

**CHARLES UNIVERSITY**  
**FACULTY OF SCIENCE**  
**DEPARTMENT OF ANALYTICAL CHEMISTRY**



**BORON DOPED DIAMOND THIN FILMS:  
PREPARATION, CHARACTERIZATION, AND  
APPLICATIONS IN ELECTROANALYSIS OF  
ORGANIC COMPOUNDS**

**HABILITATION THESIS**

**Prague, 2019**

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Prague, May 15th, 2019

RNDr. Karolina Schwarzová, Ph.D.

This Habilitation Thesis is based on the research performed and the scientific papers published in the period from 2006 to 2018. I would like to express the acknowledgements to all co-workers and co-authors of my publications, who have supported my research efforts during this time. Special thanks to my students from Charles University and also those from abroad, and colleagues from UNESCO Laboratory of Environmental Electrochemistry and Department of Analytical Chemistry, who provided inspiring and friendly atmosphere for day-to-day work.

My deep thanks belong especially to prof. Jiří Barek, the head of the UNESCO Laboratory, who supervised my master and Ph.D. theses and supported my further scientific development for all the years of my employment at the Department of Analytical Chemistry. Further, my gratitude is extended to my colleague doc. Miroslav Fojta, who encouraged me during the writing of this Thesis. I acknowledge also my colleagues from the Jaroslav Heyrovský Institute of Physical Chemistry, Institute of Biophysics and Institute of Physics of the Academy of Sciences of the Czech Republic, University Pardubice (Faculty of Chemical Technology), Slovak Technical University in Bratislava (Faculty of Food and Chemical Technology) and Palacký University Olomouc for interest and participation in my research as well as friendship and mutual support within the Czech and Slovak electroanalytical community.

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## ABSTRACT

Boron doped diamond (BDD) is a very promising electrode material with extremely broad potential window, especially in positive region, low noise and residual current, and relatively high resistance to passivation, which is the biggest obstacle in practical applications of traditional electrode materials in complex biological and environmental matrices. This Habilitation Thesis summarizes the progress in fabrication, construction and characterization of bare BDD-based electrodes and their applications with special focus on electroanalysis of organic compounds since their introduction in 1992.

The general introduction of the Thesis focuses on historical aspects, fabrication, characterization and factors influencing electrochemical properties of BDD. Further, applications of BDD in electrochemistry are presented including electrochemical oxidation of organic pollutants at BDD anodes proposed for quantitative decomposition of these compounds, electrochemical disinfection of drinking and bathing water, and electrochemical synthesis. Achievements in electroanalysis of organic compounds using BDD electrodes represent the main focus of the Thesis. This part contains an overview summarizing reviews including those published by the Author of this Thesis which are either completely devoted or at least partially touching the fields of electroanalysis by means of the BDD electrodes. Further scientific contributions of the Author in the context of related contemporary and past research are reflected in detail in two parts. The first presents electroanalytical methods developed for the determination of both oxidizable and reducible organic compounds in various matrices. In these studies, the BDD-based working electrodes were employed either in batch voltammetric methods or in amperometric detectors coupled to HPLC or capillary zone electrophoresis. The second part is devoted to important factors, such as surface pretreatment and boron-doping level, influencing the BDD electrode responses towards diverse organic analytes. Further, adsorptive features and their utilization in adsorptive stripping methods are presented and discussed.

New technologies leading to advanced BDD-based electrode materials and tailored design of BDD-based electrochemical devices assure continuing interest in their applications to improve detection of organic compounds and biomolecules in matrices of different origin as summarized in conclusions of the Thesis. Desirable expansion of developed sensing platforms and electroanalytical methods is a challenging task that requires continuous effort of researchers from academic sphere to present their advantages and versatility to service and commercial laboratories.

## **KEYWORDS**

Bare boron-doped diamond

Liquid flow techniques

Non-enzymatic electrochemistry

Organic compounds

Surface treatment

Voltammetry

## LIST OF SYMBOLS AND ABBREVIATIONS

AB	aminobiphenyl
AD	amperometric detector
AFM	atomic force microscopy
AN	aminonaphthalene
BDD	boron doped diamond
BR	Britton – Robinson (buffer)
<i>c</i>	molar concentration
CAS	Czech Academy of Sciences
CMC	critical micelle concentration
CTAB	cetyltrimethylammonium bromide
CV	cyclic voltammetry/voltammogram
CVD	chemical vapor deposition
CZE	capillary zone electrophoresis
DCV	direct current voltammetry/voltammogram
DPV	differential pulse voltammetry/voltammogram
$E_{acc}$	accumulation potential
$E_{CB}$	conduction band energy
ED	electrochemical detector/electrochemical detection
EDC	endocrine disruptor
$E_{det}$	detection potential
EF	electro-Fenton
$E_{lim,A}$	anodic potential limit
$E_{lim,C}$	cathodic potential limit
EOPG	edge plane oriented pyrolytic graphite
$E_p$	peak potential
$E_{VB}$	valence band energy
FIA	flow-injection analysis
GCE	glassy carbon electrode
H-BDD	hydrogen-terminated boron doped diamond
HER	hydrogen evolution reaction
HET	heterogeneous electron transfer
HF CVD	hot-filament chemical vapor deposition

HPLC	high-performance liquid chromatography
HRP	horseradish peroxidase
HTAB	hexadecyltrimethylammonium bromide
HVA	homovanillic acid
IARC	International Agency for Research on Cancer
$k_{app}^0$	apparent heterogeneous electron-transfer rate constant
$L_D$	limit of detection
LDR	linear dynamic range
$L_Q$	limit of quantitation
LSV	linear sweep voltammetry/voltammogram
MEA	microelectrode array
MeOH	methanol
MP CVD	microwave plasma-assisted chemical vapor deposition
O-BDD	oxygen-terminated boron doped diamond
OER	oxygen evolution reaction
PEF	photoelectro-Fenton
PGE	pyrolytic graphite electrode
ROS	reactive oxygen species
RSD	relative standard deviation
SCE	saturated calomel electrode
SDS	sodium dodecyl sulphate
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
STM	scanning tunneling microscopy
SW-AdSV	square wave adsorptive stripping voltammetry
SW-AdTSV	square wave adsorptive transfer stripping voltammetry
SWV	square wave voltammetry
$t_{acc}$	accumulation time
UNCD	ultrananocrystalline diamond
US EPA	US Environmental Protection Agency
VMA	vanillylmandelic acid
WHO	World Health Organization
XPS	X-ray photoelectron spectroscopy

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## PREFACE

Contemporary research in analytical chemistry is devoted to the development of new approaches enabling selective, sensitive, fast, and low-cost detection of target analytes, also – where appropriate and feasible – in the mode of in-field analysis. Certain renaissance of electroanalytical methods is connected with the possibility of miniaturization of electrochemical sensors and the possibility of construction of integrated devices applicable under a variety of external conditions, including *in-vitro* and *in-vivo* applications. Important is also the financial factor as both investment and running costs of electroanalytical systems are relatively low.

Since its introduction in 1992, boron-doped diamond (BDD) has been a subject of considerable interest in utilizing it as an electrode material, because in many applications its properties can be exploited to overcome disadvantages of other electrode materials. Electrochemical sensors based on BDD have been successfully developed for the determination of biologically active organic compounds important from the environmental and/or human health points of view.

UNESCO Laboratory of Environmental Electrochemistry at the Department of Analytical Chemistry led by prof. Jiří Barek has been involved in BDD-related electrochemical research practically since its foundation, as it readily established cooperation with prof. Greg M. Swain, Michigan State University, East Lansing, USA, one of the inventors of this electrode material. The Author of this Thesis has spent 6 months in 2004 in prof. Swain's group during her Ph.D. studies to gain experience in studies and applications of BDD, including preparation of this material and construction of miniaturized electroanalytical devices. The continuing interest of the Author and her activities in this field can be documented by a number of students having acquired training in BDD electrochemical research under her supervision, as well as project proposals and publications, representing the basis of this Thesis.

In the past fifteen years the Author has been delighted to participate on the contemporary BDD research from her initial experience in prof. Swain's group through expansion of the cooperation towards other research groups involved in electrochemical, material and analytical science settled abroad (prof. G. M. Swain, Michigan State University, East Lansing, USA; prof. F.-M. Matysik, Universität Regensburg, Germany; prof. Christopher M. A. Brett, University of Coimbra, Portugal) and in Czech Republic, including institutes of the Czech Academy of Science (J. Heyrovsky Institute of Physical Chemistry and

Institute of Physics (both in Prague), Institute of Biophysics (Brno)), and University Pardubice, Faculty of Chemical Technology.

The Thesis is based on 24 publications in peer-reviewed, impacted journals, 3 chapters in monographs and 4 proceeding papers, which are attached as Supplements 1-31 in Chapter 5 and abbreviated as **S1-31** when referred to in the following text. Experimental results achieved by the Author, results from 11 bachelor and 7 master theses supervised by the Authors in the period from 2007 to 2018, as well as results from 6 Ph.D. students (being in progress) have been included. The references related to these theses are highlighted in bold script. Also some of the research performed by secondary school students within the framework of their *Secondary School Special Activity* (SOČ) and by master and Ph.D. students within international student exchange programs (*e.g.*, ERASMUS+) contributed marginally to the results presented in this Thesis.

Part I of the Thesis represents a general introduction focusing on historical aspects, preparation, characterization, properties, and applications of BDD in electrochemistry.

Part II summarizes and comments results of studies led by the Author in the context of the related contemporary and past research. It is divided into two subchapters. The first one presents electroanalytical methods developed for the determination of both oxidizable and reducible organic compounds in various matrices. The second subchapter is devoted to important factors influencing the BDD electrode response towards selected organic analytes, including electrode fouling, pretreatment and activation modes, boron-doping level, adsorptive features and their utilization in adsorptive stripping methods.

The Author believes that the Thesis will represent a valuable contribution from her to the continuously growing efforts to develop reliable methods for electroanalysis of environmental, pharmaceutical and physiological matrices in the scope of long term research conducted at the UNESCO Laboratory of Environmental Electrochemistry.

## PART I

### 1. INTRODUCTION

#### 1.1. Boron Doped Diamond – Historical Overview

Diamond-based materials display owing to complete  $sp^3$  hybridization and tetrahedral bonding many unique properties including extreme hardness and thermal conductivity, chemical inertness, and low friction coefficient. Pure diamond is electrical insulator, which makes it in general unsuitable for being used as an electrode material. Nevertheless, the resistivity of diamond, with a bandgap of 5.47 eV ( $T = 300$  K) can be overcome by introduction of a dopant, most frequently boron. This enhances conductivity and electron transfer reactivity by formation of “midgap” states  $\sim 0.37$  eV above the valence band. Boron doped diamond produced by means of synthesis under high pressure or ion implantation is known since the 1970's [1]. The development of diamond deposition techniques from the vapour phase at reduced pressure in the 1980's [2, 3] has enabled introduction of semiconductive boron-doped materials deposited on various supports [2, 4]. These isolated studies were followed in 1992 by Fujishima *et al.* [5], finally drawing attention to boron-doped diamond (BDD) as an electrode material. The first studies conducted with BDD electrodes a year later outlined their suitability for electrosynthesis [6], electroanalysis [7], and electrochemical waste treatment [8]. Simultaneously, continuous fundamental research on diamond materials recognized them as potential wide band gap semiconductors with favorable electronic, chemical and mechanical properties. Intensive research especially in last ten years was focused on the use of diamond-based electronic devices in biosensing, optoelectronics, acoustics, quantum computing, and other advanced technologies. Nevertheless, applications of BDD electrodes for electrochemical sensing of both, inorganic and organic analytes hold unceasing interest acknowledged by increasing number of publications each year (Fig. 1). Relevant search in Web of Knowledge revealed that since 1987, from 5860 publications (including conference proceedings and reviews) related to boron doped diamond, 839 have been placed in the category “Analytical Chemistry”.

