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STRUCTURE-FUNCTION RELATIONSHIP OF BORON-DOPED DIMAOND THIN-FILM ELECTRODES AND APPLICATION FOR IN VITRO AMPEROMETRIC MEASUREMENTS

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STRUCTURE-FUNCTION RELATIONSHIP OF BORON-DOPED DIMAOND THIN-FILM ELECTRODES AND APPLICATION FOR *IN VITRO* AMPEROMETRIC MEASUREMENTS

By

Shihua Wang

A DISSERTATION

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Abstract

STRUCTURE-FUNCTION RELATIONSHIP OF BORON-DOPED DIMAOND THIN-FILM ELECTRODES AND APPLICATION FOR *IN VITRO* AMPEROMETRIC MEASUREMENTS

By

Shihua Wang

In this dissertation, the structure-function relationship of boron-doped diamond thin-film electrodes was studied. This includes assessing the factors that influence the properties of boron-doped diamond thin-film electrodes as well as investigating the electrical and electrochemical mechanism of these electrodes. In addition, the application of boron-doped diamond microelectrode for in vitro amperometric measurements was also studied.

The electrical and electrochemical properties of boron-doped diamond thinfilm are influenced by many factors such as growth conditions, grain size, doping level, impurities (e.g., grain defects, sp² carbon and adsorbed hydrogen) and surface chemistry. Growth condition is the primary determinant of the surface morphology of BDD thin-film, although both microcrystalline and nanocrystalline diamond thin-film can be deposited in similar hydrogen-rich gas mixtures. Microcrystalline BDD thinfilm has different Raman spectrum and carrier mobility from nanocrystalline film but their electrochemical properties are very similar in macroscopic level. Using CP-AFM and SECM, we found that the electrical conductivity and electrochemical activity for microcrystalline BDD thin-film are different from those for nanocrystalline film. Microcrystalline BDD thin-film possesses lower fraction of active regions but more active individual sites compared with nanocrystalline BDD thin-film. Doping level influences the surface morphology of BDD thin-film. More importantly, CP-AFM and SECM measurements illustrated that both the fraction of electrically conductive regions and the fraction of electrochemically active regions increase as the doping level increases and this is true for both microcrystalline and nanocrystalline BDD films.

Surface termination has a significant influence on the properties of CVD diamond. For example, the fastest electron-transfer kinetics for $Fe(CN)_6^{3./4-}$ has been recorded at hydrogen-terminated BDD electrode but very sluggish reaction has been recorded at oxygen-terminated BDD electrode. Electrochemical measurements show that O-terminated BDD electrode has a little larger background current that H-terminated BDD electrode. The reason for this might be the O-terminated surface is more hydrophilic and this may increase the dielectric constant of H₂O at the surface. CP-AFM and SECM studies show that both the fraction of electrically-active regions and the fraction of electrochemically-active regions are greater for H-terminated than for O-terminated BDD films.

As a preclusive work, the BDD microelectrode has been used to study the denervation of capsaicin on mesenteric blood vessels by monitoring the release of norepinephrine. The distribution of sensory and sympathetic nerves was visualized using glyoxylic acid fluorescence histochemistry and anti-TH, anti-substance P and anti-CGRP immunohistochemistry. The effects of 7 neuro-phamarceutical drugs on the determination of norepinephrine were also studied. We failed to show any evidence for the local communication between the sensory and sympathetic nerves by using exogenous substance P.

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Chapter 1

Introduction

1.1 Diamond and the conducting diamond electrode

1.1.1 Diamond

Diamond is a carbon allotrope with a cubic crystal structure (Fig.1.1) consisting of two interpenetrating face-centered cubic (FCC) lattices, displaced from each other by one quarter of a body diagonal. Each carbon atom is tetrahedrally coordinated (sp³ hybridized), creating strong, directed sigma bonds with its four neighboring carbon atoms. The bond length and lattice constant are 1.54 and 3.56 angstroms, respectively.¹ The outstanding mechanical, chemical and electronic properties of diamond stem from the extremely strong and tight sp³ bonding. Due to the very large activation barrier between the sp² and sp³ bonding states, diamond is for all practical purposes as a stable microstructure, although the most thermodynamically stable microstructure for carbon is graphite. Based on these facts,



Figure 1.1 Diamond cubic crystal structure.

diamond is expected to be a promising wide-band-gap semiconductor for electronic and optical devices, such as ultraviolet light emitting diodes, cold cathode electron emitters, and high-power and high-frequency devices. Diamond's well-known properties include extreme hardness, very high thermal conductivity and optical transparency, in pure form. In its natural or undoped form, diamond is an excellent electrical insulator with a bandgap of 5.5 eV.^{2, 3} When intentionally doped with boron, semiconducting or even semimetallic electrical properties can be imparted to the material.^{2, 3}

in order for diamond to be a viable wide-band-gap semiconductor or semimetallic conductor, several fundamental issues must be resolved including highquality diamond growth, different types of doping, contact fabrication and etching technology. The discovery of chemically vapor deposited diamond at high rates in 1980s^{4, 5} enabled applications such as heat sinks for electronics, wear-resistant layers on tools, and anti-corrosion layers on metals. ⁶⁻⁸ Nowadays, scientists are seeking to exploit some of the attractive properties of diamond (see Table 1.1).⁹⁻¹⁸ For example, there is a growing interest in the use of doped diamond as an electrochemical electrode.

Properties	Type IIa	CVD	Ref.
Density (g/cm ³)	3.52	3.52	9
Hardness (Gpa)	57 - 104	50 - 100	10.11
Thermal Conductivity (W/cm/K) at 298 K	20 - 23	10 - 21	10
Thermal Expansion Coefficient (10 ⁻⁶ /K)	0.8 - 1.2	~ 2.0	12
Heat Capacity (J/mol/K)	6.2	2.2	13

Table 1.1 Properties of type IIa natural and CVD diamond

Properties	Type IIa	CVD	Ref.
Optical transmissivity	225 nm to far IR	225 nm to far IR	14
Electrical Resistivity (Ω•cm)	10 ¹⁶	$10^{-2} - 10^{16}$	15
Band gap (eV)	5.45	5.5	1
Electrical breakdown field (kV/cm)	10000		9
Electron Affinity (eV) (Depends on surface termination)	0.41.3	-1.3 (H-terminated)	16
Electron mobility (cm ² /V/s)	2200	4500	17
Hole mobility (cm ² /V/s)	1600	3800	17
Electron Saturated Velocity (10 ⁷ cm/s)	2.7	2.7	18
Hole Saturated Velocity (10 ⁷ cm/s)	1.0	1.0	1

Table 1.1 Properties of type IIa natural and CVD diamond (continued)

1.1.2 Conducting diamond (Synthetic diamond)

Natural diamond is an electrical insulator with a band-gap of ~5.5 eV and a resistivity greater than $10^{12} \Omega$ -cm.⁹ However, diamond grown via CVD in hydrogenrich environments can exhibit the so-called "surface conductivity".¹⁵ The resistivity of synthetic diamond can be lowered to $10^6 \Omega$ -cm when terminated with hydrogen (or having it incorporated into the lattice). Synthetic diamond can be made more conductive via doping with elements such as boron, nitrogen and phosphorous. Diamond can be made p-type by doping with boron, $E_a = 0.37 \text{ eV}$, and n-type by

doping with nitrogen, $E_a = 1.7 \text{ eV}$, or phosphorous, $E_a = 0.56 \text{ eV}$. These are large activation energies compared to the activation energy for boron-doped Si (ca. 0.02 eV).¹⁹ The candidates for p-type doping are B, Al and heavier group III elements. Boron is the most commonly used dopant.^{2, 20} Nitrogen, phosphorous and heavier group V elements are n-type dopants but the formation of *n*-type semiconducting diamond has proven a difficult task. One reason for this is the alternation of the electric conductivity due to the incorporation of hydrogen into CVD grown films from conventional C/H source gas mixtures. Hydrogen can act as both a donor and an acceptor. Nitrogen is among a few suitable dopants for CVD diamond, but unfortunately it forms a deep donor level $\sim 1.7 \text{ eV}$ below the bottom of the conduction band. This is due to its structural distortion from the substitutional position in the diamond lattice. Therefore, achieving highly conducting (room temperature) n-type diamond had been a challenge. A breakthrough in synthesizing N-doped diamond came several years ago through the addition of N₂ to the CH₄/Ar source gas mixture for growing ultrananocrystalline diamond.²¹ Although only B and N have the required properties of a suitable dopant for diamond, surprisingly, the only proven *n*-type diamond is obtained by the introduction of phosphorus during CVD diamond growth. Koizumi et al reported the growth of n-type diamond on (111)-oriented diamond substrates by using a mixture of PH₃, CH₄ and H₂ gas in 1997. ²² Following this success, several studies have also been reported for phosphorous (P) doping during the chemical vapor deposition of diamond.^{23, 24}

The most extensively employed CVD diamond in electrochemistry is the *p*type, boron-doped material. The resistivity of highly boron-doped diamond thin films can be as low as ~0.005 Ω -cm. Both high-quality microcrystalline and nanocrystalline boron-doped diamond thin films can be routinely prepared. Diamond is, in fact, metastable with respect to graphite at low temperature and pressure as the free energy difference between the two materials at 298 K and 1 atm is only 2.900 kJ/mol (-0.03 eV per atom). However, there is a large activation barrier for conversion.^{12, 25} Thus, in theory, diamond growth can be achieved in the metastable region of the carbon phase diagram as long as graphite formation is suppressed.

Low pressure diamond synthesis via CVD dates back to the 1950s and 60s when research was conducted in both the former Soviet Union and the United States.²⁶⁻²⁸ Since then, developments in CVD technology have enabled the production of diamond for a number of applications, such as optical windows, wear-resistant coatings for cutting tools, thermistors, and electrodes.²⁹ Several CVD growth methods exist for producing diamond, all of which utilize a carbon-containing reactant source gas (e.g., methane and hydrogen), an energy source to promote reactant dissociation (e.g., microwave, hot-filament, or DC discharge), and a substrate (e.g., Si, W, Mo). High-quality (i.e., low defect density and low nondiamond carbon impurity content) CVD diamond is typically produced at low pressure (10 to 500 Torr), high gas temperature (>1700 °C), high substrate temperature (700 to 800 °C), and low carbon concentration in the source gas (e.g., 0.5%) with an energy source for gas dissociation and radical formation.^{25, 29}

1.2 Electrochemical properties and application of borondoped diamond (BDD)

The first paper on the electrochemistry of polycrystalline diamond was published by Pleskov et al. in 1987^{20, 30, 31}. This film possessed reasonable electrical conductivity but was not doped. The conductivity likely resulted from nondiamond impurity phases. Nevertheless, this demonstration of diamond electrodes spawned

conductive diamond used extensively in electrochemistry. Diamond exhibits several remarkable properties. First, it has a large potential window in aqueous solution with low background current³²⁻³⁴. Second, the electrode formed from polycrystalline diamond possesses many of the same physical properties of bulk diamond.^{12, 35-38} Third, the electrode surface microstructure is stable as there is little evidence of degradation at high potentials and current densities.³⁹⁻⁴⁴ Fourth, the electrode exhibits good activity for various redox systems without conventional pre-treatment and excellent resistance to deactivation. These characteristics make diamond useful for a number of applications.

1.2.1 Electrolytic waste water treatment

An important electrochemical application of boron-doped diamond is in the area of electrolytic water purification and decontamination.⁴⁵⁻⁵⁰ Electrolytic treatment is quite attractive for water purification and decontamination but usually is limited by the stability of the electrode. Boron-doped diamond is a good candidate electrode in this field because of its inherent properties. Our group has shown that boron-doped diamond thin film electrodes exhibit superb morphological and microstructural stability.^{51, 52} The wide potential window of boron-doped diamond has allowed poorly biodegradable compounds⁵³ and persistent contaminants⁵⁴ to be decontaminated in waste water. Ruediger et al. reported on the integrated biological and electrochemical oxidation of industrial wastewater.⁵⁵ The BDD electrode was used to transfer persistent organic compounds into a biodegradable fraction, followed by high efficient biological elimination using specialised bacteria. The advantages of the process are high efficient chemical oxidation demand (COD) removal with reduced energy consumption combined with low total residence time because the organic

compounds can be electrochemically oxidized at BDD electrode. Similarly, various chemical contaminants such as t-butanol,⁵⁶ chlorophenol,⁵⁷ phenolic compounds,⁵⁸ acetaminophen⁵⁹ and organotin compounds⁶⁰ can be oxidatively degraded with borondoped diamond. Kober et al. invented the method and device for the oxidative treatment of wastewater containing pesticides based on a boron-doped diamond electrode.⁶¹ The electrooxidation of some chemicals on boron-doped diamond electrode has also been used for decolourization in industrial wastewater. For example, Belaid and coworkers used diamond to remove phenolic compounds and decolourize olive mill wastewater.⁶² Canizares et al. reported the treatment of Fenton-refractory olive oil mill wastes by electrochemical oxidation with boron-doped diamond anodes.⁶³ More recently, Panizza et al. developed a theoretical model for organic pollutants mineralization on B-doped diamond electrodes.⁶⁴ The model was formulated for a perfect mixed electrochemical reactor operated as a batch recirculation system under multiple current steps, in which the applied current was adjusted during the electrolysis to be close to the limiting value. The model was experimentally validated by the anodic oxidation of 3, 4, 5-trihydroxybenzoic acid. Multiple current steps electrolysis and continuous current control allowed obtaining high oxidation rate and current efficiency.

1.2.2 Electroanalysis

CVD diamond has been extensively used in electroanalysis because it offers advantages over other electrodes in terms of linear dynamic range, limit of detection, response time, response precision and response stability. Some of the applications of diamond in electroanalysis reported since 2004 are highlighted below. The review for the applications reported before 2004 can be seen in the literature.^{65, 66}
A. Metal ion analysis

The electrochemical properties of CVD conducting diamond are ideally suited for the detection of trace metal ions via anodic stripping voltammetry (ASV). It has been shown that mercury ions at both the ppb and ppt level can be determined with BDD electrodes by differential pulse voltammetry (DPV).^{67, 68} A modified BDD electrode has also been used for the detection of mercury. For example, Salimi et al.⁶⁹ reported on an iridium oxide modified BDD electrode to detect Hg(I). They deposited iridium oxide films electrochemically on the electrode surface by potential cycling between -0.2 to 1.2 V from a saturated alkaline iridium (III) solution based on the following reaction:

 $Ir_2O_3 \bullet xH_2O(aq) + 2OH^- \rightarrow 2IrO_2 \bullet xH_2O(s) + H_2O + 2e^-$

The modified BDD electrode exhibited an excellent catalytic activity for oxidation of Hg(I) over a wide pH range and shows excellent analytical performance for Hg(I) amperometric detection. They suggested that IrO₂ catalyzed mercury(I) oxidation in the following electrochemical catalytic pathway:

Ir (reduced form) \rightarrow Ir (oxidized form)

Ir (oxidized form) + Hg₂²⁺ \rightarrow Ir (reduced form) +2 Hg²⁺

The detection limit, sensitivity, response time and dynamic concentration ranges are 3.2 nmol/L, 77 nA/(μ mol/L), 100 ms and 5 nmol/L – 5 μ mol/L. These analytical parameters compare favorably with those obtained with modern analytical techniques and recently published electrochemical methods.⁶⁹

Lead can be detected with BDD⁷⁰ or modified BDD⁷¹ electrodes by ASV at low pH and copper coexisting. The low limit of detection (2 nmol/L at BDD and 0.85 nmol/L at modified BDD) is an advantage compared to other electrode materials. The technique has been used for the detection of lead in tap water and blood.

Banks et al. studied the deposition of cadmium on boron-doped diamond with square-wave anodic stripping voltammetry in quiescent conditions, in the presence of an acoustic field and then in the presence of the neutral surfactant Triton[®] X-100. They found the effect of optimized insonation was to increase the sensitivity from 0.63 (under silent conditions) to $3.78 \,\mu$ A/(μ mol/L) and to reduce the limit of detection by an order of magnitude from 10^{-8} to 10^{-9} mol/L.⁷²

It has been shown that ppb levels of cadmium and lead both can be detected using square-wave anodic stripping voltammetry with a boron-doped diamond electrode.⁷³

Besides anodic stripping voltammetry, cathodic stripping voltammetry (CSV) at a boron-doped diamond electrode has been used for the detection of metal ions. For instance, free Mn (II) in seawater samples can be detected with BDD by CSV utilizing an insonated accumulation protocol. No sample pre-treatment was required with the application of ultrasound providing a sensitive and selective protocol for the analysis of Mn (II).^{74, 75}

CSV has also been used to quantify the concentration of Ni (II) in an electroless nickel deposition bath with a BDD electrode. The methodology relies on the electrodeposition of Ni onto a boron-doped diamond electrode and the subsequent oxidative conversion of the metallic layer to Ni(III). The analytical signal was derived from a cathodic stripping protocol in which the reduction of the Ni(III) layer to Ni(II) was monitored by the use of differential pulse voltammetry. The stripping peaks obtained with both solution stirring and electrode rotation were observed at +0.6 V (vs. SCE) with the response found to be linear over the range $0.3-5 \mu mol/L$ (solution

stirring) and 0.1–4 μ mol/L (electrode rotation). The viability of the technique was evaluated through the determination of nickel in an electroless nickel deposition bath solution used practically and validated by an independent comparison with the result of ICP-AES.⁷⁶

The above discussion shows that BDD electrode can be used to detect different metal ions using different detection conditions. In fact, BDD electrodes have become one of the important tools for heavy metal detection. By studying some analytical parameters of differential pulse anodic stripping voltammetry (DPASV) method, Tall et al. demonstrated that it's possible for the simultaneous determination of Zn (II), Cd (II) and Pb (II) at very low levels despite the overlapping of Zn and Cd stripping peaks. Compared to the glassy carbon electrode (without mercury plating), a lower base line current, wider potential range, higher sensitivity (3 to 5 times higher than GC) and longevity of the material were noticed for the BDD.⁷⁷

Because of the high sensitivity and low limit of detection, Hg has historically been the electrode of choice for ASV but there is an ongoing search for alternate electrodes and diamond is one of these. Our group compared the performance of boron-doped diamond for the anodic stripping voltammetric determination of heavy metal ions $(Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Ag^{+})$ with that of Hg-coated glassy carbon (Hg-GC). Despite the fundamentally different nature of the metal reduction and oxidation reactions on these two electrodes, BDD provides as good or superior analytical detection figures of merit when compared to Hg. The linear dynamic range for BDD was three to four orders of magnitude ($r^2 > 0.995$), similar to Hg-GC. Although BDD is less sensitive than Hg-GC, the lower background current and noise for BDD enabled detection limits as low as those seen for Hg-GC. The minimum concentration of each metal ion detectable (S/N \geq 3) with BDD was in the mid to low ppb range (e.g., 50 ppb Zn^{2+} , 1.0 ppb Cd^{2+} , 5.0 ppb Pb^{2+} , 10 ppb Cu^{2+} and 1.0 ppb Ag^+). BDD exhibited an electrode-to-electrode and run-to-run variability of less than 5%, which is comparable to that for Hg-GC. The results demonstrate that BDD is a viable alternate electrode to Hg for ASV.⁷⁸

B. Other inorganic species

Recently, the concept of an ion-sensitive field effect transistor (ISFET) on diamond using a thin and highly B-doped channel was described.⁷⁹ The doped channel is in direct contact with the electrolyte solution. The diamond surface is O-terminated to provide pH sensitivity and chemical stability. The first pH-sensitive ISFET microstructure with the extrinsically doped channel was fabricated on a 100-oriented single crystal diamond substrate using a solid doping source technique and a wet chemical oxidation for the O-termination. The fabricated structures showed pH sensitivity close to the Nernst's limit of 59 mV/pH. The ISFET characteristics were reproducible and did not degrade after repeated cycling between 0.1 mol/L H₂SO₄ and 0.1 mol/L KOH solutions.⁷⁹

Diamond provides a sensitive, reproducible, and stable response for the electrooxidation of azide, leading to superior detection performance compared with glassy carbon. Suzuki et al. investigated the direct detection of sodium azide using BDD electrodes in three important physiological saline buffers, ADA buffer (N-(2-acetamido) iminodiacetic acid), sodium EDTA and imidazole. Sodium azide concentrations of 502 and 1355 μ g/mL were detected in two samples with relative standard deviations (RSD) of 0.07 and 2.37%, respectively. The results show that the detection of sodium azide with BDD electrode is simple, selective, sensitive and reproducible.⁸⁰

Ivandini et al. studied Pt-modified diamond electrodes for the oxidation of hydrogen peroxide and found that the electrodes exhibited high catalytic activity and excellent electrochemical stability with a very low background current in comparison to a Pt electrode. The electrode was fabricated for electroanalytical applications by ion implantation method at 750 keV Pt²⁺ with a dose of 5×10^{14} cm⁻². Very low limit of detection, 30 nmol/L (S / N = 3), were achieved with RSD of 2.91% (n = 20).⁸¹

Sulfate, which is usually considered to be electrochemically inactive, is difficult to be detected. However, this situation has been changed because of BDD electrode. The extremely wide potential window enables BDD to be used for the electrochemical determination of sulfate according to the following reaction: ⁸²

$$2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e^-$$

Diamond electrodes allow the measurement of sulfate on the anodic side of the potential window through its oxidation into peroxodisulfate, and detection of peroxodisulfate on the cathodic side through the reverse reduction reaction. In all cases, the current density was proportional to the concentrations of sulfate and peroxodisulfate.

Our group reported an accurate method for total inorganic arsenic determination in real water samples using DPASV and a Au-coated boron-doped diamond thin-film electrode. Keys to the method are the use of a conducting diamond platform and solid phase extraction for sample preparation. In the method, the As(III) present in the sample is first detected by DPASV. The As(V) present is then reduced to As(III) by reaction with Na₂SO₃ and this is followed by a second detection of As(III) by DPASV. The method provided reproducible and accurate results for total inorganic arsenic in two contaminated water samples provided by the U.S. Bureau of Reclamation. The total inorganic As concentration in the two samples, quantified by

the standard addition method, was 23.2 ± 2.9 ppb for UV plant influent water and 16.4 ± 0.9 ppb for Well 119 water (n = 4). These values differed from the specified concentrations by less than 4%.^{47,83}

Diamond electrodes are also useful for the detection of other electroactive anion such as nitrite⁸⁴, chlorine, ⁸⁵ iodide,⁸⁶ sulfide,⁸⁷ thiosulfate,⁸⁸ sulfonamides,⁸⁹ and dodecylbenzenesulfonate.⁹⁰

C. Organic species

Boron-doped diamond electrodes have been used to detect aniline by linearsweep cathodic stripping voltammetry. The dimeric species (p-aminodiphenylamine and benzidine) was first formed by anodic oxidation of aniline during the accumulation period, and then it was reversibly reduced in acidic media. The shape of the stripping voltammetric response is suitable for aniline detection in the micromolar concentration range. The low background current of conductive diamond is an advantage compared to other electrode materials and allows a detection limit of 1 μ mol/L. Weak molecular adsorption and good electrochemical stability are additional advantages of BDD and even after long-time measurements, the electrode surface can regain its initial activity by an anodic polarization in the potential region of water decomposition.⁹¹

A mediator-free glucose biosensor, termed a "third-generation biosensor," has been fabricated by immobilizing glucose oxidase (GOD) directly onto an oxidized boron-doped diamond electrode.⁹² It is believed that the surface of the oxidized BDD electrode possesses carboxyl groups which covalently bind to GOD through glutaraldehyde. Glucose was determined in the absence of a mediator used to transfer electrons between the electrode and enzyme. The resulting biosensor exhibited fast amperometric response (less than 5 s) to glucose. The biosensor provided a linear response to glucose over the range 6.67×10^{-5} to 2×10^{-3} mol/L, with a detection limit of 2.31×10^{-5} mol/L. ^{92, 93}

Olivia et al. developed a sensitive and stable glucose biosensor for in vivo monitoring using Pt-modified BDD microfiber (Pt-BDDMF) electrodes. The electrodes were modified with Pt nano-particles to detect H_2O_2 , which was enzymically produced by glucose oxidase (GOx) immobilized on the electrode surface. The electrodes exhibited much higher sensitivity compared to Pt-microfiber electrodes, Pt electrodes and Pt-modified diamond thin film electrodes. GOx/overoxidized polypyrrole (OPPy)/Pt-modified BDDMF electrodes were applied for continuous interference-free glucose monitoring. Amperometric measurements of glucose showed a linear response between 1-70 mmol/L, with a relative standard deviation of 3.7% for five injections of 100 μ mol/L glucose. The electrodes exhibited good stability over 3 months with no detected anodic current for ascorbic acid (AA), which is an interfering compound.⁹⁴

BDD electrodes have also been used for direct and simultaneous determination of phenol (Ph), hydroquinone (HQ) and 4-nitrophenol (4-NP).⁹⁵ Results showed that the oxidative peaks of these 3 phenolic compounds can be completely separated on a BDD electrode in acidic conditions using cyclic voltammetry. The study also demonstrates that the BDD electrode is extremely easy to be refreshed to obtain current values with good reproducibility, even if it is passivated by phenolic compounds with different adsorption characteristics. For each tested phenolic compound, the concentration range with linearity is 2 or 3 orders of magnitude in the presence of other coexisting phenolic compounds with concentrations >1000 times higher than that of the tested component.

Our group reported on the analysis of chlorinated phenols (2-chlorophenol.3chlorophenol. 4-chlorophenol. 2.4-dichlorophenol. 2.4.6-trichlorophenol. pentachlorophenol) in river water using off-line solid-phase extraction (SPE) and capillary electrophoresis coupled with electrochemical detection. A key to the sensitive, reproducible, and stable detection of these pollutants was the use of a boron-doped diamond microelectrode in the amperometric detection mode. Pollutant recoveries in the 95-100% range with relative standard deviations of 1-4% were achieved. The oxidative detection of the pollutants was accomplished at +1.05 V vs. Ag/AgCl without the need for electrode pretreatment. A reproducible electrode response was observed during multiple injections of the chlorinated phenol solutions with a relative standard deviation of 5.4%. Good electrode response stability was observed over many days of continuous use with no significant electrode deactivation or fouling.96-98

Flavonoids are phenol derivatives widely distributed in fruits, nuts, seeds, flowers, vegetable peels, and beverages; they are known to exhibit high antioxidative activities. Pedrosa et al. described the use of boron-doped diamond electrode for the amperometric detection and quantification of flavonoids in tea samples using a flow injection system. The results revealed increasing peak current with rutin concentration in the interval $0.1-2.5 \times 10^{-4}$ mol/L with a detection limit of 7.7×10^{-6} mol/L. The method was used for the determination of rutin in three different green tea infusions. The repeatability of current responses for injections of 150 µL rutin was evaluated to be 2.1% (n = 20).⁹⁹

The attractive features of a boron-doped diamond (BDD) thin-film make it a good choice as a detector for microchip capillary electrophoretic (CE) separations of dye-related amino-substituted aromatic compounds. Shin et al. applied a diamond electrode for the end-column amperometric detection of 4-aminophenol (4-AP), 1, 2phenylenediamine (1,2-PDA), 2-aminonaphthalene (2-AN), 2-chloroaniline (2-CA), and o-aminobenzoic acid (o-ABA).¹⁰⁰ The diamond-based electrochemical detection system displayed a favorable analytical performance, including lower noise levels, higher peak resolution with enhanced sensitivity, and improved resistance against electrode passivation. The diamond detector displayed detection limits of 2.0 and 1.3 μ mol/L for 4-AP and 2-AN, respectively, and a wide linear response for these compounds over the 2-50 μ mol/L range. The enhanced stability was demonstrated by relative standard deviation (RSD) values of 1.4% and 4.7% for 100 μ mol/L 1,2-PDA and 200 μ mol/L 2-CA, respectively, for repetitive detections (n = 7).¹⁰⁰

D. Pharmaceuticals

Naproxen is a non-steroidal anti-inflammatory drug (NSAID) commonly used for the reduction of moderate to severe pain, fever, inflammation and stiffness and the treatment of primary dysmenorrhea. The electrooxidation of naproxen was studied, for the first time, by cyclic and differential pulse voltammetry (CV and DPV) in nonaqueous solvent supporting electrolyte system using boron-doped diamond (BDD) electrode. Naproxen undergoes one-electron transfer resulting in the formation of cation radical for the first electrooxidation step, which follows other chemical and electrochemical steps such as deprotonation, removal of another electron and the attack of nucleophile (ECEC mechanism). BDD electrode provided higher signal to background ratio, well resolved and highly reproducible cyclic voltammograms than the GC electrode. With a scan rate of 50 mV/s and pulse height of 50 ms, respectively, the DPV technique was able to determine the naproxen concentrations in the range of 0.5 to 50 mol/L with a detection limit of 30 nmol/L.¹⁰¹ The wide potential window of BDD electrode makes it very suitable for the determination of special drugs, which are usually nonelectroactive on normal carbon electrodes such as glassy carbon. Some examples are discussed here. Lincomycin is a lincosamide antibiotic that comes from the actinomyces streptomyces lincolnensis. The electroanalysis of lincomycin was investigated using BDD electrode. BDD electrode provided well-resolved oxidation irreversible cyclic voltammogram with the peak position at 1.2 V (vs. Ag/AgCl). The amperometric detection with BDD electrode was coupled with the flow injection analysis for the determination of lincomycin. A linear dynamic range of 0.5–125 μ mol/L and a detection limit of 0.02 μ mol/L were obtained. The recovery was shown to be in the range of 96–103%.¹⁰²

Lidocaine is a common local anesthetic and antiarrhythmic drug. It is used topically to relieve itching, burning and pain from skin inflammations, injected as a dental anesthetic, and in minor surgery. Recently, a new electroanalytical procedure was developed for the determination of the drug in commercial anesthetics. The procedure is based on the use of electrochemical methods, such as cyclic and square-wave voltammetry, with boron-doped diamond electrodes. The oxidation of lidocaine in Britton-Robinson buffer (0.1 mol/L) using this type of electrode gives rise to one irreversible peak in 1.68 V (vs. Ag/AgCl). The detection and quantification limits obtained from pure water were 10.0 and 34.4 μ g/L, respectively. Lidocaine recoveries ranged from 97.6% to 99.2%.¹⁰³

Aspartame (or APM) is the name for an artificial, non-saccharide sweetener, aspartyl-phenylalanine-1-methyl ester; i.e., a methyl ester of the dipeptide of the amino acids aspartic acid and phenylalanine. This sweetener is an ingredient of approximately 6,000 consumer foods and beverages sold worldwide. It is also one of the sugar substitutes used by people with diabetes. Medeiros et al. reported on the determination of aspartame in dietary products using square-wave voltammetry in conjunction with a cathodically pretreated boron-doped diamond electrode. The samples were analyzed without previous treatment in a 0.5 mol/L H₂SO₄ solution. A single oxidation peak at a potential of 1.6 V vs. Ag/AgCl with the characteristics of an irreversible reaction was obtained. The linear range is 9.9×10^{-6} to 5.2×10^{-5} mol/L of aspartame and the detection limit is 2.3×10^{-7} mol/L. The method was applied with success to the determination of aspartame in several dietary products producing results similar to those obtained by HPLC at the 95% confidence level. ¹⁰⁴

Carbaryl (1-naphthyl methylcarbamate) is a chemical in the carbamate family used chiefly as an insecticide. Originally, Union Carbide discovered carbaryl and introduced it commercially in 1958. It remains the third-most-utilized insecticide in the United States for home gardens, commercial agriculture, and forestry and rangeland protection. The anodic voltammetric behavior of carbaryl on a boron-doped diamond electrode in aqueous solution has been reported.¹⁰⁵ The square-wave voltammetric data obtained for carbaryl were typical of an irreversible electrode process with mass transport control. The results, obtained by square-wave voltammetry at 0.1 mol/L Na₂SO₄ and pH 6.0, allow the development of a method to determine carbaryl, without any previous step of extraction., clean-up, preconcentration., or derivatization, in the range 2.5-30.0 \times 10⁻⁶ mol/L with a detection limit of 8.2 µg/L in pure water.¹⁰⁵

BDD electrode has also been used in pharmaceutical formulations because of its rapidity, precise and good selectivity for electrochemical analysis. For example, methods using flow injection (FI) with amperometric detection at anodized borondoped diamond (BDD) thin films have been developed and applied for the determination of tetracycline antibiotics (tetracycline, chlortetracycline, oxytetracycline and doxycycline).¹⁰⁶⁻¹⁰⁸ The anodized BDD electrode exhibited welldefined irreversible cyclic voltammograms for the oxidation of tetracycline antibiotics with the higher currents compared to as-deposited BDD and glassy carbon electrodes. A low detection limit of 10 nmol/L (S/N = 3) was achieved for each drug when using flow injection analysis with amperometric detection using an anodized BDD electrode. Linear calibrations were obtained from 0.1 to 50 nmol/L for tetracycline and 0.5–50 nmol/L for chlortetracycline, oxytetracycline and doxycycline.¹⁰⁶⁻¹⁰⁸

Modified BDD electrode has also been used for drug determination. For example, the Ru(bpy)₃³⁺-modified boron-doped diamond electrode has strong electrocatalytic effects on the redox behavior of Vitamin B₆ (VB₆).¹⁰⁹ The oxidization and reduction peak potentials of VB₆ are 167.6 and -113 mV, respectively. In the presence of a large amount of Vitamins B₁ (VB₁) and B₂ (VB₂), the redox peak potentials of VB₆ shift slightly while VB₁ and VB₂ are not reduced or oxidized on the modified electrode. A sensitive square wave voltammetric response for VB₆ is obtained covering a linear range from 0.2775 μ mol/L to 0.3686 mmol/L with a detection limit of 6.319 × 10⁻⁸ mol/L in the presence of a large amount of VB₁ and VB₂. The modified electrode showed good stability and reproducibility with satisfactory recovery results.¹⁰⁹

E. Biosensor

Recently, diamond has been used extensively in this area due to its excellent response sensitivity, reproducibility, pH independent current and its minimal surface fouling. ^{110, 111} Dopamine is a hormone and neurotransmitter occurring in a wide variety of animals, including both vertebrates and invertebrates. In the brain, dopamine functions as a neurotransmitter, activating the dopamine receptors and their variants. Dopamine is also a neurohormone released by the hypothalamus. Its main function as a hormone is to inhibit the release of prolactin from the anterior lobe of the pituitary. The electrochemical reaction of dopamine on carbon electrodes has been extensively studied.¹¹²⁻¹¹⁸

Norepinephrine or noradrenaline is anther catecholamine with dual roles as a hormone and a neurotransmitter. It is released from the adrenal medulla into the blood stream as a hormone, and is also a neurotransmitter in the central nervous system and sympathetic nervous system where it is released from noradrenergic neurons. The actions of norepinephrine are carried out via the binding to adrenergic receptors. As a stress hormone, norepinephrine affects parts of the brain where attention and response actions are controlled. Along with epinephrine, norepinephrine also underlies the fight-or-flight response, directly increasing heart rate, triggering the release of glucose from energy stores, and increasing blood flow to skeletal muscle.¹¹⁹ Our group published several papers¹²⁰⁻¹²² on the *in vitro* continuous amperometric measurement of norepinephrine with a boron-doped diamond microelectrode. This new microelectrode, without any protective polymer coating, exhibited a sensitive and stable voltammetric response for norepinephrine released from sympathetic nerves innervating a mesenteric artery from a laboratory test animal. The background voltammetric current was low and stable over time and independent of the solution pH. The microelectrode was also used in electrochemical detection, coupled with capillary zone electrophoresis, to analyze solutions for norepinephrine, other catecholamines and their major metabolites. In the amperometric detection mode, the microelectrode exhibited good response sensitivity, low mass limits of detection (100-400 amol, S/N = 3) and excellent response reproducibility (RSD = 2-4%) without any conventional pretreatment.¹²¹ BDD electrodes have also been used to determine other biochemical species such as cysteine,¹²³ tyrosine,¹²⁴ ascorbic acid,¹²⁵ serotonin (5-HT),^{125, 126} adenosine,¹²⁷ myoglobin,¹²⁸ haemyoglobin,¹²⁸ purine,¹²⁹ and pyrimidine.¹²⁹

F. Electrosynthesis

Because of the outstanding inert chemistry of the BDD electrode, it has been used in the electrosynthesis of some chemicals. For example, Canizares et al. reported the electrosynthesis of ferrates using boron doped diamond (BDD) anodes. Their results show that BDD electrode leads to efficient processes only limited by the availability of oxidizable-iron species. The hydroxyl ion concentration, the current density and the iron raw material were found to influence greatly on the results. Thus, the efficiencies of the process were increased using high current density and high concentration of hydroxyl anions.¹³⁰

Electrolytic synthesis of ammonia with a byproduct oxygen gas from water vapor and nitrogen gas was demonstrated in LiCl-KCl-CsCl melt containing 0.5 mol/L Li₃N at 573 K under atm. pressure. Water vapor reacted with nitride ions to form ammonia and oxide ions in the melt. The consumed nitride ions were supplied by the reduction of nitrogen gas at the cathode and the formed oxide ions were oxidized to oxygen gas at a boron-doped diamond anode.¹³¹

Fardel et al. studied the anodic methoxylation of formaldehyde dimethylacetal (FADMA) to tri-Me orthoformate (TMOF) in basic MeOH on B-doped diamond electrodes. Cyclic voltammetry and preparative electrolysis showed that FADMA is electrochemically inactive in the solvent stability region; nevertheless FADMA can be oxidized in the potential region of MeOH oxidation.¹³²

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G. Spectroelectrochemistry

Spectroelectrochemistry is a hybrid of two techniques: spectroscopy and electrochemistry. The technique (transmission mode) can be used to record a change in the spectroscopic signature of an analyte associated with an alteration in redox state brought about by electron transfer with an optically transparent electrode (OTE). Boron-doped diamond (BDD) possesses attractive qualities as an OTE: a wide optical window from the near-UV extending into the far-IR (0.25-100 μ m) region of the electromagnetic spectrum, a wide working potential window (>3 V in aqueous media), low background current, microstructural stability during cathodic and anodic polarization, and resistance to molecular adsorption and fouling. Our group has been developing optically transparent diamond for use in the spectroelectrochemical measurements for some time now.¹³³⁻¹³⁶ The latest review of this field has been published by Dai et al.^{136, 137}

H. Fuel cell and power devices

In the development of fuel cells for transportation, there is a need to develop advanced catalyst-support materials that can stably function, i.e., without microstructural or morphological degradation or lost catalytic activity at the elevated temperatures (150–200 °C) in aggressive chemical environments. sp²-bonded amorphous carbons and graphite are the most commonly used support materials. A limitation of these supports is their susceptibility to corrosion, in the presence of oxygen or in aggressive chemical environments, at elevated temperature.¹³⁸ The high surface area carbon used as fuel cell electrocatalyst (nanoparticles consisting of Pt, Ru and other metals) supports are being targeted for replacement with diamond to take advantage of the superior stability and chemical modifiability of diamond.¹³⁹ The

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modification of BDD powder with metallic oxides, using the sol-gel method to prepare high area and very stable electrodes for the MeOH oxidation reaction in MeOH fuel cell, has been reported.¹⁴⁰

J. Superconductivity

Another attractive property of boron-doped diamond is its superconductivity. The recent observation of superconductivity emerging near the insulator-to-metal transition in heavily B-doped diamond has stimulated a discussion on the fundamental origin of the metallic states responsible for the superconductivity.^{141, 142} The physical properties of lightly doped semiconductors are well described by electronic bandstructure calculations and impurity energy levels. Such properties form the basis of present-day semiconductor technology. If the doping concentration (n) exceeds a critical value (n_c) , the system passes through an insulator-to-metal transition and exhibits metallic behavior; this is widely accepted to occur as a consequence of the impurity levels merging to form energy bands. Researches show that the dopingdependent occupied electronic structures are consistent with the intrinsic diamond bands, indicating that holes in the diamond bands play an essential part in determining the metallic nature of the heavily B-doped diamond superconductor. This supports the diamond band approach and related predictions, including the possibility of achieving dopant-induced superconductivity in Si and Ge.¹⁴³ This conclusion is still controversial. 136, 142

1.3 Motivation and research questions

BDD exhibits a low background current, making it useful in analytical applications where low concentrations of analyte need to be detected.^{144, 145} It also has

a wide potential window in aqueous media of 3 - 4 V, which allows electrochemically active species to be detected that may be masked by the solvent decomposition and surface reactions at other electrode materials. Other desirable properties, such as the chemical inertness, as well as its hardness and robustness, have led to applications where electrode stability is important, such as in wastewater treatment. However, the relationship between the physical, chemical and electronic properties of BDD and its electrochemical performance is still incompletely understood. In recent years, several groups have made progress learning how different factors control the electrochemical properties. For example, several authors have investigated the kinetics and mechanisms of heterogeneous redox reactions at BDD, and two general models for electron-transfer have emerged:^{3, 146-151} (i) electron-transfer mediated by electronic states within the band gap of BDD with the rate of the electron-transfer being relatively uniform across the surface but controlled by the potential-dependent density of states and (ii) electron-transfer through a partially blocked electrode that consists of highly conductive or active sites isolated by less conductive or inactive sites. Evidence supporting the second model comes from investigations of electron emission from diamond; a process that involves electron-transfer across a solidvacuum interface and is analogous to electron-transfer across a solid-liquid interface. It has been reported that boron-doped diamond films with higher electrical conductivity exhibited a lower turn-on voltage for field emission.^{152, 153} The electron emission was observed to occur from sites of high electrical conductivity. The possibility of some channel and/or grain boundary conduction was proposed.^{152, 153}

Developing an understanding of electrochemical reaction rates at diamond and their heterogeneity (i.e., the spatial nature of the electrochemical activity) across an electrode requires the ability to characterize and spatially distinguish the physical, chemical and electrical properties. Without question, polycrystalline diamond is one of the most complex carbon electrodes with factors such as the boron-doping level. hydrogen content, grain boundary density and electric double layer structure affecting electron-transfer rates. For boron-doped microcrystalline diamond, several papers describe the spatially inhomogeneous nature of the physicochemical properties, such as the variable distribution of boron in doped polycrystalline diamond.^{154, 155} Raman imaging, electrogenerated chemiluminescence imaging and photoluminescence measurements have revealed variations in the microstructure, electrical properties and electrochemical activity across a microcrystalline diamond thin-film surface.¹⁵⁶⁻¹⁵⁸ Recently reported electron emission studies from hydrogen-terminated and chemically-modified boron-doped nanocrystalline diamond films were consistent with a heterogeneous surface having different local work functions.¹⁵⁹ This conclusion was reached based on electron energy distribution measurements that were made as a function of temperature. If a complete picture of the structure-reactivity relationship at boron-doped polycrystalline diamond is to be developed, then probes of the film properties at the microscopic level are needed.

