

Synchrotron radiation X-ray analysis of boron-doped diamond films grown by hot-filament assisted chemical vapor deposition

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Abstract

This paper presents a synchrotron X-ray radiation analysis of boron-doped diamond films grown by hot-filament assisted chemical vapor deposition (HFCVD). The diamond films were grown at different doping levels with the introduction of boron to the gas mixture by bubbling hydrogen in a B₂O₃ solution in methanol. The B/C ratio in methanol varied from 2000 to 20 000 ppm and the gas flow rates were controlled so that boron incorporation to the film varied in the range from 10¹⁸ to 10²¹ boron/cm³. All other process parameters were kept unchanged to allow comparison only of the influence of the doping level. The film analyses were performed at the X-ray diffraction beamline of the Laboratório Nacional de Luz Síncrotron – LNLS, Brazil. The Debye–Scherrer configuration was used in this study. A high intensity monochromatic beam at $\lambda=1.46 \text{ \AA}$ was used and an excellent signal to noise ratio was obtained for 2θ varying from 20° to 150°. The diffractogram for the undoped diamond film show intense peaks from the (111), (220), (311), (400) and (331) crystallographic planes. For the boron-doped films a set of new diffraction lines appear and their intensities increase considerably with the doping level. The set of diffraction peaks of similar intensities are related to a hexagonal structure and were assigned with high confidence to tungsten carbide. This reveals that the boron-doping process in HFCVD facilitates the incorporation of tungsten carbide from the filament in the diamond film. The FWHM analysis of the diamond diffraction peaks shows a dependence of film crystallinity with doping level with a definite maximum at approximately 2.3×10^{19} boron/cm³. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Boron-doped diamond; Synchrotron radiation; X-Ray diffraction

1. Introduction

Diamond has various excellent physical and chemical properties such as high thermal conductivity, wide band gap, high electron and hole mobility, and chemical inertness [1]. With such properties and the possibility of doping to produce semiconductor diamond [2] by chemical vapor deposition, it is of great interest for potential use in high temperature electronics, harsh environment detectors and electrochemistry. Electronic applications need single crystal films, which nowadays are still considered a big challenge. Some alternative electronic components and detectors have already been

reported. Electrochemical applications of boron-doped diamond films have developed considerably in the last few years and are considered a very promising research area [3,4].

Boron-doped diamond electrodes present a larger potential window than any metallic or even glassy carbon electrodes. The double layer capacitance is low [5]. Its use with some metal incorporation opens a whole new area as a host material for catalysts.

Studies on the effects of boron incorporation on diamond structure and lattice parameter (a) have been performed by X-ray diffraction on CVD homoepitaxial films, CVD synthetic crystals and CVD polycrystalline films. For synthetic film Voronov et al. [6], report an increase of the lattice parameter above 1.7×10^{19} boron

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/cm³, ascribed to semiconductor-metal transition. For homoepitaxial films, Spitsyn et al. [7] report an decrease of a up to 1.7×10^{20} boron/cm³ then an increase ascribed to boron incorporation into interstitial sites. Brunet et al. [8] found a monotonic growth of a with boron concentration, especially above semiconductor-metal transition, at approximately 2.7×10^{20} boron/cm³. This expansion of the lattice was ascribed to the sum of a geometrical component, from the larger atomic size of boron compared with carbon, through Vegard's law, with, above semiconductor-metal transition, a component from the free hole concentration within the impurity band of boron. Chateigner et al. [9] found a behavior for a in polycrystalline films similar to Brunet et al.'s [8] results. They explain that lattice remains cubic but from 10^{17} to 10^{19} boron/cm³ a is smaller than in undoped films and, that boron interaction introduces additional defects which expand the lattice and progressively average the growth rate in all directions, resulting in the loss of a preferential texture.

Most doped diamond depositions systems use microwave-assisted CVD, which, in principle, minimizes the film contamination with foreign materials. However, there are several groups that use hot-filament-assisted CVD (HFCVD) to grow boron-doped diamonds, mainly for use in electrochemistry [10,11]. Angus et al. have compiled several boron-doping growth studies and reported that HFCVD is more efficient than MWCVD [12].

