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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 $D = 100\text{-}\mu\text{m}$, 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 ($D = 25\text{-}\mu\text{m}$), 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.

Keywords

Diamond; Nanocrystalline; Electrochemical; Impedance spectroscopy; Kinetics; microelectrode

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

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Conflict of interest

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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 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- μ m 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 $\text{Fe(CN)}_6^{3- / 4-}$ 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 $\text{Fe}(\text{CN})_6^{3-/4-}$ 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 ($D = 50\text{-}\mu\text{m}$), 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 $D = 100\text{-}\mu\text{m}$. 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 ($D = 25\text{-}\mu\text{m}$), 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 ($\sim 40\%$) introduce microstructural and morphological heterogeneities.

2. Experimental

2.1. UNCD microelectrode array microfabrication

Four inch silicon wafers with a surface coating of $1\text{-}\mu\text{m}$ thick thermal SiO_2 (Wafer World Inc.) were used to grow a $2\text{-}\mu\text{m}$ 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 $\sim 5\%$. 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 $\sim 0.08\Omega\text{-cm}$ 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 $\sim 800^\circ\text{C}$ with average grain size $\sim 100\text{ nm}$ and film resistivity $\sim 0.04\Omega\text{-cm}$. 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 $10\text{-}\mu\text{m}$) 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 SiO₂ 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 O₂/SF₆ 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 SiO₂ PECVD film; and (f) finally wet etch SiO₂ to open up only the UNCD microelectrodes and the contact pads using chrome-mask 2. The final SiO₂ film was 1-μm thick and found to be adequate to passivate the underlying UNCD from 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 SiO₂ 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 K₄Fe(CN)₆/5 mM K₃Fe(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 are slightly larger than the “window” dimensions of the chrome-mask used to generate the microelectrodes. For 250- μm to 25- μm microelectrodes, a deviation of up to 10% was observed. For 10- μm microelectrode, a deviation of up to 25% was observed. This is expected because to ensure the “windows” are fully developed into a proper microdisk and to produce a clean microelectrode surface that is free from SiO_2 residues and/or contamination, the etching process is usually carried out for a little longer time. This results in a somewhat larger microelectrode size. For UNCD microelectrodes used in this study, the surfaces are free of graphitic soot that are normally present after the diamond growth process and oxygen terminated due to exposure to BOE and other strong chemicals during microfabrication. Therefore, the role of oxygen-terminated grains, grain boundaries, and the morphological and microstructural defects at those grain boundaries becomes more influential on the electrode response. Fig. 1b shows the overlay of cyclic voltammograms (CVs) of UNCD microelectrodes used in this study. All nine microelectrodes in any given chip were functional, *i.e.* a 100% yield was achieved ($n = 8$). Good reproducibility in electrochemical signals were observed for the microelectrodes, based on the variability in CV parameter values. Variability of $\sim 5\%$ is seen for the forward “anodic” CV current ($I_{a,\text{exp}}$), peak potential separations (E_p) and $|E_{3/4} - E_{1/4}|$ ($E_{3/4}$ and $E_{1/4}$ are the potentials where $I = 3I_{ss}/4$ and $I = I_{ss}/4$; I_{ss} being the steady-state limiting diffusion current for UMEs) were observed ($n = 8$). Table 1 summarizes the average experimental values for different sized microelectrodes ($n = 8$).

The voltammogram shape changes from peak-shape to S-shape curve as the microelectrode size reduces, which suggests the dominance of radial diffusion at smaller microelectrodes. This is expected because at smaller (ultra) microelectrodes, the current density is larger than for a pure linear diffusion due to very high mass transfer rates and “edge effect”. Studies show that E_p and the associated slope of the cyclic voltammogram could be a good CV indicator to study electrode reaction rates [31,36]. For $D = 50\text{-}\mu\text{m}$, the voltammograms are peak-shaped and thus, E_p was used to describe the electrode kinetics. For $D = 25\text{-}\mu\text{m}$, the voltammograms are steady-state and thus, Tomeš criterion of reversibility ($|E_{3/4} - E_{1/4}|$) was used to describe the electrode kinetics. The E_p value of $\text{Fe}(\text{CN})_6^{3-/-4-}$ in KCl at the diamond surface is quite variable and can range from 60 mV to 450 mV [28,33]. For UNCD microelectrodes with $D = 50\text{-}\mu\text{m}$, higher E_p values ranging from 102 mV to 164 mV were noted (Table 1). For UNCD UMEs, the $|E_{3/4} - E_{1/4}|$ values were 91 mV and 97 mV for 25- μm and 10- μm microelectrodes, respectively. This increase (or deviation) in E_p values from the theoretical value of 59 mV for $\text{Fe}(\text{CN})_6^{3-/-4-}$ (a $1e^-$ redox reaction) is expected from diamond films that are oxygen terminated [30]. All of the microelectrodes were grown and exposed to similar microfabrication conditions, and therefore have similar surface termination, dopant level/distribution, grain boundaries, morphological and microstructural defects, and the primary crystallographic orientation. As the extrinsic and intrinsic material

