Heterogeneous distribution of surface electrochemical activity in polycrystalline highly boron-doped diamond electrodes under deep anodic polarization

Jacek Ryl[a,*], Artur Zielinski[a], Robert Bogdanowicz[b], Kazimierz Darowicki[a]

[a] Department of Electrochemistry, Corrosion and Materials Engineering, Faculty of Chemistry, Gdansk University of Technology, 11/12 Narutowicza St., 80-233 Gdansk, Poland
[b] Department of Metrology and Optoelectronics, Faculty of Electronics, Telecommunications and Informatics, Gdansk University of Technology, 11/12 G. Narutowicza St., 80-233 Gdansk, Poland

A B S T R A C T

The surface homogeneity of boron-doped diamond electrodes is variable and depends on anodic polarization conditions. The differentiation factor is the gradual and localized change in surface termination. A series of measurements under different polarization conditions was performed in order to investigate the scale of this effect. Nanoscale impedance microscopy (NIM) revealed large variation of surface resistance in individual grains. Based on the obtained results, we claim that the level of electrochemical heterogeneity significantly depends on the crystallographic texture of BDD. Modification of boron-doped diamond surface termination under anodic oxidation is assumed to be a multistage process.

1. Introduction

The majority of boron-doped diamond (BDD) electrodes in use are polycrystalline material, characterized by various grain sizes and boron dopant concentrations, which are directly influencing both local and global electric properties of these electrodes. The heterogeneity in electron-transfer rates of hydrogen terminated BDD (HT-BDD) is assumed to be mostly affected by non-uniform distribution of dopant throughout the film, preferential sp^2-carbon contamination in the inter-grain regions structural defects as well as the grain and interstitial boundaries size [1–7].

Behavior of BDD electrodes becomes more complex under electrochemical treatment, because of the presence of sp^2-carbon microdomains, which undergo dynamic removal during cyclic polarization, thereby altering the overpotential of the oxygen evolution process [8,9]. Moreover, electrochemical treatment is a common procedure to acquire oxygen terminated (OT-BDD) electrodes [10–14]. HT-BDD possess much lower surface resistivity than OT-BDD due to the presence of a superficial conductive layer in hydrogenated diamond [10,12,15,16]. Anodic polarization influences the position of conduction and valence bands as a positive flat-band potential (E_{fb}) shift [17–21], hindering the charge transfer process by OT-BDD electrode, as revealed by impedance studies [10–12,22]. Still, several reports claim that extended polarization causes the dissociation of B–H pairs, and

increases conductivity [13,14]. The formation of various oxygenated functional groups on the electrode surface can alter the electrochemically active sites and electron transfer for different adsorbed compounds. For example, when utilized for electrocatalytic processes, HT-BDD typically allows more homogeneous distribution of deposited particles [14,23–25]. Available sources report that PtNP/OT-BDD electrodes are more resistant to fouling during anodic treatment [24], while others reveal lower mechanical stability of AuNP/OT-BDD [26]. The complex nature of NPs/BDD interaction and the role of electrode termination require further studies.

The uncertainty of the overall heterogeneity level of individual electrodes often leads to the irreversibility of electrochemical processes or the lack of data reproducibility between different groups, in particular when surface-sensitive redox couples are used, such as [Fe $(CN)_6]^{4-/3-}$ [1,8,12,27,28]. Due to its non-uniform nature [1,29] BDD can be classified as an electrochemically heterogeneous electrode [30,31]. The current response of such systems depends on the shape and the time of development of the diffusion field in the vicinity sites with different activity [32,33]. The patterned microelectrode experiments confirmed the existence of discrepancies between the obtained results on the actual active surface and the estimated geometric one [33].

Crystallographic orientation of individual grains differentiates the electrode homogeneity, affecting the uptake of boron from the plasma

* Corresponding author.
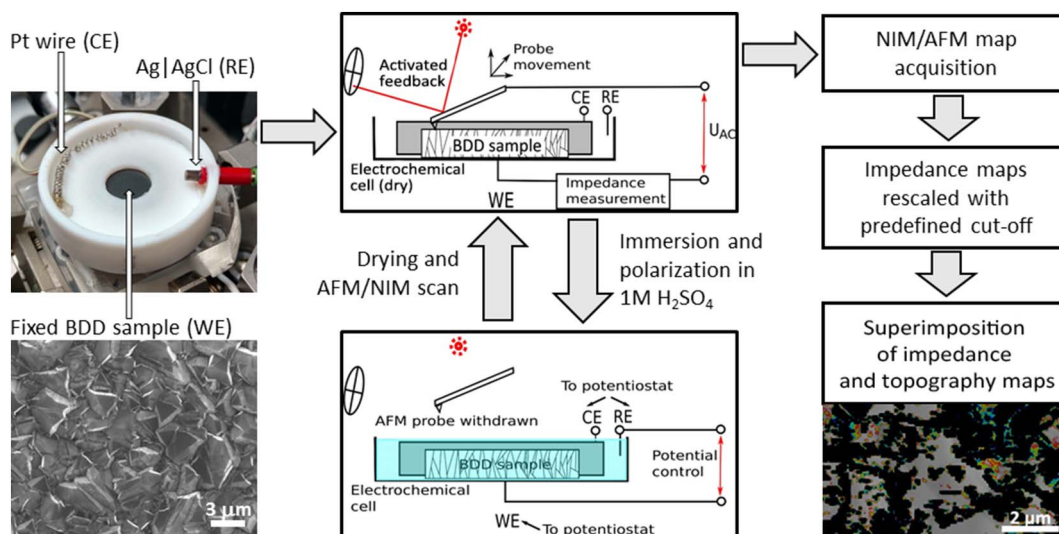 E-mail address: jacek.ryl@pg.edu.pl (J. Ryl).