Filament performance has already been extensively studied in terms of production of key growth species, such as hydrogen atom, methyl radical and acetylene [13,14]. Other practical aspects as filament stability of different refractory metals [15] and the level of metal contamination in deposited films have also been studied [16]. In particular, with boron doping it is important to quantify the metal incorporation compared to boron doping.

In this paper synchrotron X-ray radiation was used to perform X-ray diffraction (XRD) on boron-doped diamond films grown by HFCVD. The main objective was the analysis of film structure with boron doping, but, a large dependence of the level of tungsten contamination in the film with doping level was observed. This contamination is shown by high intensity peaks of a new phase assigned as tungsten carbide. The presence of tungsten carbide in the film, evaluated in up to 1% in volume for the most doped films, appears to have only a slight effect on film structure, as shown by the analysis of lattice parameter and FWHM of the diffraction peaks.

2. Experimental

The films were deposited in a HFCVD reactor, using a gas flow rate of 0.5 sccm of methane, 89.5 sccm of

pure hydrogen and 10 sccm of hydrogen passed through a bubbler containing B₂O₃ dissolved in methanol. The bubbler temperature and pressure were kept constant at 30°C and 2000 mbar, respectively, in order to guarantee the same basic gas mixture in the reactor. The B/C ratio in the gas mixture was controlled by varying the B/C ratios in the methanol solution, which were 2000, 6000, 10 000, 15 000 and 20 000 ppm. Filament temperature (2200 °C), substrate temperature (800 °C) filament to substrate distance (5 mm) and gas pressure (50 torr) were kept constant in all growth experiments. In order to keep all conditions unchanged from deposition to deposition, the single filament was changed for each deposition and a special care was taken to maintain its form. Each filament was made from 250 μm tungsten wire with seven spires and 25 mm long. Each one was carbonized in a mixture of 0.5% CH₄ in H₂ at a filament temperature of 2000 °C with great care to avoid filament deformation. Deformed filaments were discarded. Substrates were obtained from a single (100) type N, 1 Ω·cm, and 0.5-mm-thick silicon wafer. Two silicon pieces (6×6 mm² each) were used as substrate in each experiment. Since the growth conditions were tested to be very homogeneous over both substrates, both films grown on each run were considered to be alike. One of the films grown on each run was dedicated to mount an electrode for electrochemical characterization and the other was used in the synchrotron X-ray characterization.

The diamond electrodes were mounted on a brass support with contact made by silver glue on the back of the silicon substrate. A Teflon cap leaving only the diamond surface exposed covered the whole set-up. These electrodes were tested by cyclic voltammetry showing typical diamond electrodes characteristics, as shown elsewhere [17]. In particular, it is of interest for this work the electrochemical characterization of the number of carriers obtained by the Mott–Schottky plot [18]. Through this method the B/C ratio in methanol was correlated to the carrier concentration in the film, mainly for the heavily doped films.

The X-ray diffraction analysis was performed in the X-ray diffraction beamline of the LNLS – Laboratório Nacional de Luz Síncrotron [19]. The θ -2 θ goniometry of Debye–Scherrer [20,21] was chosen among the various possible set-ups available in the beamline for data acquisition and analysis of the lattice parameter and texture. The experimental details are shown elsewhere [19]. The incident beam was monochromatic, as obtained by a DCM-double crystal monochromator [22], with Si(111). The measurements were made with $\lambda = 1.46$ Å. This set-up enabled the visualization of (400) and (800) silicon peaks that were used as reference for lattice parameter measurement. The polarized beam was defined by two crossed slits. The diffractograms were obtained by two kinds of detectors: a solid state NaI-

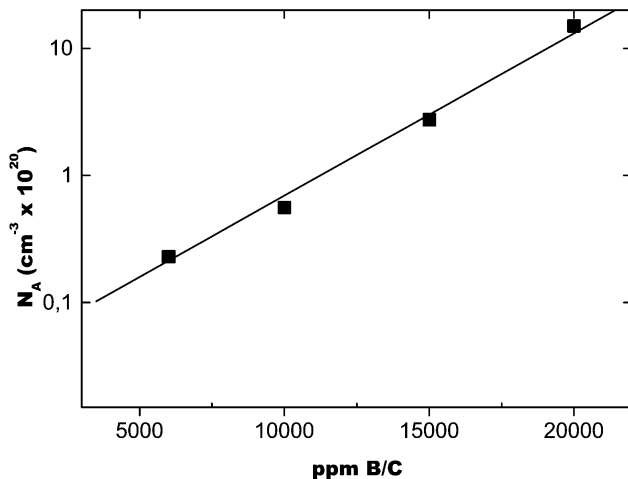


Fig. 1. Experimental correlation between the B/C ratio in methanol to the carrier concentration in boron-doped diamond films, as obtained by the Mott–Schottky plot method.

