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Influence of the Doping Level at Boron Doped Nanocrystalline Diamond Films in the Electrochemical Determination of Nitrite

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ABSTRACT

In this paper, the influence of the doping level at boron doped nanocrystalline diamond (BDND) films in the electrochemical determination of nitrite was reported. The morphology and the structure modifications as function of the boron doping level increase were observed. Two different doping levels were considered. A BDND film with a doping level of 30.000 ppm and one another with a doping level of 10.000 ppm was used. The columnar growth for the 30.000 ppm BDND led to a higher surface roughness and also to a greater grain size when compared to that 10.000 ppm BDND. The Raman spectra shown higher sp^2-bonded carbon amount in grain boundary for the 10.000 ppm BDND film due to decrease of the grain size. The morphological and structural modifications of the BDND films were crucial for nitrite oxidation process. The 30.000 ppm BDND electrode presented a better sensitivity to the nitrite oxidation and a lower detection limit (DL) on the *"as-grown"* condition, while the 10.000 ppm BDND electrode presented a better analytical sensitivity and a lower DL after the surface pre-treatment with hydrogen plasma.

INTRODUCTION

In recent years, boron-doped diamond films have been widely used as an electrode material, particularly in the eletroanalysis of numerous substances considered as environmental pollutants of great preoccupation to the human health [1-4]. This specific application is due to their intrinsic properties that include the wide potential window, the low capacitive current, the weak adsorption of molecules and the high chemical stability. In association with these properties, the increase of the electroactive surface area has been explored to increase the electroanalytical signal that is fundamental to analyze with greater sensitivity the smaller amount of the species of interest. This may be achieved with the advent of nanoscience and nanotechnology which has provided to obtain smaller and smaller structure that may exhibit new properties and behavior that are not displayed by the bulk matter with the same composition. Perhaps, one of the most intuitive effects is due to the change in the surface/volume ratio. As result of the size reduction new effects appear and play an important role. In this sense, if the surface/volume ratio increases, the surface phenomena will predominate over the chemistry and physics bulk properties [5]. Based on these considerations, the goal of this work is to evaluate the doping level effect of the BDND films as function of the electrochemical determination of nitrite. Actually, nitrite is one of nitrogen species of great preoccupation due to the eutrophication of aquatic system and the detrimental effects to the human health by the formation of carcinogenic substances (N-nitrosamines). Nitrite salts are commonly used as fertilizers, corrosion control and additive for meat products. Hence, the nitrite increase in natural water is inevitable and their control is one of fundamental importance. Among the numerous methodologies for nitrite analysis [6], the electrochemical detection presents some advantages since it offers a simple and a rapid determination.

EXPERIMENTAL

The BDND films were grown on silicon substrate by Hot Filament Chemical Vapor Deposition (HTCVD) technique. The following growth parameters, such as temperature of 900 K, pressure of 6.7 kPa, deposition time of 16h and gas mixture of $CH_4/H_2/Ar$ with flux of 1/19/80 sccm were used. Boron precursor was obtained by forcing H_2 through a bubbler with B_2O_3 dissolved in methanol. The dissolution of 10.000 ppm and 30.000 ppm of B_2O_3 covered a range of B/C ratio corresponding to the acceptor densities values with 10^{20} and 10^{21} B atoms cm^{-3} which was analyzed by Mott-Shottky plots, respectively. The morphology, the roughness and the quality of the BDND films were analyzed by scanning electronic microscopy (SEM) using a Jeol equipment JSM-5310, by atomic force microscopy (AFM) using Nanoscope V Multimode in air and operated in tapping mode and by micro-Raman scattering spectroscopy (Renishaw microscope system 2000) using the 514.5 nm line of an argon ion laser taking the spectra covering the range from 300 to 3500 cm^{-1}. The electrochemical measurements were carried out using Autolab PGSTAT 302 equipment with a three-electrode cell. The BDND films were used as a working electrode, a platinum wire served as counter electrode and Ag/AgCl electrode was used as reference. The electrochemical behavior of nitrite was evaluated using "*as-grown*" BDND and a BDND electrode pre-treated with hydrogen plasma. The hydrogen plasma pre-treatment on BDND electrode was performed using a microwave reactor with H_2 flow of 100 sccm and a pressure range from 15 to 40 Torr at a temperature around 560°C for 20 min. The response of the nitrite electrooxidation on BDND electrode was investigated by linear sweep voltammetry (LSV). All the voltammetric measurements were performed in a 0.1 mol L^{-1} Britton-Robinson buffer medium varying the pH in the interval from 2 to10. The sensibility and detection limit (DL) were determined by square wave voltammetry (SWV) by applying the best analytical conditions analyzed.

