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The effect of electrode size and surface heterogeneity on electrochemical properties of ultrananocrystalline diamond microelectrode

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ABSTRACT

We report here the effect of electrode size on electrochemical properties of boron-doped ultrananocrystalline diamond (UNCD) microelectrodes using electrochemical impedance spectroscopy (EIS). By reducing microelectrode size from 250-μm to 10-μm diameter (*D*), the shape of impedance spectra changes from linear line to two-arcs. The fitting of experimental data to electrochemical circuit model suggests that each arc likely corresponds to UNCD grains and grain boundary phases. The two phases become separable as a result of microelectrode size reduction. In addition, for $D \leq 100$-μm, microstructural and morphological defects/heterogeneities of grain boundaries and the presence of surface oxygen are also revealed in the spectra. The microelectrode size reduction specifically affect the impedance of the grain boundaries, *e.g.* for ultramicroelectrodes, UMEs ($D \leq 25$-μm), as the grain boundary impedance increases by ~30-fold. Thus, at UMEs, the grain–grain boundary properties are revealed more sensitively in the spectra. Atomic force microscopy, scanning electron microscopy, Raman spectroscopy and surface profilometry measurements were performed to study the influence of microfabrication on surface properties. A significant increase in surface roughness after microfabrication shows that heterogeneities as observed in the spectra are not only due to intrinsic UNCD properties but also arises from microfabrication.

1. Introduction

Recent advances in material engineering have driven significant progress in the development of new microelectrode technology for electrochemical sensing [1–3]. Analyte detection with high sensitivity and spatial–temporal resolution is generally achieved by reducing the size of the electrodes from micrometer to nanometer range [4]. Such electrodes are routinely fabricated by either using standard microfabrication techniques [5] (*top-down* approach) or employing nanomaterials [6] (*bottom-up* approach). The current gold standard microelectrode material are the noble metals, which exhibit fast electron-transfer kinetics and adequate sensitivity [7,8]. Unfortunately, the versatility of metal microelectrodes is tempered by increased background noise, surface oxidation and surface fouling. This results in rapid loss of analyte signals with time [9]. A promising alternative is to use carbon nanomaterials such as carbon nanotubes [10], carbon nanofibers [6,11] nanocrystalline diamond [12,13], ultrananocrystalline diamond [5,9,14–16] and graphene [17]. Among them, boron-doped diamond (BDD) exhibits excellent electronic, chemical and biological properties [18,19]. BDD is broadly classified into microcrystalline (MCD), nanocrystalline (NCD) and ultrananocrystalline diamond (UNCD) based on grain size. MCD and NCD surfaces are generally rough (arithmetic average of absolute values, R_a of ~50–1000 nm rms), whereas UNCDs with its unique nanoscale structure are inherently ultra-smooth (R_a of ~5–8 nm rms) with equiaxed grains and high-energy, mechanically-stable grain boundaries. UNCD films are grown at relatively low temperatures (300 °C–700 °C) on a wide variety of substrate materials, including small three-dimensional objects (*e.g.* wires). With the right surface chemistry, UNCD has proven to lessen non-specific adsorption of biomolecules [9,14,20–22]. Thus, UNCDs that could potentially mitigate surface biofouling problem is used in this study. One can also use (chemical)-mechanically polished MCD films with surface roughness similar to UNCD [23,24]. For ultrasensitive sensor development, several groups including ours have used microlithographic techniques to produce well-defined, reproducible microelectrode geometries on BDD films [5,25–27]. BDD coatings on microwires have been used for *in vitro* and *in vivo* neurochemical measurements [28,29].

