Production and Characterization of BDD/Si Electrodes for Environmental Analysis

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Abstract. Boron-Doped Diamond electrodes were produced on silicon substrate (BDD/Si) by Hot Filament Chemical Vapor Deposition reactor (HFCVD) using CH₄/H₂ gas mixtures. A series of experiments varying the levels of boron doping from 5000 to 25000 ppm were performed. Morphological, structural and electrochemical studies were conducted whose aim was the understanding about the film properties. The morphological and structural characterizations of these materials were made by Scanning Electron Microscopy and by Raman Scattering Spectroscopy techniques. The evaluation of the electrodes was performed using cyclic voltammetry. The electrochemical response showed the influence of boron content in the work potential window. The doped diamond films produced and characterized in this work are efficient as an electrode for environmental applications.

1. Introduction
BDD/Si electrodes have been extensively studied for their ability to oxidize a wide range of water contaminants. Contaminants can be oxidized by a combination of direct electron transfer and reaction with hydroxyl radicals (OH*) produced from water oxidation [1-3]. BDD/Si electrodes are considered as one of the most ideal electrodes for electro analysis and electrolysis [4, 5]. To date, conductive diamond has several superior characteristics compared with other carbon materials and metals, including very low background current density and wide potential window in aqueous solution [6, 7]. In this work, the experiments were carried out on a boron incorporated diamond film sample, which was produced with boric oxide (B₂O₃) dissolved in methanol (CH₃OH) in the gas phase in a hot-filament reactor during high pressure diamond deposition. The amount of incorporated boron is linear to the B/C ratio in the gas phase.

Previous papers mentioned that the boron concentration is homogeneous all over the coating film thickness [8]. The existence of boron dopants is expected to modify the atomic structure and the morphology of the diamond films. A different distribution of atomic structure in diamond films would further affect the physical properties of the diamond films.

2. Experimental procedure
The diamond electrodes doped with boron were produced by CVD (Chemical Vapor Deposition) technique in a reactor assisted by hot filament. The experimental setup is composed by the reactor comprises a stainless steel cylindrical shape with Pyrex windows and copper coil through which cooling water circulates. The internal layout of the reactor consist of five filament of tungsten with diameter of 125 µm supported with two brackets of molybdenum and a gas inlet tube located just...
above the region of the filaments. In the first step the substrate was scratched with 0.50 µm diamondsuspension for 60 min to enhance diamond nucleation.

Afterwards, the sample was ultrasonically cleaned in acetone and the substrate was placed 5 mm below the filaments and then the diamond deposition started. For the growth of BDD/Si electrodes a gas mixture of H₂ and CH₄ were used at a constant flow rate of 197 sccm and 3 sccm, respectively. The reactor temperature was of 800 °C and pressure was maintained at 40 Torr, and the deposition time was of 8 hours. For the doping of the electrodes an additional row of hydrogen was passed through a bubbler containing a boric oxide (B₂O₃) dissolved in methanol (CH₃OH), which was introduced into the gas inlet of the reactor. The temperature of the flask was maintained at 30 °C and the hydrogen flow to drag the inside of the reactor was controlled by a rotameter and kept at 35 sccm. When dissolving boric oxide (B₂O₃) in methanol (CH₃OH), trimethyl borate (CH₃)₃BO is formed which is the doping substance during the film growth. The solutions were prepared at different concentrations of B₂O₃ dissolved in methanol ranging from 5000 to 25000 ppm of boron atoms with respect to the carbon atoms (B/C) of methanol. The electrode morphology and quality were analyzed by SEM using a JEOL JSM- 5310 model, and by micro-Raman scattering spectroscopy (Renishaw microscope system 2000) using the 514.5 nm line of an argon ion laser and the spectra covered the range from 300 to 3000 cm⁻¹.

3. Results and discussion

Images of the samples presented in figure 1 refer to diamond film un-doped and the electrodes of doped diamond produced with B/C ratio with 5000 and 25000 sccm. It has been found that the films grown in the entire length of the substrate homogeneously with the formation of microcrystalline grains randomly oriented. From these images it is possible to infer that the different doping levels caused little change in the surface morphology. This behavior confirms the results observed by other researchers in the literature to BDD/Si electrodes [9,10].

![Diamond film un-doped](image1)

![5000 ppm](image2)

![25000 ppm](image3)

**Figure 1.** SEM photographs of the BDD/Si electrodes with B/C ratio of the 5000 to 25000 ppm. Magnification 5000 times.