In this field, fast progress in construction of BDD-based sensors, introduction of various approaches to surface treatment and/or surface modification, and a variety of electroanalytical methods designed for determination of specific analytes are highlighted by striking boundary stones connected with crucial roles of several research groups and recognized names, including prof. G. M. Swain (Michigan State University, East Lansing,

USA), prof. A. Fujishima (formerly the University of Tokyo, Japan), and prof. R. G. Compton (University of Oxford, UK) [9-14]. Among providers of BDD-based materials, Swiss Center of Electronic and Microtechnology (CSEM; Neuchâtel, Switzerland) [15, 16] contributed significantly in early stages of the research. In 1993, the applicability of BDD as interesting electrode material for electroanalysis has been discovered in Swains' group by observation of quasireversible response of ferro-/ferricyanide couple in the BDD electrode in aqueous media. The same group recognized the potential of BDD-based detectors for liquid flow techniques using BDD electrode housed in home-made thin layer amperometric detection cell. They coupled it to flow injection analysis to detect ethylamine and ethylenediamine (1997) [17] or to ion chromatography for azide and nitrite determination (1999) [18]. In 1998, first tested BDD microelectrodes exhibited steady-state CVs in non-aqueous media (ref. [19], Cooper and coworkers). Five years later the BDD microelectrodes were used in miniaturized detection cells for capillary zone electrophoresis (CZE) ((ref. [20], Swain and [21], Fujishima) or chip-based devices (ref. [22], Fujishima and J. Wang in cooperation). The trend of further miniaturization resulted in construction BDD microelectrode arrays (BDD MEA) in 2000 (Madore *et al.* [23]), and in 2007 in fabrication of BDD ultra $\mu$ E with disk radius of 2-7  $\mu$ m (Holt, ref. [24]). These types of miniaturized devices have been used in physiological environment for the detection of biogenic compounds under *in vitro* or *in vivo* conditions (ref. [25-27], Swain (S2)).

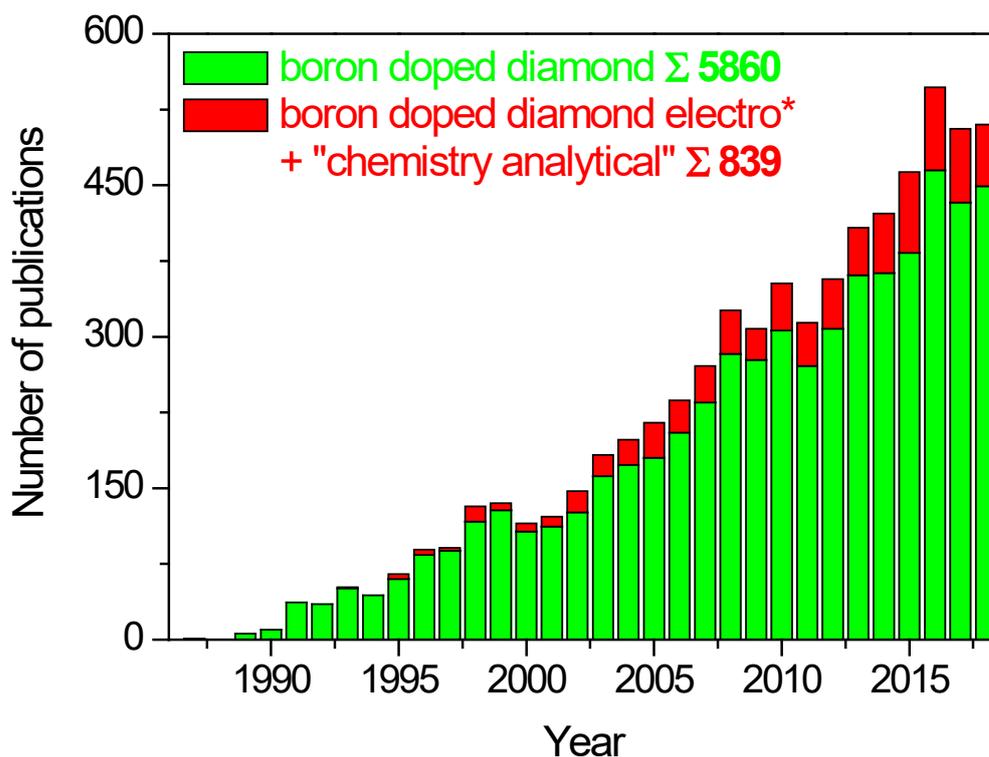
To extend sensitivity and selectivity of the BDD electrodes, intensive research on surface pretreatments and other modifications of the diamond surfaces can be traced especially in last ten years. Easy electrochemical oxidation of the BDD surface and surprising inertness of thus obtained oxygen-terminated BDD (O-BDD) surface towards adsorption of analytes was shown in 2000 by Fujishima and coworkers [28] on the example of serotonin electrooxidation. Together with earlier reports of the same group on electrochemical properties of the O-terminated surfaces [29], these observations drew attention to their use especially for electroanalysis of charged organic species (thanks to the stability of this type of surface termination it is preferred to date). On the other hand, cathodic pretreatment leading to hydrogen-termination of the BDD surface (H-BDD) has been proposed in 2006 by Avaca *et al.* [30], resulting in improvement of analytical performance of the BDD electrodes for some other organic analytes. Positive effect of BDD surface polishing at alumina was for the first time reported in 2002 for surface-sensitive redox marker and redox proteins [31, 32], and by Y. Yardim after 2010 for smaller organic molecules [33] or their associates with surfactants [34, 35]. Another approach, theoretically leading to improvement of analytical performance of

BDD materials, has emerged in last few years. It is based on increase of the specific surface area by production of nanostructured or porous BDD [36, 37].

Further functionalization (and subsequent biofunctionalization) of BDD surfaces was achieved by introduction of carboxylic (ref. [38], Swain 1999) or amino groups (ref. [39], Miller 1996). Since 1998, such functionalized surfaces have been modified by DNA [40-42], enzymes [43] or other proteins [44], which opened the way for applications of diamond-based (bio)sensors in biotechnologies.

This retrospective survey clearly demonstrates the fact that advantageous properties of BDD were shortly after its introduction recognized by the scientific community and inspired it to stunning development in both fundamental and applied research. Since 2001, this progress has been supported by wide commercial availability of BDD electrodes and BDD-based sensors. Nowadays, there are several commercial suppliers of BDD materials, including Bio-Logic SES (formerly Windsor Scientific (UK)), Element Six (formerly De Beers Industrial Diamond, UK), NeoCoat (formerly Adamant Technologies, Switzerland; spin-off company of CSEM), Condias (Germany, spin-off company of Fraunhofer Institute for Thin Films and Surface Technology), and sp3 Diamond Technologies (USA)). Many other research laboratories produce the BDD materials for their own purposes thanks to commercial availability of reactors for chemical vapor deposition (CVD) of BDD thin films for reasonable prices.

Outputs of the twenty five-year history of BDD-related research can be traced in a number of reviews devoted to the particular aspects of research. In the field of electrochemistry, reviews on general electrochemical properties [45] and surface modifications [46, 47], electrosynthesis [48] and anodic waste water treatment [49-55], electroanalytical applications including applications in biosensors [56-70] (**S4, S6, S7, S12, S25, S26, S27**) appeared in last fifteen years together with compact reviews [71-75] and books devoted to diamond electrochemistry, physics and applications [76-79].



**Figure 1.** Number of publications in database Web of Knowledge issued from 1987 to 2018 related to boron-doped diamond (“boron doped diamond”: 5 185 articles including 182 reviews, and 832 proceedings papers) and to application of boron doped diamond in electroanalysis (“boron doped diamond electro\*” + category: chemistry analytical: 741 articles including 41 reviews, and 52 proceedings papers).

## 1.2. Preparation, Characterization, and Properties of Boron Doped Diamond Thin Films

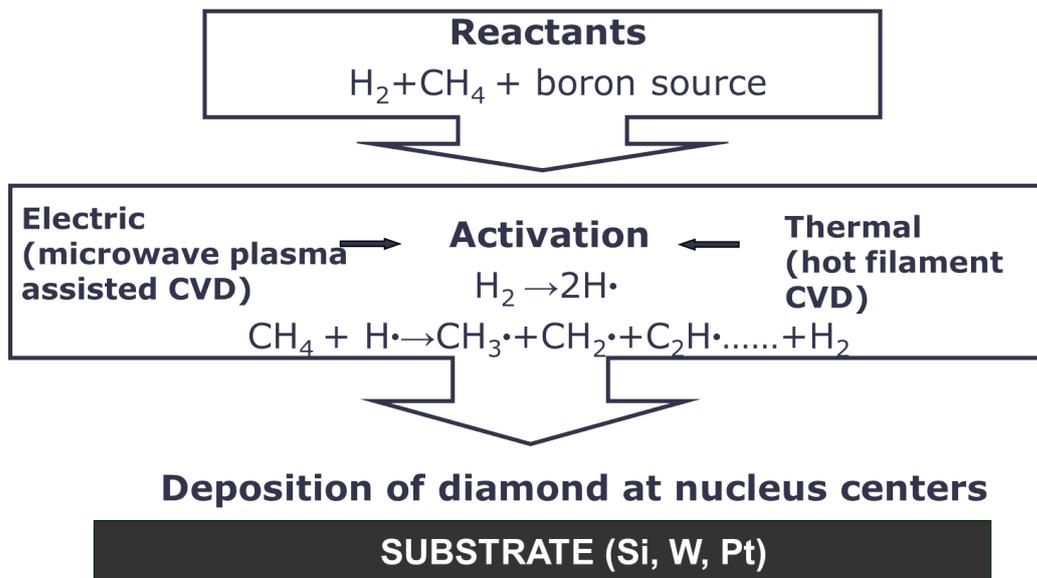
In general, diamond thin films are prepared by growing from dilute mixtures of a hydrocarbon gas in hydrogen on a suitable substrate using one of several energy-assisted CVD methods. Their advantages include relatively simple operation procedures and cheap equipment. In these processes, a carbon containing gas, most frequently methane or acetone is energetically activated to decompose the molecules into methyl-radicals and atomic hydrogen, resulting in deposition of diamond film on a suitable substrate.

