



Fabrication and characterization of boron doped diamond microelectrode arrays of varied geometry



Cory A. Rusinek^{a,*}, Michael F. Becker^a, Robert Rechenberg^a, Thomas Schuelke^{a,b}

^a Fraunhofer USA Inc., Center for Coatings and Diamond Technologies, East Lansing, MI 48824-1226, United States

^b Michigan State University, Department of Electrical and Computer Engineering, East Lansing, MI 48824, United States

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ABSTRACT

Boron doped diamond (BDD) is a well-known electrode material that exhibits an excellent electrochemical potential window with very low background current. With this, microelectrodes and microelectrode arrays (MEAs) have been found to even further lower background currents without compromising sensitivity. As such, BDD MEAs are excellent electrode materials for a variety of electroanalytical applications, capable of multi-mode detection. We fabricated BDD MEAs adapting traditional semiconductor microfabrication processes; the resulting MEAs were patterned in different geometries to find an optimum electrochemical response, depending on the application. This is demonstrated using 4 different MEA geometries of different size and spacing using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), where the charge transfer resistance (R_{ct}) increases as the electrodes are farther spaced from one another. Excellent sigmoidal voltammogram shape in CV was obtained for each BDD MEA geometry. BDD MEAs spaced farther from one another were found to give better resolution from the background in fast scan cyclic voltammetric measurements of dopamine due to the decrease in the double layer capacitance (C_{dl}) as verified with EIS. This work furthers the understanding of BDD MEAs and their pertinence to sensitive electroanalytical techniques.

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1. Introduction

Boron doped diamond (BDD) has emerged as an excellent electrochemical tool, applicable to a variety of applications including wastewater treatment, spectroelectrochemistry, heavy metal sensing, and *in vivo* neurotransmitter detection, among others [1–6]. BDD has two key advantages over other electrode materials such as gold, platinum and glassy carbon: the largest electrochemical potential window and small background current, allowing for increased signal-to-noise ratios. Other beneficial material characteristics include its biocompatibility, high chemical resistance and resistance to fouling [7,8]. In addition, BDD can be fabricated and patterned in various ways, including microfabrication as individual microelectrodes or microelectrode arrays. The combination of BDD's intrinsic low background current with that of a microelectrode, a microelectrode array (MEA), or a nanoelectrode array (NEA) can provide excellent sensitivity as the current density can significantly increase [9–14]. Over the past decade, MEAs and NEAs have garnered significant interest and various fabrication methods have been reported [15–19]. This has included BDD MEAs (including modified BDD MEAs) and NEAs for sensing of numerous analytes including manganese (Mn^{2+}), arsenic (As^{3+}), lead (Pb^{2+}), hydrogen peroxide, hydrazine, nitrate, and dopamine, among others

[20–26]. These studies, however, were completed using BDD MEAs and NEAs of fixed geometry.

In this communication, we report a traditional BDD MEA fabrication method varying the individual electrode size and center-to-center spacing, including a study on the electrochemical performance of each geometry. Using cyclic voltammetry (CV), we observed excellent microelectrode behavior and sigmoidal voltammogram shape. We also compared the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) of each MEA geometry using electrochemical impedance spectroscopy (EIS). Lastly, we also report proof of concept using dopamine and fast scan cyclic voltammetry, obtaining sharp, quantifiable peaks with all BDD MEA geometries.

2. Experimental

2.1. Boron doped diamond microelectrode array fabrication

The MEA fabrication process consists of two distinct processing sequences on a 100 mm diameter silicon wafer; each processing sequence requiring a unique photo mask. In the first processing sequence, a dual layer of electrically insulating polycrystalline diamond (PCD) and electrically conducting BDD was grown onto the substrate utilizing microwave plasma assisted chemical vapor deposition (MWPA-CVD) reactors [27]. The resulting film thicknesses were 2.5 μm for the PCD layer and 4.5 μm for the BDD layer. Photolithographic processing is

* Corresponding author.