BEDE with a Soller horizontal slit in front (0.005 degree resolution) and an Image Plate (0.01 degree resolution).

3. Results and discussion

The samples grown and analyzed in this work were one undoped and five heavily doped. The Mott–Schottky method for measurement from an electrochemical analysis was effective to determine the carrier concentration, as shown in Fig. 1. These concentrations are well correlated with the estimated B/C ratio in the gas phase and also with the comparison of the Raman spectra dependence with boron concentration, as found in the literature [23]. Even though this is not a direct measurement of the boron content in the film, it may be considered a very good estimate since carrier concentration measures effective doping in heavily doped films.

Nowadays the crystalline quality of boron-doped diamond may be easily assessed by conventional XRD. However, the limited intensity of the X-ray beam precludes the identification of phases with low concentration in the samples. For example, the conventional XRD analyses of the samples shown in this work present only the diamond peaks and for the most heavily doped samples a new and weak peak appear at approximately $2\theta = 46^\circ$. This is an indication of the formation of a new phase but its identification is very doubtful. Its position could be clearly attributed to a boron carbide (B_4C) as inferred from the gas phase used.

Synchrotron XRD enabled the identification of a whole set of peaks, as shown in Fig. 2. A logarithmic scale is used to evidence such peaks. The signal-to-noise ratio is excellent and these peaks are clearly identified. The identification of the new phase was performed by simulation with Powder Cell using the

ICSD–Inorganic Crystal Structure Database. The first attempts were made with boron compounds, including boron carbides. Some of the lines could be attributed to boron carbides but not all lines could be assigned. Several materials were tried since the set of peaks could be attributed to more than one structure, including the possible contaminants. The peaks of similar intensity suggested that a single phase of a possible hexagonal structure could be responsible for the whole set. The simulation for tungsten carbide presents complete agreement for all peaks, as shown in Fig. 3. This agreement was confirmed with comparison to standard XRD data for WC [24]. The WC peaks are relatively broadened indicating a relatively short coherence length of the crystallites. This broadening could mask some lower intensity peaks from other phases that could interfere with the WC ones. However, a detailed analysis of possible structures as boron carbides, boron oxides, tungsten oxides and tungsten have shown that interference may be present only at individual peaks of WC and since no other peaks of such structures are observed, the possible interference may be discarded. From the perfect agreement observed the new peaks are attributed to WC with 100% confidence.

The synchrotron XRD observation of WC only contamination does not discard the presence of other contaminants. It only means that the WC crystalline structure has grown to a size observable by synchrotron XRD. Other contaminants may be present in amorphous structures or isolated particles without the necessary crystalline coherence to appear in XRD analysis. The observation of WC crystalline structure is significant

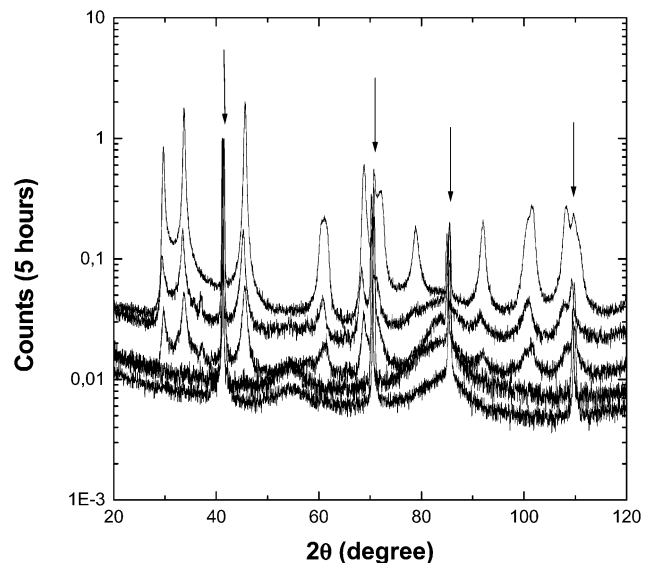


Fig. 2. Synchrotron radiation diffractograms of various boron-doped diamond films. From bottom to top: 0 ppm B/C, 2000 ppm B/C, 10 000 ppm B/C, 15 000 ppm B/C and 20 000 ppm B/C. The arrows show the position of the diamond peaks.

