Fabrication and Electrochemical Properties of Boron-Doped Diamond Hollow Fiber Wool

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Boron-doped diamond hollow fiber wool (BDD-HFW) was fabricated as a porous monolithic conductive diamond material. BDD-HFW was obtained by deposition of BDD onto a quartz wool substrate followed by removal of the substrate by chemical etching. Scanning electron microscopy observations confirmed that BDD-HFW consisted of BDD hollow fibers with diameters of several micrometers. The double-layer capacitance of a BDD-HFW electrode was estimated to be ca. 13 F g\(^{-1}\) from cyclic voltammetry measurements in an aqueous electrolyte.

Key words: boron-doped diamond, hollow fiber, porous electrode, electric double-layer capacitor

1. INTRODUCTION
Conductive boron-doped diamond (BDD) is known as a functional electrode material that exhibits a wide potential window and low background current in addition to physical, chemical and electrochemical stability.1 Based on these properties, BDD should be useful as an electrode material for electrochemical energy devices, such as fuel cells, secondary batteries and electrochemical capacitors, due to the high durability of the electrode and inertness to electrochemical decomposition of the electrolyte and solvent.2-6

In order to apply BDD electrodes in such applications, it is essential to fabricate porous BDD electrodes with large surface areas.7-9 We have reported that BDD hollow fiber membranes (BDD-HFM) can be fabricated via BDD growth on a quartz filter substrate followed by chemical etching of the substrate.10 The BDD-HFM is a conductive monolithic porous diamond material consisting of BDD hollow fibers with micrometer size diameters. Conductive monolithic porous materials should have advantages in terms of electrical conductivity compared to compacts of conductive particles, in which there may be contact resistance between the particles. BDD-HFM was found to exhibit a double-layer capacitance of ca. 13 F g\(^{-1}\) from cyclic voltammetry (CV) measurements in 0.1 M H\(_2\)SO\(_4\), which indicates that BDD-HFM can be used as a porous electrode material. However, since the quartz fibers of the quartz filter substrate were too dense, BDD could not be deposited on the entire surface of the substrate. For long deposition times, BDD formed a two-dimensional film on the substrate surface, which had less surface area per unit weight than a three-dimensional structure consisting of hollow fibers.

In an attempt to achieve such a three-dimensional structure, quartz wool consisting of quartz fibers with large voids was used as a substrate to produce a BDD hollow fiber material. BDD was deposited on the entire surface of the quartz fibers comprising the wool, and...
(MPCVD) method. 70% trimethoxyborane/methanol diluted with acetone to a B/C atomic concentration of 20,000 ppm was used as a B/C source. Considering the thermal durability limitations of the substrates, the stage temperature was set at 500 and 800 °C for the quartz filter and wool substrates, respectively. The microwave power, total pressure and H2 gas flow rate were set to 1300 W, 50 Torr and 400 sccm, respectively. After the BDD growth, the samples were immersed in a mixed solution of 1.43 M HF/1.43 M HNO3 for 24 h to dissolve the quartz fiber substrate (Fig. 1c). From an X-ray photoelectron spectroscopy result, the B/C atomic concentration ratio of a BDD-HFW was estimated to be $1.2 \times 10^{-3}$. This value corresponds to a boron concentration of $2.1 \times 10^{20}$ cm$^{-3}$ in diamond crystal, which should be sufficient for electric conductivity.11

Crystal quality of BDD hollow fibers were estimated by Raman spectroscopy (NRS-3200, Jasco). The spectra were decomposed into Voigt profiles by using a spectrum analyzing software (PeakFit 4.12, SeaSolve Software Inc.)

3. RESULTS AND DISCUSSION

For both types of substrates, SEM observations confirmed that polycrystalline BDD was grown densely on the quartz fiber surfaces (not shown). After removal of the quartz fiber substrates by chemical etching with HF/HNO3 solution, structures consisting of relatively dense BDD fibers were evident from SEM observations (Figs. 2a and 2d). Careful examination of cross-sectional SEM images (Figs. 2b, 2c, 2e and 2f) confirmed that the quartz fibers were completely removed to leave BDD hollow fibers. Therefore, the etchant is considered to percolate inside the BDD fibers from the edges and/or possible holes on the wall. The BDD-HFM fabricated using a quartz filter substrate with a 24-h deposition was a membrane consisting of BDD hollow fibers where neighboring fibers coalesced with each other. The BDD was grown only on the quartz fibers located within ca. 20 μm from the upper surface (the plasma-exposed side) of the quartz filter, although the thickness of the filter substrate was 0.45 mm. In contrast, BDD was grown on almost the entire surface of the quartz wool fiber substrate even though the deposition times were up to 48 h. As a result, the BDD-HFW produced from the quartz wool substrate had a structure in which the BDD hollow fibers were three-dimensionally entangled. Such a difference in the BDD-HFM and -HFW structures is considered to be due to the size of the voids in the substrate materials. For the quartz filter substrate with small voids, the carbon source concentration in the gas phase of the voids would be expected to decay with increasing depth from the filter substrate surface. In contrast, quartz wool possesses sufficiently large voids, so the carbon source concentration would be expected to

![Fig. 2 SEM images of (a–c) BDD-HFM (24 h deposition time) and (d–f) BDD-HFW (36 h deposition time). (a and d) Top view, (b and e) cross-sectional view and (c and f) magnified images of the cross section.](image)

![Fig. 3 Schematic illustrations of the BDD growth process on (a) quartz filter and (b) quartz wool substrates. Thicker arrows indicate a larger flux of activated carbon species during the CVD process. The top side is the plasma-exposed face.](image)
be rather homogeneous and lead to BDD growth on the entire surface of the quartz fibers (Fig. 3). The weight of the BDD-HFW increased almost linearly as the deposition time increased: 17.1, 24.9 and 30.3 mg for the deposition times of 24, 36 and 48 h, respectively, which were larger than that of the BDD-HFM (typically <10 mg). Therefore, quartz wool is a more useful template material for the fabrication of BDD hollow fiber materials with efficient and homogeneous growth than the quartz filter substrate.