The growth methods mainly differ in the manner in which the gas activation is accomplished. The most popular techniques for deposition of BDD films are hot-filament (HF CVD) and microwave plasma-assisted (MP CVD) CVD. Fig. 2 and Table I present a scheme of the CVD process and typical deposition conditions, details can be found *e.g.* in the review [80]. The most critical component in the gas mixture is hydrogen. Its atoms are capable of

cleavage of neutral hydrocarbons and creation of reactive radicals such as  $\text{CH}_3\cdot$  and  $\text{CH}_2\cdot$ . Further, they terminate the dangling carbon bonds on the surface of the diamond layer. Another purpose of hydrogen is to prevent the growth of graphite. This is possible due to the fact that atomic hydrogen etches  $\text{sp}^2$  bonded graphite much faster than diamond like  $\text{sp}^3$  carbon [80]. Therefore, the C/H ratio in the gas mixture is of great importance for the structure and quality of the deposited film. Boron doping is usually accomplished also from the gas phase by mixing boron-containing compounds such as  $\text{B}_2\text{H}_6$ , trimethylborane or  $\text{B}_2\text{O}_3$  with the source gases. The boron content is usually given by the B/C ratio in the gas phase. Typical values range from 100 ppm to 15 000 ppm resulting in boron concentration in the final film  $1\cdot 10^{18} \text{ cm}^{-3} - 1\cdot 10^{21} \text{ cm}^{-3}$  (boron concentration  $1\cdot 10^{20} \text{ cm}^{-3}$  corresponds to *ca* 1 boron atom per 1000 carbon atoms). Such films exhibit resistivities  $< 0.1 \text{ } \Omega \text{ cm}$  [81, 82]. Metallic type conductivity was reported for boundary boron content of about  $1 - 4.5\cdot 10^{20} \text{ cm}^{-3}$ . Films with lower boron concentration exhibit semiconductive properties [83-85].

The BDD films grow by nucleation at rates in the  $0.1\text{-}2 \text{ } \mu\text{m h}^{-1}$  range. To achieve continuously coating of the substrate with diamond, the nominal film thickness must be at least  $1 \text{ } \mu\text{m}$ .

Choice of the substrate is of great importance, because it has to respect the application purpose of the final BDD-based devices. Their use in electrochemistry requires sufficient conductivity of the substrate, and thus the most frequently used materials are noble or transition metals with a high thermal resistance (W, Pt, Nb, Ta). Due to the mechanical stability on one side but easy shapeability on the other, these metals can be used as supports for large-scale as well as miniaturized devices. Nevertheless, p-doped silica is the most frequently used support for BDD films prepared for electroanalytical purposes. Its fragility is compensated by other advantages including easy seeding of growth places, and low cost.



**Figure 2.** Scheme of chemical vapor deposition procedure for preparation of BDD films.

**Table I.** Parameters of thermally activated CVD processes for diamond synthesis.

Deposition parameter	
Content of CH <sub>4</sub> in H <sub>2</sub>	0.3 – 2.5 %
Total gas flow	0.1 – 0.5 SLPM
Pressure	1333 – 20 000 Pa
Microwave power (for MP CVD)	1000 – 1300 W
Filament temperature (for HF CVD)	2400 – 2800 °C
Substrate temperature	700 – 925 °C

The widespread use of BDD thin films is given by their advantageous properties [76, 81, 86, 87]:

- i) wide potential window in aqueous solutions (*ca* ~3 – 3.5 V)
- ii) low and stable background current
- iii) extreme electrochemical stability
- iv) corrosion stability in aggressive media
- v) structural stability at extreme cathodic and anodic potentials
- vi) high thermal conductivity
- vii) resistance against fouling

The main factors influencing properties of BDD thin films are closely related to boron-doping level, content of non-diamond carbon (sp<sup>2</sup>) impurities, structural defects in the diamond film, size of diamond crystallites and crystallographic orientation and surface

termination (H, O). These factors depend on the working procedure and conditions during the CVD procedure. Relation of these factors to the BDD electrochemical properties is discussed in detail in Chapter 1.3.

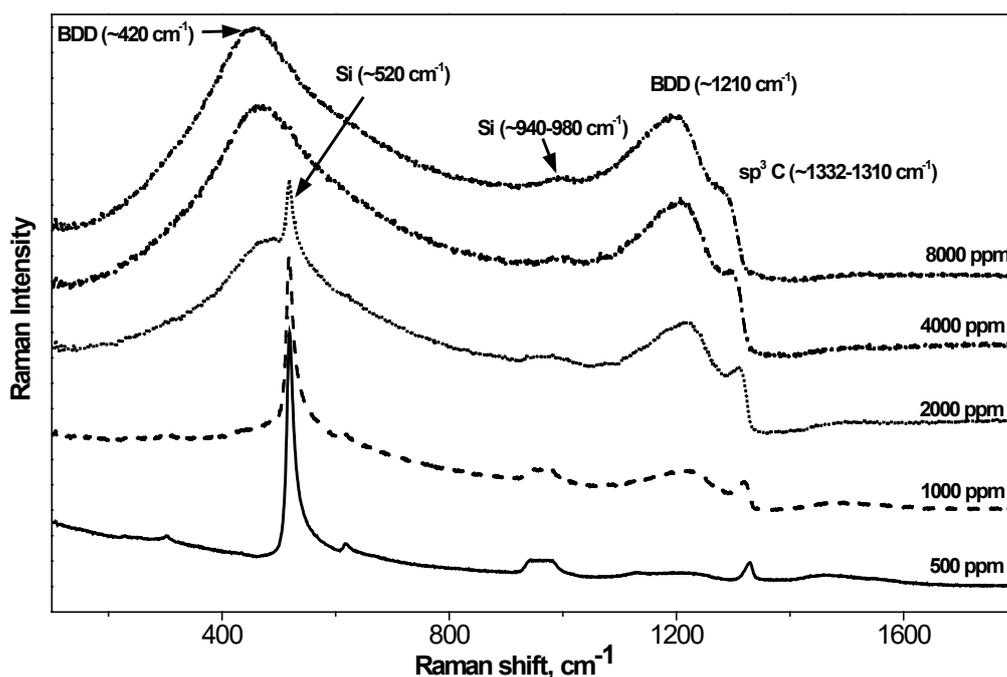
Several analytical techniques are routinely used to characterize the morphological, optical, chemical and electronic properties of diamond thin films. Raman spectroscopy is capable, at least to certain extent, of linking of the spectral features of BDD with its electrical conductivity and thus this technique represents a useful tool for electrochemists. Its fundamental merit is the sensitivity to the presence of non-diamond carbon impurities. The latter probably consist of mixtures of  $sp^3$ - and  $sp^2$ -hybridized bonding, (resembling diamond-like and amorphous carbon) and cause weak scattering intensity in the region of about  $1500\text{-}1580\text{ cm}^{-1}$ . Typical Raman spectra for high-quality diamond and BDD films miss these signals, but feature signals at  $\sim 1330\text{ cm}^{-1}$  related to the presence of  $sp^3$  carbon. The shape of the Raman spectra is further influenced by the boron content in the BDD film. Addition of boron influences the crystalline quality and thus BDD conductivity. Characteristic differences in the Raman spectra can be seen in Fig. 3, where spectra of films used for experiments in publications of the Author ([88, 89], **S21**, **S28**) are shown. Films with lower boron content exhibit semiconductive properties and their Raman spectra are characterized by one intense band at  $1332\text{ cm}^{-1}$  related to the presence of the  $sp^3$  hybridized carbon. Further, a sharp peak at  $519\text{ cm}^{-1}$  and scattering in the region  $\sim 940\text{-}980\text{ cm}^{-1}$  corresponding to Si phonon and Si 2<sup>nd</sup> order phonon might be present due to the transparency of the films with lower boron-doping level. Transition from insulating to metallically conducting state is reflected in significant changes of the Raman spectra. At the transition, the absorption coefficient of diamond at the energy of the incident light increases sharply and as a consequence, the signals associated with the presence of silica at  $\sim 940\text{-}980\text{ cm}^{-1}$  disappear from the Raman spectrum [85]. This feature is well observable at Raman spectra in Fig. 3, corresponding to films with boron doping levels 500 ppm, 1000 ppm, 2000 ppm, 4000 ppm, 8000 ppm (values related to B/C ratio in the gas phase) The boundary boron content distinguishing between semiconducting and metallically conducting BDD has been found at  $\sim 2500\text{ ppm}$ , which corresponds to the boron concentration in the film around  $3 \cdot 10^{20}\text{ cm}^{-3}$  ([88], **S21**).

Further, as the boron concentration increases, bands corresponding to the boron doping-associated vibrations start to appear around  $500$  and  $1225\text{ cm}^{-1}$  [90] and slightly shift to lower wavenumbers. At the same time the characteristic line for  $sp^3$  carbon at  $1332\text{ cm}^{-1}$  exhibits an asymmetric Fano-like line shape [90], downshifts and attenuates. Raman spectra

of BDD are also influenced by the excitation wavelength. While the 632.8 nm excitation line of He-Ne laser provides a higher sensitivity to the parasitic  $sp^2$  phase, the 514.5 nm excitation line is more sensitive to the “diamond doping” [76, 85]. Thus, combination of more excitation wavelengths is desirable for a deeper insight into the BDD composition.

Scanning electron microscopy (SEM), scanning tunneling microscopy (STM), and atomic force microscopy (AFM) are used to evaluate the film morphology and probe local electronic properties. Powder X-ray diffraction analysis is used to investigate the preferential crystallite orientation in the films. Depending on the crystallite size, polycrystalline film can be classified as microcrystalline (grain size typically 0.5  $\mu\text{m}$  – 3  $\mu\text{m}$ ), nanocrystalline (10 – 500 nm), or ultrananocrystalline (<10 nm).

Elemental composition of the surface is determined by Auger electron and X-ray photoelectron spectroscopies (XPS). Boron nuclear reaction analysis (neutron depth profiling, NDP) [91] or secondary ion mass spectrometry [85]), have been used to quantify the boron dopant concentration and probe the spatial distribution of the dopant species over the surface and within the bulk [81]. It should be always borne in mind that depending on the technique of measurement the estimated boron content represents a mean value from different growth sectors in each crystallite and for all crystallites of the films or a total mean concentration including the grains (*i.e.*, imperfectly faceted crystallites) and grain boundaries, where boron segregation may occur [85].



**Figure 3.** Raman spectra for boron doped nanocrystalline films deposited by MP CVD using  $500 \text{ ppm} \leq \text{B/C} \leq 8000 \text{ ppm}$  at 532 nm excitation wavelength. BDD films prepared at the Institute of Physics of Czech Academy of Sciences (CAS), Department of Functional Materials. Adapted from ([89], S28).

### 1.3. Electrochemistry of Boron Doped Diamond Films

Electrochemical behavior of boron doped polycrystalline diamond film electrodes strongly depends on their surface properties such as grain size, crystallographic orientation, surface termination, and  $\text{sp}^2$  content at the crystallite and grain boundaries. These are influenced by the conductive support, boron doping level, type of the CVD procedure and conditions adjusted during it.

In general, conductivity is a complex physical quantity and in the case of BDD films there are many parameters that influence charge transport [92]: (i) size of the diamond grains – conductance of microcrystalline BDD films is higher than those observed for more fine-grained films (for the same B content); (ii) grain boundaries – they contain a small volume fraction of non-diamond carbon impurities (the relative content of which depends on the B doping level); (iii) specific structures related to boron doping - defects and changed morphology of the layer (the level of added B has a strong influence on the morphology of the diamond layers grown); (iv) the surface layer of each diamond grain – may contain a higher level of B, causing specific conduction.

