

## Fabrication and Electrochemical Characterization of Boron-Doped Diamond Microdisc Array Electrodes

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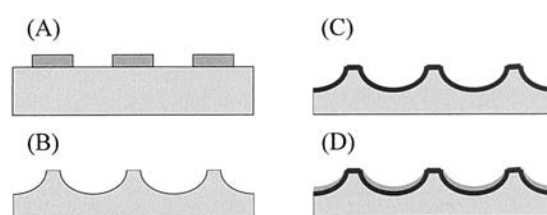
Microdisc array (MDA) electrodes of boron-doped diamond (BDD) were fabricated on structured silicon substrates. The BDD-MDA electrodes exhibited sigmoidal voltammetric curves, which show that they function as assemblies of single microelectrodes. The microelectrode behavior was also confirmed with biologically important species such as ascorbic acid and 3,4-dihydroxyphenylacetic acid, indicating its applicability in electroanalysis.

In the past few years, boron-doped diamond (BDD) electrodes have been studied with very much interest for electroanalysis. The electrochemical properties for BDD films include wide potential window in aqueous solutions, low capacitive background current and high stability.<sup>1-8</sup> These features enable BDD electrodes to be superior to other conventional electrodes such as glassy carbon and platinum in terms of sensitivity and stability. There are many reports on electroanalysis using diamond electrodes, such as electrochemical detection of NADH<sup>9</sup> and dopamine.<sup>9,10</sup>

Microelectrodes have also attracted much attention in electroanalysis, due to their small size. They possess many advantages such as steady state responses, small IR drop and small capacitance.<sup>11-13</sup> The small size of microelectrodes give them unique properties of increased rate of mass transport that results in improved signal to background current in comparison to its planar counterparts. Generally, arrays of microelectrodes are often used in order to increase the current signal, because the current at a single microelectrode is very small. Micro-array electrodes such as microdisc array (MDA) electrodes and interdigitated array electrodes can be obtained using various micro fabrication technologies.<sup>14,15</sup> Combination of the advantages of diamond and microelectrode arrays make them more attractive for electroanalytical applications. In this work, microelectrode arrays of BDD were fabricated on silicon substrates.

A schematic diagram of the procedure for fabricating the BDD-MDA electrode is shown in Figure 1. Si(100) surface was masked with patterned photoresist and etched with a mixture of HF, HNO<sub>3</sub> and H<sub>2</sub>O. The structured silicon surface was seeded with 10 nm diamond powder. BDD was deposited using a microwave plasma assisted chemical vapor deposition system (ASTeX Corp., Woburn, MA). The details of the diamond deposition have been reported elsewhere.<sup>16</sup> A 9 : 1 (v : v) mixture of acetone and methanol was used as the carbon source. Boron was doped by dissolving B<sub>2</sub>O<sub>3</sub> into the carbon source at B/C atomic ratio of 10<sup>4</sup> ppm. Diamond was deposited at a hydrogen pressure of 115 torr and microwave power of 5 kW for 3 h. After the deposition of diamond, polyimide varnish was spin-coated on

the diamond surface. The polyimide layer was mechanically polished until the diamond tips were just exposed. Electrochemical measurements were carried out at room temperature using a potentiostat and an X-Y recorder. Three-electrode configuration was used for electrochemical measurements, with Ag/AgCl (sat. KCl) electrode as reference electrode and platinum wire as counter electrode. Electrical contact from the microelectrode array was taken from the silicon substrate at the backside.

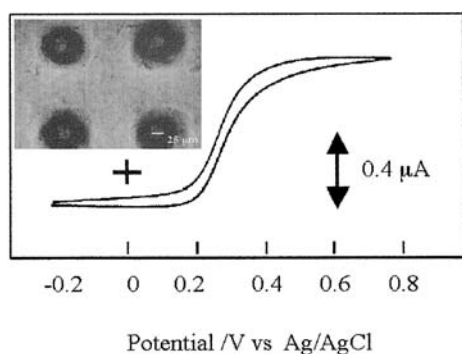


**Figure 1.** Schematic diagram of the preparation of BDD-MDA electrodes (A) Photoresist pattern formed on a silicon substrate (B) Isotropic etching of the substrate (C) Deposition of BDD (D) Spin-coating and mechanical etching of the polyimide film.

