Preparation of Boron-doped Diamond Thin Films Using BF_3 and the Electrochemical Behavior of the Semiconducting Diamond Electrodes

Fujio Okino[a], Yukio Kawaguchi[a], Shinji Kawasaki[a], Hidekazu Touhara[a], Mikka Nishitani-Gamo[b,c] and Toshihiro Ando[c]

[a]Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda 386-8567, Japan
[b]Institute of Applied Physics and Center for Tsukuba Advanced Research Alliance (TARA), University of Tsukuba, Tsukuba 305-8573, Japan
[c]CREST, National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba 305-0044, Japan

Boron-doped diamond thin films were prepared using BF_3, and the electrochemical behavior of the semiconducting diamond electrodes was investigated.

For the synthesis of CVD diamond thin films doped with boron, diborane, trimethylboron, B_2O_3, etc. are widely used as the boron source. Some halocarbons and halogens are known to lower the substrate temperature in the CVD synthesis of diamond thin films, thus economizing the process. As a typical monovalent element along with hydrogen, fluorine is expected to efficiently play the role of hydrogen that is an indispensable component of the source gas mixture in the CVD diamond synthesis. Since BF_3 contains both boron and fluorine, BF_3 can be regarded not only as a boron source but also as a fluorine source that could affect the formation of diamond significantly.

Diamond thin films were grown on a Si (100) substrate by the microwave CVD method. The following conditions were used: microwave power 450-500 W, total gas pressure 38-40 Torr, substrate temperature 1053-1093 K, gaseous mixture of methane 0.8-1.0 vol% and hydrogen gas, and reaction time10-20 h. BF_3 pre-diluted with Ar to 0.1% was used as the boron source gas. The B/C atomic ratio in the gas phase was varied in the rage of 0-10000 ppm. The products were analyzed by Raman spectroscopy, XRD and SEM. Cyclic voltammetry measurements were carried out for the B-doped semiconducting diamond electrodes using BF_3.

Figure 1 shows Raman spectra of B-doped diamond thin films with low boron concentrations (B/C = 0-625 ppm). The broad band at ca. 1500 cm^{-1} attributable to disordered graphite is strong for the undoped sample. At B/C=125 ppm the one-phonon Raman peak at 1332 cm^{-1} attributable to diamond becomes sharper. As the boron concentration further increases, the graphite band becomes undetectable, and two broad peaks around 500 and 1230 cm^{-1} appear. These features are typical of boron-doped diamond films,[1] indicating that BF_3 effectively acted as a boron source.

Although it has been found that the growth rate of diamond was reduced by small amount of diborane,[2] the SEM images of the products indicated that the growth rate was not significantly reduced by the present B-doping method, suggesting a possible involvement of fluorine in the diamond growth mechanism.

Figure 2 shows cyclic voltammograms (CVs) of 1,4-difluorobenzene in electrolyte solution $Et_4NF{\cdot}4.0HF$ using the B-doped diamond electrode. The blank CV shows only a broad and small oxidative wave above 2 V indicating the wide potential window of the diamond electrode. As 1,4-difluorobenzene is added, an oxidative wave appears at ca. 2.2 V. The peak height increases as the concentration of 1,4-difluorobenzene becomes higher from (b) to (c), indicating that this wave is attributable to the oxidation of 1,4-difluorobenzene. This electrochemical behavior is essentially the same as that of the B-doped diamond electrodes using diborane.[3]

References

1) K. Ushizawa et al., *Diamond. Relat. Mater.*, **7** (1998) 1719-1722.
2) I. Sakaguchi et al., *Diamond. Relat. Mater.*, **7** (1998) 1144-1147.
3) F. Okino et al., *Electrochem. Solid-State Lett.*, **2** (1999) 382-384.

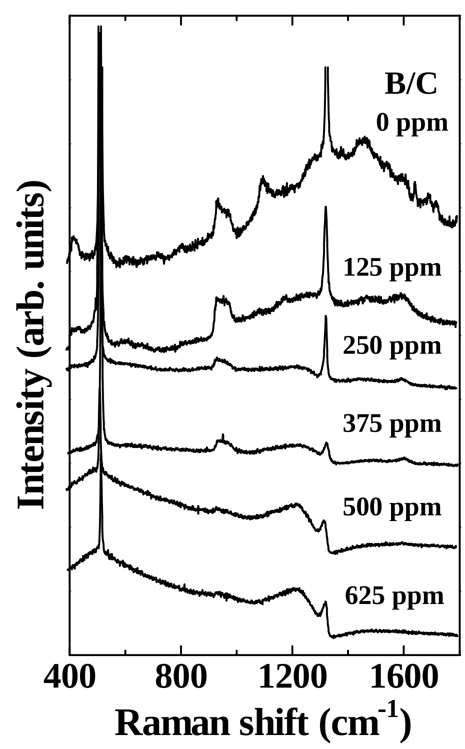

Fig. 1 Raman spectra of undoped and B-doped diamond thin films. B/C refers to the boron to carbon ratoo in the gas phase.

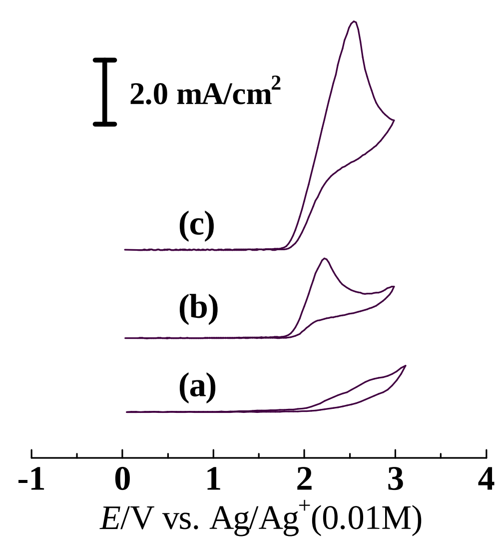

Fig. 2 Cyclic voltammograms for diamond electrode in $Et_4NF{\cdot}4.0HF$ of: (a) blank, (b) 0.012M and (c) 0.025 M of 1,4-difluorobenzene.