

# BORON DOPED DIAMOND ELECTRODES FOR THE DOPAMINE IDENTIFICATION BY ANODIC STRIPPING VOLTAMMETRY

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## 1. Introduction

Carbon based electrodes are widely used for in vivo and in vitro electrochemical studies. Similarly, glassy carbon (GC) is the preferred material for many biochemical applications, such as electrochemical detection in chromatography. More recently, nanocrystalline [1,2] diamond boron doped diamond (BDD) has been utilized for biosensing. Dopamine (DA) is an important neurotransmitter in central nervous system. A loss of DA containing neurons may result in serious disease such as Parkinson's disease. The electrochemical DA detection with carbon-based electrodes has received intense attention partially due to the possible future development of practical in vivo sensors. Major problem of electrochemical DA detection is the overlapping of oxidation waves between DA and interfering compounds (e.g. AA) at the above bare electrodes. Recently, some nano-materials, e.g. carbon nanotubes [3], gold nanoparticles [4], and polymer thin film [3] modified GC electrodes were used to carry out the selective detection of DA in the presence of AA. Complicated preparation methods and long-term stability cause still problems. Fujishima's group researched the electrochemical DA detection at BDD electrodes.

Applications and construction of various biosensors for the direct detection of biomolecules using of BDD electrodes have been summarized [5]. As we know, electrochemical reactions precede at the interface between electrolyte solutions and electrode surfaces, so the surface structures and properties of BDD electrodes are important for electrochemical detection.

## 2. Experiment

Polycrystalline BDD films 200-280 nm thick (Fig. 1) were produced in the double bias enhanced HF CVD reactor with sheet resistivity  $\sim 100 \Omega/\text{sq}$ . As a substrate, highly conductive (0.008-0.024  $\Omega\text{cm}$ ) N (100) type silicon substrate was used with  $\sim 200\text{nm}$  wet  $\text{SiO}_2$  oxide. Throughout the deposition, gas flows in reaction chamber were controlled to be 1 %  $\text{CH}_4$  in  $\text{H}_2$  and trimethylboron (TMB) in the range of 0-200 sccm (corresponding to 0-13 333 ppm of B/C), Tab 1. The total pressure in the reactor was 3 000 Pa and temperature was set to around 700 °C. Deposition process was divided into two steps: the first step was 30 min seeding with nano-powder of diamond (Sigma Aldrich, crystals  $< 10 \text{ nm}$ ) diluted in water in ultrasonic bath, the second step was growth of NCD thin layer for 2 hour. The areas which act as working electrodes were defined to be about 3x3 mm by isolation paste in 10x20 mm area. All stock solutions were prepared from analytical grade chemicals in 18 M $\Omega\text{cm}$  deionised demonized water. A three-electrode arrangement was used in all

experiments. As a reference, Ag/AgCl (0.3 M KCl) electrode and as a counter electrode, a platinum plate 10x10 mm<sup>2</sup> were used. In all experiments we have used McIlvaine buffer composed of Na<sub>2</sub>HPO<sub>4</sub>, citric acid and deionized of water with pH = 5. Before each measurement the electrode was cleaned by 30 cycles of CV (from E<sub>START</sub> = -1.5 V to E<sub>STOP</sub> = 1.5 V, scan rate was 100 mVs<sup>-1</sup>) in pure McIlvaine solution (MCII) without presence DA. Voltametric experiments were performed with an electrochemical potentiostat/galvanostat PGSTAT128N (Metrohm Autolab B.V.) controlled by a PC.

Tab. 1. Composition of process gas.

Sample	CH <sub>4</sub>	H <sub>2</sub>	TMB	B/C
1	3	290	10	667
2	3	275	25	1 667
3	3	270	30	2 000
4	3	260	40	2 667
5	3	250	50	3 333
6	3	200	100	6 667
7	3	150	150	10 000
8	3	100	200	13 333

