

# Enhanced electrochemical kinetics of highly-oriented (111)-textured boron-doped diamond electrodes induced by deuterium plasma chemistry

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## Abstract

Novel highly-oriented (111)-textured boron-doped diamond electrodes ( $BDD_D$ ) featuring high electrochemical activity and electrode stability toward electrochemical analytics were fabricated by deuterium-rich microwave plasma CVD. The high flux deuterium plasma-induced preferential formation of (111)-faceted diamond as revealed by XRD. The highly-oriented diamond surface exhibited improved boron dopant incorporation and activation, whereas the crystals showed enhanced carrier electron acceptance and donation, which accelerated the electron transfer during electrochemical redox mediation. The standard rate constant and peak-to-peak separation  $\Delta E$  for the oxidation and reduction of the  $Fe(CN)_6^{3-/4-}$  and  $Ru(NH_3)_6^{2+/3+}$  redox probes reached  $\Delta E$  values of only 60.6 and 59.8 mV, respectively. The enriched electrochemical performance of the  $BDD_D$  electrodes is an advantageous feature allowing them to be applied as ultrasensitive electrodes, demonstrated here by paracetamol determination. The differential pulse voltammetry results revealed an enhanced electrochemical oxidation effect for paracetamol at the deuterium-grown (111)-rich diamond electrode. A single linear range from 1 to 125 nM along with a low detection limit of 0.76 nM were achieved.

**Keywords:** deuterium plasma, boron-doped diamond, cyclic voltammetry, electrochemical sensors, paracetamol

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## 1. Introduction

Boron-doped diamond (BDD) has aroused the interest of scientists from around the world due to its remarkable properties such as its wide electrochemical potential window, chemical stability and inertness, and biocompatibility, among others [1–4]. Diamond films are grown mainly from a gas phase consisting of hydrogen, carbon, and a dopant source by microwave plasma-assisted chemical vapour deposition or hot filament chemical vapour deposition. The gas composition during the growth has a significant influence on the surface morphology and the electrochemical properties of the BDD films [5,6], especially the dopant concentration, surface defects, and superficial non-diamond carbon phases (NDC) [1].

It is well known that hydrogen radicals play a crucial role in high-quality diamond growth through etching NDC [7,8]. The etching of the diamond  $sp^3$  phase is much slower than the  $sp^2$  or  $sp$  phases. Due to deuterium radicals having twice the mass of hydrogen radicals, the process of etching is accelerated resulting in reduced growth rate [9].

The electrochemical properties of boron-doped diamond electrodes depend on factors such as the boron doping concentration, surface termination, and interactions of superficial non-diamond phases. Granger and Swain [1] studied the influence of surface interaction using the  $Fe(CN)_6^{-3/4}$  redox couple. The study results showed that the number of  $sp^2$  phases, and surface termination by hydrogen and oxygen had a crucial impact on BDD's electrochemical properties. Moreover, Garcia-Segura *et al.* investigated the role of  $sp^3/sp^2$  on the electrocatalytic properties, which has an impact on the potential window, pollutant mineralisation *etc.* [5].

In the literature, research efforts to enhance the boron doping can be found, which have resulted in improvements of the electronic properties which allows the doped polycrystalline diamond to be used in electronics. Teraji *et al.* [10] grew homoepitaxial diamonds (100) using high-pressure high-temperature type-Ib (100) diamond single crystal substrates to achieve a low resistance of around 1 ohm·cm by the high-power Microwave Plasma Assisted Chemical Vapor Deposition (MW PACVD) process. In the case of single-crystal diamond films, the high-power conditions are responsible for enhanced (of about one order of magnitude) boron-incorporation efficiency, resulting in a carrier concentration of  $6 \cdot 10^{15} \text{ cm}^{-3}$ . Wang *et al.* [11] used Ar-rich or  $H_2$ -rich source-gas mixtures to synthesise heavily boron-doped nanocrystalline diamond films with equivalent electrical and electrochemical properties. Furthermore, Issaoui *et al.* [12] showed



that the microwave power density is one of the key factors allowing the doping efficiencies to be tuned over a range of two orders of magnitude.

In our recent study, we investigated the plasma composition by optical emission spectroscopy during diamond film synthesis in a deuterium and hydrogen plasmas [9]. Moreover, we showed enhanced boron doping in the MW PACVD process using deuterium, achieving one order of magnitude higher charge carrier density for BDD<sub>D</sub> (deuterium boron-doped diamond) than for BDD<sub>H</sub> (hydrogen boron-doped diamond).

*Here, we report electrochemical studies of as-grown boron-doped diamond thin-film electrodes, synthesised in a deuterium-rich plasma, by means of cyclic voltammetry and electrochemical impedance spectroscopy. To the best of our knowledge, the effect of replacing hydrogen by deuterium during BDD growth on the electrochemistry of this material has not been reported. Thus, we have performed the electrochemical evaluation of BDD<sub>D</sub> including the standard rate constant ( $k^\circ$ ), and peak-to-peak separation values for the oxidation and reduction of the  $Fe(CN)_6^{3-/4-}$  and  $Ru(NH_3)_6^{2+/3+}$  redox mediators. Moreover, we also conducted the electrochemical detection of paracetamol via differential pulse voltammetry. The surface morphology, chemical composition, crystallographic orientation and sheet resistivity of the grown BDD<sub>D</sub> electrodes were also investigated along with electrochemical techniques.*

## 2. Experimental section

### 2.1 Diamond growth

*The BDD<sub>D</sub> and BDD<sub>H</sub> were synthesised in the Microwave Plasma Assisted Chemical Vapour Deposition process. Diamond films were deposited on p-type (100) silicon substrates (1 x 1 cm<sup>2</sup>). The substrates were cleaned in acetone in an ultrasonic bath for 5 minutes, and then washed in 2-propanol. The substrates were then sonicated in a water nanodiamond suspension (NanoAndo, Japan). A D<sub>2</sub>/CH<sub>4</sub> or H<sub>2</sub>/CH<sub>4</sub> gas mixture of 1% vol. At an overall gas flow rate of 300 sccm was used for the diamond film synthesis. The temperature of the heated stage was set to 700°C, the process pressure to 50 Torr (6.7 kPa), and the microwave power to 1300 W. Diborane (B<sub>2</sub>H<sub>6</sub>) was used as a boron source. The boron doping level, expressed as the [B]/[C] ratio in the gas phase, was set to 10k ppm [9]. The growth times of the BDD<sub>D</sub> and BDD<sub>H</sub> films were adjusted to achieve similar layer thicknesses, so the BDD<sub>D</sub> was grown 6 hours, and the BDD<sub>H</sub> for 2.5h,*

producing microcrystalline films with an average thickness of 650 nm and 690 nm, respectively. The cooling process took place in the CVD reactor in the constant flow of deuterium or hydrogen gas (100 sccm) at a reduced pressure of  $p=25$  Torr. The samples were removed from the reactor when the temperature of  $25^{\circ}\text{C}$  was reached.

## 2.2 Characterisation techniques

**XRD&SEM:** X-ray diffraction (XRD) analysis on the silicon plates with the deposited diamond film was carried out on a Bruker D8 Advance Eco diffractometer with Cu K radiation and a LynxEye-XE detector. The data were collected for  $2\theta$  range 42-46 deg. and 74-77 deg. where (111) and (220) reflections are observed. Scanning electron microscope (SEM) micrographs were captured using a Hitachi S-3400N microscope, operating in secondary electron mode at a 25 kV accelerating voltage.

**Raman spectroscopy:** The investigation of the molecular composition of the electrodes was carried out by means of Raman spectroscopy. A Horiba LabRAM ARAMIS Raman confocal microscope (100 $\times$ /0.95 objective, 50  $\mu\text{m}$  of confocal aperture) equipped with a 532 nm diode-pumped solid-state (DPSS) laser was used.