Conducting probe-atomic force microscopy (CP-AFM) is a technique that is useful for investigating the electrical properties of conductors and semiconductors with high spatial resolution.^{160, 161} Both nanoscale electrical characterization and topographic imaging are provided by CP-AFM. The technique usually employs a metal-coated (Pt or Au) cantilever-tip assembly that functions as both a scanning electrical contact and force sensor. Metal wire probe tips can also be used.¹⁶² Thus, direct measurements of I-V curves at specific topographical sites on an electrode are possible. CP-AFM has been used to probe the conductivity across hydrogenterminated BDD thin-film electrodes with different boron-doping levels,¹⁶³ oxygenterminated BDD¹⁶⁴ and undoped diamond films.¹⁶⁵ The general observation, at least in some of the work, is that the electrical conductivity is variable across polycrystalline diamond with a strong dependence on the grain orientation, fraction of grain boundary and the boron-doping level.^{163, 165} On the other hand, Macpherson and coworkers observed much less spatial variability in the electrical and electrochemical properties across smooth polished, oxygen-terminated diamond.¹⁰²

Our group has reported on the heterogeneous nature of the microstructure and electrochemical activity of polycrystalline BDD using Raman microprobe spectroscopy and electrogenerated chemiluminescence imaging.^{156, 157} Additionally, a pattern of variable conductivity and electrochemical activity at hydrogen-terminated boron-doped microcrystalline diamond electrodes, with different boron doping levels, were measured using CP-AFM and SECM.^{163, 166}

Although work has been performed to study the electrical and electrochemical properties of boron-doped diamond thin-film electrodes, they still possess some characteristics that are not fully understood from a fundamental view point. Principle among these is the mechanism of electron exchange between the diamond surface and solution redox species, especially the effect of the electrode surface chemistry. To gain better insight on heterogeneous electron transfer process, research was conducted to answer the following questions:

1. What is the spatial uniformity of the electrical conductivity of boron-doped microcrystalline and nanocrystalline diamond thin films?

2. What factors contribute to the electrical conductivity (e.g., boron-doping level, surface hydrogen, surface oxygen and nitrogen compensators)?

3. How does the uniformity of the electrical properties correlate with the spatial uniformity of the electrochemical reaction rates across the electrode surface for various outer-sphere redox systems?

1.4 Research goals and objectives

The research described herein investigated (i) the electrochemical behavior of BDD thin-film electrodes toward different redox systems using cyclic voltammetry, (ii) the surface chemistry of BDD electrodes and the effect on electron-transfer kinetics for various redox systems, (iii) the uniformity of the electrical conductivity and electrochemical activity across the diamond electrode and gaining a better understanding of structure-function relationship of these interesting features.

1.5 Dissertation outline

This dissertation is divided into eight chapters. Chapter 1 provides background information about boron-doped diamond: its properties and applications. In Chapter 2, experimental details are given about the growth of doped diamond and the electrochemical measurements performed. Included in this chapter are details of the surface modifications used, experimental details for the characterizations of borondoped diamond thin films including scanning electron microscopy, Raman spectroscopy and electrochemical measurements. The experimental details about the in vitro determination of norepinephrine at the blood vessel surface are also presented. Chapters 3 - 5 present results for the characterization of boron-doped diamond thin film electrodes. In this part, the physical, chemical, and electrochemical properties of two types of polycrystalline diamond thin films are studied. The surface microstructure and electrochemical characterization of microcrystalline and nanocrystalline boron-doped diamond electrodes are described in Chapter 3. Chapter 4 presents work on applying conductive-probe atomic force microscopy to two types of polycrystalline BDD thin films to investigate the relationship between electrical conductivity and doping level, morphology, bias level, bias polarity and surface termination. The relationship between electrochemical activities of BDD thin films and grain size, doping level, surface terminations and redox systems studied via scanning electrochemical microscopy is presented in Chapter 5. Chapter 6 compares the physical, chemical and electrochemical properties of two nanocrystalline BDD films from different sources. Chapter 7 describes preliminary work on the use of boron-doped diamond microelectrodes to measure norepinephrine overflow from sympathetic neuroeffector functions at mesenteric arteries and veins in the presence and absence of sensory nerve input. Chapter 8 summarizes the conclusions reached from this work and identifies future direction of the research.

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Chapter 2

Experimental Section

2.1 Preparation and characterization of boron-doped diamond thin-film electrodes

2.1.1 Chemical vapor deposition conditions

Microwave plasma-assisted CVD was used to grow both microcrystalline and nanocrystalline diamond thin films.¹⁻³ For all growths, boron was introduced by adding diborane to the source gas mixture. A block diagram of a typical reactor is shown in Figure 2.1. Briefly, the source gases (e.g., Ar, H₂, CH₄, and B₂H₆) enter the chamber at controlled rates regulated by mass flow controllers. Microwave energy is focused into the quartz cavity and ignites a plasma. The plasma, which is in close proximity to the substrate, contains the reactive species necessary for growth. The chamber pressure is maintained by a throttle exhaust valve and rotary pump that are operated continuously during film growth.

The specific deposition conditions used for the growth of each type of diamond thin film on Si are summarized in Table 2.1. All source gases were ultrahigh purity (99.999%). The substrate was highly conducting p-Si (111) (0.05 cm thick \times 1 cm² in area, \sim 10⁻³ ohm-cm, Virginia Semiconductor Inc., Fredricksburg, VA) and was prepared for film growth by mechanically scratching the surface with 0.1 μ m diameter diamond powder (GE Superabrasives, Worthington, OH) slurried in water on a felt polishing pad. The scratched substrate was then copiously rinsed with ultra-



Figure 2.1 Schematic commercial MPCVD system (ASTex Inc., Lowell, MA) used for growing microcrystalline and nanocrystalline boron-doped diamond thin films.

pure water (~18 M Ω -cm, Barnstead E-Pure), isopropyl alcohol (IPA, Fisher Scientific), acetone (Mallinckrodt), IPA, and ultrapure water to remove all polishing debris from the surface. Embedded diamond powder particles, as well as the polishing striations, serve as the initial nucleation sites for diamond growth. A high density of these sites leads to a high instantaneous nucleation density, which is necessary for forming a continuous film at a low nominal thickness. Microcrystalline boron-doped diamond was deposited at 1000 W using a $CH_4/H_2/B_2H_6$ source gas mixture consisting of 0.5% CH₄ in 99.5% H₂ with 10, 5, 1, 0.5 or 0 ppm diborane (0.1% B₂H₆ diluted in H₂) added for boron doping. The system pressure was 45 torr, the substrate temperature was ca. 750 °C, as estimated via an optical pyrometer, and the growth time was 10 h. At the end of the deposition period, the CH₄ and B_2H_6 gas flows were stopped and the films remained exposed to an H₂ plasma at 1000 W and 45 torr for an additional 10 min. The plasma power and pressure were then slowly reduced over 5 min to cool the sample in the presence of atomic hydrogen to a temperature estimated to be less than 400 °C. The plasma power was then turned off and the films were further cooled to room temperature under a flow of H₂. Post-growth annealing in atomic hydrogen served to gasify any adventious nondiamond sp² carbon impurity, to minimize dangling bonds, and to fully hydrogenate the surface.

Nanocrystalline diamond was deposited at 800 W using a $CH_4/H_2/Ar/B_2H_6$ source gas mixture consisting of 1% CH_4 and 5 % H_2 in 94% Ar, with 50, 10, 1 or 0 ppm diborane (0.1% B_2H_6 diluted in H_2) added for boron doping. The system pressure was 140 torr, the substrate temperature was ca. 750 °C, as estimated via an optical pyrometer, and the growth time was 2 h. At the end of the deposition period, the CH_4 and B_2H_6 gas flows were stopped and the film remained exposed to an Ar/H_2 plasma at 800 W and 140 torr for an additional 10 min. The Ar flow was then stopped, and the plasma power and pressure were then slowly reduced over 5 min to cool the sample in the presence of atomic hydrogen to a temperature below 400 °C. The plasma power was then turned off and the films were further cooled to room temperature under a flow of H_2 .

Boron-doped nanocrystalline diamond thin films, deposited on conducting Si, were also provided from Dr. James Butler (Naval Research Laboratory, Washington, DC, USA). The exact deposition conditions were not disclosed. These films were used for the comparison with our films, as discussed in Chapter 6.

 Table 2.1
 Growth conditions for microcrystalline and nanocrystalline boron

 doped diamond thin films deposited on Si.

	Microcrystalline	Nanocrystalline	
Microwave Power	1000 W 800 W		
Chamber Pressure	45 Torr 140 Torr		
Gas Mixture	CH ₄ /H ₂ /B ₂ H ₆ Ar/H ₂ /CH ₄ /B ₂ H		
Methane Concentration	0.5% CH ₄	CH4 1% CH4	
Total Gas Flow	200 sccm	100 sccm	
Substrate Temperature	~750 °C ~750 °C		
Growth Time	10 h	2 h	

2.1.2 Characterization of Boron-doped diamond thin films

A. Morphology

In an attempt to better understand the influence of the diamond particle size on the electrical conductivity and electrochemical activity, both microcrystalline and nanocrystalline of boron-doped diamond thin films were studied. Typical diamond film thicknesses, resistivities, carrier concentrations, and carrier mobilities are listed in Table 2.2.

Table 2.2Film thickness, resistivity, carrier concentration, and carrier mobilityfor typical microcrystalline and nanocrystalline boron-doped diamond thin films.

Туре	Film Thickness (µm)	Resistivity (Ω-cm)	Carrier Concentration (cm ⁻³)	Carrier Mobility (cm²/V-s)
Microcrystalline	~ 5-7	0.01-0.1	~10 ¹⁹	10-40
Nanocrystalline	~ 5	0.2	~10 ²⁰	0.1-1
B. Doping level

Boron is the most efficient dopant for diamond because of the high concentration that can be achieved without significant alteration in the diamond microstructure, and the low activation energy for carrier production (0.34 eV). It is not possible to uniformly dope diamond as various growth sectors uptake different concentrations of the dopant.⁷⁻⁹ Ushizawa et al. studied how the addition of boron can affect various factors including crystal morphology and quality.¹⁰ They found that a small amount of diborane added to the source gas improves the diamond crystal quality. Characteristic changes occur in the spectra for heavily doped compared to lightly doped films.¹¹ More recently, Tokuda et al. reported surface roughening of heavily boron-doped diamond films caused by the boron concentrations of 10^{17} to 5 \times 10²⁰ atoms/cm³.^{12, 13} Obviously, the most important role of boron in p-type diamond is as a dopant. The boron concentration in a film determines the electrical conductivity. Boron substitutes for carbon atoms in the growing lattice and also aggregates in grain boundaries.^{5, 14, 15} The former boron is the electrically active type. Therefore, in this work, both microcrystalline and nanocrystalline diamond films with different doping levels were studied to learn how the addition of boron affects the film morphology, electrical conductivity and electrochemical activity. The properties of the different microcrystalline and nanocrystalline diamond films used in this work are listed in Table 2.3.

The doping level (B/C ratio in the film) for both films increases proportionally with the concentration of diborane in the source gas mixture. Therefore, in this dissertation, we refer to the films in terms of the diborane concentration used during film deposition.

Туре	Film thickness (µm)	[B ₂ H ₆] in source gases (ppm)	B/C ratio in film (ppm)*	[B] in film (cm ⁻³)	Resistivity (Ω-cm)**
Microcrystalline	~ 5-7	0	48	8.5×10^{18}	5180
		0.5	230	4.0×10^{19}	37.93
		1	325	5.7 × 10 ¹⁹	0.591
		5	2280	4.0×10^{20}	0.185
		10	3285	5.8×10^{20}	0.016
Nanocrystalline	~ 5	0	58	1.0×10^{19}	14638
		1	247	4.3×10^{19}	41.81
		10	1401	2.5×10^{20}	0.264
		50	2144	3.8×10^{20}	0.0186

Table 2.3Diamond films with different doping levels used in this work.

*: Measured by boron nuclear reaction analysis at Case Western Reserve University. Courtesy of Dr. Alan Mcllwain.

**: Calculated using $\rho = 4.532 dr$, where d is the film thickness ($d = 6 \mu m$ for microcrystalline films and $d = 5 \mu m$ for nanocrystalline films), r is the resistance measured in a 4-point configuration using spring-loaded tips.

2.1.3 Surface termination

Since the discovery of "surface conductivity (SC)" by Landstrass and Ravi,^{16,} ¹⁷ many studies have shown that the surface termination can influence the electrical properties of diamond¹⁸⁻²¹. For boron-doped diamond grown via MPCVD, the "as grown" diamond surface is hydrogen-terminated because the deposition occurs in a hydrogen-rich plasma. However, this surface is not immune to oxidization. Therefore, knowledge of the interaction of hydrogen and oxygen on diamond surface is crucial to the application of BDD thin films in electrochemistry. It is well known that BDD thin films with different surface terminations exhibit different performance in electrochemistry and electron emission^{6, 14, 22, 23}, but the relationship between the electrical properties and the microstructure and the surface chemistry of polycrystalline diamond, especially for nanocrystalline diamond, remains unclear. To address the issue of surface heterogeneity, hydrogen and oxygen terminated boron-doped diamond films were prepared.

A. Oxidation of the diamond film

Surface oxidation was accomplished by exposing the film to warm (~ 60 °C) aqua regia (3 parts hydrochloric acid/1 part nitric acid, V/V) for 30 min to oxidatively remove metallic impurities. The electrode was then copiously rinsed with ultrapure water, isopropyl alcohol, acetone, IPA, and ultrapure water after cooling to room temperature. The electrode was then immersed in a warm 30% peroxide hydrogen solution (Columbus Chemical Industries, Inc.) for another 30 min for further oxidative removal of nondiamond sp² carbon impurity. This was followed by rinsing with pure water, IPA, acetone, IPA, and ultrapure water. These chemical treatments not only clean the surface but also introduce surface carbon-oxygen functional groups. For example, the XPS atomic oxygen to carbon ratio increased from <0.02 to ca. 0.15 after this wet chemical oxidation. Consistent with a hydrophilic, oxygenated surface, the contact angle for water decreased from >70° to <5°. ⁶

B. Hydrogenation of the diamond film

Surface hydrogenation was achieved by first cleaning the diamond surface in acid, as described above. This was followed by exposing the oxidized film to a hydrogen plasma. The plasma was generated by MACVD using a commercial reactor (1.5 kW, 2.54 GHz, ASTex Inc., Lowell, MA) at 1000 W using pure H_2 gas. The system pressure was 45 torr, the substrate temperature was ca. 750 °C, as estimated via an optical pyrometer, and the treatment time was 30 min. At the end of the hydrogenation, the plasma power and pressure were slowly reduced over 5 min to cool the sample in the presence of atomic hydrogen to a temperature estimated to be less than 400 °C. Surface hydrogen, which is the hydrogen bonded to the terminal carbon atoms, does not desorb at these temperatures. The plasma power was then turned off and the films were further cooled to room temperature under a flow of H_2 .

C. Heat treatment of the diamond film

In 1989, when Ravi and Landstrass first reported SC on single crystal and CVD diamond, the phenomenon was exclusively attributed to the presence of hydrogen.^{16, 17} However, in recent years the role of atmospheric species in the formation of a hole accumulation layer near the film surface has even established. It is well established that a *p*-type surface conductive layer (SCL) exists at the surface of as-grown CVD or hydrogen-terminated poly- and single-crystalline diamond, independent of crystallographic orientation, although the removal of SCL on different crystallographic orientations requires different conditions.^{21, 24, 25} The SCL has been attributed to *p*-type carriers with a lateral concentration of up 10¹³ cm⁻² and a mobility between 30 and 100 cm²/Vs showing only weak temperature dependence in the range of 120 – 400 K.^{18, 19} The mobility is similar to the hole mobility measured for boron-doped polycrystalline diamond.²⁶ Thus, there is general agreement that the carriers are holes residing in an accumulation layer close to the surface. Furthermore, it has been shown that the conductivity of the SCL is closely linked to an adsorbate layer, which covers the diamond surface when exposed to air.^{27, 28} However, the mechanism by

which the hole accumulation layer forms is still controversial. Maier *et al.*²⁹ have proposed an electrochemical model in which electrons are transferred from the diamond valence band to solvated H_3O^+ ions in a water layer that spontaneously forms in air. This model is supported by recent theoretical³⁰ and experimental studies.^{20, 21}

On the other hand, experiments have shown that exposure to different gases can affect the conductivity by many orders of magnitude,³¹ and that the SCL can be eliminated by oxidation treatments.^{16, 17} In these cases, the SCL on polycrystalline or homoepitaxial (001) diamond surfaces was removed and high resistive diamond was generated. Therefore, many researchers have pointed out that hydrogen atoms play an important role in the formation of SCL. From these results, it is generally accepted that no SCL exists on oxidized diamond surfaces. This may not be true. Recent research by Riedel et al. confirmed that the SCL can not be eliminated by oxidation treatment. Their results showed that SCL on the (001) surface was maintained in an ozone-rich atmosphere up to a partial oxygen coverage of ~40%.³²

To test the role of subsurface hydrogen, we investigated the electrochemical behavior of hydrogen terminated boron-doped diamond thin-film electrodes with different doping levels before and after annealing in Ar at 400 °C. At this temperature the chemisorbed surface hydrogen remain in tact but B-H couples are broken. Cyclic voltammograms for $Fe(CN)_6^{3-/4-}$, $Ru(NH_3)_6^{3+/2+}$ and $IrCl_6^{2-/3-}$ were recorded using hrdogen-terminated diamond electrodes. The concentration for all redox species was 0.1 mmol/L, unless otherwise stated, and the supporting electrolyte was 1 mol/L KCl. After electrochemical measurements, all electrodes were acid-washed, as described in 2.1.3A and rehydrogenated as described in section 2.1.3B. The electrodes were then heat treated in a tube furnace to desorb the hydrogen. The system is shown in Figure

2.2. Ar was passed continuously through the tube for 30 min before the furnace was switched on and adjusted to temperature. The temperature was ramped at a rate of 20 °C/min until 400 °C was reached. Once reached, the annealing was done for 30 min at 400 °C. The power of the furnace was adjusted to decrease the temperature of the chamber back to room temperature at -20 °C/min. One of the electrodes was then taken out of the chamber after cool-down and mounted in an electrochemical cell for immediate electrochemical studies. The others were kept in the furnace under an Ar purge until use.



Figure 2.2 The tube furnace heating system used for heat treating diamond thin films in Ar.

2.1.4 Boron-doped diamond microelectrodes

A. Growth of boron-doped diamond thin films on Pt wire

Boron-doped diamond microelectrodes were prepared by coating sharpened Pt wire substrates by microwave-assisted chemical vapor deposition (CVD).^{33, 34} There are only a few reports describing the preparation and basic electrochemical characterization of diamond microelectrodes³⁵⁻³⁹. Diamond microelectrodes have been found to provide superior detection figures of merit, as compared to carbon fibers in terms of linear dynamic range, limit of detection, response variability and stability⁴⁰. The Pt wire was first etched electrochemically in 1 M KOH to form a conical shape. An etching solution containing 7.0 g of CaCl₂•H₂O in a mixture of 20 mL of ultrapure water and 20 mL of acetone also functioned well.^{33, 41} A 1.4 cm long piece of Pt wire (99.99%, Aldrich Chemical, 76 µm diam) was used. Both ends of the wire were sharpened so that two electrodes could be made from one wire. The wire end was immersed to a depth of 1 to 2 mm and positioned in the center of four connected carbon rod counter electrodes during the etching, as shown in Figure 2.3. An AC polarization of 12 V (60 Hz) was applied between the wire and the counter electrodes using a variable autotransformer (Staco Energy Products, Dayton, OH). The etching procedure lasted for approximately 5 s until gas evolution visibly ceased at the tip.

The etched wire was conically-shaped near the end and cylindrically-shaped above. Prior to diamond deposition, the sharpened wire was ultrasonically cleaned in acetone (10 min) and ultrasonically seeded (30 min) in a diamond powder suspension (5 nm particles, ca. 20 mg in 100 mL of ethanol, Tomai Diamond Co., Tokyo, Japan). In order to prevent damage to the sharpened end, the wire was cleaned and seeded while vertically suspended in the agitated solution. During the seeding process, the surface was scratched by the diamond particles with some particles getting embedded. Both the scratches and the embedded particles likely serve as the initial nucleation sites for film growth. A high instantaneous nucleation density is desired because this leads to the formation of a continuous film in the shortest time with a low nominal thickness. A thin film of boron-doped diamond was then deposited on the sharpened, cleaned and seeded wire using the same commercial CVD system we used for the growth of the planar diamond thin film. The pretreated Pt wires (~ 5-6 in parallel per deposition run) were mounted horizontally on the top of a quartz plate ($10 \times 10 \times 1$ mm) in the reactor. The quartz plate was placed in the center of the reactor's molybdenum substrate stage and served to thermally isolate the wires. The thin film of boron-doped diamond was deposited from a 0.5% CH₄/H₂ (V/V) source gas mixture with 4 ~ 5 ppm of diborane (0.1 % B₂H₆ diluted in H₂) added for doping.



Figure 2.3 Schematic of the assembly used to electrically sharpen the Pt wire substrates.

Table 2.4 summarizes the growth conditions used for depositing boron-doped diamond on the Pt wires. All source gases were ultrahigh purity grade (99.999%). The system pressure was 45 Torr, the substrate temperature was ca. 300 °C, or less, (as estimated with an optical pyrometer), the microwave power was 400 ~ 600 W and the total gas flow was 200 standard cubic centimeters per min (sccm) during growth. The deposition time was 10 h. After deposition, the CH₄ and B₂H₆ gas flows were shut-off and the films cooled in the presence of atomic hydrogen (H₂ plasma) by slowly reducing the plasma power and system pressure over a 30 min period. This post-growth treatment was necessary for removing adventitious sp² carbon impurity, minimizing dangling bonds and ensuring full hydrogen termination. Under these conditions, the nominal growth rate was estimated to be about 0.3 μ m/h based on the final film thickness of 3-5 μ m. Once coated, the diameter of the cylindrical portion was approximately 80 μ m.^{33, 36, 41}

Table 2.4Growth conditions for microcrystalline boron-doped diamondmicroelectrode on *Pt* wires.

	Microcrystalline	
Microwave Power	400 ~ 600 W	
Chamber Pressure	40 ~ 45 Torr	
Gas Mixture	CH ₄ /H ₂ /B ₂ H ₆	
Methane Concentration	0.5% CH4	
B ₂ H ₆ Concentration in gas mixture	4 ~ 5 ppm	
Total Gas Flow	200 sccm	
Substrate Temperature	~300 °C	
Growth Time	10 h	

B. Insulation of boron-doped diamond microelectrode

For the electroanalytical measurements, the diamond microelectrode was attached to a Cu wire with conductive epoxy. Each electrode was then sealed in polypropylene.^{42, 43} This was accomplished by inserting the microelectrode into a pipette tip and carefully heating the tapered end using the heating coil of a P-30 micropipette puller (Sutter Instrument Co. Novato, CA).

Details of the procedure are given below:

- 1. Cut all diamond-coated Pt wires into two pieces.
- 2. Cut copper wire into pieces of appropriate length (several cm's).
- 3. Prepare conductive epoxy mixture.
- 4. Dip one end of the copper wire into the epoxy.
- 5. Contact the copper and Pt wire and allow epoxy to cure. Make sure the conical end of the Pt wire (etched end) is not contacted by the epoxy.
- 6. Leave the epoxy overnight in air.
- 7. Cut and insert the diamond/copper wire into a pipette tip.
- 8. Mount the pipette tip and wire in the micropipette puller, make sure the diamond cone protrudes from the end of the tip.
- 9. Switch on the heating coil of the micropipette puller to heat up the tip.
- 10. Gently pull up the copper wire to keep same length of coated Pt wire exposed when the micropipette tip starts to melt and shrink.

- 11. Turn off the heater when the hole in the tip is totally sealed and wait for $2 \sim 3$ s, then gently push down the copper wire to make the end of the tip a conical shape.
- 12. Fix the copper wire inside the tip with normal epoxy and wait another overnight before the microelectrode can be tested.

The final product is schematized in Figure 2.4.



Figure 2.4 Diagram of the insulated boron-doped diamond microelectrode.

2.2 Scanning Electron Microscopy (SEM)

The SEM was performed using a JSM-6300F (field emission) scanning electron microscope (JEOL Ltd., Tokyo, Japan, Center for Advanced Microscopy at Michigan State University). The images were constructed from both secondary and backscattered electrons with an accelerating voltage of 10 kV.

It is difficult to figure out the crystalline nature of nanodiamond films from the plan-view SEM images. Therefore, transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) were used to examine the phase composition of the nanodiamond films. All TEM and SAED images were performed using a JEOL2200FS transmission electron microscope (JEOL Ltd., Tokyo, Japan, Center for Advanced Microscopy at Michigan State University). The samples used for TEM were prepared involving chemically etching and ion milling, as shown below.

- Diamond thin films grown on Si were immersed in a mixed acidic solution of hydrochloride acid (HCl), hydrofluoride acid (HF) and acetic acid (HAc) to get free-standing diamond films.
- 2. Carefully cut the free-standing films into pieces of ca. $3 \times 3 \text{ mm}^2$.
- 3. Stick a small piece of diamond film onto a copper grid slot used for TEM.
- 4. Mount the grid slot to the sample holder of the ion milling instrument with melted wax.
- 5. Set the milling conditions as follow:

High voltage: 4 kV, Incident angle: 4°, Milling mode: one side.

 Carry out ion milling till the proper thickness of the diamond film reaches (~ 100 nm, the film will be totally transparent).

2.3 Raman Spectra

Raman spectra were acquired at room temperature using a RAMAN 2000 spectrograph (Chromex, Inc., Albuquerque, NM) that consisted of a diode-pumped, frequency-doubled continuous wave (CW) Nd:YAG laser (500 mW at 532 nm, COHERENT), a Chromex 500 spectrometer (f/4, 600 grooves/mm holographic grating), and a thermoelectrically cooled 1024 x 256 element charge-coupled device (CCD) detector (ANDOR Tech., Ltd., South Windsor, CT). Spectra were collected with an incident power density of ca. 500 kW/cm² (100 mW at the sample and 5 μ m diameter spot size) and a 10 s integration time. A white-light spectrum was collected under the same conditions and served as the background for spectral correction. The spectrometer was calibrated (wavelength position) with 4-acetamidophenol (CH₃CONHC₆H₄OH) and a high pressure, high temperature (HPHT), single crystal diamond sample (first-order phonon position = 1332 cm^{-1}).

2.4 Electrochemical Characterization

2.4.1 Planar boron-doped diamond electrode

Electrochemical measurements were at the core of the material characterization performed on the electrodes. Cyclic voltammetry was used to 1) assess the electrochemical reaction kinetics for several redox systems at diamond thin films deposited on Si, 2) probe the electrochemical properties of diamond microelectrodes. Basic theory and operating principles of the electrochemical techniques used in this work can be found elsewhere.^{4, 44}

All of the electrochemical measurements, were performed using a CHI650a or CHI900 computerized potentiostat (CH Instruments Inc., Austin, TX) with a graphite rod counter electrode and a Ag/AgCl reference electrode (3 M KCl, $E^{\circ'} = -56$ mV vs. SCE). All measurements were made at room temperature ($25 \pm 1 \circ C$), unless otherwise noted, and all solutions were deoxygenated with N₂ for at least 10 min prior to a measurement and blanketed with the gas during the measurement. Details of the electrochemical cells used for each type of electrode are provided below.



Figure 2.5 Design of single compartment, 3 electrode electrochemical cell.

The diamond thin film electrodes on Si were sealed against the bottom of a single-compartment electrochemical cell with a Viton® o-ring (~ 0.2 cm^2 area), as shown in Figure 2.5.³ The backside of the Si substrate was scratched, cleaned, and coated with graphite or carbon tape in order to ensure good ohmic contact with a copper current collector plate. All electrodes were tested after a 20 min soak in distilled isopropyl alcohol.

2.4.2 Microelectrode

Both boron-doped diamond coated Pt microelectrodes and carbon fiber microelectrodes were tested in a single-compartment, 3-electrode electrochemical cell as schematized in Figure 2.6.



Figure 2.6 Schematic of the electrochemical measurement with the diamond microelectrodes.

Voltammetry were performed on CHI 650a potentiostat (CH Instruments, Inc., Austin, TX) using 2 types of carbon fiber electrodes, thornel P-55s (d = 10 μ m) and T650 (d = 8 μ m) (Amoco, Greenville, SC) and boron-doped diamond microelectrode (d = 76 μ m). All measurements were recorded in a three electrode cell as shown in Figure 2.6. The scan rate used for all redox systems was 0.1 V/s. The potential was scanned between -0.2 and 0.8 V *vs.* Ag/AgCl on carbon fiber microelectrode (CFME) or -0.2 and 1.0 V *vs.* Ag/AgCl on diamond microelectrode (DME) when probed with Fe(CN)₆^{3.44}. When probed with Ru(NH₃)₆^{+3/+2}, the potential scan range was from 0.2 V to -0.4 V (CFME) or -0.6 V (DME) *vs.* Ag/AgCl. For the measurements involved Krebs buffer, the potential scan range was between 0 and 1.2 V *vs.* Ag/AgCl. Background cyclic voltammetry in 1M KCl was measured first, then the cyclic voltammogram for $Fe(CN)_6^{-3/.4}$, $Ru(NH_3)_6^{+3/+2}$, Krebs' buffer solution and NE solution were recorded, followed by the measurement of a drug. And then, cyclic voltammogram in 1M KCl, $Fe(CN)_6^{-3/.4}$, $Ru(NH_3)_6^{+3/+2}$, Krebs buffer solution, and NE redox systems were measured again to investigate the influence of the drug on the electrochemical behavior of this microelectrode. The procedure described above was one integrated measurement for one type of microelectrode in the experiment. The other two types of microelectrode will follow the same procedure as measuring the same drug. The protocol described above would be applied to other six drug measurements using three types of microelectrodes. For statistic purpose, at least three measurements were made for each drug and each type of microelectrode.

2.5 Conductive-Probe Atomic Force Microscopy (CP-AFM)

To perform CP-AFM measurements, a commercial scanning probe microscope (NanoScope IIIa scanning probe microscope, Veeco Instruments Inc., CA) was remodeled as schematized in Figure 2.7.

The conductivity measurement was made using a homemade current-tovoltage converter circuit (see Figure 2.8). This circuit converted the current flowing through the probe tip to a proportional output voltage that was then sent to a computer via a Signal Access Module (Veeco Instruments Inc., CA). The measurable current range was between $\pm 6.5 \mu$ A.



Figure 2.7 Schematic of the CP-AFM system adapted to a NanoScope IIIa scanning probe microscope.



Figure 2.8 Schematic of the home-made current-to-voltage converter.

A gold-coated, tetrahedron-shaped silicon nitride tip (Veeco NPG-20), with an apex radius of curvature less than 50 nm, a tip height of \sim 15-20 µm, and a full-tip

cone angle less than 35°, was mounted on a rectangular cantilever. The boron-doped diamond thin-film was attached to a metal pod, and electrical contact was made with carbon tape and Ag paint between the pod and backside of the conducting Si substrate (Figure 2.9). A bias voltage (sample vs. tip) of ± 0.2 or ± 2 V from an Omni 90 potentiostat (Cypress Systems, Chelmsford, MA) was applied between the sample and tip. Conductivity maps were recorded simultaneously with the topographic images. All measurements were performed in the open air.



Figure 2.9 Schematic of electrical connection between sample and tip for CP-AFM experimental setup.

2.6 Scanning Electrochemical Microscopy (SECM)

SECM^{22, 45, 46} measurements were made using a commercial microscope (CHI 900, CH Instruments Inc., Austin, TX) in a four-electrode configuration. The electrochemical cell consisted of a Pt wire auxiliary electrode and a 2 µm diameter Pt ultramicroelectrode probe tip (CH Instruments Inc.). BDD was investigated as the substrate electrode, and a homemade Ag/AgCl electrode was used as the reference.

The probe tip (2 μ m Pt ultramicroelectrode) need to be cleaned prior to any measurements. This can be achieved by running at least 20 cycles of cyclic voltammetric scanning from 1.25 V to -0.3 V (vs. Ag/AgCl) in 0.1 mol/L HClO₄ solution. Good shape of peak associated with hydrogen redox, adsorption and desorption are seen on the recorded cyclic voltammogram indicating a well-cleaned probe tip. Otherwise, the probe tip should be cleaned again or just replaced. Tip placement for all SECM images presented was performed by approaching the substrate surface in the positive-feedback mode until the current reached a value 2.3 times that for the tip far from the surface. At this point, the tip-to-substrate distance was estimated to be about 1 μ m for a 2 μ m diameter tip.⁴⁶ Once positioned, the protocol was then switched to map the electrochemical activity across the substrate electrode using the constant distance mode with Ru(NH₃)₆^{3+/2+}, Fe(CN)₆^{3-/4-}, and IrCl₆^{2-/3-} (1 mmol/L) as the redox test systems. The supporting electrolyte for all three redox systems was 1 mol/L KCl. All measurements, both tip approach curves and *x-y* images, were made in the feedback or collection mode.

2.7 Reagents for electrochemical measurements

All chemicals were analytical-grade quality, or better, and were used without additional purification. Solutions of 1 and 0.1 mmol/L potassium ferrocyanide $(Fe(CN)_6^{3-/4-}, Aldrich)$, hexaammineruthenium (III) chloride $(Ru(NH_3)_6^{3+/2+}, Aldrich)$, potassium hexachloroiridate (IV) ($IrCl_6^{2-/3-}$, Aldrich), methyl viologen (1,1'-dimethyl-4,4'-bipyridyl, $MV^{2+/+/0}$, Aldrich) in 1 mol/L potassium chloride (Spectrum), and 0.1 mol/L perchloric acid (redistilled 99.999%, Aldrich) were made. All redox analyte

solutions were prepared daily using ultrapure water (>18 MQ-cm) from an E-pure water purification system in glassware that was cleaned by a three-step process: ethanol/KOH bath, alconox/ultrapure water solution, and an ultrapure water rinse.

2.8 Experimental methods for Chapter 7

2.8.1 Animals

The University Committee on Animal Use and Care at Michigan State University approved all procedures for handling and caring for the laboratory test animals. All rats were allowed 2-3 days of acclimatization prior to entry into any experimental protocol. Pelleted rat chow (Harlan/Teklad 8640 Rodent Diet; Harlan/Teklad) and water were provided. Rats were housed in temperature and humidity controlled rooms using a 12-h on/off light cycle.

A. DOCA-salt hypertension

This model is chosen because its control state is easy to define unlike many genetic states of hypertension.⁴⁷ The DOCA-salt hypertension model is produced by surgical uninephrectomization followed by implantation of the mineralocorticoid, called deoxycorticosterone acetate (DOCA), and the administration of excess salt, NaCl, in the drinking fluid. Arterial blood pressure will significantly rise in a few weeks after such a treatment. DOCA salt-treatment causes significant changes in the cardiovascular system that contributes to the overall pathology of this model. Other details about this model can be fund in literature.^{47, 48}

B. Preparation of DOCA-salt and sham rats

Male Sprague-Dawley rats (175-200 g, Charles River Inc., Portage, MI) were exteriorized and the left kidney was removed under anesthesia with sodium pentobarbital (50 mg/kg i.p. (intraperitoneal)) after ligation of the renal artery, vein and ureter with 4-0 silk sutures. DOCA implantation was made between the back shoulder blades of the animal using a 1 cm incision. DOCA implants (600 mg/kg) were prepared by mixing deoxycorticosterone acetate in silicone rubber resulting in a dose of 200 mg/kg. DOCA-implanted rats received standard pelleted rat chow and salt water (1% NaCl + 0.2% KC1). Sham, normotensive rats also underwent left kidney removal but no DOCA pellet implantation and received unsalted tap water. The surgery was performed on a heated pad and rats recovered in a heated box. Antibiotics (enrofloxacin, 5 mg/kg s.c.(subcutaneous)) and an analgesic (butorphanol tartrate, 2 mg/kg, s.c.) were administered immediately after the surgery. After recovery, the rats were housed under the above listed conditions for 4 weeks. Systolic blood pressure was measured using the tail-cuff method four weeks after surgery. Rats with mean systolic blood pressure of > 150 mmHg were considered hypertensive.^{49, 50}

2.8.2 In vitro electrochemical and diameter measurement system

The combined use of continuous amperometry with diamond and carbon fiber microelectrodes and video imaging were used for the simultaneous in vitro measurement of NE release from sympathetic nerves innervating a rat mesenteric artery (MA) and vein (MV) and the evoked contractile response.

These techniques, along with various drugs, were employed to show the relationship between the oxidation current associated with endogenous NE overflow and blood vessel constriction. A block diagram of the experimental set-up is shown in Figure 2.10.

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Figure 2.10 Block diagram of the experimental set-up.

A. Tissue preparation

The sham and DOCA-salt rats (300 - 430 g,) were euthanized with a lethal pentobarbital injection (50 mg, i.p.). The abdomen was surgically opened, and the small intestine carefully removed and placed in an oxygenated (95% O_2 , 5% CO_2) Krebs buffer solution (pH 7.4) of the following composition: 117 mM NaCl, 4.7 mM KC1, 2.5 mM CaCl₂, 1.2 mM MgCl₂, 25 mM NaHCO₃, 1.2 mM NaH₂PO₄, and 11 mM glucose.⁵⁰ A section of the mesentery close to the ileal wall was carefully cut free from the intestine and transferred to a small silicone elastomer-lined, Teflon flow bath (5 mL volume). Secondary or tertiary arteries and veins (180-330 μ m outside diameter) were isolated for in vitro study by carefully removing the surrounding adipose and connective tissue under a dissecting microscope using fine scissors and forceps. The Krebs buffer solution entered the bath at one end (center) and flowed out the opposite end (center). The bath, containing the fixed tissue preparation, was attached to the stage of an ACCU 3030 inverted microscope (ACCU-SCOPE Inc., NY)

and superfused continuously with 37 °C Krebs buffer at a flow rate of 1.6 mL/min. The solution flow was controlled by a MasterFlex L/S Economy drive (Cole-Parmer Instrument Company, IL) peristaltic pump.

B. Assessment of electrode performance

The diamond and carbon fiber microelectrodes were cleaned by soaking in distilled isopropyl alcohol (IPA) for at least 15 min prior to a measurement.⁵¹ The microelectrode was affixed to a micromanipulator (Fine Science Tools, CA), which was used to position the electrode on the surface of the MA and MV. The microelectrode was positioned in the center of the bath containing the fixed tissue preparation, equidistant from the inlet and outlet solution ports. A Pt wire counter and a commercial "no leak" Ag/AgCl (3 M KC1, model EE009, Cypress Systems Inc.) reference electrode were also mounted in the bath to complete the electrochemical cell. All electrochemical measurements were made with a Biostat four channel potentiostat (ESA Biosciences, Inc., MA) and a computer running Biostat software (version 2.2.1, ESA Biosciences, Inc., MA). The software was used to record the continuous amperometric current-time profiles, blood vessel diameter changes and temperature of the solution in the bath. The analog output current from the potentiostat was low-pass filtered (filter parameter = 5 in Biostat). All data were digitized using a sampling rate of 100 Hz. The Krebs buffer flowed over the electrode and the tissue sample for 30 min prior to the start of a series of measurements.

C. Focal stimulation of perivascular nerves

Short trains of electrical stimulation were used to trigger NE release. Perivascular nerves were stimulated using a bipolar focal stimulating electrode positioned on the surface of the blood vessel at a distance of ca. 200 μ m from the tip of the carbon fiber. This positioning minimized the noise introduced into the current recordings. The focal stimulating electrode consisted of two AgCl-coated Ag wires inserted into double barrel glass capillary (tip diameter = 180 um). The wires were connected to a stimulus isolation unit and a Grass Instruments stimulator (S48K, Grass Telefactor W. Warwick, RI). Trains of 60 stimuli (0.3 ms duration, 30-90 V) at frequencies ranging between 2 and 20 Hz were used.

