ELECTROCHEMICAL CHARACTERIZATION OF BILAYER DIAMOND ELECTRODES

RENČIUKOVÁ Veronika[1], MORTET Vincent[1,2]

[1]*Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic, EU,*
renciukova@fzu.cz

[2]*Czech Technical University in Prague, Faculty of Biomedical Engineering, Kladno, Czech Republic, EU*

Abstract

In this work, we present fabrication and electrochemical characterization of bilayer doped diamond electrodes. The bilayers with different doping concentration have been fabricated by plasma enhanced chemical vapor deposition in two steps: namely an inner thick layer of highly boron doped diamond ([B] > $2{\cdot}10^{20}$ B atoms per cm^{-3}) and an outer thin layer with a lower boron concentration. All samples were grown on electrically conductive silicon substrate using an ASTeX 5010 deposition system. Effect of the deposition time, i.e. the thickness and doping concentration of outer thin diamond layer on electrochemical properties of the diamond electrodes have been studied by cyclic voltammetry and impedance spectroscopy. This study is motivated by the objective to produce diamond electrode with both wide potential window and high electrical conductivity using a bilayer structure.

Keywords: Bilayer diamond electrode, potential window, cyclic voltammetry, impedance spectroscopy

1. INTRODUCTION

With a wide potential window in aqueous solutions, low background current and high chemical stability, electrically conductive diamond is one optimal material choice as working electrode for electrochemical applications [1]. As a wide band gap semiconductor, conductivity of diamond can be controlled through incorporation of electrically active impurities, usually using boron atom as acceptor atoms. For boron concentration above c.a. $2{\cdot}10^{20}$ atoms per cm^{-3}, that optimally corresponds to a B/C ratio of c.a. 2000 ppm B/C in the gas phase during diamond layer synthesis, the conductivity of diamond switch from semiconducting in the freeze out regime with resistivity above 10 Ω·cm to metallic type conductivity and resistivity of 1 to 10 mΩ·cm and hence faster electron transfer [2]. However, the potential window of diamond electrodes decreases with increasing boron concentration [3]. It is also known that the sp^2-bonded carbon impurities decrease the potential window on the side of oxygen evolution reaction [4]. Pietzka et al. [5] already presented the idea of electrode with a thin low-doped layer on a highly boron-doped diamond layer. Using this approach, the bilayer diamond electrode had wider potential window than the single layer electrode with high boron doping. To characterize electrodes, they used electrochemical impedance spectroscopy and cyclic voltammetry. We extended this idea by showing a variation of electrochemical properties of bilayer diamond electrodes with thickness and boron concentration of outer diamond layer.

2. EXPERIMENTAL

2.1. Fabrication of diamond electrodes

Diamond films were grown on conductive silicon substrates (1 cm^2) in a microwave plasma enhanced chemical vapor deposition apparatus (AX5010 Seki ASTeX, San Jose, CA, USA). Prior to the deposition of diamond layers, substrates were cleaned in acetone, isopropyl alcohol and hot water for 10 min in each one of them and then seeded with a nanodiamond dispersion (4 to 6 nm). To produce bilayer diamond electrodes deposition took place in two steps. To produce the inner layer in the first step a set of seven samples was deposited under the following conditions: pressure of 50 mbar, MW power of 1150 W, gas flow rate of 500 sccm, 0.5% of CH_4 in H_2, B/C ratio of 2000 ppm and deposition time of 300 min. To produce the outer thin layer of diamond, six samples from the first step were deposited under the same conditions except the deposition time and B/C ratio in the gas phase (**Table 1**). Prior to the second deposition, the electrodes were treated by H_2 plasma for 15 min. The scheme of the fabricated bilayer diamond electrode is presented in **Figure 1**.