**Electrochemical measurements:** The electrochemical properties of the  $\text{BDD}_D$  and  $\text{BDD}_H$  electrodes were investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and differential pulse voltammetry (DPV) using a potentiostat–galvanostat (VMP-300, Bio-Logic, France) with the EC-Lab software. All electrochemical measurements were conducted in a three-electrode electrochemical cell. The Pt wire served as the counter electrode, while Ag/AgCl and Ag/AgCl/3M KCl electrodes were the reference electrodes. The geometric surface area of the working electrode was  $0.196\text{ cm}^2$ . Prior to the electrochemical measurements, the solutions were deoxygenated with argon. The cyclic voltammetry was carried out in contact with aqueous 5 mM potassium ferricyanide (III) and 5mM hexaammineruthenium (III) chlorides, both in  $0.5\text{ mol dm}^{-3}$  of  $\text{Na}_2\text{SO}_4$  solution with an applied scan rate from 5 to 300  $\text{mV s}^{-1}$ . The electrochemical impedance spectra were recorded across a wide frequency range from 0.015 Hz to 100 kHz in 5 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  with 0.5 M  $\text{Na}_2\text{SO}_4$ , and in 5 mM  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$  in 0.5 M  $\text{Na}_2\text{SO}_4$  solutions at a formal potential (held for 5 min) with a peak-to-peak amplitude of 10 mV and 6 points per frequency decade. The  $\text{BDD}_D$  electrode was also tested in 0.625 mM, 1.25 mM, 2.5 mM, 3.75 mM and 5 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  concentration with 0.5



*M Na<sub>2</sub>SO<sub>4</sub> at 50 mV s<sup>-1</sup>. The DPV measurement parameters were optimised as a pulse height of 60 mV, a pulse width of 70 ms, a step time of 1000 ms, and a scan rate equal to 5 mV s<sup>-1</sup> (see Fig. S1). The potential ranged from 0.3 to 0.9 V (vs. Ag/AgCl/3.0 M KCl).*

**Wettability:** *Angle was measured by the sessile drop method (drop volume ~50  $\mu$ L) using a self-designed tensiometer system based on a B/W CCD camera (Thorlabs, DCU223 M, USA). Determination of the angle between the BDD surface and the tangent of the drop was performed using MATLAB 6.0 (The MathWorks, USA). The contact angle was measured in three different spots, and for both sides of the drop.*

### 2.3 Preparation of PCM solutions

*For the DPV analyses, the standard stock solution of 1 mM of paracetamol (PCM) concentration was prepared in 0.1 M of phosphate buffer solution (PBS) with pH = 7. Then an aliquot volume of the standard stock solution was added to the appropriate volume of 0.1 M of PBS. The DPV measurements were conducted in 1 mL of sample solution consisting of 0 (background), 0.001, 0.002, 0.004, 0.008, 0.016, 0.032, 0.065, 0.125, 0.25, 0.5, and 1 mM of PCM.*

## 3. Results and discussion

### 3.1 Physicochemical characterisation of boron-doped diamond surfaces

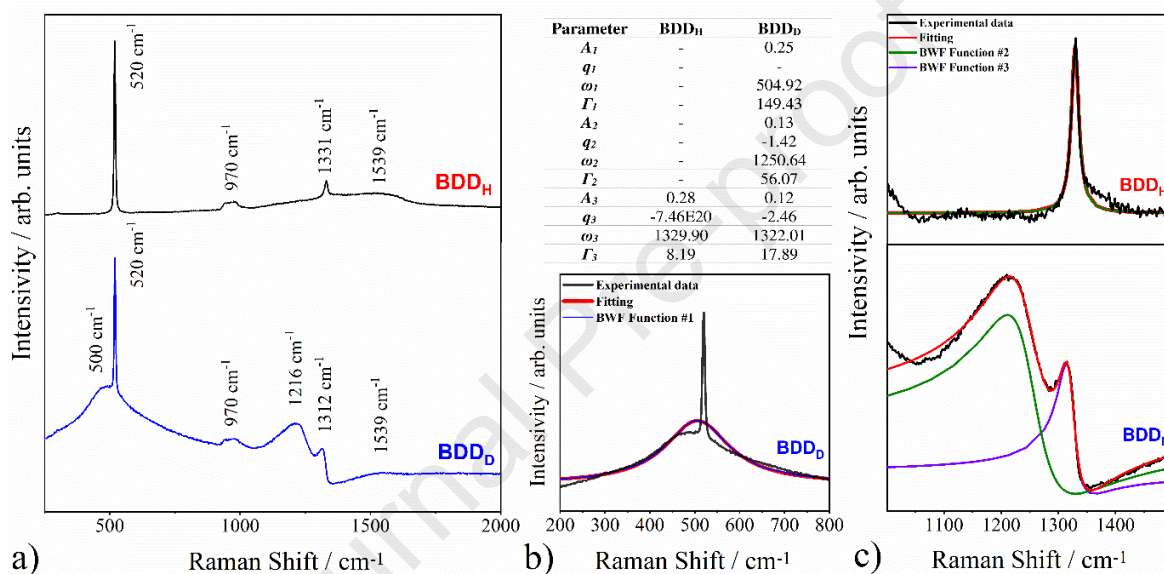
*Experimental Raman spectra are shown in Figure 1a. The sp<sup>3</sup> diamond lines are located at 1331 and 1313 cm<sup>-1</sup> for the BDD<sub>H</sub> and BDD<sub>D</sub>, respectively. The boron-doping affects the diamond line causing a shift towards lower wavenumbers. Additionally, for BDD<sub>D</sub>, the sp<sup>3</sup> peak is strongly asymmetric which is attributed to the Fano effect [13], a result of interference between the scattering by the zone-centre phonon line and the scattering by an electronic continuum [14,15]. It is worth notice that only for BDD<sub>D</sub>, we can see two broad peaks located at ca. 500 and 1200 cm<sup>-1</sup> which are attributed to the incorporation of boron in the diamond lattice [16]. According to the literature, these two broad bands are attributed to the maxima of the phonon densities of the states [17]. For both samples, peaks assigned to the first order of silicon are visible, located at 520 cm<sup>-1</sup> for one-phonon mode, and the second-order of silicon is visible at 970 cm<sup>-1</sup> in both cases.*



Additionally, the Fano-shaped peaks located at ca. 500 cm<sup>-1</sup> (BWF function #1), 1200 cm<sup>-1</sup> (BWF function #2), and 1312 and 13331 cm<sup>-1</sup> (BWF function #3) were modelled using the Breit-Wigner-Fano function (see Eq. (1)) [15,18] which is shown in Figure 1 b–c.

$$F_i(\omega) = \frac{A_i \times \left( q_i + \frac{\omega - \omega_i}{\Gamma_i} \right)^2}{1 + \left( \frac{\omega - \omega_i}{\Gamma_i} \right)^2} \quad (1)$$

In the equation,  $A_i$  is the amplitude of the Fano-shaped peaks,  $q_i$  is the asymmetric parameter,  $\omega_i$  is the position of the lines, and  $\Gamma_i$  is the width, and  $\Gamma_i$  is the position of the lines.



**Fig. 1.** a) Normalised raw Raman spectra of BDD<sub>H</sub> and BDD<sub>D</sub> electrodes, b) and c) normalised Raman spectra modeled using Breit-Wigner-Fano function, fitting (red line), different Fano-shaped peaks (BWF #1 blue line, BWF #2 green line, BWF #3 purple line); Table: Fitting parameters of BDD<sub>H</sub>, and BDD<sub>D</sub> electrodes. Indices 1, 2, and 3 correspond to the BWF#1, BWF#2, and BWF#3 bands, respectively.

The fitting parameters are shown in Fig. 1b. In the case of the BDD<sub>H</sub>, the sample's time adjustment (to have similar thickness) result in low boron incorporation into the diamond lattice that in turn results in a lack of BWF#1 and BWF#2 bands. The amplitudes of the Fano-shaped sp<sup>3</sup> (BWF#3) peak is lower for the BDD<sub>D</sub>, and the peak width ( $\Gamma$ ) is wider, which is attributed to more boron incorporation into the diamond lattice [15]. According to an investigation by Mortet et al. [18], the asymmetric parameter of the diamond sp<sup>3</sup> line ( $q_3$ ) can be used as a marker of the

carrier concentration. Only the BDD<sub>D</sub> sample indicated significant asymmetry (BDD<sub>D</sub>  $q_3 = -2.46$ ), and it should be noted that the  $q_3$  value of the BDD<sub>D</sub> electrode proves the high incorporation of boron atoms when deuterium-rich plasma is used.

Noteworthy, BDD<sub>D</sub> shows a low amount of  $sp^2$  phase despite the high boron concentration in the diamond lattice. Usually, the high boron content in the diamond film increases the amount of  $sp^2$  phase as a result of degeneration of diamond lattice [19]. In the case of BDD<sub>H</sub> sample, the  $sp^2/sp^3$  ratio reaches 0.96% which is typical for a low doped diamond film and the BDD<sub>D</sub>  $sp^2/sp^3$  ratio reaches 0.82%. For the estimation of the  $sp^2/sp^3$  ratio was used the McNamara et al. formula taking into account the cross-sections of the Raman signals of  $sp^3$  and  $sp^2$  peaks [20,21]. The formula is given by Eq. (2),