Fig. 1. Schematic representation of the applied experimental procedure and image processing.

phase in the specific facet (100, 110 or 111). The boron atoms incorporate at various substitutional sites, mainly contributing to the (111) growth sectors [7,34,35]. On the other hand, the lowest acceptor concentration occurs on the (100)-oriented faces [36,37]. This behavior was claimed as a possible reason behind a multistage mechanism of the observed oxidation process under anodic polarization [7,23,38]. Generally, the reactivity of particular surface region or facet of electrode is determined by several factors like the specific work function, number of Fermi level electrons or surface functionality etc. Due to significant variations between individual grains, one should take into consideration not only local heterogeneities at the grain boundary areas, but also the variable ratio of grain surfaces, in particular if the electrochemical treatment is applied [1]. The present work aims at evaluating development in electrode heterogeneity in relation to different conditions of anodic oxidation. It should be noted that applied measurements provide only electrical characterization of the BDD surface. Still, the results may contribute to the deeper understanding of the charge transfer process kinetics. Until now, the polarization-dependent BDD heterogeneity has not been reported.

2. Experimental

The boron-doped diamond electrodes (attn. 10,000 ppm [B]/[C] in plasma) were synthesized in an MWPECVD system (SEKI Technotron AX5400S, Japan) on p-type Si wafers as reported elsewhere [39,40]. A 6 h growth period produced microcrystalline diamond of ca. 2 μm in thickness, dominated by (110) and (111) facets, containing also (100) oriented crystals revealed by morphologic investigation [41–44]. XRD and EBSD analysis show highly randomized orientation of investigated BDD layers with no dominant texture and pole figures showing weak correlation with the (110) facets (not shown here). The applied pretreatment consisted of exposure to hot aqua regia and subsequently to microwave hydrogen plasma (1000 W, 300 sccm) to obtain H-terminated surface and to etch sp^2-carbon phase impurities, as reported elsewhere [17,45].

We have utilized novel multifrequency nanoscale impedance microscopy (NIM), which is a variation of AC signal probing implemented in contact mode atomic force microscopy (AFM) [46,47]. An impedance spectrum is attributed to each pixel of topographic image, enabling the determination of resistance maps (a sum of tip/sample contact and material spreading resistance). A similar approach was described in detail elsewhere [4]. Investigated samples underwent a topographic scan with a force of 1.24 μN, using commercially available BDD-coated conductive probes CDTP-NCHR (Nanosensors, Switzerland) [3,48]. The

impedance and topography images were synchronously recorded. AFM tip shape quality was monitored by convolution measurements on TGT1 test sample [49]. Preliminary measurements show negligible impact of scanning procedure on HT-BDD surface resistance.

Prior to measurement, BDD samples were firmly mounted inside the electrochemical cell to ensure reproducibility of the analyzed area. The electrodes were immersed in 1 M H_2SO_4 and polarized under potentiostatic conditions for 20 min between the NIM scans. When the electrochemical treatment was applied, Ag|AgCl (+ 0.23 V vs SHE) served as a reference electrode, and platinum wire as a counter electrode. The polarization potential was equal to + 1.3; + 1.6; + 1.9; + 2.2 and + 2.5 V vs Ag|AgCl. Upon completion of anodic polarization, the electrolyte was poured out and the BDD electrodes were washed with deionized water, and then left to dry. The NIM scans were carried out consecutively to investigate changes in the electric properties of electrode surface. This procedure was repeated until each of the listed polarization potentials was imposed in ascending order.

Potentiostatic polarization was performed in the electrochemical cell (volume 2.5 cm^3) connected to NTegra Prima AFM system bipotentiostat (NT-MDT, Russia). The impedance analysis was performed in real time during the image acquisition process. The generation and acquisition of signal were performed by means of PXIe-4464 and PXIe-6124 cards (National Instruments, USA). Current sensing was performed with the use of SR 570 amplifier/filter (Stanford Research System, USA).

Once the NIM-derived maps were drawn, a threshold of 19.5 MΩ was applied to raise the contrast of resistance diversity between particular grains rather than (much larger variation) between the grain interiors and grain boundaries [1,4]. Finally, the topographic and resistance maps were superimposed for visualization purposes. The complete experimental procedure is schematically shown in Fig. 1.

High-resolution X-Ray Photoelectron Spectroscopy (XPS) measurements in C1s energy range were used to evaluate surface modification of Si/BDD electrodes using Escalab 250Xi (ThermoFisher Scientific, UK), equipped with Al-Kα source (spot diameter 650 μm). The energy step size and pass energy were 0.1 and 10 eV, respectively.

3. Results and discussion

AFM contour image (deflection) in Fig. 2a reveals the grain sizes and their distribution, while Fig. 2b–e presents the local resistance values obtained for one of the investigated BDD electrodes after consecutive anodic polarizations. The black areas on the NIM maps represent regions possessing resistance below the 19.5 MΩ threshold, and