First, the distance between each microelectrode in the array and the size of each microelectrode must be considered so that the array may realize the properties of a single microelectrode. That is, if the packing density is high, the diffusion layers will overlap and the array will behave as a macro-sized electrode.<sup>13</sup> In the method used in this work, the distances between the microdisc electrodes were controlled by the mask pattern and the electrode size was controlled by the sharpness of the etched silicon substrate tips, which depend on etching conditions. A diamond array with the tip size of 25 to 30  $\mu\text{m}$  in diameter was used for electrochemical measurements. The distances between the tips were 250  $\mu\text{m}$ .

Figure 2 shows cyclic voltammograms for the oxidation of ferrocyanide at the BDD-MDA electrode. The voltammogram exhibited a sigmoidal curve, indicating that the array functions as a microelectrode. The half wave potential was +0.23 V vs Ag/AgCl, that agrees well with the value for macro-sized BDD electrodes. The calibration curve for the limiting current for oxidation of ferrocyanide was linear at a wide range of concentration from 1  $\mu\text{M}$  to 1 mM. The area of the electrode exposed to the electrolyte was 0.13 cm<sup>2</sup>, in which approximately 200 microelectrodes exist. Assuming that each of these electrodes functions as an independent microdisc electrode, the radius of each microelectrode can be estimated from the equation,  $I_{\text{lim}} = 4nFDc$ , where  $I_{\text{lim}}$  is the limiting current,  $n$  is the number of electrons,  $F$  is the Faraday constant,  $D$  is the diffusion coefficient,  $C$  is the concentration, and  $r$  is the radius of the

electrode. By using the value  $6.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  for the diffusion coefficient of ferrocyanide, the radius was calculated to be  $14 \mu\text{m}$ , which is consistent with the tip size of the electrode observed by SEM.



**Figure 2.** Cyclic voltammogram at BDD-MDA electrodes for the oxidation of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M  $\text{Na}_2\text{SO}_4$  (Potential sweep rate  $10 \text{ mV s}^{-1}$ ). Insert is a laser microscope image for the BDD-MDA electrodes.

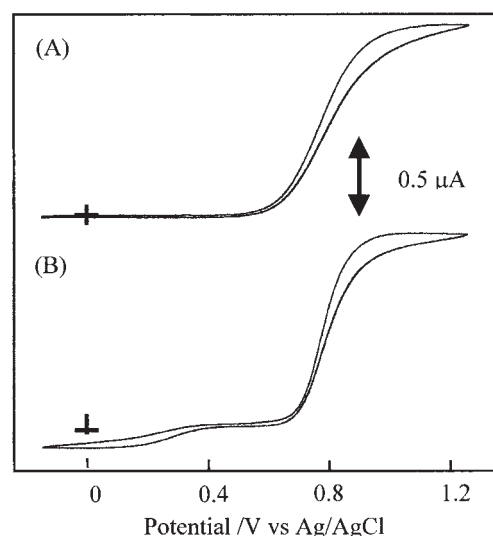
Limiting current at MDA electrodes is known to be independent of potential sweep rate for pure spherical diffusion without cross-talk between neighboring microelectrodes. The limiting current for the oxidation of ferrocyanide measured at the potential of  $+0.5 \text{ V vs Ag/AgCl}$  was constant up to  $200 \text{ mV/sec}$ . Above this sweep rate, an increase in the limiting current was observed and the voltammogram began to acquire a peak-shape. The microelectrode behavior in this study is similar to that reported for single BDD microelectrodes,<sup>17</sup> except that the observed currents were higher by two orders of magnitude. This indicates our success to increase the detection current, while the properties as microelectrodes are retained.