$$\frac{sp^2}{sp^3} = 100 \times I_G / (75 \cdot I_{diam} + I_G) \quad (2)$$

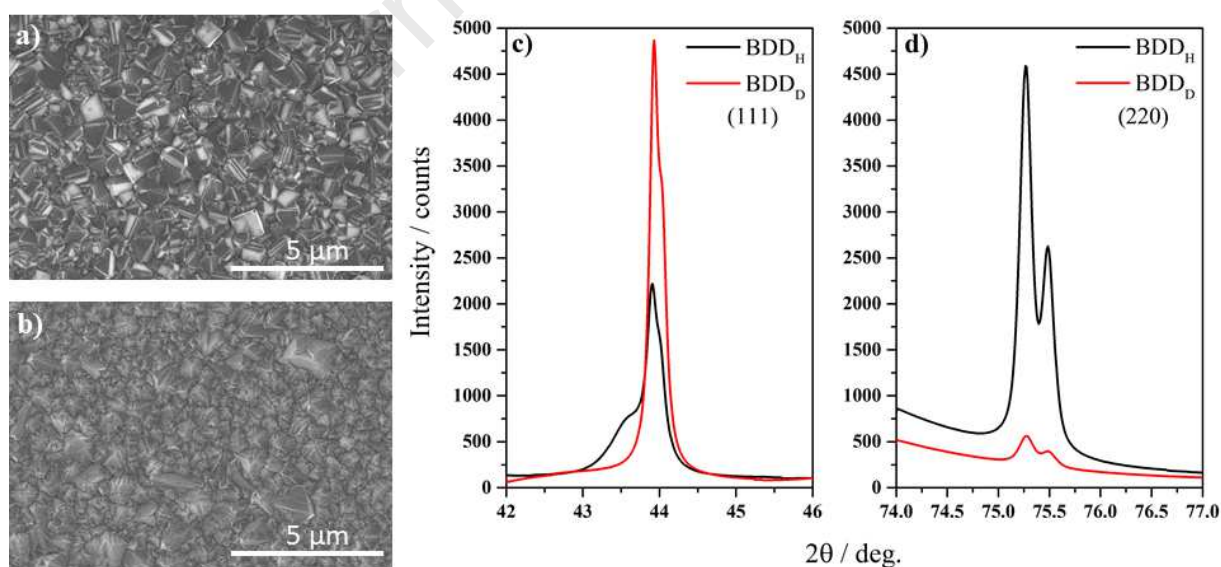
where  $I_{diam}$  is the intensity of diamond peak while  $I_G$  means the intensity of the G band. Swain and Ramesham [22] reported the  $sp^2$  phase content extending from 1 to 5% in BDD electrodes. Xu et al. [23] showed that the  $I_G/I_{Diam}$  quantitative ratio equals 0.04 for the diamond samples with 1% of boron. The grain size in this sample was ca. 8.3  $\mu m$ , while reported here BDD<sub>D</sub> electrodes exhibit grains of avg. 0.5  $\mu m$ . It should be noticed that the  $sp^2$  is predominantly localized in the inter-grain regions [24].

It was previously demonstrated that the propensity to oxidation is inseparably correlated with BDD's crystallographic texture [25–27]. SEM images presented in Fig. 2a) and 2b) reveal on average two times larger grains of BDD<sub>D</sub> than BDD<sub>H</sub>, which results in a reduced doping impact on the grain size in the case of deuterium-rich plasma synthesis. The BDD<sub>D</sub> grains are smooth and sharp, while the BDD<sub>H</sub> grains are degraded due to the dominance of the number of non-diamond  $sp^2$  phases [28,29]. According to the SEM analysis, the thickness of the BDD<sub>D</sub> and BDD<sub>H</sub> can be approximated to ~645 and ~690 nm, respectively. Authors kept a similar thickness of both samples to compare them. To achieve that, the different growth times of BDD<sub>D</sub> and BDD<sub>H</sub> were applied. It was previously found that synthesis in deuterium-rich plasma results in the growth rate of about twice as slow in comparison with hydrogen-rich conditions [9]. The deuterium has higher mass resulting from the more intensive etching of the diamond and non-diamond forms [9,30]. The Raman result also confirms Hall effect measurements resulting in one

order of magnitude higher holes concentration in BDD<sub>D</sub> reaching over  $10^{20} \text{ cm}^{-3}$  and  $10^{19} \text{ cm}^{-3}$  for BDD<sub>H</sub> [9], respectively.

The SEM micrographs reveal a significantly altered crystallographic orientation of the surface BDD grains, which was further examined through XRD studies. The crest-like grain boundaries of (111) and (220) microfacets constitute the BDD<sub>H</sub> electrode surface. On the other hand, the BDD<sub>D</sub> electrode's surface is dominated by nearly flat and crystallite edges of (111) microfacets.

The XRD analysis confirms the SEM crystallographic orientation results (see Fig. 2c-d). Only two XRD reflections of the nanodiamond films were found on the XRD patterns. Comparing the (111) reflections observed at  $2\theta = 49.3$ , we conclude that the BDD<sub>D</sub> sample has a twice more intense reflection than the BDD<sub>H</sub> sample. This phenomenon has a crucial impact on the electrical and electrochemical properties as the (111) plane is the most promoted to the incorporation of boron atoms [31–33]. Furthermore, the intensity of the (220) plane located at 75.2 and 75.5 is far stronger for the BDD<sub>H</sub> than for the BDD<sub>D</sub>, which is less promotive to the boron doping and more degenerate. For a randomly oriented polycrystalline diamond powder, the theoretical value of the  $I_{(220)}/I_{(111)}$  ratio is 0.25 according to ASTM powder diffraction data. The  $I_{(220)}/I_{(111)}$  ratio for the BDD<sub>H</sub> is 2.16, and 0.06 for the BDD<sub>D</sub>, indicating that the texture of the BDD<sub>H</sub> electrode film is oriented along the (220) direction and the BDD<sub>D</sub> along the (111) direction.



**Fig. 2.** SEM micrographs of a) BDD<sub>D</sub>, and b) BDD<sub>H</sub> with 10000x, and XRD patterns of c) (111), and d) (220) crystallographic planes.



Next, the electrical properties of the  $BDD_H$  and  $BDD_D$  electrodes were measured with a four-point probe system. The average resistivity for the sample deposited in hydrogen-based plasma was  $0.08 \text{ } \Omega \cdot \text{cm}$ , and  $2.6 \text{ m} \cdot \text{cm}$  for deuterium, which resulted in conductivities equal to  $12.5$  and  $384.6 \text{ S} \cdot \text{cm}^{-1}$ , respectively. The lower resistance of the  $BDD_D$  sample could be attributed to the direct charge transfer along the large grains, and tunneling in the intergrain region [34]. Furthermore, the lower electrical resistivity achieved for  $BDD_D$  was a result of the slightly bigger grains, which corresponds to a study reported by Habka et al. [34] in which the authors show that the grain size of polycrystalline diamond is the key parameter for efficient deuterium diffusion and trapping of boron atoms. In comparison to the  $BDD_H$  samples, we achieved one order of magnitude lower resistance for the  $BDD_D$  which is in agreement with our previous investigation showing enhanced boron-doping where the sample is grown in deuterium-rich plasma [9]. On the other hand, we achieved the same level of electrical resistivity for boron-enhanced carbon nanowalls [35] which is a hybrid material consisting of graphene nanowalls overgrown by nanodiamond clusters.

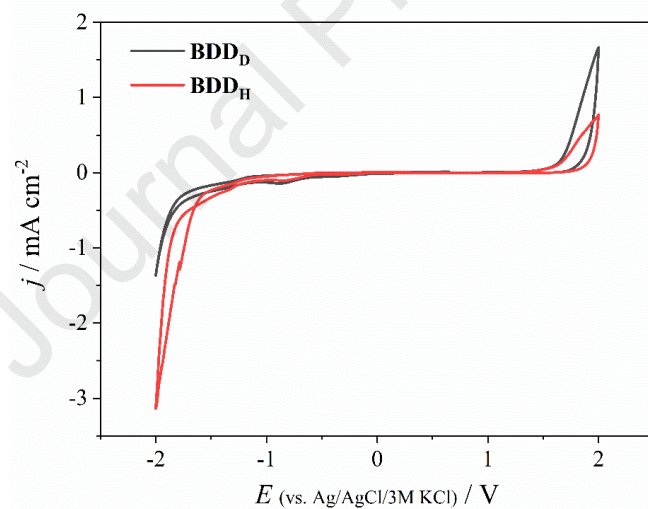
It is obvious that the variations in the isotopic composition of growth precursors drastically changes properties of deposited solid phase inducing mostly proton enhanced kinetics [36]. To improve the stoichiometric composition, the bulk diamond crystals were additionally annealed in deuterium at  $500 - 550^\circ\text{C}$  [37]. Mizuochi et al. [38] revealed that the energy of molecules and atoms in the  $D_2$  plasma are higher than those in the  $H_2$  plasma, while the etching rate by  $D$  is about 20% larger than that by  $H$  in this condition.

The contact angle was measured for the as-deposited samples (see Fig. S2). Both samples showed similar hydrophobicity with slightly higher values for the  $BDD_H$  samples. The recorded contact angle for the  $BDD_H$  was  $94.5^\circ$  and for the  $BDD_D$  was  $85.7^\circ$ . The measured angles are in agreement with other works [39,40]. The almost  $10^\circ$  difference between the contact angle can be explained by the difference in crystallite size and facet, which be determined by the amount of the surface termination by hydrogen or deuterium, resulting in different free surface energies [41].