D. In vitro video monitoring of vasoconstriction

The output of a black and white video camera (OLY 105, Olympus America Inc., USA) attached to the microscope was fed to a PC Vision Plus frame-grabber board (Picolo Pro 2 board, Euresys Inc., IL) mounted in a personal computer. Changes in blood vessel diameter of 0.1 µm could be resolved. Video images were analyzed using Diamtrak software (http://www.diamtrak.com, Adelaide, Australia). The digitized signal was converted to an analog output (NuDAQ 6208/6216 multichannel analog output card, ADLink Technology Inc., Taiwan) sent to Biostat potentiostat and analyzed in a second computer running Biostat software for a permanent recording of blood vessel diameter as function of time.

E. Protocol for in vitro electrochemical and diameter measurements

For the in vitro electrochemical and diameter measurements, we followed the protocol given below:

1. Tissue preparation,

2. Set up the measuring system (Amperometry, V = 650 mV vs. Ag/AgCl),

3. Perfuse Krebs for 30 min,

- 4. Find out proper spots for stimulation and current measuring,
- 5. Record at least 3 stimulations in a 5 ~ 10 min interval as "control",
- 6. Perfuse 1 µmol/L capsaicin in Krebs for 30 min,

7. Perfuse Krebs for 1 hr,

8. Record at least 3 stimulations as "after capsaicin",

9. Perfuse 0.4 µM Substance P in Krebs for 10 min,

10. Record at least 3 stimulations as "with substance P",

11. Perfuse Krebs for 1 hr,

12. Record at least 3 stimulations as "after substance P".

All current-time and diameter-time traces were recorded by Biostat software and stored in the computer for data treatment later.

2.8.3 Fluorescence histochemistry

A. Tissue preparation

Second or third-order veins and arteries from the ileal mesentery, were isolated by carefully clearing away the surrounding adipose and connective tissues. Red blood cells were flushed out of the blood vessel lumen with phosphate buffer (0.1 mol/L, pH 7.2) using a 30 ga. hypodermic needle and syringe, and tissues were cut to 1 cm length.

B. Glyoxylic acid fluorescence histochemistry

Catecholamine fluorescence was revealed after incubating the prepared tissues in a 2% glyoxylic acid/0.2 mol/L phosphate buffer (pH 7.0) solution for 5 minutes at room temperature. The blood vessels were stretched onto glass slides and then heated at 80 °C for 5 min. Preparations were mounted in mineral oil and observed using a fluorescence microscope (Nikon Eclipse TE 2000-U) equipped with a filter set, UV2E/C (excitation filter, 340-380 nm and emission filter, 435-485 nm).

C. Double immunohistochemistry

Mesenteric arcades were stretched tightly in a Sylgard-lined petri dish using insect pins. A 30-gauge hypodermic needle was used to cannulate the primary artery or vein and the arcade was flushed with phosphate-buffered saline (PBS, 0.01 M, pH 7.2). The tissues were then stretched tightly on small pieces of balsa wood using insect pins and were immersed in Zamboni fixative (4% formaldehyde, 2% picric acid in 0.1 M phosphate buffer, pH 7.4) overnight at 4 °C. The tissues were then cleared three times at 10-min intervals with dimethyl sulfoxide followed by 3 washes at 10min intervals with PBS. Arteries and veins were then dissected from mesenteric fat and incubated overnight with primary antibodies. We used a mouse monoclonal antityrosine hydroxylase antibody (1:200 dilution in PBS, Calbiochem, EMD Chemicals, Inc., NJ), a rat monoclonal anti-substance P antibody (1:200 dilution in PBS, Serotec Laboratories, MorphoSys US Inc., NC) and a rabbit polyclonal anti-CGRP antibody (1:200 in PBS, Chemicon, Temecula, CA) to localize immunoreactivity for SP and CGRP, respectively. After incubation with primary antibodies, tissues were washed 3 times in PBS and then incubated with goat anti-rat IgG conjugated to Cy3 (1:200 dilution in PBS; Jackson Immunoresearch Laboratories, West Grove, PA), goat antimouse IgG conjugated to Cy3 (1:200 dilution in PBS; Sigma-Aldrich, St. Louis, MO) or to goat anti-rabbit fluorescein isothiocyanate (1:40 dilution in PBS; Sigma-Aldrich, St. Louis, MO) for 1 h at room temperature. The tissues were washed 3 times with PBS and then mounted on microscope slides and coverslipped using buffered glycerol (pH 8.6). Fluorescent images were acquired using a Leitz Laborlux S upright microscope, a PL Fluotar 40× objective (0.7 N.A.), a SPOT-2 cooled color digital camera (Diagnostic Instruments, Sterling Heights, MI).

2.8.4 Chemicals and drugs

All chemicals were reagent-grade quality, or better, and used without additional purification. The chemicals and drugs used for electrode performance testing were $K_4Fe(CN)_6$ (1mmol/L) and $K_3Ru(NH_3)_6$ (1mmol/L) made with 1mol/L KCl solution, norepinephrine (20 µmol/L), pyridoxal-phosphate-6-azophenyl-2',4'disulfonic acid (PPADS, 100 µmol/L), [4-(4-amino-6,7-dimethoxy-quinazolin-2-yl) piperazin-1-yl]-(2-furyl)methanone (prazosin, 100 μmol/L), 17α-hydroxy-yohimban-16α-carboxylic acid methyl ester (yohimbine, 100 μmol/L), 5-bromo-N-(4,5-dihydro-1H-imidazol-2-yl)-6-quinoxalinamine (UK 14.304. 100 μ mol/L). methyl (1R,2R,3S,5S)-3- (benzoyloxy)-8-methyl-8-azabicyclo[3.2.1] octane-2-carboxylate (cocaine, 100 μ mol/L), (±)-2-[1,4-benzodioxan-2-yl]-2-imidazoline hydrochloride (idazoxan, 100 µmol/L) and 8-methyl-N-vanillyl-trans-6-nonenamide (capsaicin, 100 µmol/L) made with Krebs buffer solution. Krebs buffer solution has the following composition: 117 mmol/L NaCl, 4.7 mmol/L KCl, 2.5 mmol/L CaCl₂, 1.2 mmol/L MgCl₂, 25 mmol/L NaHCO₃, 1.2 mmol/L NaH₂PO₄, and 11 mmol/L glucose.⁵⁰ Capsaicin (1 µmol/L) and substance P (0.3 µmol/L) were used for in vitro study. All chemicals and drugs except substance P were obtained from Sigma Chemical Company (Saint Louis, MO). Glyoxylic acid, mouse monoclonal anti-tyrosine hydroxylase antibody, rat monoclonal anti-Substance P antibody, rabbit polyclonal anti-CGRP antibody, goat anti-mouse IgG conjugated to Cy3, goat anti-rat IgG conjugated to Cy3 or to goat anti-rabbit fluorescein isothiocyanate, Zamboni fixative (4% formaldehyde, 2% picric acid in 0.1 M phosphate buffer, pH 7.4) were used for fluorescent staining. All these chemicals, antibodies and substance P were from Dr. James J. Galligan at Department of Pharmacology and Toxicology, Michigan State University. Ultrapure water (distilled, deionized, and passed over activated carbon, 17-18 MQ, Barnstead E-PureSystem) was used for all solution preparation, and glassware and electrode cleaning.

2.8.5 Data analysis

Data were obtained from > 50 sham rats and >50 DOCA-salt rats for the research. Mean systolic blood pressure from sham and DOCA-salt rats was 121 mm Hg and 198 mm Hg, respectively. The mean weight of sham rats was 420 g, and the mean weight of DOCA-salt rats was 310 g. Data are presented as mean \pm S.E.M; where S.E.M is standard error of the mean. MA and MV constrictions are expressed as a percentage of the initial resting diameter (in µm) of the blood vessel.

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Chapter 3

Basic Properties of Boron-Doped Microcrystalline & Nanocrystalline Diamond Thin-Film Electrodes

3.1 Introduction

Developing an understanding of how the electrochemical reaction rate varies across a boron-doped diamond electrode requires that one characterize and spatially distinguish the physical, chemical, and electrical properties. Without question, polycrystalline diamond is one of the more structurally-complex carbon electrodes with factors such as the boron-doping level, hydrogen content, grain boundary density, and electric double layer structure affecting electron-transfer rates. Our group has reported on the heterogeneous nature of the microstructure and electrochemical activity of polycrystalline BDD.¹⁻¹⁰ As a follow-up to this, the present work included detailed investigation of the electrical and electrochemical properties of boron-doped diamond thin film. In this chapter, we report the effect of boron-doping level and surface termination on the physical and electrochemical properties of boron-doped diamond electrodes fabricated by CVD. The diamond thin films were comprehensively characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and cyclic voltammetry. Several specifically selected, aqueous-based redox couples, including $Fe(CN) = \frac{3}{6} e^{-3}$, $\operatorname{Ru}(\operatorname{NH3})_6^{3+/2+}$, $\operatorname{IrCl}_6^{2-/3-}$ and methyl viologen, were used to evaluate the electrochemical properties of boron-doped diamond thin-film electrodes.

3.2 Scanning Electron Microscopy (SEM) Images

3.2.1 SEM images for microcrystalline boron-doped diamond thin films

SEM images of typical microcrystalline BDD films are presented in Figure 3.1. Triangular crystalline facets, typical of polycrystalline diamond grown from hydrogen-rich CH₄/H₂ source gas mixtures, are apparent. Many of the microcrystallites have a base diameter of ca. 1 μ m. The triangular {111}-oriented crystal facets are the preferred growth phase, which is independent of the doping level. The grain boundaries and facet surfaces, for the most part, are devoid of smaller secondary diamond growths at all doping levels. As a general rule, the fraction of large grains ($\sim 1 \mu m$) increases but the fraction of small grains (less than 500 nm) decreases as the doping level increases. The exception is the sample with a doping level of 5 ppm (see Figure 3.1B). In other words, the surface of boron-doped diamond became rougher when the doping level increased from 0 to 10 ppm (concentration of diborane in source gas mixture). This is consistent with the results reported by Kim et al.¹¹ They observed nanoscale secondary grains to be on top of the isolated crystal, and surface roughness generally increased with increasing doping concentration. Twinning, which is evident as re-entrant grooves at the edge of some of the triangular crystallites, is clearly seen for 10 ppm diamond film but is not so apparent for other films.¹²

On the basis of the SEM images, several conclusions can be drawn:

1. The triangular $\{111\}$ crystal facets are the preferred growth phase for 0.5 - 10 ppm films, which suggests that boron-doping, at least within this range, doesn't significantly influence the growth orientation, although the addition of boron does



Figure 3.1 SEM images for microcrystalline diamond thin films grown by microwave-assisted chemical vapor deposition with different diborane levels in the source gas: (A) 10, (B) 5, (C) 1, (D) 0.5, and (E) 0 ppm. The source gas composition was 0.5% CH₄ + 99.5% H₂, the plasma power was 1000 W, and the pressure was 45 torr. Growth time was 10 hours.

influence the growth rates of {111} facets (triangular) and {100} facets (square). ^{13,14} In fact, Wurzinger et al. found out that {111} facets predominate with increasing boron concentration.¹³ Ushizawa et al. reported that {100} facets tend to predominate when the boron-to-carbon ratio (B/C) in the source gas mixture is less than 80 ppm but the situation reversed when B/C increased to 200 ppm.¹⁴ In other words, {111} facets are the preferred growth phase. Our results are very similar to this because, in our system, 0.5 ppm B_2H_6 concentration corresponds to a B/C of 200 ppm in the gas phase. Therefore, having {111} facets predominate is not unexpected.

2. The surface of boron-doped diamond became rougher with increasing diborane in the source gas, which indicates that the incorporation of boron does influence the morphology of the diamond surface. This is also consistent with the literature. Tokuda et al. studied the surface roughening of heavily boron-doped diamond films using atomic force microscopy (AFM). Their results showed that the root mean square (RMS) value of the heavily boron-doped diamond surfaces increased with the increasing B/C ratio in the gas phase.^{15, 16}

3. Twinning is clearly evident in Figure 3.1. A twin band is a structure with a pair of stacking errors in parallel {111} planes containing numbers of layers of correct stacking between the errors.¹² A single stacking error is a rotation of adjacent layers by 60° from their correct positions in the diamond-cubic crystal. The intersection of a pair of parallel {111} stacking errors with the surface of a diamond-cubic crystal gives rise to a re-entrant corner and these re-entrant corners play a critical role in the growth of {111} faceted diamond crystals from the vapor because the re-entrant corner provides a self-regenerating site for the nucleation of new layers and leads to the rapid growth of the crystal within the plane of the twin band. Therefore, twin bands can be easily seen in any growth where {111} facet is preferred. This is true for all growths studied here. From the twining mechanism, one would expect that boron would not influence the twin structure too much. As shown in Figure 3.1, all images
show {111} facets dominating the surfaces and many re-entrant grooves can be seen independent of the boron concentration, except for undoped diamond film (Figure 3.1E) because {111} facets didn't dominate the surface.

3.2.2 SEM images for nanocrystalline boron-doped diamond thin films

The nanocrystalline diamond film, compared to the microcrystalline film, is much smoother and has feature sizes of around 50 nm, as shown in Figure 3.2. These nodular features are actually aggregates of diamond grains about 15-20 nm in diameter.^{5, 7} The smaller feature and grain size is typical of diamond films deposited from hydrogen-poor CH_4/H_2 +Ar source gas mixtures and results from a high renucleation rate during growth.¹⁷

This set of SEM micrographs demonstrates the transition of the nanocrystalline diamond microstructure as a function of the dopant concentration in the source gas mixture. For the undoped nanocrystalline diamond film, most of the individual particles were found to be polycrystals, which had rugged surfaces, showing little indication of well-developed crystal facets. This is a characteristic of diamond single crystals (See Figure 3.2E). When 1 ppm diborane was added, particles with rugged facets largely decreased in number although most of the individual particles were still polycrystals with a smaller grain size (See Figure 3.2D). Dramatic changes happened when more than 5 ppm diborane was added to the source gas mixture. Particles with rugged facets disappeared and the particle size decreased. More importantly, a new morphology, a nodular structure emerged. The sizes of these nodular features are ca. 50 nm which made a cauliflower-shape surface of the nanocrystalline diamond film (See Figure 3.2A, B and C).

It is difficult to determine the crystalline nature of these films from the planview SEM images shown in Figure 3.2 because of the nodular features. Instead, transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) were used to examine the phase composition of the nanodiamond films.



Figure 3.2 SEM images of boron-doped nanocrystalline diamond thin films grown by microwave-assisted chemical vapor deposition with different diborane concentrations in the source gas: (A) 50, (B) 10, (C) 5, (D) 1, and (E) 0 ppm. The source gas composition was 1% CH₄ and 5 % H₂ in 94% *Ar* with diborane, the plasma power was 800 W, and the pressure was 140 torr. Growth time was 2 hours.

Figure 3.3 is a bright-field transmission electron micrograph of a 10 ppm boron-doped diamond film with a fairly uniform distribution of conglomerates made up of diamond crystallites. The black area in the center of the image was from the instrument not the sample. The small dots uniformly distributed over the whole image are diamond particles introduced in seeding procedure before the growth. The bright traces are grain boundaries or caused by overlapping of different grains along the incident electron beam direction.¹⁷ TEM image showed the structural homogeneity of the nanocrystalline film because of higher spatial resolution.



Figure 3.3 Bright-field TEM image revealing the plan-view morphology of the nanodiamond thin film. The grain boundary contrast reveals that the film possesses a granular structure.

Selected-area electron diffraction (SAED) was used to reveal the phase purity of the nanodiamond thin film. The technique was used because either sp^2 -bonded glassy carbon or predominantly sp^3 -bonded diamond-like amorphous carbon (ta-C) gives rise to recognizable diffraction intensities at positions different from those of the crystalline carbons.¹⁷ Figure 3.4 is a SAED pattern obtained from a typical nanocrystalline diamond film. Sharp Bragg reflections are located in concentric circles, indicative of the ramdomness of the crystallite orientation. No appreciable scattering intensity from either graphite crystallites or amorphous carbon (glassy carbon or diamond-like amorphous carbon) was observed, suggesting that the film is phase-pure diamond.



Figure 3.4 SAED pattern from the nanodiamond thin film. Sharp Bragg reflections are visible indicating good crystallinity.

3.2.3 SEM images for boron-doped diamond microelectrodes

Figure 3.5A shows SEM images of a boron-doped diamond microelectrode grown on a 76 µm diam. Pt wire and insulated by polypropylene. The conical shape and the polycrystalline morphology are evident. There are two regions: the exposed diamond and the isolated diamond. Because the polymer coating was not electrically conductive, it appears brighter in SEM image. The exposed microelectrode, on the other hand, is conductive so it appears darker. The polymer layer appears thin and uniform over the electrode. The microelectrode diameter at the narrowest point is 10 μ m and at the widest point is ca. 80 μ m. The length of this particular exposed electrode is ~50 μ m.

A higher magnification image of the coated wire is presented in Figure 3.5B. The polycrystalline film consists of randomly oriented, well-faceted crystallites ranging in diameter from 0.5 to 2 μ m. Triangular crystalline facets, typical of polycrystalline diamond grown from hydrogen-rich CH4/H₂ source gas mixtures, are seen. Twinning is evident as re-entrant grooves at the edge of some of the triangular crystallites. In contrast to the planar films, there is a wide crystallite size distribution with smaller secondary crystallites existing on the larger primary crystallite facets.



Figure 3.5 SEM images of a boron-doped diamond microelectrode grown on a *Pt* wire and insulated using polypropylene. The white line indicates the boundary between polypropylene coating and exposed diamond film.

3.3 Raman Spectra

3.3.1 Raman spectra for microcrystalline boron-doped diamond films

on Si substrates

Raman spectroscopy is frequently used to characterize CVD diamond films, because of its sensitivity to the carbon microstructure. Raman scattering in the visible region is ca. 50 times more sensitive to the presence of sp^2 -bonded carbon than sp^3 -bonded carbon, which makes the technique a very useful probe of the nondiamond phase in diamond thin films.¹⁸⁻²⁶ The Raman spectrum obtained for a 10 ppm boron-doped microcrystalline diamond film is shown in Figure 3.6.

The sharp peak at 1332 cm⁻¹ with a full width at half maximum of 8 cm⁻¹ is the characteristic one-phonon diamond line. This line is asymmetric with a dip on the low wavenumber side of the peak and a shoulder on the high wavenumber side. Similar to heavily doped silicon,²⁷ this asymmetry is attributed to a Fano-type interference between the scattering by the zone-center optical phonon and scattering by an electronic continuum (related to the formation of an impurity band above 10^{19} B cm⁻³) whose energy overlaps that of the phonon.²⁸



Figure 3.6 Raman spectrum for a highly boron-doped microcrystalline diamond

film on Si, deposited from a 10 ppm diborane source gas mixture.

Beside the appearance of a Fano asymmetry, a band near 1200 cm⁻¹ is another feature present in the spectrum for heavily doped films. Along with this band, a very broad and intense band around 500 cm⁻¹ is also seen. Some have attributed the band at 1200 cm⁻¹ to bonds between boron atoms.²⁹ However, a similar band was reported by Buckley and co-workers for undoped diamond films.³⁰ Consequently, these bands do not appear to be related to boron. The theoretical phonon density of states for diamond³¹ shows a maximum around 1200 cm⁻¹, which matches closely with the band observed for this film. Gonon et al. proposed that the bands observed at 1200 and 500 cm⁻¹ are related to maxima in the phonon density of states of diamond and arise from scattering by phonons outside the center of the Brillouin zone.²⁸ May et al. gave another explanation for these bands. They also noted that the band is near two maxima in the phonon density of states (PDOS). They attributed these bands to relaxation of the wavevector selection rules caused by boron incorporation into the lattice, rather than the hole concentration.³²

Recently, Vlasov et al. studied the vibrational modes of heavily boron-doped diamond using isotopic substitution of boron and carbon.³³ They observed that none of the bands in the Raman spectra shifted upon ¹⁰B-substitution, whereas the bands shifted to lower frequency upon ¹³C-substitution. These isotopic substitution experiments are consistent with the 500 cm⁻¹ and 1200 cm⁻¹ bands being associated with diamond phonons, revealing the phonon density of states, and not with boron.

From the above discussion, we may interpret these bands in the following way: In relatively small regions of the crystal, a high boron concentration causes structural disorder (SD) which breaks the translation symmetry of the crystal lattice. As a consequence, the wave-vector conservation rule for Raman scattering is broken. As a result, phonons with a large range of wave vectors in the Brillouin zone are excited and the resultant bands tend to be broad and reflect the phonon density of states. In general, the 500 and 1200 cm⁻¹ bands do not directly arise from but are related to boron atoms incorporated into the lattice.

The broad peak around 1500 cm⁻¹ is attributed to non-diamond sp² carbon in the grain boundaries. It is known that the Raman scattering cross-section for graphite is about 50 times higher than that for diamond.³⁴ The low intensity of this peak indicates the dominance of the sp³ bonding in boron-doped microcrystalline diamond films. The sharp peak at 522 cm⁻¹ is from the one-phonon mode of Si ^{28, 35} and the broad peak centered at 950 cm⁻¹ is the second-order scattering peak of Si.²⁹

To further reveal the influence of boron on the Raman spectrum, Figure 3.7 shows Raman spectra for microcrystalline boron-doped diamond films grown from different diborane concentrations in the source gas mixture. The broad band centered ca. 1500 cm⁻¹, assigned to the nondiamond sp² carbon, is strong for the undoped sample (0 ppm diamond film). The influence of boron is clearly revealed in the spectral features. The graphite band decreased in intensity with increasing boron concentration. Above 10^{20} B cm⁻³ (5 ppm diamond film, see Table 2.3 in section 2.3.2), the graphite band almost diminished, while the one-phonon Raman peak at 1332 cm⁻¹ slightly shifted to lower wavenumbers. This shift is in accordance with the observation in previous Raman studies of boron-doped polycrystalline diamond films and is typically attributed to internal tensile strain.²² At the same time, the full width at half maximum increased with increasing boron concentration. The intensity of the one-phonon diamond line decreased with increasing boron concentration due to the greater optical density. This makes the penetration depth less with increasing boron concentration so the number of scatterers is less. Table 3.1 summarizes the position

and width for the diamond line observed for microcrystalline boron-doped diamond thin films.



Figure 3.7 Raman spectra for microcrystalline diamond films grown with different source gas diborane levels. The greater the source gas diborane concentration, the higher the doping level.

As the boron-doping level is increased, a new, broad band emerged around 1200 cm⁻¹ appeared and its intensity increased indicating a high concentration of impurities or lattice defects, as discussed before.

Table 3.1One-phonon diamond line position and width observed in Ramanspectra from microcrystalline diamond films with different doping levels.

[B ₂ H ₆] in the source gas (ppm)	10	5	1	0.5	0
Peak position (cm ⁻¹)	1330.2	1330.7	1331.8	1331.9	1332.0
FWHM (cm ⁻¹)	12.7	10.8	10.1	10.0	8.9

The spectra also reveal that the presence of boron enhanced the growth of sp³band carbon, as shown in Figure 3.8. Although the intensity of one-phonon diamond line decreased with increasing diborane concentration, the background photoluminescence also decreased. The ratio of the peak-to-baseline (P/B) near 1332 cm⁻¹ increases with increasing diborane concentration from 0 to 5 ppm. When the boron-doping concentration increased to 10 ppm, the ratio of the peak-to-baseline decreased indicates the gradual degradation in diamond microstructure in the film.



Figure 3.8 Relationship between peak-to-baseline (P/B) ratio of Raman spectrum and the diborane concentration in the source gas mixture for microcrystalline diamond films. The P/B ratio is defined as the ratio of the intensity of the peak at 1332 cm^{-1} and the intensity of the baseline at the peak position.

3.3.2 Raman spectra for nanocrystalline boron-doped diamond films on Si substrates

Raman spectra for nanocrystalline boron-doped diamond films with different doping levels are shown in Figure 3.9. Several distinct, broad peaks can be seen: 1145, 1330, 1469, and 1545 cm⁻¹. The peak at 1545 cm⁻¹ is clearly the G-band Raman peak, which is well known for disordered carbon films and arise from the in-plane stretching modes of the sp²-bonded carbon at the grain boundaries of nanocrystalline diamond.³⁶



Figure 3.9 Raman spectra for nanocrystalline diamond films grown with different source gas diborane levels. The greater the source gas diborane concentration, the higher the doping level.

The broad peak at 1330 cm⁻¹ has been attributed to two different origins: the one-phonon diamond line that is broadened and down-shifted from the expected 1332 cm⁻¹ position because of the small size of the diamond grains, or the D-band (1350 cm⁻¹) scattering by graphitic edge plane phonons. In disordered sp²-bonded carbon, D-

band stretching arises from the breathing modes in small aromatic clusters. The argument for the assignment of the broad peak at 1330 cm⁻¹ to the sp²-bonded carbon D-band Raman peak is based on the fact that the peak is absent in the UV Raman spectra³⁷ because the D-peak is believed to arise from a double resonant Raman process (when the incident photon wave vector k=0.5q), where the intensity is highest for low energy excitation and decreases strongly with increasing excitation energy.³⁶

The shoulder at 1145 cm⁻¹ and the smaller peak observed at 1470 cm⁻¹, often observed for nanocrystalline diamond films, have been attributed to trans-(CH)_x (trans-polyacetylene) at grain boundaries.³⁸ The evidence from Ferrari and Robertson, and Birrell is that these peaks arise from sp²-bonded carbon of the grain boundaries and not sp³-bonded carbon.

Some changes were observed when the concentration of diborane in the source gas mixture increased. Comparing the 0 to 50 ppm samples in Figure 3.9, we notice that the shoulder at 1145 cm⁻¹ and the smaller peak observed at 1470 cm⁻¹ decreased in relative intensity to the D-band peak (at 1330 cm⁻¹) as the doping level increased. The origins of these peaks has been attributed in the literature to various features, either due to relaxation of the phonon selection rules for nanocrystalline materials or due to the presence of specific carbon–hydrogen bond in the grain boundaries of nanocrystalline diamond.³⁸⁻⁴¹ We believe that the changes of the peaks at 1145 and 1470 cm⁻¹ are due to the presence of greater amounts of boron at the grain boundaries of nanocrystalline diamond for two reasons. First, the intensities of these peaks in the visible Raman spectra correlates with the amount of boron used during growth; and second, there is no evidence for these peaks in the UV Raman spectrum.^{23, 32} This reduction in intensity with excitation wavelength is consistent with the results that assign the peak to sp²-bonded carbon, although the exact nature of these bands is as yet unknown.

3.3.3 Raman spectra for boron-doped diamond films on Pt substrates

Figure 3.10 shows Raman spectra for several diamond films deposited on the 76 μ m diam. Pt wires. All spectra possess an intense one-phonon diamond line at 1331 cm⁻¹. The fact that there is only small downshift of the peak position (1 cm⁻¹) means that the diamond films are not under significant tensile or compressive stress.⁴² There is some scattering intensity near 1580 cm⁻¹, which is attributable to amorphous sp²-bonded carbon impurity. We suppose that much of this impurity responsible is located at the interface between the *Pt* and diamond film, and does not reside on the film surface. The linewidth, or the full width at half maximum (FWHM), is inversely related to the phonon lifetime. The larger linewidth for the films on *Pt* is caused by increased phonon scattering as a result of the grain boundaries and defects in the polycrystalline film.^{6, 43}

A broad but weakly intense peak around 586 cm⁻¹ is seen in all the spectra. We believe this peak is of a similar origin to the peak at 522 cm⁻¹ seen for the microcrystalline boron-doped diamond films. In other words, this peak does not arise from boron itself, but appears whenever a high concentration of impurities or lattice defects is present. Table 3.2 summarizes the Raman spectra analysis for microcrystalline boron-doped diamond thin films on *Pt* substrate.

Table 3.2 One-phonon diamond line position and width in Raman spectra.

Sample	1	2	3	4
Peak position (cm ⁻¹)	1330.8	1330.9	1330.7	1330.6
FWHM (cm ⁻¹)	12.9	13.0	12.7	12.5



Figure 3.10 Raman spectra for four boron-doped microcrystalline diamond films deposited on *Pt* wires. The diborane concentration in the source gas was 4 ppm.

3.4 Electrochemical Characterization

3.4.1 Background CV for boron-doped diamond thin-film on Si

Figure 3.11 shows the background cyclic voltammetric *i-E* curves for "as grown" microcrystalline and nanocrystalline BDD thin-films in 1 mol/L KCl at 0.1 V/s. Curves for glassy carbon are shown for comparison. The geometric area of both electrodes was the same (0.183 cm²). The curves for both electrodes are featureless between -200 and 800 mV (vs. Ag/AgCl). There are no redox peaks for diamond as there are for glassy carbon due to the presence of redox-active surface carbon-oxygen functionalities that populate the edge plane sites.^{44, 45} The background current for the nanocrystalline BDD thin-film electrode is slightly larger than that for the microcrystalline electrode. In the absence of any redox-active solution species, the

background voltammetric current (i_{bkg}) is related to the electrode area (A, cm²), the double-layer capacitance (C_d, F/cm²) and the potential scan rate (υ , V/s), and is given by the following equation:⁴⁶

$$i_{bkg} = AC_d \upsilon \tag{3.1}$$

There are two reasons for the difference in background current between the two diamond film types. First, as revealed in CP-AFM measurements (see Chapter 4), the fraction of area that is highly conducting is larger for the nanocrystalline film because of the smaller grain size. Second, the nanocrystalline film, because of the π states in the grain boundary, likely has a higher carrier concentration than does the microcrystalline film and this leads to a greater excess surface charge density at a given potential. This results in a greater double layer capacitance and a larger voltammetric background current. Even though the background current for nanocrystalline diamond is slightly larger than that for microcrystalline diamond, both currents are approximately a factor of 5 - 10 less that that for comparably-sized glassy carbon.⁴ The larger current for glassy carbon results in large part from the pseudocapacitance associated with electroactive and/or ionizable surface carbonoxygen functionalities.^{3, 47} Diamond is devoid of such functionalities. The lower background current for diamond leads to improved signal-to-background ratios in electroanalytical measurements.



Figure 3.11 Background cyclic voltammetric *i*-E curves for planar diamond films. Supporting electrolyte: 1 mol/L KCl. Scan rate: 0.1 V/s. The geometric area of all electrodes was ca. 0.2 cm².

It is well-known that the surface termination of diamond films strongly influences their properties. This was confirmed in the present work. Figure 3.12 compares background cyclic voltammetric *i-E* curves for hydrogen- and oxygen-terminated nanocrystalline and microcrystalline BDD thin-film electrodes in 1 mol/L KCl at 0.1 V/s. Clearly, the background current for nanocrystalline electrode is influenced by the surface termination as the current for the oxygen-terminated electrode is larger by a factor of 2-3. Hydrogen- and oxygen-terminated microcrystalline electrodes show similar results. The increased background current does not appear to be due to increased surface area because of any surface roughening, as SEM images of films before and after oxidation revealed no morphological changes.⁴ It seems that the oxygen termination increases the apparent electrode

capacitance possibly by causing an increase in the water contact area. The contact angle decreases significantly after oxidation, which is consistent with a more hydrophilic surface. Yagi et al. reported similar results that showed the background current for oxidized diamond electrode was 3-5 times larger than that for the asgrown electrode.⁴⁸



Figure 3.12 Background cyclic voltammetric *i*-*E* curves for H- and O-terminated (a) nanocrystalline and (b) microcrystalline diamond films. The curves were recorded in 1 mol/L KCl at a scan rate of 0.1 V/s starting from -0.2 V (vs. Ag/AgCl).

Gerischer and coworkers demonstrated that the double layer capacity of graphite is relatively low in comparison to metal electrodes because of a low electron density of states (DOS) near the Fermi level.⁴⁹⁻⁵¹

Another possibility is the increase in the dielectric constant of water at the hydrophilic diamond surface. The organization of water at the hydrophobic hydrogenterminated surface is expected to be different from that at the hydrophilic oxygenterminated surface. The ability of water to isolate charge at the hydrophilic surface would be greater, hence the larger dielectric constant.

3.4.2 Electrochemical behavior of boron-doped diamond thin-films with different doping levels

Four specifically chosen redox systems were used to evaluate the electrochemical behavior of the BDD electrodes: $Fe(CN)_6^{3./4-}$, $Ru(NH_3)_6^{3+/2+}$, $IrCl_6^{2./3-}$ and methyl viologen.^{3, 4, 7} For carbon electrodes, the heterogeneous electron-transfer rate constant is known to be strongly influenced by the amount of exposed edge plane on sp² carbon electrodes (i.e., electronic properties), but weakly influenced by the oxygen functionalities terminating the edge plane carbon atoms.⁵²⁻⁵⁴ Surface cleanliness is also important as are the electrolyte type and concentration.⁵²⁻⁵⁴ Fe(CN)₆^{3./4-} was used as a probe because the electrode reaction kinetics for this couple are strongly influenced by the amount of exposed edge plane on sp²-bonded carbon, as well as the surface cleanliness.⁵⁴ Therefore, its heterogeneous electron-transfer rate constant is quite sensitive to the surface cleanness and chemistry of sp² and sp³ carbon electrodes.^{4, 54-57} This redox system often behaves anomalously on carbon electrodes and should not be considered typical outer-sphere. The electrochemical kinetics of Fe(CN)₆^{3./4-} has been studied extensively. For example, studies show that there are

several factors that can influence the electrode kinetics at metal and sp² carbon electrodes. First, the rate constant is strongly influenced by the fraction of edge plane exposed on sp² carbon electrodes (i.e., electronic properties), but relatively insensitive to the surface oxygen functionalities terminating the edge plane carbon atoms as long as a thick, anionically charged oxide film is not present.^{52, 53, 58, 59} Second, surface cleanliness is important, as are the electrolyte type and concentration.^{52-54, 60, 61} For example, the involvement of specifically adsorbed cations (e.g., K⁺) through a possible surface-bridging interaction has been proposed.⁶⁰ The rate of reaction increases with electrolyte composition in the order of LiCl < NaCl < KCl.^{60, 61} At the 1 mol/L electrolyte concentration, the rate is a factor of ~10 higher in KCl than in LiCl at both gold and glassy carbon electrodes.⁶⁰ Third, adsorbed monolayers on sp² carbon electrodes can decrease the rate of reaction. The McCreery group observed an increase in ΔE_p from 5 to 140 mV after modification of the polished glassy carbon surface with adsorbed monolayers.^{52, 53} The level of increase depends on the type and coverage of the adsorbate.

Different from sp²-bonded carbon electrodes, the physicochemical properties of boron-doped diamond strongly influence the electrode kinetics of Fe(CN)₆^{3-/4-}. ΔE_p of Fe(CN)₆^{3-/4-} is very sensitive to the surface termination with the smallest ΔE_p observed at the clean, hydrogen-terminated surface. After oxygen termination, ΔE_p increases by over 125 mV but is reversibly reduced to the original value after removal of the oxygen functionalities by hydrogen plasma treatment.⁶² The sensitivity of the electrode kinetics to surface oxygen at diamond is in sharp contrast to the minor effects these functionalities have on the response at sp² carbon electrodes.

The $Fe(CN)_6^{3-/4-}$ rate constant is also sensitive to the electrolyte composition and ionic strength with the largest values observed in KCl and the smallest in LiCl. This dependence is presumed to result from the formation of a dimeric species consisting of both the oxidized and reduced forms of the anion coupled through a bridging cation and sabilized by some specific surface interaction.⁶⁰ However, the difference at the 1 mol/L concentration level is only a factor of 2-3 rather than 10, as is the case for metal and glassy carbon electrodes.⁶³ All the evidence at sp² carbon and diamond electrodes suggests the involvement of a clean, non-oxide surface site.

In the present work, we investigated the influence of the boron-doping level on the electrochemical activity of diamond thin-film electrode using 0.1 mmol/L $Fe(CN)_6^{3/4}$ in 1 mol/L KCI. The results are shown in Figure 3.13 and Table 3.3. Our results show that the cyclic voltammetric ΔE_p decreases with increasing the diborane concentration in the source gas (i.e., increased doping level). For a film grown with 0.1 ppm diborane, ΔE_p was 420 mV possibly indicating a sluggish electron-transfer kinetics or an increased iR effect. As doping level increased to 0.5 ppm, well-defined peak shape *i-E* curve was recorded and ΔE_p was 208 mV implying much faster electron transfer kinetics. Another explanation for the reduced ΔE_p with increased doping level is a reduced iR effect. When doping level increased over 1 ppm, ΔE_p decreased to less than 82 mV (Table 3.3). The near-Nernstian ΔE_p indicates that these boron-doped diamond electrodes possess the requisite surface structure and properties for a relatively rapid rate of charge transfer.



Figure 3.13 Cyclic voltammetric *i-E* curves for 0.1 mmol/L $Fe(CN)_6^{3-/4-}$ in 1 mol/L KCl for microcrystalline boron-doped diamond films grown with different diborane concentrations.

Table 3.3 Cyclic voltammetric ΔE_p values for different redox couples (0.1 mmol/L analyte in 1 mol/L KCl) at microcrystalline boron-doped diamond films grown with different diborane concentrations. Measurements were made with one film at each doping level.

	$\Delta \mathbf{E}_{\mathbf{p}} (\mathbf{mV})$				
DIAID IIIIIS	Fe(CN) ₆ ^{3-/4-}	Ru(NH ₃) ₆ ^{3+/2+}	MV ^{2+/+}	IrCl ₆ ^{2-/3-}	
10 ppm	72	56	51	64	
5 ppm	78	61	52	63	
1 ppm	82	68	57	63	
0.5 ppm	208	76	62	76	
0.1 ppm	420	78	59	N/A	

 $Ru(NH_3)_6^{3+/2+}$ involves simple electron transfer at most electrodes including diamond^{1-3, 57, 64} and sp² carbon.^{52-54, 65} The electrode kinetics for $Ru(NH_3)_6^{3+/2+}$ are relatively insensitive to the surface microstructure, surface oxides, and adsorbed monolayers on sp² carbon electrodes.^{52-54, 65} The electron transfer rate constant of this redox couple is insensitive to surface modification, which strongly implies that electron transfer does not depend on an interaction with a surface site or functional group.⁵⁴ The most important factor affecting the rate of reaction is the electronic properties of the electrode, specifically the density of electronic states near the formal potential of the redox system.

For metal and glassy carbon electrodes, a low density of electronic states is seldom an issue. However, for semiconducting/semimetallic diamond, the potential dependent electronic density of states is an important factor governing the response. This is why ΔE_p increases at boron-doped diamond thin film electrodes with decreasing boron doping level.⁶⁴ ΔE_p for 10 ppm diamond film was 56 mV (Table 3.3) and increased to 78 mV when the doping level decreased to 0.1 ppm. The formal potential (i.e., cyclic voltammetric $E_p/2$ value) for this couple is -218 mV vs. SCE. The valence band position of boron-doped polycrystalline diamond has been estimated to be ~550 mV vs. SCE.^{2, 66} Considering the 5.4 eV band gap, this means that the formal potential falls within the band gap (i.e., between the valence and conduction band positions). Therefore, this redox system is not expected to exchange charge directly with either the valence or the conduction band. The nearly reversible response indicates that there must be a sufficient density of electronic states present within the band gap at this potential (Figure 3.14). The midgap density of states in the polycrystalline films can be influenced in a combined way by the boron-doping level and lattice hydrogen content, the inherent grain boundaries and other morphological

defects, and the nondiamond carbon impurity phases at the surface. However, in this case, surface nondiamond carbon phases are clearly not an important factor influencing the density of states since Raman spectra showed that the films were sp³⁻-band carbon dominated especially for the 5 and 10 ppm films (Figure 3.7). As will be discussed below, the evidence suggests that the boron-doping level and the chemisorbed hydrogen are the most important factors controlling the density of electronic states in this potential region.



Figure 3.14 Cyclic voltammetric *i-E* curves for 0.1 mmol/L Ru(NH₃) $_{6}^{3+/2+}$ in 1 mol/L KCl at microcrystalline boron-doped diamond films grown with different diborane concentrations in the source gas.

Similar to $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{IrCl}_6^{2-/3-}$ involves simple electron transfer at most electrodes including diamond^{3, 66} and sp² carbon.⁵⁴ The k⁰_{app} is relatively insensitive to the surface microstructure, surface oxides, and adsorbed monolayers on sp² carbon

electrodes.^{52-54, 65} Surface cleanliness is important, although to a lesser degree than for $Fe(CN)_6^{3-4}$. The most influential factor is the electronic structure of the electrode. As shown in Figure 3.15, all electrodes showed near-Nernstian responses to this redox couple. ΔE_p changed from 63 to 76 mV when the diborane concentration in the source gas decreased from 10 ppm to 0.5 ppm (Table 3.3). Table 3.3 also shows that ΔE_p was largely unaffected by changing boron-doping level. The formal potential of this redox couple is 767 mV vs. Ag/AgCl, which is positive of the proposed valence band position.⁶⁶ This means that charge exchange for this couple likely occurs through the valence band and not through midgap states.



Figure 3.15 Cyclic voltammetric *i-E* curves for 0.1 mmol/L $IrCl_6^{2-/3-}$ in 1 mol/L KCl at microcrystalline boron-doped diamond films grown with different diborane concentrations in the source gas.

Methyl viologen involves simple electron transfer at diamond and most other electrodes. The k_{app}^0 at diamond is relatively insensitive to surface oxides, grain boundaries, and defect density and the presence of nondiamond carbon impurities. Like Ru(NH₃)₆^{3+/2+}, the most important factor influencing the rate is the density of electronic states at the formal potential. The formal potential of -685 mV vs Ag/AgCl for MV^{2+/+} is well into the band gap region, even more negative than the formal potential for Ru(NH₃)₆^{3+/2+}. Therefore, methyl viologen likely undergoes charge transfer through midgap surface states.



