Available online at www.sciencedirect.com
ScienceDirect
Diamond & Related Materials 16 (2007) 174–180
DIAMOND AND RELATED MATERIALS
www.elsevier.com/locate/diamond

Detection of N and B in doped diamond films by ERDA method and related electrochemical characteristics

Leide Lili G. Silva [a,b,*], V.J. Trava-Airoldi [b], E.J. Corat [b], N. Added [c], P.T.A. Sumodjo [a]

[a] *IQUSP, Av. Lineu Prestes, 748, CEP: 05508-900, São Paulo/SP, Brazil*
[b] *LAS–INPE, Av. dos Astronautas 1758, C.P. 515, 12245-970, São José dos Campos/SP, Brazil*
[c] *IFUSP, Rua do Matão, Travessa R, 187, Butantã, CEP: 05508-900, São Paulo/SP, Brazil*

Received 20 July 2005; received in revised form 11 January 2006; accepted 24 April 2006
Available online 5 June 2006

Abstract

Boron and nitrogen incorporation in diamond films grown by hot filament chemical vapor deposition (HFCVD) was investigated by elastic recoil detection analysis (ERDA). Boron concentration of only B-doped films ranges from 0.3% to 1.7%, which is related to the increase of B concentration into the gas phase from 0.2% to 1.5%. Two different sets of diamond films co-doped with B and N were investigated. The B incorporation into the films varied from 0.17% to 0.29% while the B concentration in the gas phase is increased from 0.2% to 2.0% and the N concentration in the films remains fixed. If the N_2 concentration of gas phase increases from 0.7% to 4.8% at a fixed B concentration, the B/C ratio of the films remains virtually unchanged (0.1 to 0.17%). Our results obtained from Scanning Electron Microscope (SEM), Raman Spectroscopy and 4 points resistivity measurements demonstrated that nitrogen incorporation modifies the characteristics of B-doped diamond films. In this article we also discuss the effect of film doping on the diamond electrode working potential window, which has been extended from 3.0 V to 3.5–4.0 V.

Keywords: Hot filament CVD; Diamond film; ERDA; Diamond electrodes

1. Introduction

Diamond films grown by chemical vapor deposition have attained much attention because of their excellent physico-chemical properties which turn them very attractive for several applications [1–3]. An important application is as an electrode material due to its wide working potential window and high corrosion resistance. The diamond electrodes have been widely applied in electroanalysis [4] and electrosynthesis [5]. Boron and nitrogen are used as dopant to turn the diamond film as a semiconductor by introducing free electrons or holes into the diamond crystal lattice. The characteristics of the diamond films doped with only boron [6–9], only nitrogen [6,10,11] or co-doped with N and B [12] have been studied by many research groups. However few works are dedicated on quantitative determination of boron [13] and nitrogen [14,15] using Elastic Recoil Detection analysis (ERDA). For diamond films doped with only B, Liao et al. [13] observed that boron depth profile is uniform and B content varied from 4.4×10^{17} B/cm^3 for slightly doped film up to 2.3×10^{20} B/cm^3 for the highly doped film. The N doped diamond films were obtained by Bergmaier et al. [15] by adding during the growth process a mixture of N_2 in H_2 (N_2 content from 0.0025% up to 0.5%). In the same paper the probability of N incorporation into the film was estimated to be 0.4% in relation to the carbon.

The existing works that employ the ERDA analysis for light elements detection in diamond films are mostly related to the determination of hydrogen [13,17–20] and in some cases, oxygen [14] and deuterium [16]. Hydrogen content is rather evaluated because it is a growth precursor for CVD diamond films. Its content affects the physical, mechanical and electrical properties of the films [13], such as the thermal conductivity coefficient and the resistivity that decrease with increasing H content in the films [21].

The main objective of the present study is to determine B and N contents by ERDA analysis in two different types of diamond films, films doped only with boron and co-doped with B and N. Additionally, it is explored the effect of film doping on the electrochemical characteristics of diamond electrode, because

* Corresponding author. Tel.: +55 12 3945 6676; fax: +55 12 3945 6710.
E-mail address: leide@plasma.inpe.br (L.L.G. Silva).

0925-9635/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2006.04.010

Table 1
Experimental conditions of the feeding gases during the diamond films growth; B/C and N/C ratios in the films

Samples	Set 1	Set 2	Set 3
B/C ratio (%) in the feeding gas	0.2–2.0	0.2–2.0	1.0.
B/C ratio (%) in the diamond films	0.3–1.7	0.17–0.29	0.2–0.28
N_2 concentration (%) in the feeding gas	–	0.7	0.7–4.8
N/C ratio (%)in the diamond films	–	0.07–0.1	0.1–0.17

such a relation has not yet been investigated in previous studies. The films were characterized by SEM, Raman spectroscopy and resistivity measurements, while the electrochemical measurements were performed by cyclic voltammetry.

