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Determination of chemical oxygen demand (COD) at boron-doped diamond (BDD) sensor by means of amperometric technique

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Abstract

A boron-doped diamond (BDD) sensor was proposed for effective detection of chemical oxygen demand (COD) by means of amperometric technique. Thin boron doped diamond active sensor layer was deposited on Si wafer and glassy carbon substrate by Microwave Plasma Enhanced Chemical Vapor Deposition (MW PE CVD). The structure of BDD was confirmed by Raman spectra analysis. Broad Raman bands centered at 482 cm⁻¹ and 1219 cm⁻¹ are typical for boron-doped diamond layers. The BDD deposition onto the glassy carbon gives the maximum oxygen reduction peak current with the lowest background signal. The reduction of O₂ on boron-doped diamond electrode was studied in DMSO solution. The reduction of oxygen at boron-doped diamond predominantly involves the 1e⁻ reduction of oxygen to superoxide. The lowest COD detection limit was about 0.3 mg/l.

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Keywords: CVD diamond, Boron-doped diamond electrode, amperometric techniques, chemical oxygen demand

1. Introduction

Detection of COD in water and wastewater is crucial parameter for water quality control and environmental monitoring. The conventional dichromate methods of COD determination have several inherent drawbacks. It causes incomplete oxidation of volatile compounds and requires high-cost (Ag₂SO₄) and toxic (Cr and Hg) compounds. Furthermore, the dichromate technique is time consuming and the equipment should be operated by skilled personnel to reduce analysis errors [1]. Yu et al. [2,3] employed boron doped diamond (BDD) to determine chemical oxygen demand. Test of standards samples, a wide range of 20-9000 mg l⁻¹ COD to detection limit at 7,5 mg l⁻¹. Samples for calibration was

used: glucose, KPH, glutamic acid, the second ones was pollutants usually exiting in waster: phenol, PNP, salicylic acid and cysteamine. The BDD film was synthesized by the HFCVD on Ti substrate with gas composition of 1% CH₄ with total flow of 200 sccm and B₂H₆ diluted in H₂ was employed as doping agent at a consternation of 10 ppm. The electrochemical measurements were carried out in 10ml of sodium sulfate (0.1 M) solution. Potential rating for 50um of glucose was 2.2 V to 2.5 V (vs. SCE). Correlation between the COD obtained by the BDD sensor and the COD values measured by the convectional dichromate method is linear. Szunerits et al. [4] reports the influence of the surface termination of BDD electrodes on the oxygen reduction reaction in alkaline solution. The NH₂ BDD surface displays a higher oxygen reduction current density and positive shift in the oxygen reduction potential compared to H- and H₆- terminated BDD surfaces.

Authors performed electrochemical experiments using deposited BDD layers. Cyclic voltammograms were measured to determine the chemical oxygen demand (COD) by amperometric technique. Cyclic voltammograms were measured in dimethyl sulfoxide solution in the negative region of potential related to the reference electrode. Apart from the electroanalytical work, we have made investigation of quality of BDD electrodes. Film quality was analyzed by scanning electron microscope and Raman spectroscopy confirmed structure of boron doped diamond.

