 M\( \Omega \)-cm, was used throughout.

8.2.1 Electrode preparation

Prior to processing, organic contaminants were removed from the BDD and pBDD surfaces with a ‘Piranha’ clean (3:1 v/v of 98% HCl and 30% \( \text{H}_2\text{O}_2 \)) for 10 min [135].

The graphitic carbon content in the surface of each BDD and pBDD substrate was qualitatively assessed with a Renishaw micro-Raman spectrometer (532 nm laser source). The Raman analysis was performed with 20\( \times \) magnification, 10 s exposure and an average was taken over ten accumulations, the microscope was calibrated using a silicon substrate. WiRE (v 2.0) software was used for data acquisition.

It has previously been shown that gold nanoparticles (AuNPs) have stronger adherence to BDD surfaces when they are hydrogen terminated [178]. The BDD and pBDD substrates were hydrogen terminated in an AX5010 Seki Technotron
Inc. reactor with H-plasma for 10 min at 700 °C platen temperature (Williamson Dual wavelength pyrometer), 800 W power, 40 Torr pressure. A non-continuous 5 nm gold film was sputtered onto one each of the BDD and pBDD electrodes with an Emscope SC500 gold sputter coater. The gold films were segregated into gold nanoparticles (AuNPs) by an annealing process (often referred to as ‘de-wetting’, due to the role of surface tension) in a Solaris 150 Rapid Thermal Processing System, under nitrogen at 400 °C for 5 min.

A Zeiss XB1540 Crossbeam scanning electron microscope (10 kV operation voltage) was used to quantify the size and dispersion of AuNPs on the electrode surfaces. Scans from five random locations across each substrate were analysed with ImageJ software to calculate the average size and surface coverage of the AuNPs on each electrode.

8.2.2 EIS measurements

The EIS measurements were made with a three-electrode setup, controlled by a Metrohm Autolab PGSTAT204 potentiostat, using the FRA32M EIS module, and NOVA 2.1 software. A BDD-based working electrode, with 0.14 cm² surface area exposed to the electrolyte, a Ag/AgCl KCL (3 M) reference electrode and a platinum counter electrode with 1 cm² surface area were used. The experiments were conducted in a 0.1 M HNO₃ electrolyte, which was sequentially doped with increasing concentrations of mercury nitrate, from 1 pM – 1 mM Hg(NO₃)₂. Four BDD-based electrodes were used: a bare BDD electrode, a BDD electrode decorated with 30 nm AuNPS, a bare pBDD electrode, and a pBDD electrode decorated with 30 nm AuNPs.

At each concentration of mercury, the EIS measurements were performed after the application of each of three potentials for 10 min: an open circuit potential control, a deposition potential of 0.35 V, at which the mercury ions in the electrolyte were pre-concentrated onto the surface of the BDD-based working electrode and a stripping potential of 1.0 V, at which all of the pre-concentrated mercury will have been stripped from the surface of the BDD-based working electrode. After the application of each of these potentials for 10 min an EIS measurement was performed over the frequency range 50 kHz – 50 mHz, with 8 points per decade and 10 mV amplitude [144]. Between each addition of mercury nitrate the working electrode was cleaned by the application of 150 current pulses, lasting 100 ms, which alternated between 10 mA cm⁻² and -10 mA cm⁻², as has been previously shown to be effective [10].

The progress of the EIS measurements were monitored in real time with a
Lissajous plot, to identify noise in the system and to ensure that the response was linear [12]. A Konig-Kramers (KK) test was performed to determine if the recorded EIS data satisfied the conditions of being linear, causal and stable, which is required for equivalent circuit modelling to be an appropriate analysis method [22].

EIS Spectrum Analyser (ABC Chemistry) software was used to fit the EIS results using equivalent circuit modelling. The quality of the fit for each set of experimental data is defined by a $\chi^2$ value, with the quality of each fit below the limit $\chi^2 < 0.1$. The parameters of each equivalent circuit are quantified and used to calculate the electron transfer rate ($k_0$) at each electrode.

8.3 Results and discussion

8.3.1 Electrode characterisation

The relative proportions of sp$^3$ diamond carbon and sp$^2$ non-diamond carbon at the surface of the BDD and pBDD electrodes was assessed with Raman spectroscopy (Figure 8.2a). Visible Raman spectroscopy is known to overemphasise the size of the sp$^2$ origin peaks as compared to those derived from the sp$^3$ phase, due to the differing cross sections for Raman excitation of the two carbon phases [99]. It is clear from Figure 8.2a that both films are predominantly diamond (sp$^3$) in character. Crystalline quality can be estimated from the full width at half maximum (FWHM) of the 1332 cm$^{-1}$ sp$^3$ peak; in this case the values of 8.39 $\pm$0.11 cm$^{-1}$ and 12.10 $\pm$0.18 cm$^{-1}$ for the BDD and pBDD substrates respectively. These verify the relatively high diamond crystalline quality despite the presence of very high levels of the boron dopant [174]. Figure 8.2b and 8.2c reveal the morphological differences between the polished and unpolished samples using SEM analysis.

The characteristic 1332 cm$^{-1}$ diamond carbon peak is clearly displayed in the Raman spectra for both substrate types (Figure 8.2a). The non-diamond carbon G peak at 1575 cm$^{-1}$ is also present in both spectra, but at greater intensity in the spectra for the pBDD substrate. The ratio between the intensities of the 1332 cm$^{-1}$ and 1575 cm$^{-1}$ peaks can only be used to qualitatively assess the relative proportions of these two carbon bond types. It is not possibly to quantify this ratio because the intensity of each peak is dependent on the grain size, film stress, doping density, and excitation wavelength used [18]. When the excitation wavelength is in the visible spectrum, as in this paper where a 532 nm laser source was used, the sensitivity to sp$^2$ materials is approximately 100× higher than for sp$^2$ material [141].

Due to the higher sensitivity of the excitation wavelength used for the sp$^2$ car-
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Figure 8.2: a) Raman spectra of the unpolished BDD substrate revealing the distinctive 1332 cm\(^{-1}\) peak of the diamond carbon phase, and (inset) second order Raman spectrum (black) and similar measurements for the polished pBDD substrate (red), with the corresponding SEM images of b) the BDD substrate and c) the polished pBDD substrate.

bon bonds in these spectra, we can confidently say that as the intensity of the sp\(^3\) diamond peak at 1332 cm\(^{-1}\) is significantly greater than the 1575 cm\(^{-1}\) peak that there is a low proportion of sp\(^2\) carbon at the surface of these electrodes, compared to the bulk sp\(^3\) carbon. The intensity of the 1575 cm\(^{-1}\) peak is higher relative to the 1332 cm\(^{-1}\) peak for the pBDD substrate, meaning that there is a higher proportion of non-diamond carbon at the surface of this substrate. This is likely due to the polishing process introducing damage to the diamond surface [161].

The high boron doping concentration in the BDD and pBDD substrates ([B] > 10\(^{20}\) cm\(^{-3}\)) is confirmed by the asymmetry at the base of the 1332 cm\(^{-1}\) peak, known as the Fano resonance, which corresponds to the onset of metal-like conductivity in the diamond as a result of the boron impurity band transitioning into a continuum state [1].

The average size and percentage coverage of the AuNPs produced on the BDD and pBDD substrates by the annealing process described in section 8.2.1 were calculated using ImageJ to analyse the SEM images of each surface (Figure 8.3). An average value was calculated from the size and surface coverage of the AuNPs on each electrode, from five scans at random locations on the substrate surfaces. On the BDD substrate, the average AuNP diameter was 30 ± 14 nm, with a percentage coverage of 44 %. On the pBDD substrate, the average AuNP diameter was 30 ± 11
nm, with a percentage of 42%.

Figure 8.3: SEM images of a) the BDD substrate decorated with AuNPs, average diameter 30 nm, and b) the pBDD substrate decorated with AuNPs, average diameter 30 nm. The SEM images were obtained from a Zeiss XB1540 Crossbeam scanning electron microscope (10 kV operation voltage) and analysed with ImageJ software.