BDD-MDA electrodes are useful for electrochemical detection of various biologically and environmentally important chemical species with high sensitivity and stability. Sigmoidal voltammograms could be obtained for (A) ascorbic acid and (B) 3,4-dihydroxyphenylacetic acid (DOPAC), as shown in Figure 3. Steady state current was observed even at potentials as high as  $+1.2 \text{ V vs Ag/AgCl}$ , due to the wide potential window of BDD. Electrochemical sensing of chemical species with high oxidation potentials and trace metal analysis are major applications for both microelectrodes and BDD electrodes. These electrodes are also expected to exhibit high stability as their planar counterpart.<sup>9</sup> The work on electroanalysis using BDD-MDAs is in progress.

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#### References and Notes

- 1 N. Spataru, B. V. Sarada, E. Popa, D. A. Tryk, and A. Fujishima, *Anal. Chem.*, **73**, 514 (2001).
- 2 A. Fujishima and T. N. Rao, *Diamond. Relat. Mater.*, **10**, 1799



**Figure 3.** Cyclic voltammogram at BDD-MDA electrodes for the oxidation of (A) 1 mM ascorbic acid in 0.1 M  $\text{Na}_2\text{SO}_4$  and (B) 1 mM DOPAC in 0.1 M  $\text{Na}_2\text{SO}_4$  (Potential sweep rate  $10 \text{ mV s}^{-1}$ ).

- (2001).
- 3 T. N. Rao and A. Fujishima, *Diamond Relat. Mater.*, **9**, 384 (2000).
- 4 M. C. Granger, M. Witek, J. Xu, J. Wang, M. Hupert, A. Hanks, M. D. Koppang, J. E. Butler, G. Lucazeau, M. Mermoux, J. W. Strojek, and G. M. Swain, *Anal. Chem.*, **72**, 3793 (2000).
- 5 B. V. Sarada, T. N. Rao, D. A. Tryk, and A. Fujishima, *Anal. Chem.*, **72**, 1632 (2000).
- 6 Y. V. Pleskov, *Russian Chem. Rev.*, **68**, 381 (1999).
- 7 J. C. Angus, H. B. Martin, U. Landau, Y. E. Evstefeeva, B. Miller, and N. Vinokur, *New Diamond and Frontier Carbon Technol.*, **9**, 175 (1999).
- 8 R. Tenne and C. Lévy-Clément, *Israel J. Chem.*, **38**, 57 (1998).
- 9 A. Fujishima, T. N. Rao, E. Popa, B. V. Sarada, I. Yagi, and D. A. Tryk, *J. Electroanal. Chem.*, **473**, 179 (1999).
- 10 E. Popa, H. Notsu, T. Miwa, D. A. Tryk, and A. Fujishima, *Electrochem. Solid State Lett.*, **2**, 49 (1999).
- 11 A. M. Bond, *Analyst*, **119**, R1 (1994).
- 12 R. M. Wightman, C. Amatore, R. C. Engstrom, P. D. Hale, E. W. Christensen, W. G. Kuhr, and L. J. May, *Neuroscience* **25**, 513 (1988).
- 13 "Microelectrodes: Theory and Applications," ed. by M. I. Montenegro, M. A. Queiros, and J. L. Daschbach, Kluwer Academic Publishers, The Netherlands (1991).
- 14 M. Wittkamp, K. Cammann, M. Anrein, and R. Reichelt, *Sensors and Actuators B*, **40**, 79 (1997).
- 15 G. C. Fiaccabrino, X. M. Tang, N. F. de Rooij, and M. Koudelka-Hep, *Sensors and Actuators B*, **35-36**, 247 (1996).
- 16 T. Yano, E. Popa, D. A. Tryk, K. Hashimoto, and A. Fujishima, *J. Electrochem. Soc.*, **146**, 1081 (1999).
- 17 B. V. Sarada, T. N. Rao, D. A. Tryk, and A. Fujishima, *J. Electrochem. Soc.*, **146**, 1469 (1999).