As a whole, B doping produces materials with many different conducting regions and

entities, at which the charge transport may follow different pathways and mechanisms. In electrochemistry, these different entities may be involved to different extents in electron transfer processes characteristic for different classes of redox probes or analytes (see below). In the following subchapters the main factors influencing electrochemical properties of BDD thin films *i.e.*, boron doping level and surface termination, are addressed.

### 1.3.1. Boron Doping Level

Boron content in BDD is considered to be one of the main factors influencing substantially the film morphology, conductivity, and electrochemical properties [85, 91, 93-98]. Depending on the boron-doping level, the electrical conductivity of the BDD films ranges from insulating to metallic. The boron dopant atoms act as electron acceptors and form a band located  $\sim 0.37$  eV above the valence band edge. At low boron concentrations ( $< 10^{17} \text{ cm}^{-3}$ ) conduction occurs through holes in the valence band contributed by ionized substitutional B. At higher doping levels, conduction occurs by nearest-neighbor and variable range hopping of holes between ionized B sites [99, 100]. At very high doping levels, an impurity band is formed, giving rise to metallic conductivity with the activation energy of electrical conduction falling from  $\sim 0.37$  eV to  $\sim 0.1$  eV [2, 90]. The threshold for the semiconductive/metallic transition was theoretically predicted to be  $2 \cdot 10^{20} \text{ cm}^{-3}$  in 1970 [84]. Practically, the critical boron content of about  $1 - 3 \cdot 10^{20} \text{ cm}^{-3}$  [83] or  $4.5 \cdot 10^{20} \text{ cm}^{-3}$  [85] were reported and it seems that these concentrations are sufficient to achieve fast electron transfer typical for metallic-type conductivity. Films with more than  $3 \cdot 10^{20}$  boron atoms per  $\text{cm}^3$  are sometimes denoted as “heavily doped BDD films” [97].

Several studies were published investigating the location, configuration, and bonding structure of boron in BDD layers, as the B atoms might be located within the core or at the surface of diamond crystallites as well as within grain boundaries of thin films which always contain a small-volume fraction of conductive non-diamond impurities. As the grain size in the film became smaller, abundance of the boundaries increases and their contribution to the overall properties gain importance. In addition, the amount of conductive graphitic carbon at the grain boundaries increases with boron doping level which supports further the charge transport mechanisms. Further, it should be kept in mind that the crystallographic orientation itself influences the boron uptake with  $\{111\} > \{110\} > \{100\}$  (ref. [101, 102]), thus poly- (or nano-)crystalline BDD material has a boron content which varies heterogeneously. Taken together, the net conductivity is a combination of effects related to boron-doping level, which results in many different conducting regions, and possibly different conducting pathways and

mechanisms.

Recently, several papers were published concerning the influence of boron content on the physical and electrochemical characteristics of BDD films [93-96, 103], resistance towards electrochemical corrosion [95], surface resistance towards fouling [104], effectivity of electrocatalytic anodic oxidation of organic compounds (utilized in degradation of pollutants [105-108]), and favorable analytical parameters of determination of selected inorganic ions [103, 109]. Despite the fact that increased interest in these topics can be traced in last seven years and information on boron doping level is usually given in electroanalytical publications (at least as B/C ratio during deposition procedure), only few studies address its influence on electroanalytical characteristics such as width of the potential window [110-112], or on voltammetric responses of organic analytes. Examples of such studies include floroquinolone enrofloxacin [113], dopamine [104], uric acid [114], nitrofurantoin [115] or in our laboratory studied benzophenone-3 ([116], **S17**) 5-nitroquinoline ([117], **S19**), 4-chloro-3-methylphenol ([118], **S20**), and 2-aminobiphenyl ([88, 89], **S28**, **S21**). The latter studies of the Author and coworkers are closer commented in Chapter 2.2.

### 1.3.2. Surface Termination and Its Characterization by Redox Probes

BDD surfaces resulting from the standard CVD procedures are hydrogen terminated (H-terminated) and most of BDD-related pioneering studies published in 1990's were performed with these "as-grown" surfaces (*e.g.*, [7, 119, 120]). Nevertheless, the H-termination in above mentioned studies is questionable because later [121, 122] it was established that conversion of the "as grown" to oxygen terminated (O-terminated) surface proceeds very easily upon applying potentials more positive than potential of anodic decomposition of water due to the massive oxidation of the electrode surface by hydroxyl radicals formed under such conditions (eq. 1):



Nowadays, BDD pretreatment and (re)activation in electroanalysis between individual potential scans is one of the main factors influencing successful development of electroanalytical methodology. These procedures, usually adjusted empirically, are applied to condition the electrode surface and to prevent its passivation, to obtain best developed voltammetric signals, and to ensure desirable repeatability and reproducibility of response of particular analytes. Most frequently applied strategies involve (i) anodic pretreatment or (ii) cathodic pretreatment of the bare BDD surface. In addition, minority of studies employ (iii)

manual polishing of the BDD surface. The procedure of surface pretreatment influences strongly hydrophobicity/hydrophilicity of the surface and thus its wettability. Further it influences the polarity of surface bonds, which is reflected in occurrence of electrostatic interactions. The latter can raise or lower the energy levels of the valence ( $E_{VB}$ ) and conduction bands ( $E_{CB}$ ) of the BDD which leads to changes in its conductivity and thus influences the electron transfer rate (reflected in positioning and intensity of redox signal of electroactive species).

*Ad (i):* Anodic pretreatment relies on incorporation of oxygen atoms on the BDD surface mostly *via* carbon reaction with HO $\cdot$  radicals. The latter are produced *via* transfer of one electron from water (eq. 1) as the first step of oxygen evolution reaction (OER) at high anodic potentials in the region of water instability (in aqueous media of pH < 9.0 (ref. [123])). Quasi-free HO $\cdot$  radicals are confined to the BDD surface. Subsequent reactions include HO $\cdot$  reactions with each other, reactions with other intermediates *e.g.*, H<sub>2</sub>O<sub>2</sub> molecules or O<sub>2</sub>H $\cdot$  radicals and further electron transfers leading to production of O<sub>2</sub> (described in detail in [124, 125]). As a consequence of interaction of the mentioned radical species with BDD surface, their stabilization occurs *via* formation of various oxygenous functional groups, with the prevalence of ether bonds, ketonic, alcoholic and carboxylic groups [122, 126, 127]. These anodized, O-terminated BDD surfaces are most frequently used in electroanalysis of organic compounds. They can easily be obtained using inherently simple electrochemical procedures involving application of highly positive potentials ( $\sim < \pm 2.0$  V; in the region of water decomposition reaction) or current densities applied for seconds to minutes. It was reported that even tens of seconds may lead to almost complete oxidation of the surface when sufficiently high potentials are applied ( $\sim < +3.0$  V *vs.* Ag|AgCl reference electrode in 1 mol L<sup>-1</sup> sulfuric acid/0.5 mol L<sup>-1</sup> nitric acid solution) [128]. Once the O-terminated surface is obtained, its re-hydrogenation is achievable only by hydrogen-flame annealing or hydrogen-plasma treatment, which requires adequate equipment, when omitting the electrochemical way described and commented below in (ii).

The O-termination has a major influence on physico-chemical properties of the BDD surface. The polarity of the C $\delta^+$ -O $\delta^-$  bonds causes lowering of the energy levels  $E_{VB}$  and  $E_{CB}$  and introduces a positive electron affinity. Nevertheless, oxygen termination does not result in a measurable surface conductivity, in contrast to H-termination [127].

*Ad (ii):* The importance of H-termination was raised by Suffredini *et al.* in 2004, who presented faster electron transfer for [Fe(CN)<sub>6</sub>]<sup>4-/3-</sup> and signal increase at a H-terminated BDD electrode, and improved repeatability for measurements of selected chlorophenols

[129]. Properties and use of cathodically pretreated BDD surfaces were reviewed by Andrade *et al.* [130].

The H-termination can be achieved using highly negative potentials ( $\sim < -2.0$  V; in the region of hydrogen evolution reaction) or negative current densities up to  $-2.5$  A cm<sup>-2</sup>, or potentials generating such high densities, even as negative as  $-35$  V [131, 132]. Such current densities represent a transfer of several thousand electrons per second and carbon atom on the surface. Some reports speculate that surfaces undergoing such severe pretreatment are re-hydrogenated similarly as when exposed to hydrogen plasma or hydrogen dose during the CVD procedure [132]. Nevertheless, in general the resemblance of the cathodically pretreated to the “as grown” H-terminated surfaces is still questionable (see above).

Naturally, H-terminated surfaces are more hydrophobic than the O-terminated ones. Further, a noticeable surface conductivity was reported for H-terminated surface. The polarity of the C<sup>δ-</sup>-H<sup>δ+</sup> results in a rising of both  $E_{VB}$  and  $E_{CB}$ , with the latter sitting above the vacuum level. As a results, electron transfer between the  $E_{VB}$  and H<sub>3</sub>O(aq)<sup>+</sup> becomes possible and a positively charged accumulation layer (sub-surface) is formed, resulting in measurable surface conductivity [74]. Analogous effects were reported even for undoped diamond, insulating when O-terminated, but exhibiting substantial surface conductivity when H-terminated with surface conductivity in the order of  $10^{-5}$  Ω<sup>-1</sup> [ref. 133, 134].

A number of studies has been devoted to (in)stability of the H-termination. Instability of the surface conductivity during exposure to air for a long time was reported for both boron doped [30] and undoped diamond [135]. For cathodically pretreated BDD exposed to air for 30 days, increase of the content of oxygen on the surface was detected by XPS measurements [30]. The loss of surface hydrogen is caused by oxidation of the surface by atmospheric oxygen or by other species (HCO<sub>3</sub><sup>-</sup>, OH<sup>-</sup>) contained in a thin layer of water naturally formed on the surface of solids exposed to air [133, 134]. Further, it seems that increased boron content has stabilizing effect on the H-termination [30, 93].

The H-termination may facilitate interactions and adsorption of electrochemical species on the electrode surface and thus clearly leads to an apparently higher electrochemical activity for a number of organic compounds [74, 117, 129, 136, 137]. A high number of studies demonstrating the favorableness of cathodic pretreatment was published by the Brazilian group headed by O. Fatibello-Filho; some of the recent summarized in the Table II. In general, it is difficult to predict for which molecular structure motives the cathodic pretreatment will be advantageous. With a certain probability, positive effects can be expected for reducible compounds, typically azo dyes [138, 139], which is also supported by our

experience with tartrazine and allura red ([140], **S30**, see Chapter 2.1.2.). Some reports exist on advantageous properties of cathodically pretreated BDD films for the detection of phenolic compounds *e.g.*, 4-nitrophenol [141, 142], chlorophenols [129, 143, 144], bisphenol A [145], or total phenolic antioxidants [137] and total phenols in food [146]. These reports usually mention oxidation or reduction potentials being located closer to 0 V and faster electron transfer on the cathodically pretreated BDD electrodes, compared to anodically pretreated ones. Importantly, due to the above discussed instability of the H-termination in air, the cathodic pretreatment should be applied just before the electrochemical experiments to ensure reliable and reproducible results, especially when the electrode has not been used for a long period of time.