8.3.2 EIS measurements
The Bode impedance and phase plots for each electrode are consistent under all configurations of mercury concentration and potential at which the EIS measurements were made. An example of these plots, made at the deposition potential (0.35 V) when the mercury concentration in the electrolyte was 1 mM, is shown in Figure 8.4. The Bode plots for each electrode in the control blank electrolyte and over the full range of mercury concentrations and potentials tested are provided in Appendix B.

The raw EIS data is presented in the Bode plot format in Figure 8.4. In the high frequency region of the Bode impedance plots (Figure 8.4a) a horizontal amplitude is reached and in the high frequency region of the Bode phase plots (Figure 8.4b) the phase angle tends to 0°. These responses are typical of uncompensated resistance, which in this experiment will predominantly be due to the solution resistance through the electrolyte (R_s) [140]. In the low frequency region of the Bode impedance plots the curve is horizontal and the impedance is therefore independent of frequency, which corresponds to the total impedance of the system. In the middle frequency region, the Bode impedance plots are linear (slope close to -1) and the phase angle tends to -90° in the Bode phase plots. These characteristics are typical of a capacitor, which in this system is due to the double layer capacitance at the surface of the diamond-based working electrodes [144].

The EIS results for each of the electrodes, at the mercury concentrations 1 µM, 500 µM, and 1 mM are presented in the Nyquist plot format in Figure 8.5. In the
8.3. Results and discussion

Figure 8.4: a) The Bode impedance plots and b) the Bode phase plots of the data for each electrode resulting from an EIS measurement performed at a mercury concentration of 1 mM, applied potential 0.35 V. The EIS measurement was conducted over the frequency range 50 kHz –50 mHz, with 8 points per decade and 10 mV amplitude.

The frequency range used here (50 kHz –50 mHz), which is standard for the analysis of Faradaic processes in aqueous systems with EIS, only one semicircle is seen on the Nyquist plots [49]. The Warburg impedance discussed in section 4.4.2 is not seen on the Nyquist plots in Figure 8.5 because an additional fast redox couple was not added to the electrolyte [12]. The measurements conducted in this study follow the methodology of Petovar et al. to use EIS to investigate how the response of the working electrode changes during the deposition and stripping steps of the SWASV measurements conducted in previous work, using this electrochemical system to detect mercury ions in aqueous solution (Chapter 7) [144]. The low frequency, semi-infinite diffusion that is modelled by the Warburg impedance element was not an important factor to analyse during this study [53][144]. Here, the focus has been on identifying the changes that occur at the surface of the diamond electrodes and determining the influence of AuNPs during SWASV measurements for mercury ion detection. The key parameters that give insight into the nature of the interaction between the diamond working electrode surfaces and the mercury ions in the solution are the charge transfer resistance and capacitance values extracted from the EIS data (see Tables 8.2 and 8.3) [49].

The Nyquist plots for the EIS measurements made in the control blank electrolyte and the other mercury concentrations tested (1 pM and 1 nM) are presented in Appendix B.
Figure 8.5: Nyquist plot presentation of the EIS data from measurements made over the frequency range 50 kHz – 50 mHz, with 8 points per decade and 10 mV amplitude, for each of the electrodes. The results presented here are from EIS measurements made at a) open circuit potential, 1 µM Hg concentration, b) deposition potential (0.35 V), 1 µM Hg concentration, c) stripping potential (1.0 V), 1 µM Hg concentration, d) open circuit potential, 500 µM Hg concentration, e) deposition potential (0.35 V), 500 µM Hg concentration, f) stripping potential (1.0 V), 500 µM Hg concentration, g) open circuit potential, 1 mM Hg concentration, h) deposition potential (0.35 V), 1 mM Hg concentration and i) stripping potential (1.0 V), 1 mM Hg concentration. The Nyquist plots for the other mercury concentration and potentials tested with EIS are presented in Appendix B.
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The Nyquist plots in Figure 8.5 show that generally, the bare diamond electrodes (both BDD and pBDD) have significantly higher charge transfer resistance ($R_{ct}$) than the electrodes decorated with AuNPs. This means that the bare electrodes will be slower to respond to a change in mercury concentration in the solution than the electrodes coated with AuNPs. The semicircle on the Nyquist plots for the bare BDD electrode are the highest and correspond to the highest $R_{ct}$ at the surface of that electrode. This is because the higher proportion of sp$^2$ carbon at the surface of the pBDD-based electrodes and the presence of the gold nanoparticles on the decorated electrodes improves their reactivity, so these electrodes will have lower $R_{ct}$ than the bare BDD electrode [118][178].

The Nyquist plots for the EIS data recorded for the mercury concentrations between 1 pM and 1 µM are consistent and very similar to the Nyquist plots for the data recorded during the control measurements in the blank electrolyte, when no mercury was present (see Appendix B). This means that within this concentration range each of the working electrodes tested were passive, with no change in the electron transfer rate at their surface with the increasing mercury concentration and so, no mercury would have been detected in an electrochemical measurement.

When the concentration of mercury in the electrolyte was increased to 500 µM there was a significant reduction in the size of the part of the semicircle presented in the Nyquist plots, for the EIS measurements at the deposition potential (0.35 V, Figure 8.5e). At this potential, the mercury ions in the solution were pre-concentrated onto the surface of the electrodes. The reduction in the size of the semicircle is due to a decrease in $R_{ct}$ at the surface of the electrodes. $R_{ct}$ values are smaller for the decorated electrodes, as the AuNPs act catalytically during the application of the deposition potential. Therefore, more mercury ions became more strongly attached to the AuNP decorated electrode surface, meaning that mercury was detected at lower concentrations when the AuNPs were present [118]. The Nyquist plot recorded at the stripping potential (1.0 V) at this concentration is similar to the one recorded at open circuit potential. This shows that all of the mercury has been stripped from the surface of the electrodes and that no further reaction is taking place at their surface.

When the concentration of mercury in the electrolyte was increased to 1 mM there was a further reduction in the size of the semicircles on the Nyquist plot recorded at the deposition potential (Figure 8.5h). The $R_{ct}$ values extracted from this plot are smaller for the pBDD-based electrodes than the BDD electrodes, whether or not the electrodes were decorated with AuNPs. Therefore, at this higher concentration of mercury the higher proportion of sp$^2$ carbon at the surface of the pBDD-based electrodes had a greater impact on the electron transfer kinetics than
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The AuNPs. It has previously been shown that the presence of sp² carbon can lead to the adsorption of analytes onto the electrode surface, commonly referred to as fouling [52]. In the case of the pBDD electrodes here this could mean that at the higher mercury concentrations mercury is pre-concentrated onto the sp² regions of the pBDD surface during the application of the deposition potential (0.35 V), which is conventionally only the case when AuNPs are present. This requires further investigation. Again, the Nyquist plot recorded at the stripping potential is similar to that recorded at an open circuit potential. However, it appears that not all of the mercury has been removed from the surface of the bare BDD electrode, as the $R_{ct}$ value is lower than that recorded at the open circuit potential, indicating that some reaction may still be happening at this electrode surface.

![Lissajous plot](image)

**Figure 8.6:** Lissajous plot produced during the EIS measurement over frequency range 50 kHz –50 mHz, 8 points per decade and 10 mV amplitude with the bare BDD electrode, in the blank 0.1 M HNO₃ electrolyte at open circuit potential. The Lissajous plots generated during all of the EIS measurements are shown in Appendix B.

During the EIS measurements, a Lissajous plot was used to monitor the response of the electrochemical system, to test if the response was linear and to identify noise in the data set. An example Lissajous plot, from the EIS measurement using the bare BDD electrode in the blank 0.1 M HNO₃ electrolyte at open circuit potential is shown in Figure 8.6. The Lissajous plots produced during the other EIS...
measurements are presented in Appendix B.