E-mail address: crusinek@fraunhofer.org (C.A. Rusinek).

used to pattern the diamond layers into individual areas, which later serve as substrate dies for individual MEAs. A patterned 2 μm thick aluminum layer serves as an etch mask and the diamond layers are dry-etched in a low pressure plasma system [28]. The individual BDD areas are fabricated to ensure complete electrical insulation of the fully processed electrode. In the second processing sequence, a 1.5 μm thick insulating layer such as silicon dioxide or silicon nitride is applied on top of the wafer, entirely enclosing the BDD areas. Subsequent photolithographic patterning of the insulating layer defines the final electrode structures. The same etcher as previously used for the diamond layers was used for the insulating layer etching where a patterned 4.5 μm thick SPR220 photoresist layer serves as an etch mask. As a final step, the individual MEAs are laser cut out of the wafer.

2.2. Materials and instrumentation

All electrochemical experiments (CV and EIS) were conducted using a custom-made glass cell consisting of a BDD MEA working electrode, a Ag/AgCl reference electrode (3.0 M KCl solution), and a platinum (Pt) wire counter electrode. The BDD MEAs were hexagonal patterns of the following geometries: 15 μm diameter \times 150 μm center-to-center spacing (15 \times 150), 15 μm diameter \times 200 μm center-to-center spacing (15 \times 200), 15 μm diameter \times 250 μm center-to-center spacing (15 \times 250), and 20 μm diameter \times 250 center-to-center spacing (20 \times 250). All CV and EIS measurements were performed with a CH Instruments, Inc. (Austin, TX) 660C potentiostat. For the CV and EIS measurements, a 2.5 mM, 1:1 mixture of $\text{K}_3\text{Fe}(\text{CN})_6$: $\text{K}_4\text{Fe}(\text{CN})_6$ in 1.0 M KCl solution was used. For the EIS measurements, the frequency range was set from 100 kHz to 1 Hz. For dopamine measurements, a 10 mM stock solution was diluted in pH 7.4 phosphate buffered saline (PBS) where appropriate. A scan rate of 300 V/s was used.

3. Results and discussion

3.1. Surface and electron transfer properties

The final photolithographic patterning step of BDD MEA fabrication is crucial to quantitative analysis of the material. Over or under-etching of the top insulating layer can cause the individual electrodes to vary in diameter which can effect several major parameters. Fig. 1A and B show SEM images of the 20 \times 250 MEA. The hexagonal MEA pattern shows no evidence of over or under etching. Fig. 1B shows a highly symmetrical individual BDD microelectrode well with the targeted 20 μm diameter, also indicative of proper etching. The well depth was 1.5 μm .

Diamond surface roughness and well depth were analyzed using a surface profilometer, resulting in a R_a of 60 nm and R_z of 500 nm. It should be considered that as the fabricated diamond layer grows, the surface roughness increases. Four point probe analysis of the BDD layer showed a sheet resistance of 1.5 $\text{m}\Omega\text{-cm}$, indicating a highly boron doped diamond layer.

To compare the electrochemical surface properties of the BDD MEAs as the geometry is changed, electrochemical impedance spectroscopy (EIS) measurements were executed and the data are shown in Fig. 1. For this communication, we focused on the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}). The frequency range was set to 100 kHz to 1 Hz for EIS measurements. This reduces the non-planar mass transfer effect observed at microelectrodes, enabling a Randle's circuit (inlay of Fig. 1C) to be used for a semi-infinite diffusion case. Fig. 1C shows Nyquist plots of each BDD MEA geometry. When comparing the electrodes of similar diameter but different center-to-center spacing, R_{ct} increases as the electrodes are farther spaced apart, while C_{dl} decreases. This is expected because as the electrodes are farther spaced from one another, the electrical double layer should be smaller and/or thinner.