The electrode kinetics of BDD is dependent on several factors such as (i) nondiamond carbon impurity phases, (ii) the surface termination (H *vs* O), (iii) the dopant type, level, and distribution, (iv) grain boundaries and other morphological/microstructural defects, and (v) the primary crystallographic orientation [30–32]. Extensive research has already been conducted on how some of these factors can be controlled during growth using *macro-sized* electrode films [18,26,28,31]. Nonetheless, there is no literature on how these factors alter the electrochemical properties of microfabricated microelectrodes. The current body of work covers methods to fabricate BDD microelectrodes and their basic

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electrochemical behavior [5,24,25]. But identifying the smallest microelectrode size that offers robust electrochemical performance with highest sensitivity and lowest damage to surrounding microenvironment (*e.g.* tissue) is critically needed for emerging applications such as chronic neurochemical monitoring.

In this article, we study the electrode size effect on electrochemical properties of UNCD microdisk microelectrodes by systematically varying their size to 250, 200, 150, 100, 50, 25 and 10-μm in diameter (*D*). Variations in the surface morphology and diamond film quality are monitored using scanning electron microscopy (SEM), atomic force microscopy (AFM), surface profilometry and Raman spectroscopy. Electrochemical behavior is obtained in 5 mM $Fe(CN)_6^{3-/4-}$ redox species in 1 M KCl solution using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Since, the main goal of this paper is to study the surface effects (including surface oxygen coverage) on diamond microelectrode response at different electrode sizes, we use $Fe(CN)_6^{3-/4-}$ redox couple because it is sensitive to surface chemistry and surface oxides of carbon materials [28,33].

The work reported here provides several new observations of the electrochemical properties of *micro-patterned* boron-doped UNCD films. First, for very small microelectrodes ($D \leq$ 50-μm), two distinct arcs in the Nyquist plot and corresponding two phase peaks in the Bode phase plot are observed. Each arc likely correspond to impedance due to diamond grains (*G*) and grain boundaries (*GB*) phases. Thus, as the microelectrode size is reduced, the two phases of UNCD become separable electrochemically. Second, *GB* impedance drastically increased for microelectrodes with $D \leq$ 100-μm. The circuit fitting of impedance data suggests that at these electrode dimensions, microstructural and morphological defects/heterogeneities at *GB* behave as pores similar to defects in coatings. These defects play a significant role in controlling the conductivity of grain boundaries. Further understanding of these defects and their influence on charge carrier pathways will assist in precisely controlling the electrochemical properties of grains and grain boundaries. Third, surface oxygen functionalities are revealed only in the impedance spectrum of ultramicroelectrodes UME ($D \leq$ 25-μm), where current density is high. Thus, at UMEs, one expects a very sensitive impedance response to surface changes, *e.g.* surface oxidation, surface fouling and/or chemical modification. Fourth, AFM, Raman, SEM and profilometry demonstrate microfabrication generated surface roughness increase (~40%) introduce microstructural and morphological heterogeneities.