The shape of the example Lissajous plot in Figure 8.6 (which is similar to the other Lissajous plots, shown in Appendix B) shows that the response of the system is linear [12]. The symmetrical, tilted oval, is repeatedly traced over during the EIS experiment, with each frequency measured. In a non-linear system the Lissajous plot would not be symmetrical [121]. The smooth oval shape of the plot indicates that there is little noise within the system [51].

For EIS data to be analysed using equivalent circuit modelling it must satisfy the conditions of being linear, causal, and stable, which was determined for these experiments using Kronig-Kramers (KK) testing [140]. In most electrochemical systems the current response will vary non-linearly with the applied potential, however, when the amplitude is kept as low as possible (10 mV in this case) the response can be kept near-linear [22].

The KK relations, which are the basis for the test, are integral equations that explain the interdependence between the real and imaginary parts of the total impedance (explained in more detail in section 4.3.2). Calculation of the KK transformation would require integration over the frequency range \(0 \rightarrow \infty\), so for the KK test the measured data is instead modelled with a chain of series connected, parallel RC circuits, with one RC circuit for every recorded data point. This is a slight approximation, however, as each RC circuit is KK transformable the entire circuit must also be KK transformable [22]. The quality of the fit of the equivalent circuit to the experimental data is assessed with \(\chi^2\) values. The \(\chi^2\) values are calculated for the real and imaginary components of the impedance, which are then combined to give an overall \(\chi^2\) value for the equivalent circuit model fit. The overall \(\chi^2\) values from the KK tests at open circuit potential, over the full mercury concentration range tested, are shown for each electrode in Table B.2.

The \(\chi^2\) values for the KK test equivalent circuit fitting to the experimental data sets (Table B.2) are used to determine whether the data set satisfies the conditions of being linear, causal and stable. Determination of whether a \(\chi^2\) value is ‘large’ or ‘small’ is dependent on the number and value of the data points used in the KK test, however, it is convention that when \(\chi^2 > 10^{-4}\) the data set is considered to have a poor fit to the equivalent circuit model used in the KK test and therefore equivalent circuit modelling is not an appropriate analysis method for that data set [123]. When the \(\chi^2\) values are between \(10^{-4} \rightarrow 10^{-5}\) the fit is generally considered to be ‘reasonable’, and a ‘good’ fit is classified as \(\chi^2\) between \(10^{-5} \rightarrow 10^{-6}\) [22].

The \(\chi^2\) values for each of the electrodes in Table B.2 are all \(\leq 10^{-4}\), with the majority being \(10^{-5}\), meaning that every data set recorded during the EIS measure-
8.3. Results and discussion

Table 8.1: The $\chi^2$ values corresponding to the quality of the equivalent circuit model fit to the experimental data during Kronig-Kramers (KK) tests of the EIS data sets recorded at open circuit potential for each of the diamond electrodes, over the full mercury concentration range tested. The results of the KK tests on the data sets recorded at the other potentials (0.35 V and 1.0 V) are presented in Appendix B.

<table>
<thead>
<tr>
<th>Mercury concentration</th>
<th>BDD ($\chi^2$)</th>
<th>BDD + AuNP ($\chi^2$)</th>
<th>pBDD ($\chi^2$)</th>
<th>pBDD + AuNP ($\chi^2$)</th>
</tr>
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<tbody>
<tr>
<td>0 M (control)</td>
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<td>1.16$^{-4}$</td>
<td>1.48$^{-5}$</td>
<td>4.23$^{-5}$</td>
</tr>
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<td>1 pM</td>
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<td>4.11$^{-5}$</td>
<td>1.29$^{-5}$</td>
<td>8.39$^{-5}$</td>
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<tr>
<td>500 µM</td>
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<td>4.79$^{-5}$</td>
<td>1.73$^{-5}$</td>
<td>1.03$^{-5}$</td>
</tr>
<tr>
<td>1 mM</td>
<td>8.17$^{-5}$</td>
<td>4.37$^{-5}$</td>
<td>2.72$^{-5}$</td>
<td>1.24$^{-5}$</td>
</tr>
</tbody>
</table>

ments satisfies the conditions of being linear, causal, and stable to an acceptable level for equivalent circuit modelling to be appropriate for analysis of the experimental results.

The equivalent circuit models that were used to make the fits to the Bode and Nyquist plots in Figures 8.4 and 8.5 are presented in Figure 8.7. The fits of the equivalent circuits to the raw data all fit the criteria of $\chi^2 < 0.1$. In both of the equivalent circuit models (Figure 8.7) a constant phase element ($Q$) has been used to represent the double layer capacitance at the surface of the diamond electrodes, as is convention for rough electrode surfaces and polycrystalline materials [10]. The impedance of $Q$ is calculated using Equation 8.1, in which $Y_0$ is a constant, $j$ is the imaginary number $\sqrt{-1}$, $\omega$ is the angular frequency and $N$ is the exponent (0 –1).

$$Z_Q = \frac{1}{Y_0 (j\omega)^N}$$  \hspace{1cm} (8.1)

$Q$ is used to calculate the effective capacitance using Equation 8.2, in which $C_{eff}$ is the effective capacitance, $R_s$ is the solution resistance and $R_{ct}$ is the charge transfer resistance at the diamond-based electrode.

$$C_{eff} = Y_0^{\frac{1}{2}} \cdot \left[\frac{1}{R_s} + \frac{1}{R_{ct}}\right]^{\frac{N-1}{N}}$$  \hspace{1cm} (8.2)
The BDD and BDD + Au electrodes are modelled with a modified simple Randles equivalent circuit, made up of a series resistor ($R_s$) to represent the solution resistance of the electrolyte, a parallel resistor ($R_{ct}$) to represent the charge transfer resistance at the surface of the diamond electrodes, and a constant phase element ($Q_{dl}$), which represents the capacitance of the double layer at the surface of the diamond electrodes (Figure 8.7a). An additional RC circuit is added in parallel for the equivalent circuit designed to model the EIS data for the pBDD and pBDD + Au electrodes. This is necessary due to the higher proportion of sp$^2$ carbon at the surface of these electrodes, which has been shown to have a significant effect on the electrode reaction kinetics of some redox systems [119][15]. The additional parallel resistor ($R_3$) represents the charge transfer resistance at the sp$^2$ carbon regions on the surface of the pBDD-based electrodes and the parallel capacitor (C) represents the double layer capacitance at the sp$^2$ carbon regions of the pBDD-based electrode surfaces (Figure 8.7b).

**Figure 8.7:** a) The equivalent circuit used to model the EIS data for the BDD electrode and the BDD electrode decorated with 30 nm AuNPs and b) the equivalent circuit model for the pBDD electrode and the pBDD electrode decorated with 30 nm AuNPs.