*Ad (iii):* Mechanical polishing is another way to obtain a clean and defined BDD surface. This possibility has stayed aloof from the interest of analytical chemists, as it partially devalues one of the main advantages of BDD electrodes – the possibility to get rid of manual manipulation with the electrode and to use solely electrochemical activation *in-situ*. Nevertheless, at least for certain analytes or redox systems the mechanical cleaning appears to be well suited. Observation of reversible electron transfer for  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox couple in heme units of cytochrome *c* at alumina-polished BDD surface was reported already in 2002 [31]. Later published studies also revealed potential shift closer to 0 V and current increase of voltammetric signal of different oxidisable compounds on polished BDD surfaces, *e.g.* for chlorogenic acid [147] or *m*-cresol studied by Author (closer in Chapter 2.2.1.). Nevertheless, only recently attention has been paid to characterization of such surfaces and their utilization in electroanalysis, mainly for the determination of associates of organic molecules with surfactants [34, 35] including our study on benzophenone-3 ([116], **S17**) and 4-chloro-3-methylphenol ([118], **S20**, closer introduced in Chapter 2.2.3.).

It was documented that properties of polished BDD surface differ significantly from those of the electrochemical pretreated ones. The polished surfaces exhibit faster electrode response for selected redox markers ([116, 127], **S17**). Results from XPS show a dramatic difference between the alumina-polished surface and anodically polarized surface, although both have been reported to be oxygen terminated. The main  $\text{sp}^3$  C–C peak attributed to C present in the diamond bulk shifts slightly to a lower binding energy at the polished surface, indicating charging effects or a change in the valence band position. Presence of C–O–C, C–OH, and C=O groups, but absence of COOH groups was proved for the alumina-polished surface. Further, concentrations of these groups are substantially lower compared to anodically polarized surface [127], and are not sufficient to hinder heterogeneous electron

transfer (HET) of some inner-sphere redox mediators as  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  (while such hindrance has been reported for the anodized BDD surface).

This redox probe and several others, including dopamine,  $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ ,  $[\text{IrCl}_6]^{2-/3-}$ , are used to evaluate the electrode kinetics, thus giving an insight into the properties of BDD surface. The HET of the latter two probes proceeds by an outer-sphere electron-transfer pathway with the electrode kinetics being relatively insensitive to the physicochemical properties of electrode surfaces [148], including BDD ones [74]. Formal potential of  $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$  couple ( $E^0 = -0.16$  V vs. saturated calomel electrode (SCE)) lies in the band gap of the BDD, and thus it is capable of showing differences in electrochemical characteristics of differently doped electrodes. Apparent heterogeneous electron-transfer rate constants,  $k_{\text{app}}^0$ , between 0.01 and 0.2  $\text{cm s}^{-1}$  are commonly observed for conducting polycrystalline films (both microcrystalline or nanocrystalline) without extensive pretreatment for this outer-sphere redox marker ([86, 88, 149], **S21**).

Cyclic voltammetric response of the  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  redox couple has been largely studied at BDD electrodes [32, 74, 86, 122, 129] as the charge transfer proceeds through a more inner-sphere electron transfer pathway. In contrast to the outer-sphere redox probe  $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ , for  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  the electrode kinetics is highly sensitive to the diamond surface termination. It should be noted that the latter redox couple is traditionally treated as outer-sphere, but it behaves anomalously at carbon-based electrodes. Thus, the range of observed  $k_{\text{app}}^0$  values spans several orders of magnitude, depending on the BDD surface characteristics [29, 131, 150]. The  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  redox couple is thus an excellent system for probing the electronic properties, surface cleanliness, and surface chemistry of BDD electrodes.

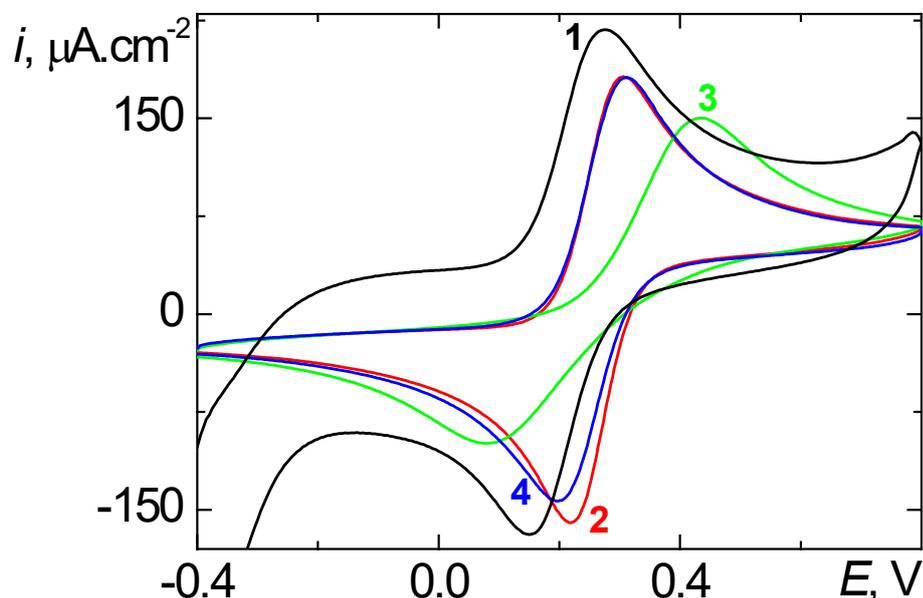
An example of cyclic voltammograms of the  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  redox couple recorded at a commercially available BDD electrode [151] subjected to different pretreatment modes is shown in Fig. 4, together with response measured on a glassy carbon electrode (GCE). The latter electrode exhibits substantially higher background current, but similar current densities for signal of the redox probe on the BDD electrode. Differences between the potentials of anodic and cathodic peaks ( $\Delta E_p$ ) of 120 mV were obtained for GCE, and  $\Delta E_p = 85$  mV for polished and  $\Delta E_p = 110$  mV for H-terminated BDD surface, witnessing the high quality of the investigated BDD thin films. These values are relatively close to the theoretical value of 59 mV for one-electron reversible process. Anodic pretreatment leading to O-termination (without subsequent polishing) causes remarkable increase of  $\Delta E_p$  to 350 mV. Values

approaching or reaching 59 mV, indicating fast electron transfer, were reported for “as grown” or cathodically pretreated *i.e.*, predominantly H-terminated BDD films already in the early stages of BDD-related research [112, 131, 152]. The origin of such behavior has been considered to be based on specific ion-dipole interactions including [153]: (i) interactions between the redox ion and surface hydrogen atoms on diamond [18], and (ii) electrostatic repulsion between dipoles at O-terminated diamond surfaces and negative charges on the redox ion [32, 154, 155]. Nevertheless, effect of introduction of oxygen-containing groups on the HET of redox markers is still subject of continuous research. Recently, reversible voltammetric behavior was obtained for  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  for relative level of surface oxidation of about 15%, which indicates that BDD surfaces do not need to be completely hydrogenated to ensure a fast electron transfer kinetics [131].

Besides those of H-termination, positive effect of BDD surface polishing on HET has been reported in isolated studies [32]. For  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ ,  $\Delta E_p$  of 65 mV was reported for microcrystalline BDD with  $[\text{B}] > 1.9 \times 10^{20} \text{ cm}^{-3}$  [127]. In our study ([116], **S17**), time dependence of alumina polishing for conversion from the O-terminated surface on  $\Delta E_p$  is presented. The  $\Delta E_p$  value decreases from 397 mV (obtained for freshly anodized surface) to 114 mV within fifteen minutes of polishing. Similarly high  $\Delta E_p$  value for O-terminated surface (340 mV) is obvious also in Fig. 4. Thus, presence of C–O–C, C–OH, C=O and COOH groups is responsible for the decrease in HET for  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  that is known to be sensitive on the presence of surface oxides on carbon surfaces in general. On the other hand, the HET for  $\text{Fe}^{3+/2+}$  (coordinated by water molecules) is favored at O-terminated surface, as the carbonyl groups are known to mediate the HET for this redox couple [72, 127, 153]. Clearly, the surface chemistry affects significantly the electron transfer rates by electrostatic and other interactions between the redox species and the functional groups present on the surface. Thus, only combination of methods characterizing the surface and using different types of redox probes can clarify the factors influencing HET on carbonaceous materials, including BDD.

Prediction of the suitability of a given type of BDD surface pretreatment for particular organic analytes is difficult and frequently both modes of electrochemical pretreatment are tested. From the practical point of view the cathodic pretreatment is less user-friendly, as it has to be applied just before the electrochemical experiments to ensure reliable and reproducible results, especially when the electrode has not been used for a longer period of time due to instability of H-termination in air [30]. Questions involving the influence of

surface termination of the BDD films on electrochemical processes occurring on these electrodes are still controversial, needing to be further investigated.



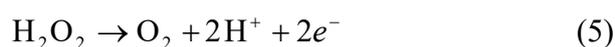
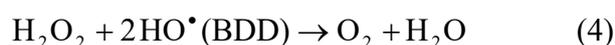
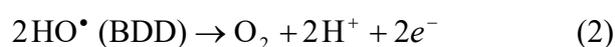
**Figure 4.** Cyclic voltammograms of  $1 \text{ mmol L}^{-1} [\text{Fe}(\text{CN})_6]^{3-/4-}$  in  $0.1 \text{ mol L}^{-1} \text{ KCl}$  (GCE) and in  $1 \text{ mol L}^{-1} \text{ KCl}$  (BDD) measured on (1) GCE, (2) newly obtained, H-terminated BDD electrode, (3) after anodic pretreatment of BDD electrode at  $+2.4 \text{ V}$  for 20 min in  $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ , (4) after polishing at alumina slurry for 8 min. Commercial BDD<sub>ws</sub> electrode [151], scan rate  $\nu = 100 \text{ mV s}^{-1}$ .

### 1.3.3. Potential Window of BDD Electrodes

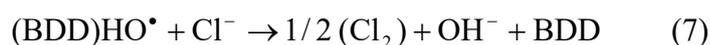
The width of the potential window is being referred as one of main benefits of the BDD electrodes. Naturally, it is influenced by solvent and supporting electrolyte used on one side, and by electrochemical properties of BDD films given by their surface morphology and termination, boron-doping level and conductivity on the other. Isolated studies touching particular factors can be found in the literature rather than those investigating systematically the effect of their changes on cathodic and anodic potential limits ( $E_{\text{lim,C}}$  and  $E_{\text{lim,A}}$ ).