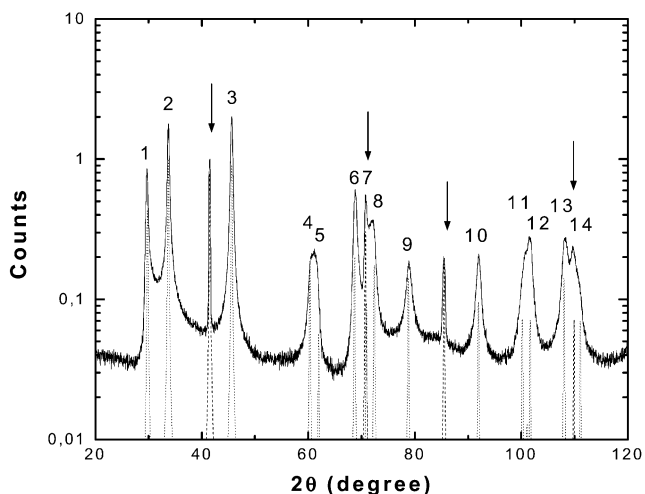


Fig. 3. Comparison of the diffractogram of 20 000 ppm B/C boron-doped diamond film with simulation with Powder Cell using the ICSD-Inorganic Crystal Structure Database. The simulated peaks correspond to WC (dotted line) and diamond (dashed line). The arrows show the diamond peaks ($2\theta = 41.52/d = 2.06 \text{ \AA}$, $2\theta = 70.74/d = 1.261 \text{ \AA}$, $2\theta = 85.50/d = 1.075 \text{ \AA}$, $2\theta = 109.9/d = 0.892 \text{ \AA}$). The numbers show the WC peaks: 1, $2\theta = 29.82/d = 2.837 \text{ \AA}$; 2, $2\theta = 33.72/d = 2.517 \text{ \AA}$; 3, $2\theta = 45.62/d = 1.883 \text{ \AA}$; 4, $2\theta = 60.30/d = 1.453 \text{ \AA}$; 5, $2\theta = 61.94/d = 1.419 \text{ \AA}$; 6, $2\theta = 68.70/d = 1.294 \text{ \AA}$; 7, $2\theta = 70.90/d = 1.259 \text{ \AA}$; 8, $2\theta = 72.42/d = 1.236 \text{ \AA}$; 9, $2\theta = 78.76/d = 1.151 \text{ \AA}$; 10, $2\theta = 91.96/d = 1.015 \text{ \AA}$; 11, $2\theta = 100.20/d = 0.952 \text{ \AA}$; 12, $2\theta = 101.68/d = 0.941 \text{ \AA}$; 13, $2\theta = 108.04/d = 0.902 \text{ \AA}$; 14, $2\theta = 111.10/d = 0.885 \text{ \AA}$.

because it shows that the whole environment favors its growth.

Because of the concern with other contaminants a XPS analysis was performed to verify, at least on the surface, the presence of boron carbides. This analysis has shown only a very faint signal at B–C binding energy, indicating that its contribution to synchrotron XRD is not significant. Also, recent elastic recoil detection analysis (ERDA) analysis has shown oxygen in the film.

From synchrotron XRD it is observed that tungsten carbide incorporation increases monotonically with doping level. Fig. 4 shows this relative increase, which has an exponential behavior. The evaluation of the spectrum for the most doped sample shows up to 1% of WC in the diamond film. This is a very high value considering that tungsten contamination at the ppm level has been measured for undoped films. It is also a very high value compared with boron incorporation. The evolution of the WC contamination with boron-doping level clearly indicates that there is a mechanism that facilitates WC incorporation. The nature of this mechanism is not so clear. Since all other experimental parameters were rigorously the same, only the boron oxide concentration in methanol was varied, some suppositions may be depicted. Most likely there is an increase of filament etching with a consequent increase of the available

tungsten in the gas phase to co-deposit with diamond. The filament etching by oxygen is well known [25], and could be thought as a first candidate to promote this process. However, according to the experimental conditions, this is not a straightforward conclusion.