The parameters extracted from the equivalent circuit fits for the EIS results at open circuit potential of the BDD-based and pBDD-based electrodes are presented in Table 8.2 and 8.3 respectively. The parameters extracted from the equivalent circuit fits of the EIS results conducted at the deposition potential (0.35 V) and the stripping potential (1.0 V) are provided in Appendix B.
Table 8.2: The parameters extracted from the equivalent circuit (Figure 8.7a) fit of the raw EIS data for the BDD and BDD + Au electrodes at open circuit potential. The parameters extracted from the equivalent circuit fit of the EIS data for these electrodes at the other potentials tested are presented in Appendix B.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Hg concentration</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ M(Ω)</th>
<th>$C_{eff}$ (µF)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDD</td>
<td>0 M (control)</td>
<td>38.1</td>
<td>1.61</td>
<td>0.30</td>
<td>0.07</td>
</tr>
<tr>
<td>BDD + Au</td>
<td>0 M (control)</td>
<td>36.8</td>
<td>0.52</td>
<td>0.05</td>
<td>0.10</td>
</tr>
<tr>
<td>BDD</td>
<td>1 pM</td>
<td>61.1</td>
<td>2.89</td>
<td>0.30</td>
<td>0.02</td>
</tr>
<tr>
<td>BDD + Au</td>
<td>1 pM</td>
<td>86.8</td>
<td>0.69</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>BDD</td>
<td>1 nM</td>
<td>87.7</td>
<td>4.69</td>
<td>0.31</td>
<td>0.01</td>
</tr>
<tr>
<td>BDD + Au</td>
<td>1 nM</td>
<td>105.0</td>
<td>0.70</td>
<td>0.06</td>
<td>0.02</td>
</tr>
<tr>
<td>BDD</td>
<td>1 µM</td>
<td>99.6</td>
<td>4.97</td>
<td>0.31</td>
<td>0.01</td>
</tr>
<tr>
<td>BDD + Au</td>
<td>1 µM</td>
<td>123.0</td>
<td>0.73</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>BDD</td>
<td>500 µM</td>
<td>107.0</td>
<td>2.41</td>
<td>0.32</td>
<td>0.03</td>
</tr>
<tr>
<td>BDD + Au</td>
<td>500 µM</td>
<td>121.0</td>
<td>0.46</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>BDD</td>
<td>1 mM</td>
<td>126.0</td>
<td>0.98</td>
<td>0.29</td>
<td>0.06</td>
</tr>
<tr>
<td>BDD + Au</td>
<td>1 mM</td>
<td>129.0</td>
<td>0.44</td>
<td>0.06</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Table 8.3: The parameters extracted from the equivalent circuit (Figure 8.7b) fit of the raw EIS data for the pBDD and pBDD + Au electrodes at open circuit potential. The parameters extracted from the equivalent circuit fit of the EIS data for these electrodes at the other potentials tested are presented in Appendix B.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Hg concentration</th>
<th>$R_1$ (Ω)</th>
<th>$R_2$ M(Ω)</th>
<th>$R_3$ k(Ω)</th>
<th>$C_{eff}$ (µF)</th>
<th>C (µF)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pBDD</td>
<td>0 M (control)</td>
<td>46.7</td>
<td>0.38</td>
<td>0.02</td>
<td>3.58</td>
<td>9.40</td>
<td>0.03</td>
</tr>
<tr>
<td>pBDD + Au</td>
<td>0 M (control)</td>
<td>21.8</td>
<td>0.51</td>
<td>1.76</td>
<td>0.07</td>
<td>2.78</td>
<td>0.04</td>
</tr>
<tr>
<td>pBDD</td>
<td>1 pM</td>
<td>71.3</td>
<td>2.24</td>
<td>0.03</td>
<td>4.24</td>
<td>6.93</td>
<td>0.08</td>
</tr>
<tr>
<td>pBDD + Au</td>
<td>1 pM</td>
<td>60.3</td>
<td>0.38</td>
<td>1.98</td>
<td>0.10</td>
<td>2.07</td>
<td>0.03</td>
</tr>
<tr>
<td>pBDD</td>
<td>1 nM</td>
<td>87.8</td>
<td>3.11</td>
<td>0.04</td>
<td>4.37</td>
<td>6.54</td>
<td>0.08</td>
</tr>
<tr>
<td>pBDD + Au</td>
<td>1 nM</td>
<td>87.8</td>
<td>0.42</td>
<td>2.16</td>
<td>0.10</td>
<td>2.02</td>
<td>0.02</td>
</tr>
<tr>
<td>pBDD</td>
<td>1 µM</td>
<td>107.0</td>
<td>4.01</td>
<td>0.04</td>
<td>4.62</td>
<td>6.35</td>
<td>0.07</td>
</tr>
<tr>
<td>pBDD + Au</td>
<td>1 µM</td>
<td>111.0</td>
<td>0.33</td>
<td>1.89</td>
<td>0.10</td>
<td>2.06</td>
<td>0.04</td>
</tr>
<tr>
<td>pBDD</td>
<td>500 µM</td>
<td>116.0</td>
<td>0.91</td>
<td>0.04</td>
<td>4.64</td>
<td>7.06</td>
<td>0.03</td>
</tr>
<tr>
<td>pBDD + Au</td>
<td>500 µM</td>
<td>109.0</td>
<td>0.32</td>
<td>3.85</td>
<td>0.03</td>
<td>2.43</td>
<td>0.06</td>
</tr>
<tr>
<td>pBDD</td>
<td>1 M</td>
<td>123.0</td>
<td>2.80</td>
<td>0.03</td>
<td>4.78</td>
<td>7.37</td>
<td>0.06</td>
</tr>
<tr>
<td>pBDD + Au</td>
<td>mM</td>
<td>115.0</td>
<td>0.27</td>
<td>5.70</td>
<td>0.13</td>
<td>1.98</td>
<td>0.07</td>
</tr>
</tbody>
</table>
The equivalent circuits used to model the electrochemical systems in this work are based on the simple Randles equivalent circuit [154]. A constant phase element was used in place of a traditional capacitor to represent the double layer capacitance at the surface of the diamond-based electrodes. This is common practice for polycrystalline materials, for which the double layer capacitance is non-homogenous across their surface [10]. An additional RC circuit was added in parallel to the modified simple Randles equivalent circuit for the pBDD-based electrodes, to more accurately model their surfaces, which have a larger proportion of sp² carbon, introduced during the polishing process. The additional RC circuit models the charge transfer resistance and double layer capacitance at the sp² carbon regions of these electrodes. For each electrode type, BDD or pBDD, the same equivalent circuit model could be used for the bare electrode or when decorated with AuNPs. This demonstrates that although the presence of the AuNPs improves the sensitivity of the electrodes by aiding the pre-concentration of mercury ions in the bulk electrolyte onto the electrode surfaces, the response of the mercury detection measurements is dominated by the diamond electrodes.

The resistance values extracted from the equivalent circuits fits of the EIS data for each electrode are of similar magnitudes. The significant difference between the bare and AuNP decorated electrodes of each type (BDD or pBDD) is the capacitance values. In each case the capacitance or effective capacitance is higher for the bare BDD and pBDD electrodes. A high quality BDD electrode, with a low concentration of sp² impurities, will have a capacitance <10 µF cm⁻². This is the case for each electrode, over the full mercury concentration range tested. As the capacitance values are much smaller for the AuNP decorated electrodes this means that lower detection limits are possible using these electrodes, compared to the bare BDD and pBDD electrodes [109].

The electron transfer rate (kₒ) was calculated using Equation 8.3, in which R is the universal gas constant, T is the absolute temperature, F is Faraday’s constant, n is the number of electrons transferred, S is the surface area of the working electrode exposed to the electrolyte and C₀ is the concentration of the redox couple in the electrolyte. For the kₒ calculations here mercury has been considered as the redox couple in the electrolyte, as there is an established redox transition between Hg²⁺ and Hg⁰ during the SWASV measurements and from CV measurements in other literature [94][111][178]. Although, it has been shown elsewhere that including a fast redox couple such as Fc/Fc⁺ in the electrolyte can aid in establishing the exact electron transfer rate at the working electrode [12]. When included, the concentration of the fast redox couple would be used in place of the concentration of mercury.
8.3. Results and discussion

in the solution as $C_0$.

$$k_0 = \left( \frac{RT}{nF} \right) \cdot \frac{1}{nSFR_c C_0}$$  \hspace{1cm} (8.3)

The $k_0$ values calculated from the parameters extracted from the equivalent circuit modelling of each of the electrodes, from the EIS measurements at a mercury concentration of 1 µM in the electrolyte, are displayed in Table 8.4.