RESULTS AND DISCUSSION

The morphology, roughness and quality of the "*as-grown*" BDND films were analyzed prior to electrochemical experiments with respect to nitrite electrooxidation.

Figures 1(a) and (b) show the SEM images of the 10.000 and 30.000 ppm BDND films, respectively. The morphological aspect shows a significant difference in the texture and also in the grain size. For the 10.000 ppm BDND film, a structure type cauli-flower composed by clusters of small particles with crystallites size around few nanometers was verified. On the other hand, by increasing the boron doping level, a significant change on the morphology was observed, due to its effect on the growth mechanism. In particular, the resulting columnar growth for the 30.000 ppm BDND, as can be seen in Figure 1 (b), led to a structure formed with clusters composed of diamond crystallites with different size in nanometer scale, resulting in clusters with a medium diameter at around 1.0 μm. The average size of the crystallites for the BDND films was determined with the X-ray diffraction analysis (not shown). The Scherrer equation has been used by some authors to determinate the crystal size using the most intense diffraction peak, i.e., the (111) diamond peak [7,8]. The average value of the crystallite size calculated for the 10.000 ppm and 30.000 ppm BDND films was around 14 nm and 35 nm, respectively. This increase in the crystallite size cannot be related only to the influence of boron. A small amount of oxygen from the solution (B_2O_3 + methanol) can also contribute to the growth rate variation since with increasing boron doping in the gas mixture, the oxygen also increases. Oxygen is known to lead to potential chemical reactions with species in the gas phase and to the consumption of some carbon and boron species in the plasma, which usually modified the diamond growth rate [9]. The presence of oxygen from the solution in the growth gas mixture could be activated the intermediate species containing oxygen, which enhanced the etch rate of the nondiamond carbon component by improving the quality of the deposited film.

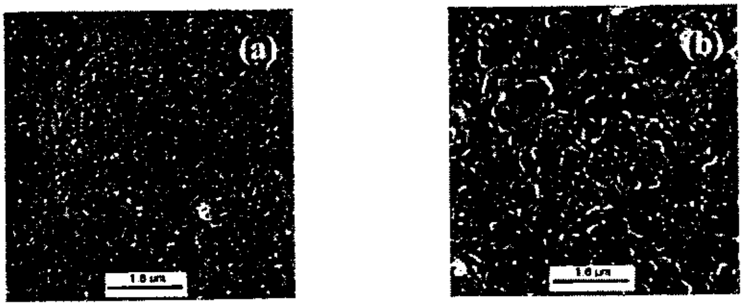

Figure 1. SEM images of the (a) 10.000 ppm BDND and (b) 30.000 ppm BDND.

A better visualization of the morphological change of the BDND films can be seen with the AFM images, as shown in Figures 2 (a) and 2 (b). According to the AFM images, the estimated values for the root mean square roughness (R_{rms}) measured over an area of 30 µm x 30 µm corresponding to 30.000 and 10.000 ppm BDND were 150.0 nm and 22.8 nm, respectively.