2. Experimental

2.1. UNCD microelectrode array microfabrication

Four inch silicon wafers with a surface coating of 1-μm thick thermal SiO_2 (Wafer World Inc.) were used to grow a 2-μm thick UNCD film by Hot Filament Chemical Vapor Deposition (HFCVD) technique [5,16,33]. UNCD film is synthesized by CH_4/H_2 gaseous mixture with a ratio of ~5%. The boron doping was realized by introducing Trimethylboron (TMB) gas with a fixed C/H ratio of ~3000 ppm to achieve the minimum film resistivity of ~0.08Ω·cm as measured by a 4-point probe from witness wafer (Pro4, Lucas Labs, Gilroy, CA). The filament at deposition glows with approximately 2200 °C, which effectively cracks gas molecules into diamond precursors before they approach the substrate. The substrate temperature of a witness wafer (defined as a reference or a control wafer used for post-deposition characterization) was measured as 700 °C. The average roughness of the UNCD film was <10 nm rms based on AFM measurements (Digital Instruments, Santa Barbara, CA). For MCD films, the reactor setup and processes are similar to those reported previously by Hongjun et al. [34]. To keep the grain size larger in MCD films, the C/H gas ratio is maintained at or below 5% [35]. The MCD are grown at ~800 °C with average grain size ~100 nm and film resistivity ~0.04 Ω·cm. Optical microlithography was used to fabricate 21 chips per wafer. Each chip was micro-patterned into nine individually addressable disk microelectrodes of varying diameters (250, 200, 150, 100, 50, 25 and 10-μm) in a 3 × 3 microelectrode array (MEA) format (Fig. 1a, details described elsewhere [5]). Note: For simplicity, these values represent the "window" dimensions of the chrome-mask used to micro-pattern the UNCD microelectrodes. The actual values of the microelectrode diameter or size are slightly larger than the chrome-mask "windows" (details in Section 3.1). Briefly, the microfabrication steps were as follows: (a) deposit a 500 nm thick SiO_2 layer using Plasma Enhanced CVD (PECVD) on UNCD coated silicon wafer; (b) pattern oxide using a 1.7-μm thick positive resist using chrome-mask 1; (c) wet etch the oxide in 10:1 buffered oxide etchant for 15 min; (d) dry etch the UNCD with reactive ion etching (ICP-RIE) of O_2/SF_6 gas mixture through the oxide hard mask formed in the previous steps to form MEAs, electrical contact pads and the electrical lines between them; (e) deposit another 500 nm thick SiO_2 PECVD film; and (f) finally wet etch SiO_2 to open up only the UNCD microelectrodes and the contact pads using chrome-mask 2. The final SiO_2 film was 1-μm thick and found to be adequate to passivate the underlying UNCD form the electrolyte solution.

2.2. Morphological and structural characterization

The surface morphology of the UNCD was examined using field-emission scanning electron microscope (FESEM: Hitachi S-4800). In addition, the films were further characterized by Raman spectroscopy (Control Development 2DMPP with λ: 532 nm) and atomic force microscope (Agilent AFM/SPM-5420).

2.3. Reagents and chemicals

All chemicals were reagent grade and purchased from Sigma Aldrich Chemical Co. The chemicals were used as received unless otherwise specified. Deionized (DI) water was prepared using a three-filter purification system from Continental Water Systems (Modulab DI recirculator, service deionization polisher). Buffered oxide etchant was CMOS electronic grade (from MicroChem, Inc.).

2.4. Electrochemical measurements

All EC experiments were carried out with an Autolab potentiostat (PGSTAT 302N, Metrohm USA) in a three-electrode setup using a Pt coil (Alfa Aesar) counter-electrode and a saturated calomel electrode (SCE, Accumet, New Hampshire, USA) as the reference electrode. The potentiostat was equipped with Frequency Response Analyzer 2, ECD and Multiplex modules and Nova 1.10.3 software. The UNCD MEA was used as the working electrode. The microelectrode surfaces were exposed to the solution and sealed with a 4 mm diameter O-ring in a Teflon cell. For each sensor array chip, the electrical isolation of the pads was checked using a two-point probe multimeter. This ensures the integrity of the SiO_2 passivation, which is essential for stable sensors. Prior to characterization, MEAs were briefly sonicated in ethanol for 30 s and dried in nitrogen. Cyclic voltammograms (CVs) were recorded between −1.0 and +1.2 V *vs* SCE with a scan rate of 100 mV/s. The EIS spectra were recorded between 100 kHz and 100 mHz at 10 mV ac signal amplitude (rms value) at open circuit potential (OCP). All values in Nyquist plots are normalized to the geometric area of the microelectrodes. All measurements were carried out in a solution of 5 mM $K_4Fe(CN)_6$/5 mM $K_3Fe(CN)_6$ in 1 M KCl. All solutions were freshly prepared on the same day of the experiment. All experiments were replicated at least 8 times ($n = 8$) using four different UNCD chips.

3. Results and discussion

3.1. Cyclic voltammetry measurements

Surface characterization using SEM (Fig. 1a) and optical microscopy (data not shown) showed no major defects and/or contamination of microelectrode surfaces. SEM images show the microelectrode sizes