Table 1 Parameters of the growth of diamond films

	Inner layer	Outer layer					
B/C (ppm)	2000	0	0	0	200	200	200
Deposition time (min)	300	6	9	12	6	9	12

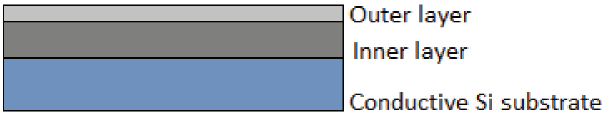

Figure 1 Scheme of the fabricated bilayer diamond electrodes

2.2. Electrochemical measurements

Electrochemical measurements were performed using a three-electrode setup. A platinum mesh was used as the counter electrode, an Ag/AgCl (sat. KCl) electrode was used as the reference electrode and as-grown diamond films were used as the working electrode. The geometric area of exposed working electrodes was 0.5024 cm^2. The electrodes were connected to a Gamry Reference 600+ potentiostat controlled by the Gamry Framework software (Gamry Instruments, PA, USA). All the electrochemical measurements were carried out in 0.5 M H_2SO_4 deaerated by nitrogen bubbling. Electrochemical impedance spectroscopy (EIS) was used to determine the capacitance of the double layer. Impedance data were recorded at the open circuit potential over the frequency range of 10^5 to 10^{-2} Hz. The amplitude of the applied potential signal was 10 mV. Cyclic voltammetry (CV) was used to measure the potential window of the diamond electrodes, and therefore followed the impedance measurements. The CV measurements were recorded at a scan rate of 100 $mV \cdot s^{-1}$ between −1.75 V and 2.75 V vs reference electrode for 15 cycles.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry

The cyclic voltammograms of the diamond electrodes in 0.5 M H_2SO_4 are shown in **Figure 2**. The values of the current were normalized to the geometric area of the diamond electrodes. In general, the width of the potential window increased with the thickness of the outer layer when compared with the single layer electrode (2000ppm-300’). On the contrary, the potential window decreased with the boron concentration of the outer layer. This trend was the opposite of that previously reported in the literature [3].

The general trends described above does not seem clear because of higher current density of hydrogen evolution reaction of the 2000ppm/0ppm-6’ electrode than of the 2000ppm-300’ electrode at −1.0 V. However, the onset of the hydrogen evolution started earlier in the case of 2000ppm-300’ than 2000ppm/0ppm-6’ electrode. The overall situation on the side of oxygen evolution is similar to the side of the hydrogen evolution. The onset of the oxygen evolution of 2000ppm-300’, 2000ppm/0ppm-6’ and 2000ppm/200ppm-6’ electrodes is shifted at least 300 mV in negative direction to c.a. 1.75 V (**Figure 2**, inset). The anodic peak around 2.1 V is attributed to the sp^2 carbon. In the case of 2000ppm-300’, 2000ppm/0ppm-6’, 2000/0ppm-9’ and 2000ppm/200ppm-6’ the sp^2 peak was mildly reduced in the voltammograms after 15 cycles. In the case of the other electrodes the sp^2 peak was strongly reduced.