properties remain same for all the microelectrodes, their kinetic rate constant also remains the same.

3.2. Effect of buffered oxide etchant (BOE) on UNCD surface properties

Numerous studies have reported the electrical heterogeneity in micro- and (ultra)nanocrystalline diamond electrodes [30,33,38–40]. The literature on microfabrication-induced surface heterogeneity is sparse. So, we studied its effect by treating UNCD with 1:10 BOE for 10 min, which represents the last microfabrication step. Being corrosive, we expect BOE to alter the surface morphology/microstructure and introduce surface defects. Raman spectroscopy showed M-shaped Raman signature of UNCD [34] was preserved with no significant change in the intensity of the peaks after the BOE treatment (Fig. 2e). The Raman spectrum consists of peaks at 1150, 1310–1355, 1470 and 1560 cm^{-1} . The two major peaks 1310–1355 and 1560 cm^{-1} represent a broad combination of D-band (disorganized graphite) and the diamond peak at 1332 cm^{-1} , and G-band (crystalline graphite), respectively [34]. AFM measurements showed a change in the surface morphology to a line-granular structure after the treatment (Fig. 2b, d). This might be due to the selective chemical etching of GB, which reveals the line-granular grain structure. Surface profilometry showed a corresponding increase in average surface root-mean-square (rms) roughness from 9.5 nm to 14.7 nm rms ($n = 8$, 3–5% variation in data values) after the treatment. Even though we expect this high surface roughness to be present in all microelectrode sizes, again their influence on electrochemical properties is found to be significant at smaller microelectrodes. Thus, surface properties and defects of UNCD grains and grain boundaries, which could be significantly altered during microfabrication should also be considered during material design and application development of UNCD UMEs. This conclusion agrees well with the electrochemical impedance studies performed on these microelectrodes (details in the next section).

3.3. Electrochemical impedance spectroscopy measurements

The shape of the impedance spectra (Nyquist plots) changes as the size of the UNCD microelectrode is reduced (Fig. 3). The spectra can be broadly classified into three types, where each type of spectra exhibit unique characteristic properties. *Note:* Experiments were performed in replicates ($n = 8$) from 4 different chips. The general behavior of the spectra is very reproducible for any sized microelectrode. For example, Fig. 4 demonstrates the high reproducibility of impedance data collected from 25- μm microelectrodes ($n = 8$). Additionally, the values of circuit elements showed a small difference of 1–5%, which ensures that the conclusions drawn are sound and statistically significant. Therefore, we only report typical spectra and circuit element values in Tables 2–4.

The spectra of the first set of microelectrodes of sizes 250- μm , 200- μm and 150- μm are similar (henceforth called spectra 1, Fig. 3a). The spectra of 250- μm and 200- μm consist of a very small arc at very high frequencies, followed by a big arc at low frequencies, and that of 150- μm consists of a relatively small arc at very high frequencies, followed by a big arc. $[R_s(C[R_{ct}Q])]$ is the equivalent circuit that fits well to the experimental data. The four elements of this fitted circuit are solution resistance (R_s), capacitance (C), charge transfer resistance (R_{ct}) and constant phase element (Q) and the values are shown in Table 2. The R_s

