THE DEPENDENCE OF CATHODIC PRE-TREATMENT ON H-TERMINATED DIAMOND SURFACE FOR DIFFERENT DOPING LEVELS

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The electrochemical behavior of boron doped polycrystalline diamond (BDD) electrodes strongly depend on its surface properties such as the grain size, crystallographic orientation and sp^2 content at the film grain boundary. The cause of different electrochemical behaviors corresponding to different surface-terminated diamond films is far from being clarified [1,2]. So, complementary studies are justified to correlate the electrode response and its surface termination evolution taking into account how the doping levels may influence the diamond surface after cathodic treatment (CT). This study is presented for BDD electrodes produced at four different doping levels, called as A,B,C and D, with acceptor concentrations of 10^{18} up to 10^{20} atoms. cm^{-3} . This range was estimated from Mott-Schottky plots using frequencies of 1, 10 and 50 kHz.

The films were prepared by hot filament CVD technique using the standard mixture of H_2/CH_4 with an additional H_2 flux passing through a bubbler containing different concentrations of B_2O_3 dissolved in methanol. Diamond quality, morphology and crystallinity were characterized by scanning electron microscopy, Raman spectroscopy and x-ray diffraction techniques while the changes in film surfaces were analyzed by contact angle, cyclic voltammetry and synchrotron X-ray photoelectron spectroscopy (XPS). The cathodic pre-treatment was performed in $0.5\text{ mol L}^{-1} H_2SO_4$ at -3.0 V x $Ag/AgCl$ for 30 min. The BDD hydrophobicity, reversibility, work potential window characteristics, as a function of the doping level, were related with its physical properties and its chemical surface; mainly associated with its natural oxidation (as-grown BDD) or with its changed behavior forced by the cathodic pre-treatment.

The relationship between the BDD electrochemical response and its surface bond termination is presented comparing Mott-Schottky plots (MSP) and XPS for the lightly (10^{17} - electrode A) and heavily (10^{20} - electrode D) BDD films. Figure 1 shows the MSP obtained before and after the CT in $0.5\text{ mol L}^{-1} H_2SO_4$ at 1 kHz for these two samples. The measurements revealed a classical Mott-Schottky behavior. The two samples presented a small shift to more negative values for flat band potentials after the cathodic polarization. The space charge density values determined after treatments for

both samples are very similar to those previously measured on the as-grown electrodes.

The proportions of C1s and O1s contributions for BDD as-deposited and electrochemically treated are presented in Tables 1 and 2. These values were obtained by peak fitting to identify the presence of different chemical states in the electrode surfaces. For C1s spectra, the more intense peak was centered at 284.8 eV attributed to the bulk diamond component. Considering the C1s region spectra the peaks studied were C-Hx (polyhydride), "C-O" (hydroxyl or ether groups), and "C=O" (carbonyl, carboxylic or ester carbon). These as-grown BDD films may be considered as hydrogen terminated since the O_{1s}/C_{1s} ratio is smaller than 2.0 at. %. Nonetheless, after CT the oxygen amount increased for the all samples, with a higher content for film D. This behavior is explained by the natural oxidation of diamond after the acid etching process that may expose more active sites in the sp^2 content at the diamond grain boundary, mainly for heavily doped films.

Fig. 1. Mott-Schttky representations of BDD electrodes before and after cathodic treatment.

	A	D
as-grown	1.18	2.68
CT	8.8	9.5

Table 1. Oxygen relative proportion O1s/C1s (%) from XPS measurements

	A	D
As-grown	5.7	8.4
CT	12	14.2

Table 2. Proportions of "C-O" (hydroxyl or ether groups) contribution by peak fitting of C1s (%)

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- [2] H. Girard, N. Simon, D. Ballutaud, M. Herlem, A. Etcheberry, *Diam. Rel. Mat.*, 16 (2007) 316.