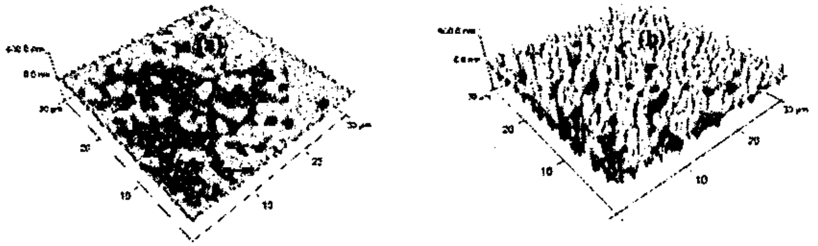

Figure 2. AFM images of the (a) 10.000 ppm BDND and (b) 30.000 ppm BDND.

The quality of 30.000 and 10.000 ppm BDND analyzed with Raman spectroscopy is presented in Figure 3.

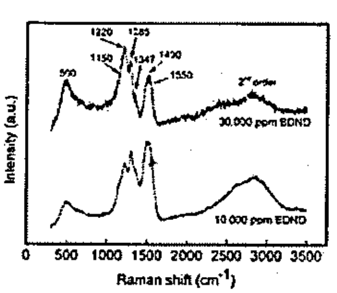

Figure 3. Raman spectra of the BDND films.

Both spectra do not have prominent diamond one-phonon line at 1332 cm^{-1} as it is verified for single crystal diamond. The diamond peak shifts to lower wavenumber (1285 cm^{-1}) because the high impurities levels present in the film [10]. Besides the broadening of this peak, related to the D band present at 1347 cm^{-1}, overlap the diamond peak. In addition, the spectra also exhibited a broadening band at 1500 cm^{-1}, due to the overlap of the peak at 1490 cm^{-1} related to transpolyacetlylene segments at the grain boundaries of nanocrystallines diamond films and of the G peak at 1550 cm^{-1} [11]. In the spectrum of the 10.000 ppm BDND, the lower intensity of the diamond peak (1285 cm^{-1}) in comparison to the broad band located at 1500 cm^{-1} indicate a higher proportion of sp^2-bonded carbon when compared to the 30.000 ppm BDND, that also is confirmed by the high intensity of the second order Raman spectrum at around 2800 cm^{-1}. The broad band at around 500 cm^{-1} and 1220 cm^{-1} have been associated with the actual boron incorporation in the lattice, rather that the role concentration [12].

The effect of boron doping level of nanocrystalline diamond films on the nitrite electrochemical determination was analyzed by using *"as-grown"* BDND electrode and the BDND electrode after the surface treatment with hydrogen plasma. The purpose of surface treatment is to evaluate the contribution of hydrogenated surface terminations on the electroanalytical sensitivity. The morphological and structural modification of the BDND electrode, particularly, due to the decrease in the grain size, may lead to a greater amount of the impurities which is associated to the presence of sp^2 carbon in grain boundary resulting in a more oxygenated surface and, hence, affecting the electrochemical behavior. Firstly, the electrochemical response of nitrite was evaluated by LSV (not shown) using BR buffer solution covering a wide pH range (3 to12). According to reaction mechanism, the nitrite electrooxidation is strongly influenced by pH solution [13]. Based on voltammetric results, it is possible to verify that independent of the boron doping level and also of the surface pre-treatment condition on BDND electrodes, the highest oxidation current of nitrite was observed in BR buffer solution with pH 6.0. Considering the best voltammetric response, the electroanalytical sensitivity and detection limit of nitrite were analyzed by using the optimized parameters for SWV (frequency of 80 Hz, pulse amplitude of 50 mV and scan increment of 5 mV). Figure 4 presents the square wave votammograms for the nitrite oxidation on (a) 10.000 and (b) 30.000 ppm *"as-grown"* BDND electrodes at different nitrite concentrations. The SWV for the nitrite oxidation on hydrogen plasma treatment BDND electrodes were not presented in this paper. The inset in Figure 4 corresponds to the analytical curves, whose the linear dependence of current intensity with nitrite concentration was verified in the interval of 9.0 x 10^{-5} to 5.0 x 10^{-3} mol L^{-1} for the 10.000 ppm BDND and 9.0 x 10^{-5} to 2.0 x 10^{-3} mol L^{-1} for the 30.000 ppm BDND electrode.