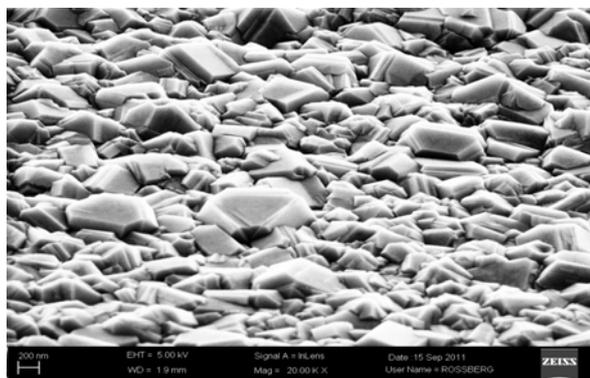


Fig.1: SEM image of BDD film

### 3. Results and discussion

Fig. 2 shows typical cyclic voltammograms for 0.1 mM DA in MCII after 10 cycles of electrode without TMB. The oxidation peak for DA was found at  $460 \pm 2$  mV (n=10), the reduction peak at  $85 \pm 0.18$  mV (n=10). The tendencies to increase sweep rate to 100, 400 and 900 mV (Fig.3) predict to use NCD electrode for high-speed DA detection. The anodic peak current increased linearity  $R^2 = 0.996$  with the square root of the potential sweep rate for DA. The current density (Fig. 4) and FWHM (Fig. 5) of all types of electrodes with different B/C ratio from 667 to 13 000 ppm clearly show a fact that only highly doped BDD with more than 6 000 ppm gives better results.

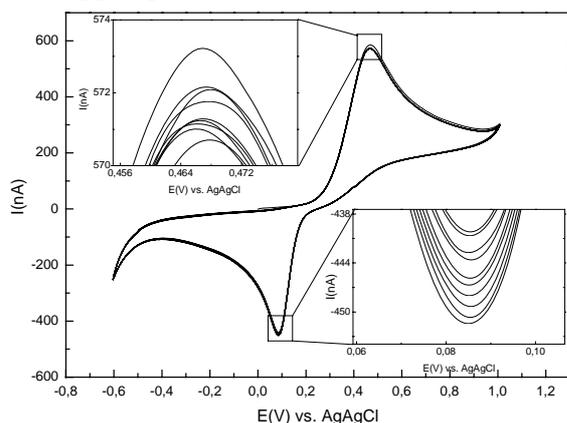


Fig.2: Cyclic voltammograms for 667 ppm B/C, 0.1 mM DA in MCII, pH = 5 after 10 cycles, sweep rate 100 mVs<sup>-1</sup>.

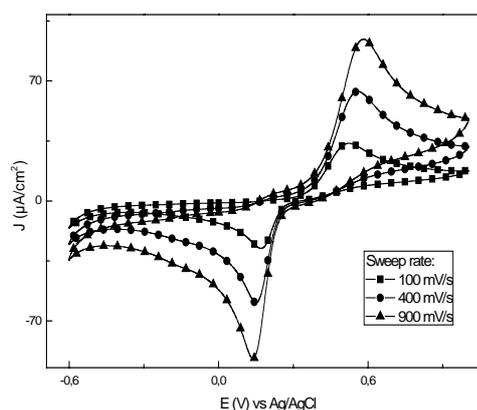


Fig.3: Cyclic voltammograms for 667 ppm B/C, 0.1 mM DA in MCII, pH = 5, 10 cycles, sweep rates: 100, 400 and 900 mVs<sup>-1</sup>

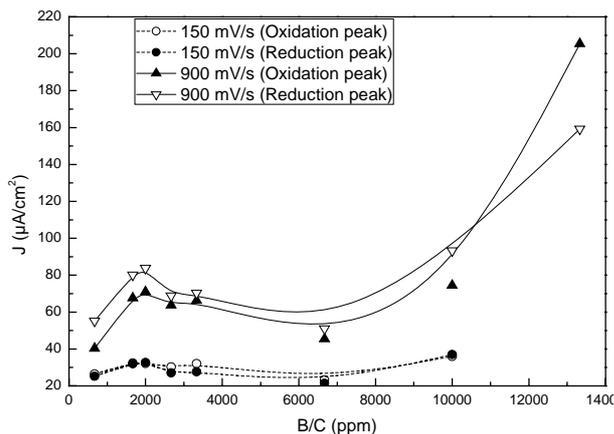


Fig.4: Current density of electrodes from CV measurements with presence of 0.1 mM DA in MCII, for 150 (dashed line) and 900 mV (full line) sweep rates as a function of B/C ratio.

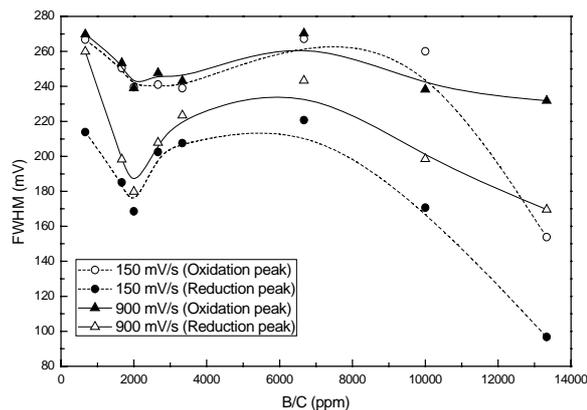


Fig.5: FWHM of electrodes from CV measurements with presence of 0.1 mM DA in MCII, for 150 (dashed line) and 900 mV (full line) sweep rates as a function of B/C ratio.