More attention has been paid to investigation of reactions limiting the positive edge of the potential window due to the utilization of BDD electrodes for decomposition of organic compounds by quasi-free  $\text{HO}^\bullet$  radicals formed by reaction (1) [123-125, 156] or their role in anodic oxidation of the BDD surface [126]. Potential of formation of the  $\text{HO}^\bullet$  radicals is  $E^0_{\cdot\text{OH}/\text{H}_2\text{O}} = +2.38 \text{ V vs. SHE}$  [125] and it is known that their adsorption (as well as adsorption of  $\text{H}_2\text{O}$ ) on the electrode surface decreases this value [157, 158]. Thus, adsorption of both species decreases the thermodynamic potential of  $\text{HO}^\bullet$  formation and consequently the

potential of oxygen evolution reaction (OER). The latter is initiated by the adsorption of water and formation of the HO• radicals, which may subsequently undergo a subset of reactions leading to oxygen, hydrogen peroxide or ozone production, and possibly corrosion of the BDD material to form CO<sub>2</sub> in dependence on the supporting electrolyte and pH of the aqueous solution (details can be found for example in ([124, 159])). In the most simplified way the oxygen evolution can be described by eq. 2 with formation of HO• radical (eq. 1) being the rate determining step of the OER. It proceeds through H<sub>2</sub>O<sub>2</sub> formation *via* recombination of two quasi-free HO• radicals (eq. 3) in the close vicinity of the electrode surface. Their further reaction with the formed H<sub>2</sub>O<sub>2</sub> leads to O<sub>2</sub> formation (eq. 4), as well as direct electrochemical oxidation of H<sub>2</sub>O<sub>2</sub> (eq. 5)



The thermodynamic potential for O<sub>2</sub> formation is only +1.23 V *vs.* SHE and thus large overpotential of oxygen evolution is observed at the BDD electrodes exhibiting onset of anodic current typically at +1.9 V to +2.3 V *vs.* SHE in aqueous acidic to neutral media. In basic media the anodic potential limit can be as low as +1.2 V to +1.5 V *vs.* SHE [160]. Naturally, not only pH value but also the supporting electrolyte composition influences the value of  $E_{\text{lim,A}}$ . In non-oxidizable supporting electrolytes (*e.g.*, containing NO<sub>3</sub><sup>-</sup> or ClO<sub>4</sub><sup>-</sup> ions) the HO• radicals, primary products of water decomposition (eq. 1), are the main oxidants. In oxidizable electrolytes the situation can be more complex, as also the electrogenerated products of electrolyte oxidation participate in reactions influencing  $E_{\text{lim,A}}$ . Typical example are Cl<sup>-</sup> ions, at the anode being converted into reactive Cl<sub>2</sub> by direct anodic oxidation (eq. 6) or *via* a reaction with HO• radicals (eq. 7).

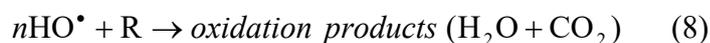


These reactions narrow significantly the potential window at the anodic side [161, 162].

In the systematic study of Author ([88], **S21**) effects of boron doping level on  $E_{\text{lim,A}}$  were investigated for a set of five BDD films (deposited at B/C 500 ppm – 8000 ppm) in aqueous solutions of different pH values and different supporting electrolytes. The difference

of  $E_{lim,A}$  between the electrode with the lowest and the highest boron-doping level varied, depending on the medium composition, from 0.2 V (acetate buffer pH 4.0) to 0.42 V (1 mmol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>). This difference reflects the decline of  $E_{lim,A}$  from values observed for 500 ppm and 1000 ppm semiconductive electrodes to values characteristic for metallic-type 2000 ppm to 8000 ppm films (the latter exhibiting comparable values of  $E_{lim,A}$  for all tested electrolytes). Water adsorption associated with boron-rich sites, facilitating its oxidation to HO• radicals (eq. 1) presumably the rate determining step of OER [124] is obviously limited at the (poor in boron content) semiconductive electrodes which results in positive shift of  $E_{lim,A}$ . It should be mentioned that positive shifts of oxidation potentials at the semiconductive electrodes in comparison with the metallic-type BDD electrodes were observed also for oxidizable phenolic and other organic compounds (closer commented in Chapter 2.2.2.). For metallic-type BDD films the  $E_{lim,A}$  value is practically independent on the boron content and the activity of these conductive electrodes towards OER is controlled by other factors such as pH of the solution and presence of other ions in the solution.

Another important factor influencing the width of the BDD potential window is the presence of organic co-solvents, frequently added to the media to increase solubility of organic analytes. In the presence of organic compounds (R), the electrogenerated HO• radicals initiate their oxidation (eq. 8):



Such oxidation can lead to fragmentation of the organic reactant(s), finally resulting in production of H<sub>2</sub>O and CO<sub>2</sub> *via* various intermediates. These processes are used for anodic decomposition of organic compounds, with prospective application for their removal from polluted water (as mentioned in Chapter 1.4.). Thus, in mixed aqueous-organic media the potential window at the anodic side can be limited by reactions of the organic solvents. Among those frequently used in electroanalysis, acetonitrile is not oxidizable and thus is recommended when the mixed organic-aqueous media are needed. On the other hand, aliphatic alcohols (methanol, ethanol, isopropyl alcohol), often used as co-solvents due to their miscibility with water, are oxidizable by the HO• radicals and thus their presence in the solution decreases the anodic potential limits [125, 160]. As it has been calculated for formic acid, methanol and ethanol, the higher is the rate of reactions between the organics and the HO• radicals, the higher is the shift of the *I-E* curves towards less positive potential (with respect to oxygen evolution). For methanol and formic acid, the calculated shifts of  $E_{lim,A}$  were confirmed experimentally. Negative shift of *ca* 0.22 V (from *ca* +2.62 V to +2.4 V *vs.*

SHE) was observed upon the change of methanol concentration from 0 to 50 mol L<sup>-1</sup> in perchloric acid solution [125]. The width of potential window of the BDD electrode was further compared with the potential window of GCE in aqueous-methanol mixtures of different pH values. While in acidic media with 50:50 methanol:water content the potential window on the anodic side was by almost 0.4 V wider on the BDD electrode compared to GCE (+2.1 V or +1.74 V, respectively, vs. SHE)). This difference decreases upon increasing the methanol content and increasing pH. In neutral, and particularly in alkaline methanolic solutions the differences between the anodic potential limits reached at the BDD and at the GC electrodes were only ~0.1 V or even less [160].

Less attention has been paid to the mechanism of hydrogen evolution reaction (HER) at the cathodic side of the BDD potential window [156, 163]. In acidic media the HER proceeds *via* Volmer-Heyrovsky mechanism (equations 9 and 10), where (BDD) represents active site at the BDD surface:



The reaction proceeds *via* initial adsorption of a water molecule/proton (eq. 9) [112, 156] and further, the weakly adsorbed H atoms presumably catalyze reduction of further protons and thus the HER (eq. 10) [163]. In contradiction, both reaction were found to be the rate determining steps: Volmer reaction (eq. 9) due to a high apparent energy of the [BDD...H<sup>+</sup>] intermediate calculated from Tafel plots [156]. On the other hand, lower calculated activation energy for the reaction described by eq. 9, compared to activation energy of reaction described by eq. 10, indicates the Heyrovsky step as the rate limiting one [163]. Adsorption of H atoms is associated with near-subsurface substitutional boron defects and thus can be directly related to the boron-doping level [112]. This was confirmed in our study ([88], S21), where a well pronounced dependence of cathodic potential limit for HER on the boron content was proved for a set of two semiconductive BDD films (deposited at B/C ratio 500 ppm and 1000 ppm) and three BDD films with metallic-type conductivity (2000 ppm, 4000 ppm, and 8000 ppm) in aqueous solutions of different pH values and supporting electrolytes. Differences in the cathodic potential limits  $E_{\text{lim,C}}$  between these films were in the range from 0.83 V (0.1 mol L<sup>-1</sup> phosphate buffer pH 7.0) to 0.58 V (1 mol L<sup>-1</sup> KCl). The decline of  $E_{\text{lim,C}}$  values was observed to be continuous, with higher differences of observed for 500 ppm to 4000 ppm electrodes.

In [160] it was shown that  $E_{\text{lim,C}}$  at BDD electrode was *ca*  $-1.15$  V,  $-1.45$  V, and  $-1.65$  V *vs.* SHE in acidic, neutral and basic media, respectively. When compared to GCE, these values, show differences ranging from *ca*  $0.6$  V in acidic medium to almost  $1.0$  V in neutral and alkaline media (for the BDD electrode being more negative). The addition of methanol had a small effect on the cathodic potential limit. Thanks to relatively negative values of  $E_{\text{lim,C}}$ , BDD electrodes can be applied for investigation of reductive processes, which has been up to now rather marginalized field in electrochemistry of organic compounds (see Chapter 2.1.2.).

To conclude, the fact that BDD electrodes exhibit wide potential window, especially in the anodic region, is generally accepted. Nevertheless, on one side its limitations at the positive potentials in the presence of some organic solvents and in alkaline media should be considered when developing electroanalytical procedures based on electrooxidations. On the other side the relatively wide potential window in cathodic region is worth highlighting to stimulate studies utilizing the BDD electrodes for reducible species.

#### 1.3.4. Adsorption Features on BDD Surfaces

Bare BDD surfaces have been considered for a long period as relatively inert to the adsorption for organic compounds of low molecular weight. Nevertheless, a few examples on the use of adsorptive stripping voltammetry for oxidizable or reducible compounds have been reported in last seven years. These include utilization of (i) the adsorption of the analyte itself or (ii) the adsorption of surfactants interacting with organic analytes, thus mediating their accumulation on the BDD surface. Further, attention has been paid to adsorbability of large biomolecules and their constituents.

*Ad* (i): Reports on adsorption of low-molecular-weight organic compounds on BDD surface are still relatively scarce and are limited to phenolic and polyphenolic compounds, and polyaromatic compounds with flat molecules. The latter group is represented by quinizarine that adsorbs on the electrode surface in dependence on its pre-exposure to organic solvents [164]. The significance of surface termination was emphasized in the case of methyl viologen (MV). It can exist in three forms (redox states),  $MV^{2+}$ ,  $MV^+$ , and  $MV^0$ , the latter representing the neutral form that adsorbs efficiently on some electrode surfaces. Thus, voltammetric signals of reduction/oxidation between  $MV^+$  and  $MV^0$  are used to distinguish between diffusion and adsorption processes [165]. It was found that  $MV^0$  adsorbs on microcrystalline BDD, BDD powder, and detonation nanodiamond powder if they are hydrogen terminated, but not if they are oxygen terminated [166]. The strong adsorption

arises probably from the interaction between the hydrophobic hydrogen-terminated diamond surface and hydrophobic and low-polar  $MV^0$ , forming multiple layers adsorbed on the H-BDD electrode. Formation of these layers is driven by  $\pi$ - $\pi$  interactions between adjacent  $MV^0$  molecules. This tendency was previously generally assigned to favorable accumulation of hydrophobic compounds on H-terminated diamond surface in order to decrease the overall hydrated surface area [165]. For 9,10-anthraquinone-2,6 disulfonic acid disodium salt, no adsorption was found on the microcrystalline BDD electrode, although significant adsorption was again noted on the above mentioned powder electrodes, provided they were hydrogen terminated [166].