### 3.2 Electrochemical studies: $BDD_D$ versus $BDD_H$

Cyclic voltammetry testing of the bare  $BDD_D$  and  $BDD_H$  electrodes in a neutral electrolyte ( $0.5 \text{ M Na}_2\text{SO}_4$ ) was performed to examine the electrochemical potential window (EPW), and

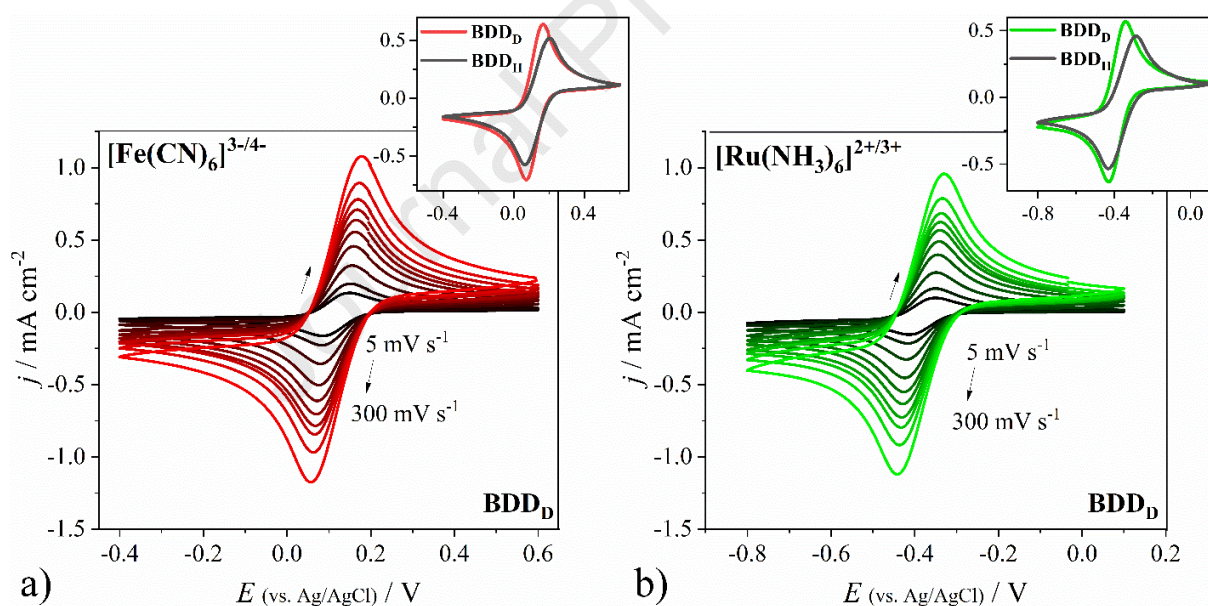
the magnitude of the background current. The results are presented in Fig. 3. As can be seen, a low background current value and very wide working potential windows (up to 3.8 V) can be observed for both diamond electrodes. However, the  $BDD_H$  layer is unstable at a deep cathodic potential (below -1.6 V), whereas the  $BDD_D$  can be polarised to -1.8 V. Wider EPW of deuterium boron-doped diamond may be caused by lower amount of  $sp^2$  when compared to the  $BDD_H$  electrode [42]. Furthermore, the presence of non-diamond carbon in both electrodes is confirmed by a weak cathodic peak at ca. -0.85 V, which may be assigned to the oxygen reduction reaction [33]. The wide EPW is related to the overvoltage of water decomposition. The oxygen electrode reaction and the hydrogen electrode reaction belong to the inner-sphere reaction. The rates of such reactions depend on the electrode surface structure (the reactions require the adsorption process of the reaction intermediates) [43]. Thus, a wide EPW value of water stability indicates a high-quality diamond layer with a low number of defects and grain boundary density [2,44].



**Fig. 3.** Cyclic voltammetry of  $BDD_D$  and  $BDD_H$  electrodes immersed in 0.5 M  $Na_2SO_4$ ; scan rate  $100\text{ mV s}^{-1}$ .

The electrochemical reactivity of the  $BDD_D$  and  $BDD_H$  electrodes was investigated using electroactive species characterised with differently charged inner-sphere and outer-sphere electron transfer: 5 mM  $K_3[Fe(CN)_6]$  in 0.5 M  $Na_2SO_4$ , and 5 mM  $[Ru(NH_3)_6]Cl_3$  in 0.5 M  $Na_2SO_4$ , respectively. Both potassium ferricyanide (III) and hexaammineruthenium (III) chloride

undergo a one-electron reversible redox reaction. The  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  redox couple represents the outer-sphere redox reaction and the kinetics of the electron transfer does not depend on the interaction with superficial functional moieties. Thus, the adsorbed  $sp^2$  carbon layers, the surface microstructure, and the surface oxides have relatively little influence on the rate of the reaction of  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  oxidation and reduction. However, the rate of the reaction depends on the electronic features of the electrode, especially the density of the electronic states [2,45]. The  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox mediator, in turn, belongs to the inner-sphere redox reaction. The  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox reaction is accompanied by the break-up and formation of the inner coordination sphere. Such reactions usually involve the adsorption process on the electrode surface and strongly depend on the surface chemistry of diamond, because the transfer of the electron requires direct interactions with the reactive sites on the electrodes [2,33,46]. The cyclic voltammetry of both redox systems recorded on  $\text{BDD}_D$  is presented in Figure 4, whereas the results of  $\text{BDD}_H$  are shown in Fig. S3.



**Fig. 4.** CV curves of  $\text{BDD}_D$  electrodes immersed in: a) 5 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  + 0.5 M  $\text{Na}_2\text{SO}_4$  (inset:  $\text{BDD}_D$  vs.  $\text{BDD}_H$  electrode at  $100 \text{ mV s}^{-1}$ ); and b) 5 mM  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$  + 0.5 M  $\text{Na}_2\text{SO}_4$  as a function of scan rates (inset:  $\text{BDD}_D$  vs.  $\text{BDD}_H$  electrode at  $100 \text{ mV s}^{-1}$ ).

In our case, the deuterium-terminated boron-doped diamond electrode exhibited extraordinary peak-to-peak separation values ( $E$ ) in both  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  and  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox couple (Table

1). The  $E$  value obtained for  $10 \text{ mV s}^{-1}$   $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  was equal to 60 mV, which is expected for a Nernstian one-electron reaction. The separation between the oxidation and reduction peak potentials obtained on the  $\text{BDD}_D$  electrode increased with the rising scan rate from 60 mV to 114 mV for  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ , and from 61 mV to 121 mV for the  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox system. The narrow peak-to-peak separation indicates that the  $\text{BDD}_D$  electrode showed desirable electronic properties and surface structure, which supported fast electron transfer for both: inner- and outer-sphere redox systems. However, better catalytic properties were observed for the  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  redox probe. Worse catalytic effect of BDD electrodes towards surface-sensitive  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox mediator can be explained by the presence of edge plane on  $\text{sp}^2$  carbon and surface defects on BDD electrodes [44,46]. Increasing peak-to-peak separation at high scan rates may be due to the presence of the Ohmic potential drop [47,48] the presence of which is confirmed by the voltammogram in Fig. S4.

It is known that the anodic and cathodic peaks should be independent of the scan rate for a reversible redox reaction [49]. For the  $\text{BDD}_D$  electrode response, there was a slight shift in the peak maximum with the increasing sweep rate. The results suggest that the interfacial charge transfer was rather fast for both redox couples and the redox couples behaved in a quasi-reversible manner (the redox reactions were limited by the slow mass transfer of the reactants from the solution to the surface of the electrode).

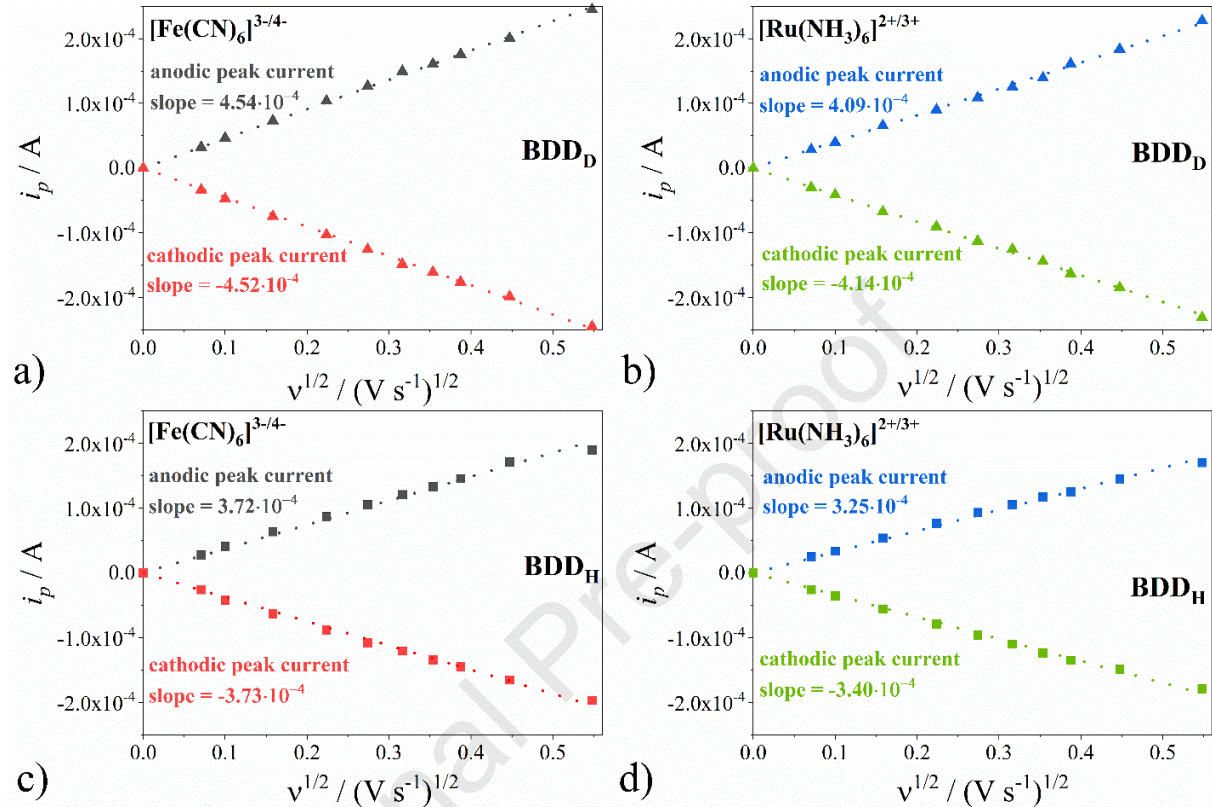
**Table 1.** Values of oxidation ( $E_{ox}$ ) and reduction potentials ( $E_{red}$ ) and the resulting peak-to-peak separation depending on the scan rate.