is mainly due to electrolyte and does not vary much for microelectrodes of different sizes. Diamond grains are mainly comprised of highly ordered, sp^3 -bonded carbon atoms, where each carbon atom is tightly bonded to four other atoms. Due to such strong bonds, the grains have fewer number of impurities and defects [41,42]. Thus, the surface of grains is chemically homogeneous and has a single RC time constant. Therefore, capacitance in the circuit can be attributed to grains. Conversely, grain boundaries comprise of nondiamond carbon impurities, *i.e.* highly disordered, sp^2 -bonded carbon atoms. It is generally believed that a majority of boron dopants, impurities and defects reside at or near grain boundaries [35,43,44]. Such a surface is chemically, microstructurally and morphologically heterogeneous and causes RC time constant dispersion, which is variation along the electrode surface of reactivity or of current and potential. The presence of time constant dispersion is modeled by constant phase element (CPE). Thus, CPE in the circuit is attributed to grain boundaries. In our previous studies, [5] we demonstrated a similar two-phase response of 200- μm UNCD microelectrodes. However, the two phases were unseparable at such large-sized microelectrodes. As electrode size reduces from 250- μm to 10- μm , the capacitance of grains decreases. However, for 250 and 200- μm microelectrodes, the capacitance of grains remains almost the same and also has a lower value compared to smaller-sized microelectrodes. This could be possibly explained in terms of variability in boron uptake and microfabrication processing. It is well-known from the work of Unwin et. al and others that boron uptake is nonuniform across the electrode surface [38,45]. This nonuniformity in boron uptake in the grains causes a large variation in the grain conductivity. Hence, the microelectrode with high boron uptake in the grains exhibits more conductance, *i.e.* low impedance and high capacitance. Therefore, the low capacitance values observed in larger microelectrodes could be due to factors such as low boron uptake and microfabrication induced surface heterogeneities. The capacitance of the grains for $D = 150\text{-}\mu\text{m}$ to $10\text{-}\mu\text{m}$ decreases consistently with the electrode area and satisfies the Helmholtz model.

Next, the circuit element R_{ct} is due to both grains and grain boundaries. As shown in the Table 2, the value of R_{ct} does not change significantly as the electrode size is reduced. The Q due to grain boundaries decreases by 2.5 times for the 150- μm microelectrode, but still remains in the μmho range. This suggests that the resistivity of the GB phase increases as a result of reduction in microelectrode area. Here, the values of circuit elements may not depict the exact values of the physical properties, but nevertheless provide a good qualitative understanding of how the electrochemical activity responds to electrode size changes.

The second type of spectra (henceforth called spectra 2, Fig. 3b) is for microelectrodes of sizes 100- μm and 50- μm . With a significant reduction in diameters, spectra 2 is quite different from spectra 1. The fitted circuit [$R_s(C[R_{ct}(R_{GBD}Q)])$], is similar to the one used for fitting impedance data to a polymer-coated metal surface [46]. This circuit is very commonly used to detect defects or pores due to delamination in surface coatings [47–49]. The circuit has five elements, namely R_s , C , R_{ct} , Q and solution resistance due to GB defects (R_{GBD}). In this study, the GB and the microstructural defects at or near the GB collectively behave similar to a pore, *i.e.* it represents a heterogeneous rough surface that causes an increase in the impedance. In the literature, several models have been developed to describe a pore [50,51]. The impedance spectra of pore models have a component which can be approximated by a CPE of $N = 0.5$. In Tables 1 and 2, the N value becomes approximately

half when the *GB*/defects start to behave as a pore. This value of $N = 0.5$ further confirms the pore-like behavior of UNCD *GB*/defects. In addition, the impedance of grain boundaries from the circuit of spectra 1 is given by Eq. (1):

$$Z_{GB} = \frac{1}{Q(j\omega)^N} \quad (1)$$

Here, Q is constant phase element, N is a parameter ($0 < N < 1$) and ω is the frequency.

The impedance of grain boundaries from the circuit of spectra 2 can be given by Eq. (2):

$$Z_{GB} = \frac{R_{GBD}}{1 + R_{GBD}Q(j\omega)^N} \quad (2)$$

From Eq. (1), it is clear that the impedance of grain boundaries is mainly imaginary and varies at low and high frequencies. However, the impedance of grain boundaries as shown in Eq. (2) is quite different from the impedance in Eq. (1). According to Eq. (2), at low frequencies, the impedance of grain boundaries is real and equal to the resistance due to *GB*/defects (R_{GBD}). The denominator of Eq. (2) is simply 1 at low frequencies because $1 \gg R_{GBD}Q(j\omega)^N$ and the imaginary part can be neglected. Thus, the impedance due to *GB* at low frequencies is real and simply behaves as a resistor of about MΩs called as *GB* defect resistance or pore resistance. However, at high frequencies, the impedance of grain boundaries in Eq. (2) ($1 \ll R_{GBD}Q(j\omega)^N$), is the same as that for the grain boundaries in Eq. (1). This is because at high frequencies, the signal does not penetrate the pore, and thus provides the impedance of the surface of the pore. However, at low frequencies, the signal gets sufficient time to penetrate the pore and thus, provides the resistance of the pore.

