



# Chemical-Assisted Mechanical Lapping of Thin Boron-Doped Diamond Films: A Fast Route Toward High Electrochemical Performance for Sensing Devices



Jacek Ryl<sup>a,\*</sup>, Artur Zielinski<sup>a</sup>, Lukasz Burczyk<sup>a</sup>, Robert Bogdanowicz<sup>b</sup>, Tadeusz Ossowski<sup>c</sup>, Kazimierz Darowicki<sup>a</sup>

<sup>a</sup> Department of Electrochemistry, Corrosion and Materials Engineering, Faculty of Chemistry, Gdansk University of Technology, 11/12 Narutowicza St., 80-233 Gdansk, Poland

<sup>b</sup> Department of Metrology and Optoelectronics, Faculty of Electronics, Telecommunications and Informatics, Gdansk University of Technology, 11/12 Narutowicza St., 80-233 Gdansk, Poland

<sup>c</sup> Department of Analytical Chemistry, Faculty of Chemistry, University of Gdansk, 63 Wita Stwosza St., 80-952 Gdansk, Poland

## ARTICLE INFO

### Article history:

Received 1 March 2017

Received in revised form 14 April 2017

Accepted 6 May 2017

Available online 8 May 2017

### Keywords:

boron doped diamond  
electrode homogeneity  
spreading resistance  
impedance monitoring

## ABSTRACT

There is an urgent need for an effective and economically viable increase in electrochemical performance of boron-doped diamond (BDD) electrodes that are used in sensing and electrocatalytic applications. Specifically, one must take into consideration the electrode heterogeneity due to nonhomogeneous boron-dopant distribution and the removal of  $sp^2$  carbon impurities saturating the electrode, without interference in material integrity. In this work, authors describe a detailed study on electrochemical performance and the enhancement of electrochemical active surface area in the BDD electrodes that have been pretreated via chemical-assisted mechanical lapping.

The effect of lapping on both surface chemistry and oxidation processes at the BDD surface was assessed by means of chronovoltammetry, instantaneous impedance monitoring, and X-Ray photoelectron spectroscopy. Next, atomic force microscopy and scanning electron microscopy were employed to produce data on spreading resistance and surface geometry, respectively.

While the analyzed interactions are very complex and multi-level, authors suggested that the main observed effect was due to the removal of *non-diamond* carbon impurities from the electrode surface, decreased grain size, and heterogeneous conductivity. Short-duration pretreatments were found to be an effective route towards more efficient surface activation with negligible alterations in the diamond film structure. A prolonged pretreatment led to a decrease in grain size and lowered contribution of (111) and (110) facets, which in turn influenced the electrode kinetics.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Recently, the electrochemical applications of boron-doped diamond (BDD) electrodes attract much attention not only in the field of electrochemistry, but also in other areas such as functional materials, analytical and environmental chemistry, biomedical and biological sciences. Since the properties of BDD are combined with its inert surface characteristics, the BDD electrodes display intriguing electrochemical features, *inter alia*, the widest solvent window of all electrode materials in aqueous solutions, low

background and capacitive currents, reduced fouling and the ability to withstand extreme potentials, while at the same time retaining the excellent mechanical robustness. Thus, BDD is slowly rising in prominence in the electrochemical arena, predominantly where longevity and low maintenance are key attributes [1,2].

The electrode preparation step is often applied to remove  $sp^2$ -carbon impurities saturating the BDD electrode during the CVD process [3,4], which can be found in particular, but are not limited to, inter-grain regions [5]. Usually, the pretreatment of BDD electrode surface for electrochemical measurements is carried out via one or several of the following mechanisms: (I) mechanical polishing and lapping; (II) acid washing and rehydrogenation; (III) heat treatment; and (IV) electrochemical polarization [6–11] (Supporting Information, Section I). These methods are often

\* Corresponding author.

E-mail address: [jacek.ryl@pg.gda.pl](mailto:jacek.ryl@pg.gda.pl) (J. Ryl).

found to be destructive as they introduce stresses to the BDD film, which may lead to the formation of cracks and film discontinuities. The destructive nature of the pretreatment process depends on many factors, such as growth method, film thickness and the presence of  $sp^2$ -carbon phase.

The numerous types of chemical and mechanical pretreatments are characterized by distinctive disadvantages [12–16]. The final surface finish and the level of interference into the material's physico-chemical properties greatly depends on the chosen pretreatment method. This, in turn, affects the factors such as grain size or oxidation of termination bonds [17], both being of key interest to electrochemical performance of BDD electrodes. The termination bonds not only substantially influence the electrochemical properties of diamond [18,19] but also factors such as hydrophilicity or adhesion and durability of organic compounds attached to the electrode surface [20,21]. For example, Bogdanowicz et al. [22] reported that the difference in anodic polarization of even 0.2 V may lead to an almost complete detachment of functionalized amine film from the electrode surface.

The numerous indirect analytical approaches have demonstrated the occurrence of heterogeneity of physico-chemical properties within grain boundaries in polycrystalline BDD films [23,24]; the resulting effect can be critical in cases when high performance is expected in electrochemical applications. It is assumed that polycrystalline boron-doped diamond surfaces exhibit heterogeneity in electron-transfer rates over the surface due to non-uniform distribution of dopant throughout the film, with local highly-doped sites of fast (reversible) kinetics and the slow sites (irreversible) containing less dopant [25–27]. Recently, nanoscale impedance microscopy (NIM) allowed the observation of differences in impedance modulus between the areas of different boron-dopant concentration, which amounted to three orders of magnitude between the grain boundaries and inter-grain regions [5]. This phenomenon originates from the higher boron incorporation at the grain boundaries, which results in the much lower charge transfer resistance. In addition, the preferential  $sp^2$ -carbon contamination in the inter-grain regions plays a significant role. Based on the above mentioned results, it has been assumed that the electrochemically active surface area is much smaller than the geometrical surface area. As a consequence, large heterogeneities of electric properties should be expected for high local current densities at conductive regions [28,29], leading to the lowered electrode efficiency and accelerated electrode aging. The effective reaction rate constant strongly depends on the coverage of inactive area. Furthermore, the heterogeneity of physico-chemical properties occurs at the level of particular grains. Szunerits et al. [30] claim that the dopant level in particular grains varies which can result in the two types of region, with different metallic and semiconducting properties next to each other.