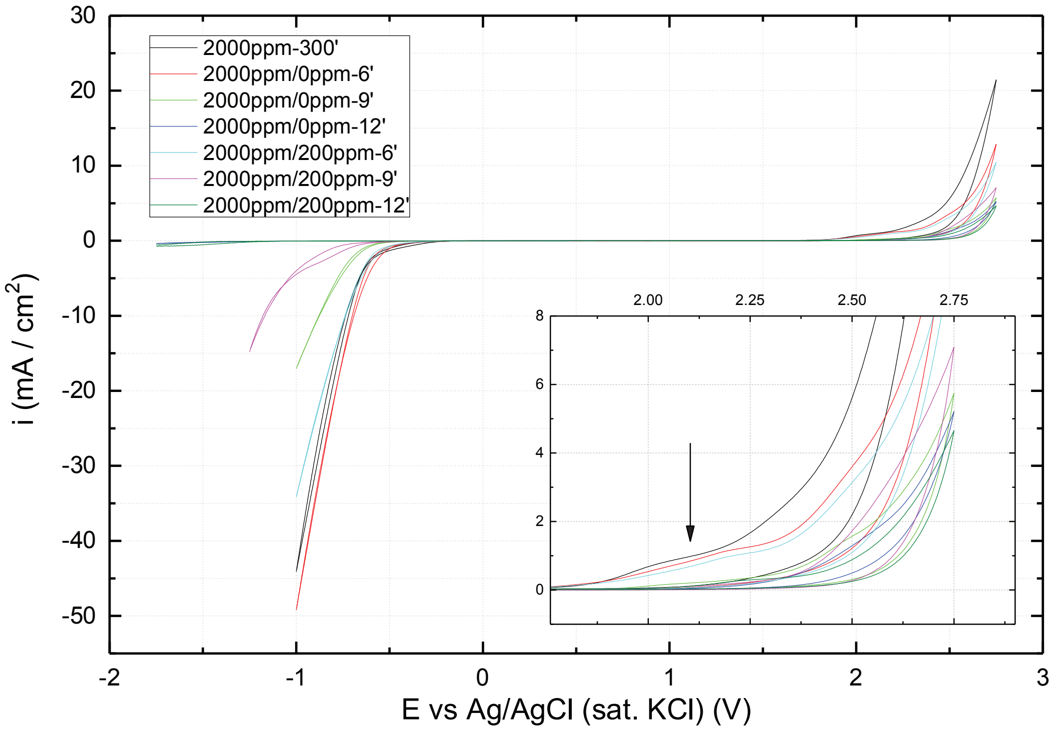

Figure 2 Cyclic voltammogram of diamond electrodes measured in 0.5 M H_2SO_4, 15th cycle. The scan rate was 100 mV·s^{-1}. The inset shows the variation of anodic current peak with thickness and doping concentration of the outer diamond layer.

3.2. Electrochemical impedance spectroscopy

Experimental impedance data of the diamond electrodes are shown in **Figure 4**. Data are in the form of Bode plot, i.e. the dependency of the modulus of impedance and phase shift on the frequency. The phase shift of 6', 9' electrodes and 2000ppm-300' electrode reached almost the maximum of −90°, i.e. of an ideal capacitor. The impedance data were fitted by the models of an equivalent circuit (EC) shown in **Figure 3** and the results are reported in **Table 2**. The impedance spectra of 12' electrodes were complicated by the formation of the second time constant in the low frequencies of the spectra. This second time constant will be the object of the future characterization of the bilayer diamond electrodes, and therefore it was not fitted by models of equivalent circuit.

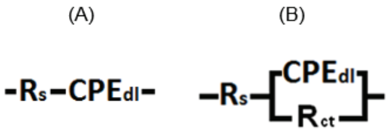

Figure 3 Models of equivalent circuit (EC); R_s, series resistance, *CPE*, constant phase element, R_{ct} charge transfer resistance

The constant phase element, *CPE*, is more flexible for the approximation of the dispersive impedance data than the "ideal" capacitance. Impedance of the *CPE* element is expressed as:

$$Z_{CPE} = Q^{-1}(j\omega)^{-n} \tag{1}$$

where Q is *CPE* coefficient and n is *CPE* exponent with $0 < n < 1$. The exponent n is a measure of the capacitance dispersion. The coefficient Q has dimension of capacitance when $n = 1$, and resistance when

n = 0 and the Warburg impedance, W, when n = 0.5, respectively. The charge transfer resistance, R_{ct}, was in the range of MΩ·cm^2 for 2000ppm/200ppm-9' electrode. The dispersion exponent n differed slightly from the ideal case (n = 1). This is often attributed to the roughness of the film surface. The value of the non-ideal capacitance was in the range of μF·s^{n-1}·cm^{-2}, which corresponds to the expected value of the capacitance of the diamond, i.e. 10 μF.cm^{-2} [6]. The 2000ppm/200ppm-6' electrode showed the lowest value of the capacitance of the double layer.