Interestingly, the effect of nondiamond carbon and defects on the *GB* impedance and its pore-like behavior is revealed only in the impedance spectrum of $D = 100\text{-}\mu\text{m}$. The increase in impedance of *GB* by ~30-fold as observed in the decrease of constant phase element (Q) from $Q = 13.2\text{ }\mu\text{mho}$ to $0.44\text{ }\mu\text{mho}$ of the fitted circuit (Tables 2 and 3) and appearance of R_{GBD} could be due to *GB*'s inability to conduct the vast majority of the current due to the high current density and the "edge-effect". Further this can be seen as blockage of carrier pathways arising from their scattering at the *GB* defects due to high current density. The conduction mechanism, which is also described as transport of charge carriers in UNCD is not well understood [52,53]. It is generally believed that there are several pathways that lead to conduction in grains and grain boundaries [44,49,52]. One of the pathways in grain boundaries is due to the hopping of charge carriers between acceptors [42]. Thus, addressing critical questions such as What is the role of *GB* defects in electron scattering?, What are the charge carrier pathways in grain and *GB* phases? and What are the critical parameters that control the conductivity in UNCD microelectrodes? would be key towards developing applications for such nanomaterials. However, from this study, it is clear that these (ultra)microelectrodes could be an important investigative tool to study UNCD conduction mechanism.

By further reducing the electrode size to $50\text{-}\mu\text{m}$, the Nyquist plot shows two distinct arcs. One of the arcs is likely from grains and the other from grain boundaries. These two arcs

become more prominent as the electrode size is reduced further. Also, corresponding to these two phases in Nyquist plot, two distinguished phase peaks, one at high frequency and the other at low frequency are observed in the Bode phase plot. The phase peak (phase angle θ of 34°) at a frequency of 24.4 kHz is sharper and it is likely from grains. While, the phase peak (θ of 30.8°) at a lower frequency of 1.67 Hz is broader and mainly due to heterogeneity (*i.e.* CPE) and it is most likely from grain boundaries. Thus, grains participate in the charge carrier transport at higher frequencies whereas grain boundaries participate at lower frequencies. The R_{ct} of 50- μm microelectrode is ~ 4 times larger than that of 100- μm microelectrode. By reducing the microelectrode size, the exchange current I_0 , which depends on the electrode area reduces ($I_0 = nFAK^0[C]$, where n is the number of electrons transferred per molecule of the redox probe, F is Faraday constant, A is electrode area, K^0 is heterogeneous electron transfer rate constant, $[C]$ is bulk concentration)[37]. This reduction in I_0 appears in terms of an increase in charge transfer resistance, R_{ct} ($R_{ct} = RT(nFI_0)^{-1}$, where R is universal gas constant, T is temperature). Since R_{ct} is inversely proportional to the electrode area at OCP, the $4\times R_{ct}$ increase witnessed at 50- μm microelectrode could be due to the corresponding one-fourth reduction in the electrode area. It is interesting to see that the circuit element has predicted such a precise increase in the R_{ct} value. Also, the capacitance of the grains of the electrode decreases with area as shown by the circuit values in Table 3.

The third type of spectra (henceforth called spectra 3) was experimentally fitted to EIS data collected from ultramicroelectrodes (UMEs, $D = 25\text{-}\mu\text{m}$ and $10\text{-}\mu\text{m}$). These UMEs, which exhibited a steady-state cyclic voltammogram have characteristics similar to other microelectrodes. Again, the Nyquist plot shows that the two arcs are more separable now (Fig. 3c). To further confirm that the two separable arcs in Nyquist plot are unique to polycrystalline materials with distinct phases, we compared the impedance characteristics of 10- μm UNCD UME to a 10- μm MCD and 10- μm platinum metal UME (Fig. 5). The two-arc behavior was observed in all three polycrystalline materials, albeit with different degrees of distinguishability (UNCD N MCD N Pt). This is expected because the two phases in the UNCD are very distinct in terms of their electrochemical activity when compared to the MCD or Pt.