A large amount of oxygen atoms (approx. 1%) is admitted in the reactor, through the methanol, for all experiments. This large oxygen amount is not significant to tungsten filament etching because of the high stability of CO in the gas phase. Diamond growth using HFCVD with methanol/hydrogen only is very peculiar because the gas phase is just on the CO-tie line in the Bachmann [26] diagram. With this mixture a new tungsten filament does not carbonize but a pre-carbonized filament does not de-carbonize, indicating that there is no significant oxygen available for filament attack. In the gas mixture used in this work we added 0.5% of CH_4 just to obtain more carbon available for diamond growth, going over the CO-tie line in the Bachmann diagram. In all experiments the base gas mixture was the same, with the same concentrations of CH_4 and methanol in hydrogen, so that the increase of WC content in the film may not be attributed to the variation of the oxygen content added through the methanol.

More oxygen is added to the system through the boron oxide dissolved in methanol. The amount added is quite small. In the worst case, with 1% B_2O_3 (20 000 ppm B/C) dissolved in methanol, the additional oxygen atoms in the gas mixture is close to 0.03%. The B_2O_3 dissolved in methanol converts into trimethyl boride $[(\text{CH}_3)_3\text{BO}_3]$ which is probably the form added to the gas phase in the reactor. The chemical kinetics of such species in the gas phase have not been studied, but may be that there is a reaction mechanism that may prevent oxygen from a direct conversion from the boride to CO in the gas phase. If so, may be that this oxygen added through the boron oxide is responsible for filament

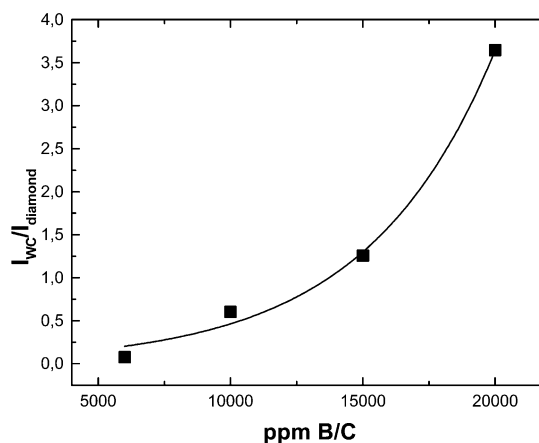


Fig. 4. Variation of the intensity of WC diffraction peaks relative to intensity of diamond diffraction peaks for the heavily doped diamond films.

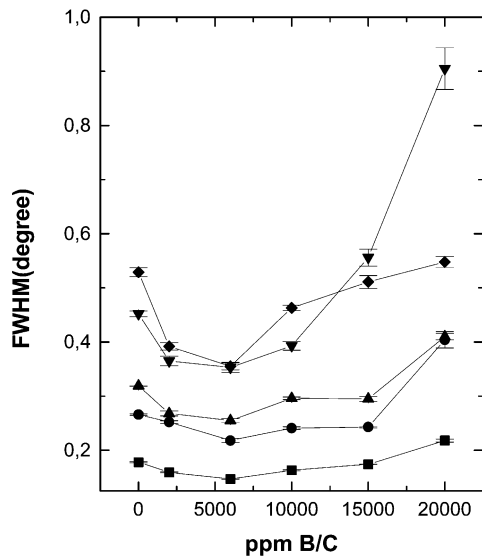


Fig. 5. Dependence of full width at half maximum (FWHM) of the diamond peaks with the B/C ratio in methanol, for various diamond crystallographic planes: ■ (111), ● (220), ▲ (311), ▼ (400), ◆ (331).

attack and WC incorporation in the film. However, this is only speculation and further studies are necessary to identify the correct mechanism.

In most cases the main interest is to avoid contamination. One alternative study is to identify if other filament materials are also potential contaminants under boron doping with B_2O_3 dissolved in methanol. Another alternative is to observe if other doping sources may induce less contamination.

Besides the presence of the WC peaks in the diffractograms, the peaks from the following diamond crystalline planes were observed with a high signal-to-noise ratio: (111), (220), (311), (400) and (331). This observation allowed the analysis of the diamond crystallographic quality. The relative peak intensities show that there is no preferential orientation under the growth conditions for these heavily doped films, corroborating the results of Chateigner et al. [9].