2. Experimental

Three sets of diamond films were grown on a silicon substrate by hot filament chemical vapor deposition (HFCVD) using a basic mixture of 0.5% of CH_4 diluted in H_2. The filament temperature (2200 °C), substrate temperature (750 °C), 6 h deposition time, tungsten filament, to substrate distance of 5 mm, and 50 Torr gas pressure were kept constant for all experiments. The growth rate was approximately 1 μm/h and the layers morphology presents a columnar structure. A cooling system is installed in the reactor. The sample holder is sustained on copper rods, which are water cooled. The experimental conditions of the feeding gases during the diamond films growth are shown in Table 1. Nitrogen doping of the diamond films was performed by introducing N_2 gas directly into the reactor. Boron doping of the diamond films was carried out by addition of B_2O_3 dissolved in methanol. The solution with boron was introduced to the gas phase during the diamond growth by dragging in H_2. The B/C ratio in the mixture was controlled by ranging the B/C ratio in the methanol solution as presented in Table 1. Total carbon concentration, including the carbon of CH_4 and that one introduced by the methanol, was kept constant in all doping processes.

The Raman spectra of the samples were obtained using the Renishaw 2000 micro-Raman system with Ar^+ laser (λ=514.5 nm) as an excitation source. Surface morphology of the films was examined by SEM using a LEO 440 scanning microscope and the film resistivity was measured by Matheson RTM 111 model.

The electrochemical measurements were performed by cyclic voltammetry using a potentiostat (EG and G PAR, 273A). The cyclic voltammetry was made using a conventional three electrode cell. Diamond film samples with geometric area of 0.28 cm^2 were employed as working electrode. The reference and counter electrodes were the Ag|AgCl and platinum, respectively. The electrolytic solutions applied in the electrochemical measurements were 1.0 M H_2SO_4 or KCl. The electrolyte was deoxygenated with N_2 prior to the experiments. All the experiments were performed at room temperature.

Elastic Recoil Detection Analysis (ERDA) has a high efficiency to identify and quantify implanted ions or deposited films on the substrate surface [22,23]. This method is specially indicated to investigate light elements (Z<10), in which other techniques such as Rutherford Backscattering Spectrometry (RBS) [24] have low efficiency. B and N doped diamond films were analyzed by ERDA method to detect quantitatively B, C, N and O elements in the diamond films. In this technique, high-energy Cl^{35} ions (54 MeV) were used as incident beam on the samples at 60° angle in relation to the normal. An ionization camera was arranged at 40° angle in the laboratory referential to detect and identify the scattering particles (projectile and recoil). The ERDA results correspond to the energy of the recoil detection particles through the Silicon Surface Barrier Detector (SSBD), which serves to generate an initial signal.

The data reduction software (SCAN/DAMM) allowed to obtain energy spectra for each element obtained in the reaction. The atoms number for each element in the sample was attained by SIMNRA 4.4 to reproduce the counts integral for each energy spectrum. The analyses considered Rutherford scattering shock section as a homogeneous distribution of the elements in the samples.

The last uncertainty in the elements percentual values was defined by counts integral statistic of the elements energy spectra. It was admitted a general uncertainty in the order of 5% related to the energy loss calculation. The bidimensional spectra showed a heavy element contribution, which was assumed as tungsten, from [28].

The data are compiled and presented relative to carbon concentration in the film, so that the ratios B/C, N/C, O/C and W/C are obtained.

3. Results and discussion

3.1. Characterization of diamond films

The ERDA results presented homogeneous films with uniform distribution of the dopant in the bulk of the film for all samples investigated. In summary, the B/C and N/C ratios in the diamond films obtained by ERDA analyses are shown in Table 1. Fig. 1 depicts the B/C ratio in the films as a function of the B/C ratio in the feeding gases (B/C = 0.2–2%) obtained

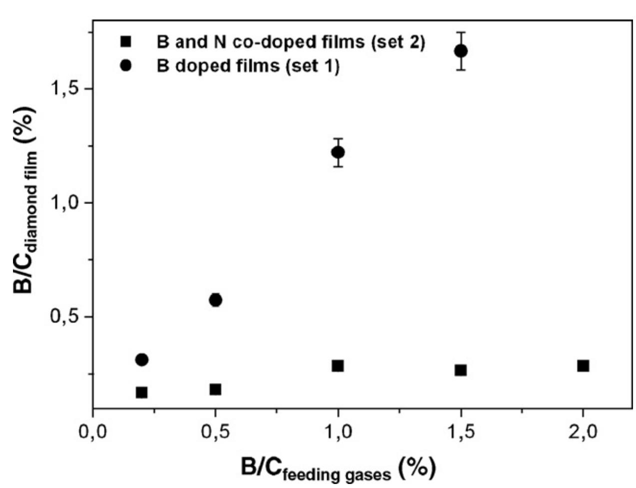

Fig. 1. Variation of the B/C incorporation in the films as a function of B/C ratio in feeding gases (0.2–2.0%); for the B-doped diamond films (circle = set 1) and B and N doped diamond films (square = set 2), (N_2 concentration = 0.7%).