

BORON DOPED MICRO-AND NANO-CRYSTALLINE DIAMOND ELECTRODES: CORRELATION BETWEEN SURFACE PROPERTIES AND SURFACE MODIFICATIONS USING ELECTROCHEMICAL TREATMENTS

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1. Introduction

Boron doped micro- and nano-crystalline diamond (BDD and BDND) films have attracted attention as electrode materials for application in electroanalysis due to its many outstanding properties, such as high corrosion resistance, wide potential window of water stability and low background currents. However, its electroanalytical application strongly depends on their surface properties determined by factors including doping level, morphology, grain size of diamond, sp² carbon impurities in grain boundary, etc [1,2]. The influence of these several factors becomes the electroanalytical reproducibility very difficult to be controlled due to surface modifications which gradually occur with natural oxidation as well after the use of these electrodes. Based on these considerations, this work has as goal to evaluate the influence of the surface properties of the BDD and BDD electrodes on the charge transfer kinetic of the ferri/ferro cyanide (Fe(CN)₆^{-3/-4}) redox couple from the H- and O-terminated surface modifications carried out through electrochemical treatments (cathodic – CT and anodic – AT, respectively).

2. Experimental

BDD and BDND films were obtained by Hot Filament Chemical Vapor Deposition and grown using different CH₄/H₂ ratios in the reaction mixture. The boron doping was carried out using two B/C ratios of 2,000 ppm (2k) and 20,000 ppm (20k). The doping level, morphology, grain size of diamond, sp² carbon impurities in grain boundary were analyzed using different techniques such as, scanning electronic microscopy, atomic force microscopy and Raman spectroscopy. The cathodic and anodic treatments were carried out to apply different current densities using aqueous solution containing 0.5 mol L⁻¹ H₂SO₄. After each CT and AT, the BDD and BDND electrodes were evaluated by cyclic voltammetry as function of the charge transfer kinetic of the ferri/ferro cyanide [Fe(CN)₆^{-3/-4}] redox couple.

3. Results and Discussions

The cyclic voltammetry results of the BDD and BDND electrodes after to be submitted to CT revealed that the hydrogenation process was determinant to increase of the charge transfer rate of the Fe(CN)₆^{-3/-4} redox system only for diamond films grown using B/C ratio of 2k, due to more contribution of the H-terminations on the electric conductivity (Fig. 1). On the other hand, the AT decreased the charge transfer rate of the Fe(CN)₆^{-3/-4} redox system (Fig. 2), independent of doping level and grain size of the diamond films. The reversible Fe(CN)₆^{-3/-4} redox process was reached again after re-hydrogenation process (*Inset* in Fig. 2) with the CT. However, this reversible condition of the [Fe(CN)₆^{-3/-4}] redox couple was achieved only after to apply mild ATs.

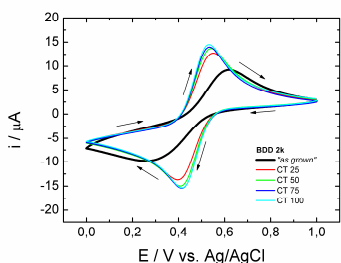


Fig. 1. Cyclic voltammograms obtained in 1mM K₃[Fe(CN)₆] + 0.5 M H₂SO₄ on BDD 2k ppm submitted to different cathodic current cathodic. Scan rate of 50 mVs⁻¹

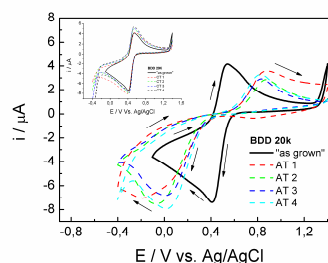


Fig. 2. Cyclic voltammograms obtained in 1mM K₃[Fe(CN)₆] + 0.5 M H₂SO₄ on BDD 20k ppm. *Inset:* after cathodic treatment subsequent to anodic treatment. Scan rate of 50 mVs⁻¹

4. References

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