All characteristic parameters of BDD electrodes were summarized in Tab. 2. Detection limits LOD for 10 000 ppm B/C ratio with highest sensitivity of 1.04 and 0.9  $\mu\text{A}\cdot\text{M}\cdot\text{cm}^{-2}$  DA were 6.02 and 7.66  $\mu\text{M}$  calculated from calibration curves of oxidation peak (Fig 6) and reduction peak (Fig. 7). All electrodes were measured in extremely wide range of dopamine (1-300  $\mu\text{M}$ ). High stability and linear response of hydrogenated BDD electrodes was observed for 6 000 and 10 000 ppm oxidation peaks.

Possible explanation of the detection for DA is that the interaction between the ammonium groups of DA is relatively strong with hydrogenated BDD surface, which acquires surface dipoles as a result of introducing C-O functional groups. High level of BDD doping (10 000 ppm) from Raman spectra of B concentration of  $8.32 \times 10^{20} \text{ cm}^{-3}$ , was calculated. Valence band edge at hydrogen terminated diamond electrode lies at a greater energy than the aqueous  $\text{H}^+/\text{H}_2$  couple, this would result in hydrogen terminated diamond always being in accumulation when in an aqueous electrolyte. Thus any applied potential would be dropped across the Helmholtz layer and reversible electrochemical behavior observed for simple redox couple. Indeed an accumulation of holes at hydrogen terminated diamond surfaces exposed to the atmosphere has been used to explain surface conductivity of the material [6].

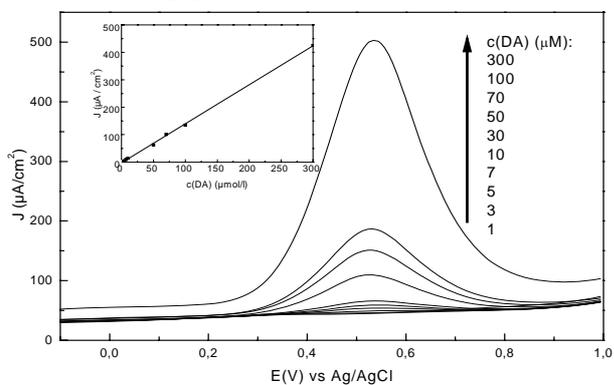


Fig.6: Current density of oxidation peak for 10 000 ppm B/C ratio BDD and calibration curve from SWASV measurements with presence of 1–300  $\mu\text{M}$  DA.

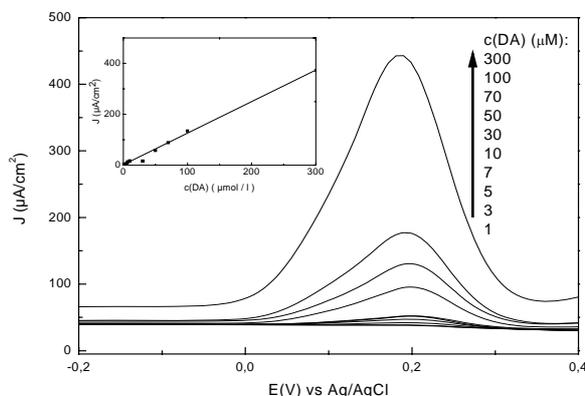


Fig.7: Current density of reduction peak for 10 000 ppm B/C ratio BDD and calibration curve from SWASV measurements with presence of 1–300  $\mu\text{M}$  DA.

Tab. 2. *SW ASV results for reduction of DA in MCII*

B/C[ppm]	Oxidation peak			Reduction peak		
	Sensitivity ( $\mu\text{A.M.cm}^{-2}$ )	Linearity $R^2$	LOD ( $\mu\text{M}$ )	Sensitivity ( $\mu\text{A.M.cm}^{-2}$ )	Linearity $R^2$	LOD ( $\mu\text{M}$ )
2 000	1.04	0.9985	18.97	0.90	0.9982	15.44
6 667	0.75	0.9926	4.10	0.83	0.8856	4.24
10 000	1.42	0.9921	6.02	1.88	0.9953	7.66

#### 4. Conclusions

We have compared different measurements in presence of biological molecules (DA) with various BDD electrodes. These electrodes exhibited very high sensitivity, long-term stability and high reproducibility. A very good performance (LOD = 6.02,  $R^2=0.9921$ ) of the BDD surface has been demonstrated only for very high 10 000 ppm B/C ratio (B doping levels  $n = 3.6 \times 10^{21} \text{ cm}^{-3}$ ) for surface sensitive reactions in complex biological matrices.

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