**Table 8.4:** The electron transfer rates ($k_0$) of each of the electrodes tested, calculated from the parameters extracted from equivalent circuit modelling fits of the raw EIS data (see Appendix B) at a mercury concentration of 1 µM in the electrolyte.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$k_0$ at open circuit potential (cm/s)</th>
<th>$k_0$ at deposition potential (0.35 V) (cm/s)</th>
<th>$k_0$ at stripping potential (1.0 V) (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDD</td>
<td>9.56x10$^{-08}$</td>
<td>1.04x10$^{-07}$</td>
<td>9.70x10$^{-07}$</td>
</tr>
<tr>
<td>BDD + Au</td>
<td>6.51x10$^{-07}$</td>
<td>9.70x10$^{-07}$</td>
<td>6.60x10$^{-07}$</td>
</tr>
<tr>
<td>pBDD</td>
<td>1.19x10$^{-07}$</td>
<td>1.51x10$^{-07}$</td>
<td>1.89x10$^{-07}$</td>
</tr>
<tr>
<td>pBDD + Au</td>
<td>1.44x10$^{-06}$</td>
<td>1.22x10$^{-06}$</td>
<td>1.19x10$^{-06}$</td>
</tr>
</tbody>
</table>

The electron transfer rates ($k_0$) calculated for each of the electrodes are provided in Table 8.4. These values were determined using the concentration of the mercury in the electrolyte as the redox couple in this electrochemical system. The $k_0$ values reported here are lower than documented elsewhere, when a fast redox couple has been added to the system, because in these cases the complexity of the mass transport of the mercury ions through the solution was not a factor in the rate of electron transfer at the working electrode surfaces [155]. For the bare BDD and pBDD electrodes there is little variation ($\pm 8x10^{-09}$ cm$^{-1}$ and $\pm 7x10^{-08}$ cm$^{-1}$ respectively) in $k_0$ at each of the potentials at which the EIS measurements were made. Therefore, the kinetics and charge transfer resistance at the surface of these electrodes did not change when the mercury was pre-concentrated onto or stripped from their surface. This demonstrates that the BDD and pBDD electrodes must be decorated with gold for the pre-concentration of mercury ions from the bulk electrolyte to occur. When the electrodes are not decorated with AuNPs the mercury ions are not pre-concentrated onto their surface, meaning that mercury will not be detected until a larger concentration has been added to the electrolyte. At each potential the $k_0$ of the AuNP decorated electrodes is higher, showing that even when the mercury ions in the electrolyte are not pre-concentrated onto the electrode
surface the decorated electrodes induce lower charge transfer resistance and faster kinetics at their surface.

8.4 Conclusion

This work presents a detailed EIS study investigating the role of AuNPs deposited onto the surface of diamond electrodes for electrochemical mercury detection. The systems analysed used BDD and polished pBDD electrodes, both bare and decorated with 30 nm AuNPs, for EIS measurements in a 0.1 M HNO$_3$ electrolyte which was sequentially doped with increasing concentrations of mercury nitrate from 1 pM – 1 mM.

It is demonstrated that the mercury detection process is dominated by the reactivity of the diamond electrodes, as the same equivalent circuit type can be used for the bare and AuNP decorated electrodes of each substrate type (BDD and pBDD). The AuNPs improve the efficiency of the mercury detection process at each electrode, with a corresponding reduction in the $R_{ct}$ value when they are present. The AuNPs do not change the reaction pathway at the diamond electrodes, but improve the sensitivity of the electrodes by aiding the pre-concentration of mercury ions from the bulk electrolyte, causing mercury to be detected at lower concentrations than when a bare diamond electrode is used. The electrodes decorated with AuNPs have lower capacitance and electron transfer rates, meaning that these electrodes have higher sensitivity for mercury detection than the bare BDD and pBDD electrodes. When the electrolyte is doped with higher concentrations of mercury (> 500 µM) the relative proportions of sp$^2$/sp$^3$ carbon have a greater influence on the sensitivity of the electrode for mercury detection than the presence of the AuNPs. The pBDD-based electrodes, which have a higher proportion of sp$^2$ carbon at their surface, are shown to have lower charge transfer resistance than the BDD-based electrodes, at higher mercury concentrations. It is suggested that at the higher concentrations of mercury the application of the deposition potential (0.35 V) causes mercury ions in the bulk electrolyte to become pre-concentrated onto the sp$^2$ regions of the pBDD surfaces.

The exceptional capacitance values and low $k_0$ values reported highlight how robust diamond electrodes can be optimised for high sensitivity detection. These electrodes are ideal for the development of commercial mercury sensors in aquatic environments.
Conclusion

This thesis has focused on analysing and improving the electrochemical performance of boron doped diamond (BDD) electrodes. The influence of surface preparation by polishing, hydrogen and oxygen termination, and the decoration of BDD electrodes with gold nanoparticles (AuNPs) on the electrochemical performance of BDD electrodes have been directly compared throughout this work.

The properties of heavily-doped, quasi-metallic BDD make it an optimal material for the development of sensors for use in extreme environments. The need for such sensors is particularly great in the oil industry, where high temperatures are the major challenge in the development of down-well sensors. Whilst BDD electrodes are known to be stable at the high temperatures experienced in this environment, the influence of these elevated temperatures on the electrochemical performance of BDD is not well understood. This is addressed in Chapter 6, in which the electrochemical windows of BDD electrodes, with a series of surface modifications, are measured during cyclic voltammetry measurements up to 125 °C.

In this work, the influence of surface polishing and termination on the electrochemical window of BDD were investigated. BDD substrates in their as grown state (surface roughness $R_A \sim 50 \mu \text{m}$) and BDD substrates mechanically polished to a surface roughness $R_A \sim 50 \text{ nm}$ were used, with the surface of one substrate of each type hydrogen terminated and the other oxygen terminated. The widest electrochemical windows are reported for the unpolished electrodes, which have a lower proportion of sp$^2$ carbon at their surfaces in comparison to the polished electrodes. The influence of the ratio between sp$^2$ and sp$^3$ carbon at the electrode surfaces was shown to have a much more significant impact on the electrochemical window reported than the hydrogen or oxygen termination of the diamonds. Increasing the proportion of sp$^2$ carbon in a BDD electrode has been shown to favour electrochemical oxidation and have a significant effect on the electrode reaction kinetics of some redox systems. Therefore, some reactions (such as the electrolysis of water) will occur at
lower overpotential when there is a greater proportion of sp$^2$ relative to sp$^3$ carbon at the surface of the working electrode. This means that for high temperature sensing, the quality of the diamond substrate used is the most important parameter to control when developing a sensor with the potential to detect the broadest range of analytes. Higher quality diamond will have a significantly higher proportion of sp$^3$ carbon relative to sp$^2$ carbon at its surface and so, the electrochemical window will be wider.

In addition to the exceptional electrochemical performance of BDD electrodes at elevated temperatures, they also have extremely high sensitivity for analyte detection under standard laboratory conditions (21 °C). In Chapter 7, BDD electrodes decorated with AuNPs were used for the detection of mercury with extremely high sensitivity. In this research, a novel method of producing 10 nm AuNPs on BDD surfaces was developed, using a TEM grid as a shadow mask. Two BDD substrate types were used: as grown with surface roughness $R_A \sim 50$ µm, and mechanically polished to a surface roughness $R_A \sim 50$ nm, each of which was decorated with two sizes of AuNPs (four electrodes total). The substrates were all hydrogen terminated for this study, as AuNPs have previously been demonstrated to adhere more strongly to a hydrophobic diamond surface. This is due to a combination of the electrostatic and hydrophobic interactions between the AuNPs and the diamond surface when it is hydrogen terminated, which result in the formation of a non-covalent bond. The AuNPs are known to improve the sensitivity of BDD electrodes for mercury detection, as they act catalytically during the pre-concentration step of the square wave anodic stripping voltammetry (SWASV) measurements. In this step, application of a reducing potential causes the Hg$^{2+}$ ions in the electrolyte to concentrate onto the surface of the BDD working electrode as Hg$^0$. The mercury is detected when a sufficiently oxidising potential is applied to the BDD electrode and the mercury is stripped back into the bulk electrolyte.

The results of this research showed that the size of the catalytically active AuNPs on the electrode surfaces had a less significant effect on the sensitivity for mercury detection than the surface preparation of the BDD. This was proven to not be caused by the diffusion of ions to the electrode surface, through repetition of the SWASV measurements with the BDD electrode decorated with 22 nm AuNPs at a 20× slower scan speed. The same sensitivity was achieved as during the SWASV measurements using the same electrode at the higher scan rate, meaning that it is not necessary to reach saturation of the sensor to achieve repeatable results. This demonstrates that these BDD electrodes are well suited to rapid in situ measurements for mercury detection in aqueous environments. It was concluded
that, like in Chapter 6, the relative proportions of sp$^2$ and sp$^3$ carbon at the surface of the unpolished and polished BDD surfaces has a much greater influence on the electrochemical performance of the electrode than other surface modifications; the termination or presence of nanoparticles.