Figure 2 shows the Raman spectra of the BDD/Si electrodes that exhibit a characteristic diamond peak at 1332 cm⁻¹ and a band at 1200 cm⁻¹ attributed to the disorder induced in the diamond lattice due to the incorporation of boron [11]. It is observed from this figure that the band at 1200 cm⁻¹ becomes steeper and wider by increasing the doping concentration, and this effect is associated to a reduction of the diamond peak and related to the locally disordered structures induced by the heavily boron doping [10, 12]. A band around 500 cm⁻¹ is also observed, which can be attributed to the vibration modes of pairs of boron, causing a distortion in the diamond network [13]. A complete absence of peaks around 1500 cm⁻¹ can also be noticed related to the graphitic bonds, indicating the quality of the electrode [14].
The cyclic voltammograms (CV) for the BDD/Si electrodes at different B/C ratio were performed in an aqueous solution of H\textsubscript{2}SO\textsubscript{4} 0.5 M, with a scan rate of 10 mVs\textsuperscript{-1}. We obtained a value of window work potential around 3.0 V for the various BDD/Si electrodes. This broad potential window value (E) allows the detection of redox reactions in addition to the potential range of working potential of conventional electrodes, which is around 2.0 V for platinum and graphite [15].

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This broad potential window value (E) allows the detection of redox reactions in addition to the potential range of working potential of conventional electrodes, which is around 2.0 V for platinum and graphite [15]. Figure 3 shows the voltammograms for the BDD/Si electrodes at different scanning speeds in the presence of [K\textsubscript{4}Fe(CN)\textsubscript{6}] 1 mM in H\textsubscript{2}SO\textsubscript{4} 0.5 M electrolyte. In this figure, it is observed that the increase in the scan rate of potential causes an increase in the intensity of the peak currents for the cathodic and anodic BDD/Si electrodes. It is found that the anodic peak shift occurs to more positive potentials by increasing the anodic current, and the displacement direction for the cathodic peak potential becomes smaller with the increase in the cathodic current. The anodic and cathodic peaks occur due to the charge transfer reactions (oxidation and reduction) of one electron during the application cycle potential.

Figure 4 shows the variation of potential (ΔEp) as a function of the scan rate (V) solution of ferrocyanide 1 mM/H\textsubscript{2}SO\textsubscript{4} 0.5 M to BDD/Si electrodes. It is observed in Figure 4 that there is an increase in the amount of ΔEp analyzed for all electrodes when the scan speed is increased. The BDD/Si electrodes produced at 5000 to 15000 ppm doping of B/C ratio showed lower values of ΔEp (60-70 mV) when compared to BDD/Si electrodes at 20000, and 25000 ppm at low speed scanning (10-50 mV/s), which shows that, under these conditions, these electrodes are reversible. ΔEp values can be taken as a criterion of reversibility, even when they deviate from the theoretical value, since this deviation is not too large [16].
Therefore, it can be inferred that according to this criterion BDD/Si electrodes produced at 20000, and 25000 ppm are almost reversible, i.e., they have a slower kinetic charge transfer reactions on ferrocyanide. Taking this criterion only as a reference, it can be stated that the BDD/Si electrodes produced at 5000 to 15000 ppm are more reversible. The behavior of the anodic peak current (I_{pa}) as a function of the square root of scan speed (V^{1/2}) in ferrocyanide solution for the BDD/Si electrodes is shown in figure 5. In this figure, it can be seen that there was a linear increase in the anodic peak current as a function of the square root of the scan speed for all electrodes analyzed. The fact that the graph (I_{pa} x V^{1/2}) present a line for all electrodes examined, confirms that the ratio I_{pa} / V^{1/2} independent from the scan rate, which is a criterion of reversibility. This result suggests that these electrodes may be reversible only at low scan speeds.
According to Yagi et al. (1999), the diamond electrodes in hydrogen terminations are more reversible with respect to the system [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ than to the diamond film endings in oxygen, which can be understood when considering the nature of the connections established in each case [17]. In the diamond electrode formed by a high-carbon sp³ hybridized as the functional group formed by carbon atoms bonded with oxygen tend to form bonds at the ends of the flat sites linked together by carbon double bond, i.e. that contain sp2 bonds, which results in diamond lattice oxygen terminations. The terminal oxygen atoms thus established are sites available for the establishment of new connections among the species present in the solution, which leads to the establishment of parallel reactions and/or for electron capture. The high electronegativity of the terminal oxygen atoms may be responsible for obstructing the exit of electrons associated with them, which in turn has a direct influence on the low-speed transfer of these electrons in the system.

4. Conclusions
In all Raman spectra is present the strong band at 1332 cm⁻¹, characteristic of the first order Raman scattering due to the optical vibrations of sp³-bonded carbon atoms in diamond crystal structure. All characteristic peaks of boron-doped diamond films were found features in the Raman spectrum including the broad band around at 500 cm⁻¹ and 1200 cm⁻¹ with a reduction of the diamond peak. The BDD/Si electrodes produced in this work can be considered as great anodic materials for the electro degradation of because of the high value of the anodic threshold the extensive electrochemical window and low values of capacitive currents.

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