For phenolic compounds, adsorption was proved at oxygen terminated BDD surface [167] or BDD surface polished by alumina slurry [33]. In general, acidic solutions of supporting electrolytes are being used to keep the phenolic species in non-ionized form. Adsorptive transfer stripping voltammetry and polishing of BDD surface was used for determination of antioxidant capacity in coffee samples based on the oxidation peaks of present phenolic compounds – chlorogenic, caffeic, and gallic acid [33]. Other phenolic compounds, *e.g.* vanilline [167, 168], were determined simultaneously with caffeine in various commercially available food and beverage products using the same conditions (O-terminated surface and square wave adsorptive stripping voltammetry (SW-AdSV) using open circuit accumulation for maximum time of 60 s). Another compound capable of adsorption on O-BDD is quinine, as reported in a study performed under supervision of the Author [169]. Low detection limit of  $1.03 \cdot 10^{-8}$  mol L<sup>-1</sup> was achieved by SW-AdSV using accumulation time  $t_{acc} = 5$  s and accumulation potential  $E_{acc} = +1.2$  V. Interestingly, this method did not succeed for quinoline, the aromatic heterocyclic skeleton of quinine (structure in Chapter 2.1.1.), lacking the quinuclidine moiety, which is probably significantly contributing to the adsorbability of quinine on the O-BDD surface. This indicates its importance, as well as the importance of other functional groups making the difference between quinine and quinoline.

*Ad (ii):* Ionic surfactants, as amphiphilic molecules with a long hydrophobic tail on one side and polar head on the other, are capable of adsorption onto hydrophobic substrates from aqueous solutions. Presumably, at low concentrations below critical micelle concentration (CMC), the surfactant monomers adsorb to form a lower-density adsorbed layer on the substrate surface, which is oriented with the hydrocarbon chains parallel to the substrate plane (*via* hydrophobic interactions), while the charged head groups are oriented toward outside. As the surfactant concentration is increased, this first layer acts as a template for subsequent surfactant adsorption (forming hemicylindrical structures, such as

conventional and gemini ones for ionic surfactant chains longer than 12 carbon atoms). This explanation is widely accepted for structures of hemimicelles (monolayer formation). At higher concentrations (but well below CMC), bilayer aggregates, sometimes called admicelles, are formed due to favorable interactions between the surfactant tail groups [170-173].

Applications of surfactants in electroanalytical chemistry have been widely reported. The interaction of a surfactant and an organic compound can change redox potential of the latter, influence charge transfer coefficient or diffusion coefficient of the electrode processes, and thus may lead to improved analytical figures of merit. Nevertheless, little work has been carried out to utilize surfactant adsorption on BDD surfaces. Cationic surfactants were used for detection of resorcinol [174] (hexadecyltrimethylammonium bromide (HTAB)), pterostilbene [170] and benzophenone-3 [175] in the reductive detection mode (cetyltrimethylammonium bromide (CTAB)). Voltammetric response of capsaicin [34], benzo(*a*)pyrene [35], and ambroxol [176] was enhanced in the presence of sodium dodecylsulfate. The main disadvantage of this approach is the necessity of manual polishing of the BDD surface after each scan. On the other hand, the interaction with the surfactant and/or transfer of the adsorbed species from a matrix to pure supporting electrolytes can substantially increase the selectivity of the method.

#### *1.3.4.1 Adsorption and Electrochemistry of Biomolecules and Their Constituents on BDD Electrodes*

Adsorption (either utilizable or undesired) at electrode surfaces plays important roles in electrochemistry of biomacromolecules (peptides, proteins, oligonucleotides, and nucleic acids) and their constituents. These species are capable of adsorption on  $sp^2$  carbon materials. Electrochemical activity of peptides and proteins relies on oxidation of tyrosine, tryptophan, and cysteine [177]. Histidine, methionine and disulfide bridges are oxidizable at far positive potentials, and although they exhibit anodic signals at carbon-based materials including BDD [178-182], in proteins these species are rather inactive with exception of -S-S- bridges on BDD electrodes [155, 183-187].

In specific proteins, oxidation/reduction of incorporated metallic units, sometimes coupled to catalytic processes, is observed. It has to be emphasized that, particularly in the case of BDD electrodes, the interplay among surface termination, morphology, electron transfer kinetics, and adsorption of biomolecules is sparingly discussed and especially older studies suffer from insufficient information on these issues. This is valid especially for the

surface pretreatment, as its importance for interaction with the redox active species and influence on charge transfer was not recognized in the early stages of BDD-related research. An illustrative example of the development of the knowledge of electrochemistry of a biomolecule is that of cytochrome *c* at BDD-based materials. Its ferric (Fe<sup>3+</sup>)/ferrous (Fe<sup>2+</sup>) heme unit may undergo reversible or quasireversible redox process, influenced by accessibility (*i.e.* orientation and distance of the heme unit from the electrode surface) for the electron transfer. The latter is believed to occur at the solvent-exposed edge of the heme group by an outer-sphere mechanism [188]. It has been shown on metallic and some sp<sup>2</sup> carbon electrodes that highly pure cytochrome *c* solution and hydrophilic/oxophilic (and/or negatively charged) surface obtained by electrochemical pretreatment or other modification exhibit a rapid electrode reaction kinetics [188, 189]. For example, two-fold increase of the kinetics in the electron-transfer rate of cytochrome *c* at the edge oriented pyrolytic graphite (EOPG) with higher O/C ratio was reported in comparison with freshly cleaved, hydrophobic basal plane pyrolytic graphite [190]. Chemically modified electrodes with negatively charged COO<sup>-</sup> terminal groups showed adsorption of cytochrome *c* and an increase in the electron transfer rate, compared to mixed surfaces containing hydroxyl groups [191]. Deprotonated carboxylates enable electrostatic interaction between the positively charged heme edge and the negatively charged electrode surface and thus result in fast electron transfer kinetics ( $k = 10^{-3} \text{ cm s}^{-1}$ ).

Electrochemistry of cytochrome *c* on BDD surface was for the first time reported in 1992 by Swain *et al.* only for the H-terminated mode. The study revealed a fast, quasi-reversible ( $k = 10^{-3} \text{ cm s}^{-1}$ ), stable, diffusion-controlled kinetics contrary to expectations of sluggish kinetics [192]. These findings were revised by the same group fourteen years later, when the hydrogen-termination of BDD surface was confirmed by XPS and negligible cyclic voltammetric response of cytochrome *c* was obtained [188]. This revision was inspired by studies of other authors, who in general reported fast electron transfer only at BDD electrodes functionalized with carbon-oxygen groups or molecular linkers that were oxygenated or charged [193-197] or at alumina polished surface [31]. Further, the inactivity of the H-terminated surface was in concordance with results of Nebel group [194, 195]. They reported on differences observed in cytochrome *c* redox reaction and conformation in dependence on oxygenation of BDD surface. Efficient immobilization and fast electron transfer was observed only at moderately oxidized surface, enabling adsorption of the protein by electrostatic interactions and a good electronic coupling of the heme unit. The later was located in

hydrophobic environment and thus took advantage of hydrophobic interaction with the BDD surface, favorable for a conformation enabling electron transfer. Such arrangement mimicked the binding of cytochrome *c* to its natural binding partner cytochrome *c* oxidase. Interaction of the protein with the H-terminated surface led to its denaturation and thus in a loss of redox activity. Strongly oxidized surface enables adsorption of the protein in its native form, but does not favor proper orientation of the heme unit to facilitate electron transfer. Thus, it has been concluded by Swain *et al.* that in their original study [192] the allegedly hydrogen-terminated surface obtained by hydrogen plasma treatment was in fact insufficiently terminated by C-H bonds and surface oxygen was likely introduced upon exposure of the films to the air as a consequence of the cool-down procedure after BDD deposition [188]. In this study it was confirmed that O-terminated surface enables relatively rapid rates of electron transfer due to close positioning of the Fe heme edge close to electrode surface through electrostatic and hydrogen bonding interactions. Moreover,  $k$  values ( $k = 2-4 \cdot 10^{-3} \text{ cm s}^{-1}$ ) were comparable for microcrystalline and ultrananocrystalline BDD thin films, indicating independence of the electron transfer kinetics on morphologies of BDD films investigated.

Several other reports exist on the preference of O-BDD surface for adsorption of enzymes used for construction of biosensors. A mediator-free glucose biosensor was fabricated by immobilizing glucose oxidase cross-linked with oxidized BDD surface through glutaraldehyde [198]. BDD electrodes coated with adsorbed heme undecapeptides exhibited lower responses to  $\text{H}_2\text{O}_2$  reduction for the H-BDD (as grown) surface than the O-BDD surface, in the latter case comparable with those of an EOPG electrode (despite much lower roughness). However, electron transfer to oxidation products of horseradish peroxidase (HRP) from the BDD electrodes proceeded much slower than that from EOPG or glassy carbon, suggesting that the  $\pi$  electrons present on  $\text{sp}^2$  carbon may play an important role in the direct electron transfer to the heme moiety of HRP [199].

On the other hand, several reports have been published on preference of H-termination over O-termination in studies of proteins and peptides, as reported *e.g.*, for oxidation of immunoacidic suppressive protein, and for bovine serum albumin [200]. Ricin, a lectin with two polypeptide chains is oxidizable probably due to redox activity of tryptophan residues in ricine A chain [201]. Importantly, its accumulation can be performed only on H-BDD; on O-BDD the oxidation signal is negligible probably due to partially negative charge of the surface, repelling the negatively charged protein in borate buffer pH 9.0. Alumina polished BDD surface also enables adsorption of protein. Such surface was employed to study direct electron transfer of the heme unit and catalytic reduction of oxygen by myoglobin and

hemoglobin. In addition, polishing was the only procedure used to remove adsorbed protein to obtain clean electrode surface [202]; no other surface pretreatment was tested.

Similarly as for proteins and peptides, the behavior of DNA, RNA, and their constituents on BDD surfaces has been investigated since 2002. These studies dealt with different terminations and morphologies, but consistent studies comparing response of these biomolecules at different surfaces are scarce [203-214]. These molecules have been largely investigated on  $sp^2$  carbon materials, as reviewed in [215]. Their electrochemical activity in anodic region relies on oxidation of DNA bases, mostly guanine and adenine, in less frequent cases thymine and cytosine using specific conditions. Especially the latter two nucleobases are oxidized at fairly positive potentials, giving rise to problems such as interference with oxygen evolution, large background currents, or slow electron transfer kinetics. Further, adsorption of nucleic acids or their reaction products (leading to electrode passivation) is characteristic for  $sp^2$  carbon materials, including pyrolytic graphite electrode [216], glassy carbon electrode [217, 218], or carbon paste electrode [219]. The adsorption can be exploited to attain analyte accumulation and apply adsorptive stripping chronopotentiometric or voltammetric techniques, as demonstrated for glassy carbon electrode after anodic electrochemical activation *e.g.*, for adenine and guanine [217] or for all DNA nucleotides [218].

Using BDD electrodes, purine and pyrimidine bases were investigated by Ivandini *et al.* [206] in ammonium acetate buffer solution (pH 4.25), who reported on the importance of surface termination and ionic strength of electrolyte for their electrochemical oxidation. All four nucleobases were detected on O-BDD but not on H-BDD (as deposited) surface, where thymine was overlaid by earlier onset of background current. In the mild acidic conditions used, these bases behave as neutral or very slightly positively charged molecules which has been ascribed to electrostatic bonding with water molecule. Therefore, their electrostatic interactions with the surface are of minor importance and diffusion-controlled oxidation process was recognized for both surfaces. Slight enhancement of oxidative current on the O-BDD compared to that observed on the H-BDD was attributed to the elimination of non-diamond impurities at the former surface during the pretreatment [206], which is, however, questionable with respect to the current knowledge on importance of the surface termination of BDD surface on electron transfer processes. Also on the polished BDD surface, the oxidation process was reported to be driven by diffusion for both adenine and guanine [207]. The peak-to-peak separation 0.2 V of these bases enables their voltammetric determination in native, thermally, and acid denatured chromosomal DNA.