The full widths at half maximum (FWHM) of each peak were obtained directly from the spectra and are plotted in Fig. 5 as a function of doping level. The FWHM of diffraction peaks are influenced by crystallite size and stress distribution. For all diamond crystalline planes the behavior of the FWHM are similar. There is a decrease of FWHM with doping level, up to 6000 ppm, followed by an increase from 6000 to 20 000 ppm. The existence of a definite minimum FWHM indicates that there is a definite maximum of film crystalline quality in this range. The diffraction peak profiles are influenced by crystalline size and microstrain. Brunet et al. [27], have performed a detailed study of the contribution of both and concluded that the main effect of

boron doping is to modify the crystalline size or coherence domains with almost no influence on microstrain. Therefore, the use of the Scherrer equation enables the analysis of the apparent crystallite size or coherence domain at each crystallographic plane. This is a measure of the average length of crystalline diamond grains between adjacent defects. A definite maximum crystallite size is observed at 6000 ppm for all crystalline planes as shown in Fig. 6. This observation agrees with other authors that concluded, from Raman or XRD analysis, that interaction of defects with boron incorporation is responsible for the improvement of crystalline quality in this doping range [28].

This coherence domain has no or little correlation with the diamond film morphology, as seen by scanning electron microscopy (SEM). Fig. 7 shows the average grain size dependence on doping level as measured from SEM images. The film grain size decreases monotonically, but above approximately 5000 ppm it is almost constant. Neither the coherence domain or the average grain size present a definite correlation with the tungsten carbide formation observed in Fig. 4, which means that the presence of WC does not contribute significantly for the increase of defect density in the diamond film or to define the grain size. Fig. 8 shows the lattice parameter (a) dependence on doping level. The a values were obtained with close agreement for (111), (220) and (311) crystallographic planes. The average values with the corresponding error bars are also plotted in Fig. 8. No definite tendency is observed with the increase of boron concentration. The a value is relatively constant

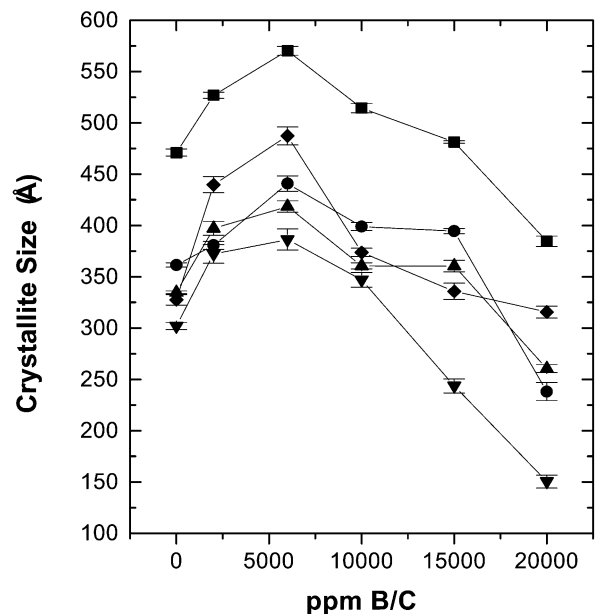


Fig. 6. Dependence of the crystallite size (coherence domain) obtained by the Scherrer equation with the B/C ratio in methanol, for various diamond crystallographic planes: ■ (111), ● (220), ▲ (311), ▼ (400), ◆ (331).

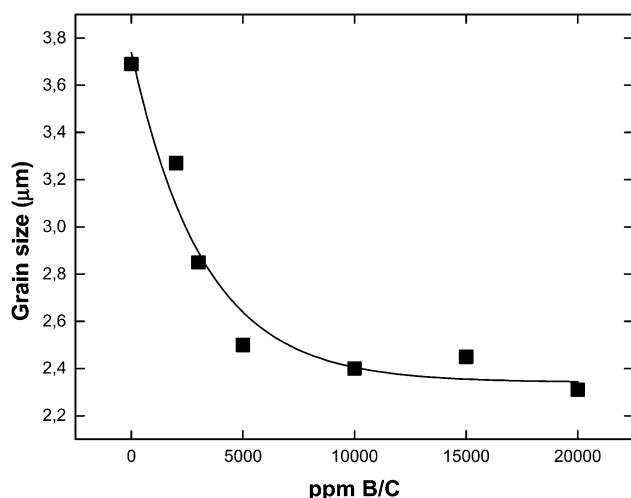


Fig. 7. Dependence of the diamond grain size obtained from SEM images of diamond films grown at different B/C ratio in methanol.

for most B/C ratios which means that probably there is no influence of the increasing WC content on diamond lattice parameter. These observations may be an indication that the WC phase forms in the grain boundary with little influence on grain crystalline structure.