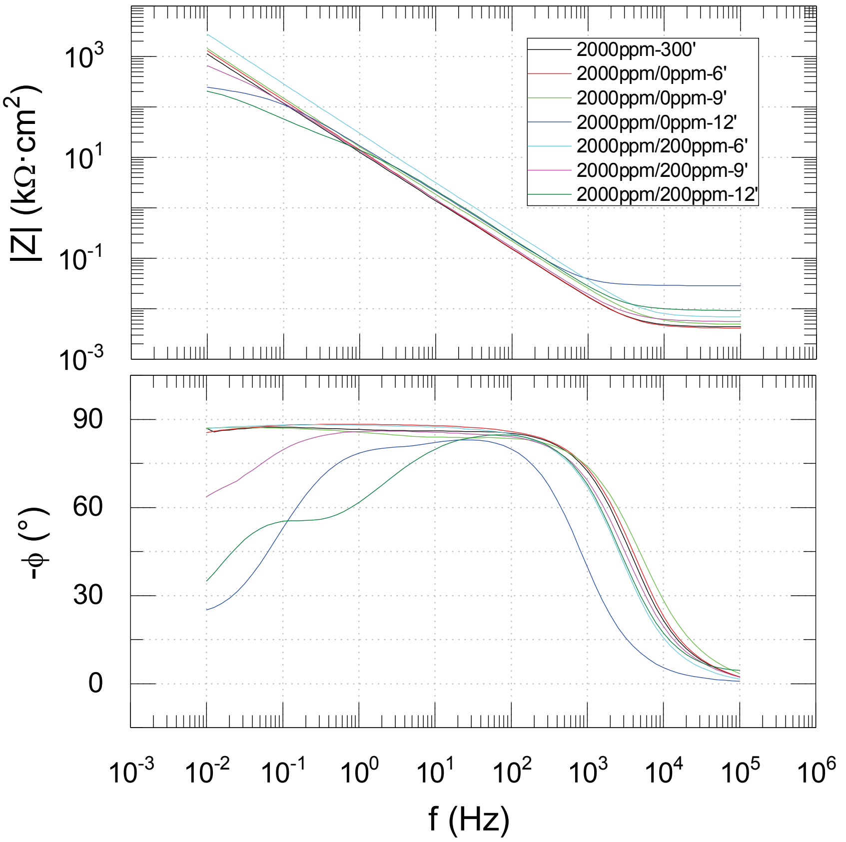

Figure 4 Bode plot of diamond electrodes measured in 0.5 M H_2SO_4

Table 2 Fitting parameters of the impedance data

	EC	R_s / (Ω·cm^2)	Q_{dl} / (μF·s^{n-1}·cm^{-2})	n_{dl} / (-)	R_{ct} / (MΩ·cm^2)
2000ppm-300'	A	4.40	13.3	0.96	
2000ppm/0ppm-6'		4.19	11.7	0.98	
2000ppm/0ppm-6'		4.97	10.4	0.95	
2000ppm/200ppm-6'		6.86	5.46	0.98	
2000ppm/200ppm-9'	B	5.61	13.3	0.95	1.35

4. CONCLUSION

To increase the width of potential window, the bilayer diamond electrodes has been fabricated in two deposition steps. The electrodes were characterized using cyclic voltammetry and electrochemical impedance spectroscopy. The width of the potential window depends both on the thickness and boron concentration of the outer diamond layer. Our further research will deal with the characterization of the electrodes with two time constants in the impedance spectra is the object of the future work.

ACKNOWLEDGEMENTS

This work was supported by the Czech Science Foundation (contract No. 13-31783S), the Czech Ministry of Industry and Trade (contract No. FV - TRIO FV10312), the Technology Agency of the Czech Republic (contract No. TH02030874), and the J.E. Purkyně fellowship awarded to V. Mortet by Academy of Sciences of the Czech Republic.

REFERENCES

[1] PLESKOV, Y.V. Electrochemistry of Diamond: A Review. *Russian Journal of Electrochemistry*, 2002, vol. 38, no. 6, pp. 1275-1291.

[2] MACPHERSON, J.V. A practical guide to using boron doped diamond in electrochemical research. *Physical Chemistry Chemical Physics*, 2015, vol. 17, no. 5, pp. 2935-2949.

[3] SALAZAR-BANDA, G.R., ET AL. On the activation and physical degradation of boron-doped diamond surfaces brought on by cathodic pretreatments. *Journal of Applied Electrochemistry*, 2010, vol. 40, no. 10, pp. 1817-1827.

[4] DUO, I., FUJISHIMA A., COMNINELLIS C. Electron transfer kinetics on composite diamond (sp3)-graphite (sp2) electrodes. *Electrochemistry Communications*, 2003, vol. 5, no. 8, pp. 695-700.

[5] PIETZKA C., ET AL., Nano-crystalline diamond electrodes with cap layer decorated by gold particles. *Diamond and Related Materials*, 2010, vol. 19, no. 1, pp. 56-61.

[6] DENISENKO A., ET AL. The electronic surface barrier of boron-doped diamond by anodic oxidation. *Journal of Applied Physics*, 2008, vol. 103, no. 1, pp. 014904/1-014904/8.