The lowest limits of mercury detection reported in Chapter 7 were achieved with the polished BDD electrodes. The superior sensitivity of the pBDD electrodes is explained by the higher graphitic carbon content at the surface of these electrodes (compared to the BDD-based electrodes), which was caused by polishing damage and characterised with Raman spectroscopy. The high sensitivity displayed by the pBDD electrodes, allied to the demonstrated tenacious nature of the attached AuNPs during repeated measurement cycles suggests a promising future for this approach for the realisation of robust trace mercury detectors for a wide range of aqueous environments.

It is generally understood that there is a ‘high affinity’ between gold and mercury, which is hypothesised to be the reason that modification with AuNPs improves the sensitivity of carbon-based electrodes for mercury detection. However, the mechanism by which the AuNPs influence the sensitivity of the BDD electrodes in Chapter 7 is not fully understood. To gain further insight into the role of the AuNPs during these measurements an electrochemical impedance spectroscopy (EIS) study was conducted in Chapter 8, using the same conditions and similar electrodes to those utilised in Chapter 7. For each substrate type (as grown and polished) both bare electrodes and electrodes decorated with 30 nm AuNPs were used, to investigate the role of AuNPs during mercury sensing with diamond electrodes. In the SWASV measurements conducted for mercury detection in Chapter 7 the mercury ions in the electrolyte were deposited onto, then stripped from the diamond electrode surface. To investigate the different electrode performances during these steps the EIS measurements were made following application of the deposition and stripping potentials, alongside scans at open circuit potential for comparison.

It has been demonstrated that the mercury detection process is dominated by the reactivity of the diamond electrodes, as the same equivalent circuit type could be used for the bare and AuNP decorated electrodes of each substrate type (as grown and mechanically polished). Modification of the electrode surfaces with AuNPs has been shown to improve the efficiency of the mercury detection process, with a corresponding reduction in the charge transfer resistance at the surface of each electrode when the AuNPs were present. Lower capacitance values and electron transfer rates are reported for the electrodes decorated with AuNPs, meaning that these electrodes have higher sensitivity for mercury detection than the bare BDD
electrodes. However, when the electrolyte was doped with higher concentrations of mercury (>500 µM) the relative proportions of sp$^2$/sp$^3$ carbon at the electrode surfaces were shown to have a greater influence on the sensitivity of the electrode for mercury detection than the presence of the AuNPs. The electrodes made from the polished BDD substrates were shown to have a higher proportion of sp$^2$ carbon at their surface with Raman spectroscopy. These electrodes had lower charge transfer resistance at the higher mercury concentrations tested than the unpolished, as grown substrates. It is suggested that at the higher concentrations of mercury, the application of the deposition potential caused mercury ions in the bulk electrolyte to become pre-concentrated onto the sp$^2$ regions of the polished electrode surfaces, which was previously believed to only happen at the sites of AuNPs.

The exceptional capacitance values and low k$_0$ values reported in Chapter 8 highlight how robust diamond electrodes can be optimised for high sensitivity detection. These electrodes are therefore ideal for the development of commercial mercury sensors in aquatic environments.

The overall conclusion from this thesis is that the quality of the diamond substrates used to make electrodes is the most important parameter to control when designing an electrochemical sensor. For the high sensitivity detection of mercury a lower quality diamond, with a higher proportion of sp$^2$ carbon at it’s surface, was shown to be superior. However, a balance must be reached as increasing the sp$^2$ carbon content of a diamond electrode (such as by mechanical polishing) will reduce the electrochemical window available at the electrode, therefore reducing the range of chemical processes that it will be possible to detect. This is particularly important for high temperature measurements, as the electrochemical window of the sp$^3$ carbon is also reduced above room temperature. Although slightly higher concentrations of sp$^2$ carbon at the electrode surfaces were concluded to improve the performance of these electrodes, the Raman spectra in this thesis show that the proportion of sp$^2$ carbon is still very low in all of the substrates used.
Future Work

The research presented in this thesis shows how robust diamond sensors can be optimised for high sensitivity detection in extreme environments.

The work presented in Chapter 6 demonstrates the potential for BDD electrodes to be used in the development of electrochemical sensors for use in high temperature environments. These experiments were conducted at 5 bar pressure, to ensure that the water in the aqueous system did not boil. However, in the proposed application of these electrodes (down-well sensing in the oil industry) the pressure is likely to be significantly higher. Before these electrodes are used commercially this research should be extended to investigate how elevated pressures, coupled to high temperatures, affect the electrochemical window of the electrodes and therefore the potential range in which chemical reactions can be detected.

Exceptionally high sensitivity for mercury detection was achieved under laboratory conditions in Chapter 7. For the electrodes used in this work to be developed into commercial sensors for mercury detection they must first be tested in real water samples. A comparison study is required, in which different water samples are collected from sites where there is mercury contamination and analysed alongside ‘clean’ (mercury free) samples of similar water, which would be doped with known concentrations of mercury to calibrate the BDD sensor. For example, in the River Thames there are areas with significant oil contamination from the shipping industry, where mercury concentrations above those detected in Chapter 7 would be expected, as crude oil contains between 0.1 - 20,000 µg/kg. The mercury concentration in water collected along the length of the River Thames could be compared to calibration data recorded using water from closer to the source of the river, before the water is contaminated, which would be doped with known concentrations of mercury.

This thesis has focused on modifying BDD surfaces to improve their electrochemical performance. A further parameter that has been shown to influence the
Electrochemical performance of BDD electrodes is the boron concentration within the diamond lattice. It has previously been shown that the mechanism of charge transfer differs at lower boron doping concentrations compared to more heavily boron doped samples. In the literature there is evidence that when the boron concentration is low (<10 ppm) the electrode surface is predominantly insulating, with electroactive areas spaced out across it causing there to be a radial element to diffusion at its surface [70]. A valuable study that would extend the literature in this field would be to investigate the electrochemical performance of BDD electrodes with different concentrations of boron in their structure, combined with surface modification with AuNPs. This could be done with EIS and electrochemical detection measurements, in addition to simulation work.
Appendix A

Supplementary information to Chapter 6

Figure A.1: Combined spectra of the CV average scans and standard deviation across the full temperature range measured for each electrode a) unpolished BDDH, b) polished BDDH, c) unpolished BDDO and d) polished BDDO at a scan rate of 0.1 Vs⁻¹.
Figure A.2: Combined spectra of the CV average scans and standard deviation across the full temperature range measured for each electrode a) unpolished BDDH, b) polished BDDH, c) unpolished BDDO and d) polished BDDO at a scan rate of 1.0 Vs⁻¹.
Appendix B