Figure 3.16 Cyclic voltammetric *i-E* curves for 0.1 mmol/L MV in 1 mol/L KCl at microcrystalline boron-doped diamond films grown with different diborane concentrations in the source gas.

Figure 3.16 shows the cyclic voltammetric i-E curves for methyl viologen on different boron-doped diamond thin film electrodes. Both near-Nerstian redox waves

associated with the $MV^{2+/4}$ and $MV^{+/0}$ transitions were observed. The near-Nernstian ΔE_p values indicated that all films showed semimetal behavior at the $E^{0^{\circ}}$ values of ca. -0.7 and -1.0 V (vs. Ag/AgCl) for methyl viologen. Figure 3.16 and Table 3.3 also clearly shows that the positions of the redox waves, and therefore the electron transfer kinetics, were largely unaffected by changing the boron doping level, similar to the observation for $IrCl_6^{2-/3-}$. Therefore, we can conclude that the rate constant for this system is relatively insensitive to surface sites and chemical functionality. Surface cleanliness and electronic effects appear to be the most influential factors determining the rate, and this redox system behaves as outer-sphere.



Figure 3.17 Cyclic voltammetric *i-E* curves for (a) 1 mmol/L $Fe(CN)_6^{3-/4-}$, (b) 0.1 mmol/L Ru(NH₃) $_6^{3+/2+}$, (c) 0.1 mmol/L IrCl $_6^{2-/3-}$, and (d) 0.1 mmol/L methyl viologen with 1 mol/L KCl at nanocrystalline diamond thin film electrodes grown with different diborane concentrations in the source gas.

Similar voltammetric measurements were made to evaluate and compare the response of nanocrystalline boron-doped diamond thin films. The results for $Fe(CN)_6^{3/4-}$, $Ru(NH_3)_6^{3+/2+}$, $IrCl_6^{2-/3-}$, and methyl viologen are presented in Figure 3.17 and Table 3.4. For all the redox systems except $Fe(CN)_6^{3/4-}$, the data shown were acquired in 0.1 mmol/L redox couple with 1 mol/L KCl at a scan rate of 0.1 V/s. The data for $Fe(CN)_6^{3/4-}$ were obtained in 1 mmol/L analyte with 1 mol/L KCl at a scan rate of 0.1 V/s.

It can be seen that similar results were obtained with 1, 5 and 10 ppm nanocrystalline boron-doped diamond films, as compared to the microcrystalline boron-doped diamond films with corresponding boron-doping level. ΔE_p 's for Fe(CN)₆^{3-/4-}, Ru(NH₃)₆^{3+/2+} and methyl viologen at both types of films are nearly the same. This means that the electrode resistance is largely unchanged by the change in doping level. The big difference between the nanocrystalline and microcrystalline films is the ΔE_p 's for IrCl₆^{2-/3-}, which are 10 mV larger at nanocrystalline films.

Table 3.4 Cyclic voltammetric ΔE_p 's for different redox couples (0.1 mmol/L analyte in 1 mol/L KCl) at nanocrystalline boron-doped diamond films grown with different diborane concentrations in the source gas. Measurements were made with one film at each doping level.

BND films	$\Delta \mathbf{E}_{\mathbf{p}} (\mathbf{mV})$				
	*Fe(CN)6 ^{3-/4-}	Ru(NH ₃) ₆ ^{3+/2+}	MV	IrCl ₆ ^{2-/3-}	
10 ppm	68	60	55	74	
5 ppm	75	59	56	74	
1 ppm	94	62	54	80	

*: the concentration for $Fe(CN)_6^{3-4-}$ was 1 mmol/L.

The near-Nernstian responses for $Fe(CN)_6^{3-/4-}$, $Ru(NH_3)_6^{3+/2+}$, $IrCl_6^{2-/3-}$ and methyl viologen all indicate that resistance or semiconductor effects are minimal even at very negative potentials when the boron-doping level is over 1 ppm for both microcrystalline and nanocrystalline diamond films. The hydrogen terminated (or new as grown) diamond surface is chemically inert, hydrophobic, and resists adsorption of impurities such that a high degree of surface cleanliness is maintained. This avoids the need for frequent surface pretreatment in order to active the electrode.

The voltammetric data presented above reveal that, for $Fe(CN)_6^{3/4-}$, $Ru(NH_3)_6^{3+/2+}$, $IrCl_6^{2-/3-}$ and methyl viologen, the clean, as-grown microcrystalline and nanocrystalline boron-doped diamond thin films possess similar macroscopic electrochemical properties.^{5, 7}

3.4.3 Electrochemical activities for planar boron-doped diamond thinfilm on Si substrate with different surface terminations

The surface chemistry of carbon materials and its effect on the electrochemical behavior is a complicated issue. For example, glassy carbon needs to be activated to create reproducibly active electrodes due largely to the complex nature of the surface chemistry. To activate glassy carbon, usually, mechanical polishing with successively smaller grades of alumina is first used, often followed by additional treatments such as heat treatment,⁶⁷ electrochemical polarization,⁶⁸ plasma treatment⁶⁹ or laser activation.⁷⁰ Although it's not normally necessary to activate a boron-doped diamond electrode, the electrode response can be affected by surface contaminants, surface functional groups, and microstructural defects. Oxygen from air or H₂O chemisorbs to most sp² carbon surfaces, so it is very difficult to avoid oxygen functional group formation when using these electrodes in air. The same holds true for diamond but the

oxidation reaction rate is slower than that for other sp²carbon materials. In addition, there is often a low level of sp^2 carbon impurity present on CVD diamond electrodes. which is located mainly in the grain boundary and has been reported to be more active than sp³ diamond,⁶⁶ especially for nanocrystalline diamond. The presence of oxygen on the diamond surface has a significant influence on the chemical reactivity,⁴⁴ electrical conductivity.⁴⁵ and electron affinity.⁷¹ On the other hand, oxidation is a means to clean the BDD surface. At present, several procedures have been used by different labs to oxidize the boron doped diamond surface including: (i) chemical treatment, (ii) electrochemical treatment, and (iii) oxygen plasma treatment. These procedures can remove all detectable impurities except oxygen but form hydroxyl and ether functional groups, carbonyl and carboxyl groups on the diamond surface. The distribution of particular oxygen containing functional groups is fairly difficult to be determined and may itself vary with time and sample history. This makes the relationship between the electrochemical properties and the surface chemistry of boron doped diamond more complicated. The "as grown" diamond surface is hydrogen-terminated because the deposition of diamond films is undertaken in hydrogen plasma. However, this surface is not resistant to oxidization. Therefore, knowledge of the interaction of hydrogen and oxygen on diamond surface is crucial to the application of BDD thin-films in both electrochemistry and electron emission fields. It is well known that BDD thin-films with different surface terminations exhibit different performance in electrochemistry and electron emission,⁴ but the relationship between the electrical properties and the microstructure and the surface chemistry of polycrystalline diamond, especially for nanocrystalline diamond, remains unclear.

In the present work, we characterized highly boron-doped microcrystalline and nanocrystalline thin-film electrodes with H- and O-terminations using cyclic voltammetric method. Our results show that O-termination blocked the electrochemically-active sites on the electrode surface that lowered the electrontransfer rate and this inhibiting effect was much more pronounced for nanocrystalline diamond than for microcrystalline diamond.

Figure 3.18 shows the cyclic voltammetric *i-E* curves for 1 mmol/L Fe(CN)₆³⁻ ^{/4-} in 1 mol/L KCl at a scan rate of 0.1 V/s at H-terminated microcrystalline and nanocrystalline BDD electrodes. Well-defined, peak-shape voltammograms are observed for both electrode types without any conventional treatment. ΔE_p values of 73 ± 5 mV (n = 3) were seen for the microcrystalline BDD electrode, while the peak separation for the nanocrystalline BDD electrode was 73 ± 4 mV (n = 3). The small ΔE_p value is indicative of relatively rapid electrode-reaction kinetics.⁵ Currents limited by semi-infinite linear diffusion were found as the peak current for the forward scan varied proportionally with the square root of the potential sweep rate.⁴⁶ Based on the conductivity maps (see section 4.6), it appears that the current passed flows through only selected regions of the diamond surface. In other words, the effective current density is locally high in some regions.

Similar results were obtained for 1 mmol/L Ru(NH₃)₆^{3+/2+} in 1 mol/L KCl as shown in Figure 3.19. ΔE_p value of 63 ± 4 mV and 69 ± 6 mV (n = 3) were observed for microcrystalline and nanocrystalline BDD electrodes, respectively. These results show that, for "as grown" or H-terminated BDD electrode, the macroscopic electrochemical properties of both BDD types are similar.^{5, 7}



Figure 3.18 Cyclic voltammetric *i*-*E* curves for 1 mmol/L $Fe(CN)_6^{3-/4-}$ in 1 mol/L KCl at 0.1 V/s for 10 ppm micro- and nanocrystalline BDD thin-film electrodes. Both electrodes were H-terminated.



Figure 3.19 Cyclic voltammetric *i-E* curves for 1 mmol/L Ru(NH₃) $_{6}^{3+/2+}$ in 1 mol/L KCl at 0.1 V/s for 10 ppm micro- and nanocrystalline BDD thin-film electrodes. Both electrodes were H-terminated.

Figure 3.20 shows the cyclic voltammetric *i-E* curves for 1 mmol/L Fe(CN)₆³⁻ ^{/4-} in 1 mol/L KCl at 0.1 V/s for H- and O-terminated nanocrystalline BDD. A nearly reversible response was seen for the H-terminated electrode. After oxidation, a large increase in ΔE_p was observed indicating that this surface termination causes a significant decrease in rate of electron transfer for this redox couple. The anodic peak current decreased from 330 ± 21 μ A/cm² (n = 3) for the hydrogen termination to 202 ± 11 μ A/cm² (n = 4) for oxygen termination and ΔE_p increased from 73 ± 4 mV (n = 3) to 289 ± 31 mV (n = 4) after oxidation. The data show that the electrochemical kinetics for this redox couple strongly depends on the surface termination.⁶²



Figure 3.20 Cyclic voltammetric *i-E* curves for 1 mmol/L $Fe(CN)_6^{3-/4-}$ in 1 mol/L KCl at 0.1 V/s for 10 ppm H- and O-terminated nanocrystalline BDD thin-film electrodes.

When probed using 1 mmol/L Ru(NH₃)₆^{3+/2+} in 1 mol/L KCl, similar trends were found (Figure 3.21). The anodic peak current changed from $358 \pm 25 \,\mu$ A/cm² (n = 4) for the H-terminated electrode to $206 \pm 30 \,\mu$ A/cm² (n = 3) for O-terminated electrode, and ΔE_p increased from 71 ± 6 mV (n = 4) to $180 \pm 47 \, \text{mV}$ (n = 3). These data clearly revealed a comprehensive effect of termination change from H to O and surface carbon-oxygen functionalities. Oxygen blocks the reactive sites of the diamond surface which makes more sluggish reaction on O-terminated than that on Hterminated BDD electrode.



Figure 3.21 Cyclic voltammetric *i-E* curves for 1 mmol/L Ru(NH₃) $_{6}^{3+/2+}$ in 1 mol/L KCl at 0.1 V/s for 10 ppm H- and O-terminated nanocrystalline BDD thin-film electrodes.

The cyclic voltammetric *i-E* curves for 1 mmol/L $Fe(CN)_6^{3-/4-}$ in 1 mol/L KCl at H and O-terminated microcrystalline boron-doped diamond thin-film electrodes at

a scan rate of 0.1 V/s are shown in Figure 3.22. The anodic peak current decreased from $331 \pm 8 \,\mu\text{A/cm}^2$ (n = 3) for the H-terminated electrode to $295 \pm 28 \,\mu\text{A/cm}^2$ (n = 3) for the O-terminated electrode, and ΔE_p changed from $73 \pm 5 \,\text{mV}$ (n = 3) for Hterminated electrode to $106 \pm 12 \,\text{mV}$ (n = 3) for O-terminated electrode. These are surprising results compared with those for nanocrystalline BDD films. It seems that O-termination of microcrystalline BDD film has much less influence on the electrochemical kinetics of $\text{Fe}(\text{CN})_6^{3/4}$. A possible reason for this is that the microcrystalline BDD film is more resistive to surface oxidation such that there is less oxide coverage. This is partially confirmed by XPS measurements on a set of similar BDD films, as shown in Table 3.5.

The cyclic voltammetric *i-E* curves for 1 mmol/L Ru(NH₃)₆^{3+/2+} in 1 mol/L KC1 at 0.1 V/s on H- and O-terminated microcrystalline BDD confirmed this hypothesis. ΔE_p changed from 63 ± 4 mV (n = 4) for H-terminated electrode to 71 ± 6 mV (n = 3) for O-terminated electrode revealed that only few active sites were blocked by oxygen (Figure 3.23).

 Table 3.5
 XPS results for microcrystalline and nanocrystalline BDD thin films

 with different surface treatments.*

		C1s (%)	O1s (%)	O/C
BMD	As grown	97.96	2.04	0.02
	Rehydrogenated	98.07	1.93	0.02
	Acid washed	87.52	10.79	0.12
BND	As grown	95.04	4.96	0.05
	Rehydrogenated	97.56	2.09	0.02
	Acid washed	80.32	13.58	0.17

*: The author acknowledges Yingrui Dai, a member of Dr. Swain's group, who provided the XPS data.



Figure 3.22 Cyclic voltammetric *i-E* curves for 1 mmol/L Fe(CN) $_6^{3-/4-}$ in 1 mol/L KCl at 0.1 V/s for H- and O-terminated microcrystalline BDD thin-film electrodes.



Figure 3.23 Cyclic voltammetric *i*-*E* curves for 1 mmol/L Ru(NH₃) $_{6}^{3+/2+}$ in 1 mol/L KCl at 0.1 V/s for H- and O-terminated microcrystalline BDD thin-film electrodes.



Figure 3.22 Cyclic voltammetric *i-E* curves for 1 mmol/L $Fe(CN)_6^{3-/4-}$ in 1 mol/L KCl at 0.1 V/s for H- and O-terminated microcrystalline BDD thin-film electrodes.



Figure 3.23 Cyclic voltammetric *i-E* curves for 1 mmol/L Ru(NH₃) $_{6}^{3+/2+}$ in 1 mol/L KCl at 0.1 V/s for H- and O-terminated microcrystalline BDD thin-film electrodes.
3.5 The Effect of surface hydrogen on the properties of planar boron-doped diamond thin-film on Si substrate

Surface conductivity (SC) on single crystals and chemical vapor deposition diamonds was first reported in 1989 by Ravi and Landstrass. The phenomenon was exclusively attributed to the presence of hydrogen at the begining.^{72, 73} However, in recent years the role of atmospheric species on the formation of a hole accumulation layer has become known. In several experiments it has been demonstrated that exposure to different gaseous species varies the SC by many orders of magnitude.⁷⁴ Maier et al.⁷⁵ have proposed an electrochemical model in which electrons are transferred from the diamond valence band to solvated H_3O^+ ions in a solution layer that forms spontaneously in air (condensation). This model is supported by recent theoretical⁷⁶ and experimental studies.^{77, 78} Both physisorbed and chemisorbed hydrogen exist in diamond films grown by CVD. Although the influence of adsorbed hydrogen on the properties of diamond films has been studied by several groups, however, few investigations about the effect of the surface hydrogen on boron-doped diamond films have been done. Here we investigate the properties of boron-doped diamond thin films upon annealing in Ar and exposure to lab atmosphere. Our goal is to distinguish the different influences of physisorbed hydrogen and chemisorbed hydrogen on the physical and chemical properties of boron-doped diamond thin films.

3.5.1 Contact angle measurement

The hydrogen-terminated diamond surface is hydrophobic and resists adsorption of polar molecules such that a high degree of surface cleanliness is maintained. On the other hand, the oxygen-terminated diamond surface is hydrophilic and is less resistant to the adsorption of polar impurities because of the terminal oxygen functional groups. This difference of wettability was confirmed by contact angle measurements in distilled and deionized H_2O , as shown in Table 3.6.

The contact angles were measured by commertial instrument, FTA200 (Edmund Scientific Co., Barrington, NJ), using ultrapure water. The "as grown" films were stored in the laboratory atmosphere for weeks prior to the measurements so the surface had been partially oxidized. Our results show that the as grown diamond films were highly hydrophobic and the film became more hydrophilic as the doping level increased. A possible explanation for this is that the defects introduced by boron on the surface, especially in the grain boundaries, increase as the concentration of boron increases. These defects are more hydrophilic than those terminated hydrogen because the interstitial boron (aggregated mostly in the grain boundaries) tends to introduce the sp² bond⁷⁹ resulting in more hydrophilic surface. After annealing at 400°C, the contact angle significantly decreased for all tested samples. This can be attributed to the removal of physisorbed hydrocarbon species and the partial oxidation of the surface as the gas ambient used for heating was not totally devoid of oxygen. For example, physisorbed hydrocarbon species desorb from the diamond surface lower than 400°C⁸⁰ but oxygen-containing species do not.⁸¹

Table 3.6Contact angles of microcrystalline boron-doped diamond thin filmswith different doping levels and annealing treatment.

Film	Contact angle (degree, aver. ± std., n=6)			
	As grown	After annealing		
0.1 ppm	60.3 ± 2.0	42.4 ± 4.0		
0.5 ppm	60.8 ± 2.5	38.5 ± 3.4		
1 ppm	62.3 ± 1.9	33.2 ± 1.7		
5 ppm	48.5 ± 2.4	32.0 ± 3.1		
10 ppm	49.7 ± 1.3	31.0 ± 3.6		

3.5.2 Four-point resistivity measurements

Table 3.7 summarizes the electrical resistivity data for two microcrystalline boron-doped diamond thin films with different doping levels. The resistivity of the film was measured using a home-made 4-point probe, with spring-loaded tips, in combination with a Hewlett Packard 3478 multimeter (HP, USA). The resistivity was calculated using the following equation:

$$\rho = 4.532 dr \tag{3.2}$$

where ρ is the resistivity ($\Omega \cdot cm$), *d* is the film thickness (for microcrystalline diamond thin film, $d = 6 \mu m$), *r* is the resistance measured in a 4-point probe configuration (Ω).

The data show that annealing in Ar at 400°C significantly increased the resistivity of 0.5 ppm boron-doped diamond thin film (from 6.4 ± 1.4 to 11.6 ± 1.3 $\Omega \cdot \text{cm}$) but did not change the resistivity of 5 ppm boron-doped diamond thin film. A possible interpretation for this is that the surface conductivity induced by hydrogen has a greater influence on the resistivity of 0.5 ppm diamond film because of the

lower doping level and hence a weaker conductivity. In other words, surface hydrogen acting as an electron acceptor is the "extra" dopant here. During annealing surface hydrogen (i.e., electron acceptors) is desorbed and the surface conductivity was decreased.^{80, 82} For the 5 ppm boron-doped diamond film, because of the high doping level, the contribution to the electronic properties by the boron dopant was great enough that the desorption of hydrogen had little effect on the resistivity.

Table 3.7 Surface resistivity of boron-doped diamond thin films (n = 6).

Film	0.5	ppm BMD	5 ppm BMD		
Resistivity	As-grown	After annealing	As-grown	After annealing	
Average (Ω·cm)	6.4	11.6	0.150	0.148	
S.D. (Ω·cm)	1.4	1.3	0.006	0.007	

3.5.3 Cyclic voltammetric characterization

The electrochemical response for 0.5 and 5 ppmboron-doped microcrystalline diamond film electrodes towards $Fe(CN)_6^{3.44}$, $Ru(NH_3)_6^{3+/2+}$ and $IrCl_6^{2.43-}$ was measured before and after the annealing treatment and shown in Figure 3.24a - c. Figure 3.24a shows voltammetric *i-E* curves for 0.1 mol/L $Fe(CN)_6^{3.44-}$ with 1 mol/L KCl. $Fe(CN)_6^{3.44-}$ is an inner-sphere redox system^{4, 6, 62} with a heterogeneous electron-transfer rate constant that is sensitive to the electronic properties, surface cleanliness and the presence of surface oxides on diamond electrodes as discussed before (see section 3.4.2). At 0.5 ppm diamond electrode, a sluggish curve and a large peak separation (225 mV) were recorded. While large ΔE_p values can be related to both sluggish kinetics and to the presence of the ohmic potential loss (iR), the large value for this film is mainly due to surface contamination.



Figure 3.24 Electrochemical response of 0.5 and 5 ppm microcrystalline BDD thinfilm electrodes before and after annealing in Ar flow at 400°C for 30 min. a) 0.1 mmol/L Fe(CN)₆^{3./4-}, b) 0.1 mmol/L Ru(NH₃)₆^{3+/2+} and c) 0.1 mmol/L IrCl₆^{2./3-}. The supporting electrolyte solution was 1 mol/L KCl and the scan rate was 0.1 V/s.

After annealing at 400°C in Ar, it appeared that physisorbed hydrocarbon species are removed⁸⁰ creating clean "sites" for $Fe(CN)_6^{3-/4-}$ electron-transfer. However, annealing at 400°C in Ar may only remove the physisorbed hydrocarbon species but not oxygen-containing species and chemisorbed hydrogen.^{80, 81, 82} In other words, this treatment may just partly change the surface conductivity induced by hydrogen-termination. It's possible that this change has significant influence on the electrochemical response of diamond film with a low doping level such as 0.5 ppm when probed with a inner sphere redox couple like $Fe(CN)_6^{3/4}$. For highly doped diamond electrode (5 ppm in our case), the effect of annealing is weak enough to be negligible even when probed with $Fe(CN)_6^{3/4-}$ because of the high density of electrochemically active sites induced by boron doping. This can also explain why there was no significant difference for the electrochemical response of diamond electrodes recorded in Figure 4.24 b and c. As discussed in section 4.4.2, $Ru(NH_3)_6$ $^{3+/2+}$ and $IrCl_6^{2-/3-}$ are both out sphere redox couples and involve simple electron transfer on most electrodes including diamond^{1-3, 57, 64} and sp² carbon.^{52-54, 65} The electrode kinetics for these two redox couples are relatively insensitive to the surface microstructure, surface oxides, and adsorbed monolayers on sp² carbon electrodes.^{52-54,} ⁶⁵ The most important factor affecting the rate of reaction is the electronic properties of the electrode. We also demonstrated in section 4.4.2 that, for these redox species, a doping level of 0.5 ppm was good enough for diamond electrodes to obtain near-Nernstian response. Annealing in Ar at 400°C did not destroy the hydrogen termination, which meant the electronic properties of the electrodes were largely unaffected by this treatment. Therefore, the peak separations and peak currents for $Ru(NH_3)_6^{3+/2+}$ and $IrCl_6^{2-/3-}$ did not change too much as did $Fe(CN)_6^{3-/4-}$ before and after the annealing treatment.

Table 3.8 summarizes the changes of peak separation (ΔE_p) and peak current for 0.5 and 5 ppm boron-doped diamond thin film electrodes before and after annealing at 400 °C in Ar flow.

Table 3.8 Cyclic voltammetric peak separation (ΔE_p , mV) and peak current (μA) data for 0.1 mmol/L analytes in 1 mol KCl at 0.5 and 5 ppm boron-doped microcrystalline diamond thin-film electrodes before and after annealing in *Ar* flow at 400°C.

Redox	film	As grown			After Annealing		
		ΔE _p	i _{p,a}	i _{p,c}	ΔE _p	i _{p,a}	i _{p,c}
Fe(CN) ₆ ^{3-/4-}	0.5 ppm	225	3.35	3.31	123	4.53	4.39
	5 ppm	82	6.74	6.6	72	6.97	6.92
Ru(NH ₃) ₆ ^{3+/2+}	0.5 ppm	74	5.57	5.88	66	5.86	5.98
	5 ppm	62	6.48	6.57	64	6.78	6.80
IrCl ₆ ^{2-/3-}	0.5 ppm	76	5.54	5.95	74	5.54	5.98
	5 ppm	68	5.84	6.71	64	6.01	6.42

3.6 Conclusions

Boron-doped microcrystalline and nanocrystalline diamond thin-film electrodes with different doping levels were evaluated using Raman, SEM, TEM and cyclic voltammetry. The microcrystalline diamond films possessed some sp^2 carbon impurity at lower doping levels (< 0.5 ppm diborane in source gas mixture), but this impurity was reduced at higher doping levels (> 1 ppm diborane in source gas mixture), based on Raman spectrum. The nanocrystalline diamond films have Raman spectra dominated by the sp^2 -bonded carbon in the grain boundaries. The one-phonon peak at 1332 cm⁻¹ was partially buried by the stronger scattering by grain boundary carbon in Raman spectra. Although lots of nodular features were seen in SEM for nanocrystalline diamond films, TEM and SEAD images demonstrated that these films consisted of phase-pure cubic diamond crystallites. Additionally, electrochemical characterization with $Fe(CN)_6^{3./4-}$, $Ru(NH_3)_6^{3+/2+}$, $IrCl_6^{2./3-}$ and MV showed that the clean, as-grown microcrystalline and nanocrystalline boron-doped diamond thin films possess similar macroscopic electrochemical properties. The present study also showed that the surface termination strongly affected the electrochemical properties of boron-doped diamond thin film electrodes, especially when probed with $Fe(CN)_6^{3-}$ ^{/4-}. The oxygen-terminated diamond electrodes had greater voltammetric background currents than the hydrogen-terminated counterparts. Annealing at 400 °C in *Ar* flow influenced the physical and electrochemical properties of boron-doped diamond electrodes with a low doping level (0.5ppm), but did not affect the highly doped diamond electrodes (5 ppm).

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Chapter 4

Heterogeneous Electrical Conductivity of Polycrystalline Boron-Doped Diamond Films

4.1 Introduction

Polycrystalline, boron-doped diamond (BDD) thin film, grown by chemical vapor deposition (CVD), has been used as an electrochemical electrode material for more than 10 years.¹⁻⁷ However, the relationship between the physical, chemical, and electronic properties of BDD and its electrochemical performance is still incompletely understood. In recent years, much has been learned about how different factors control the electrochemical properties. For example, several authors have investigated the kinetics and mechanisms of heterogeneous redox reactions at BDD, and two general models have been proposed: ⁸⁻¹⁴ (i) electron transfer via potential-dependent electronic states within the band gap with a relatively uniform rate constant across the surface and (ii) electron transfer through a partially blocked electrode consisting of highly conductive or active sites separated by less conductive or less active regions. In our early work, we hypothesized that the first model explained the electrochemical behavior of BDD.⁶ Now, based on recent work and results presented herein, we suppose a combination of these two models best describes electron transfer at diamond. Additional evidence in support of the second model comes from investigations of electron emission from diamond, an analogous process that involves electron transfer across a solid-vacuum interface.

It has been reported that BDD films with higher electrical conductivity exhibit a lower turn-on voltage for field emission.^{15, 16} The electron emission was observed to occur from sites of high electrical conductivity. The possibility of some channel and/or grain boundary conduction was proposed.^{15, 16}

Developing an understanding of how the electrochemical reaction rate might vary across the diamond electrode requires that one be able to characterize and spatially distinguish the physical, chemical, and electrical properties. Without question, polycrystalline diamond is one of the more structurally complex carbon electrodes with factors such as the boron-doping level, hydrogen content, grain boundary density, and electric double layer structure affecting electron-transfer rates. For boron-doped microcrystalline diamond, a few papers have described spatially inhomogeneous physicochemical properties, such as a variable distribution of boron in doped polycrystalline diamond.^{17, 18}

Raman imaging, electrogenerated chemiluminescence imaging, and photoluminescence measurements have revealed variations in the microstructure, electrical properties, and electrochemical activity across a microcrystalline diamond thin-film surface.¹⁹⁻²¹ Recently, electron emission studies from hydrogen-terminated and chemically-modified boron-doped nanocrystalline diamond films were consistent with a heterogeneous surface having different local work functions.²² This conclusion was reached based on electron energy distribution measurements that were made as a function of temperature. If a complete picture of the structure-reactivity relationship at boron-doped polycrystalline diamond is to be developed, then probes of the film properties at the microscopic level are needed. Conducting probe-atomic force microscopy (CP-AFM) is one such technique that is useful for investigating the electrical properties of conductors and semiconductors with high spatial resolution.²³.

²⁴ Both nanometer electrical characterization and topographic imaging are provided by CP-AFM. The technique usually employs a metal-coated (Pt or Au) cantilever-tip assembly that functions as both a scanning electrical contact and force sensor. Metal wire probe tips can also be used.²⁵ Thus, direct measurements of I-V curves at specific topographical sites on the sample are possible.

CP-AFM has been used to probe the conductivity across hydrogen-terminated microcrystalline diamond thin-film electrodes with different boron-doping levels,²⁶ oxygen-terminated BDD,²⁷ and undoped diamond films.²⁸ The general observation, at least in some of the work, is that the electrical conductivity is variable across polycrystalline diamond with a strong dependence on the grain orientation, fraction of grain boundary, and boron-doping level.^{26, 28} These studies highlight the importance of charge carrier concentration and mobility in BDD in controlling electrochemical activity.²⁷ Local electrochemical activity is clearly linked to the underlying conductivity of individual grains, which is governed by the boron incorporation.

Our group has reported on the heterogeneous nature of the microstructure and electrochemical activity of polycrystalline BDD using Raman microprobe spectroscopy and electrogenerated chemiluminescence imaging.^{19, 20} Additionally, a pattern of variable conductivity and electrochemical activity at hydrogen-terminated microcrystalline diamond electrodes, doped with boron at different concentrations, was measured using CP-AFM and SECM.²⁶ As a follow-up to this, we report herein on a detailed investigation of the electrical properties of boron-doped diamond thin films using CP-AFM.

CP-AFM was used to simultaneously map the topography and electrical conductivity of the thin films as a function of the boron-doping level. The dependence

of the electrical conductivity on the boron-doping level, surface topography, and the bias voltage (sample vs. tip) polarity was investigated.

4.2 CP-AFM images of nanocrystalline films

Figure 4.1A-D shows conductivity maps (different current scales) for nanocrystalline BDD films grown with 50, 10, 1 or 0 ppm diborane added to the source gas mixture. The boron-doping level decreased with decreasing B_2H_6 concentration in the source gas. The image contrast results from different levels of current flow between the sample and tip, which is dependent on the contact resistance between sample and tip (a value that is inversely related to the contact radius of the tip), the local charge carrier concentration at the electrode surface and the bias voltage.^{27, 29} In all of these images, the sample was biased +0.2 V relative to the tip. To ensure that removal of the Au coating from end of the tip was not a complicating factor, a new tip was used for imaging each film and was checked for integrity by multiple-scan imaging an area of the surface with multiple scans. Importantly, as has been observed in recent work with hydrogen-terminated microcrystalline films.²⁶ the images reveal variable electrical conductivity across the film surface with regions of high conductivity isolated by regions of low conductivity. The ability of the film to support current flow increased proportionally with the boron-doping level as the current was highest for the 50 ppm film and lowest for 0 ppm film at the 0.2 V bias. Some of the more conductive regions are clustered together, whereas others are more isolated. Some of more conducting regions have lateral dimensions of 2 to 4 μ m, which means they encompass multiple grains and grain boundaries (refer to 50 ppm boron doped film). The more conducting zones are separated from one another, in many cases, by a micrometer or less. Only the undoped film possesses very few

conductive regions and, since there is little boron-doping (there will be some due to reactor contamination with the species), we suppose the conductive regions are associated almost exclusively with the grain boundaries in this film. A similar conclusion was reached by Ternyak et al. in their CP-AFM imaging work of undoped nanocrystalline diamond film.²⁸ The resolution of the conductivity maps in the present work was not high enough to reveal the grain boundaries.



Figure 4.1 CP-AFM images $(10 \times 10 \ \mu\text{m}^2)$ of nanocrystalline BDD thin films grown with different source gas B₂H₆ concentrations (i.e., different doing levels): (A) 50, (B) 10, (C) 1 and (D) 0 ppm B₂H₆. The bias voltage used for all images was +0.2 V vs. the tip. The current ranged from 0 to 6.5 μ A. (Reprinted with permission from *J. Phys. Chem.* 111, 3986 (2007). Copyright (2007) American Chemical Society.) (From Ref. 49).

The fact that the contact resistance between the diamond and tip decreased with increasing boron-doping level indicates that the electrical properties are strongly influenced by the boron-dopant and not solely by the existing grain boundary or any adventitious non-diamond sp² carbon impurity. Therefore, we conclude, as was the case in past work, that the conduction pathway is not solely through the grain boundary but rather through a combination of the doped diamond grains as well as the grain boundary.³⁰ The same conclusion has been reached by Macpherson and coworkers in their work with doped diamond electrodes.²⁷ It is expected that the boron substitutionally inserted into the diamond grains is the primary contributor to the charge carrier concentration in the film, but it is also possible that aggregated boron atoms in the grain boundary could also contribute to the carrier concentration by increasing the sp² carbon bonding (π states).³¹

The contact area between the tip and sample is an influential factor when measuring polycrystalline diamond because of the tip curvature, which is ca. 50 nm. This can be seen below in the expression that describes the contact resistance, R,

$$R = 4\rho l/3\pi a^2 \tag{4.1}$$

where ρ and *l*, respectively, denote the resistivity and the electron mean free path in the electrode, and *a* is the tip radius.²⁹ The radius of curvature of the tips used in our work is comparable to the roughness of the nanocrystalline film. The pattern of conductivity indicates that the thin film consists of regions of high electrical conductivity isolated from one another in a more insulating matrix, at least within our detection ability, which is < 0.1 μ A for current or > 10 M Ω for resistance. One reason for the differential conductivity is the possibility of boron-rich regions due to inhomogeneous boron-doping.^{17, 18, 20} This will produce regions of higher charge

carrier concentration (i.e., holes). Consistent with this is previous Raman imaging work that revealed an inhomogeneous distribution of boron dopant in mechanically polished polycrystalline diamond.²⁰ Another possible reason for the differential conductivity, and one consistent with the electron emission studies published recently, is a variable work function across the surface.²² It has been reported that the work function of diamond depends on the crystallographic orientation.³² There are two reasons for this. First, the (100) face has the highest density of dangling bonds while the (111) face has the lowest.^{33, 34} Second, polycrystalline films that are hydrogenterminated exist with a less than full coverage on the (100) surface³³ as compared to the (111) surface,³⁵ with the work function being dependent on the surface coverage. In fact, hydrogen is a ubiquitous elemental component of diamond. Chemisorbed hydrogen serves to maintain the sp^3 bonding on the surface and prevents formation of π -bonded carbon. Therefore, its presence has a significant influence on the local work function. Furthermore, it has been known for some time that the electrical properties of diamond surfaces are strongly modified by the presence of hydrogen.³⁶⁻³⁸ Hydrogenation leads to an increase in surface conductivity through increased hole conduction as the element acts as an electron acceptor with an activation energy lower than that for boron. ³⁶⁻³⁸ The surface conductance can also be influenced by electrochemical transfer doping by surface adsorbates.³⁹ Finally, hydrogen can reduce the conductivity of boron-doped diamond by forming acceptor-donor complexes with substitutionally-inserted boron.⁴⁰ Differential local work functions would contribute to variable electrical conductivity across the surface (i.e., from facet-to-facet). Several groups have reported work function variations for hydrogen and oxygen-terminated diamond when imaged by Kelvin probe microscopy.^{41, 42} Based on such measurements, Brandes and Mills concluded that defects and/or oxygen on the surface likely produce the surface states that create the positive electrical field due to surface electron occupying these surface states.⁴³ This would decrease the surface conductivity. Although these measurements were performed on undoped diamond, it's reasonable to expect that the accumulation of boron on the surface will increase the surface states and change the surface conductivity of boron-doped diamond.⁴⁴ Wang et al. reported, based on field emission imaging and scanning tunneling spectroscopy studies, that the dominant emission sites in boron-doped p-type diamond are located at or near the grain boundaries due to a lower work function than the surrounding grains.⁴⁵ Finally, Ternyak et al. mentioned another possible reason for the differential conductivity and that is inhomogeneous hydrogen and impurity coverage across the surface, which could affect the surface conductivity in CP-AFM measurements made in air.²⁸

4.3 CP-AFM images of microcrystalline films

Figure 4.2 shows conductivity maps of microcrystalline films grown with 10, 5, 1, 0.5, and 0 ppm B₂H₆ added to the source gas mixture. A bias voltage of +2.0, rather than +0.2 V, was needed to image these films. This is because there was a greater tip-electrode contact resistance with the microcrystalline films. Therefore, instead of measuring a current from 0 to 6.5 μ A, as was the case for nanocrystalline diamond doped with 50 ppm B₂H₆, the current measured for microcrystalline diamond ranged only from 0 to 0.65 μ A. We attribute this increased resistance to a reduced tip contact area with the rough microcrystalline surface. The images reveal a pattern of heterogeneous conductivity similar to that of the nanocrystalline films and similar to that of other previously imaged microcrystalline films.²⁶ Some of the conductive regions are clustered together, whereas others are more isolated. The conductive

regions for the highly doped films are several micrometers in lateral dimension meaning that the sites comprise both faceted crystallites and the grain boundary between them. As was the case for the nanocrystalline films, the fraction of highly conductive area decreased with decreasing boron-doping level.



Figure 4.2 CP-AFM images $(10 \times 10 \ \mu\text{m}^2)$ of microcrystalline BDD thin films grown with different source gas B₂H₆ concentrations (i.e., different doing levels): (A) 10, (B) 5, (C) 1, (D) 0.5 and (E) 0 ppm B₂H₆. The bias voltage used for all images was +2.0 V vs. the tip. The current ranges from 0 to 0.65 μ A. (Reprinted with permission from *J. Phys. Chem.* 111, 3986 (2007). Copyright (2007) American Chemical Society.) (From Ref. 49).

On the basis of the conductivity data reported above, several points of comparison can be made between the two diamond film types, although it should be re-emphasized that both highly doped film types function well as electrochemical electrodes.^{6, 14, 30} First, the contact resistance between the diamond and the Au tip was

greater for the microcrystalline film. Second, the fraction of the imaged area that exhibited high electrical conductivity was less for microcrystalline diamond. As discussed above, there are several possible reasons for the differential conductivity across the surface of a boron-doped film. CP-AFM is sensitive to the contact resistance between the tip and electrode, which is proportional to $\rho l/a^2$. The resistivity, ρ , of the film in the vicinity of the tip is proportional to the product of the local carrier concentration and the carrier mobility. Since both film types have approximately the same macroscopic resistivity (ca. $10^2 \Omega cm$), we suppose that the difference in contact resistance for the two film types is related to the size and shape of the tip relative to the grain size and morphology of the film surface. To address this issue more clearly, a SEM image for the conductive tip used in this study is shown in Figure 4.3.



Figure 4.3 SEM image of a gold-coated, tetrahedral-shaped silicon nitride tip (Veeco NPG-20) with an apex radius of curvature less than 50 nm and a tip height of ~15-20 µm.

The apex radius of curvature is approximately 50 nm, which is much smaller than the grain size (ca. 1 μ m) of the microcrystalline film but comparable to the nodular features (ca. 50 nm) of the nanocrystalline film. Therefore, the contact area between the tip and the sample for microcrystalline diamond films is likely greater than that for nanocrystalline diamond films. This is schematically depicted in Figure 4.4. When the tip scans over a microcrystalline film, the tip interacts with the surface using a smaller contact area (Figure 4.4A) than when imaging a nanocrystalline film (Figure 4.4B). The smaller contact area gives rise to a higher contact resistance and lower current for a given bias voltage. The difference in contact area could also explain why the microcrystalline film has a less conductive area.

A. CP-AFM tip interaction with a microcrystalline BDD film



B. CP-AFM tip interaction with a nanocrystalline BDD film



Figure 4.4 Schematic representation of how the tip interacts with the (A) rougher and faceted microcrystalline diamond film and (B) smoother nanocrystalline diamond film. (Reprinted with permission from *J. Phys. Chem.* 111, 3986 (2007). Copyright (2007) American Chemical Society.) (From Ref. 49).

4.4 CP-AFM images and topography

Figure 4.5 shows topographical (A) and conductivity (C) maps for a nanocrystalline diamond film grown with 10 ppm B_2H_6 in the source gas, along with line profiles through each image (B and D). The bias voltage was +0.2 V, and the scan size was 500 × 500 nm². In the topographical map, nodular features of 50-100 nm in the lateral dimension are seen. The boundaries between these features are also clearly visible, as is a depression in the topography in the upper right quadrant of the image. This region is about 50 nm in width and 250 nm in length. Some of the least conducting regions in the image are actually associated with features of greatest topographical height. These are the sites where presumably the tip would have the least area in contact with the surface, hence a greater contact resistance. In contrast, many of the most conducting regions are associated with low points in the topography where the contact area with the tip would be greatest. The exception to this is point d where a relatively high topographical feature exhibits high conductivity. The contact resistance at the highly conducting regions is approximately the same over the surface as evidenced by the constant magnitude of the current. By use of the equation

$$R = V_{bias}/i \tag{4.2}$$

where V_{bias} is the applied voltage and *i* is the measured current, a contact resistance of $\sim 1 \text{ M}\Omega$ was calculated. It is supposed that this contact resistance also reflects the resistance of current flow from the tip to the electrode and then through the diamond bulk, the diamond/Si interface, and the conducting Si substrate before reaching the metal current collector (see Section 2.5 and Figure 2.9). Importantly, not all of the nodular features and surrounding grain boundaries exhibit high conductivity. For

example, it can be seen in Figure 4.5D that the line scan passes through a nodular feature on the left that exhibits low conductivity. At its boundary (mark a), high conductivity is exhibited. The line scan then goes through another nodular feature on the right (mark d) that exhibits high conductivity. This again maybe related to inhomogeneous boron dopant distribution in the nanocrystalline film.⁴⁶⁻⁴⁸



Figure 4.5 Topographical (A) and conductivity maps (C) for a $0.5 \times 0.5 \text{ }\mu\text{m}^2$ region of a nanocrystalline BDD thin film grown with 10 ppm B₂H₆ in the source gas. Corresponding line profiles through the image (B and D) are also presented. The bias voltage used to obtain the conductivity map was +0.2 V vs. the tip. The Z-axis scales are 0 to 50 nm for height image and 0 to 0.65 μ A for the current image. (Reprinted with permission from *J. Phys. Chem.* 111, 3986 (2007). Copyright (2007) American Chemical Society.) (From Ref. 49).