| $v / \text{mV s}^{-1}$ | $\text{Fe}(\text{CN})_6^{3-/4-}$ |                        | $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ |                        |
|------------------------|----------------------------------|------------------------|------------------------------------|------------------------|
|                        | $\text{BDD}_D$                   | $\text{BDD}_H$         | $\text{BDD}_D$                     | $\text{BDD}_H$         |
|                        | $\Delta E / \text{mV}$           | $\Delta E / \text{mV}$ | $\Delta E / \text{mV}$             | $\Delta E / \text{mV}$ |
| 5                      | <b>61 ± 1</b>                    | <b>73 ± 4</b>          | <b>60 ± 1</b>                      | <b>77 ± 3</b>          |
| 10                     | <b>66 ± 2</b>                    | <b>77 ± 5</b>          | <b>65 ± 2</b>                      | <b>87 ± 5</b>          |
| 25                     | <b>74 ± 1</b>                    | <b>100 ± 5</b>         | <b>70 ± 1</b>                      | <b>107 ± 4</b>         |
| 50                     | <b>82 ± 0</b>                    | <b>115 ± 3</b>         | <b>80 ± 0</b>                      | <b>126 ± 6</b>         |
| 75                     | <b>89 ± 3</b>                    | <b>130 ± 5</b>         | <b>86 ± 1</b>                      | <b>139 ± 6</b>         |
| 100                    | <b>95 ± 1</b>                    | <b>141 ± 2</b>         | <b>89 ± 2</b>                      | <b>151 ± 7</b>         |
| 125                    | <b>98 ± 2</b>                    | <b>147 ± 1</b>         | <b>93 ± 3</b>                      | <b>160 ± 8</b>         |
| 150                    | <b>103 ± 1</b>                   | <b>154 ± 1</b>         | <b>97 ± 1</b>                      | <b>166 ± 7</b>         |

|     |                |                |                |                |
|-----|----------------|----------------|----------------|----------------|
| 200 | <b>110 ± 3</b> | <b>167 ± 1</b> | <b>102 ± 3</b> | <b>182 ± 7</b> |
| 300 | <b>121 ± 2</b> | <b>184 ± 2</b> | <b>114 ± 3</b> | <b>203 ± 6</b> |

The  $BDD_D$  electrode's almost linear dependence ( $R^2=0.9995-0.9997$ ), with the zero intercept, of the growth of the anodic and cathodic peak current density with the increasing square root on the scan rate is shown in Fig. 5. A linear dependence of the logarithm of the anodic and cathodic peak current densities vs. the logarithm of the scan rate is also observed (Fig. S5). As can be seen, the cathodic and anodic peak currents increased with the sweep rate. Moreover, there is a symmetry between the oxidation and reduction peaks, which demonstrated a nearly reversible electron transfer reaction. There is a high degree of symmetry of the  $BDD_D$  reaction in both electrolyte systems. For  $Ru(NH_3)_6^{2+/3+}$  redox mediator, the anodic slope was equal to  $4.09 \cdot 10^{-4} A V^{-1/2} s^{1/2}$ , while the cathodic was  $-4.14 \cdot 10^{-4} A V^{-1/2} s^{1/2}$ , whereas for the  $Fe(CN)_6^{3-/4-}$  redox couple, the anodic slope was  $4.54 \cdot 10^{-4} A V^{-1/2} s^{1/2}$ , and the cathodic was equal to  $-4.52 \cdot 10^{-4} A V^{-1/2} s^{1/2}$ . Generally, the  $BDD_H$  electrode exhibited worse electrochemical behaviour. The value of the peak-to-peak separation increased from 73 to 184 mV for the  $Fe(CN)_6^{3-/4-}$  redox couple, and from 77 to 203 mV for the  $Ru(NH_3)_6^{2+/3+}$  redox system. The slopes in the  $Fe(CN)_6^{3-/4-}$  electron mediator were equal to  $3.72 \cdot 10^{-4} A V^{-1/2} s^{1/2}$  and  $-3.73 \cdot 10^{-4} A V^{-1/2} s^{1/2}$ , whereas in the  $Ru(NH_3)_6^{2+/3+}$  redox couple, the slopes were  $3.25 \cdot 10^{-4} A V^{-1/2} s^{1/2}$  and  $-3.40 \cdot 10^{-4} A V^{-1/2} s^{1/2}$ . The difference in the electrochemical response of the  $BDD_D$  and  $BDD_H$  electrodes may be related to the different electrochemical kinetics, which strongly depends on their boron-doped level, surface termination, diamond grain size, crystallographic orientation, surface resistivity, and presence of NDC impurity phase [1,3,33,43,50].  $BDD_D$  electrode shows much lower surface resistivity, higher boron concentration and lower NDC amount than  $BDD_H$  as confirmed by Raman, XRD and CV data. Moreover, works by Zieliński et al. [51] and Ryl et al. [52] showed the influence of surface termination on the electrochemical performance. Moreover, the crystal configuration also plays a crucial role due to the oxidation propensity sequence (110)>(100)>(111). Also, Invandini et al. [46] investigated the influence of surface orientation on the electrochemical properties and concluded that the (111) plane is more reactive than the (100) plane independent of the type of surface termination (H- and O-). According to work by Brillas and Martinez-Huitle [43], the fastest rates of redox reactions should be observed for the (111) crystal configuration, which refers to the metallic behaviour of the diamond layer. In agreement with the XRD studies, the crystallographic structure of the deuterium-terminated

diamond is dominated by the (111) configuration. The reactivity of the (111) boron-doped diamond is associated with the high amount of boron built into the carbon structure.



**Fig. 5.** Dependence of the peak current on the scan rate obtained for  $BDD_D$  electrodes immersed in: a) 5 mM  $K_3[Fe(CN)_6]$  + 0.5 M  $Na_2SO_4$ ; and b) 5 mM  $[Ru(NH_3)_6]Cl_3$  + 0.5 M  $Na_2SO_4$ ; and  $BDD_H$  electrodes immersed in: c) 5 mM  $K_3[Fe(CN)_6]$  + 0.5 M  $Na_2SO_4$ ; and d) 5 mM  $[Ru(NH_3)_6]Cl_3$  + 0.5 M  $Na_2SO_4$ .