2. Experimental

The BDD electrodes were synthesized in an PE MW CVD system (SEKI Technotron AX5200S) on highly doped single-crystal p-type Si <111> substrates and glassy carbon. Both sides of the substrates were covered, essentially providing a full encapsulation of the substrate. The silicon substrate was seeded by sonication in nanodiamond suspension of 5–10 nm grain size for a 2h [5,6]. Substrate temperature was kept at 1000°C during deposition process. Highly excited plasma was ignited by microwave radiation (2.45 GHz) [7,8]. The plasma microwave power, optimized for diamond synthesis, was kept at 1300 W. The molar ratio of CH₄-H₂ mixture was kept in this study at 1 % of gas volume at 300 sccm of total flow rate. The base pressure was about 10⁻⁶ Torr and the process pressure was kept at 50 Torr. The doping level of boron in the gas phase, expressed as B/C ratio, was about 10 000 ppm using diborane (B₂H₆) dopant precursor. Investigation of molecular composition of the electrodes was carried out by Horiba LabRAM ARAMIS Raman confocal microscope (100x/0.95 objective, 50 μm of confocal aperture) equipped with a 532 nm diode pumped solid state (DPSS). The scanning electron microscope (S-3400N, HITACHI, Japan) with tungsten source and variable chamber pressure (VP-SEM) was utilized to define the surface of synthesized BDD electrode. The electrochemical investigations of oxygen reduction were carried out in a single-compartment, three-electrode cell. The potential was applied with an Autolab potentiostat/galvanostat PGSTAT30 (Eco Chemie B.V., The Netherlands) controlled with General Purpose Electrochemical System (GPES 4.9) software. Platinum wire served as the counter electrode and a Ag/Ag(I) system (AgCl in 0.1 M dm⁻³ KCl, 0.05 M dm⁻³ tetrabutylammonium perchlorate in DMSO) was used as the reference electrode. The solutions consisted of a 0.1 mol dm⁻³ tetrabutylammonium perchlorate in DMSO as a base electrolyte. The DMSO was dried over molecular sieves (Aldrich, 4A °) prior to use. Experiments were performed at room temperature (~24 °C). Voltammograms were scanned in a negative direction from 0.5V to -1.5V at a scan rate of 0.1 Vs⁻¹.

Results and discussion

The scanning electron microscope analysis of the electrode surface showed (see Fig. 1a.) that the doped diamond layer was continuous and crystalline clusters have an average size of 1 micron. The layer was 3D and no discontinuity was observed. Such a crystal size enables higher surface area and increase

amount of active sites where electrochemical reactions could be carried out [9]. The closed film surface prevents electrochemical system against the influence of substrate.

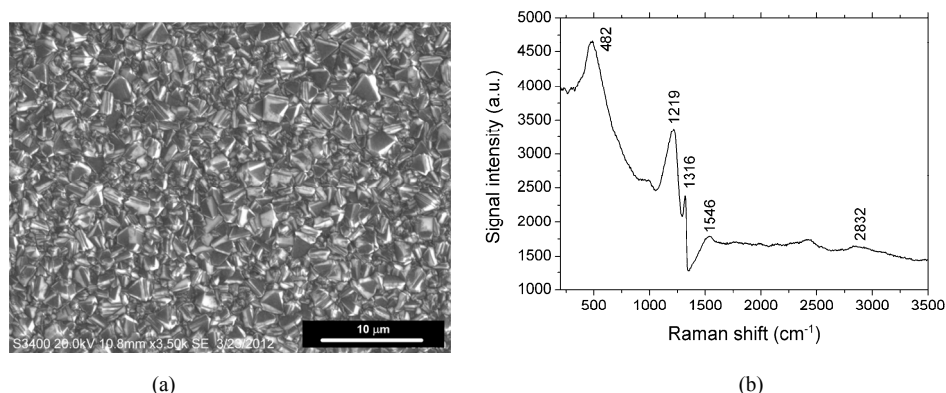


Fig. 1: Pictures of BDD diamond layer taken by scanning electron microscopy with 3500x magnification (a) and Raman spectrum of the boron diamond doped electrode deposited on silicon (b)

The molecular structure of BDD films including (content of sp^2 and sp^3 carbon phases, content of C-H bonds and efficiency of boron doping) was investigated by Raman spectra analysis. Spectrum of a BDD film deposited on silicon is shown in Fig. 2b. A narrow band assigned to diamond (1315 cm^{-1}) is shifted towards lower wavenumbers in comparison with pure undoped diamond (1332 cm^{-1}) when content of boron is high. It is related to stress of distorted diamond lattice [10,11]. Broad Raman bands centered at 482 cm^{-1} and 1219 cm^{-1} are typical for boron-doped diamond layers. Their intensity and position of the latter band can be used to evaluate doping efficiency. The origins of the bands at 482 cm^{-1} and 1219 cm^{-1} are not fully understandable [12]. Hypotheses include phonon scattering at boron-induced structural modifications and electronic transitions involving boron [10,11]. However, such features are typical for heavily boron-doped diamond layers and have been previously described [13,14]. Wide bands at 1546 cm^{-1} (assigned to “G”-band of amorphous carbon) and 2832 cm^{-1} (assigned to C-H stretching) can be used for this purpose.