The relationship between the conductivity and topography of microcrystalline films was also examined by CP-AFM. Figure 4.6 shows the conductivity (A) and deflection mode (B) maps of microcrystalline film doped with 10 ppm diborane added to the source gas mixture. The bias voltage applied to BDD thin-film was +0.2 V relative to the tip and the scan size was $2 \times 2 \mu m^2$. For microcrystalline diamond films, only one or two grains can be imaged within this scan size. The grain boundaries can be imaged clearly in this range and this helps to study the relationship between the topography and conductivity of the sampled surface. The deflection image is shown here because it more clearly reveals the grain boundaries. The deflection image is gained by measuring the twisting motion of the tip as it travels across a surface. Therefore, it is more sensitive to the grain boundary because big changes of the surface curvature exist in boundaries causing much bigger twisting of the cantilever. There is evidence of this in the images in Figure 4.6, where some correlation is observed between the surface topography and conductivity, with many areas of high conductivity being associated with grain boundaries between diamond crystallites. Most of crystalline facets do not show high conductivity. A possible reason for the lower conductivity of the facets is that continuous electrical pathways from these areas to the conductive substrate might not exist. In the present work, electrical contact was made from the bottom of the silicon substrate by carbon tape and silver paint (see Fig. 2.9), and this means that conduction is only possible through certain pathway on the diamond film from the substrate to the surface. Therefore, areas of conductivity imaged by CP-AFM may correspond to sites where surface boron dopant (or other impurity such as sp^2 carbon) sites can establish electrical contact to the silicon substrate through the film. Another reason might be the boron aggregation in grain boundaries, as mentioned above.^{17, 18, 20}



Figure 4.6 Conductivity (A) and topographical maps (B) for a $2 \times 2 \mu m^2$ region of a microcrystalline BDD thin film grown with 10 ppm B₂H₆ in the source gas. The bias voltage was +0.2 V vs. the tip. The current scale was 0 to 0.65 μ A.

4.5 Effect of bias voltage polarity

When a p-type semiconductor electrode is positively biased, electrons should easily flow from the conducting tip into acceptor states at the electrode surface. However, when the electrode is negatively biased, current flow should be inhibited due to a depletion of charge carriers at the surface (this is true for the case of $\Phi_s < \Phi_m$, where Φ_s is the work function of the semiconductor, i.e., diamond, and Φ_m is the work function of gold, i.e., the tip used in present work). On the other hand, a conductor will obey Ohm's Law, which means the current flow will be proportional to the bias voltage and that the polarity only changes the direction of current flow, not the magnitude. Experiments were performed with both diamond film types to study how the conductivity maps changed as a function of the bias voltage polarity. Both highly doped microcrystalline and nanocrystalline BDD showed conductive features that did not change in size or number with the bias polarity. Figure 4.7 shows a typical example for a nanocrystalline film grown using 10 ppm B₂H₆ in the source gas. Conductivity maps were recorded over the same region at +0.2 and -0.2 V (parts A and C). Line profiles of the current response are also presented (parts B and D). The conductivity maps and the current-line plots are nearly mirror images of one another. The same regions of the film exhibited high conductivity at both bias voltages regardless of the polarity. This means that the conducting sites are ohmic in nature and possess metal-like electronic properties. Furthermore, the current magnitudes at the conducting sites were similar for a given bias voltage and no new conductive regions appeared or disappeared with change in bias voltage.



Figure 4.7 Conductivity maps $(2 \times 2 \ \mu m^2)$ obtained from CP-AFM images of the same area of a nanocrystalline BDD thin film grown with 10 ppm B₂H₆ in the source gas at bias voltages of (A) +0.2 V and (C) -0.2 V vs. the tip. Corresponding line profiles of the same region are presented in (B) and (D). The Z-axis scale was 0 to 0.65 μ A for both A and C. (Reprinted with permission from *J. Phys. Chem.* 111, 3986 (2007). Copyright (2007) American Chemical Society.) (From Ref. 49).

The dependence of the current magnitude on the bias voltage was also investigated. Parts A-C of Figure 4.8 show three conductivity maps at bias voltages of +0.2, +1.0, and +2.0 V vs. the tip for the same region of a nanocrystalline BDD grown with 10 ppm B₂H₆ in the source gas mixture. The circles in every panel mark the same conductive area in each image.

The current flow at the marked site increased from 0.11 to 0.54 to 1.21 μ A with increasing bias voltage. This corresponds to a relatively constant contact resistance of 1.82, 1.85, and 1.65 M Ω , respectively. The ratio of the current magnitudes was 11:5:1, which is close to the ratio of the applied bias voltages, 10:5:1. This is the expected behavior for a metallic conductor. Even with the image drift, these images also show that no new conductive sites appear with increasing bias voltage. A fixed number of conducting areas exist in each film, particularly for the more highly doped ones. In other words, the fraction of conducting area does not vary with the magnitude of the bias voltage. This is different from the continuous image tunneling spectroscopy (CITS) results (discussed later in Section 4.8).



Figure 4.8 CP-AFM section analysis of $(1 \times 1 \ \mu m^2)$ of a nanocrystalline BDD thin film grown with 10 ppm B₂H₆ in the source gas at bias voltages of (A) +0.2, (B) +1.0 and (C) +2.0 V vs. the tip. The measurements were made on the same area of the film. (Reprinted with permission from *J. Phys. Chem.* 111, 3986 (2007). Copyright (2007) American Chemical Society.) (From Ref. 49).

4.6 CP-AFM images and surface termination

Conductivity maps for "as grown", hydrogen-terminated and oxygenterminated microcrystalline and nanocrystalline boron-doped diamond thin films were also acquired. Figure 4.9a and c show $1 \times 1 \mu m^2$ conductivity maps for "as grown" microcrystalline and nanocrystalline diamond thin films (stored in lab atmosphere for weeks), respectively. These images were collected with the sample biased at 0.2 V positive relative to the tip. This means that the electrons were flowing from the tip into the diamond film. The map of the microcrystalline diamond film surface reveals considerable electrical heterogeneity. There are regions of high electrical conductivity (the bright areas) isolated by regions of significantly lower conductivity. It can be seen from the scale bar that currents approaching 0.65 μ A are flowing through the conducting regions (Figure 4.9b). Similar heterogeneity was observed in images over a larger area $(10 \times 10 \ \mu m^2)$. Variable conductivity is also seen for the nanocrystalline film. However, the fraction of area that is conducting is greater for the nanocrystalline film. It can be seen from the profile (Figure 4.9d) that the current passed through the conducting regions of the nanocrystalline film is lower than that for the microcrystalline film. This could be due to the difference in contact area between the pyramidally-shaped tip and the rough microcrystalline surface and the smooth nanocrystalline surface. The tip curvature is approximately 50 nm, which is much smaller than the grain size (ca. 1 µm) of the microcrystalline film but comparable to the nodular features (ca. 50 nm) of the nanocrystalline film. When the tip scans over a microcrystalline film, the tip may interact with the surface using a larger contact area than for the nanocrystalline film in some special regions (e.g., grain boundaries) as shown in Figure 4.4.⁴⁹ The higher contact area gives rise to a lower contact resistance and a larger current for a given bias voltage.



Figure 4.9 CP-AFM images $(1 \times 1 \mu m^2)$ for "as grown" (a) microcrystalline and (b) nanocrystalline BDD thin films. A bias voltage of 0.2 V vs. the tip was used for all images. The current ranged from 0 to 0.65 μ A.

Figure 4.10a and c show $1 \times 1 \mu m^2$ conductivity maps for a freshly rehydrogenated and an oxidized nanocrystalline diamond thin film. In these images, the sample was biased 0.2 V positive to the tip. It's noteworthy that, compared to the "as grown" films (see Figure 4.9), the rehydrogenated film is less in surface oxygen while the oxidized film is rich in surface oxygen. This is why these images are so different from those in Figure. 4.9. Although the map of the H-terminated surface reveals heterogeneous conductivity, the fraction of area that is conducting is much greater than that for the O-terminated nanocrystalline film. It can be seen from the scale bar (Figure 4.10b) that the conducting regions are passing currents near 0.65 μ A for the H-terminated nanocrystalline film, whereas the currents passed for the Oterminated film are around just 0.1 µA (factor of 6 times less, see Figure 4.10d).



Figure 4.10 CP-AFM images $(1 \times 1 \ \mu m^2)$ for (a) hydrogen-terminated and (b) oxygen-terminated nanocrystalline BDD thin films. A bias voltage of 0.2 V vs. the tip was used for all images. The current ranged from 0 to 0.65 μ A for H-terminated film and 0 to 0.16 μ A for O-terminated film.

Figure 4.11a and c show $1 \times 1 \mu m^2$ conductivity maps for freshly hydrogenated and oxidized microcrystalline diamond thin films. In these measurements, the bias potential applied was 0.2 V relative to the tip. The map of the H-terminated diamond surface reveals that the surface is not uniformly conducting. There are regions of higher electrical conductivity isolated by



Figure 4.11 CP-AFM images $(1 \times 1 \ \mu m^2)$ for (a) hydrogen-terminated and (b) oxygen-terminated microcrystalline BDD thin films. A bias voltage of 2.0 V vs. the tip was applied for hydrogen-terminated film and the currents at some sites were out of range (> 3.25 μ A). For the oxygen-terminated film, a bias voltage of 0.2 V vs. the tip was applied and the current ranged from 0 to 0.65 μ A.

regions of lower conductivity. The image for the O-terminated microcrystalline film also shows isolated conducting regions. Although the currents passed through the Oterminated film are lower than those for the H-terminated film, the O-terminated microcrystalline film shows a lower fraction of conducting area than does the Hterminated microcrystalline film (Figure 4.11b and d). Comparing with the conductive map of the O-terminated nanocrystalline film (Figure 4.10c and d), the conductive map of O-terminated microcrystalline film reveals higher fraction of conductive area and larger current for the former when probed at same bias potential (Figure 4.11c and d). However, these changes in conductivity are reversible. High conductivity can be recovered after removal of the oxygen functionalities by rehydrogenation.

4.7 Special issues with CP-AFM measurements

There are several critical issues when imaging polycrystalline diamond by CP-AFM. One of these is the tip chemistry and shape. The tip used in this work was a gold-coated, tetrahedral-shaped silicon nitride tip (Veeco NPG-20), with an apex radius of curvature less than 50 nm, a tip height of ~15-20 μ m, and a full-tip cone angle less than 35°, mounted on a rectangular cantilever. In limited scans, this type of tip worked well, as shown in Figure 4.12.



Figure 4.12 CP-AFM images during 2 consecutive scans over the same area of a 10 ppm boron-doped nanocrystalline diamond thin film (rehydrogenated). The bias voltage applied was +0.2 V vs. the tip.

However, because of the hardness of diamond, the Au coating over the tip as well as its tetrahedral shape is adversely affected by the mechanical action with the
surface. Au is removed and the sharp tip is smoothed and flattened during scanning over the hard surface. This causes the CP-AFM image to change over time. For example, it is observed that the conducting regions of a particular film decrease in number and size with increasing scan number (Figure 4.13). In general, we found that stable conductivity maps could be obtained with a tip for both film types for up to 4 scans over a 10 × 10 μ m² area. All CP-AFM maps presented herein were recorded over an area at least twice to make sure the image features were real and were not artifacts of the tip condition.



Figure 4.13 CP-AFM images as a function of the scan number for a 10 ppm borondoped nanocrystalline diamond thin film. (A) 1st scan, (B) 5th scan and (C) 10th scan. It shows that the CP-AFM images changed after 5th scan. The bias voltage applied was +0.2 V vs. the tip.

Another issue is the overloaded current. The conductivity may be very high for some highly doped diamond nanocrystalline films (e.g. 50 ppm hydrogenated nanofilms). In this case, a bias of just 0.2 V vs. the tip produces a large current that can damage the Au overlayer on the tip. In our work, we experienced an extremely serious case where the current flow ceased before one image could be completed. Using SEM, we found the tip was total etched away, as shown in Figure 4.14. The part of the tip itself and the Au coating on it might be melted and etched away at a high temperature due to the large current.



Figure 4.14 SEM images for (A) an original CP-AFM tip and (B) a damaged tip after one scan with an overloaded current. The image was taken using a JSM-6300F (field emission) scanning electron microscope in the Center of Advanced Microscopy at Michigan State University.

4.8 Continuous imaging tunneling spectroscopy (CITS)

images

The results that were obtained by CP-AFM on boron-doped diamond thin films conflicted, to some extent, with results published in the literature.^{27, 50} For example, we observed that the grain boundary area possesses special features of electrical conductivity.⁴⁹ Using the same technology (i.e. conducting probe AFM), Macpherson and coworkers observed no difference between the grain boundaries and other areas on a film.^{27, 50} A noteworthy fact is that their sample was a polished, oxygen-terminated boron-doped diamond film, which was quite different from our samples. Second, Schottky I-V curves have been recorded for undoped,^{51, 52} oxidized⁵¹, hydrogen-terminated⁵³ and boron-doped diamond samples.⁵⁴ Baker et al. reported Schottky I-V curves for an oxidized synthetic boron-doped diamond ([B] was 3 - 1500 ppm as measured by secondary ion mass spectroscopy) with a threshold voltage greater than +3.8 V.⁵⁴ Our CP-AFM measurements showed a linear relationship between the applied bias and the recorded current. This observation held true both from -2.0 to -0.2 V and +0.2 to +2.0 V vs. the tip. We did not test the electrical properties of our samples between ± 0.2 V vs. the tip. In other words, we observed metallic-like properties for our boron-doped diamond films (Figure 4.6).

CITS⁵⁵ is a good choice for us to check if our results reliable. CITS is a scanning probe microscopy developed from scanning tunneling microscopy by Hamers et al. in 1986.⁵⁵ The principle of CITS is very similar to that of STM. Usually, CITS works in a constant-current STM mode but the feedback control circuit used for constant-current STM is gated so that it is only active in a part time (e.g., 30%). When the feedback loop is active, a constant voltage is applied. When it is inactive, the position of the tip is held stationary and the tunneling current is measured at various bias voltages. Repeating this sequence at a certain frequency, a constant sample-tip distance is maintained during all i-V measurements and the i-V characteristics of each point along the scan are determined simultaneously with the topography. This method can record the real-space images of the tunneling current directly reflecting the spatial

distribution of the surface states at different potentials. In other words, the technique can be used to measure current-voltage characteristics at each point in the scanned area. Therefore, this technique is a powerful tool to determine whether the nature of a metal-semiconductor contact is ohmic (linear response of current to voltage) or Schottky (nonlinear response of current to voltage).⁵⁴ In fact, Iseri et al. recorded both ohmic and Schottky I-V curves on different sites in the same microcrystalline diamond film.¹⁶ To further study the electrical properties of our diamond films and to confirm our CP-AFM measurements, we sent a batch of microcrystalline and nanocrystalline BDD diamond thin films to Prof. Steven Prawer's laboratory (University of Melboune, Australia). All CITS images presented here were obtained by Prof. Prawer's group.

4.8.1 CITS measurements for microcrystalline boron-doped diamond films

Figure 4.15 shows $2 \times 2 \ \mu m^2$ CITS and topographic images obtained for a microcrystalline boron-doped diamond film grown on a highly doped Si substrate. The bright region in Figure 4.15A indicates the high tunneling current area. It can be seen that most of the film, except the middle region at top right of the image emitted electrons. Figure 4.15 C shows a superimposed image of tunneling and topography. It clearly shows that some grain boundaries on some specific facets emit electrons strongly.

According to the CITS measurement, two specific regions were selected: one of high conductivity and one of low conductivity, respectively. The I-V characteristics for these two regions were measured and shown on Figure 4.16. The I-V curves shown in Figure 4.16 are the averaged results over the selected region, respectively. Figure 4.16A shows a selected grain boundary and its I-V characteristics. An almost perfect linear relationship between the tunneling current and the applied sample voltage indicates that this region possesses typical ohmic (metallic) nature within the applied voltage (± 2.5 V). Figure 4.16B shows a selected facet with low electron emission and its I-V characteristics. The I-V curve clearly shows that the tunneling current is near to zero from -0.7 to +0.5 V for this region. When the applied voltage is higher than +0.5 V or lower than -0.7 V, the tunneling current increases exponentially, indicating this region possesses Schottky (semiconductor) electrical properties.



Figure 4.15 (A) CITS and (B) topographic images for microcrystalline borondoped diamond thin film grown by CVD on highly doped Si substrate. (C) is the superimposing image of (A) and (B).



Figure 4.16 Differential electrical properties of two regions of a microcrystalline BDD thin film. (A) a selected region on the topographic map (white square) and its I-V characteristics showing ohmic behavior, and (B) a selected region on topographic map (white square) and its I-V characteristics showing schottky behavior.

More interesting images were acquired for a microcrystalline diamond thin film with higher boron doping level. Figure 4.17 shows the topographic images ($10 \times 10 \text{ } \text{µm}^2$) and I-V curves (averaged) for selected regions on this film. In a grain boundary region (Figure 4.17A), the I-V curve shows linear relationship over ±2.0 V except when the polarity of the testing voltage changes. The current jumped from ca. -1 nA to +2.0 nA as the polarity of voltage changed from negative to positive. On the other hand, the current was near zero over this voltage range at a crystalline facet but increased at more positive and more negative bias voltages. There is clearly a gap where current flow is negligible. It's noteworthy to mention that the current scale for Figure 4.17B was 2 orders of magnitude smaller than that for Figure 4.17A.



Figure 4.17 Differential electrical properties of two regions of a microcrystalline BDD thin film. (A) a selected region with high electron emission on the topographic map and its I-V characteristics, and (B) a selected region with low electron emission on the topographic map and its I-V characteristics. Scanned size: $5 \times 5 \ \mu m^2$.

All of the above results suggest that some grain boundary regions are much more electrically conductive than some of the crystals of the microcrystalline borondoped diamond thin film.

4.8.2 CITS measurements for nanocrystalline boron-doped diamond thin films

Nanocrystalline boron-doped diamond thin films were also imaged by CITS to study the relationship between the topography and electronic properties. Figure 4.18 shows $1 \times 1 \,\mu\text{m}^2$ topographic images for a nanocrystalline boron-doped diamond film grown on highly doped Si substrate. Two representative regions were selected (regions within white rectangle) and their I-V curves (averaged results over the selected region) were recorded and also shown in Figure 4.18. From the topographic images, nodular features with different sizes (50 \sim 250 nm) are clearly seen. Both selected regions consisted of nodular surfaces and boundaries, expected a nanocrystalline diamond film grown from an Ar-rich source gas. But the CITS measurements revealed quite different electron tunneling in these two regions. For the selected region shown in Figure 4.18A, a linear relationship between the tunneling current and the applied sample voltage was recorded indicating a typical ohmic (metallic) nature within the applied voltage (± 2.0 V). Figure 4.18B shows a different image of electron emission on this diamond film. The I-V curve clearly shows that the tunneling current is near to zero from -0.7 to +0.5 V. When the applied voltage becomes greater than +0.5 V or less than -0.7 V, the tunneling current increases exponentially, indicating this region possesses Schottky (semiconductor) electrical properties. Different from what was observed for microcrystalline diamond film (Figure 4.16), where different current scales were recorded for different regions indicating high or low electron emission. The currents for two different selected regions at same bias voltage were similar except for the inhibiting voltage. This means that these two regions both possess high electron emission but they emitted electrons through different mechanisms.



Figure 4.18 Different electrical properties of two representative regions on a nanocrystalline boron-doped diamond thin film. (A) a selected region with ohmic behavior on the topographic image and its I-V characteristics, and (B) a selected region with Schottky behavior on the topographic image and its I-V characteristics.

Prof. Prawer's group also probed our nanocrystalline films in contact mode with a conductive cantilever (W₂C). Just like CP-AFM, this technique can investigate the electrical conductivity and topography spatially over the sample surface. Figure 4.19 shows (A) a current image, (B) a topographic image and (C) a merging of these two images. In the current image, the current level is indicated by the brightness. "CITS" data were acquired with bias voltage from -2 to +2V.



Figure 4.19 CITS images probed in contact mode with a conductive tip for a nanocrystalline boron-doped diamond thin film. (A) current image, (B) topographic image, and (C) superimposing of (A) and (B).

As seen in Fig. 4.19A, current was observed over most regions of the surface indicating a pretty high fraction of conductive area. However, levels differed from site to site. At the top right corner, an area of $100 \times 30 \text{ nm}^2$ corresponding to part of a nodular structure has only a few conductive points. Low conductive or insulating area is also seen in the bottom of left corner including several nodular boundaries. The relationship between electrical conductivity and topography can be seen more clearly in Figure 4.19C. Most boundary and grain regions are conductive, but low conductive or insulating areas.

A section analysis is shown in Figure 4.20. Figure 4.20A and C show the topographic and current images with a diagonal line (white line) selected for section analysis. Figure 4.20B shows the height profile and Figure 4.20D shows the current profile for the selected line. 4 nodular structures were probed in this measurement. As seen in Figure 4.20, neither the nodule nor the boundary in the upper left possessed any conductivity. On the other hand, a near-saturated current was recorded for the second nodular structure (on the top left, next to the first one) and boundary. The third nodular structure in the center of the scanned area did not show high conductivity except for several individual points. The forth nodular structure on the right bottom corner showed good conductivity although the conductive regions were discrete and the recorded currents were half of the saturated current.



Figure 4.20 Topographic and current images obtain by CTIS in contact mode for a nanocrystalline highly boron-doped diamond thin film. (A) height image with a marked line selected for section analysis, (B) height profile for the selected line, (C) current image with a marked line selected for section analysis, (D) current profile for the selected line.

The results presented here indicated that the electrical properties of nanocrystalline boron-doped diamond thin film are different from those of microcrystalline boron-doped diamond thin film. For microcrystalline diamond, almost all grain boundary regions are conductive with many of the crystals possessing low conductivity. However, most regions of the nanocrystalline diamond film exhibit high electrical conductivity. There are some nodules and boundaries in the nanocrystalline film that possess low conductivity or are insulating, but the fraction of conductive area is greater than that for microcrystalline films. More importantly, all these results are consistent with the observation we got from our CP-AFM measurements although CITS revealed the local work function of the sample instead of the electrical conductivity directly. In fact, the local work function can be associated with the local conductivity because lower work function means electrons can escape or cross the surface of interface of a contact easier, which corresponds higher electrical conductivity.

4.9 Conclusions

CP-AFM was used to investigate the spatial heterogeneity of the electrical conductivity of microcrystalline and nanocrystalline BDD thin films as a function of the boron-doping level, surface morphology, polarity of the applied voltage and surface terminations. All films were characterized by a fixed number of isolated conductive regions separated from one other by less conducting zones. The fraction of highly conductive area increased with increasing boron-doping level. The current at the conducting sites increased proportionally with the bias voltage, and was the same magnitude and independent of the bias voltage polarity indicating the conductive sites possess metal-like electronic properties. Each film was characterized by a fixed number of conductive sites as no new sites emerged with increasing bias voltage of both polarities. Similar observations were made for microcrystalline BDD. CP-AFM measurements also show that the fraction of highly conductive area depends on the surface termination and diamond particle size. The results clearly show that the

fraction of highly conductive area for nanocrystalline BDD thin film is higher than that of microcrystalline BDD thin-film. The morphology of CP-AFM images for nanocrystalline diamond films is also a little different from that for microcrystalline diamond films. For microcrystalline diamond films, most highly conductive regions are located at the grain boundary area but this association is much weaker for nanocrystalline diamond films. In other words, the highly conductive area is somewhat independent on the topographic features for nanocrystalline diamond films.

CITS measurements were also applied to our microcrystalline and nanocrystalline boron-doped diamond thin films. CITS measurements revealed both microcrystalline and nanocrystalline diamond films with both metallic and semiconducting properties. This is an important observation. These results partially confirmed our CP-AFM measurements. For example, Schottky behavior was recorded on some grain facets within ± 2 V (see Figure 4.16). These facets are poorly conductive or insulating when probed by CP-AFM because of the Schottky effect. CITS measurements revealed that these facets emitted electrons after the applied voltage increased over 2. 0 V. Therefore, these facets may be non conductive when probed using CP-AFM with a bias voltage less than 2.0 V.

4.10 Reference

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Chapter 5

Heterogeneous Electrochemical Activity of Polycrystalline Boron-Doped Diamond Films

5.1 Introduction

Several authors have investigated the charge transfer kinetics for different redox couples at BDD electrodes using a variety of electrochemical methods.¹⁻⁶ Much has been learned about how different factors control the electrochemical properties of BDD. Depending on the redox molecule, factors such as the boron-doping level, surface chemistry, nondiamond sp² carbon impurity and film morphology can be influential.

One model of electron transfer at BDD involves mediation via impurity states present within the band gap. These states could arise from the boron doping or from impurities present, such as sp²-bonded carbon,¹ so the rate of the charge transfer is dominated by the available density of states near the formal potential of the redox couple. More accurately, the heterogeneous electron-transfer rate constant will depend on the availability of states of the correct energy relative to the potential of the redox couple. Such states could arise from the overlapping of wave functions of neighboring boron atoms and hence result in the formation of an impurity band. In fact, van de Lagemaat et al.⁵ suggested that interfacial states (at or near the surface), distributed in energy throughout the band gap, mediate electron transfer between the valence band and the redox system at a boron-doped, single-crystal diamond electrode. The surface states are supposed to be associated with defects or impurity sites located very close to the surface, perhaps caused by hydrogen, boron, oxygen, or carbon inclusions. Such an exchange may take place by multiple-electron-hopping (a model developed by Mott⁷ to describe electrical conduction in strongly disordered systems with localized states). The act of electron-transfer is usually considered as tunneling of the electron between states of the electrode and those of the reactant. Therefore, heterogeneous electron-transfer kinetics are highly dependent on the rate of tunneling of electrons to and from the redox species in solution. Electron tunneling typically follows an expression of the form:⁸

$$p(i) \propto \exp(-\beta x)$$
 (5.1)

where p(i) is the probability of tunneling, x is the distance over which tunneling occurs, and β is the height of the energy barrier and the nature of the medium between the states. Thus, if deep boron dopant sites are involved in the electron-transfer, then the kinetics may be slow and limited by the rate at which the carrier can migrate to the surface. The electron transfer rate will also be sensitive to the state of the surface. For example, the heterogeneous electron-transfer rate constants for BDD electrodes are generally lower than those for noble metals. An explanation for this is that there is a lower density of electronic states (DOS) of an appropriate energy. The available DOS and carrier migration will depend on the dopant concentration. Thus, as the boron content is increased, a greater density of states may be available for electron transfer, although the charge carrier mobility will decrease as the charge carrier concentration increases with the concentration of boron.

In the second model, polycrystalline boron-doped diamond surfaces exhibit heterogeneity in electron-transfer rates over the surface due to nonuniform distribution of dopant throughout the diamond film. In other words, the surface may consist of sites of fast (reversible) kinetics where the dopant level is high and sites of very slow kinetics (irreversible) where there is less dopant. This model arises due to the observation that boron incorporates into the diamond structure in different concentrations depending on the crystal face of the diamond. For example, the boron concentration in {111} growth sectors is five or more times greater than that found in {100} sectors.⁹ Additionally, dopant may also accumulate in the grain boundaries, crystal edges, and other defects, but these atoms are not expected to be electronically active. Macroscopically, different crystal faces are exposed on the polycrystalline surface, resulting in a heterogeneous electron-transfer rate that is an average value for the whole electrode area. In other words, any heterogeneity in the electron transfer kinetics can not be directly observed in electrochemical measurements. Becker et al. studied diamond films with doping levels between 200 and 6000 ppm using cyclic voltammetry and electrochemical impedance spectroscopy.³ They observed strong deviations from reversible charge transfer for "outer-sphere" reactions (Fe(CN)₆^{3/4-} and $Ru(NH_3)_6^{3+/2+}$ with decreasing doping level. Limiting current densities that were lower than predicted and the existence of an additional capacitive element in the impedance spectra at higher frequencies led to the suggestion of a geometric surfaceblocking model, where only limited areas of the diamond film are believed to be electrically conducting. Hence this model suggests that the rate of electron transfer is not limited by the migration of carriers to the electrode surface but more by the availability of active surface sites for reaction. These may be sites where boron dopant has accumulated and where conductive pathways are available through the film.

Both of these models suggest that the rate of heterogeneous electron transfer will depend on boron concentration within the film. However, the mechanism for electron transfer might be different at different doping levels. For example, an electron-hopping mechanism may dominate at low boron levels, whereas conduction via the impurity band or surface states may be the main mechanism at higher doping levels.

Some redox couples, such as $Fe(CN)_6^{3-4-}$, which are traditionally treated as outer-sphere, behave anomalously at carbon-based electrodes and may change to an inner-sphere electron-transfer mechanism at diamond electrodes, where some degree of interaction occurs between the redox species and the electrode surface.^{1, 10} In these cases, factors such as the termination of the surface and presence of oxygen functionalities can influence the reaction kinetics.

As the redox systems, such as $Ru(NH_3)_6^{3+/2+}$, $IrCl_6^{2-/3-}$ and methyl viologen, are relatively insensitive to surface structure,¹¹ the most important factor affecting the heterogeneous electron-transfer rate constant is the electronic properties of the electrode, which depend on the dopant concentration and distribution.

This chapter describes the application of scanning electrochemical microscopy (SECM) to image diamond thin-film electrode surfaces, doped with varying gas-phase B_2H_6 concentrations from 0 to 10 ppm. These measurements produced maps of the electrochemical activity across the surface as a function of the boron-doping level. Combined with results from electrochemical characterization and CP-AFM, a microscopic partial blocking model is applied to interpret the electrochemical properties of boron-doped diamond thin film electrode.

5.2 Details of the scanning electrochemical microscopy measurements

5.2.1 Scanning electrochemical microscopy (SECM)

Scanning electrochemical microscopy (SECM) is type of scanning probe microscopy (SPM). SECM makes use of a microelectrode tip that approaches to within a few micrometers of a substrate and probes the electrochemical activity across the surface.¹²⁻²⁰ This technique was developed by the Bard group at the University of Texas at Austin in the late 1980s.¹²⁻¹⁴ SECM has been used in a variety of ways to study heterogeneous and homogeneous electrochemical reactions. A comprehensive review of the technique was published in 2001.²¹ The principle of SECM and all concepts and terms used in this chapter can be found therein.

Typically, the tip potential is chosen to oxidize or reduce a mediator species in a solution, with the measured current being controlled by the flux of the mediator. This flux depends on the properties of the substrate and the distance between the microelectrode and the substrate. Keeping the distance constant, the microelectrode current will be controlled by the substrate only. In other words, monitoring the current of the microelectrode reveals information about the activity of the substrate for the redox probe. There are several imaging modes with the two most common being the tip generation and tip collection modes. The tip generation mode involves holding the tip at a potential where an electrode reaction occurs. If the substrate is conductive and held at a different potential where a product of the tip reaction will react (be collected), the product of the substrate reaction will diffuse to the tip and cause an increase of the tip current. This is the so called positive feedback tip-generation/substrate-collection (TG/SC) mode. Figure 5.1 shows the general principle of this mode. On the other hand, if the tip is near an electrically insulating substrate, the substrate will hurdle diffusion of redox species to the tip and causes a decrease of the tip current (negative feedback). Therefore, scanning over the surface of a substrate and recording the tip current, one can obtain a current map revealing the electrochemical activity of the substrate.



Conductive substrate

Figure 5.1 General principle of the positive feedback tip-generation/substratecollection mode for SECM. The tip is near a conductive substrate, feedback diffusion leads to a larger tip current than when the tip is far away from the substrate.

5.2.2 Tip cleaning and activation

As mentioned before SECM involves the measurements of the current at a microelectrode probe. The properties of the substrate (working electrode) are revealed by the current changes resulting from the perturbation of the substrate. It's reasonable to expect that the microelectrode itself will strongly influence the current too. In fact, the electrochemical behavior of the microelectrode mostly depends on its configuration. Therefore, the roughness of the microelectrode surface, the thickness of the glass sheath and the isolation (sealing) of the microelectrode are very important

factors that influence the SECM measurements. One can find details about this in the book edited by Bard and Mirkin.²¹ Different materials including Pt, Au, carbon fiber etc. have been used as microelectrode tip with different configurations in SECM. All microelectrodes used in the present work were purchased from a commercial source (2 μ m diam. Pt microelectrodes, CH Instruments, Texas). Figure 5.2 shows the schematic diagram of the microelectrode probe tip.



Figure 5.2 Schematic of the *Pt* microelectrode probe tip used for imaging. All *Pt* microelectrodes were commercial products (CH Instruments Inc., Austin, TX). The nominal diameter of the microelectrode (*Pt* wire) was ca. 2 μ m sealed in glass sheath. The end of the assembly was treated by a special polishing procedure to make a flat disk shape.

All microelectrodes were cleaned before use. The method used to clean or activate the microelectrodes is discussed in Section 2.6. Below is shown a representative cyclic voltammetric *i-E* curve for a Pt microelectrode after cleaning. Figure 5.3 shows the last cycle of a series of repetitive cyclic voltammograms used to clean the Pt microelectrode. The cycles were performed in 0.1 mol/L HClO₄ at 0.1 V/s. All characteristic features of Pt are present, particularly the Hadsorption/desorption peaks near -0.1 V. This is consistent with the Pt being clean.



Figure 5.3 Typical cyclic voltammetric *i*-*E* curve for the Pt microelectrode after potential cycle cleaning in 0.1 mol/L HClO₄ at 0.1 V/s. All features of *Pt* are present indicative of a clean surface.

5.2.3 Calibration of the microelectrode

The nominal diameter of the microelectrode (Pt wire) is not known precisely due to variability in the manufacturing. In practice, the diameter of a microelectrode needs to be determined before it can be used for SECM imaging. In the present work, three redox couples $(Fe(CN)_6^{3-/4-}, Ru(NH_3)_6^{3+/2+} and IrCl_6^{2-/3})$ were used for SECM imaging; therefore, the microelectrode diameters were also determined using these three redox couples.

Aoki and Osteryoung^{22, 23} showed that the current-time curve for diffusion limited current at a disc microelectrode followed the following expression:

$$i = \frac{4nFADC^*}{\pi r_0} f(\tau)$$
(5.2)

where r_0 is the radius of the disc microelectrode, A is the area of the disc, D and C^{*} are the diffusion coefficient and bulk concentration of the redox species, respectively. τ is a dimensionless parameter defined as

$$r = \frac{4Dt}{r_0^2} \tag{5.3}$$

And at long times, $f(\tau) \approx 1$, equation (5.2) can be simplified to:²¹

$$i_{T,\infty} = 4nFDCr_0 \tag{5.4}$$

 $i_{T,\infty}$ is the steady-state current for a disk-shaped microelectrode. Equation (5.4) indicates that the limiting current is related to the radius of the tip, the diffusion coefficient and concentration of the redox species.

Applying equation (5.4), the diameter of the microelectrode can be determined by acquiring a cyclic voltammogram when the microelectrode is far away from the substrate and the concentration of the redox species is known. Figure 5.4 shows typical cyclic voltammetric i-E curves for the different redox species recorded at a Pt microelectrode. Sigmoidal-shaped curves were observed for all three. The small size of microelectrode makes diffusional mass transport extremely efficient. At relatively long experimental time scales, the dimensions of the diffusion layer exceed the radius of the microelectrode, and the planar diffusion field transforms into a spherical diffusion field. Consequently, the flux of electroactive species to the microelectrode is substantially higher than that for the pure planar diffusion case that is typical of a macroelectrode. This efficient mass transport allows one to observe steady-state responses when the applied potential is slowly scanned in cyclic voltammetry. The sigmoidal-shaped responses observed in these experiments are analogous to the polarograms obtained using a dropping mercury electrode, or a rotating disk electrode, but they are observed under entirely quiescent conditions. In fact, mass transport rates to a microelectrode are comparable with those of a conventional macroelectrode that is being rotated at several thousand r.p.m. The high flux at a microelectrode means that one does not observe a reverse wave under steady-state conditions (Figure 5.4), because the electrolysis product diffuses completely away from the electrode on the time scale of the measurement.

The steady-state limiting current is directly proportional to the analyte concentration (Equation 5.4), making it useful for analysis and determination of the microelectrode diameter. Table 5.1 summarizes the calibration results with different redox couples for a microelectrode with a nominal diameter of 2 μ m. The results show that the measured radius is pretty close to its nominal radius, although the values depend on the redox species.



Figure 5.4 Cyclic voltammetric *i-E* curves for (a) 1 mmol/L Ru(NH₃)₆^{3+/2+}, (b) 1 mmol/L Fe(CN)₆^{3-/4-}, and (c) 1 mmol/L IrCl₆^{2-/3-}, all in 1 mol/L KCl, at a *Pt* microelectrode. Scan rate = 0.1 V/s.

 Table 5.1
 Limiting current and calculated microelectrode radius determined by

 different redox systems.

Redox	i (pA)	D [*] (10 ⁻⁶ cm/s)	r₀ (μm)
Ru(NH ₃) ₆ ^{3+/2+}	23.15	5.50	1.09
Fe(CN) ₆ ^{3-/4-}	24.40	7.60	0.83
IrCl ₆ ^{2-/3-}	20.42	6.80	0.78

* Data from reference 6.

5.2.4 Tip approach curves

A plot of the experimental tip current vs. tip-substrate separation is called an approach curve and it can provide information about the nature of the substrate. Approach to an insulating surface typically results in negative feedback, where diffusion of fresh mediator species to the tip is blocked as it moves within a few tip radii of the substrate. In this case, the current rapidly drops to zero as the tip approaches the surface. If the substrate is a conductor, its potential can be selected so that it re-oxidizes or re-reduces the species being produced at the tip. In this case, as the tip approaches the surface, positive feedback results and the current increases as the tip approaches the surface. Therefore, when the microelectrode is several tip diameters from the surface, a steady-state current $i_{T,\infty}$ is observed. When the tip approaches a surface, the tip current i_T differs from $i_{T,\infty}$, and it depends on both the distance of separation, and the electrochemical activity of the surface. If the surface is an electronic insulator, $i_T/i_{T,\infty}$ will be less than unity. If the surface is an electronic conductor, then the flux of the redox species to the tip will be enhanced, and $i_T/i_{T,\infty}$ will be larger than unity. The actual current-distance relationship depends on the tip shape and on the heterogeneous electron-transfer rate constant of the 'feedback' reaction that occurs at the substrate surface.

The SECM instrument can record the current and the displacement of the microelectrode as it approaches a substrate. These data need to be treated and converted to a current-distance (between the microelectrode and the substrate) curve (approach curve).

Experimental approach curves can be compared to theory in order to accurately determine the height of the tip above the substrate surface. In fact, before performing SECM imaging of a substrate, one needs to generate the tip approach curve mode to accurately determine the microelectrode position near the substrate surface.

Figure 5.5 shows four approach curves recorded at the same position on a nanocrystalline BDD deposited with 10 ppm B_2H_6 in the source gas mixture. The curves were acquired with different engaging currents (approach stopped automatically according to a prescribed set-point). Ru(NH₃)₆^{3+/2+} was used as the redox system. The potential of the tip was -0.3 V vs. Ag/AgCl (mass-transfer limited reduction of Ru(NH₃)₆³⁺), and the potential of the diamond electrode was 0 V vs. Ag/AgCl (mass-transfer limited oxidation of Ru(NH₃)₆²⁺). The approach curves were acquired until the limiting current reached a value that was 2.3 times the value measured with the tip far away from the surface. At this point, the distance between the tip and the substrate was calculated to be ~1.0 µm using the following equation¹⁴

$$(i_T/i_{T,\infty}) = (\pi/4)(a/d) + 0.901 + 0.099 \exp[-0.16(a/d)] - 0.29 \exp[-0.39(d/a)]$$
(5.5)

where i_T is the tip current at any position, $i_{T,\infty}$ is the limiting current measured when the tip is positioned far from the surface, a is the tip radius, and d is the distance between the tip and the substrate.



Figure 5.5 SECM tip approach curves at the same position on a "as grown" nanocrystalline BDD thin film electrode in 1 mM Ru(NH₃)₆^{3+/2+} + 1 M KCl. The nominal diameter of the microelectrode was 2 μ m. The microelectrode was held at - 0.3 V, and the diamond electrode potential was held at 0 V vs. Ag/AgCl. i_T is the tip current, $i_{T,\infty}$ is the limiting current, and L = d/a, where d is the distance between the tip and substrate, a is the radius of the tip. The engaging current ratio for 1st to 4th approach was 1.5, 1.8, 2.5 and 2.2, respectively.