However, the presence of WC phase on grain boundary should influence the stress behavior of the diamond films. An independent stress analysis of boron-doped films obtained in the same conditions of the ones studied in this work have been presented elsewhere [29]. This analysis has been performed by X-ray diffraction using the $\sin^2\psi$ technique. This technique is very effective in analyzing the global stress since it samples a relatively large volume. The results show a relatively constant tensile stress up to 5000 ppm B/C and it become increasingly compressive for higher boron concentrations. For the range of film thickness ($\sim 6 \mu\text{m}$) of this study the stress would be expected to be increasingly tensile since it is dominated by grain boundary effects and boron incorporation tends to decrease grain size, or conversely, increase grain boundary. The observed behavior is opposite to the expected and this result may be related to the presence of other phases in the grain boundary that could relax the tensile stress and compress the film structure. In the discussion presented by Ferreira et al. [26] this effect was related to the probable presence of boron clusters or non-diamond carbon phases in the grain boundary. However, the observation of this work of a significant WC content in the film and that it is probably concentrated in grain boundary may indicate that this phase may have a significant influence on film stress.

Despite the WC presence in the boron-doped diamond films its behavior as electrodes for electrochemistry is very compatible with studies presented in the literature: the electrodes are very stable, present a wide potential

window and a low background current. Electrochemical results with these electrodes are presented elsewhere [30].

4. Conclusion

Boron-doped diamond grown by HFCVD with tungsten filament was analyzed by X-ray diffraction in a synchrotron radiation beam line. The main effect observed was the incorporation of tungsten carbide in the film. The WC content in the film increased monotonically with boron oxide addition to methanol. At this point it is not possible to explain a mechanism for this observation. All growth runs have been performed in very typical growth conditions, which means that this effect is probably found in many films observed in the literature. HFCVD is extensively used for the growth of diamond electrodes and some studies have shown that boron doping is more effective in this kind of reactor. Most studies that analyzed the presence of film contamination with filament material have been performed at low doping levels in which contamination by WC is still low. From this study it may be concluded that the contamination increases exponentially with boron oxide content and has to be considered, at least at higher doping levels.

The X-ray diffraction analysis has shown that the incorporation of the WC contaminant has no direct correlation with the crystallite size and the lattice parameter and, also, no correlation was found with the grain size. Therefore, the WC phase is expected to be concentrated in the grain boundaries, which would influence the stress behavior of the film.

Further studies are necessary to observe the influence of filament material and temperature on WC incorporation into the diamond film and also the effect of other boron sources. Clearly the objective of such studies will

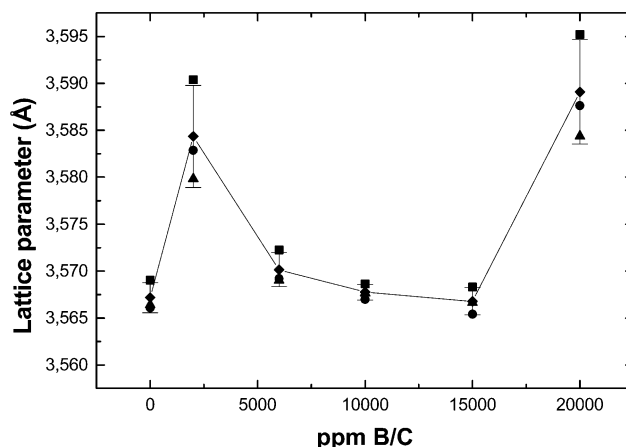


Fig. 8. Variation of the lattice parameter with the B/C ratio in methanol, as obtained for various crystallographic planes: ■ (111), ● (220), ▲ (311). The line (-♦-) shows the average value.

be to avoid or minimize contamination in heavily boron-doped diamond films.

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