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Diamond-derived microelectrodes array for electrochemical analysis

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Abstract

Two types of diamond electrodes were fabricated and characterized for electrochemical analysis; diamond ultramicroelectrode arrays (D-UMEAs) and nano-diamond-coated microprobes. Array parameters such as electrode geometry, electrode–electrode spacing, and array size are established through design and fabrication, and their relation to electrochemical analysis is evaluated. The superior detection figures of merit for diamond, particularly the limits of detection and sensitivity, have been achieved by shrinking electrode geometries with microfabrication techniques. The D-UMEAs were shown to display ultramicroelectrode (UME) behavior when individual active electrode was placed at a sufficient distance from each other. The D-UMEAs were also found to display higher current density for detection of analyte in comparison with a conventional diamond planar macroelectrode. Diamond ultramicroelectrodes in array configurations have potential applications in electrochemical analysis including the study of fast electron transfer reactions, electrocatalysis, and as a sensor in flow systems. The boron-doped nano-diamond-coated microprobe was fabricated with plasma-enhanced chemical vapor deposition (PECVD). The nano-diamond-coated microprobe showed good sensitivity to analytes with reversible electron transfer and a large potential window.

Keywords: Diamond ultramicroarray electrodes; Nano-diamond microprobe; Electrochemical analysis; Potential window; Increased sensitivity; Spherical diffusion

1. Introduction

The work of Wightman and Fleishman on ultramicroelectrodes (UMEs) in the 1980s brought about a new stage of development for electrochemical science. UMEs are smaller than normal electrodes. Bard and Faulkner [1] define UME as an electrode having at least one dimension smaller than 25 μm. This is known as the critical dimension of the electrode. When the critical dimension becomes equivalent or smaller than the thickness of the diffusion layer, the UME will exhibit different experimental behavior from that of a macroelectrode. Due to its small geometry, it has low current, small ohmic drop, and small time constant. Although the low ohmic drop is desirable, the small current is not. This problem can be overcome by using an array of the UMEs, or UME array (UMEA), which increases the active electrode area. UMEA is an array of the individual UMEs, each isolated from the others by dielectric materials such as silicon nitride or silicon dioxide. According to the early works on UMEAs [2–6], they have several advantages over macroelectrodes, one of great interest is the increase in sensitivity.

Also UMEAs have a higher signal-to-noise (S/N) ratio, which ultimately leads to lower limits of detection than macroelectrodes [3,4]. Increased sensitivities and decreased limits of detection can be achieved due to enhanced mass transport to the interfacial reaction zone. As the electrode dimension becomes smaller than the diffusion length, relative to the time scale of the measurement, the flux of reactant to the electrode becomes dominated by spherical

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diffusion. The background signal is low due to decreased overall active area, relative to the geometric area. Both of these factors lead to enhanced signal/background ratios.

The advantage of using UMEAs over macroelectrode is further improved by the excellent properties of boron-doped diamond, achieving a superior working electrode for electrochemical analysis. Among the outstanding electrochemical properties of high quality, boron-doped, hydrogen-terminated diamond in aqueous media are (i) low and stable voltammetric and amperometric background current, (ii) a wide working potential window, (iii) quasi-reversible to reversible electron transfer kinetics for several redox systems without conventional pretreatment and with enhanced signal-to-background ratios due to the low background signal, (iv) long-term response stability, (v) morphological and microstructural stability during anodic polarization, and (vi) weak adsorption of polar molecules [7].

This work reports on the fabrication and experimental evaluation of (i) diamond microelectrode arrays and (ii) nano-diamond-coated microprobe for electrochemical sensing. Array parameters such as electrode geometry, electrode–electrode spacing, and array size are established through design and fabrication and their relation to electrochemical analysis evaluated.

2. Experimental

2.1. Fabrication of diamond ultramicroelectrode arrays (D-UMEAs)

The fabrication process for the D-UMEA is outlined in Fig. 1. First, a 2-μm-thick dry oxide was deposited on the n++ silicon wafer. Following that, photolithography was performed. The mold is then sonicated in a diamond powder suspension. Diamond powder on the oxide was removed by photoresist lift-off before diamond deposition. The diamond growth was performed at temperature=800 °C, pressure=120 torr, methane and hydrogen flow rate=18/478 sccm and microwave power=5000 W. Boron doping was achieved using a gaseous dopant; trimethylboron (TMB)=20 sccm. Diamond deposition duration is 1 h. The fabrication of planar diamond film for electrochemical analysis, using these growth parameters has been presented elsewhere [7].

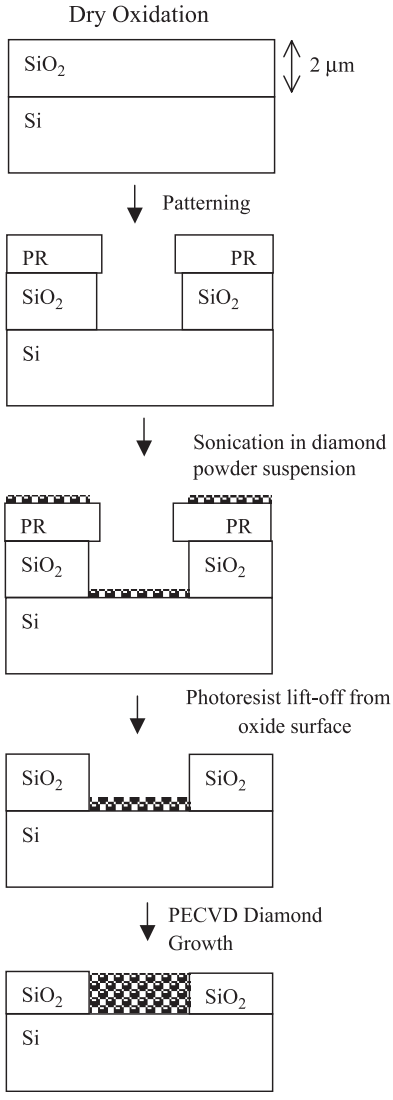

Fig. 1. Fabrication process for D-UMEA.

2.2. Fabrication of nano-diamond microprobe

Diamond-coated metallic microprobes were fabricated by CVD diamond deposition on tungsten wires, using selective growth techniques. The tungsten wires (130 μm diameter, 5.5 cm long) were electrochemically sharpened to a tip diameter of approximately 0.5 μm [8]. The CVD diamond deposition was performed on the tungsten wire in ASTEX 1500 W machine with H_2=138 sccm, CH_4=15 sccm, and TMB=10 sccm for 10 min. The pressure was maintained at 14 torr with the microwave power at 400 W for first 5 min without TMB and 550 W for the next 5 min with TMB.

2.3. Diamond electrode characterization method

Electrochemical measurements were carried out in a single-compartment, three electrode, cylindrical cell (50 ml) similar to the one used by Granger et al. [9]. The Ag/AgCl (3 M) reference electrode and the platinum (Pt) wire counter electrode were purchased from CH Instruments. $K_4Fe(CN)_6 \cdot 3H_20$, KCl, and KNO_3 were purchased from Fisher Scientific. All solutions were prepared with DI water (18 MΩ). The D-UMEAs were rinsed with DI water prior to use without further surface pretreatment.

Electrochemical measurements for the diamond-derived electrodes were made using Electrochemical Analyzer (Model 620A) from CH Instruments. The supporting electrolyte was 0.1 M KNO_3 and the analyte was 1 mM $Fe(CN)_6^{4-}$. The D-UMEA working electrodes were clamped