The curves are normalized to the limiting current in order to more clearly reveal the trends. The current at the tip is a function of the solution composition, the distance between the tip and the electrode, as well as the morphology and electronic properties of the diamond electrode.²⁴ With the tip many diameters away from the diamond electrode, a steady-state current was recorded at -0.3 V that increased proportionally with the analyte concentration. Far away from the diamond electrode, the diffusion layer near the tip is hemispherical, but this changes as the tip approaches the surface. If the diamond film is a conductor (boron-doped) and if the potential applied is sufficient to oxidize $Ru(NH_3)_6^{2+}$ back to $Ru(NH_3)_6^{3+}$ (0 V vs. Ag/AgCl in our case), then the current at the tip will increase due to recycling of the redox system (positive feedback). The opposite trend (negative feedback) will be observed if diamond is an insulator (e.g., undoped diamond). The positive increase in current as the tip approaches the diamond electrode is due to redox system recycling at the tip and means that region of the diamond electrode is electrochemically active (i.e., rapid rate of electron transfer) for this redox system. A theoretical approach curve for this redox system with positive feedback is shown, for comparison.

Once the tip current increases to the ratio of $i_T/i_{T,\infty} > 2.3$, which means the distance between the tip and the substrate is about 1 µm for a 2 µm tip, the scan was initiated in the constant height mode.

5.3 SECM images for boron-doped diamond thin films

5.3.1 Reproducibility of SECM imaging

The SECM is capable of measuring very fast heterogeneous electron-transfer reactions at a substrate surface by moving the tip close to the substrate. This SECM method of measuring heterogeneous electron-transfer rates relies on a steady-state response, and is therefore less sensitive to double-layer charging effects and adsorption of electroactive species, than transient techniques. To make sure our SECM measurements were reliable, the reproducibility of SECM imaging was examined first.

Figure 5.6 shows two consecutive SECM images acquired for a 10 ppm microcrystalline boron-doped diamond thin film probed with 5 mmol/L Ru(NH₃) $e^{3r/2*}$ + 1 mol/L KCI. The tip was scanned at a distance of about 1 µm above the surface of each film (determined by approach curve). The bright and brown regions represent the regions showing high electrochemical activity on the surface of the diamond film. These images clearly reveal that most of areas of the diamond film exhibit electrochemical activity but there are several regions with extremely high electroactivity (one possibility is that the microelectrode was closer to the substrate at these regions because of the roughness of the diamond film). These highlight areas are repeated in consecutive images indicating good measurement reproducibility. These images reveal that small drifts (several microns) existed in both x and y directions when the microelectrode was scanned over the surface of the substrate.



Figure 5.6 SECM images $(25 \times 25 \ \mu\text{m}^2)$ of a microcrystalline BDD thin film grown with 10 ppm B₂H₆ in the source gas in 5 mmol/L Ru(NH₃)₆^{3+/2+} + 1 mol/L KCl. The *Pt* diameter was 2 μ m. The tip potential was -0.3 V and the diamond electrode potential was 0 V vs. Ag/AgCl. The two images were recorded consecutively.

5.3.2 Effect of morphology of diamond thin-film

It has been reported that the electrochemical activity of a boron-doped microcrystalline diamond film for Ru(NH₃)₆^{3+/2+} is heterogeneous across the surface.^{25, 26} In the present work, we sought to learn if there are factors that affect this heterogeneity for boron-doped diamond films. The first factor considered was the morphology of the diamond thin film. To assess this, the electrochemical activity of microcrystalline and nanocrystalline boron-doped diamond thin films was probed in TG/SC mode. A series of tip-approach curves were first recorded at different regions on the film in the feedback mode. Ru(NH₃)₆^{3+/2+} was used as the test redox system. The approach curves were acquired until the limiting current reached a value that was 2.3 times the value measured with the tip far away from the surface. At this point, the distance between the tip and the substrate was calculated to be ~1.0 μ m, as discussed above.

Figure 5.7A and B show $10 \times 10 \ \mu\text{m}^2$ maps of Ru(NH₃)₆^{3+/2+} electrochemical activity across microcrystalline and nanocrystalline BDD electrodes, respectively. The maps were obtained when a 2 μ m diameter Pt tip was rastered across the surface at 50 μ m s⁻¹. Both films were deposited with 10 ppm B₂H₆ in the source gas mixture. The tip potential was -0.3 V and the substrate potential was 0 V vs. Ag/AgCl. The images reveal that most areas of both electrodes exhibit electrochemical activity for this redox system as the current is greater than the 1.1 nA limiting current measured when the tip was many diameters away from the surface. However, there are some regions that exhibit a higher level of activity than others with positive feedback currents as high as 11 nA. There are very few regions of negative feedback where the current is less than 1.1 nA. The nanocrystalline diamond film possesses a greater fraction of active areas than does the microcrystalline film. On the basis of the CP-AFM images, one may



Figure 5.7 SECM images $(10 \times 10 \ \mu\text{m}^2)$ of a (A) microcrystalline and (B) nanocrystalline BDD electrode, both grown with 10 ppm B₂H₆ in the source gas, in 5 mM Ru(NH₃)₆^{3+/2+} + 1 M KCl. In all cases, the *Pt* tip diameter was 2 μ m. The tip potential was -0.3 V and the diamond electrode potential was 0 V vs. Ag/AgCl. (Reprinted with permission from *J. Phys. Chem.* 111, 3986 (2007). Copyright (2007) American Chemical Society.) (From Ref. 26).
conclude that the majority of the current flow through the diamond films occurs primarily at a fixed number of highly conducting sites. For the highly doped film, the spacing between the conductive sites is approximately a micrometer or less. This same level of heterogeneity is not seen in the SECM image because the tip diameter is greater than the lateral spacing of the conducting sites. In other words, this tip does not afford the sub-micrometer spatial resolution that would be needed to probe the electrochemical activity of the individual conducting sites. The nonuniform electrochemical activity is, however, consistent with the differential electrical conductivity.

5.3.3 Effect of boron doping level

Figure 5.8A-C shows SECM images for nanocrystalline boron-doped diamond films grown with 10, 5 and 1 ppm diborane added to the source gas mixture. The boron-doping level decreased with decreasing B_2H_6 concentration in the source gas. In all of these images, the microelectrode potential was -0.3 V and the diamond electrode potential was 0 V vs. Ag/AgCl. The mediator used for imaging was 1 mmol/L Ru(NH₃)₆^{3+/2+} in 1 mol/L KCl. Importantly, as was observed in recent work with hydrogen-terminated microcrystalline films,^{25, 26} the images reveal variable electrochemical activity across the film surface with regions of high activity isolated by regions of lower activity. The ability of the film to support the electrochemical reaction (i.e., current flow) increased proportionally with the boron-doping level as the fraction of highly active regions was highest for the 10 ppm film and decreased progressively with decreased doping level, although, the difference between the 5 and 1 ppm films is not so obvious. Some of the more active regions are clustered together, whereas others are more isolated. Some of more active regions have lateral dimensions of 5 to 10 μ m, which may result from the low resolution of SECM. The more active zones are separated from one another, in many cases, by tens of micrometers or less.



Figure 5.8 SECM images $(100 \times 100 \ \mu\text{m}^2)$ of nanocrystalline BDD thin films grown with (A) 10 ppm, (B) 5 ppm and (C) 1 ppm B₂H₆ in the source gas mixture using 1 mmol/L Ru(NH₃)₆³⁺²⁺ + 1 mol/L KCl as the test redox system. The *Pt* tip diameter was 2 μ m. The microelectrode potential was -0.3 V and the diamond electrode potential was 0 V vs. Ag/AgCl. Images were recorded in the TG-SC mode.

Similar results were obtained when probed with 1 mmol/L $\text{Fe}(\text{CN})_6^{3/4}$ or IrCl₆^{2/3-} in 1 mol/L KCl, as shown in Figure 5.9. The images reveal a pattern of heterogeneous electrochemical activity similar to that probed by 1 mmol/L Ru(NH₃)₆^{3+/2+} in 1 mol/L KCl. Some of the electrochemically active regions are clustered together, whereas others are more isolated. The electrochemically active regions for the highly doped films are 5 to 10 micrometers in lateral dimension. As was the case probed by Ru(NH₃)₆^{3+/2+}, the fraction of highly conductive area decreased with decreasing boron-doping level.



Figure 5.9 SECM images $(100 \times 100 \ \mu\text{m}^2)$ for nanocrystalline BDD thin films grown with 10 ppm (A and D), 5 ppm (B and E), and 1 ppm (C and F) B₂H₆ in the source gas mixture using either 1 mmol/L Fe(CN)₆^{3/4} (A, B and C) or 0.5 mmol/L IrCl₆^{2/3} (D, E and F) as the test redox system. The supporting solution was 1 mol/L KCl. The *Pt* diameter was 2 μ m. $E_{tip} = -0.3$ V and $E_{substrate} = 0$ V vs. Ag/AgCl when tested with Fe(CN)₆^{3/4}. $E_{tip} = 0.8$ V and $E_{substrate} = 1.0$ V vs. Ag/AgCl when tested with IrCl₆^{2/3}. Images were recorded in the TG-SC mode.

5.3.4 Effect of surface termination

The above results suggest that the boron-doped diamond electrode is heterogeneous in terms its electrochemical activity and that redox reactions may be limited by the availability of these reactive sites, rather than by slow heterogeneous electron-transfer caused by limitation in either the carrier concentration or the migration of carriers to the electrode surface. Electrochemical measurements revealed that the surface chemistry of boron-doped diamond thin film can also strongly influence its electrochemical activity (see Section 4.4.1 and 4.4.3). Therefore, to further evaluate this, the electrochemical activity of both film types was studied using different redox systems: $Ru(NH_3)_6^{3+/2+}$ and $Fe(CN)_6^{3/4-}$.

Figure 5.10 shows SECM images for hydrogen- and oxygen-terminated nanocrystalline BDD electrodes recorded in 1 mmol/L Ru(NH₃)₆^{3+/2+} (Figure 5.10A and B) and Fe(CN)₆^{3-/4-} (Figure 5.10C and D). The supporting electrolyte solution was 1 mol/L KCl. The maps were generated using a 2 μ m diameter Pt tip that was rastered across the surface at 50 μ m s⁻¹. The tip was scanned at a distance of about 1 μ m above the surface of each film, using a tip potential of -0.3 V and a substrate potential of 0 V vs. Ag/AgCl when probed with Ru(NH₃)₆^{3+/2+}. When probed by Fe(CN)₆^{3-/4-}, the tip potential was 0.5 V, and the substrate potential was 0 V vs. Ag/AgCl. (Both are working in tip generation-substrate collection mode). The images clearly show that the H-terminated BDD electrode possesses a greater number of active regions in comparison with the O-terminated BDD electrode regardless of the redox probe. Similar measurements were performed using H- and O-terminated microcrystalline BDD electrodes, with slightly different results being obtained (Figure 5.11). It's noteworthy that the engaging current was set at i_T/i_{T,x} = 1.8, which meant the distance between the tip and the substrate was 1.25 μ m according to equation 5.5. The purpose

of this change of the engaging current is to protect the tip because the surface roughness of microcrystalline BDD film is ca. 1 µm. More active regions were found on H-terminated BDD electrode but the fraction of active area for the O-terminated microcrystalline diamond electrode was greater than that for the O-terminated nanocrystalline electrode. These results matched our electrochemical measurements very well and clearly show that the redox processes are limited by the availability of sites (or density of active sites) for electron transfer on the surface of boron-doped



Figure 5.10 SECM images $(50 \times 50 \ \mu m^2)$ for 1 mmol/L Ru(NH₃) $e^{3+2*} + 1$ mol/L KCl at nanocrystalline BDD thin films: (a) hydrogen-terminated and (b) oxygen-terminated ($E_{tip} = -0.3$ V and $E_{substrate} = 0$ V vs. Ag/AgCl). SECM images $(50 \times 50 \ \mu m^2)$ for 1 mmol/L Fe(CN) $e^{3+4*} + 1$ mol/L KCl at nanocrystalline BDD thin films: (c) hydrogen-terminated and (d) oxygen-terminated ($E_{tip} = 0.5$ V and $E_{substrate} = 0$ V vs. Ag/AgCl). In all cases, the *Pt* tip diameter was 2 μ m. The *z*-axis scale shows the tip current. Images were recorded in the TG-SC mode.

diamond. More active sites were mapped out on H-terminated than on O-terminated boron-doped diamond when imaged by SECM, while much smaller peak separations (faster kinetics) were recorded for the H-terminated boron-doped diamond electrode when characterized by cyclic voltammetry. This suggests that faster kinetics of electron-transfer on boron-doped diamond electrode may be related to a higher number of active sites on the electrode surface.



Figure 5.11 SECM images $(100 \times 100 \ \mu\text{m}^2)$ for 1 mmol/L Ru(NH₃)₄3³⁺²⁺ + 1 mol/L KCl at microcrystalline BDD thin films: (a) hydrogen-terminated and (b) oxygen-terminated ($E_{tip} = -0.3 \ \text{V}$ and $E_{substrate} = 0 \ \text{V}$ vs. Ag/AgCl). SECM images ($100 \times 100 \ \mu\text{m}^2$) for 1 mmol/L Fe(CN)₆3³⁺⁴⁺ + 1 mol/L KCl at microcrystalline BDD thin films: (c) hydrogen-terminated and (d) oxygen-terminated ($E_{tip} = 0.5 \ \text{V}$ and $E_{substrate} = 0 \ \text{V}$ vs. Ag/AgCl). In all cases, the *Pt* tip diameter was 2 μ m. The z-axis scale shows the tip current. Images were recorded in the TG-SC mode.

5.3.5 Effect of redox system

The electrochemical activity of both film types, highly boron-doped and Hterminated, were further evaluated using different redox systems: $Ru(NH_3)_6^{3+/2+}$, $Fe(CN)_6^{3-4-}$, and $IrCl_6^{2-3-}$. The cyclic voltammetric response for these redox systems at both types of conducting diamond has been discussed in detail elsewhere.^{6, 27-29} $Ru(NH_3)_6^{3+/2+}$ and $IrCl_6^{2-/3-}$ are so-called outer-sphere redox systems on diamond with heterogeneous electron-transfer rate constants that depend primarily on the density of electronic states. $^{6, 27-29}$ Fe(CN) $_{6}^{3-/4-}$ is a more complicated, so-called inner-sphere redox system on carbon electrodes, with a heterogeneous electron-transfer rate constant that strongly depends not only on the density of states but also the surface cleanliness and surface oxygen coverage. ^{6, 10, 27-29} Figure 5.12 shows electrochemical activity maps for a nanocrystalline BDD grown with 10 ppm B₂H₆ in the source gas mixture. In all cases, the image features were reproducible with scanning and they cover the same region of the electrode. Figure 5.12A shows an image recorded in 1 mmol/L Ru(NH₃) $_{6}^{3+/2+}$ and 1 mol/L KCl. Much of the electrode exhibits high activity for this redox analyte, as evidenced by the positive feedback current. The active regions are distributed randomly over the surface with some of them being close enough together to create a rather large zone (multiple micrometers in dimension). Figure 5.12B shows a map of the same electrode area for 1 mmol/L $Fe(CN)_6^{3/4-}$ and 1 mol/L KCl. The fraction of the surface exhibiting high electrochemical activity for this redox system appears greater than that for $Ru(NH_3)_6^{3+/2+}$ or $IrCl_6^{2+/3-}$ (see below). Figure 5.12C shows a map of the same electrode area for 1 mmol/L $IrCl_6^{2-/3-}$ and 1 mol/L KCl. It can be seen that over half the surface exhibits high electrochemical activity for this redox system. The fraction of active area in this image appears less than that for the $Fe(CN)_6^{3/4-}$ probe but larger than that for the $Ru(NH_3)_6^{3+/2+}$ probe.



Figure 5.12 SECM images $(10 \times 10 \ \mu\text{m}^2)$ of a nanocrystalline BDD thin film grown with 10 ppm B₂H₆ in the source gas in (A) 1 mmol/L Ru(NH₃) e^{3+2+} , (B) 1 mmol/L Fe(CN) e^{3+4-} and (C) 1 mmol/L IrCl e^{2-3-} . The supporting electrolyte in all cases was 1 mol/L KCl. The *Pt* tip diameter was 2 μ m. The z-axis scale in all three images is the same. Images were recorded in the TG-SC mode. (Reprinted with permission from *J. Phys. Chem.* 111, 3986 (2007). Copyright (2007) American Chemical Society.) (From Ref. 26).

For $Fe(CN)_6^{3/4-}$ and $IrCl_6^{2/3-}$, as was the case for $Ru(NH_3)_6^{3+/2+}$, nearly all of the imaged area exhibit positive feedback current indicating that all regions are electrochemically active. Noteworthy, though, is the fact that the most of the active regions are different for each redox system even though the same area of the electrode was imaged. The exact reason for this is unclear at present but may be related to different electric double layer structures locally on the surface.

The results clearly show that the electron-transfer mechanism of these commonly used redox systems at diamond, and other carbon electrodes, is more complex than previously thought. In the case of diamond, these three redox systems undergo electron-transfer at different sites on the surface.

5.3.6 Comparison with other electrode materials

The SECM images acquired for the nanocrystalline diamond film revealed different electrochemically-active areas for the three redox systems. These results suggested the mechanism of electron transfer on diamond electrode might be different for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{IrCl}_6^{2-/3}$, even though they are considered as outersphere redox couples on other electrodes,³⁰ the exception being $\text{Fe}(\text{CN})_6^{3-/4-}$.

Our SECM images were acquired when a microelectrode scanned over the surface of a substrate in the constant distance mode. In other words, the height of the microelectrode is kept constant relative to the starting point (where approach curve was taken), hence the distance between the microelectrode and the point or region being measured varied according to the roughness of the substrate surface. From the theory of SECM, we know that this distance change will strongly affect the tip current,¹³ therefore, the film morphology could influence the SECM image although

this is less likely for the smooth nanocrystalline diamond electrodes (~ 100 nm rms). One possibility is that the different images obtained for the same area of the diamond electrode with different redox couples may result from changes in the surface roughness. Therefore, to better understand the variations in electrochemical activity, studies were performed to learn what role the electrode roughness has on the image features. To study the effect of surface roughness, we applied SECM measurements on smoother, non-diamond electrodes using Ru(NH₃)₆^{3+/2+}, Fe(CN)₆^{3-/4-} and IrCl₆^{2-/3-} as probes. Glassy carbon has more uniform electronic properties and smoother surface than does diamond after special polishing procedure. Therefore, the first material studied was glassy carbon (GC-30, Tokai Ltd. Japan) prepared by polishing with successively smaller grades of alumina powder slurried in ultrapure water (1.0, 0.3, and 0.05 μ m) on separate felt pads. The electrode was rinsed thoroughly with and ultrasonically cleaned for 5 min in ultrapure water after each polishing step.³¹

Representative electrochemical activity maps are shown in Figure 5.13. A 10 \times 10 μ m² image recorded in 1 mmol/L Fe(CN)₆^{3.44} and 1 mol/L KCl is shown in Figure 5.13A. Much of the electrode exhibits high activity for this redox analyte, as evidenced by positive feedback current. The active regions are distributed randomly over the surface with few of them being close enough together to create an active zone (less than 1 micrometer in dimension). There are some noisy signals in the horizontal (scanning) direction that may result from the movement of the microelectrode or the polishing residue. Figure 5.13B shows a 100 \times 100 μ m² map recorded in 1 mmol/L Ru(NH₃)₆^{3+/2+} and 1 mol/L KCl. Only several points exhibit high activity. Most of the area is green color, which means that the current is close to the current limit of the measurement. It can be seen from the current scale bar that the lowest current limit is 0.14 nA, which is about the limiting current for the

microelectrode positioned far away from the substrate. It's hard to figure out if the regions showing green color in this image are electrochemically active or non-active because of the low color resolution of SECM image. Figure 5.13C shows a map of $10 \times 10 \ \mu\text{m}^2$ recorded in 0.5 mmol/L IrCl₆^{2-/3-} and 1 mol/L KCl. It can be seen that much of the surface exhibits high electrochemical activity for this redox system. The fraction of highly active area in this image is greatest for the three probes. The results shown in Figure 5.13 indicate that glassy carbon exhibits similar heterogeneous electrochemical activity as diamond, which is reflected in the SECM images. This is different from the SECM image of GC reported by Hočevar et al.³² It's noteworthy that they performed SECM imaging on GC with a 25 µm diam. Pt microelectrode at a distance of 10 µm.

As expected, very uniform images were obtained, as shown in Figure 5.13D, E and F when we reduced all current scales with a factor of 1/10. Figure 5.13D shows that current larger than 1.19 nA (>> 0.2 nA, the limiting current) was recorded over the scanned area when probed using $Fe(CN)_6^{3/4-}$ except some regions near the center of the image that show smaller current (ca. 0.94 nA). Figure 5.13E shows that current larger than 0.82 nA (>> 0.2 nA, the limiting current) was recorded over half of the scanned area when probed using $Ru(NH_3)_6^{3+/2+}$. Half of the scanned area (right part in Figure 5.13E) shows smaller current (ca. 0.6 nA). More uniform image was recorded when probed using $IrCl_6^{2/3-}$ and only a few points show lower current (Figure 5.13F). These images clearly show that the whole scanned area exhibits high activity for all redox couples, as evidenced by positive feedback current.



Figure 5.13 SECM images of glassy carbon in (A) 1 mmol/L Ru(NH₃)₆^{3+/2+}, (B) 1 mmol/L Fe(CN)₆^{3+/4-} and (C) 0.5 mmol/L IrCl₆^{2-/3-}. The supporting electrolyte in all cases was 1 mol/L KCl. The *Pt* tip diameter was 2 μ m. Images were recorded in the TG-SC mode. The left column shows the original images recorded by SECM. These images were replotted in right column with a reduced current scale by a factor of 1/10. Note that the scan size for (B) and (E) is 100 × 100 μ m² and the other are 10 × 10 μ m².

To better compare the glassy carbon and diamond electrode results, the diamond images were replotted with an enhanced current axis. The surprising results are shown in Figure 5.14. Figure 5.14A shows a $10 \times 10 \ \mu m^2$ image of highly doped nanocrystalline diamond film recorded in 1 mmol/L Fe(CN) $_{6}^{3/4}$ and 1 mol/L KCl. Much of the electrode exhibits high activity for this redox analyte, as evidenced by positive feedback current. The active regions are distributed randomly over the surface with some of them being close enough together to create a rather large zone (multiple micrometers in dimension). When the current scale was reduced by a factor of 1/10, a very similar image was obtained, as shown in Figure 5.14D. There were no new active regions evident except the weak, streamlined wave-lines resulting from the scanning of the microelectrode. This is very different from the result for glassy carbon. These results revealed that there were certain regions on the doped diamond electrode that show very high electrochemical activity. These regions were so active that the current reached a very high level (11.9 nA in this case) when the microelectrode was scanned over the surface. The activity of other areas was very different with less tip current being observed. Because of the low color resolution, when a high current scale was used, the SECM image showed lots of bright brown islands (high active regions) surrounded by green ocean (low active regions). When the current scale reduced an order of magnitude, the glassy carbon electrode showed uniform activity. On the other hand, diamond electrode showed non-uniform activity (Figure 5.14D). These results demonstrate that glassy carbon electrode has a greater fraction of electrochemically active area than does the diamond electrode, even though the most active regions possessed the same level of current flow for both electrodes.



Figure 5.14 SECM images of a nanocrystalline BDD thin film grown with 10 ppm B_2H_6 in the source gas mixture in (A) 1 mmol/L Fe(CN)₆^{3/4+}, (B) 1 mmol/L Ru(NH₃)₆^{3+/2+} and (C) 1 mmol/L IrCl₆^{2/3-}. The supporting electrolyte in all cases was 1 mol/L KCI. The *Pt* tip diameter was 2 µm. Images were recorded in the TG-SC mode. The left column shows the original images recorded by SECM. These images were replotted in the right column with a reduced current scale by a factor of 1/10.

This observation was further confirmed by SECM measurements using $Ru(NH_3)_6^{3+/2+}$ and $IrCl_6^{2-/3-}$ as probes (Figure 5.14E and F). The SECM images with 10 times lower current scales still show similar images to the original ones, which were different from the same measurements on glassy carbon electrode. The images are consistent with lower electrochemical activity at diamond electrode than at glassy carbon for these redox systems.

These results also suggest that the surface roughness of diamond does not strongly contribute to the image features. The glassy carbon electrode used here was polished by a standard procedure,³¹ so it's reasonable to assume the surface roughness was at 50 nm level, which is comparable to the roughness of nanocrystalline diamond thin film. If the non-uniformity of the SECM image essentially resulted from the roughness of the electrode surface, glassy carbon should show similar properties to diamond and this was not the case.

To further validate our observations, we recorded electrochemical activity maps of a thin Au-film electrode. The Au was sputter-coated onto a clean Si substrate. Ohmic contact was made directly though the Au film by contacting with copper foil. The resulting images are shown in Figure 5.15.

A 100 × 100 μ m² image recorded in 1 mmol/L Fe(CN)₆^{3-/4-} and 1 mol/L KCl is shown in Figure 5.15A. Much of the electrode exhibits high activity for this redox analyte, as evidenced by positive feedback current. The active regions are distributed randomly over the surface with some of them being close enough together to create active zones. Figure 5.15B shows a 10 × 10 μ m² map recorded in 1 mmol/L Ru(NH₃)₆^{3+/2+} and 1 mol/L KCl. Only several points exhibit high activity that can be shown. Most of the area shows a green color indicating the current close to the steadystate current of the measurement. It can be seen from the current scale bar that the least current limit is 0.17 nA that is close to the limiting current of the microelectrode far away from the substrate. It's hard to distinguish the area showing green color as electrochemically active or non-active because of the low color resolution. In general, heterogeneity is seen for Au as was the case for diamond and glassy carbon.



Figure 5.15 SECM images of a gold film deposited on a conducting Si substrate in (A) 1 mmol/L Fe(CN) $_{6}^{3\cdot/4}$ and (B) 1 mmol/L Ru(NH₃) $_{6}^{3\cdot/2^{*}}$. The supporting electrolyte was 1 mol/L KCI. The *Pt* tip diameter was 2 µm. Images were recorded in the TG-SC mode. The left column shows the original images recorded by SECM. These images were replotted in the right column with a reducd current scale by a factor of 1/10.

As expected, very uniform images were obtained, as shown in Figure 5.15C and D when we reduced all current scales with a factor of 1/10. Figure 5.15C shows that current larger than 1.19 nA (>> 0.2 nA, the limiting current) was recorded over the scanned area when probed using $Fe(CN)_6^{3/4}$ except some regions near the right corner of the bottom that show smaller current (ca. 0.4 nA). Figure 5.15D shows that current near 1.11 nA (>> 0.2 nA, the limiting current) was recorded over half of the scanned area when probed using $Ru(NH_3)_6^{3+/2+}$. Half of the scanned area show lower current shows smaller current (ca. 0.8 nA). Different from the SECM image for GC, this image shows that the more active regions intermixed the less active regions each other.

5.4 Mechanism of electron-transfer on polycrystalline borondoped diamond

Both the CP-AFM and SECM images revealed that there are randomly distributed electrically- and electrochemically-active sites on the films that are surrounded by less active regions. We suppose that electron-transfer reactions at diamond can be considered to occur at a partially blocked electrode. In fact, a macroscopic, partially-blocking model was proposed several decades ago.³³⁻³⁵ However, partial coverage of the electrode surface may result in non-linear diffusion effects. This effect may result in the extension of analysis of macroscopic blocking to microscopic inhomogeneities unsatisfactory. To solve this problem, Amatore et al.³⁶ proposed a microscopic model. In this section, we applied this model to boron-doped diamond electrode. We sought to theoretically interpret the electrochemical properties of boron-doped diamond thin film electrodes.

In this model, it is assumed that a microscopic configuration for the borondoped diamond electrode consists of active sites in a disc-like shape of the same size evenly distributed over the surface. This assumption simplifies the theoretical calculations even though CP-AFM and SECM images showed active sites with different shapes and sizes randomly distributed over boron-doped diamond surface. This model and the diffusion volume unit are shown in Figure 5.16. In this model, the radius of an active site is R_a and the distance between the centers of two adjacent active sites is $2R_0$, which are assumed to be small compared to the thickness of the diffusion layer. It is assumed that beyond a distance $L \approx 2R_0$ from the electrode surface, diffusion can be regarded as linear and semi-infinite. Within a distance less than L, diffusion is non-linear and a stationary situation exists because L is much smaller than the thickness of the diffusion layer.



Figure 5.16 Model of a boron-doped diamond electrode surface and a diffusion volume unit for an active site. Black dots represent active sites.

Consider the single, reversible electron-transfer reaction

$$O + e \leftrightarrow R$$
 (5.6)

and assign C_0 as the concentration of O at any distance from the electrode surface with C_0^* being the bulk concentration of O. There is no R present at the beginning of the reaction. E^0 is the standard reduction potential, α is the transfer coefficient, k^0 is the standard heterogeneous electron-transfer rate constant, t_c is the time of the electrolysis ($t_c = RT/Fv$ for cyclic voltammetry with a scan rate of v), and D is the diffusion coefficient. It is assumed $D = D_0 = D_R$. θ is the fraction of the electrode surface occupied by non-active sites and S is the total area of the electrode. To simplify the calculations, the following dimensionless parameters were used:

$$c = C_0 / C_0^{\bullet}$$
(5.7)

$$\tau = t/t_c \tag{5.8}$$

$$x = X(Dt_c)^{-1/2}$$
 (5.9)

$$\psi = i/[FSC_0^{\bullet}(D/t_c)^{-1/2}]$$
(5.10)

$$\Lambda = k^0 (t_c/D)^{1/2}$$
(5.11)

$$\xi = -(F/RT)(E - E^{0})$$
(5.12)

Under these conditions, for a normal planar electrode (i.e., linear and semiinfinite diffusion apply), integration of the linear and semi-infinite diffusion equation (Fick's Law) gives

$$c(0,t) = 1 - \pi^{-1/2} \int_0^t \psi(t)(t-\tau) d\tau = 1 - I \Psi$$
 (5.13)

where $I\Psi$ is the convolution integral.⁸ On the other hand, the Butler-Volmer equation can be expressed as

$$\psi = \frac{\partial c}{\partial x}\Big|_{x=0} = \Lambda \exp(\alpha\xi)[c_O - c_R \exp(-\xi)]$$
(5.14)

and because there is no R present initially,

$$c_0 + c_R = 1$$
 (5.15)

Substituting (5.15) to (5.14) gives

$$\psi = \Lambda \exp(\alpha \xi) \{ c_0 [1 + \exp(-\xi)] - \exp(-\xi) \}$$
(5.16)

and thus to

$$\psi = \Lambda \exp(\alpha \xi) [1 - I \Psi - I \Psi \exp(-\xi)]$$
(5.17)

Now returns to the partially blocking model, at $x = \mu = 2R_0$, linear and semiinfinite diffusion still apply and similarly, we have³⁶

$$c_{\mu} = 1 - \pi^{-1/2} \int_0^t \frac{\partial c}{\partial x} \Big|_{\mu} (t - \tau) d\tau$$
(5.18)

The conservation of the concentration flux in the stationary diffusion region ($x \le \mu$) leads to

$$\psi = \frac{\partial c}{\partial x}\Big|_{\mu} = \frac{\partial c}{\partial x}\Big|_{0}(1-\theta)$$
(5.19)

where $\frac{\partial c}{\partial x}|_0$ is the average value of the dimensionless current density at the active

sites. At the active sites, the Butler-Volmer relationship still applies; therefore,

$$\frac{\partial c}{\partial x}\Big|_{0} = \Lambda \exp(\alpha\xi) [\overline{c_{o}} - \overline{c_{R}} \exp(-\xi)]$$
(5.20)

again,

$$\overline{c_o} + \overline{c_R} = 1 \tag{5.21}$$

combine (5.20), (5.21) with (5.19), one gets

$$\psi = \Lambda(1-\theta)\exp(\alpha\xi)\{\overline{c_0}[1+\exp(-\xi)]-\exp(-\xi)\}$$
(5.22)

The problem then becomes figuring out what $\overline{c_o}$ is. Amatore et al. solved this problem in their paper.³⁶ They gave the relationship between $\overline{c_o}$ and c_{μ} for disc-type active sites as follows,

$$\overline{c_o} = c_{\mu} - \mu \psi [1 + \frac{1}{2} \sum_{n=1}^{\infty} B_n(\eta)]$$
(5.23)

where $B_n(\eta)$ is the Bessel function with $\eta = (1-\theta)^{1/2}$. In our case, $\mu = 2R_0$ and assume θ is close to unity, then the sum of the Bessel function can be approximated by 0.3(1- θ)^{-1/2}, hence,

$$\overline{c_o} = c_{\mu} - 2R_0 \psi[0.3(1-\theta)^{-1/2}]$$
(5.24)

Combining (5.18), (5.22) and (5.24) leads to the final expression of the currentpotential curves:

$$\psi = \Lambda(1-\theta) \exp(\alpha\xi) \{ [1-I\Psi - 0.6R_0\psi(1-\theta)^{-1/2}] - [I\Psi + 0.6R_0\psi(1-\theta)^{-1/2}] \exp(-\xi) \}$$
(5.25)

where $I\Psi$ is the convolution integral as defined by (5.13).

The significance of equation (5.25) can be identified by comparing the polarization curves having a reaction scheme as follows

$$I \stackrel{k_{1}}{\underset{k_{2}}{\overset{\otimes}{\leftarrow}}} O (\mathbf{K} = \frac{\mathbf{k}_{1}}{\mathbf{k}_{2}})$$

$$O + e \in R (E^{0}, \alpha, k^{0})$$

$$R \stackrel{k_{2}}{\underset{k_{1}}{\overset{\otimes}{\leftarrow}}} J (\mathbf{K} = \frac{\mathbf{k}_{1}}{\mathbf{k}_{2}})$$
(5.26)

Saveant et al.³⁷⁻³⁹ studied this reaction scheme and gave a general expression for the "pure kinetic" polarization curves

$$\Psi = \Lambda[K/(1+K)]\exp(\alpha\xi)\{[1-I\Psi - (\Psi/K\lambda^{1/2})] - [I\Psi + (\Psi/K\lambda^{1/2})]\exp(-\xi)\}$$
(5.27)

with

$$\lambda = (k_1 + k_2)t_c \tag{5.28}$$

the form of equation (5.25) is the same as equation (5.27).

Based on the similarity of equation (5.25) and equation (5.27), it's possible to characterize the electrochemical properties of boron-doped diamond electrodes as follows:

1. The "pure kinetic" conditions for reaction scheme (5.26) means the chemical reactions are so fast that the two equilibria are perturbed only in a thin reaction layer adjacent to the electrode surface.³⁷⁻³⁹ On BDD electrode, there is a stationary non-linear diffusion layer that corresponds to this thin layer. In fact, similar results were obtained for partially blocked electrode system in macroscopic view.³³⁻³⁵

2. When $0.6R_0\psi(1-\theta)^{-1/2} \ll 1$, equation (5.25) becomes

$$\psi = \Lambda(1-\theta)\exp(\alpha\xi)[1-I\Psi-I\Psi\exp(-\xi)]$$
(5.29)

Comparing equation (5.29) with equation (5.17), we conclude that the borondoped diamond electrode simply results in an apparent decrease of the standard rate constant of electron-transfer. In other words, the voltammograms for boron-doped diamond electrodes are the same as those obtained on a perfect electrode of same surface area S (no non-active sites, e.g. a noble metal electrode) with a decreased standard rate constant $k_{app}^{0} = k^{0}(1-\theta)$. Without question, the decrease is dependent on θ , i.e., the larger θ , the larger peak separation, which is exactly the cases for borondoped diamond with decreasing doping level or the surface termination changed from hydrogen to oxygen. θ can be calculated from an SECM image using a graphical software and k_{app}^{0} for a certain BDD film can be determined from SECM measurements. Assuming GC as a uniformly electroactive electrode, i.e. using k⁰ obtained from GC as the rate constant of an ideal carbon electrode without blocking, one can validate the partial blocking model for BDD thin-film electrodes with different doping levels. This will be a future work.

3. As θ increases, which corresponds to the cases for boron-doped diamond electrode at low doping level (e.g., < 1 ppm or undoped) and oxidized nanocrystalline BDD, R₀ will increase greatly. All these will make $0.6R_0\psi(1-\theta)^{-1/2}$ can not be neglected and $k_{app}^{0} = k^0(1-\theta)$ tends to 0. Under these conditions, the shape of voltammogram changes as the peak separation increases and peak current decreases. These have been confirmed by our electrochemical measurements, CP-AFM and SECM images for low boron-doped or oxidized nanocrystalline diamond electrodes.

4. SECM images clearly show the partially blocked electrochemically-active surface of BDD thin-film electrode and the coverage of blocked area decreases as the doping level increases. Besides SECM image, the tip-approach curve can also reveal a certain region electrochemically-active or not. Approach curves recorded at nanocrystalline BDD thin-film grown with 1 ppm diborane in the source gas confirmed this, as shown in Figure 5.17. Figure 5.17A and B show the tip-approach curves recorded in 1 mmol/L Ru(NH₃)₆^{3+/2+} and 1 mol/L KCl at different positions of the same BDD film. The curves are normalized to the limiting current in order to more clearly reveal the trends. With the tip many diameters away from the diamond electrode, a steady-state current was recorded at -0.3 V that increased proportionally with the analyte concentration. Far away from the diamond electrode, the diffusion

layer near the tip is hemispherical, but this changes as the tip approaches the surface. The positive increase in current as the tip approaches the diamond electrode is due to redox system recycling at the tip and means that region is electrochemically-active (i.e., rapid rate of electron transfer, Figure 5.17A) for this redox system. On the other hand, at another position (Figure 5.17B), the tip current decreases as the tip approaches the diamond electrode due to the blocking effect of the substrate and the absence of the redox system recycling at the tip, which means that region of the diamond electrode is not electrochemically-active for this redox system. Theoretical approach curves for this redox system with positive and negative feedback are shown in both Figure 5.17A and B, for comparison.

Similar results were recorded at a nanocrystalline BDD film grown with 5 ppm diborane in the source gas but we did not recorded negative feedback approach curve at the diamond film grown with 10 ppm diborane in the source gas. A possible reason is that the coverage of the blocked area is too low at this doping level. Another possible reason might be the microelectrode probe tip used in this study (2 μ m in diam.) is too big that can not distinguish the non-active area at this film.



Figure 5.17 Tip-approach curves at (A) a conductive site and (B) a non-conductive site of a nanocrystalline BDD thin film electrode in 1 mM Ru(NH₃)₆^{3+/2+} + 1 M KCl. The nominal diameter of the microelectrode was 2 μ m. The microelectrode was held at -0.3 V, and the diamond electrode potential was held at 0 V vs. Ag/AgCl. i_T is the tip current, $i_{T,\infty}$ is the limiting current, and L = d/a, where d is the distance between the tip and substrate, a is the radius of the tip. Theoretical curves are calculated according to the models given in Ref. 21.

5.5 Conclusions

SECM was used to investigate the spatial heterogeneity of the electrochemical activity across the microcrystalline and nanocrystalline BDD thin films as a function of the boron-doping level, surface morphology and chemistry, and the redox system. All films were characterized by a fixed number of isolated electrochemically-active regions separated from one other by less active zones. The fraction of highly active area increased with increasing boron-doping level. Similar observations were made for microcrystalline and nanocrystalline BDD electrodes. SECM measurements also showed that the fraction of highly active area depends on the surface termination and diamond crystal size, which are consistent with the results of electrochemical measurements (nanocrystalline BDD electrode has lightly greater peak current that microcrystalline BDD electrode with same geometric area) and CP-AFM images. The results clearly show that the fraction of highly active area for the nanocrystalline BDD thin film is larger than that for microcrystalline BDD thin film. The pattern of SECM images for nanocrystalline diamond films is also a little different from that for microcrystalline diamond films. For nanocrystalline diamond films, most highly active regions are more evenly distributed in smaller cluster size compared with microcrystalline diamond electrode. The morphology of SECM images for nanocrystalline diamond films also show that the redox systems used as mediators have strong influence on the SECM images.

A microscopic partial blocking model was applied to the boron-doped diamond electrode. The theoretical results deduced from this model matched well with our results obtained from electrochemical measurements and SECM images for both microcrystalline and nanocrystalline boron-doped diamond thin film electrodes. Especially, both the effect of surface termination and the influence of doping level on the electrochemical properties of boron-doped diamond electrode can be explained by this model.

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Chapter 6

The Physical and Electrochemical Properties of Two Types of Boron-Doped Nanocrystalline Diamond Thin-Film Electrodes

6.1 Introduction

It has been reported that diamond films from different sources exhibit quite reproducible electrochemical behavior.^{1, 2} Therefore, it has been shown that borno-doped microcrystalline and nanocrystalline diamond film electrodes possess similar properties. Several factors can influence the electrochemical response of a polycrystalline diamond film: (i) the presence of any non-diamond sp² carbon impurity phases, (ii) the surface termination (H vs. O), (iii) the dopant type, level, and distribution, (iv) grain boundaries and other morphological defects, and (v) the primary crystallographic orientation. The extent to which any one of these factors influences the response will depend on the charge-transfer mechanism of a particular redox analyte.³⁻⁷ In 2000, our group published a paper titled *"Standard Electrochemical Behavior of High-Quality, Boron-Doped Polycrystalline Diamond Thin-Film Electrodes*" and suggested that the data presented serve as a benchmark for research groups evaluating the electrochemical properties of polycrystalline, hydrogenterminated, boron-doped diamond electrodes.¹

To better understand the relationship between the microstructure of borondoped diamond thin film, and its electrical and electrochemical properties, we used CP-AFM and SECM to study the spatial heterogeneity in the electrical and electrochemical properties. In previous chapters, it was shown that these two techniques, combined with SEM, Raman spectroscopy and electrochemical measurements, provide researchers with a more complete picture of the structure-function relationship at diamond thin-film electrodes. In this chapter, we report on the use of these methods to investigate the properties of boron-doped, nanocrystalline diamond thin films produced by two different methods. One high-quality nanocrystalline film was produced by the Naval Research Laboratory (NRL) group using a conventional CH_4/H_2 source gas mixture. The other was produced using a $CH_4/H_2/Ar$ source gas mixture, a method pioneered by the Argonne group. CP-AFM was used to examine the morphology and electrical conductivity of both film types. SECM and visible-Raman spectroscopy were employed to probe the film morphology and microstructure. Electrochemical measurements were used to assess the electrochemical properties.