Next, in the bode phase plot (Fig. 6), the phase peak due to grain boundaries is suppressed. This might be due to the fact that it has become more resistive (confirmed by a high impedance value in bode modulus plot) and does not contribute much to conductivity at lower frequencies. Whereas, the peak due to grains is shifted, and its phase angle value is ~ 2 -fold than that of grains in the 100- μm and 50- μm microelectrodes. A new circuit that fits well to the experimental data of UMEs, $[R_s(C_{ot}R_{ov})(C[R_{ct}(R_{GBD}Q)])]$ (Table 4).

The fitted circuit comprises of seven elements with the additional capacitance (C_{ot}) and resistance (R_{ov}) coming from the surface oxygen terminated functional groups [51] along with the pore circuit. Since all the microelectrodes experienced similar microprocessing conditions, it is more likely that they also sustained similar surface oxidation. However, only the impedance spectra of UMEs reveal the presence of surface oxygen. Thus, one expects the impedance values at UNCD UMEs to respond more sensitively to any surface changes or modifications. This electrode-size dependence of impedance sensitivity could be attractive

for ultrasensitive biosensing applications. Specifically, the implications for biosensing are: (i) the distinction between the impedance of grain and grain boundaries at smaller microelectrodes assists in identifying the signal from noise. Because the probes-target are specifically attached to the grains whereas non-specifically adsorbed biomolecules are preferentially present at grain boundaries. Therefore, the change in the impedance of grains is the detection signal and the change in impedance of GB is simply noise; (ii) at smaller microelectrodes, the grain boundaries acquire high impedance which could reduce detection signal because of overall reduction in electrode conductivity. So, one has to tune the grain boundaries properties as well to enhance the signal; (iii) for chemical sensing (e.g. dopamine), the selectivity and reaction kinetics depend on the surface termination (oxidation) and surface fouling of the electrode material. The two-arc behavior will allow for the first time to evaluate the surface oxidation and fouling of grains and grain boundaries separately. This new understanding is important for advanced chemical sensing such as chronic *in vivo* neurotransmitter monitoring.

Finally, we correlate the absolute value of impedance ($|Z|$) with frequency (Fig. 6). At lowest frequency of 0.1 Hz, we found $|Z|$ to be at maximum. From the plot, it is quite interesting that as the microelectrode size reduces 10-fold from 250- μm to 25- μm , $|Z|$ increases ~ 10 -fold. Thus, we suggest an empirical relationship between $|Z|$ at the lowest frequency and microelectrode size, which is $|Z| \propto D^{-1}$ or $|Z| = B/D$, where B is the constant of proportionality. The constant B needs to be studied experimentally. This relationship implies that $|Z|$ at lowest frequency might lead to gaining important information about how much active electrode area contributes to impedance, which is a subject of our current studies.

4. Conclusions

The two main conclusions of the experimental investigation in this work are the following: (1) as the UNCD microelectrode size is reduced from 250- μm to 10- μm , impedance spectra changes to two arcs and each arc likely represents the impedance of grain and grain boundary phases, and (2) only for ultramicroelectrodes (UMEs, $D \leq 25\text{-}\mu\text{m}$), microstructural and morphological defects and surface oxygen groups are revealed in the spectra. This clearly demonstrate the effect of electrode size reduction on the electrochemical properties of UNCD microelectrode. Also, we note that, UMEs could be used as an investigative tool to study electrical and chemical properties of UNCD grains and grain boundaries phases separately. Additionally, a drastic increase in the impedance of grain boundaries (~ 30 -fold increase) is observed at UMEs. This implies that the conductivity of grain boundaries plays a critical role in the electrochemical response. AFM, SEM and profilometry measurements show that microfabrication processing induces heterogeneities and therefore one needs to consider surface pretreatments for application development.

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Fig. 1.

(a) SEM image of one of the chips showing the nine individually addressable 200-μm microelectrodes in 3×3 array format. The inset SEM image shows the UNCD surface morphology. (b) Cyclic voltammograms of UNCD microelectrodes of varying diameters (10, 25, 50, 100, 150, 200 and 250 μm). The inset shows the voltammograms of smaller size microelectrodes (c) The E_p values for different sized microelectrodes. The solution is 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 1 M KCl electrolyte. Scan rate is 100 mV/s. The scale bar in (a) is 200-μm and 1-μm (inset).

Fig. 2.

Effect of buffered oxide etchant (BOE) on UNCD surface morphology. UNCD film was exposed to freshly prepared 10:1 BOE. AFM images of surfaces with no treatment, (a,c) and 10 min treatment (b,d). The scan size is $25 \mu\text{m}^2$. (e) Raman spectra of UNCD microsurface before (black curve) and after 10 min BOE treatment (blue curve).

