Diamond & Related Materials 19 (2010) 1021–1026

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Transparent diamond microelectrodes for biochemical application

Z. Gao [a,*], V. Carabelli [b], E. Carbone [b], E. Colombo [a,b], F. Demaria [c], M. Dipalo [a], S. Gosso [b], Ch. Manfredotti [d], A. Pasquarelli [a], S. Rossi [a], Y. Xu [a], E. Vittone [d], E. Kohn [a]

[a] Institute of Electron Devices and Circuits, University of Ulm, Germany
[b] Department of Neuroscience and Nanostructured Interfaces and Surfaces Excellence Centre, University of Torino, Italy
[c] Institute of Optoelectronics, University of Ulm, Germany
[d] Experimental Physics Department and Nanostructured Interfaces and Surfaces Excellence Centre, University of Torino, Italy

ARTICLE INFO

Available online 17 March 2010

Keywords:
Diamond
Transparency
MEA

ABSTRACT

In this investigation a technology has been developed to use diamond electrodes in Micro Electrode Arrays (MEAs) on a transparent sapphire substrate, thus combining the outstanding electrochemical properties of boron-doped diamond electrodes (BDD) with the transparency needed for simultaneous fluorescence analysis. Nanodiamond films were grown on double side polished sapphire substrates by hot filament CVD (HFCVD) and Bias Enhanced Nucleation (BEN). A simple four microelectrode array (quadrupole) has been fabricated, fully characterized in optical and electrochemical properties, and tested with adrenal chromaffin cells, identifying amperometric spikes by the four recording diamond electrodes, corresponding to the oxidation current of catecholamine molecules.

1. Introduction

Boron-doped diamond electrodes have been extensively investigated for electroanalytical applications for many years and their characteristics well analyzed, especially their large potential window to water dissociation, their low background current and their high corrosion resistance, allowing high anodic overpotentials, out of reach of noble metal or glossy carbon electrodes [1,2]. High oxidation potentials are for example needed for the detection of organic molecules like phenol [3,4] or glutathione [5]. The low background current and the high corrosion resistance enable high sensor stability and reproducibility as well as a high signal to noise ratio [6,7]. Diamond electrodes use quasi-metallic boron doping levels (above 10^{20} cm^{-3}) to enable high electron transfer rates. They can be functionalized in various ways by nano-patterning as well as by defined terminations, like H, O or F [8–10], and can thus be tailored to specific requirements. They are therefore ideally suitable for the use in Micro Electrode Arrays especially and applied to biochemical analysis [11,12]. Such arrays have been realized on Si substrates [13]. More recently a prototype grown on glass has been reported [14], which might allow simultaneous fluorescence and bioelectrical investigations, but the functional properties of this MEA where not yet described.

Diamond is a semiconductor with a wide bandgap and thus a transparency window between the far-IR and 225 nm in the UV. Moderate doping with boron is responsible for the blue color of natural stones, while high doping levels (10^{20} cm^{-3} and above) will result in black stones. To preserve the transparency of undoped diamond, the quasi-metallically doped electrode layers have to be of limited thickness. Therefore, in this study the electrode structure has been a stack of an undoped nanocrystalline diamond (NCD) support layer and an approximately 350 nm thin boron-doped electrode layer. In addition, the limited grain size, the surface roughness and possibly embedded graphitic phases of the NCD film can cause light attenuation [15–17]. NCD needs to be seeded with nanoparticles or nucleated by a nucleation layer, if grown on a non-diamond substrate. Here, Bias Enhanced Nucleation (BEN) has been chosen, needing a conductive carbon forming nucleation layer. In our case, this has been a thin plasma deposited Si-based layer [18]. This layer takes part in forming the diamond nanoclusters, which are then outgrown in the following step, and it may be widely consumed during this nucleation process [19]. Thus, this layer should be as thin as possible, even though it may still cause optical absorption.

NCD layers in the past have been deposited onto transparent substrates like sapphire, quartz and bio-glass and their transparency measured [15,20,21]. Although in general seeded by diamond nanoparticles, their absorption spectrum is quite similar to the one measured in this case. This indicates the possibility to maintain a high transparency by downscaling the electrode layer stack thickness while still maintaining "electrochemically grade" BDD electrode surface conditions, providing low background current, a wide potential window of water dissociation and high corrosion resistance. In turn, this has been one of the incentives for this study eventually allowing simultaneous fluorescence measurements from the backside of the sample and amperometric measurements from the front side.

* Corresponding author. Tel.: +49 731 502 6181; fax: +49 731 502 6155.
E-mail address: zi-yao.gao@uni-ulm.de (Z. Gao).

0925-9635/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2010.03.014