The electroactive surface area of the  $BDD_D$  electrode,  $A_e$  ( $cm^2$ ), was calculated using the modified Randles-Sevcik equation for quasi-reversible reactions (2) [53,54]:

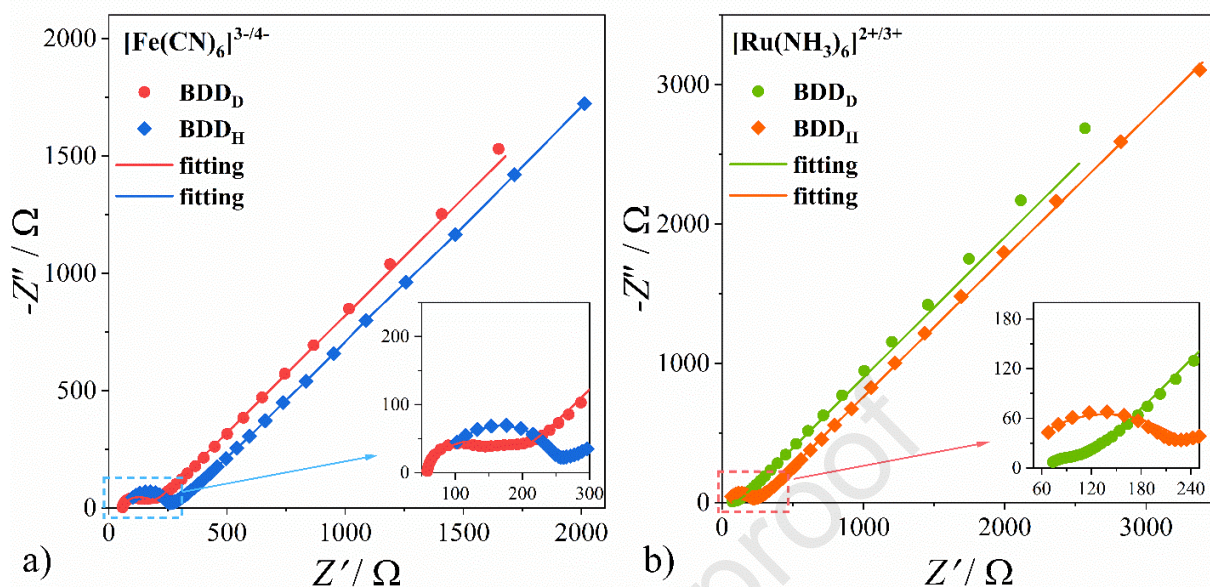
$$i_p = 0.4463 \cdot n \cdot F \cdot A_e \cdot C \cdot D^{\frac{1}{2}} \cdot \sqrt{\frac{n \cdot F}{R \cdot T}} \cdot v^{\frac{1}{2}} \cdot \kappa(\Lambda, \alpha), \quad (2)$$

where  $i_p$  is the peak current (A),  $F$  corresponds to Faraday's constant ( $96485 \text{ C mol}^{-1}$ ),  $R$  is gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $T$  is the temperature (298 K),  $C$  is the concentration ( $\text{mol cm}^{-3}$ ),  $D$  is the diffusion coefficient ( $\text{cm}^2 \text{ s}^{-1}$ ),  $n$  is the number of electrons,  $v$  is the scan rate ( $\text{V s}^{-1}$ ),  $\kappa$  and  $\alpha$  are parameters introduced by Matsuda and Ayabe [55], and  $\Lambda$  is charge transfer coefficient

assumed as 0.5 [56,57]. The diffusion coefficients were taken as  $7.6 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , and  $4.96 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  for  $\text{Fe}(\text{CN})_6^{4-/3-}$ , and  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ , respectively [58,59]. In the  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$  redox couple, the determined electroactive surface areas for  $\text{BDD}_D$  and  $\text{BDD}_H$  are equal to  $0.14 \text{ cm}^2$  and  $0.11 \text{ cm}^2$ , respectively. In the  $\text{Fe}(\text{CN})_6^{4-/3-}$  electron mediator, the  $A_e$  values were lower and amounted to  $0.12 \text{ cm}^2$  for  $\text{BDD}_D$ , and  $0.10 \text{ cm}^2$  for  $\text{BDD}_H$ . There were no differences between the  $A_e$  obtained for the anodic and cathodic currents in both solutions, which indicates comparable electroactive surface areas regardless of the oxidation and reduction process. The values of  $A_e$  indicate that 39%, and 29% of the geometric surface area of the  $\text{BDD}_D$  electrode, in  $\text{Fe}(\text{CN})_6^{3-/4-}$ , and  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ , respectively, were blocked towards electron transfer between the electrode and electrolyte. According to the literature, different polycrystalline crystal faces are incorporated during the growth of boron-doped diamond by chemical vapour deposition. The presence of point defects, non-diamond carbon phases, and grain boundaries may result in heterogeneity in the local concentration of charge carriers [1]. In agreement with the literature, this phenomenon can be explained by heavily overlapping diffusion layers with the characteristics of linear diffusion [60–62]. In this case, the average size of the unblocked areas and the average distance between them are relatively small.

Electrochemical impedance spectroscopy was carried out in 5 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  with 0.5 M  $\text{Na}_2\text{SO}_4$ , and 5 mM  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$  in 0.5 M  $\text{Na}_2\text{SO}_4$  at the formal potential of the redox reaction for  $\text{BDD}_D$ . Simultaneously, the measurement was also conducted on the reference  $\text{BDD}_H$  electrode. The Nyquist plots are depicted in Fig. 6. Quantitative data were estimated using an electric equivalent circuit (EEQC) in the ZSimpWin analyser software. The EEQC used for fitting  $R_e(\text{CPE}(R_{ct}W))$  is shown in inset Fig. S6. The fitting procedure gave normalised fitting errors  $\chi^2$  at the level of  $10^{-4}$ - $10^{-3}$ . The values of the electrical parameters evaluated using the aforementioned EEQC are collected in Table 2.





**Fig. 6.** Nyquist plots registered and fitted for  $BDD_D$  and  $BDD_H$  electrodes immersed in: a) 5 mM  $K_3[Fe(CN)_6] + 0.5 M Na_2SO_4$ ; and b) 5 mM  $[Ru(NH_3)_6]Cl_3 + 0.5 M Na_2SO_4$ .

The EIS spectra include a semicircle region lying in the high-frequency regime followed by a straight line with a  $45^\circ$  slope (at a lower frequency). The semicircle represents the electron-transfer-limited process, while the line corresponds to the diffusion-limited process. The electrolyte resistance,  $R_e$ , is an element arising in the high-frequency range. The value of  $R_e$  is ca.  $12 \text{ } \Omega \cdot \text{cm}^2$ , and  $13 \text{ } \Omega \cdot \text{cm}^2$  for  $Ru(NH_3)_6^{2+/3+}$ , and  $Fe(CN)_6^{3-/4-}$ , respectively. A low electrolyte resistance indicates a good attachment of the  $BDD_D$  to the silicon substrate. Furthermore, it suggests a low contamination level of the surface. The charge-transfer resistance  $R_{ct}$  is equal to the diameter of the aforementioned semicircle. The  $R_{ct}$  value is significantly lower for the  $BDD_D$  electrode and is equal to  $9.8 \text{ } \Omega \cdot \text{cm}^2$  in  $Ru(NH_3)_6^{2+/3+}$ , and  $18.2 \text{ } \Omega \cdot \text{cm}^2$  in  $Fe(CN)_6^{3-/4-}$ , which indicates better electron transfer processes. The impedance spectra show that the capacitance of both diamond electrodes depends on frequency. Thus, the electrical equivalent circuit of the electrodes includes a frequency-dependent constant phase element (CPE) which also reflects the distribution of reactivity caused by the surface electrochemical heterogeneity [63–67]. The CPE impedance ( $Z_{CPE}$ ) is defined as  $Z_{CPE} = 1/Q(j\omega)^{-n}$ , where  $Q$  and  $n$  are the constant phase element parameters,  $\omega$  is the angular frequency, and  $j$  is the imaginary number. The Warburg impedance ( $Z_w$ ) describes a diffusional resistance. This element was used only in terms of the correct fitting procedure of the other elements.



**Table 2.** Mean values of selected electric parameters calculated on the basis of  $R_e(CPER_{ct}W)$  equivalent circuit.

|   | $Fe(CN)_6^{3-/4-}$  |                     | $Ru(NH_3)_6^{2+/3+}$ |                     |
|---|---------------------|---------------------|----------------------|---------------------|
|   | BDD <sub>D</sub>    | BDD <sub>H</sub>    | BDD <sub>D</sub>     | BDD <sub>H</sub>    |
| $R_{ct} / \Omega \text{ cm}^2$                    | 18.2                | 79.3                | 9.8                  | 43.9                |
| $CPE / \Omega^{-1} \text{ cm}^{-2} \text{ s}^n$   | $2.0 \cdot 10^{-4}$ | $1.1 \cdot 10^{-6}$ | $3.9 \cdot 10^{-4}$  | $7.1 \cdot 10^{-6}$ |
| $n$   | 0.8                 | 0.8                 | 0.8                  | 0.8                 |
| $W / \Omega^{-1} \text{ s}^{0.5} \text{ cm}^{-2}$ | $5.5 \cdot 10^{-3}$ | $2.4 \cdot 10^{-3}$ | $5.9 \cdot 10^{-3}$  | $4.4 \cdot 10^{-3}$ |