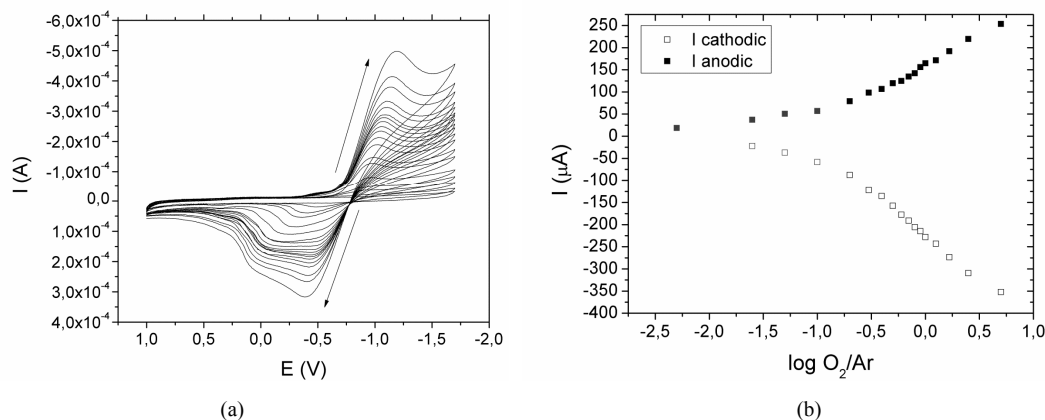


Fig. 3: Cyclic voltammogram recorded for increasing oxygen concentration reduction in DMSO with TBAP as electrolyte on BDD electrode (a) and the plot of cathodic height (I_c) and anodic height (I_a) peak as a function of log ratio oxygen concentration to Ar (b).

Cyclic voltammetry was employed to investigate the BDD electrode substrate for reduction of molecular oxygen. Molecular oxygen is reduced in a solution of DMSO in the one-step, reversible redox process in the mechanism [4,15]. The presence of small amounts of oxygen cause the increasing of the

height of cathodic and anodic peak, related to the generation of the superoxide anion on the BDD electrode. Fig. 3a. illustrates the voltammetry of O_2 on BDD electrode in DMSO and how this voltammetry changes with increasing oxygen concentration in the $2.2 \cdot 10^{-5} \div 4.4 \cdot 10^{-3}$ M range. The reduction of oxygen starts at a potential ca. $-1.06V$ vs. Ag/Ag(I) electrode, representing the reduction of O_2 to O_2^- ; while the oxidation peaks occurs at a potential $-0.4V$, representing the reoxidation of O_2^- to O_2 . This provides yields a $DE= 52mV$ for DMSO solution saturated with oxygen by passing $5:200 \text{ cm}^3 \cdot \text{min}^{-1}$ $O_2 : Ar$ through the liquid to $DE= 80 \text{ mV}$ for DMSO solution saturated with oxygen by passing $100 : 100 \text{ cm}^3 \cdot \text{min}^{-1}$ $O_2 : Ar$; and it's typical for quasi-reversible process. The voltammogram are represented by peak, the first cathode, designated I_c , with a related anodic peak (I_a). The oxidation peak of O_x has good linear correlation between peak current and concentration of O_x . Fig. 4b was obtained in a linear range from $1 \cdot 10^{-3} \div 4.4 \cdot 10^{-3}$ M. In such a case the lowest detection limit was about 0.3 mg/l . It has been demonstrated that the reduction of oxygen at the BDD electrode in DMSO occurs via the one electron reduction to superoxide. It's seems that kinetic for this process is slow.

3. Conclusions

The reduction of O_2 on boron-doped diamond electrode was studied in DMSO solution The reduction of oxygen at boron-doped diamond predominantly involves the $1 e^-$ reduction of oxygen to superoxide. The reduction of oxygen was found to be quasi-reversible on boron - doped diamond ($\Delta E = 52 \div 80mV$). The lowest detection limit was about 0.3 mg/l . Molecular composition and quality of the electrode were investigated by micro-Raman spectroscopy, which confirmed that carbon phase ratio and efficiency of boron doping was sufficient while amount of the film defects (amorphous carbon and C-H bands) was very low. Only weak bands/shoulders were observed for Raman wavenumber referring to the defects.

Acknowledgements

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