To the best of our knowledge, there has been no earlier contribution to the discussion on the effect of chemical-assisted mechanical lapping (CAML) on electrochemical properties of BDD electrodes. The authors have proposed this particular pretreatment technique as a possible route to increase the electrode's performance in a fast and effective way, taking into consideration that the removal of  $sp$ - and  $sp^2$ -hybridized carbon is much faster than the removal of stable  $sp^3$  phase, while lapping itself does not strongly affect the material integrity [31,32]. The CAML effect has been studied with AC and DC electrochemical techniques as well as various microscopic and spectroscopic tools. The presented work demonstrates the changes in electrochemical properties of as-prepared Si/BDD electrodes, while the applied pretreatment technique is shown to be even more efficient in the case of electrodes that have become degraded due electrochemical fouling.

## 2. Experimental

The boron-doped diamond was synthesized in an MWPECVD system (SEKI Technotron AX5400S, Japan) on p-type Si substrates with (111) orientation. The seeding process included spinning of thin film of DND seeding media by means of a spin-coater (Laurell WS-400B, USA). The home-made DMSO-PVA-DND suspension with nanodiamond concentration of 0.25% w/w in DMSO/PVA was used in the experiments. The procedure for DND slurry preparation has been reported elsewhere [33]. The selected substrates were etched in hydrogen plasma for 1 min. The optimized power of microwave plasma for diamond synthesis was kept at 1300 W. Excited plasma was ignited by microwave radiation (2.45 GHz). The total flow of gas mixture, containing 1% of the molar ratio of  $CH_4$ - $H_2$ , was kept at 300 sccm. Diborane ( $B_2H_6$ ) was used as dopant precursor, and the [B]/[C] ratio of boron level in the gas phase was kept at 10 000 ppm. The used growth time of 6 h produced microcrystalline hydrogen-terminated diamond films of ca. 2  $\mu m$  in thickness.

The Si/BDD electrodes underwent chemical-assisted mechanical lapping on an own-designed lapping machine. Samples had surface area of 1  $cm^2$ . The rotational speed of pad and carrier (rotating in opposite directions) equaled to 40 rpm, while the down pressure was 40 kPa. Samples were attached to the carrier with silver paste and subjected to CAML for different time periods ( $t$ ), i.e. 3, 10, 30, 80 and 120 min. The cloth was moistened at a rate of 100  $ml h^{-1}$  with an alkaline colloidal silica solution. The size of silica particles (Akasol, Denmark) was 50 nm in diameter. Buehler 40-7212 PSA polymer microcloth was used. Immediately after the CAML pretreatment, samples were degreased in acetone with an ultrasonic cleaner.

Selection of lapping parameters was based on a procedure carried out for nanocrystalline diamond [34,35] and it might require further optimization for different types of diamond-based electrodes. According to Thomas et al. [34] this inexpensive and efficient method is based on the chemical-assisted mechanism, consisting of wet oxidation of the surfaces with the polishing fluid, followed by the formation of  $Si(OH)_4$  passive layer and eventually shearing silanol molecules with bonded carbon atoms from the electrode surface. It is concluded that the lapping does not significantly change the chemical composition of NCD surface, and thus the graphite and graphite-related defects were not developed.

The chronovoltammetric and impedance measurements were performed by means of an Autolab 302N potentiostat/galvanostat (Ecochemie, The Netherlands). In the case of impedance measurements, the system was expanded with PXIe-4464 and PXIe-6124 (National Instruments, USA) measurement cards for AC signal generation and acquisition, respectively. The aforementioned cards were operating in PXIe-1073 chassis. The measurements were carried out in a three-electrode cell, with Si/BDD as a working electrode,  $Ag|Ag_2SO_4$  as a reference electrode (+0.273 V vs SHE), and the platinum mesh as a counter electrode. The sample area submitted to electrochemical investigations was 0.50  $cm^2$ ; it was limited by the geometry of electrochemical cell. The volume of electrochemical cell was 50 ml. The  $Ag|Ag_2SO_4$  reference electrode was prepared in accordance with the methodology presented elsewhere [36,37] in order to avoid chloride contamination. Chronovoltammetry served as a tool to define changes in the active surface area due to lapping. The scan rate was set between 5 and 100  $mV s^{-1}$ , while the polarization ranged from  $-0.6$  to  $+1.2$  V vs  $Ag|Ag_2SO_4$ . A solution of 5 mM  $K_4[Fe(CN)_6]$  + 0.5 M  $Na_2SO_4$  was used as an electrolyte. Ferri/ferrocyanide remains the most often used redox couple to investigate BDD electrodes, although a number of sources fairly report its lack of reproducibility if electrodes have different electrochemical history [38–40]. To avoid it, a new electrode was used for each subsequent measurement.

Download English Version:

<https://daneshyari.com/en/article/6471198>

Download Persian Version:

<https://daneshyari.com/article/6471198>

[Daneshyari.com](https://daneshyari.com)