The apparent heterogeneous electron transfer rate constant  $k_{app}^{\circ}$  was calculated using Eq. (3) [68,69]:

$$k_{app}^{\circ} = \frac{R \cdot T}{n^2 \cdot F^2 \cdot A \cdot C \cdot R_{ct}}, \quad (3)$$

where  $R$  is the molar gas constant ( $8.32 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the electrolyte temperature (K),  $n$  is the number of electrons exchanged during the reaction,  $F$  is the Faraday constant (96,500 C),  $A$  is the geometric electrode area, and  $C$  is the concentration ( $\text{mol cm}^{-3}$ ). The standard rate constant values for the BDD<sub>D</sub> were equal to  $5.84 \cdot 10^{-3} (\pm 0.56 \cdot 10^{-3}) \text{ cm s}^{-1}$  for  $Ru(NH_3)_6^{2+/3+}$ , and  $2.93 \cdot 10^{-3} (\pm 0.86 \cdot 10^{-3}) \text{ cm s}^{-1}$  for the  $Fe(CN)_6^{3-/4-}$  redox system, respectively. The BDD<sub>H</sub> electrode gave a  $k_{app}^{\circ}$  of  $1.213 \cdot 10^{-3} (\pm 0.026 \cdot 10^{-3}) \text{ cm s}^{-1}$  for  $Ru(NH_3)_6^{2+/3+}$ , and  $6.72 \cdot 10^{-4} (\pm 3.41 \cdot 10^{-4}) \text{ cm s}^{-1}$  for the ferri-ferrocyanide system. According to work by Alehashem et al. [70], the achieved in the  $Fe(CN)_6^{3-/4-}$  redox system  $k_{app}^{\circ}$  value is one order of magnitude higher for the BDD<sub>D</sub> than for the standard BDD<sub>H</sub> resulting in a higher heterogeneous electron transfer rate constants. The value of  $k_{app}^{\circ}$  is heavily dependent on the chemical and physical properties of the diamond-based electrodes [1]. Also,  $k_{app}^{\circ}$  is strongly sensitive to the amount of exposed edge plane on  $sp^2$  carbon electrodes [71]. The high value of  $k_{app}^{\circ}$  indicates a low amount of surface  $sp^2$  phase on the BDD<sub>D</sub>, which is in agreement with the Raman spectroscopy investigations.

The calculated values are in agreement with the standard rate constants found in the literature for boron-doped diamond (from  $10^{-5}$  to  $10^{-2} \text{ cm s}^{-1}$ ) [49,63,71]. Moreover, the value of  $k_{app}^{\circ}$  confirms the reversibility of the electrochemical processes, which should be between  $10^{-1}$  and  $10^{-5} \text{ cm s}^{-1}$  [49].

**Table 3.** Comparison of the physicochemical and electrochemical properties of polycrystalline boron-doped diamonds.

| Sample           | Process                       | Post-treatment  | [B]: [C]<br>ratio /<br>ppm | [B] / B<br>atoms<br>cm <sup>-3</sup>           | Grain<br>size / $\mu$ m | R /<br>m $\Omega$ ·cm | EPW /<br>V | $\Delta E$<br>Fe(CN) <sub>6</sub> <sup>3-/4-</sup><br>/ mV | $\Delta E$<br>Ru(NH <sub>3</sub> ) <sub>6</sub> <sup>2+/3+</sup><br>/mV | $k_{app}^{\circ}$<br>Fe(CN) <sub>6</sub> <sup>3-/4-</sup><br>/ cm·s <sup>-1</sup> | $k_{app}^{\circ}$<br>Ru(NH <sub>3</sub> ) <sub>6</sub> <sup>2+/3+</sup><br>/ cm·s <sup>-1</sup> | Ref.         |
|------------------|-------------------------------|---|----------------------------|--|-------------------------|-----------------------|------------|--|---|---|---|--------------|
| BDD              | MW PACVD                      | annealed under a N <sub>2</sub><br>atmosphere   | 1,100                      | n/d  | 1-10                    | 10 <sup>4</sup>       | 1.2        | 104  | n/d   | n/d   | n/d   | [72]         |
| BDD              | MACVD <sup>1</sup>            | aqua regia;<br>H <sub>2</sub> SO <sub>4</sub> /HNO <sub>3</sub> /NaNO <sub>3</sub> ; H <sub>2</sub><br>plasma               | n/d                        | 10 <sup>19</sup> –10 <sup>20</sup>             | 3                       | 10 <sup>2</sup>       | 1.4        | 70   | 70  | n/d   | n/d   | [1]          |
| BDD              | MW PACVD                      | H <sub>2</sub> O <sub>2</sub> /H <sub>2</sub> SO <sub>4</sub> ;<br>H <sub>2</sub> plasma                                    | 10,000                     | 3.4·10 <sup>17</sup> –<br>1.8·10 <sup>21</sup> | 1-2                     | 7                     | n/d        | 243  | n/d   | n/d   | n/d   | [73]         |
| BDD              | MW PACVD                      | no  | 600                        | 1.0·10 <sup>20</sup>                           | 11                      | n/d                   | 4.9        | 980  | 380   | n/d   | n/d   | [23]         |
| BDD              | MW PACVD                      | H <sub>2</sub> SO <sub>4</sub> /HNO <sub>3</sub> ;<br>HNO <sub>3</sub> /HCl; HF; H <sub>2</sub><br>plasma                   | n/d                        | 7.6·10 <sup>20</sup>                           | 5                       | 6                     | n/d        | 60   | 60  | n/d   | n/d   | [46]         |
| BDD              | MACVD                         | H <sub>2</sub> SO <sub>4</sub> /HNO <sub>3</sub> /NaNO <sub>3</sub> ; H <sub>2</sub><br>plasma                              | n/d                        | 10 <sup>19</sup> –10 <sup>20</sup>             | 2-4                     | 10 <sup>2</sup>       | 3.8        | 64   | 65  | 10 <sup>-3</sup> –10 <sup>-2</sup>  | 10 <sup>-3</sup> –10 <sup>-2</sup>  | [71]         |
| BDD              | HFCVD <sup>3</sup>            | H <sub>2</sub> plasma   | 10,000                     | n/d  | n/d                     | n/d                   | 2.8        | 473  | 61  | 1.1·10 <sup>-4</sup>  | 9.7·10 <sup>-2</sup>  | [74]         |
| BDD              | Commercial<br>Element Six Ltd | H <sub>2</sub> SO <sub>4</sub> ; lapped   | n/d                        | 1.9·10 <sup>20</sup>                           | n/d                     | 60                    | 3.5        | n/d  | 68  | n/d   | 4.0·10 <sup>-2</sup>  | [75]         |
| BDD              | MW PACVD                      | aqua regia; HNO <sub>3</sub> /HCl;<br>H <sub>2</sub> O <sub>2</sub> /H <sub>2</sub> SO <sub>4</sub> ; H <sub>2</sub> plasma | 10,000                     | 2.0·10 <sup>21</sup>                           | n/d                     | n/d                   | n/d        | 108  | n/d   | 6.1·10 <sup>-3</sup>  | n/d   | [63]         |
| BDD              | HFCVD                         | Cathodic treatment HNO <sub>3</sub>   | 5,000                      | 4.0·10 <sup>18</sup>                           | 8–4.5                   | n/d                   | 3.5        | 68   | 92  | 1.0·10 <sup>-2</sup>  | 1.31·10 <sup>-3</sup>   | [76]         |
| BDD              | MW PACVD                      | n/d   | n/d                        | n/d  | 0.5-1.5                 | 10-20                 | n/d        | 149  | n/d   | 1.4·10 <sup>-3</sup>  | n/d   | [77]         |
| BDD <sub>H</sub> | MW PACVD                      | no  | 10,000                     | 1.5·10 <sup>19</sup>                           | 0.1                     | 0.08                  | 3.5        | 73   | 74  | 6.7·10 <sup>-4</sup>  | 1.2·10 <sup>-3</sup>  | this<br>work |
| BDD <sub>D</sub> | MW PACVD                      | no  | 10,000                     | 7.9·10 <sup>20</sup>                           | 0.5                     | 2.6                   | 3.8        | 61   | 59.4  | 2.9·10 <sup>-3</sup>  | 5.8·10 <sup>-3</sup>  | this<br>work |

<sup>1</sup> Microwave assisted chemical vapour deposition; <sup>2</sup> Plasma assisted chemical vapour deposition; <sup>3</sup> Hot filament chemical vapour deposition



Table 3 enumerates a detailed list of parameters of different polycrystalline boron-doped diamond electrodes reported in the literature comparing them with as-grown BDD<sub>D</sub> surfaces. The cleaning, pre-treatment, boron content and structure morphology clearly affects electrochemical parameters like EPW value, peak-to-peak separation, etc.. The most of reported diamond electrodes were subjected to a multi-step cleaning process using an aggressive chemical like hot aqua regia or concentrated, hot sulfuric acid (VI). Xu et al. used “as grown” BDD electrode, but as a result the oxidation and reduction reactions were sluggish ( $\Delta E_{[Fe(CN)_6]^{3-/4-}} = 980$  mV,  $\Delta E_{[Ru(NH_3)_6]^{2+/3+}} = 380$  mV) [23].

