Advanced Microelectrodes for Chemical and Biological Detection

We are evaluating robust, highly sensitive microelectrode materials for detection of chemical or biological threats. Boron doped diamond (BDD), in the form of chemical vapor deposited (CVD) films, has been extensively studied as an electrode material in electrochemical environments. At high boron-doping levels, BDD has been shown to exhibit metal-like conductivity. BDD further exhibits a wide electrochemical window in water and other solvents, enabling a broader range of voltage sweep, with low background current. Furthermore, BDD is phenomenally durable under harsh electrochemical conditions. Such properties make BDD an attractive candidate as a microelectrode sensor material. We use reactive ion etch (RIE) of BDD films to make electrode structures that can be tested and integrated within microfluidic configurations compatible with existing systems for collection and separation of potential threats.

This realm is not without its drawbacks, however. As electrode size decreases, any lack of electrode durability exacerbates problems with device service life, and places limits on size and operating conditions. Graphite microelectrodes are prone to fouling and corrosion, and noble metals experience dissolution over time in environments, such as biological systems, that contain chloride. Integrated BDD microelectrode sensors may offer a compact, ultrasensitive alternative to detection of chemical and biological threats.

Figure 1. SEM image of BDD film before RIE etching.

Project Goals

The goal of this work is to demonstrate the fabrication and performance of diamond microelectrode arrays for the detection of chemical and biological samples. We will further determine the limits of detection for the BDD electrode configurations we choose.

Relevance to LLNL Mission

Microelectrodes offer many possibilities for increased sensitivity and flexibility in electrochemical detection, an area of interest to LLNL.

FY2005 Accomplishments and Results

BDD microelectrodes have been fabricated and characterized. Comparison of BDD microelectrode performance to other metal electrodes

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demonstrates metal-like behavior under nominal testing conditions.

The as-deposited nanocrystalline CVD BDD film is illustrated in Fig. 1. The process is as follows: Microelectrode arrays are formed in the BDD film using RIE. The electrode patterns are formed using photolithography and electroplating to create a thick gold hardmask pattern. RIE is then used to remove the diamond everywhere except beneath the gold patterns. After etching, the gold masking layer is stripped off, leaving the BDD microelectrodes (Fig. 2). To determine the electrochemical behavior of the BDD microelectrodes, cyclic voltammetry (CV) is performed by sweeping the voltage on one of the diamond strip electrodes and measuring the resulting current.

Figure 3 compares voltammograms for BDD microelectrodes and gold electrode structures in a hydroquinone solution. BDD is a very inert electrode surface. In the case of hydroquinone, it is a two-electron reaction, and requires the intermediate, semiquinone, to stay stuck to the electrode long enough for the second electron to come off/get put on. The hydroquinone and semiquinone adhere well to the gold electrode and, hence, easily undergo the electrochemistry on gold electrodes. Their lack of adhesion to BDD greatly retards the kinetics of this process on BDD electrodes. The result is that a higher voltage is needed on either side of the reaction, to speed up the process. Thus, compared to the gold electrodes, the BDD electrode exhibited sluggish kinetics, resulting in an asymmetric voltammogram with a peak separation of > 700 mV, while a gold electrode in the same solution displayed reversible behavior.

For the case of simple, one-electron, outer-sphere transfers we anticipate a fast reaction. Using a ruthenium hexamine solution, the BDD electrode was compared to a platinum electrode under similar conditions. In this case, the BDD electrode exhibited the typical fast, metallic-like kinetics expected of a highly-boron-doped-diamond electrode, comparable to that of a platinum electrode under the same conditions.

In summary, we've shown that BDD microelectrodes will prove to be a robust, low-noise detection technique for a variety of potential chemical- and biological-sensing applications.

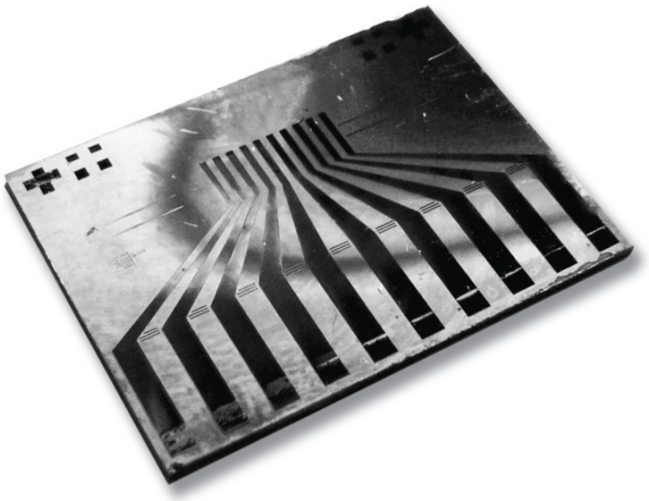

Figure 2. RIE-fabricated multi-electrode BDD array on SiO_2/Si wafer. The dark areas are the BDD electrodes.

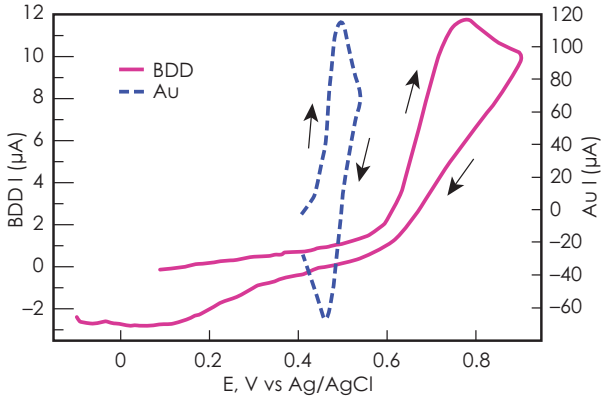

Figure 3. CV of 1mM hydroquinone in 1 M sulfuric acid, with RIE BDD electrode (~ 0.5 mm x 2 mm) and a 5-mm diameter Au electrode. Scan rate is 50 mV/s. Scan directions are as marked.