Einaga *et al.* [220] used cyclic voltammetry to compare oxidation of adenosine phosphates on H-BDD (cathodically pretreated) and O-BDD. A typical oxidation peak at the potential of about +1.3 V (*vs.* Ag | AgCl) attributable to the oxidation of adenine base moiety was observed in phosphate buffer solution pH 7.4. However, at low pH the oxidation peak could be well observed for all adenosine monophosphate (AMP), adenosine diphosphate (ADP), and ATP on H-BDD, whereas on O-BDD it was only found for the oxidation of AMP. Such results indicated that the negatively charged surface of BDD slows down the oxidation kinetic of the adenosine phosphates, possibly due to the repulsion effects between the O-BDD surface and the phosphate (particularly di- and triphosphate) functional groups. For free adenine base, only small differences between the two surface modes were observed.

While the nucleobases seem not to adsorb on BDD surfaces regardless of the surface pretreatment, their nucleoside and nucleotide forms exhibit proclivity to adsorption of themselves or their electrochemical reaction products. Prado *et al.* [204] focused on H-BDD surface. Deoxyguanosine monophosphate was oxidized in adsorbed state through two successive electrochemical processes at potentials of +1.1 V and +1.3 V (*vs.* SCE). Analogous two-step mechanism was also observed for guanine-containing RNA as well as ssDNA and dsDNA. These potentials are more positive than those obtained for guanosine oxidation by Dryhurst *et al.* [221], who proposed a mechanism of the nucleoside oxidation on PGE, where three oxidation waves were recorded at potentials of +0.81 V, +1.00 V, and +1.20 V (*vs.* SCE) at pH 7. In general, positive potential shifts at BDD electrodes compared to  $sp^2$  carbon materials were also observed for other oxidizable substances and may be attributed to larger hindrance of the electron transfer at the heterogeneous BDD surface. This applies also to the report by Fortin *et al.* [210] on electrooxidation of nucleoside and nucleotide forms of 2'-deoxyguanine and 2'-deoxyadenine on O-BDD, where positive shifts of peak potentials by  $\sim 0.15$  V were reported for both nucleosides, compared to respective signals measured at the PGE [221]. In general, nucleotide oxidation signals appear even at higher potentials and the recorded peak intensity is markedly lower, which is a common feature for these biomolecules, reflecting the lower diffusion coefficient of larger molecules and decreased accessibility to electron transfer at the oxidation site [213, 222]. For all mentioned studies, adsorption of the nucleos(t)ides on BDD surface was reported with the exception of [213], who used microchip CE-EC setup with BDD electrode employed in amperometric mode for detection of purine derivatives including guanosine and synthetic oligonucleotides. In studies dealing with electrochemistry of native and denaturated DNA or oligodeoxynucleotides, O-BDD electrodes were used for adsorptive sensing of purine bases in their sparingly soluble Cu(I)

complexes [212] or for investigation of electrochemical behavior of native and thermally denatured fish DNA in the presence of free cytosine and selected porphyrins [205].

#### 1.4. Applications of Boron Doped Diamond Electrodes

Over the past twenty five years, it has become apparent that the BDD is, in many ways, almost ideal electrode material displaying advantageous mechanical, physical, and electrochemical properties. To exploit them, four main directions of the BDD use have been established: (i) Electrochemical oxidation of organic pollutants at BDD anodes proposed for their quantitative conversion or destruction in wastewaters, (ii) electrochemical disinfection of drinking and bathing water, (iii) electrochemical synthesis, particularly *via* production of strong oxidizing agents or in electroorganic synthesis [48, 223-226] and, (iv) use of BDD electrodes in electroanalysis for the detection of both organic and inorganic species in environmental, biological, and pharmaceutical matrices (in more detail introduced in Chapter 2). Extremely important reaction characteristic of the BDD anodes, especially for the application fields (i) and (ii) listed above, is the formation of HO<sup>•</sup> radicals by water decomposition (eq. 1).

*Ad* (i): The principal aim of the wastewater treatment is complete oxidation of a variety of pollutants to produce CO<sub>2</sub>, water, and inorganic ions, or conversion of the pollutants to biocompatible compounds (eq. 8). BDD electrodes are extremely suitable for this purpose, because the high overpotential for water oxidation at the BDD favors generation of large quantities of the HO<sup>•</sup> radicals (eq. 1). These powerful oxidants ensure non-selective direct oxidation of the organics on the BDD anode surface so that its passivation is prevented. The HO<sup>•</sup> radicals are relatively weakly adsorbed and consequently available for organic oxidation, which proceeds not only directly on the BDD surface, but also in its vicinity [227]. Further, the number of active sites for the adsorption (*e.g.*, regions with higher content of sp<sup>2</sup> carbon) of reactants and/or products decreasing the efficiency of the degradation process is minimized. Besides BDD, only SnO<sub>2</sub> and PbO<sub>2</sub> anodes were reported to exhibit a Faradaic efficiency in direct electrochemical oxidation of organic compounds. These electrodes also produce HO<sup>•</sup> radicals as intermediates of oxygen evolution; nevertheless, they have substantial drawbacks such as short service life (SnO<sub>2</sub>) or release of toxic ions (PbO<sub>2</sub>) during electrolysis [228].

Other approaches aiming at the increase of concentration of the HO<sup>•</sup> radicals in solutions include electro-Fenton (EF) and photoelectro-Fenton (PEF) oxidation processes

(reviewed in [229-231]). In the EF process on BDD anodes, the production of HO• radicals by reaction of H<sub>2</sub>O<sub>2</sub> (generated as one of products of water decomposition) and Fe<sup>2+</sup> complements their direct formation on BDD surface, thus augmenting their effect in the electrochemical cell. In the PEF processes, artificial UVA light or sunlight is used to induce photo-reduction of iron species in high oxidation state to form of Fe<sup>2+</sup> and consequently the HO• radicals *via* the Fenton reaction, again supporting the electrocatalytic effect of the BDD anode [53, 232].

For all modes of the above mentioned oxidation processes, operative characteristics (anode/cathode material, applied current density, initial concentration of the pollutant, pH, temperature, and composition of supporting electrolyte and its stirring (flow) rate, cell design) are being evaluated to optimize the degradation efficiency. These studies are frequently accompanied by voltammetric studies in order to elucidate the electrochemical oxidation mechanism involved in the degradation process. Several reviews have been devoted to this topic in previous years for oxidation processes performed by means of BDD-based anodes [49-55, 228, 233, 234] showing that these methods lead to almost complete mineralization of organic compounds. The latter include pesticides and their degradation products, environmental pollutants (chlorophenols, polyaromatics and their derivatives), various dyes, surfactants, selected drugs and many others. Most of these studies have been performed on BDD anodes deposited on silica supported devices (showing limitations connected with fragility or relatively low conductivity of silica), or on titanium. The latter substrate suffers from short service time due to large thermal residual stress caused by the substrate cooling from about 850°C to ambient temperature, as well as due to the formation of a TiC interlayer reducing diamond film adhesion to the substrate [233]. Further, the sp<sup>2</sup>/sp<sup>3</sup> ratio in the BDD film is discussed with respect to its electrocatalytic properties, as these characteristics influence the degradation pathway followed during electrooxidation of the pollutant as well as during production of the vigorous oxidants [234, 235]. Thus, development of BDD-based anode material deposited on sufficiently stable and conductive support is still subject of continuous research so that BDD can serve as anode material for large-scale degradation of organic compounds in industrial applications.

*Ad (ii):* The objective of water treatment is inactivation or removal of pathogenic microorganisms to prevent the spread of waterborne disease. Chlorination as the most common method of water disinfection is worldwide discussed with respect to the identification of potentially toxic products associated with this chemical method, *e.g.*, halomethanes or chloroform [236]. Thus, alternative disinfection technologies are being

developed to minimize these risks using less chemicals and save energy. The electrochemical treatment has gained widespread acceptance since 1950, especially that based on electrogeneration of disinfecting agents as it was proven to inactivate a wide variety of microorganisms ranging from viruses to bacteria and algae [237]. The efficiency of the process is largely dependent on the design of the electrochemical reactor, anode material, electrolyte composition, and electrolysis conditions. As the anode materials, metals and mixed metal oxides, or carbonaceous materials including BDD films are being used. Electrochemical disinfection is most effective in waters containing chlorides, as by their oxidation at the anode active chlorine species such as  $\text{Cl}_2$ ,  $\text{HOCl}$ ,  $\text{OCl}^-$ , and  $\text{ClO}_2$  are formed which are recognized as key oxidants responsible for inactivating the microorganisms. Again, besides these species, reactive oxygen species (ROS) can be formed from water decomposition at the anode including  $\text{HO}^\bullet$  radicals, atomic oxygen,  $\text{O}_2$ , hydrogen peroxide, and/or ozone, depending on the anode material and composition of the solution. Production of similar spectra of reactive species was reported for many anode materials, as reviewed *e.g.*, in [237]. Strikingly, even in chloride-free media (or media with very low concentrations of  $\text{Cl}^-$ ), remarkable effectiveness of the electro-disinfection was observed at BDD and other anodes [237, 238]. On BDD surface a large spectrum of other ROS can be formed (in addition to those mentioned above), as well as weaker oxidants such as peroxodisulfate, peroxodicarbonate, or peroxodiphosphate from the oxidation of sulfate or bisulfate, bicarbonate, or phosphate, respectively [237]. For *Escherichia coli*, an indicator microorganism for sanitary water quality, significant decrease of concentration by  $\geq 3$  log units after 60 s of electrolysis was reported in  $\text{Na}_2\text{SO}_4$  medium [238], or by  $\geq 5$  log units after 60 min of electrolysis using the BDD anode. Similar efficiencies were observed for other Gram-negative bacteria (*Pseudomonas aeruginosa*), as well as Gram-positive ones (*Bacillus atrophaeus*, *Staphylococcus aureus* and *Enterococcus hirae*) under acidic and neutral conditions [239]. In chloride-containing solutions, the BDD anodes proved high disinfection ability [240-242]. Nevertheless, during the electrochlorination processes, higher amounts of undesired chlorate ( $\text{ClO}_3^-$ ) and perchlorate ( $\text{ClO}_4^-$ ) are formed at the BDD anode compared to metal oxide anodes [243-245]. Recent studies suggest that the  $\text{sp}^3/\text{sp}^2$  ratio is a key parameter influencing their production, favoring use of electrodes with a high  $\text{sp}^3$  content and applying low current densities to limit production of  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  [246]. The  $\text{sp}^3/\text{sp}^2$  ratio plays also role in production of some ROS, as proved for  $\text{H}_2\text{O}_2$  [247].

The achievements using BDD-based materials in the application fields described above definitely demonstrate their potentialities in minimizing human health risks associated with the presence of pathogenic microorganisms and bio-refractory compounds in the environment. They represent the driving force for continuous research in this area, leading to industrial applications of BDD anodes.