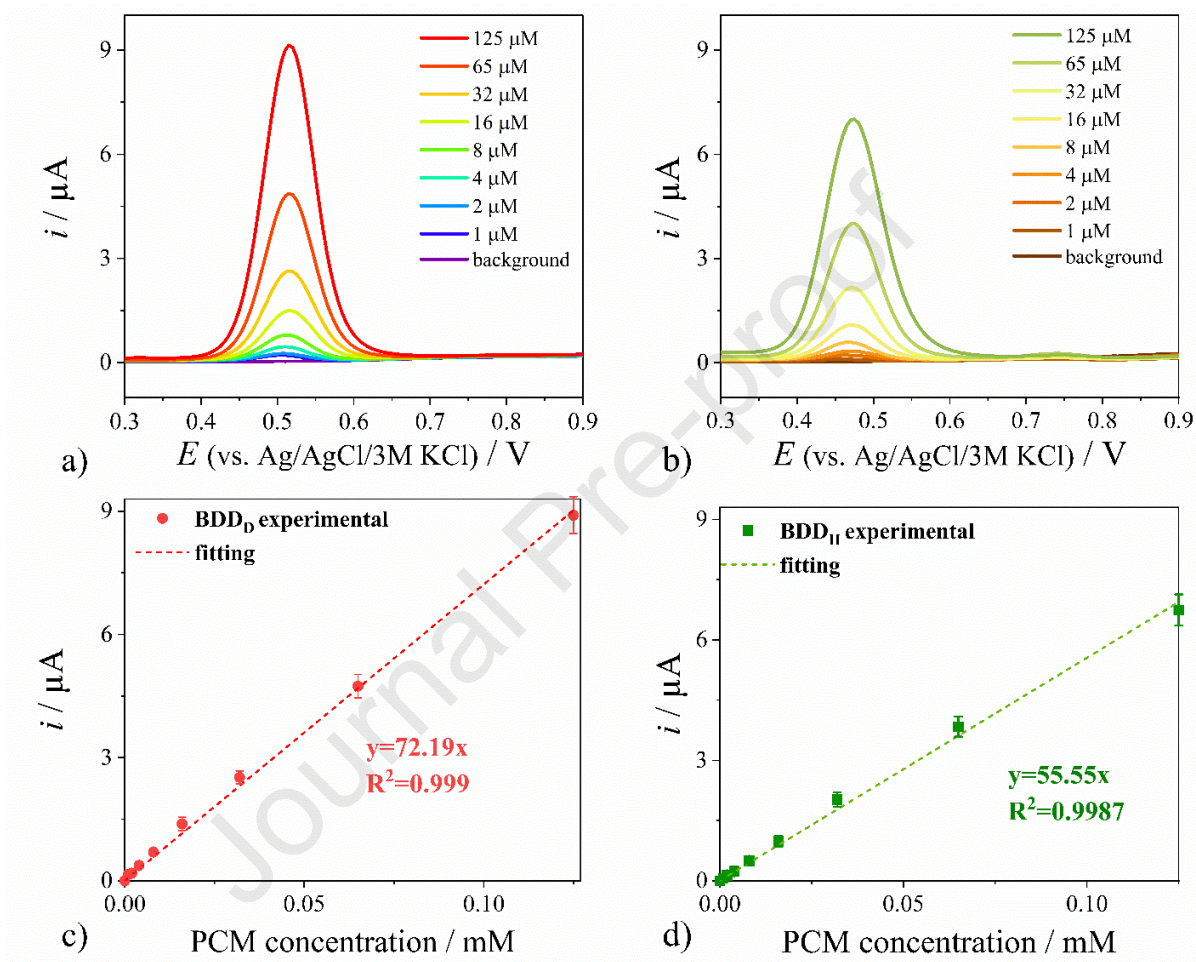
### 3.2.1 Electrochemical determination of paracetamol

The as-deposited BDD<sub>D</sub> and BDD<sub>H</sub> electrodes were used as an electrochemical sensor for the detection of paracetamol. The DPV technique was used for this purpose. The oxidation peak of the analyte was presented at about +0.49 V (vs. Ag/AgCl/3M KCl). The anodic peak currents of PCM recorded on both types electrode were linear to their concentrations in a wide linear range from 1 to 125  $\mu$ M in 0.1 M PBS (pH 7) (see Fig. 7). The additional anodic peak at ca. +0.62 V of PCM oxidation was observed for both electrodes for high-concentrated samples (see Fig. S7), which can be attributed to by-products of PCM electropolymerisation [4].

Both electrodes exhibited a wide linear range from 1 to 125  $\mu$ M, and the corresponding linear regression equations were given as  $i_p [\mu A] = (72.19 \pm 0.92) c_{PCM} [mM]$  for BDD<sub>D</sub> (correlation coefficient = 0.9993) and  $i_p [\mu A] = (55.55 \pm 0.98) c_{PCM} [mM]$  for BDD<sub>H</sub> ( $R^2 = 0.9987$ ). Thus, the electrodes differ in the sensitivity of PCM detection, which was equal to  $367.85 \pm 4.69 \mu A mM^{-1} cm^{-2}$  for BDD<sub>D</sub> electrode and  $283.06 \pm 4.99 \mu A mM^{-1} cm^{-2}$  for BDD<sub>H</sub> electrode. The limit of detection (LOD) was estimated using the equation  $LOD = 3.3 s_b/a$ , where  $s_b$  is the standard deviation of a blank solution (based on 10 blank readings), and  $a$  denotes the slope of the calibration curve [78–80]. The value of LOD calculated for the BDD<sub>D</sub> electrode was 765 nM, whereas for the BDD<sub>H</sub> was 2510 nM. Moreover, the relative standard deviation (RSD), obtained for five separated BDD<sub>D</sub> electrodes used for 125  $\mu$ M PCM determination, was equal to 5.5%. These results indicate that BDD<sub>D</sub> electrode exhibits significant electrocatalytic activity towards paracetamol. Furthermore, BDD<sub>D</sub> electrode shows better sensing performance towards PCM comparing to BDD<sub>H</sub> electrode. The difference in the behaviour of the electrodes may result from

the higher amount of electroactive zones on deuterium-terminated diamond strictly related to (111) crystal facets [46,81].

Table 4 presents a comparison of the PCM detection performances from the present and previously reported electrochemical sensors on different diamond electrodes.



**Fig. 7.** DPV of PCM recorded on a)  $BDD_D$ , b)  $BDD_H$  electrode; and concentration dependence of PCM on c)  $BDD_D$ , and d)  $BDD_H$  electrode (the error bars represent the standard deviation).

**Table 4.** Comparison of the electroanalytical detection of PCM on different BDD electrodes.

| Electrode   | Method             | Linear range / $\mu\text{M}$ | LOD / $\mu\text{M}$ | Reference |
|---|--------------------|------------------------------|---------------------|-----------|
| $BDD$ electrode                                       | Cyclic Voltammetry | 100–8000                     | 10                  | [82]      |
| Commercial $BDD$ electrode by Windsor Scientific Ltd. | DPV                | 10–100                       | 0.85                | [83]      |



|  |                                 |                     |                    |                         |
|--|---------------------------------|---------------------|--------------------|-------------------------|
| <i>Cathodically Pretreated Boron-Doped Diamond Electrode</i> | <i>Square-Wave Voltammetric</i> | 0.2–97.3            | -                  | [84]                    |
| <i>BDD electrode</i>   | <i>DPV</i>                      | 50–83               | 49                 | [85]                    |
| <b><i>BDD<sub>H</sub> electrode</i></b>                      | <b><i>DPV</i></b>               | <b><i>1–125</i></b> | <b><i>2.51</i></b> | <b><i>This work</i></b> |
| <i>BDD<sub>D</sub> electrode</i>                             | <i>DPV</i>                      | 1–125               | <b><i>0.76</i></b> | <i>This work</i>        |

#### 4. Conclusions

In summary, the boron-doped diamonds synthesised in the deuterium-rich plasma exhibited activity towards  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  and  $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$  redox couples, reaching peak-to-peak separation values of only 60.6 mV, and 59.8 mV, respectively. The substitution of hydrogen to deuterium in the gas phase is primarily responsible for the enhanced boron doping and significantly decrease of nondiamond  $sp^2$  phase in diamond films. This phenomenon is also visible in the Raman spectra followed by a strongly shifted diamond peak from  $1332\text{ cm}^{-1}$  to  $1312\text{ cm}^{-1}$ , and resistivity of  $2.6 \cdot 10^{-3}\text{ cm}$ . It is worth noting that the amount of (111)-oriented crystals are higher for  $\text{BDD}_D$  compared to  $\text{BDD}_H$ . It should also be noted that a low value of background currents leads to an enhanced signal-to-background ratio which allows  $\text{BDD}_D$  to be used in the application of sensors. The boron-doped diamond grown in deuterium-rich plasma shows very promising electrical and electrochemical properties which can be applied to the thin, sensitive electrochemical sensor with a great linearity range equal to 1–125  $\mu\text{M}$  achieved for PCM.

#### CRediT authorship contribution statement

**A. Dettlaff:** Conceptualisation, Methodology, Resources, Investigation, Writing - original draft; **M. Sobaszek:** Conceptualisation, Methodology, Resources, Investigation, Writing - original draft; **T. Klimczuk:** Investigation; **R. Bogdanowicz:** Funding acquisition, Project Administration.

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**Highlights:**

- Novel deuterium-plasma-grown diamond electrodes were prepared.
- Deuterium enriched electrode exhibited high electroactivity and stability.
- Enhanced electrochemical mechanism of the diamond electrodes was elaborated.
- Wide linear range of sensing of paracetamol from 1 to 125  $\mu\text{M}$  was achieved.

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