B AND N CODOPED DIAMOND FILMS: AN EXTENSION OF THE WORK POTENTIAL WINDOW

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Nitrogen and boron-codoped diamond films were produced to obtain an extension of the diamond electrode work potential window (>3,0 V). These electrodes will be applied in electrosinthesis [1]. Diamond films were grown on silicon substrate by hot filament CVD method. The deposition temperature of the polycrystalline films was around 700° C during 6 hours. Boron source was achieved using a solution of boric trioxide dissolved in methanol and placed in a bubbler. N2 gas was introduced simultaneously with B doping. The CH₄; H₂ and B₂O₃/CH₃OH/H₂ flows are kept at 0.5, 100 and 44 sccm (standard cubic centimeters per minute), respectively. The N₂ flow is varied from 1.0 to 3.0 sccm. All diamond films exhibited an uniform surface containing faceted grains, their grain size was approximately 2.5 - 3.5 µm. Nitrogen and boron-codoped diamond films are more resistive than boron doped ones. The resistivity increases with the N₂ concentration increase. Raman spectroscopy results (figure 1) demonstrated a diamond characteristic line at 1332 cm⁻ for all the diamond films and two broad peaks, around 490 and 1220 cm^{-1} were observed due the boron incorporation in the diamond crystalline structure, mainly for the highly doped electrodes (2000000 ppm B/C). Another band was observed around 2452 cm^{-1} (2.1 eV). This band was also observed by other authors [2-3] and was attributed to the nitrogen-vacancy complex. The figures 2 and 3 show the cyclic voltammetry for the diamond electrode (10000 ppm B/C) in KCl (1 mol.l⁻¹) and H_2SO_4 (1 mol.l⁻¹), respectively, obtained in the potential range between -3,0 and 3,0 V in a scan rate of 100 mV/s. In figure 2, it was observed a work potential window nearly 4,0 V, larger than observed with B-doped electrode (3,0 V). The oxygen evolution for the N and Bcodoped diamond electrodes occurs nearly 2.0 V and the hydrogen evolution in -2.0 V while for B-doped one, these reactions occur in 1.6 and -1.4 V, respectively. In figure 3, it was observed a work potential window nearly 3.6 V. The oxygen evolution for the N and B-codoped diamond electrodes occurs nearly 2.6 V and the hydrogen evolution in -1.0 V while for B-doped one, these reactions occur in 2.2 and -0.7 V, respectively. The extension of the work potential window due to N2 introduction in the film is not well understood in the literature, although, some authors[3] inferred from luminescence studies of N and B-doped diamond films that a competition between the boron acceptors and nitrogen donors can occur in diamond crystalline structure, moving the position of the Fermi level. This way, the film become more resistive and causes the extension of the work potential window.

References

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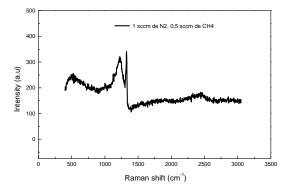


Fig. 1: Extended Raman spectra of N_2 and B-doped diamond electrode (20000 ppm B/C) with nitrogen concentration of 1.0 sccm N_2

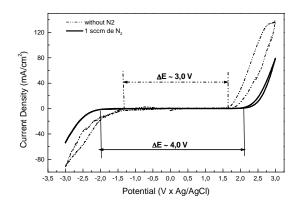


Fig. 2. Cyclic voltammogram for the diamond electrodes (10000 ppm B/C) in KCl (1 mol.l⁻¹); 100 mV/s.

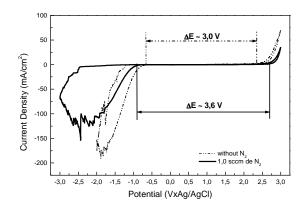


Fig. 3. Cyclic voltammogram for the diamond electrodes (10000 ppm B/C) in H_2SO_4 (1 mol.l⁻¹); 100 mV/s.

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