Supplementary information to Chapter 8
Figure B.1: Bode impedance plot presentation of the EIS data from measurements made over the frequency range 50 kHz - 50 mHz, with 8 points per decade and 10 mV amplitude, for each of the electrodes. The results presented here are from EIS measurements made at a) open circuit potential, 0 M Hg concentration, b) deposition potential (0.35 V), 0 M Hg concentration, c) stripping potential (1.0 V), 0 M Hg concentration, d) open circuit potential, 1 pM Hg concentration, e) deposition potential (0.35 V), 1 pM Hg concentration, f) stripping potential (1.0 V), 1 pM Hg concentration, g) open circuit potential, 1 nM Hg concentration, h) deposition potential (0.35 V), 1 nM Hg concentration and i) stripping potential (1.0 V), 1 nM Hg concentration.
Figure B.2: Bode impedance plot presentation of the EIS data from measurements made over the frequency range 50 kHz –50 mHz, with 8 points per decade and 10 mV amplitude, for each of the electrodes. The results presented here are from EIS measurements made at a) open circuit potential, 1 µM Hg concentration, b) deposition potential (0.35 V), 1 µM Hg concentration, c) stripping potential (1.0 V), 1 µM Hg concentration, d) open circuit potential, 500 µM Hg concentration, e) deposition potential (0.35 V), 500 µM Hg concentration, f) stripping potential (1.0 V), 500 µM Hg concentration, g) open circuit potential, 1 mM Hg concentration, h) deposition potential (0.35 V), 1 mM Hg concentration and i) stripping potential (1.0 V), 1 mM Hg concentration.
Figure B.3: Bode phase plot presentation of the EIS data from measurements made over the frequency range 50 kHz – 50 mHz, with 8 points per decade and 10 mV amplitude, for each of the electrodes. The results presented here are from EIS measurements made at a) open circuit potential, 0 M Hg concentration, b) deposition potential (0.35 V), 0 M Hg concentration, c) stripping potential (1.0 V), 0 M Hg concentration, d) open circuit potential, 1 pM Hg concentration, e) deposition potential (0.35 V), 1 pM Hg concentration, f) stripping potential (1.0 V), 1 pM Hg concentration, g) open circuit potential, 1 nM Hg concentration, h) deposition potential (0.35 V), 1 nM Hg concentration and i) stripping potential (1.0 V), 1 nM Hg concentration.
Figure B.4: Bode phase plot presentation of the EIS data from measurements made over the frequency range 50 kHz – 50 mHz, with 8 points per decade and 10 mV amplitude, for each of the electrodes. The results presented here are from EIS measurements made at a) open circuit potential, 1 µM Hg concentration, b) deposition potential (0.35 V), 1 µM Hg concentration, c) stripping potential (1.0 V), 1 µM Hg concentration, d) open circuit potential, 500 µM Hg concentration, e) deposition potential (0.35 V), 500 µM Hg concentration, f) stripping potential (1.0 V), 500 µM Hg concentration, g) open circuit potential, 1 mM Hg concentration, h) deposition potential (0.35 V), 1 mM Hg concentration and i) stripping potential (1.0 V), 1 mM Hg concentration.
Figure B.5: Nyquist plot presentation of the EIS data from measurements made over the frequency range 50 kHz – 50 mHz, with 8 points per decade and 10 mV amplitude, for each of the electrodes. The results presented here are from EIS measurements made at a) open circuit potential, 0 M Hg concentration, b) deposition potential (0.35 V), 0 M Hg concentration, c) stripping potential (1.0 V), 0 M Hg concentration, d) open circuit potential, 1 pM Hg concentration, e) deposition potential (0.35 V), 1 pM Hg concentration, f) stripping potential (1.0 V), 1 pM Hg concentration, g) open circuit potential, 1 nM Hg concentration, h) deposition potential (0.35 V), 1 nM Hg concentration and i) stripping potential (1.0 V), 1 nM Hg concentration.
Figure B.6: Lissajous plots produced during EIS measurements with a) BDD electrode, b) BDD + AuNP electrode, c) pBDD electrode and d) pBDD + Au electrode, over frequency range 50 kHz –50 mHz, 8 points per decade and 10 mV amplitude with the bare BDD electrode, at open circuit potential.

Table B.1: The $\chi^2$ values corresponding to the quality of the equivalent circuit model fit to the experimental data during Kronig-Kramers (KK) tests of the EIS data sets recorded at the deposition potential (0.35 V) for each of the diamond electrodes, over the full mercury concentration range tested.

<table>
<thead>
<tr>
<th>Mercury concentration</th>
<th>BDD ($\chi^2$)</th>
<th>BDD + AuNP ($\chi^2$)</th>
<th>pBDD ($\chi^2$)</th>
<th>pBDD + AuNP ($\chi^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 M (control)</td>
<td>2.78$^{-5}$</td>
<td>3.04$^{-5}$</td>
<td>1.46$^{-5}$</td>
<td>5.81$^{-5}$</td>
</tr>
<tr>
<td>1 pM</td>
<td>2.14$^{-5}$</td>
<td>4.17$^{-5}$</td>
<td>4.19$^{-6}$</td>
<td>1.49$^{-5}$</td>
</tr>
<tr>
<td>1 nM</td>
<td>1.55$^{-5}$</td>
<td>1.96$^{-5}$</td>
<td>5.59$^{-6}$</td>
<td>1.01$^{-5}$</td>
</tr>
<tr>
<td>1 µM</td>
<td>1.53$^{-5}$</td>
<td>2.34$^{-5}$</td>
<td>4.14$^{-6}$</td>
<td>2.21$^{-5}$</td>
</tr>
<tr>
<td>500 µM</td>
<td>7.40$^{-6}$</td>
<td>4.85$^{-5}$</td>
<td>1.73$^{-5}$</td>
<td>1.58$^{-5}$</td>
</tr>
<tr>
<td>1 mM</td>
<td>1.39$^{-5}$</td>
<td>4.55$^{-5}$</td>
<td>1.20$^{-5}$</td>
<td>1.64$^{-5}$</td>
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Figure B.7: Lissajous plots produced during EIS measurements with a) BDD electrode, b) BDD + AuNP electrode, c) pBDD electrode and d) pBDD + Au electrode, over frequency range 50 kHz –50 mHz, 8 points per decade and 10 mV amplitude with the bare BDD electrode, at the deposition potential (0.35 V).

Table B.2: The $\chi^2$ values corresponding to the quality of the equivalent circuit model fit to the experimental data during Kronig-Kramers (KK) tests of the EIS data sets recorded at the stripping potential (1.00 V) for each of the diamond electrodes, over the full mercury concentration range tested.

<table>
<thead>
<tr>
<th>Mercury concentration</th>
<th>BDD ($\chi^2$)</th>
<th>BDD + AuNP ($\chi^2$)</th>
<th>pBDD ($\chi^2$)</th>
<th>pBDD + AuNP ($\chi^2$)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>$9.65^{-5}$</td>
<td>$8.67^{-6}$</td>
<td>$2.15^{-5}$</td>
</tr>
<tr>
<td>1 pM</td>
<td>$2.42^{-5}$</td>
<td>$9.27^{-5}$</td>
<td>$6.59^{-6}$</td>
<td>$1.43^{-5}$</td>
</tr>
<tr>
<td>1 nM</td>
<td>$1.61^{-5}$</td>
<td>$2.05^{-5}$</td>
<td>$5.82^{-6}$</td>
<td>$1.13^{-5}$</td>
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<tr>
<td>1 µM</td>
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<td>$2.00^{-5}$</td>
<td>$6.21^{-6}$</td>
<td>$2.51^{-5}$</td>
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<td>$2.78^{-5}$</td>
<td>$4.20^{-5}$</td>
<td>$7.76^{-6}$</td>
<td>$7.82^{-6}$</td>
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<tr>
<td>1 mM</td>
<td>$1.76^{-5}$</td>
<td>$7.99^{-5}$</td>
<td>$7.67^{-5}$</td>
<td>$1.08^{-5}$</td>
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Figure B.8: Lissajous plots produced during EIS measurements with a) BDD electrode, b) BDD + AuNP electrode, c) pBDD electrode and d) pBDD + Au electrode, over frequency range 50 kHz – 50 mHz, 8 points per decade and 10 mV amplitude with the bare BDD electrode, at the stripping potential (1.00 V).
Table B.3: The parameters extracted from the equivalent circuit of the raw EIS data for the BDD and BDD + Au electrodes at the deposition potential (0.35 V).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Hg concentration</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ M(Ω)</th>
<th>$C_{eff}$ (µF)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDD</td>
<td>0 M (control)</td>
<td>39.8</td>
<td>2.04</td>
<td>0.30</td>
<td>0.06</td>
</tr>
<tr>
<td>BDD + AuNP</td>
<td>0 M (control)</td>
<td>22.0</td>
<td>0.54</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>BDD</td>
<td>1 pM</td>
<td>64.2</td>
<td>2.99</td>
<td>0.30</td>
<td>0.03</td>
</tr>
<tr>
<td>BDD + AuNP</td>
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<td>36.3</td>
<td>0.52</td>
<td>0.05</td>
<td>0.08</td>
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<tr>
<td>BDD</td>
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<td>89.3</td>
<td>4.23</td>
<td>0.31</td>
<td>0.02</td>
</tr>
<tr>
<td>BDD + AuNP</td>
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<td>103.0</td>
<td>0.49</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>BDD</td>
<td>1 µM</td>
<td>99.9</td>
<td>4.58</td>
<td>0.61</td>
<td>0.01</td>
</tr>
<tr>
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<td>1 µM</td>
<td>122.0</td>
<td>0.49</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>BDD</td>
<td>500 µM</td>
<td>108.0</td>
<td>3.23</td>
<td>0.31</td>
<td>0.03</td>
</tr>
<tr>
<td>BDD + AuNP</td>
<td>500 µM</td>
<td>123.0</td>
<td>0.58</td>
<td>0.05</td>
<td>0.07</td>
</tr>
<tr>
<td>BDD</td>
<td>1 mM</td>
<td>128.0</td>
<td>2.28</td>
<td>0.28</td>
<td>0.10</td>
</tr>
<tr>
<td>BDD + AuNP</td>
<td>1 mM</td>
<td>127.0</td>
<td>0.56</td>
<td>0.06</td>
<td>0.06</td>
</tr>
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</table>

