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Electrochemistry Communications 8 (2006) 375–382
electrochemistry communications
www.elsevier.com/locate/elecom

Electrochemical characterization of mechanically implanted boron-doped diamond electrodes

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Received 15 November 2005; received in revised form 21 December 2005; accepted 21 December 2005
Available online 24 January 2006

Abstract

A new, low production cost, technique for the preparation of boron-doped diamond electrodes (BDD) is presented. The technique is based on mechanical implantation of BDD particles into a titanium substrate. The electrochemical characterization of low coverage mechanically implanted boron-doped diamond electrodes was performed using the $Fe(CN)_6^{4-/3-}$ redox couple and compared with the BDD thin-films electrodes. The interpretation of the recorded voltammetric responses was based on microelectrodes-array theory. The thickness of the diffusion layer, the spacing of particles and equivalent particle dimension was considered. Depending on the potential scan rate the linear or spherical diffusion with partial overlap was observed.

Keywords: Boron-doped diamond electrodes; Random microelectrodes-array; Mechanical implantation; Spherical diffusion

1. Introduction

Synthetic boron-doped diamond electrodes (BDD) are characterized by high anodic stability, a wide working potential window and low and stable voltammetric background current in aqueous media [1,2]. For these reasons, the electrochemical behaviour of BDD electrodes have been investigated with the goal of developing applications in electrosynthesis [3–5], incineration of organic pollutants for wastewater treatment [6–8], water disinfection [9], preparation of powerful oxidants [10], recovery of heavy metals [11] and electroanalysis [12–15].

BDD thin-film electrodes, deposited on an appropriate substrate (p-Si, Ti, Nb, Ta, Mo, W) by chemical vapour deposition (CVD), are the most widely studied and well reported in the literature [16]. Two main techniques have been used for the CVD deposition; the hot-filament chemical vapour deposition and the microwave-assisted plasma-enhanced chemical vapour deposition [11,17]. Although these electrodes have shown excellent electrochemical performances, they have some limitations, mainly due to the complexity of the preparation procedure of the BDD films (900 °C in the presence of large excess of hydrogen). In a recent paper, an alternative technique has been proposed by Swain et al. [18] for fuel cell applications. In this method, BDD electrodes are produced by coating the diamond powder on Si substrate using a Teflon binder.

Recently a new preparation mode for BDD electrodes, named mechanically implanted boron-doped diamond electrodes (MI-BDD), has been proposed [19] for electrolysis with application in wastewater treatment and electrosynthesis. In this process, boron-doped diamond crystals are firstly prepared then mechanically implanted into a titanium substrate and finally an electrically non-conducting silicon based coating is applied in order to cover the space between the diamond crystals (Fig. 1) [19]. The main advantages of this technique are:

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doi:10.1016/j.elecom.2005.12.013

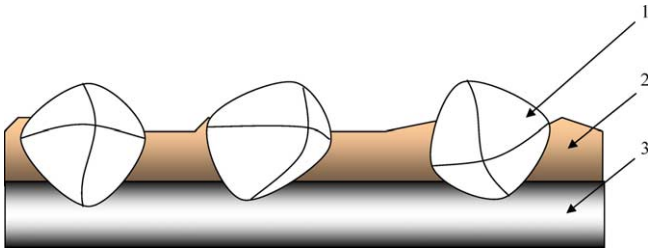

Fig. 1. Schematic representation of the mechanically implanted boron-doped diamond electrode (1) boron-doped diamond crystals (2) non-conducting silicon based coating (3) titanium substrate.

(a) Low production cost due to the fact that the preparation of diamond crystals is already a relatively cheap high volume technology [20].
(b) Easy preparation of large surfaces (order of square meters).
(c) Avoids problems inherent to the CVD deposition technique at 900 °C in presence of excess hydrogen (hydrogen embrittlement, phase transformation of the substrate, formation of non diamond impurities at the grain boundaries of the coating, formation of carbides at the substrate coating interface, difference in the thermal expansion coefficient between the substrate and the coating).
(d) Possibility to control the surface density of diamond crystals for an optimal utilisation of diamond particles.