This would then cause a slight decrease in the ionic strength at the surface of each individual microelectrode well in the array. As a result, a slight increase in resistance should be observed. This explains the increase in R_{ct} and decrease in C_{dl} from the 15 \times 150 geometry (442 Ω , 23 nF) to the 15 \times 250 geometry (582 Ω , 9 nF), as listed in Table 1. Also noted in Table 1, the 15 \times 200 and 20 \times 250 BDD MEAs have similar electrochemical performances in both CV and EIS as they both have a similar overall electrode area ($\approx 0.03 \text{ mm}^2$). R_{ct} and C_{dl} are nearly identical for both geometries but the slight increase in R_{ct} and subsequent decrease C_{dl} with 20 \times 250 could be due its larger edge-to-edge distance (230 μm) compared to 15 \times 200 (185 μm). This also suggests that the ratio of center-to-center spacing to individual microelectrode well diameter can predict the relative behavior of the BDD MEAs and where these ratios are similar, electrochemical performance should also be similar (20 \times 250 = 12.5, 15 \times 200 = 13.3). These resistance and capacitance values are not significantly different but do confirm that R_{ct} and C_{dl} are dependent on both the individual electrode well diameter and the center-to-center spacing of the MEA.

3.2. Cyclic voltammetry of BDD MEA geometries

To evaluate how the BDD MEA electrode geometry affects electrochemical performance, CV studies were conducted and the data are shown in Fig. 2. For the $\text{Fe}(\text{CN})_6^{3-/4-}$ CVs, each MEA was pre-treated in a 1.0 M H_2SO_4 solution where the potential was cycled from 0 mV to -2400 mV. This was done to create a predominantly hydrogen terminated BDD surface, which is optimal for electron transfer with $\text{Fe}(\text{CN})_6^{3-/4-}$ [3]. In Fig. 2A, a CV comparison is shown using 2.5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ with BDD MEAs of different microelectrode well diameters and center-to-center distances. Excellent steady state behavior is observed on each BDD MEA geometry and the electrodes with closer center-to-center spacing exhibit larger currents. This is a result of the increase in overall electrode area as the individual microelectrode wells are spaced closer together (as listed in Table 1). Due to similar surface area, the CVs in Fig. 2A for the 15 \times 200 and 20 \times 250 geometries nearly overlay one another and i_{ss} is almost identical. In addition to this, the electron transfer kinetics are nearly identical for all BDD MEA geometries as the steady state current is reached at the same potential in both the oxidation and reduction waves.

Fig. 2B shows a scan rate study of 2.5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ completed with the 15 \times 250 BDD MEA. A range of 5 mV/s to 1000 mV/s scan rates was completed and the results for the 5, 100, 1000 mV/s scan rates are shown. It can be seen from the 1000 mV/s scan rate that quantifiable voltammetric peaks are observed because the diffusion profile $(Dt)^{1/2}$ is smaller than the radius of the electrode [29–32]. With such short measurements, the potential is swept faster than the analyte can diffuse to the electrode surface and macroelectrode-like behavior is observed. However, as the scan rate is decreased to 100 mV/s, the sigmoidal CV shape appears because $(Dt)^{1/2}$ is now larger than the radius of the electrode [29–32]. As the scan rate is decreased to 5 mV/s, overlap of the diffusion profile of each microelectrode on the MEA can occur (transition from radial diffusion at each individual microelectrode to planar diffusion at the entire MEA surface) [32]. This can be seen in Fig. 2B as well where the capacitance is larger with the 5 mV/s scan rate than that observed at the 100 mV/s scan rate.

The featureless background current of BDD MEAs has significant potential for fast scan cyclic voltammetric (FSCV) measurements of neurotransmitters. To show this, we demonstrated a proof of concept using FSCV of dopamine in pH 7.4 PBS buffer (Fig. 2C & D). Voltammetric peaks are obtained for each BDD MEA due to the increased speed of the scan rate (300 V/s), as discussed above. It can be seen from Fig. 2C that as the microelectrode wells are spaced closer to one another, both current and capacitance increase (see EIS data in Table 1 above). For the 20 \times 250 geometry, the capacitance and background current were slightly higher than the 15 \times 250 values, but current measurements remained nearly the same. Although the current response is higher

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