Table B.4: The parameters extracted from the equivalent circuit of the raw EIS data for the BDD and BDD + Au electrodes at the deposition potential (1.0 V).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Hg concentration</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ M(Ω)</th>
<th>$C_{eff}$ (µF)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDD</td>
<td>0 M (control)</td>
<td>42.0</td>
<td>2.61</td>
<td>0.30</td>
<td>0.03</td>
</tr>
<tr>
<td>BDD + AuNP</td>
<td>0 M (control)</td>
<td>28.5</td>
<td>0.42</td>
<td>0.05</td>
<td>0.07</td>
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<tr>
<td>BDD</td>
<td>1 pM</td>
<td>67.6</td>
<td>3.38</td>
<td>0.31</td>
<td>0.02</td>
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<tr>
<td>BDD + AuNP</td>
<td>1 pM</td>
<td>46.3</td>
<td>0.51</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>BDD</td>
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<td>90.6</td>
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<td>0.31</td>
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<td>BDD + AuNP</td>
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<td>106.0</td>
<td>0.69</td>
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<tr>
<td>BDD</td>
<td>1 µM</td>
<td>101.0</td>
<td>4.68</td>
<td>0.31</td>
<td>0.01</td>
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<td>BDD + AuNP</td>
<td>1 µM</td>
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<td>0.06</td>
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<td>0.81</td>
<td>0.30</td>
<td>0.04</td>
</tr>
<tr>
<td>BDD + AuNP</td>
<td>500 µM</td>
<td>126.0</td>
<td>0.49</td>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td>BDD</td>
<td>1 mM</td>
<td>132.0</td>
<td>2.04</td>
<td>0.29</td>
<td>0.01</td>
</tr>
<tr>
<td>BDD + AuNP</td>
<td>1 mM</td>
<td>129.0</td>
<td>0.48</td>
<td>0.06</td>
<td>0.02</td>
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</table>
Table B.5: The parameters extracted from the equivalent circuit fit of the raw EIS data for the pBDD and pBDD + Au electrodes at the deposition potential (0.35 V).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Hg concentration</th>
<th>R₁ (Ω)</th>
<th>R₂ M(Ω)</th>
<th>R₃ k(Ω)</th>
<th>Cₑffective (µF)</th>
<th>C (µF)</th>
<th>χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>pBDD</td>
<td>0 M (control)</td>
<td>49.0</td>
<td>0.55</td>
<td>0.02</td>
<td>3.85</td>
<td>8.79</td>
<td>0.04</td>
</tr>
<tr>
<td>pBDD + AuNP</td>
<td>0 M (control)</td>
<td>34.1</td>
<td>0.52</td>
<td>2.06</td>
<td>0.04</td>
<td>2.10</td>
<td>0.04</td>
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<tr>
<td>pBDD</td>
<td>1 pM</td>
<td>73.7</td>
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<td>0.03</td>
<td>4.23</td>
<td>6.79</td>
<td>0.09</td>
</tr>
<tr>
<td>pBDD + AuNP</td>
<td>1 pM</td>
<td>64.5</td>
<td>0.44</td>
<td>2.37</td>
<td>0.09</td>
<td>1.96</td>
<td>0.03</td>
</tr>
<tr>
<td>pBDD</td>
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<td>88.8</td>
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<td>0.04</td>
<td>4.41</td>
<td>6.57</td>
<td>0.08</td>
</tr>
<tr>
<td>pBDD + AuNP</td>
<td>1 nM</td>
<td>89.8</td>
<td>0.43</td>
<td>2.29</td>
<td>0.10</td>
<td>1.96</td>
<td>0.03</td>
</tr>
<tr>
<td>pBDD</td>
<td>1 µM</td>
<td>108.0</td>
<td>3.15</td>
<td>0.04</td>
<td>4.61</td>
<td>6.53</td>
<td>0.05</td>
</tr>
<tr>
<td>pBDD + AuNP</td>
<td>1 µM</td>
<td>107.0</td>
<td>0.39</td>
<td>2.32</td>
<td>0.10</td>
<td>2.32</td>
<td>0.04</td>
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<td>pBDD</td>
<td>500 µM</td>
<td>116.0</td>
<td>0.52</td>
<td>0.03</td>
<td>4.64</td>
<td>6.59</td>
<td>0.08</td>
</tr>
<tr>
<td>pBDD + AuNP</td>
<td>500 µM</td>
<td>109.0</td>
<td>0.27</td>
<td>2.33</td>
<td>0.15</td>
<td>2.33</td>
<td>0.08</td>
</tr>
<tr>
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<td>1 M</td>
<td>123.0</td>
<td>0.19</td>
<td>0.03</td>
<td>4.80</td>
<td>8.63</td>
<td>0.06</td>
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<tr>
<td>pBDD + AuNP</td>
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<td>2.31</td>
<td>0.16</td>
<td>2.31</td>
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</table>
Table B.6: The parameters extracted from the equivalent circuit fit of the raw EIS data for the pBDD and pBDD + Au electrodes at the deposition potential (0.35 V).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Hg concentration</th>
<th>$R_1$ (Ω)</th>
<th>$R_2$ M(Ω)</th>
<th>$R_3$ k(Ω)</th>
<th>$C_{eff}$ (µF)</th>
<th>C (µF)</th>
<th>$\chi^2$</th>
</tr>
</thead>
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<tr>
<td>pBDD</td>
<td>0 M (control)</td>
<td>33.3</td>
<td>1.45</td>
<td>0.02</td>
<td>3.39</td>
<td>0.17</td>
<td>0.02</td>
</tr>
<tr>
<td>pBDD + AuNP</td>
<td>0 M (control)</td>
<td>38.4</td>
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<td>0.04</td>
</tr>
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<td>1 pM</td>
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<td>6.68</td>
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<td>4.44</td>
<td>6.43</td>
<td>0.08</td>
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<td>0.10</td>
<td>2.01</td>
<td>0.03</td>
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<td>1 µM</td>
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<td>0.04</td>
<td>4.64</td>
<td>6.75</td>
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<td>1.56</td>
<td>0.10</td>
<td>2.21</td>
<td>0.03</td>
</tr>
<tr>
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<td>117.0</td>
<td>0.63</td>
<td>0.04</td>
<td>4.63</td>
<td>6.76</td>
<td>0.07</td>
</tr>
<tr>
<td>pBDD + AuNP</td>
<td>500 µM</td>
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<td>5.87</td>
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<tr>
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<td>0.03</td>
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<td>7.89</td>
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<td>7.53</td>
<td>0.12</td>
<td>1.64</td>
<td>0.08</td>
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References


[189] C. Van Nguyen, R. Bartali, L. Crema, and G. Speranza. Effect of glass surface treatments on the deposition of highly transparent reduced graphene ox-