In this work the electrochemical characterization of mechanically implanted boron-doped diamond electrodes (MI-BDD) has been investigated using the ferri-ferrocyanide $Fe(CN)_6^{4-/3-}$ redox couple and compared with the BDD thin-film electrodes, deposited on p-Si by the hot-filament chemical vapour deposition technique (Si/BDD). It has been found that the electrochemical response of low coverage electrodes (LC-MI-BDD) is different form that of Si/BDD (CVD), revealing rather microelectrodes behaviour. The main parameters such as thickness of diffusion layer δ; average distance between particles (d) and equivalent particle dimension (R) have been evaluated [21,22]. Taking all advantageous of microelectrodes behaviour, these electrodes can be applied for wastewater treatment or electrolysis. In a next paper the high coverage mechanically implanted boron-doped diamond electrodes (HC-MI-BDD) will be treated.

2. Experimental

2.1. Preparation of boron-doped diamond thin film electrodes on Si substrate (p-Si/BDD)

The boron-doped diamond thin film electrodes were synthesized at the Centre Suisse de Electronique et Microtechnique SA (CSEM) Switzerland by the hot-filament chemical vapour deposition technique using a low-resistivity p-Si substrate (p-Si/BDD). The filament temperature was 2500 °C and that of the substrate was about 830 °C. The reactive gas was a mixture of 1% CH_4 in H_2 containing trimethylboron as a boron source. A gas flow of 5 $dm^3\ min^{-1}$ was supplied to the reaction chamber giving the diamond film growth rate of 0.24 $\mu m\ h^{-1}$. The thickness of randomly textured, polycrystalline diamond layer was about 1 μm with the grain size from 200 to 800 nm (doping level $2 \times 10^{20}\ cm^{-3}$).

2.2. Preparation of the mechanically implanted boron-doped diamond electrodes (MI-BDD)

The implanted boron-doped diamond electrodes have been synthesized at Pro Aqua GmbH, Niklasdorf, Austria. The conductive diamond particles (doping level $3 \times 10^{20}\ cm^{-3}$), with a particles size in the range from 100 to 150 μm, have been prepared by the high temperature high pressure technique [19]. The titanium substrate, before implantation, has been treated in boiling oxalic acid solution (10%) for 30 min in order to increase the surface roughness and to eliminate the surface oxide layer (TiO_2). The diamond particles have been implanted on the pretreated Ti substrate by rolling. All spaces between the diamonds particles were filled with electrical non-conductive silicon based coating Tyranno coat ST-100 Standard. Finally the electrodes were heated in argon atmosphere during 30 min at 350 °C and polished mechanically by a grinding machine until the tops of the diamonds were visible. More details concerning the preparation technique are given elswhere [19].

2.3. Electrochemical measurements

Electrochemical measurements were carried out in a single-compartment, three-electrode cell (50 ml) using an Autolab PGSTAT 30. The counter electrode was a Pt wire and the reference electrode was mercury sulphate electrode (MSE) $Hg/Hg_2SO_4/K_2SO_{4(sat)}$ (0.64 V vs NHE). The geometric electrode area (projected area) was 0.785 cm^2.

The measurements were performed at room temperature using 0.5 M H_2SO_4 as a supporting electrolyte. All solutions were prepared from deionized water, sulphuric acid (Fluka Chemie), $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]{\cdot}3H_2O$ (Merck).

3. Results and discussion

3.1. Morphological characterization

Fig. 2a and b shows SEM micrograph for both high and low coverage mechanically implanted boron-doped diamond electrodes respectively. In this work the low coverage mechanically implanted electrodes (LC-MI-BDD) will be investigated (Fig. 2b). In a next paper the high coverage mechanically implanted boron-doped diamond electrodes (HC-MI-BDD) will be treated.