

Behavior of a Boron-Doped Diamond Monocrystals in Mineral and Organic Acid Solutions

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Boron-doped diamond (BDD) electrodes are promising new tools in the electrochemical water treatment market. A BDD monocrystal has been characterized and tested in order to improve the understanding of the electrode surface behavior during electrolysis. Two different typical acid or organically charged solutions were used.

BDD electrodes enable new applications in electrolysis thanks to their wide working window and their capacity to generate very active oxidative species such as OH. radicals^[1]. The BDD films used as electrodes are polycrystalline. Their behavior during electrolysis and in particular the role played by the different crystal faces of the grains is still poorly understood. In order to progress in this field, boron-doped monocrystalline diamond (100) grown homo-epitaxially by CVD was characterized using SEM and AFM. Cyclo-voltammetry was performed in acidic and organic solutions in order to study the monocrystal behavior and its stability when used as an electrode. Particular attention was paid to changes in the working window and the surface topography during the tests.

The BDD monocrystal was grey in color (due to the boron doping); its dimensions were 3 x 3 x 1mm. It was fixed on a printed circuit board to carry out the cyclo-voltammetry measurements.

The first experiment was carried out using cyclo-voltammetry in perchloric acid solution (HClO₄ 1M; -3V to +7V at a sweep rate of 1V/s), from 0 to 28500 scans:

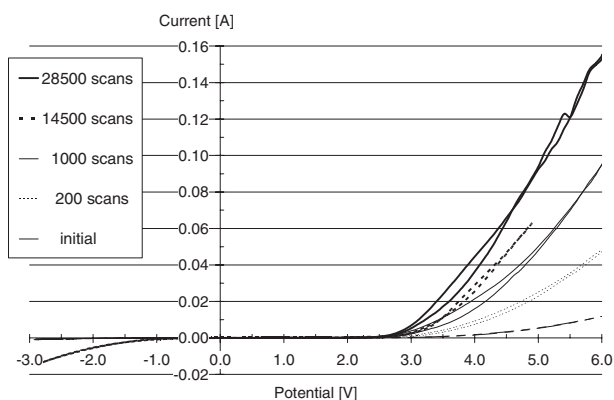


Figure 1: Changes in the cyclo-voltammograms as a function of number of cycles in HClO₄ 1M – Ag/AgCl-KCl 3M - 1V/s.

The working window, initially from ~-2 to ~+3.2V, was reduced during the electrochemical cycles to ~-1 to ~+2.7V after 28500 scans (equivalent to 17.85 Ah/cm²). This indicates a reduction of the crystal surface activity due to the treatment in acidic solution. The surface roughness measured by AFM changed from Ra=2.8nm initially to Ra=2.6nm after 28500 scans, indicating a good stability. No corrosion related to the specific crystal planes (100), (111) or (110) was observed.

A second experiment consisted of cyclo-voltammetry in 1M acetic acid solution with 75 g/l Na₂SO₄ as a supporting electrolyte in order to observe corrosion effects on the crystal faces or their boundary regions.

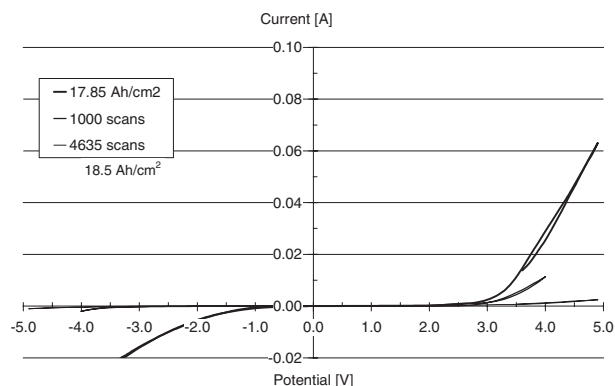


Figure 2: Changes in the cyclo-voltammograms as a function of number of cycles in CH₃COOH 1M – Ag/AgCl-KCl 3M – 1V/s.

In acetic acid, the working window increased during electrochemical cycling: from ~-1 to ~+2.7V initially to ~-3V to more than +3V with only 0.65 Ah/cm². This results shows is the opposite to that seen in perchloric acid solution: the reactions induced at anodic potentials degrade the organic compound.

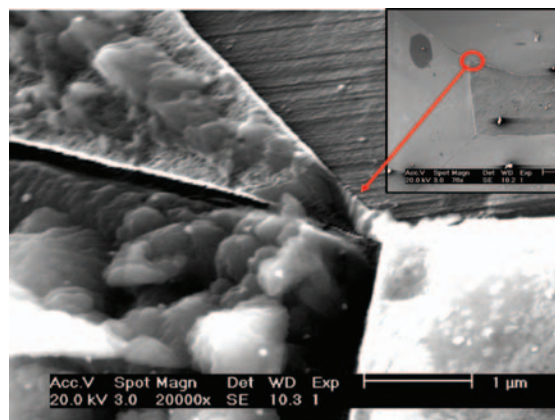


Figure 3: SEM after treatment in CH₃COOH 1M.

SEM analysis shows preferential corrosion at the grain boundaries of 2-3 orientation planes. The planes themselves are not affected by this corrosion.

The effect of multiple cyclo-voltammetry scans on a monocrystal in a mineral acidic medium (HClO₄) is significantly different to the effect in an organic acid (CH₃COOH). Perchloric acid allows the production of OH. radicals, which recombine to give H₂O₂ or ozone without affecting the perchloric acid molecule. In contrast, the acetic acid medium is degraded, initiating the Kolbe reaction (ethane production) and CO₂ production. Grain and plane boundaries have been identified as preferential sites for corrosion.

The support of OFES is gratefully acknowledged.

^[1] Béatrice Marselli, "Electrochemical Oxygen Transfer Reaction on Synthetic Boron-doped Diamond Thin Film Electrode", Thesis EPFL 2004