6.2 **Results and discussion**

6.2.1 Morphology

The MSU diamond film was deposited by microwave-assisted chemical vapor deposition (CVD), as described in Chapter 2. The NRL film (grown on 3 in Si wafer) was provided by Dr. James Butler. This film was cut into small pieces (1 cm² in area) for all tests described herein. Figure 6.1 shows representative AFM images (contact mode in air) of the two films. Clearly, the morphology of the MSU film is quite different from that of the NRL film. The image of the MSU film shows cauliflower-like structures consisting of many nodular features. TEM images (not shown here) revealed that these nodular features are aggregates of smaller diamond grains (grain size is 15 - 20 nm).^{8, 9} On the other hand, the image of the NRL film shows more uniform morphology, consisting of crystal-like grains with different grain sizes (i.e. more

nanofaceted). The grain size is 50 - 200 nm which is of the same order as the cauliflower-like structures found in the MSU film. The biggest difference between the two films is the faceted crystallites of the NRL film.



Figure 6.1 AFM mages for MSU (left) and NRL (right) boron-doped nanocrystalline diamond films.

Because of the cauliflower-like structure, the roughness of the MSU film is greater than that of the NRL film as evidenced by the large nominal roughness factor and maximum feature height. These data are summarized in Table 6.1.

Table 6.1 Roughness analysis of MSU and NRL films.

Film	RMS* (Avg. ± SD, nm)	R _{max} ** (Avg. ± SD, nm)
MSU (n=4)	19.9 ± 2.3	128.4 ± 18.9
NRL (n=3)	8.3 ± 0.9	53.8 ± 2.2

* RMS = Root mean square of surface roughness over a scan area of $1 \times 1 \ \mu m^2$.

**R_{max} = Maximum height.

The nanocrystalline diamond film grown from an Ar-rich source gas results from a high rate of renucleation during growth.⁹ C₂ dimer is the primary growth species. In the Ar environment, large crystals never have an opportunity to grow as new nuclei frequently form. The nanocrystalline diamond film grown from the H₂-rich source gas was achieved by a special seeding process that produces a high initial nucleation density. Therefore, a large number of nuclei initially form and a continuous film is achieved within a short growth period.¹⁰ Even that faceted crystals are present, one can conclude that the rate of renucleation is low and the rate of crystal growth is fairly uniform across the surface.

Representative images of the two film types are presented in Figure 6.2. The MSU film has feature sizes of around 50 nm, which is consistent with the AFM images. These nodular features are actually aggregates of diamond grains^{2, 8} The smaller feature and grain size is typical of films deposited from an *Ar*-rich source gas mixtures and results from a high renucleation rate during growth.⁹ On the other hand, the NRL film shows a much larger grain size with some secondary nucleation in the grain boundaries. Different from the MSU film, crystal facets are clearly visible on the NRL film. These features are typical of films deposited from hydrogen-rich CH₄/H₂ source gas mixtures and result from a low renucleation rate during deposition.



Figure 6.2 SEM images of the (A) MSU and (B) NRL nanocrystalline borondoped diamond films.

6.2.2 Raman Spectra

Raman spectroscopy was used to probe the film microstructure. Spectra for the MSU and NRL films are displayed in Figure 6.3. The spectrum for each film is quite different from the typical spectrum for single crystal diamond, which consists of single, narrow band at 1332 cm⁻¹. This band is attributed to the first-order lattice phonon of cubic diamond.¹¹ A broad peak centered at 1331 cm⁻¹ is seen in Figure 6.3A, which is typical of nanocrystalline boron-doped diamond deposited from an Arrich CH₄/H₂+Ar source gas mixture. This broad peak is likely a convolution of the 1332 cm⁻¹ diamond phonon peak with scattering by the sp²-bonded carbon in the grain boundaries. The peak is broadened in energy because of the small size of the diamond grains.¹² Other researchers argued for a different assignment for this peak.¹³ Birrell et al. assigned this broad peak to sp²-bonded carbon (i.e., D-band Raman peak).¹⁴ The argument for this assignment is based on the observation that the peak is absent from the Raman spectrum when using UV excitation.¹⁴ The D-peak is believed to arise from a double resonant Raman process, where the intensity is highest for low energy excitation and decreases strongly with increasing excitation energy.¹³

The shoulder at 1155 cm⁻¹, often observed for nanocrystalline diamond, has been assigned to transpolyacetylene segments at the grain boundaries.¹² The peak at 1550 cm⁻¹ is clearly the G-mode Raman peak, which is well known for disordered carbon films and arises from the in-plane stretching modes of the sp²-bonded carbon at the grain boundaries of nanocrystalline diamond.¹³



Figure 6.3 Raman spectra (visible excitation, 514.4 nm) for the (A) MSU and (B) NRL boron-doped diamond films.

The Raman spectrum for the NRL film is very different from that for the MSU film, as shown in Figure 6.3B. An asymmetric peak at 1312 cm⁻¹ is seen that can be attributed to the one-phonon Raman diamond line. The asymmetry of the one-phonon band is caused by the Fano interference induced by quantum mechanical interference between the discrete phonon state and electronic continuum. The band width, Raman frequency shift and asymmetry of the peak are all affected by the Fano interference.¹⁵

The broad band around 1215 cm⁻¹ and the broad and intense band around 500 cm⁻¹ are two other typical bands observed for highly boron-doped diamond films. The origins of these two bands are still open to debate. To date, several assignments have
been proposed by different research groups. First, the band at 1215 cm⁻¹ was proposed to arise from boron atoms by Ager III et al.¹⁶ However, a similar band along with a band around 500 cm⁻¹ are often observed for undoped diamond films, as reported by Buckley and co-workers.¹⁷ Therefore, these bands are not directly related to boron bonding in the film. Second, Gonon et al. suggested that these bands are related to maxima in the phonon density of states of diamond and arise from scattering by phonons outside the center of the Brillouin zone.¹⁸ This is based on the theoretical phonon density of states for diamond,¹⁹ which has a maximum around 1200 cm⁻¹ and matches quite closely the band observed in the spectrum. May et al. gave another explanation for these bands. They noted that the positions of these two bands agreed with the two maxima in the phonon density of states (PDOS) and claimed that these bands may be connected with a relaxation of the wavevector selection rules. Therefore, they may be associated with the actual boron incorporation in the lattice, rather than the hole concentration.²⁰ More recently, Vlasov et al. studied the vibrational modes of heavily boron-doped diamond using isotopic substitution of boron and carbon. They found none of the bands in the Raman spectra shifted upon ¹⁰B-substitution, whereas shifts to lower frequency were observed for all bands upon ¹³C-substitution, as compared to a sample with natural isotope abundancies. Their results supported the assignment of these bands to perturbed diamond lattice phonons. Therefore, they ascribed these bands to vibration modes in maxima of the phonon DOS of diamond.²¹ The broad peak at 477 cm⁻¹ is the one-phonon mode of Si^{18, 22} and the broad peak centered at 1010 cm⁻¹ is the second-order scattering from the silicon substrate.¹⁶

As evidenced by the AFM and SEM images, the morphology of the MSU and NRL films is very different. There are also microstructural differences, as confirmed

by Raman spectroscopy. The Raman spectrum for the MSU film is strongly influenced by sp² bonded carbon in the grain boundaries but the Raman spectrum for NRL film is identical to that for highly boron-doped microcrystalline diamond. The morphology of NRL film is very similar to that for a highly boron-doped microcrystalline diamond film except the grain size is much smaller. This may explain why the Raman spectrum for NRL film is more similar to that for a highly boron-doped microcrystalline rather than a nanocrystalline diamond film.

6.2.3 Electrochemical Characterization

Background cyclic voltammetric *i-E* curves are useful for examining the diamond film quality because the electrochemical response is highly sensitive to physicochemical properties of the surface. The magnitude of the background current, the working potential window, and the voltammetric features present within the working potential window are all sensitive to the presence of nondiamond (amorphous or graphitic) sp² carbon impurity.²³⁻²⁷ Figure 6.4 shows representative background cyclic voltammetric *i-E* curves for MSU and NRL nanocrystalline BDD thin-film electrodes in 1 mol/L KCl at 0.1 V/s. The geometric area of both electrodes was the same (0.183 cm²), although the currents in Figure 6.4 are not normalized to this area. The background current for the NRL film is low and featureless between -0.8 and 2.0 V. There is no evidence for any surface redox processes; therefore, the film appears to be ideally polarizable in this potential region. A similarly low and featureless background current is observed for the MSU film between -1.3 and 1.8 V. The MSU film shows an anodic peak on the forward sweep at 1.5 V. This peak is assigned to the oxidation of the grain boundary sp² carbon, where electrochemically-active carbon-oxygen

functionalities can form (e.g., quinine/hydroquinone couple).^{23, 26-28} The MSU film has more of this type of sp^2 carbon than does the NRL film.

The background currents for both electrodes are a factor of ~10 lower than freshly polished glassy carbon of the same geometric area. No change in the shape of the traces was observed during multiple cycles suggestive of a very stable surface structure. The working potential window (\pm 500 µA/cm² geometric area) for these two films is 3.0 (NRL film) and 3.4 V (MSU film), respectively. The NRL film has a less negative onset potential for hydrogen evolution but more positive onset potential for oxygen evolution, in comparison with the MSU film. We suppose this is due, in part, to more conductive sites on NRL film maybe because of higher doping level (refer to the CP-AFM images in next section), which would increase the density of electronic states at negative potentials. But we can't explain why NRL film has a slightly more positive onset potential (oxygen evolution) at present. The potential windows for the MSU and NRL films are within the range of 3—4 V typical of good quality boron-doped polycrystalline diamond.²³⁻²⁷



Figure 6.4 Background cyclic voltammetric *i-E* curves for the MSU and NRL nanocrystalline boron-doped diamond films in 1 mol/L KCl at 0.1 V/s.

Panels A-F of Figure 6.5 show cyclic voltammetric *i-E* curves for Fe(CN)₆^{3/4-}, Ru(NH₃)₆^{3+/2+}, IrCl₆^{2-/3-}, methyl viologen, dopamine, and Fe^{3+/2+}, respectively, at the two films. The voltammetric data are summarized in Table 6.2. As an example, Figure 6.6 shows the cathodic current vs. $v^{1/2}$ for the two films in 0.1 mmol/L Ru(NH₃)₆^{3+/2+} + 1 mol/L KCl (scan rate v: 0.1 to 0.9 V/s). These redox systems were selected for testing because of the known sensitivity or insensitivity of each to the electronic properties, surface microstructure, and surface chemistry of sp² and sp³ carbon electrodes (HOPG, glassy carbon, and diamond).^{3-7, 23, 24}



Figure 6.5 Cyclic voltammetric *i-E* curves for (A) 1 mmol/L $Fe(CN)_6^{3-/4-}$ in 1 mol/L KCl, (B) 1 mmol/L Ru(NH₃)_6^{3+/2+} in 1 mol/L KCl, (C) 1 mmol/L IrCl_6^{2-/3-}+ 1 mol/L KCl, (D) 1 mmol/L methyl viologen in 1 mol/L KCl, (E) 1 mmol/L dopamine in 0.1 mol/L HClO₄, and (F) 1 mmol/L Fe^{3+/2+} in 0.1 mol/L HClO₄. Scan rate: 0.1 V/s.

	NRL (mV)	MSU (mV)
Fe(CN) ₆ ^{3-/4-}	61 ± 3	64 ± 3
Ru(NH ₃) ₆ ^{3+/2+}	57 ± 1	59 ± 2
IrCl ₆ ^{2-/3-}	60 ± 2	57 ± 5
MV	59 ± 2	66 ± 5
DA	513 ± 15	577 ± 18
Fe ^{3+/2+}	603 ± 25	663 ± 22

Table 6.2Peak separations of the MSU and NRL films in different redoxsystems*.

* Scan rate: 0.1 V/s, Solution: 1 mmol/L analyte + 1 mol/L KCl (for $Fe(CN)_6^{3./4-}$, $Ru(NH_3)_6^{3+/2+}$, $IrCl_6^{2./3-}$ and MV) and 0.1 mol/L HClO₄ (for DA and $Fe^{3+/2+}$). The data are presented as average value ± standard deviation with n =3.



Figure 6.6 Relationship between the cathodic peak current and the square root of the scan rate for the two BDD electrodes in 0.1 mmol/L Ru(NH₃)₆^{3+/2+} + 1 mol/L KCl. The scan rate was valued from 0.1 to 0.9 V/s.

 $Fe(CN)_6^{3/4}$ was used as a redox probe because the electrode reaction kinetics for this couple are strongly influenced by the fraction of exposed edge plane on sp^2 bonded carbon electrode, as well as the surface cleanliness.⁵ Therefore, its heterogeneous electron-transfer rate constant is quite sensitive to the surface cleanliness and chemistry of sp² and sp³ carbon electrodes.^{1, 5, 25, 29, 30} Compared to other outer-sphere systems, this redox system often behaves anomalously on carbon electrodes and should not be considered outer-sphere. The physicochemical properties of boron-doped diamond also strongly influence the electrode kinetics of $Fe(CN)_6^{3/4-}$. For example, the cyclic voltammetric ΔE_p is very sensitive to the surface termination with the smallest value observed at the clean, hydrogen-terminated surface. After oxygen termination, ΔE_p increases by over 125 mV but is reversibly reduced back to the original value after removal of the oxygen functionalities by hydrogen plasma treatment.³¹ The ΔE_p for the curves in Figure 6.5 are 64 mV for the MSU film and 61 mV for the NRL film. The near-Nernstian ΔE_p indicates that both boron-doped diamond electrodes possess the requisite surface structure and properties to support rapid charge transfer.

Ru(NH₃) $_{6}^{3+/2+}$ involves simple electron transfer on most electrodes including diamond^{23-26, 32} and sp² carbon.³⁻⁶ The electrode kinetics are relatively insensitive to the surface microstructure, surface oxides, and adsorbed monolayers on sp² carbon electrodes.³⁻⁶ The fact that the electron-transfer rate constant is relatively insensitive to surface chemistry indicates the electrode reaction does not involve a specific interaction with a surface site or functional group.⁵ The most important factor affecting the kinetics is the electronic properties of the electrode, specifically the density of electronic states near the formal potential of the redox system. The ΔE_p values are nearly the same, 57 and 59 mV, for the NRL and MSU film, respectively.

Similar to Ru(NH₃) $_{6}^{3+/2+}$, IrCl $_{6}^{2-/3-}$ involves simple electron transfer at most electrodes including diamond^{26, 33} and sp² carbon.⁵ The electron-transfer rate constant is relatively insensitive to the surface microstructure, surface oxides, and adsorbed monolayers on sp² carbon electrodes.³⁻⁶ Surface cleanliness is important, although to a lesser degree than for Fe(CN) $_{6}^{3-/4-}$. The most influential factor is the electronic structure of the electrode. As shown in Figure 6.5C, both the MSU and NRL electrodes showed near-Nernstian responses for this redox couple with a ΔE_p of 60 and 57 mV for the NRL and MSU film, respectively.

Methyl viologen involves simple electron transfer at diamond and most other electrodes.^{7, 31, 34} The rate of reaction at diamond is relatively insensitive to surface oxides, grain boundaries, defect density, and the presence of nondiamond carbon impurity^{1, 7, 31, 34}. Like Ru(NH₃)₆^{3+/2+}, the most important factor influencing the rate is the density of electronic states near the formal potential. Near-Nerstian cyclic voltammetric i-E curves are seen for both electrodes with a ΔE_p of 59 and 66 mV for the NRL and MSU film, respectively. The near-Nernstian ΔE_p values indicate that both films possess similar electronic properties and similar activity for this redox system.

The near-Nernstian responses for $Fe(CN)_6^{3-/4-}$, $Ru(NH_3)_6^{3+/2+}$, $IrCl_6^{2-/3-}$ and methyl viologen all indicate that ohmic resistance within the film is minimal even at very negative potentials.

Dopamine exhibits much more electrochemical irreversibility, as evidenced by the relatively large ΔE_p . This more irreversible behavior is characteristic of all the catechols and catecholamines investigated so far at diamond.^{25, 26, 33, 35} ΔE_p is 513 mV for the NRL film and 577 mV for the MSU film. For comparison, ΔE_p , at polished glassy carbon under identical conditions is in the range of 125-175 mV.³⁶ The formal potential is positive of that for Fe(CN)₆³⁻⁴⁻ so a low density of electronic states is not the reason for the larger ΔE_p . We suppose that minimal adsorption on diamond is the reason for the sluggish kinetics. Recent work in our group with several catechols and catecholamines has revealed no evidence for adsorption at solution concentrations as low as 1×10^{-6} mol/L. Hunt-Duvall and McCreery have presented a detailed study showing that low ΔE_p values correlate with catechol and catecholamine adsorption on glassy carbon, and surface treatments that decreased adsorption also increased ΔE_p .³⁷

 ΔE_p for DA is quite sensitive to the presence of nondiamond sp² carbon impurity at which adsorption can occur.³⁸ Therefore, this is a good redox system to test the MSU film against the NRL film. The MSU film has a high fraction of sp² bonded carbon in grain boundary, more than the NRL film. If grain boundaries dominate the electrochemical properties of the film, then one might expect a smaller ΔE_p for DA at the MSU film. This is not true for the results present here, which suggest that electrochemical activity of the MSU film is dominated by boron-doping rather than sp² carbon in grain boundary.

Very sluggish electrode kinetics are also observed for $Fe^{3+/2+}$ on diamond, as evidenced by the large ΔE_p of 603 mV for NRL and 663 mV for MSU film. The electrode kinetics for $Fe^{3+/2+}$ are highly sensitive to the presence of oxides on sp^2 carbon electrodes. The McCreery group has shown that electron transfer for this system is catalyzed by a specific chemical interaction with surface carbonyl functionalities.^{4,5} Therefore, we conclude that the sluggish electrode kinetics at diamond are due to the absence of mediating surface carbon-oxygen functionalities, specifically carbonyl groups. The voltammetric data presented above reveal that for $Fe(CN)_6^{3.44}$, $Ru(NH_3)_6^{3+/2+}$, $IrCl_6^{2.43-}$ and MV, the clean, hydrogen-terminated NRL and MSU films are very active without any conventional pretreatment prior to use. On the other hand, the relatively large peak separation observed for $Fe^{3+/2+}$ at hydrogen-terminated diamond is presumably because of the absence of surface carbonyl functional groups, which are known to catalyze this reaction.³⁹ Relatively slow electrode reaction kinetics are also observed for dopamine, presumably due to weak adsorption on hydrogen-terminated diamond.²⁸

6.2.4 CP-AFM measurements

Figure 6.7 shows the topographical (A) and conductivity (B) maps for the MSU boron-doped diamond nanocrystalline thin film obtained by CP-AFM. The bias voltage was ± 0.2 V (sample vs. tip), and the scan size was 200 \times 200 nm². In the topographical map, nodular features of 50-100 nm in the lateral dimension are seen. The boundaries between these features are also clearly visible. In the conductive map, nonuniformly distributed conductive sites are seen. Although the most of conductive sites appear to be associated with grain boundaries (most of small conductive regions in Figure 6.7B are associated with grain boundaries in Figure 6.7A), Figure 6.7B shows evidence that several nodular features are conductive (e.g., the particle in the middle right and the nodular feature in the lower left quadrant of the image). On the other hand, some of the least conducting regions in the image are actually associated with nodular features and even grain boundaries (see the upper edge area of Figure 6.7B).



Figure 6.7 CP-AFM images for the MSU nanocrystalline boron-doped diamond thin film. (A) Height image and (B) Conductivity map.

Generally, not all of the nodular features and surrounding grain boundaries exhibit high conductivity. This may be related to inhomogeneous boron dopant distribution in the film,⁴⁰⁻⁴² as was discussed in Chapter 4.

Figure 6.8 shows the topographical (A) and conductivity (B) maps for the NRL boron-doped diamond nanocrystalline thin film. The bias voltage was +0.2 V (sample vs. tip), and the scan size was 200 × 200 nm². In the topographical map, a few of the small crystals are seen . In the conductive map, nonuniformly distributed conductive regions are seen. Most of grains are conductive, which is a little different from the MSU film. Therefore, the fraction area that is conductive appears higher for the NRL film. This is one reason why the nominal ΔE_p values were smaller for the NRL film when probed with Fe(CN)₀^{3,24}, dopamine and Fe^{3+r2+} (refer to section 6.2.3). Similar to the MSU film, most of the imaged area, including crystal facets and boundary areas, are conductive. There are some grains and boundaries showing lower conductivity (see the grains at the middle of the upper edge and lower left corner of Figure 6.8A and B). We suppose there are two possible reasons for this observation. First, there may be less boron aggregates in these regions, which results in a lower charge carrier concentration. Second, the contact area between the CP-AFM tip and the sample may play a role because of the bigger grain size as we discussed in Chapter 4.



Figure 6.8 CP-AFM images of an NRL nanocrystalline boron-doped diamond thin film. (A) Height image and (B) Conductivity map.

6.3 Conclusions

The electrochemical properties of high-quality, boron-doped nanocrystalline diamond thin films produced by two different growth methods were compared. Several factors, such as the grain size, morphology, microstructure and electrical conductivity that influence the electrode kinetics for several aqueous-based redox systems, were investigated. The similarity of the voltammetric data for the NRL and MSU films indicates the high quality and electrical conductivity of both films. Several important conclusions regarding the structure-reactivity relationship of these nanocrystalline films can be made. First, similar CVs for Ru(NH₃)₆^{34/2+}, IrCls^{24/2-} and

methyl viologen were obtained for both films. These redox systems appear to involve simple electron-transfer that is relatively insensitive to surface oxides, grain boundaries and other defects including nondiamond carbon impurities present in the polycrystalline films. Therefore, our results suggest that the electrochemical properties of the MSU film are similar to those of the NRL film, even the two films show different microstructures because of the different growth conditions. $Ru(NH_3)_6^{3+/2+}$ and methyl viologen have formal potentials that fall well into the midgap region of diamond. The near-Nerstian responses for both redox systems suggest a sufficient density of electronic states exists near the formal potentials of each. These midgap states result mainly from the boron doping and the lattice hydrogen, rather than from non-diamond carbon impurity phases or grain boundaries and other defects. Second, $Fe(CN)_6^{3-/4-}$ involves more complex, surface-sensitive electrontransfer that is highly sensitive to the presence of surface oxides but insensitive to non-diamond carbon impurity phases. The fastest kinetics were observed for the hydrogen-terminated surface. Third, $Fe^{3+/2+}$ undergoes sluggish electron-transfer at both the NRL and MSU films consistent with the absence of carbonyl groups on the surface as electron-transfer kinetic of $Fe^{3+/2+}$ are known to be strongly influenced by these groups.³⁹ Fourth, the slow electrode reaction kinetics for dopamine may be due a lack of adsorption on the relatively non-polar surfaces. Both SEM and AFM images show the difference of the morphologies of two films, which may result from different growth conditions. CP-AFM images revealed that although most of the imaged area was conductive for both films, there were some grains and boundaries showing low conductivity. The fraction of highly conductive regions for the NRL film was greater than that for the MSU film.

The key finding was that nanocrystalline boron-doped diamond films produced by two different growth procedures possess similar electrochemical and electrical properties.

6.4 Reference

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Chapter 7

Diamond Microelectrodes for Continuous Amperometric Recording at Blood Vessel Surfaces

7.1 Introduction

The peripheral nervous system (PNS) consists of sensory nervous system, which sends information to the central nervous system (CNS) from internal organs and from external stimuli, and the motor nervous system, which carries information from the CNS to organs, muscles, and glands. The motor nervous system is divided into the somatic nervous system and the autonomic nervous system. The somatic nervous system controls skeletal muscle as well as external sensory organs, such as the skin. The autonomic nervous system controls involuntary muscles, such as smooth and cardiac muscle. The autonomic nervous system can further be divided into the parasympathetic and sympathetic divisions. The sympathetic nervous system is concerned especially with preparing the body to react to situations of stress or emergency, which contains chiefly adrenergic fibers and tends to depress secretion, decrease the tone and contractility of smooth muscle, increase heart rate and blood pressure. The parasympathetic nervous system, on the other hand, is evident when a person is resting and feels relaxed, and is responsible for such things as the constriction of the pupil, the slowing of the heart, the dilation of the blood vessels, and the stimulation of the digestive and genitourinary systems.

Sympathetic nerves are responsible for acute changes in blood pressure and they contribute to long-term blood pressure regulation. Peripheral sympathetic nerves travel along arteries and veins, and are present near the adventitial-medial border to make close contact with vascular smooth muscle cells. The nerves communicate with the effector cells of the resistance (arteries) and capacitance (veins) vessels through the release of norepinephrine (NE), a vasoconstrictor neurotransmitter, as shown in Figure 7.1. This is the typical pattern for the sympathetic innervation of blood vessels.¹ Only the smooth muscle cells located at the adventitial/medial border are directly innervated.^{2, 3} The appearance and arrangement of sympathetic nerves associated with the veins is similar to that of arteries, although nerve density in veins is generally less than that observed in the adjacent arteries.^{4, 5}



Figure 7.1 Schematics for (A) the distribution of sensory and sympathetic nerves around a blood vessel, (B) an arterial neuroeffector junction, and (C) a venous neuroeffector junction.

Sensory nerves arising from neurons in the dorsal root ganglia (DRG) supply most blood vessels and these nerve fibers contain and release the neuropeptides, substance P (SP) and calcitonin gene related peptide (CGRP).⁶ Activation of perivascular sensory nerves causes arterial dilation.⁷ While sympathetic nerve activity is an important determinant of systemic blood pressure, sensory nerves may also contribute to the regulation of vascular tone. For example, CGRP levels are increased in DRG of deoxycorticosterone acetate (DOCA)-salt rats and treatment of these animals with a CGRP receptor antagonist increases blood pressure.⁸

The communication between sensory and sympathetic nerves is accomplished along a pathway called the reflex arc. A normal reflex arc, as schematized in Figure 7.2, involves the afferent nerve carrying nerve impulses from receptors or sense organs toward the CNS and the efferent nerve carrying nerve impulses away from the CNS to effectors, such as muscles or glands. It has been known that repetitive activation of afferent nerve fibers can cause cross-excitation of neighbors not stimulated directly.⁹ This cross-excitation has been demonstrated at sites of peripheral nerve injury and sensory ganglia.^{10, 11} However, it is still unclear if sensory nerves directly communicate with sympathetic nerves locally near the neuroeffector junctions. One of the specific aims of our research was to determine if there is local (direct) communication between sensory and sympathetic nerves that innervate mesenteric blood vessels of rats when the connections from both sensory and sympathetic nerves to the CNS are severed (no reflex arc).

In this chapter, progress toward this specific aim is discussed including determining the distribution of sensory and sympathetic nerves along blood vessels,

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understanding the effects of drugs used in the work on the diamond electrode's response for norepinephrine.



Figure 7.2 An illustration of a simple reflex arc.

7.2 Effects of drugs on the electrochemical responses of carbon fiber and diamond microelectrodes

7.2.1 Norepinephrine and drug effect

Norepinephrine (NE) functions as both a hormone and neurotransmitter. It is secreted by the adrenal medulla and released from sympathetic nerves. It plays a key role in the regulation of vascular tone, heart rate, blood pressure, and blood sugar level.^{12, 13} NE levels have been measured in tissue and biological fluids because of its involvement in stress related diseases, such as, hypertension, depression and cardiovascular disease.^{12,}

¹⁴ In the past, measurements of NE in plasma were done by high performance liquid chromatography (HPLC) or with radioactive labeling methods. These so-called "overflow" measurements provide little information about real-time, local release of NE.¹⁴⁻¹⁶

Since NE can be oxidized via a 2H⁺/2e redox reaction, it can be detected electrochemically as an oxidation current. Since the pioneer work of Gonon *et al.*,^{17, 18} on NE release from rat tail artery as measured by continuous amperometry, electrochemical measurements with carbon fiber microelectrodes have been widely employed for *in vitro* studies of NE release and clearance from sympathetic nerves innervating mesenteric arteries and veins.¹⁹⁻²³ Unlike the "overflow" methods, the electrochemical methods provide information on dynamic changes in neurotransmitter concentrations near the sites of release.

Two types of carbon electrodes have been used: carbon fiber and boron-doped diamond. Carbon fiber has been routinely used for *in vivo* and *in vitro* electrochemical measurements since the 1970's.²⁴⁻²⁷ Recently, diamond has been used because of its excellent response sensitivity, reproducibility, pH-independent current response and its resistance to fouling.²⁸⁻³² Drugs are routinely used with the electrochemical measurements to pharmacologically characterize the neuroeffector junction. It is unclear how these drugs might affect the microelectrode response for NE .^{21, 22, 31-34} There have been reports in the dopamine studies that some drugs decrease the carbon fiber microelectrode sensitivity, which leads to decreased dopamine current measured *in vitro*.^{35, 36} Previous studies have discussed the influence of some drugs on electrochemical measurement.^{26, 37} Among the drugs that show electroactivity, some of them don't have

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significant effects on the sensitivity of the microelectrode, however, some other drugs, like GBR 12909 and nomifensine, the effect of the drug is quite strong that it needs to be considered if the current change is due to both pharmacological effect and the change of microelectrode sensitivity.³⁶ Non-electroactive drugs may also change the responsivity of the microelectrode.¹⁷ The mechanisms that cause electrode fouling drop are not fully understood.

We recently found that in addition to the pharmacological effect, some commonly used drugs also changed the surface chemistry of the microelectrode and thus changed the NE oxidation current. For some drugs, even after washing out, the NE current could not be totally recovered. In this work, we systematically studied if and how drugs commonly used to study sympathetic neuroeffector transmission affect the electrode response for NE oxidation. Seven drugs were investigated: prazosin, an α_1 adrenergic receptor antagonist; yohimbine, an α_2 adrenergic receptor antagonist; idazoxan, an α_2 adrenergic antagonist; UK, 14,304, and α_2 adrenergic agonist; cocaine, NE transporter antagonist; PPADS, a P2X-purinoceptor antagonist and capsaicin, a drug used for TRPV 1 channel.^{32, 34, 38, 39} The electroactivity of these drugs and their effect on the electrode response for NE were studied using both carbon fiber and diamond microelectrodes.

Table 7.1 shows the molecular structure and function of the neuropharmacological agents. Two types of carbon fiber were used: Thornel P55 pitch-based fibers and Thornel T650 PAN-based fibers. Both types have been widely used to investigate neurotransmission in biological environments.^{40, 41}

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Chemicals	Function	Structure
NE	Neurotransmitter in sympathetic nervous system	HO HO
Capsaicin	Agonist for TRPV 1 channel	F 3 C C CH3 C CH3 C CH3
Cocaine	Antagonist for NE transporter	N-CH ₃ O
Idazoxan	Antagonist for α-2 autoreceptor	
PPADS	Antagonist for P2X purinergic receptor	HO HO H ₃ C N NaO ₃ S SO ₃ Na

Table 7.1The structures and functions for NE and seven studied drugs.

Chemicals	Function	Structure
Prazosin	Antagonist for α-1 receptor	CH ₃ NH ₂ CH ₃
UK 14,304	Agonist for α-2 autoreceptor	H N N N H N N N H N
Yohimbine	Antagonist for α-2 autoreceptor	H H H ₃ COOC OH

Table 7.1The structures and functions for NE and seven studied drugs (continued).

Refer to Chapter 2 for more information about the drugs.

7.1.2 Results

A. Raman spectroscopy

The carbon microelectrodes were first characterized by Raman spectroscopy. Figure 7.3 shows characteristic spectra for diamond and two types of carbon fiber microelectrode. Figure 7.3a shows an intense one-phonon diamond line at 1332 cm⁻¹.⁴²⁻⁴⁴ There is minimal scattering intensity observed between 1500 and 1600 cm⁻¹, which arises from amorphous nondiamond carbon (i.e., sp² bonded carbon) impurity.^{31, 43, 45} Figure 7.3b shows P55 carbon fiber and Figure 7.3c shows T650 carbon fiber microelectrode microstructure. The exterior of the carbon fibers is an amorphous carbon network with a majority of sp² hybridized bonds and of nanocrystalline graphite regions. The G band peak, as the peak around 1583 cm⁻¹ shown in Figure 7.3b and the peak around 1587 cm⁻¹ in Figure 7.3c, represent the crystal graphite structure.⁴⁶⁻⁴⁸ The peaks shown around 1350 cm⁻¹ in Figure 7.3b and 1370 cm⁻¹ in Figure 7.3b are D band peaks, which are good indicators of disorder in the crystal structure. The higher I_D/I_G ratio suggests the more disordered structure of T650 carbon fiber, of which we suppose to have higher electroactivity.^{46, 47} This may explain why the E_{1/2} values of T650 carbon fiber microelectrode for NE redox systems are lower comparing with P55s carbon fiber and diamond microelectrodes (Table 7.2).

E _{1/2} (mV) vs. SCE	P55S	T650	Diamond
FeCN	255 ± 5	229 ± 5	283 ± 13
Ruhex	-240 ± 2	-223 ± 2	-251 ± 4
NE	137 ± 4	98 ± 7	294 ± 10
Capsaicin	563 ± 16	494 ± 19	548 ± 21
PPADS	N/A	N/A	805 ± 10
Prazosin	772 ± 10	794 ± 17	751 ± 2
UK 14,304	893 ± 6	877 ± 9	876 ± 4
Yohimbine	703 ± 12	696 ± 12	637 ± 13

Table 7.2 $E_{1/2}$ values of seven drugs, $Fe(CN)_6^{3-/4-}$ and $Ru(NH_3)_6^{3+/2+}$ on three types of microelectrodes.



Figure 7.3 Raman spectra of (a) a boron-doped diamond thin film deposited on a Pt wire, (b) a P55 carbon fiber, and (c) a T650 carbon fiber.

B. Electrochemistry

Figure 7.4 shows cyclic voltammetric *i-E* curves for a 0.1 mmol/L concentration of the drug in Krebs' buffer (0.1 V/s) at P55 (Figure 7.4a and b), T650 (Figure 7.4c and d) and diamond (Figure 7.4e and f) microelectrodes. The curves indicate that capsaicin, prazosin, yohimbine and UK 14,304 are electrochemically-active at both carbon fiber and diamond microelectrodes. Capsaicin can be oxidized between 0.5 and 0.8 V (vs. Ag/AgCl) on both carbon fiber and diamond. However, the oxidation current is significantly lower than that for the other three drugs at equal concentration. Prazosin, UK 14,304 and yohimbine can be oxidized between 0.7 and 1.0 V (vs. Ag/AgCl) on carbon fiber and between 0.8 and 1.1 V (vs. Ag/AgCl) on diamond. Figure 7.4 also shows that cocaine and idazoxan are electrochemically inactive on carbon fiber and diamond electrodes within 0 - 1.2 V (vs. Ag/AgCl) window and PPADS is electrochemically inactive on carbon fiber 0.9 and 1.1 V (vs. Ag/AgCl).

Effects of Capsaicin and Prazosin. Figure 7.5 shows the cyclic voltammetric i-E curves for $0.02 \text{ mmolL}^{-1} \text{ NE}$, $0.02 \text{ mmolL}^{-1} \text{ NE} + 0.1 \text{ mmolL}^{-1}$ capsaicin or prazosin, and $0.02 \text{ mmolL}^{-1} \text{ NE}$ after capsaicin or prazosin exposure at P55 (Figure 7.5a and b), T650 (Figure 7.5c and d) and diamond (Figure 7.5e and f) microelectrodes. These data show that the oxidation current peak of NE could not be distinguished when capsaicin or prazosin was present except on T650 carbon fiber electrode, on which the oxidation current peak of NE could be seen but significantly decreased when capsaicin was present.



Figure 7.4 Cyclic voltammetric *i-E* curves for the drugs at carbon fiber (P55, T650) and diamond microelectrodes. (a) Capsaicin, prazosin, UK 14,304 and yohimbine on P55 carbon fiber electrode. (b) Idazoxin, PPADS and cocaine on P55 carbon fiber electrode. (c) Capsaicin, prazosin, UK 14,304 and yohimbine on T650 carbon fiber electrode. (d) Idazoxin, PPADS and cocaine on T650 carbon fiber electrode. (e) Capsaicin, prazosin, UK 14,304 and yohimbine on diamond microelectrode. (f) Idazoxin, PPADS and cocaine on diamond microelectrode. (f) Idazoxin, PPADS and cocaine on diamond microelectrode. All curves were acquired in Krebs solution at 0.1 V/s. The concentration of the drug was 0.1 mmol/L.



Figure 7.5 Cyclic voltammetric *i*-*E* curves for NE at P55 (a), T650 (c) carbon fiber electrode and diamond microelectrodes (e) with and without capsaicin and Cyclic voltammetric *i*-*E* curves for NE at P55 (b), T650 (d) carbon fiber electrode and diamond microelectrodes (f) with and without prazosin. All curves were acquired in Krebs' buffer at 0.1 V/s. The concentration of NE was 0.02 mmol/L and the concentration of each drug was 0.1 mmol/L.

The data in Figure 7.6 summarize how the NE oxidation response at all three electrodes was affected by exposure to capsaicin and prazosin. Results are presented as a shift in $E_{1/2}$ and a ratio of $ip^{ox}_{(with or after drug)} / ip^{ox}_{(before drug)}$. Both capsaicin and prazosin significantly affect the detection of NE at their presence at carbon fiber and diamond electrodes (Figure 7.6a and b). The peak current of NE could not be determined using P55s and diamond microelectrode with these two drugs. NE could be measured using T650 microelectrode, however, the current amplitude has been significantly diminished. After washing out drugs (Figure 7.5c and d), the effects of capsaicin on the detection of NE with three types of electrodes were reversed, however, the inhibitory effect of prazosin on P55s and diamond microelectrodes were hard to be reversed ($E_{1/2}$ of NE right-shifted and the current decreased).

To test if the adsorption of the drug species to the electrode surface is physically or not, we used two redox systems, $Ru(NH_3)_6^{3+/2+}$ and $Fe(CN)_6^{3-/4-}$ to characterize the drug effect on the microelectrode sensitivity. The mechanisms that how these two redox systems work will be discussed later. Data are shown in Table 7.3. These results show that capsaicin significantly deactivates the diamond microelectrode ($E_{1/2}$ for $Fe(CN)_6^{3-/4-}$ is right-shifted and $Ru(NH_3)_6^{3+/2+}$ is left-shifted significantly) but they have negligible effect on carbon fiber electrodes ($E_{1/2}$ is shifted only slightly). Prazosin deactivated all three types of microelectrode. The effects of capsaicin on three types of electrode were reversed when the drug was washed out but not for prazosin, suggesting that prazosin changed the electronic state of the microelectrode.

Table 7.3 Statistical data (n=3) for $E_{1/2}$ values and current changes for $Fe(CN)_6^{-3/4}$ and $Ru(NH_3)_6^{+3/42}$ before and after exposure to capsaicin and prazosin at P55, T650 carbon fiber and diamond microelectrodes.

Drug	Probe	P55	T650	Diamond
		ΔE _{1/2} (mV)	ΔE _{1/2} (mV)	ΔE _{1/2} (mV)
Capsaicin	Fe(CN)6 ^{3-/4-}	18.3 ± 9.7	-7.5 ± 20.7	89.7 ± 9.5 *
	Ru(NH3)6 ^{3+/2+}	1.0 ± 6.0	0 ± 0.6	-12.7 ± 2.9
Prazosin	Fe(CN)6 ^{3-/4-}	69.7 ± 13.5 *	7.0 ± 5.0	251.3 ± 30.3 *
	Ru(NH3)6 ^{3+/2+}	-6.7 ± 1.9	-5.7 ± 1.2	-29.0 ± 10.0



Figure 7.6 Statistical results (n = 3) for the effect of capsaicin and prazosin. (a) $\Delta E_{1/2}$ before and after drug on P55, T650 and diamond electrode for NE detection. (b) Peak current changes before and after drug for NE detection on three types of electrode. (c) $\Delta E_{1/2}$ before and after drug was applied for NE detection. (d) Peak current changes before and after drug was applied for NE detection using three types of electrode.

Effects of UK 14,304 and Yohimbine. Figure 7.7 shows cyclic voltammetric *i-E* curves for 0.02 mmolL⁻¹ NE, 0.02 mmol/L NE + 0.1 mmol/L UK 14,304 or yohimbine, and 0.02 mmol/L NE after UK 14,304 or yohimbine was applied on P55 (Figure 7.7a and b), T650 (Figure 7.7c and d) and diamond (Figure 7.7e and f) microelectrodes. These data show that the oxidation current peak of NE was reduced when UK 14,304 or yohimbine was present. It seems that UK 14,304 and yohimbine can be reversibly adsorbed on the surface of the electrode and occupied the active sites because the oxidation current peak of NE can be reversed after the drug is washed out.