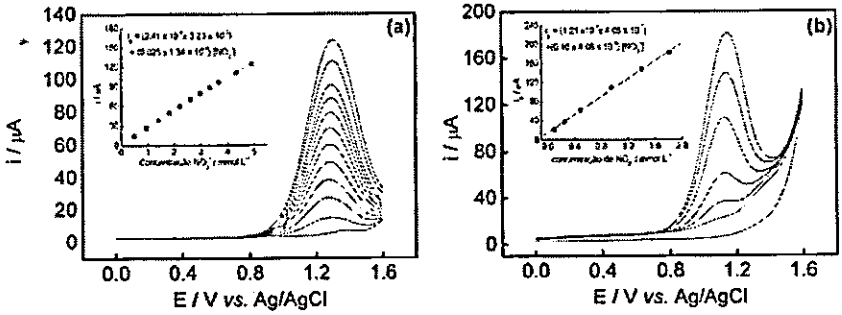

Figure 4. SWV (a) 10.000 ppm BDND and (b) 30.000 ppm "*as-grown*" BDND in 0.1 mol L^{-1} BR buffer with the nitrite concentration in the interval from 9.0 x 10^{-5} to 2.0 x 10^{-3} mol L^{-1}. f = 80 Hz, pulse amplitude = 50 mV and scan increment = 5 mV. *Inset*: the analytical curves.

Remembering that the DL values was determined using the standard deviation of the mean value of currents measured at the peak oxidation potential for ten voltammograms of the blank solution (S_b) and the slope of the analytical curve (b) by the $DL = 3S_b/b$ equation [14]. The 30.000 ppm BDND electrode showed a better sensitivity for analytical curve in the "*as-grown*" condition. The DL for the nitrite oxidation process in this condition was of 4.7 µmol L^{-1} smaller than that determined for the 10.000 ppm BDND electrode in the same condition. This behavior may be attributed to better morphological and structural conditions that were associated to electroactive area, surface roughness, sp^2 carbon amount and surface terminations. On the other hand, 10.000 ppm BDND electrode showed a higher sensibility to nitrite oxidation process after the surface treatment with hydrogen plasma.

Based on these results, the predominant factor to improve the analytical sensitivity is related to the surface modification, particularly, regarding the sp^2-bonded carbon impurities in the grain boundary that are more susceptible to be removed by the hydrogen plasma treatment. Thus, the parameters that predominated on the better analytical sensitivity to nitrite oxidation process (59.0 ± 0.002 nA L μmol^{-1}) and the lower detection limit (5.0 µmol L^{-1}) for the 10.000 ppm BDND may be related to the hydrogenated surface terminations after the hydrogen plasma treatment, leading to an increase in the electroactive area due to a smaller grain size of this film.

CONCLUSIONS

According to the results, the analytical sensitivity and the DL values were influenced by the boron doping level of the BDND films, due to the morphological and structural modifications that were associated to the electroactive area, the surface roughness, the amount of sp^2-bonded carbon in the grain boundary and surface terminations. The 30.000 ppm BDND electrode presented a better sensitivity to nitrite oxidation and a lower DL value in the "*as grown*" condition, due to a higher electroactive area justified to a higher grain size that favored a smaller amount of sp^2-bonded carbon in the grain boundary. On the other hand, after the surface pre-treatment with hydrogen plasma, the 10.000 ppm BDND electrode showed a better analytical sensitivity and a lower DL value when compared to *"as-grown"* condition due to the efficiency of the hydrogen plasma for the removing of sp^2-bonded carbon impurities that, probably, was the predominant factor on the analytical sensitivity for nitrite oxidation.

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