Figure 4 shows Raman spectra of BDD-HFM and -HFW, which were decomposed into six Voigt profiles. The spectra are decomposed into six Voigt profiles. In both spectra, a sharp phonon band for diamond is seen at ca. 1332 cm\(^{-1}\), which indicates successful growth of BDD crystals on both quartz fiber substrates. However, D and G bands for graphite appear at 1360 and 1580 cm\(^{-1}\), respectively. According to a peak identification of CVD diamond films reported by Das et al.,\(^{12}\) these spectra can be decomposed into bands for disordered graphitic carbon (1280 cm\(^{-1}\)), polyacetylene (1500 cm\(^{-1}\)) and amorphous carbon (1530 cm\(^{-1}\)), in addition to diamond, graphite D and G bands. Based on the peak area of the bands and the relative scattering cross-section,\(^{12}\) the fraction of diamond was estimated to be 68% and 78% for BDD-HFM and -HFW, respectively. According to a peak identification of CVD diamond films reported by Das et al.,\(^{12}\) these spectra can be decomposed into bands for disordered graphitic carbon (1280 cm\(^{-1}\)), polyacetylene (1500 cm\(^{-1}\)) and amorphous carbon (1530 cm\(^{-1}\)), in addition to diamond, graphite D and G bands. Based on the peak area of the bands and the relative scattering cross-section,\(^{12}\) the fraction of diamond was estimated to be 68% and 78% for BDD-HFM and -HFW, respectively. When the spectra were decomposed into Gaussian and Lorentzian profiles, these values were calculated to be 57% and 76% (Gaussian), and 71% and 79% (Lorentzian), respectively. Although the values varied more or less depending on the type of profile used for curve fitting, however, the results indicated that the fraction of diamond was larger at the BDD-HFW than at the BDD-HFM. During the CVD process, graphite can also be deposited on the substrate, and is etched by activated hydrogen species in the plasma at a larger rate than diamond. Thus, exposure to activated hydrogen species is essential to lower graphitic carbon impurities. For the quartz filter substrate, the quartz fibers may be so dense that the fiber surfaces on the backside were not exposed to the activated hydrogen species effectively, which resulted in a significant amount of graphitic impurities. On the other hand, the quartz wool substrate has sufficient void volume, which makes it suitable for exposure to the activated hydrogen species to etch graphitic carbon. Graphitic carbon impurities in BDD electrodes may cause poor electrochemical performance with a narrow potential window compared to that for high quality BDD electrodes. Thus, the deposition of graphitic carbon impurities in BDD hollow fibers must be suppressed to obtain BDD electrode materials with a wide potential window. In this respect, quartz wool is a better substrate material than quartz filter.

The double-layer capacitance (\(C_{dl}\)) of the BDD-HFM and -HFW in an aqueous electrolyte was estimated using CV measurements. The BDD growth time was 24 h for both samples. Each sample was pasted on a carbon tape.
for immobilization and electrical contact (Fig. 5a). Figure 5b shows CV curves measured in 0.1 M H₂SO₄, in which the current was normalized according to the weight of the BDD-HFM or -HFW on the electrodes. The potential window was found to be ca. 1.5 V, and was narrower than that typical for a polycrystalline BDD thin film (ca. 3.5 V). This is most likely due to the graphitic impurities contained in the BDD-HFM and -HFW electrode materials, as indicated by the Raman spectra (Fig. 4). The \( C_d \) estimated from the anodic current at +0.5 V vs. Ag/AgCl in the CV measurements was 12.7 F g⁻¹ for the BDD-HFW, which was larger than that for the BDD-HFM (3.0 F g⁻¹). The difference in the \( C_d \) value is considered to be due to the specific surface area of BDD. The SEM images show that the BDD-HFM fabricated by a 24-h deposition was a two-dimensional membrane (Figs. 2b and 2c). Thus, the specific surface area per unit weight would not be as large as for BDD-HFW with a three-dimensional structure. Therefore, quartz wool with sufficient void volume among the fibers was determined to be a suitable substrate and template material for the fabrication of porous monolithic BDD with a three-dimensional structure.

4. CONCLUSIONS
BDD-HFW, a porous monolithic conductive diamond material, was fabricated using the MPCVD method with quartz wool as a substrate. CV analysis of the BDD-HFW electrode in an aqueous electrolyte indicated that BDD-HFW is a porous electrode material with a double-layer capacitance of 12.7 F g⁻¹, which is larger than that measure for BDD-HFM (3.0 F g⁻¹) fabricated with the same deposition time.

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References