Fig. 3.

Nyquist plot of UNCD microelectrodes: (a) EIS spectra 1 for 250- μm (black dotted), 200- μm (green dotted), 150- μm (brown dotted). (b) EIS spectra 2 for 100- μm (orange dotted), 50- μm (red dotted). (c) EIS spectra 3 for 25- μm (gray dotted) and 10- μm (purple dotted). The inset in (c) shows the expanded view of 25- μm plot. The solid curves are fitted to experimental data. The electrolyte is 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 1 M KCl. 10 mV amplitude, 0.1 Hz–100 kHz.

Fig. 4.

Overlay of Nyquist plots of 25- μm UNCD microelectrodes. The eight spectra were collected from 4 different UNCD chips. The electrolyte is 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 1 M KCl. 10 mV amplitude, 0.1 Hz–100 kHz.

Fig. 5. Nyquist plots of 10- μm UNCD (blue), MCD (brown) and platinum (black) microelectrodes. The electrolyte is 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 1 M KCl. 10 mV amplitude, 0.1 Hz–100 kHz.

Fig. 6. Bode and Bode phase plots of UNCD microelectrodes: 250- μm (black), 200- μm (green), 150- μm (brown), 100- μm (orange), 50- μm (red), 25- μm (gray) and 10- μm (purple). The solid curves are fitted to the experimental data. The electrolyte is 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 1 M KCl. The inset shows the SEM image of MCD microelectrode surface. The scale bar is 1- μm .

Table 1

Cyclic voltammogram data (averaged, $n = 8$) from UNCD microelectrodes of varying sizes. The % variation of the data is 1–5%.

Microelectrode size, D [μm]	E_p [mV]	$ E_{3/4} - E_{1/4} $ [mV]	$I_{a,exp}$ [A]
250	123		1.0E-06
200	127		7.1E-07
150	102		4.1E-07
100	113		2.0E-07
50	164		5.2E-08
25 ^a		91	3.5E-08
10 ^a		97	1.6E-08

^aSteady-state voltammograms.

Table 2

Typical values of interfacial parameters of UNCD microelectrodes obtained by fitting $[R_s(C[R_{ct}Q])]$ circuit to experimental data. The % errors for R_s , C , R_{ct} , Q and N are 0–7%, 15–20%, 3–5%, 1–3% and 1–3%, respectively.

Microelectrode size, D [μm]	R_s [$\text{K}\Omega$]	C [pF]	R_{ct} [$\text{K}\Omega$]	Q [μmho]	N
250	7.6	350	14.4	13.2	0.44
200	15.4	302	15.3	9.1	0.44
150	9.7	751	21	5.0	0.48

Table 3

Values of interfacial parameters of UNCD microelectrodes obtained by fitting $[R_s(C[R_{ct}(R_{GBD}Q)])]$ circuit to experimental data. The % errors for R_s , C , R_{ct} , R_{GBD} , Q and N are 3%, 3–4%, 2–4%, 7–11%, 5–7% and 2–4%, respectively.

Microelectrode size, D [μm]	R_s [$\text{K}\Omega$]	C [pF]	R_{ct} [$\text{K}\Omega$]	R_{GBD} [$\text{M}\Omega$]	Q [μmho]	N
100	9	485	30.5	1	1.6	0.48
50	10.3	311	128	1.7	0.44	0.49

Table 4

Values of interfacial parameters of UNCD ultramicroelectrodes obtained by fitting $[R_s(C_{ot}R_{ot})(C[R_{ct}(R_{GBD}Q)])]$ circuit to experimental data. The % errors for R_s , C_{ot} , R_{ot} , C , R_{ct} , R_{GBD} , Q and N are 0%, 6–12, 7–8%, 2–4%, 4–8%, 5–7%, 9–12% and 4–7%, respectively.

Microelectrode size, D [μm]	R_s [$\text{K}\Omega$]	C_{ot} [pF]	R_{ot} [$\text{K}\Omega$]	C [pF]	R_{ct} [$\text{K}\Omega$]	R_{GBD} [$\text{M}\Omega$]	Q [nmho]	N
25	11.7	179	25.6	165	447	3.4	105	0.51
10	11.6	133	33.4	113	6440	6.4	31	0.47