The statistic data shown in Figure 7.8a and b indicate that at the presence of UK 14,304 and yohimbine, NE could be determined in most situations but the current was significantly decreased. Figure 7.8c and d show that the effects of UK 14,304 and yohimbine on the determination of NE at three types of microelectrodes were reversed to some extent after the drug was washed out.



Figure 7.7 Cyclic voltammetric *i*-*E* curves for NE at P55s (a), T650 (c) carbon fiber electrode and diamond microelectrodes (e) with and without UK 14,304. Cyclic voltammetric *i*-*E* curves for NE at P55 (b), T650 (d) carbon fiber electrode and diamond microelectrodes (f) with and without Yohimbine. All curves were acquired in Krebs' buffer at 0.1 V/s. The concentration of NE was 0.02 mmol/L and the concentration of the drug was 0.1 mmol/L.



Figure 7.8 Statistical results (n = 3) for the effects of UK 14,304 and yohimbine. (a) $\Delta E_{1/2}$ before and with drug on P55, T650 and diamond electrodes for NE. (b) Peak current changes before and after drug on NE detection using three types of microelectrode. (c) $\Delta E_{1/2}$ before and after drug was applied for NE. (d) Peak current changes before and after drug was applied for NE detection using three types of microelectrode.

Effects of Cocaine, Idazoxan, and PPADS. As shown in Figure 7.4, idazoxan and PPADS are electrochemically inactive on carbon fiber and diamond electrodes within the voltage range studied. PPADS is electrochemically-inactive at carbon fiber but has an oxidation peak around 805 mV vs. Ag/AgCl at diamond. This may be due to the different adsorption ability of PPADS to three types of microelectrode surface. We anticipate that

these three drugs should not affect the determination of NE too much, at least for carbon fiber microelectrode. Our measurements confirmed this. Figure 7.9 shows the cyclic voltammetric i-E curves for 0.02 mM NE, 0.02 mM NE + 0.1 mM idazoxan or PPADS and 0.02 mM NE after idazoxan or PPADS was applied on P55S (Figure 7.9a and b), T650 (Figure 7.9c and d) and BDD (Figure 7.9e and f) electrodes. As expected, idazoxan and PPADS show little effects on the oxidation current peak of NE on all electrodes. Figure 7.9 also shows that the cyclic voltammetric i-E curves of NE, NE with and after these drugs are not exactly identical, therefore, calibrations should be performed before and after the drug is applied for the determination of NE.

Cocaine is also electrochemically inactive on carbon fiber and diamond electrodes as shown in Figure 7.4d, e and f. Different from idazoxan and PPADS, cocaine activated all electrodes in our experiments. The oxidation current peak of NE increased slightly after cocaine was applied as shown in Fig 7.10 (except for BDD microelectrode). This activation effect was also confirmed when probed by $Fe(CN)_6^{3-/4-}$ and $Ru(NH_3)_6^{3+/2+}$ as summarized in Table 7.4. Both of the oxidation peak current $Fe(CN)_6^{3-/4-}$ and the reduction peak current of $Ru(NH_3)_6^{3+/2+}$ increased slightly after cocaine was applied. It's noteworthy that these increases are not significant when checked with ANOVA.

Figure 7.10 also shows that the cyclic voltammetric i-E curves of NE, NE with and after cocaine are not exactly identical, therefore, calibrations should be performed before and after the drug is applied for the determination of NE.
Drug	Probe*	P55S		T650		Diamond	
		ΔE _{1/2} (mV)	İ _{ratio}	ΔE _{1/2} (mV)	i _{ratio}	ΔE _{1/2} (mV)	İ _{ratio}
Idazoxan	F	29.5 ± 26.4	0.89 ± 0.06	10.8 ± 7.2	0.93 ± 0.04	79.0 ± 4.6	1.00 ± 0.08
	R	-3.8 ± 3.7	1.00 ± 0.03	1.3 ± 0.6	1.00 ± 0.01	-4.3 ± 4.3	0.97 ± 0.02
PPADS	F	6.3 ± 9.4	0.96 ± 0.05	7.7 ± 2.7	0.88 ± 0.03	8.3 ± 16.2	0.98 ± 0.04
	R	0.3 ± 1.7	1.02 ± 0.02	-0.7 ± 14	0.99 ± 0.03	7.0 ± 3.8	1.05 ± 0.03
Cocaine	F	-15.3 ± 9.2	1.07 ± 0.11	4.3 ± 3.5	1.08 ± 0.05	16.5 ± 2.5	1.03 ± 0.05
	R	6.8 ± 4.8	1.05 ± 0.05	0.6 ± 0.9	1.03 ± 0.01	-5.7 ± 27	1.01 ± 0.01

Table 7.4Effects of Idazoxan, PPADS and Cocaine on the electrochemicalproperties of carbon fiber and BDD microelectrodes probed by $Fe(CN)_6^{3-/4-}$ and $Ru(NH_3)_6^{3+/2+}$.

F: Fe(CN)₆^{3-/4-}

R: $Ru(NH_3)_6^{3+/2+}$



Figure 7.9 Cyclic voltammetric *i-E* curves for norepinephrine at P55 (a), T650 (c) carbon fiber and diamond microelectrodes (e) with and without idazoxan. Cyclic voltammetric *i-E* curves for norepinephrine at P55 (b), T650 (d) carbon fiber and diamond microelectrodes (f) with and without PPADS. All curves were acquired in Krebs' buffer at 0.1 V/s. The concentration of norepinephrine was 0.02 mmol/L and the concentration of each drug was 0.1 mmol/L.



Figure 7.10 Cyclic voltammetric *i*-*E* curves for norepinephrine at P55 (a), T650 (b) carbon fiber and diamond microelectrodes (c) with and without cocaine. All curves were acquired in Krebs' buffer at 0.1 V/s. The concentration of norepinephrine was 0.02 mmol/L and the concentration of each drug was 0.1 mmol/L.

7.1.3 Discussion

As shown in Table 7.1, the chemical structure of the neuropharmacological agents can be divided into three categories: 1) the $-NH_2$ group in prazosin, -OH group in capsaicin, and -OH group in vohimbine make these drugs oxidizable; 2) although PPADS also have -OH group in a pyridine structure, N=N group which connects with this pyridine make --OH group really difficult to be oxidized; and the -- NH group in five member ring both in UK 14,304 and idazoxan make these two drugs also not easy to be oxidized; 3) there is no function group in cocaine which could be oxidized. Since these drugs may possess different electrochemistry property, we predict that they may have different effects on the responsivity of the microelectrode when used in biological environment. Normally, in the electrochemical measurement of NE in vitro, the electrode used should possess good biocompatibility, good sensitivity, low limit of detection, stable and low background current which is not affected by the changes in surrounding solution and resistance to the adsorption, either by the interested redox species and their products or the components of the background solution (e.g. Krebs' buffer)^{22, 34, 49, 50}. However, when there are various redox system in the biological buffer (e.g. drug application), there are changes, more or less, to the sensitivity of microelectrode. The concern that if and how these commonly used drugs affect the NE oxidation current measurement and their effect on the microelectrode sensitivity drives us doing this study.

Our results show that according to the effect on the determination of NE on carbon fiber and boron-doped diamond microelectrodes, the seven drugs can be classified into 3 categories: 1) capsaicin and prazosin, which voltammagrams immerge the oxidation current peak of NE; 2) UK 14,304 and yohimbine, which voltammagrams

partially overlap the oxidation current peak of NE; 3) Cocaine, Idazoxin, and PPADS which have no significant effect on the determination of NE.

Capsaicin and prazosin can be oxidized, as shown in Figure 7.4. At the presence of capsaicin, the oxidation current peak of NE could not be distinguished except on T650 carbon fiber microelectrode, on which the oxidation current peak of NE could be seen but significantly decreased (Figure 7.5a, c and e). But after drug washing out, the effects of capsaicin on three types of microelectrode were reversed (Figure 7.6a and b). One reason for this might be capsaicin has a phenol structure, which is really similar to the structure of NE. This makes capsaic behave similarly as NE and has similar $E_{1/2}$ value (Table 7.2). In this case, the competition of being oxidized for these two species depends largely on their concentration. In our experiment, we tried to mimic the situation in *in vitro* NE measurement, the ratio of capsaicin and NE is around 5, which suggest more capsaicin is prone to be oxidized on the surface of microelectrode. Thus, there would be a great interference on NE measurement at the presence of capsaicin and our data proved this. Figure 7.5b, d and f show that the oxidation current peak of NE could neither be distinguished at the presence of prazosin. However, we think the reason for this is not exactly the same as what we saw from capsaicin. Because after drug washing out, the inhibitory effect of prazosin on all 3 electrodes were difficult to be reversed (Figure 7.6c and d) and the response to NE was also diminished (Figure 7.5b, d and f) except for T650.

The mechanism of how these drugs affect the NE detection is not clear. However, we think one potential reason is the adsorbed drug occupied the activation points on the surface of the microelectrode which influenced the efficacy of NE detection. The

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recovered currents after capsaicin washed out are consistent with this hypothesis. McCreery and DuVall have shown that the specific molecular features present at the carbon surface plays an important role in determining the kinetics of heterogeneous reactions. The adsorption may involve a distribution of interaction strengths between each type of carbon surface site and adsorbed analyte species ^{51, 52}. While there is only NE in the solution, NE bind with those activation sites, and reodx reaction happens at the surface of the electrode. However, at the presence of adsorbing electroactive drugs, the efficacy of NE being oxidized depends on the adsorption competition between the drug and NE. If the adsorption ability of the drug to the electrode surface is comparable with NE, then at the presence of this drug, how much NE would be oxidized depends on the kinetics, which is related with the concentration of both drug and NE; and after drug washing out, the response to NE could recover, e.g. capsaicin. However, if the drug could be strongly adsorbed on the surface of the electrode, then NE has less chance to bind with activation sites. As a consequence, once equilibrium is established, the strongly held drugs remain on the surface, and only the weaker adsorbing carbon surface sites remain exposed for NE adsorption, and thus there is a right shift NE $E_{1/2}$ value and a decrease of current amplitude. To the maximum, the NE current is decreased to the extent that it is totally merged and could not be distinguished from the drug peak, e.g. prazosin. And what's more, since the adsorption to the electrode are so strong, even after washing out, some drug species are still adsorbed on the electrode surface. As a consequence, the response to NE could not get back, no matter for $E_{1/2}$ or oxidation current.

In order to verify our hypothesis, we also used two redox systems, $Ru(NH_3)_6^{3+/2+}$

and $Fe(CN)_{6}^{3./4-}$ to characterize the drug effect on the microelectrode sensitivity which has a great influence on NE measurement. That is because how the chemical and physical properties affect the electrochemical response of sp² (e.g. carbon fiber) and sp³ (e.g. diamond) carbon electrodes depends to some extent on the electron transfer mechanism for the specific redox system ⁵¹⁻⁵³. Ru(NH₃)₆^{3+/2+} is an outer-sphere redox systems on both carbon fiber and diamond with heterogeneous electron-transfer rate constant depend primarily on the density of electronic states and is less affected by the physical and chemical properties of the electrode surface ^{43, 44, 51-53}. Fe(CN)₆^{3./4-} is a more complicated, inner sphere redox system, with a heterogeneous electron-transfer rate constant highly sensitive to the surface cleanliness, surface oxygen coverage and microstructure, as well as the density of electronic states ^{31, 43, 44, 51}. Thus, these two redox systems could characterize both the change of density of electronic states and surface cleanliness of the microelectrode under the effect of drugs.

After capsaicin was washed out, both the $E_{1/2}$ and oxidation current recovered suggest that neither the electronic structure nor the surface of the electrode had been changed after drug application. So the adsorption of capsaicin on the electrode surface was reversible and the interference in NE detection at its presence was mainly caused by the competition between these two species. While after prazosin washed out, there was only a current decrease for $Fe(CN)_6^{3-/4-}$ but not for $Ru(NH_3)_6^{3+/2+}$ on T650 microelectrode indicated that prazosin molecules only bind and contaminate the surface of the electrode but didn't change electrode electronic structure. However, the current significantly decreased for both $Ru(NH_3)_6^{3+/2+}$ and $Fe(CN)_6^{3-/4-}$ comparing to original at P55 carbon fiber and diamond miecroelectrode demonstrated that prazosin molecules

were not only physically adsorbed on the electrode, but also changed the electrode electronic density of states. This process was not reversible.

The differences of the influence on the NE detection with the same drug among these three types of microelectrode are mostly caused by their different microstructures. Carbon fiber surface is polar and hydrophilic due to its sp² bonded carbon structure with a π -electron system and also a variety of oxygen functional groups. As a consequence, these properties promote the adsorption of polar molecules by hydrogen bonding, dipole-dipole and ion-dipole interactions ^{52, 53}. As shown in Figure 7.3, T650 carbon fiber possesses a higher I_D/I_G ratio suggesting a more disordered structure, which was supposed to have stronger electroactivity. This may explain why the $E_{1/2}$ value for NE at T650 carbon fiber microelectrode is lower comparing with P55s carbon fiber microelectrodes (Table 7.2). And also because of the disordered structure, the adsorption of drugs to the electrode surface is not that stable, which may be the reason of why T650 carbon fiber microelectrode could recover better from drug application (Figure 7.6c and d). Sp³ bonded carbon microstructure and little π -electron density make diamond more stable and not prone to be adsorbed, especially by catecholamines, e.g. NE^{30, 33, 54}. The $E_{1/2}$ value for NE is around 150 mV more positive for diamond than for carbon fiber due to the more sluggish electrode reaction kinetics, which might be caused by the weak NE adsorption on the diamond surface. However, the $E_{1/2}$ value for each drug is comparable at these three types of microelectrodes (Table 7.2). And our data suggest that drug species we studies here are easier to be adsorbed on diamond comparing with NE and that is maybe why applied drug influence diamond microelectrode more comparing with T650 carbon fiber microelectrode (Figure 7.6c and d).

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Both UK 14,304 and yohimbine have a – NH (or – OH) group within and out of a five member ring which could be oxidized (Table 7.1). So we predicted that these two drugs would have some effects on NE detection and our results verified this. The data shown in Figure 7.7 and Figure 7.8 suggested that the adsorption ability for both UK 14,304 and yohimbine are comparable with NE at the surface of diamond and T650 carbon fiber microelectrodes. So NE could be determined at the presence of these drugs although the oxidation current peak of NE was flattened and reduced. This is not true with P55s carbon fiber microelectrode. The almost non-distinguishable NE current peak at the presence of UK 14,304 and yohimbine indicate the adsorption to the electrode surface for these two drugs are stronger than that for NE. It seems that UK 14,304 and yohimbine could be reversibly adsorbed on the surface of the electrode and occupy the active sites because the oxidation current peak of NE can be reversed after the drug was washed out, although there was still current decreases (Figure 7.8). Data from Ru(NH₃)₆^{3+/2+} and Fe(CN)₆^{3-/4-} are consistent with this conclusion (not shown here).

Cocaine and idazoxan have very stable structures which make them almost non-electroactive, at least in the potential range we employed (Figure 7.4). Although PPADS has a –OH group which could be oxidized, it needs relatively high voltage, where its oxidation peak may have negligible effect on the oxidation peak of NE. In this case, the adsorption to electrode competition between drugs and NE are mild and NE is prone to adsorb first on the electrode surface and undergo the redox reaction at the detection potential area. As expected, idazoxan and PPADS showed little effects on the oxidation current peak of NE on all electrodes no matter with or after their present (Table 7.4). And the fouling effect was much weaker as the consequence of the less efficient binding between drug and microelectrode. Data from $Ru(NH_3)_6^{3+/2+}$ and $Fe(CN)_6^{3-/4-}$ are consistent with this conclusion (not shown here). A little different from idazoxan and PPADS, cocaine activated all electrodes in our experiments although not all of the statistic data mean significantly different (Table 7.4). The reason why cocaine may potentially activate the electrode might be that it could increase the activation sites while binding with the electrode surface or there are high electron density points in cocaine molecule which could make the electron transfer between NE and electrode more efficiently.

To conclude, we have found capsaisin and prazosin have severe effect on the measurement of NE at the surface of both carbon fiber and diamond microelectrode at their presence; UK 14,304 and yohimbine could reduce the response of NE to the electrode, but washing out will reverse this effect; cocaine, idazoxan and PPADS do not influence the detection of NE. These data suggest that, in voltammetric and amporometric experiments, consideration should be make wherever possible a drug is electroactive. Direct effect of a drug on electrode response sensitivity should be determined before measuring NE level. Therefore, at the similar situation, it may be more secure to use the drug which is not electroactive or at least electrochemically inactive with the potential range of NE detection. Calibrations should be performed before and after that drug is applied for the precise determination of NE level.

7.2 Distribution of sympathetic and sensory nerves

7.2.1 Glyoxylic acid fluorescence histochemistry

Glyoxylic acid (GA) is a reagent for the fluorescent histochemical visualization of biogenic monoamines.⁵⁵ GA reacts with indolylethylamines and catecholamines to produce a fluorescence product that can be used for histochemical visualization. NE can be converted into the intensely fluorescent 2-carboxymethyl-dihydroisoquinoline derivative by GA,⁵⁵ as shown in Figure 7.10. Therefore, the distribution of GA-induced fluorescence of neuronal stores of NE was used to assess the distribution of periarterial and perivenous sympathetic nerves.



Figure 7.11 Reaction mechanism for GA and norepinephrine. The circled groups represent the fluorophore in the molecule.

Figure 7.12 shows GA-induced fluorescence images of mesenteric arteries (MA)

and veins (MV), which reveal a network of varicose nerve fibers. The periarterial nerve plexus consists of bundles of several axons arranged in a net-like manner.^{4, 56} For a Sham or normotensive rat, the nerve plexus for MA consists of bundles of axons arranged in network-like distribution with nerve fibers equally likely to pass parallel or perpendicular to the longitudinal axis of the vessel. The perivenous plexus is less dense than in arteries and consists of individual varicose axons largely oriented circumferentially around the vessel. This does not necessarily mean that the density of innervation of MV is less than that of MA. MV is thinner than MA so the number of axons per smooth muscle cell could be similar. This suggestion is supported by the fact that ultrastructural studies have shown that in guinea pigs, the density of neuromuscular junctions is similar for MA and MV.⁵⁷ Similarly, for DOCA-salt rat, the nerve plexus for MA consists of bundles of axons arranged in a mesh-like network with nerve fibers parallel or perpendicular to the longitudinal axis of the vessel. On the other hand, the plexus for MV consists of single axons with more of a circumferential arrangement and few axons are localized along the longitudinal axis of the blood vessel.



Figure 7.12 Glyoxylic acid-induced fluorescence images of catecholamines in the perivascular sympathetic nerves of Sham MA (A), Sham MV (B), DOCA-salt MA (C) and DOCA-salt MV (D). The nerve plexus in arteries has a mesh-like arrangement with fibers oriented along both the longitudinal and circular axes of the blood vessel. The plexus in veins has a circular arrangement with very few fibers oriented longitudinally.

7.2.2 Immunohistochemistry

Glyoxylic acid-induced fluorescence imaging can be used to determine the distribution of sympathetic nerves but not sensory nerves. A different procedure was needed to visualize the sensory nerves arrangement along arteries and veins. This is described below. Tyrosine hydroxylase (TH) is the first enzyme involved in catecholamine (CA) biosynthesis. It catalyses the conversion of L-tyrosine to L-3,4-dihydroxyphenylalanine (L-DOPA). Tyrosine hydroxylase is, therefore, a useful marker of all CA-containing neurons.^{57, 58} An Immunohistochemical imaging method was used that involved bonding an anti-TH antibody with TH. The resulting complex was then reacted with a secondary antibody conjugated with a special fluorescent dye. The TH complex becomes fluorophoric allowing one to spatially image the fluorescence locations by microscopy.

In a similar way, the occurrence of substance P (SP) and calcitonin gene-related peptide (CGRP) immunoreactive varicose fibers were localized by double immunohistochemistry using anti-substance P and anti-CGRP antibody conjugated with different fluorescent dyes, respectively.

Theoretically, because of the high selectivity of antigen-antibody reaction, the distribution of TH, SP and CGRP containing nerve fibers can be localized in the same preparation, respectively, by choosing different fluorescent dyes and excitation wavelengths. In this study, we used three different secondary antibodies with two different fluorescent dyes to localize the distribution of TH-containing nerve fibers (sympathetic nerves) and SP- or CGRP-containing nerve fibers (sensory nerves) around the mesenteric blood vessels of rats. The mechanisms behind these measurements are diagramed in Figure 7.13. We were specifically interested in the arrangement of TH-, SP- and CGRP-containing nerve fibers associated with mesenteric arteries and veins from Sham and DOCA-salt rats.

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Figure 7.13 Schematic of immunohistochemical staining of TH, SP and CGRP. In the sympathetic nerve varicosity, anti-TH antibody (primary antibody) binds to TH, followed by binding of a secondary antibody with a fluorescent dye, which generated fluorophoric complex. In the sensory nerve varicosity, anti-SP antibody binds to SP, followed by binding of a secondary antibody with a fluorescent dye, which generated fluorophoric complex. Also in the sensory nerve varicosity, anti-CGRP antibody binds to CGRP, followed by binding of a secondary antibody with a fluorescent dye, which generated fluorophoric complex. The fluorescence intensity depends on the concentration of fluorescent complex at a particular excitation wavelength.

Examination of whole mount preparations from Sham rats revealed a dense plexus of varicose nerve fibers containing TH-immunoreactivity (TH-ir) was associated with mesenteric arteries (Figure 7.14A and Figure 7.15A) and veins (Figure 7.14D and Figure 7.15 D). Also, a dense plexus of varicose nerve fibers containing CGRP-immunoreactivity (CGRP-ir) was associated with mesenteric arteries (Figure 7.14B and Figure 7.15B) and veins (Figure 7.14E and Figure 7.15E). Overlay of these images reveal that the sensory nerves have a similar net-like distribution and there is significant co-localization of sensory and sympathetic nerves (right column in Figure 7.14 and Figure 7.15).



Figure 7.14 Immunohistochemical localization of TH and CGRP in whole mount preparations of mesenteric artery and vein from a Sham rat. (A) Localization of TH-ir in Sham MA. (B) Localization of CGRP-ir in the same tissue. While there are much higher dense TH-ir nerve fibers, CGRP-ir are less dense. (C) Overlay of (A) and (B). (D) Localization of TH-ir in Sham MV. (E) Localization of CGRP-ir in the same tissue. (F) Overlay of (C) and (D). Scale bars in all images are 50 µm.



Figure 7.15 Immunohistochemical localization of TH and CGRP in whole mount preparations of mesenteric artery and vein from a DOCA-salt rat. (A) Localization of TH-ir in MA. (B) Localization of CGRP-ir in the same tissue. While there are much higher dense TH-ir nerve fibers, CGRP-ir are less dense. (C) Overlay of (A) and (B). (D) Localization of TH-ir in MV. (E) Localization of CGRP-ir in the same tissue. (F) Overlay of (C) and (D). Scale bars in all images are 50 µm.

Our results show that the distribution of the TH-containing nerve fibers (sympathetic nerves) for the artery is different from that for the vein, which is similar to the GA histochemical results. There is no significant difference in the distribution of CGRP-containing nerve fibers (sensory nerves) between arteries and veins except that the density of CGRP in DOCA-salt MV (Figure 7.15E) seems less than that in Sham MV (Figure 7.14E).

Figure 7.16 shows the immunohistochemical localization of TH and SP in whole mount preparations of mesenteric vein from a DOCA rat. There are very weak fluorescent lines shown in Figure 7.16 indicating that rare SP can be detected in DOCA-salt mesenteric vein. In fact, we did not get obvious SP-ir image from Sham mesenteric blood vessels. This is consistent with the literature reports. Galligan et al. published their immunohistochemical research on Sham and DOCA-salt mesenteric blood vessels. They found very little SP-ir in the nerve fibers in arteries or veins in tissues from Sham rats, however, there was clear evidence that the intensity of nerve fiber staining for SP was higher in veins from DOCA-salt rats.⁵⁹



Figure 7.16 Immunohistochemical localization of TH and SP in whole mount preparations of mesenteric vein from a DOCA-salt rat. (A) Localization of TH-ir. (B) Localization of SP-ir in the same tissue. (C) Overlay of (A) and (B). Scale bars in all images are 200 µm.

Figure 7.17 shows the immunohistochemical localization of TH and SP in whole mount preparations of mesenteric artery from a DOCA rat. Although the dense of SP-ir is much lower that that of CGRP-ir, the overlay image clearly shows that the SP-containing varicosities are exactly consistent with those CGRP containing varicosities, which demonstrates SP and CGRP exist in the same nerve fibers (Figure 7.17C).



Figure 7.17 Immunohistochemical localization of SP and CGRP in whole mount preparations of DOCA-salt mesenteric arteries. (A) Localization of SP-ir. (B) Localization of CGRP-ir in the same tissue. While there are numerous CGRP-ir nerve fibers, SP-ir is rare. (C) Overlay of (A) and (B). Note the yellow lines which are combinations of the red lines (SP-ir) in (A) and green lines (CGRP-ir) in (B). Scale bars in all images are 50 µm.

7.3 Vasoconstriction and norepinephrine oxidation current at MA and MV

7.3.1 Determination of norepinephrine

As we mentioned before, one of the specific aims in our group's research is to determine if there is local communication between sensory and sympathetic nerves at mesenteric blood vessels of rats when the connections from both sensory and sympathetic nerves to the CNS were severed. Researches have found that repetitive activation of afferent nerve fibers can cause cross-excitation of neighbors not stimulated directly.⁹⁻¹¹ It was hypothesized that local communication may exist between sensory and sympathetic nerves using the SP or CGRP neurotransmitters released by sensory nerves. Therefore, if release of SP and CGRP is inhibited then the response of mesenteric blood vessels to stimulations may change and this change may be recovered by exogenous SP application. The effects of substance P and CGRP on NE release from sympathetic nerves were assessed using continuous amperometry with a diamond microelectrode.

Norepinephrine (NE) functions as both a hormone and neurotransmitter. It is secreted by chromaffin cells produced in the adrenal medulla and at the sympathetic nerve endings. It is a vasoconstrictor and increases in heart rate, blood pressure, and the sugar level in the blood.¹ NE levels has been measured in tissue and biological fluids because of its involvement in the stress related-diseases, such as hypertension, depression and cardiovascular disease.⁶⁰⁻⁶² Previous measurements of NE in plasma have been performed using high performance liquid chromatography (HPLC)^{63, 64} or radioactive labeling methods.^{65, 66} These overflow techniques provide little information about real-time local release of NE from sympathetic nerves. NE can be oxidized via a 2H⁺/2e

redox reaction, as shown below.



In other words, norepinephrine is electrochemically active and can be detected electrochemically. To date, electrochemical measurements using fast scan cyclic voltammetry and continuous amperometry with carbon fiber microelectrodes have been widely used in *vitro* to study the release and clearance mechanisms for NE in the sympathetic nervous system because of the high spatial and temporal resolution this technique provides.⁶⁷⁻⁷⁰ Previous work in our group demonstrated that boron-doped diamond microelectrodes could be used for sensitive, reproducible and stable electrochemical determination of NE.⁷¹⁻⁷⁶ In this work, all measurements of NE were performed using 76 µm Pt wire microelectrodes coated with boron-doped diamond.

7.3.2 Sensory nerve denervation by capsaicin

A. Hydrodynamic and calibration curves for NE determination

To determine an optimal detection potential for the determination of NE, hydrodynamic *i-E* curves for NE, substance P (SP) and capsaicin at a BDD microelectrode were first recorded, as shown in Figure 7.18. The curves were generated by measuring the current of a BDD microelectrode in 0.1 mmol/L analyte (NE, SP or capsaicin) in Krebs' buffer with a 50 mV potential step starting from 0 V vs. Ag/AgCl.

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Figure 7.18 Hydrodynamic *i-E* curves for NE, SP and capsaicin at a BDD microelectrode. The measurements were performed in 0.1 mmol/L NE, SP or capsaicin in Krebs' buffer with a 50 mV potential step starting from 0 V vs. Ag/AgCl, respectively.

Figure 7.18 shows that SP is not electroactive and has no influence on the determination of NE. Capsaicin, on the other hand, seriously affect the determination of NE as we discussed in Section 7.1.2. Capsaicin is an agonist of vanilloid receptors localized at sensory (SP/CGRP-containing) nerve endings and activation of these receptors leads to SP and CGRP release.⁷⁷ Perfusing capsaicin for a long period (usually 30 min) will deplete the finite stores of SP and CGRP in sensory nerves, a chemical denervation. After that, capsaicin can be washed out.

To quantitatively determine NE, all BDD microelectrode should be calibrated before used. A representative calibration curve is shown in Figure 7.19.



Figure 7.19 Calibration curve for NE oxidation at a BDD microelectrode. The oxidation currents were measured amperometrically by perfusing Krebs' buffer with different NE concentrations.

B. vasoconstriction and NE overflow from Sham and DOCA-salt mesenteric blood vessels

We studied the relationship between sensory and sympathetic nerves of mesenteric blood vessels following the protocol given in Section 2.8.2E. 14 Sham rats and 15 DOCA-salt rats were examined. Figure 7.20 shows typical experimental results recorded from a Sham mesenteric artery. The results demonstrate that the blood vessel constriction (top curves) did not significantly change after capsaicin treatment and wash

out (Figure 7.20, top panel in column B). The artery constricted reproducibly by ca. 20%. Substance P did not influence sympathetic nerve activity either (Figure 7.20, top panel in column C). This was confirmed by the current traces as the oxidation current did not significantly change in all cases.



Figure 7.20 Typical vasoconstriction and NE overflow results recorded for a Sham mesenteric artery. The top panels show the blood vessel constriction and the bottom panels show the recorded NE oxidation current after electrical stimulation. The dash lines indicate when the electrical stimulus was applied. Column A shows the diameter and current traces for the blood vessel control. Column B shows the diameter and current traces after 1 μ mol/L capsaicin was applied (30 min) and washed out (perfused with Krebs' solution for 1 h). Column C shows the diameter and current traces after SP wash out. The time axis and baseline for each current trace were adjusted for comparison.

Similar results were obtained on DOCA-salt mesenteric artery, as shown in Figure 7.21. The only difference is that we observed that capsaicin obviously dilated the blood

vessel (Figure 7.21, top panel in column B).



Figure 7.21 Typical results recorded from a DOCA mesenteric artery. The top panels show the blood vessel constriction and the bottom panels show the recorded NE oxidation current after electrical stimulation. The dash lines indicate when the electrical stimulus was applied. Column A shows the diameter and current traces for control. Column B shows the diameter and current traces after 1 μ mol/L capsaicin was applied (30 min) and washed out (perfused with Krebs' solution for 1 hour). Column C shows the diameter and current traces during perfusion of 0.4 μ mol/L SP. Column D shows the diameter and current traces after SP wash out. The time axis and baseline for each current trace were adjusted for comparison.

Figure 7.22 and 7.23 show results for Sham and DOCA mesenteric veins. Different from the results for the arteries, the diameters of both Sham and DOCA veins significantly increased after capsaicin was applied. On the other hand, when Substance P was perfused, both tissues constricted strongly. The effects of capsaicin and substance P were not obviously evident on the oxidation current of NE for these two tissues.



Figure 7.22 Typical results for a Sham mesenteric vein. The top panels show the blood vessel constriction and the bottom panels show the recorded NE oxidation current after electrical stimulation. The dash lines indicate when the electrical stimulus was applied. Column A shows the diameter and current traces for the control. Column B shows the case after 1 μ mol/L capsaicin was applied and washed out. Column C shows the case when 0.4 μ mol/L Substance P was perfused. Column D shows the cases after Substance P was washed out. The time axis and baseline current for each trace were adjusted for comparison.



Figure 7.23 Typical results for a DOCA-salt mesenteric vein. The top panels show the blood vessel diameter and the bottom panels show the recorded NE oxidation current after electrical stimulation. The dash lines indicate when the electrical stimulus was applied. Column A shows the diameter and current traces for the control. Column B shows the case after 1 μ mol/L capsaicin was applied and washed out. Column C shows the case when 0.4 μ mol/L Substance P was perfused. Column D shows the cases after substance P was washed out. The time axis and baseline current for each trace were adjusted for comparison.

C. Statistical analysis of the results

The statistical analysis of the results for mesenteric arteries from 10 Sham rats and 11 DOCA-salt rats are shown in Figure 7.24. These results are the ratio of the constriction and oxidation current after capsaicin or substance P were applied to control values (no any drugs were applied). Our results show that after denervation of the sensory nerves, the exogenous Substance P does not influence sympathetic nerve activity. There is no difference in the vasoconstriction or oxidation current for NE after the application of capsaicin, and with or without Substance P perfusion for both Sham and DOCA-salt mesenteric arteries, as shown in Figure 7.24. Figure 7.24A also shows that the NE oxidation current for Sham artery is reduced after capsaicin and Substance P were applied. The reason for this is not clear yet.

The statistic results for mesenteric veins from 4 Sham rats and 4 DOCA-salt rats are shown in Figure 7.25. Similar to mesenteric artery, after capsaicin or substance P was applied, the constrictions and oxidation currents of NE for mesenteric veins from both Sham and DOCA-salt rats did not change too much. But different from mesenteric artery, when substance P was applied, the constriction and NE oxidation current for mesenteric veins from both Sham and DOCA-salt rats strongly decreased. No difference for this change was found between Sham rats and DOCA-salt rats.



Figure 7.24 Percent change in the NE oxidation current (left) and the blood vessel constriction (right) for mesenteric arteries from 10 Sham rats and 11 DOCA-salt rats.



Figure 7.25 Percent change in the NE oxidation current (left) and the blood vessel constriction (right) for mesenteric veins from 4 Sham rats and 4 DOCA-salt rats.

7.3.3 Discussion

In DOCA-salt hypertensive rats, venomotor tone is increased.⁷⁸ Venomotor tone is a function of the structural properties of veins and also of constrictor input to venous smooth muscle cells.⁷⁹ The primary determinant of venomotor tone is sympathetic nerve activity and it has been shown that sympathetic input to veins is elevated in DOCA-salt⁷⁸ and spontaneously hypertensive rats (SHRs).⁸⁰ It is known that in hypertensive rats, CGRP released from sensory nerves acts as a vasodilator to attenuate elevated blood pressure.⁸¹ The function and disposition of perivascular sensory nerves can be altered in hypertension and these changes might contribute to the development of maintenance of elevated blood pressure.⁸² CGRP and Substance P are two neurotransmitters released from sensory nerves. In this study, we focused on Substance P but not CGRP. Our results show that Substance P affects sympathetic nerve activity at mesenteric veins but not arteries (both constriction and oxidation current decreased when Substance P exogenously administrated after senserory nerves were denervated by capsaicin, Figure 7.25). Substance P is a vasodilator peptide that acts on NK-1 receptors localized to endothelial cells to cause release of nitric oxide (NO) and other vasodilator substances.⁶ There is an upregulation of SP-ir in perivascular nerves in tissues from DOCA-salt rats.⁵⁹ Galligan et al. investigated the distribution of SP in sensory nerve fibers around mesenteric blood vessels and the venoconstrictor effects of SP. They concluded that SP acts to constrict mesenteric veins via an action at NK-3 receptors.⁵⁹ This conclusion is similar to that reached by others about venoconstrictor NK-3 receptors in rat mesenteric veins.⁸³ The results we obtained on mesenteric veins clearly show that substance P affects the sympathetic nerve activity and this suggests that it's possible that there is a local communication between sensory and sympathetic nerves. We failed to observe any change of sympathetic nerve activity on mesenteric artery. However, this should not serve as a conclusion that there is no communication between sensory nerves and sympathetic nerves because previous researchers demonstrated that Substance P only contracts veins but not arteries.⁵⁹ Positive results may be observed by exogenous administration of CGRP on mesenteric arteries because CGRP acts as a strong vosadilator on mesenteric arteries. This need to be confirmed in the future research.

7.4 Reference

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Chapter 8

Conclusions

Natural diamond is an electrical insulator with a band-gap of ~5.5 eV and a resistivity greater than $10^{12} \ \Omega$ -cm.¹ However, synthetic diamond can be made electrically conducting via doping with a dopant, such as boron, nitrogen and phosphorous.

The most extensively employed CVD diamond in electrochemistry is the *p*type, boron-doped diamond. The resistivity of highly boron-doped diamond thin film can be as low as ~0.005 Ω -cm. Both high-quality microcrystalline and nanocrystalline boron-doped diamond thin films can be prepared by CVD. Born-doped diamond thin films show low capacitive background current, a wide potential window in aqueous media of 3 - 4V, chemical inertness, extreme hardness and robustness, and dimensional stability at high potentials and current densities.

The electrical and electrochemical properties of boron-doped diamond thinfilms are influenced by many factors, such as the growth conditions, grain size, doping level, impurities (e.g., grain defects, sp^2 carbon and adsorbed hydrogen), and surface chemistry. The growth conditions are the primary determinant of the surface morphology, although both microcrystalline and nanocrystalline diamond thin-films can be deposited in similar hydrogen-rich gas mixtures. Nanocrystalline diamond thin-film can be deposited from a hydrogen-rich or an *Ar*-rich source mixture (Chapter 6). We demonstrated that the two types of nanocrystalline BDD thin films have very electrochemical properties, although their grain size and surface morphology are very different as revealed by SEM images and Raman spectra.

According to the grain size, microcrystalline and nanocrystalline BDD thinfilms can be classified. Microcrystalline BDD thin-film has a different Raman spectrum than the nanocrystalline film grown from an *Ar*-rich gas but their electrochemical properties are similar. Using CP-AFM and SECM, we found that the electrical conductivity and electrochemical activity of both microcrystalline and nanocrystalline BDD thin-films are variable across the surface. Microcrystalline BDD thin-film possesses lower fraction of active regions but more active individual sites than do the nanocrystalline films. On the other hand, nanocrystalline BDD thin-film shows greater fraction of electrically-active regions.

The doping level influences the surface morphology of BDD thin-film. Increasing boron-doping level increases the surface roughness of the film. This was observed for both microcrystalline and nanocrystalline films. More importantly, the doping level influences the electrical and electrochemical properties of BDD thin film. CP-AFM and SECM measurements illustrated that both the fraction of electrically conductive area and the fraction of electrochemically active regions increase as the doping level increases for both microcrystalline and nanocrystalline films.

The impurities in BDD thin-film have various effects on the physical and chemical properties. The Raman spectrum for the nanocrystalline BDD thin-film is very different from that for microcrystalline BDD thin film. One reason for this is that the content of sp² carbon in nanocrystalline film is much higher than that in microcrystalline film. CP-AFM images showed that the electrically conducting sites are associated with the grain boundaries of microcrystalline BDD thin film. Comparing the electrochemical reaction of dopamine at the MSU and NRL BDD thin-

film electrodes, it was found that sp² carbon impurity does not dominate the electrochemical activity. Other important impurities in BDD thin-film are hydrogen and hydrocarbon species. Hydrogen can be physisorbed and chemisorbed on the surface or in the bulk of the thin-film. Heating treatment at 400 °C in Ar can desorb the physisorbed hydrogen and hydrocarbon species making the thin-film surface more hydrophilic (contact angle decreases). The desorption of physisorbed hydrogen and hydrocarbon species also influence the electrochemical properties of BDD thin-film electrodes with a low doping level but this effect can be negligible on BDD thin-film electrodes with higher doping levels (> 5 ppm). We did not investigate how the absorbed hydrogen influence the electrical conductivity of BDD film with CP-AFM because we do not have an oxygen-free, isolated system to perform the measurement. Therefore, to further study what role hydrogen play for the electrical conductivity of boron-doped diamond can be one of the future work.

The surface termination had a significant influence on the properties of CVD diamond. For example, the fastest electron-transfer kinetics for $Fe(CN)_6^{3.44}$ has been recorded at hydrogen-terminated BDD electrode but very sluggish reaction has been recorded at oxygen-terminated BDD electrode. Electrochemical measurements show that O-terminated BDD electrode has a little larger background current that H-terminated BDD electrode. The reason for this might be the O-terminated surface is more hydrophilic and this may increase the dielectric constant of H₂O at the surface. CP-AFM and SECM studies show that both the fraction of electrically-active regions and the fraction of electrochemically-active regions are greater for H-terminated than for O-terminated BDD films.

In general, the present work answered the following questions:

1. What is the spatial uniformity of the electrical conductivity of boron-doped microcrystalline and nanocrystalline diamond thin films? The electrical properties of boron-doped microcrystalline and nanocrystalline diamond thin films are not uniform over the surface.

2. What factors contribute to the electrical conductivity (e.g., boron-doping level, surface hydrogen, surface oxygen and nitrogen compensators)? Factors such as boron doping level, surface hydrogen, surface oxygen and sp² carbon contribute to the electrical conductivity but boron-doping level is the determinant.

3. How does the uniformity of the electrical properties correlate with the spatial uniformity of the electrochemical reaction rates across the electrode surface for various outer-sphere redox systems? The electrochemical properties of boron-doped microcrystalline and nanocrystalline diamond thin films are also not uniform over the surface. Because the spatial resolution of the SECM used in the present work (in micrometer level) does not match the spatial resolution of CP-AFM (in nanometer level), we can not associate the electrical conductivity with the electrochemical activity of BDD films. SECM with a resolution in nanometer level is available now. Therefore, using SECM with a higher spatial resolution and CP-AFM to investigate the spatial relationship between the electrical conductivity and electrochemical activity of boron-doped diamond may be another future work.

