Pt-implanted Boron-doped Diamond Electrodes for Electrochemical Oxidation of Hydrogen Peroxide

Tribidasari A. Ivandini, Rika Sato, Yoshihiro Makide,† Akira Fujishima,†† and Yasuaki Einaga*
Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Yokohama 223-8522
†Radiaisotope Center, The University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo 113-0032
††Kanagawa Academy of Science and Technology, KSP 3-2-1 Sakado, Kawasaki 213-0012

(Received May 10, 2004; CL-040522)

Pt-modified diamond electrodes were fabricated for electroanalytical applications by implantation method with a dose of 5×10^{14} cm^{-2}. The electrochemical behavior has been studied for oxidation of hydrogen peroxide by using cyclic voltammetry in phosphate buffer solution. With very low background current in comparison to that of Pt metal electrode, the electrode exhibited higher signal to background ratio (≈3.8 times) as well as better electrochemical and physical stability.

Metal modification of boron-doped diamond (BDD) electrode has attracted much attention since it had been reported that dispersion of metallic particles within an organic polymer or an inert surface resulting in drastic increase of the catalytic activity and sensitivity of the electrode.[1,2] BDD is known to have superior properties, including a wide electrochemical potential window in aqueous and non-aqueous media, very low capacitance and extreme chemical and electrochemical stability.[3] Furthermore, whereas some metals, such as platinum, are known to oxidize peroxide and methanol, BDD electrode is found completely inactive for those catalytic reactions. Therefore, BDD film should be the best support for the deposition of metal electrocatalysts.

Preparation of some metal-modified BDD electrodes for electroanalytical purposes by using chemical precipitation and electrochemical deposition method had been reported.[4] However, the stability is limited since the metal particle is detached or dissolved under strong stimulation condition.[5] Our group had recently reported metal-modification of BDD electrode by using implantation method for electrochemical detection of glucose.[4,6] In addition to its high catalytic activity, the electrode exhibit excellent electrochemical stability with low background current even after ultrasonic treatment indicates the stability of metal position at the diamond surface.

The present work is focused on the fabrication of platinum-implanted BDD for the detection of hydrogen peroxide. Sensitivity and stability have also been observed in comparison to those of platinum metal electrode.

Highly boron-doped diamond electrode were deposited on Si(100) wafers in a microwave plasma-assisted chemical vapor deposition (MPCVD) system (ASTeX Corp.) Detail of the preparation has been described elsewhere.[3] A mixture of acetone and methanol in the ratio of 9:1 (v/v) was used as the carbon source. B_2O_3, used as the boron source, was dissolved in the acetone-methanol solution at B/C atomic ratio of 1:100. These films were implanted with 750 keV Pt^{2+} with a dose of 5×10^{14} cm^{-2} (Tandetron 4117-HC, HVEE) by using platinum rods as targets. Annealing process was performed at 850 °C for 45 min in an H_2 ambient (80 Torr).

After Pt-implantation process, SEM images had shown the presence of small holes on the BDD surface. However, the metal particles were not observed. Although diameter changes of the holes (diameter is between 10–30 nm) were not significant, the number of holes increased after annealing process in H_2 plasma (data is not shown).

An annealing process is particularly required to rearrange the metastable states diamond produced by implanted process back to diamond structure.[7] We believe that during annealing process the metal particles is lifted up to the surface, resulting in more number of holes appeared. In previous studies with nickel implantation, annealing in H_2 atmosphere was enough to lift the Ni particles up to the surface, which was demonstrated by the presence of Ni catalytic effect after annealing.[5,6] However, in Pt implantation-BDD, the process is not enough to present Pt electrocatalyst effect in hydrogen peroxide oxidation. An annealing in H_2 plasma, which involved etching process, is required. Probably, since Pt is much heavier metal than Ni, implantation method caused Pt particles to be buried more stable in the near surface of BDD film.

Figure 1 shows Raman shift of the BDD film before and after annealing process. In comparison to the previous result with Ni implantation,[5,6] Figure 1 shows that implantation of Pt caused more surface disordered at BDD film. The Raman spectrum before annealing shows sharp first-order peak (single-phonon scattering) at 1332 cm^{-1}, which provides strong evidence for well-crystallized diamond, and sp^2 related band at 1550 cm^{-1}, and also some other peaks between 1000 and 1300 cm^{-1} which shows the strained of BDD film. However, after 45 min annealing at 850 °C, the characteristic peak of sp^2 band disappeared and the spectra is comparable to that of as-deposited BDD. This implies that the strained diamond film generated by irradiation has been partially relieved by annealing.

The presence of Pt particles on BDD surface was further

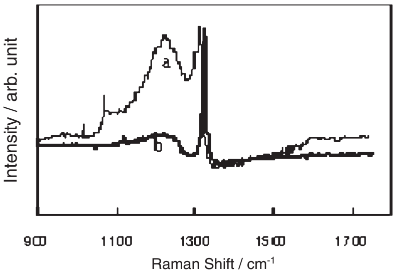

Figure 1. Raman spectra observed at Pt implanted BDD (a) before and (b) after annealing process in H_2 plasma.

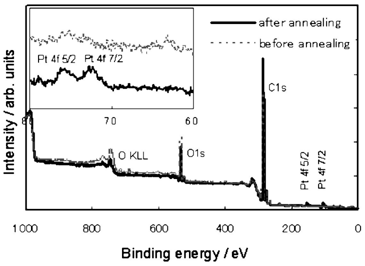

Figure 2. XPS spectra of Pt-implanted BDD before and after annealing.

confirmed by XPS, which after annealing shows significant peaks at binding energy 73 and 76 eV corresponding to Pt $4f_{7/2}$ and Pt $4f_{5/2}$, respectively (Figure 2). While, before annealing the Pt peaks observed were very small.

Electrochemical behavior of the films is investigated for hydrogen peroxide oxidation in phosphate buffer solution (PBS) pH 5. Figure 3 shows cyclic voltammetric responses of 10 mM H_2O_2 in the 0.1 M PBS at Pt-implanted BDD and Pt metal, recorded along with the background voltammograms. Well-defined peaks were observed at the potentials of 1.0 V and 1.2 V (vs Ag/AgCl) at Pt-implanted BDD and Pt metal, respectively.

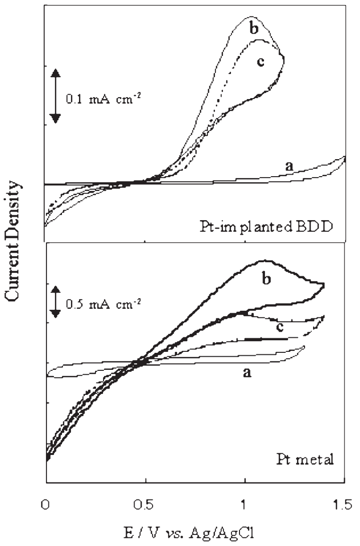

Figure 3. Cyclic voltammograms of 10 mM H_2O_2 at Pt-implanted BDD and Pt metal in 0.1 M PBS pH 5 (a) and in similar electrolyte with the presence of 10 mM H_2O_2 for the 1st cycle (b) and the 10th cycle (c). Scan rate is $100\,\mathrm{mV\,s^{-1}}$.

Although the working potential window for the Pt-implanted BDD remained essentially the same as that for the Pt metal, a very low background current is observed at Pt-implanted BDD electrode ($\approx 5.2\,\mu A$), which is much lower than that at Pt-metal ($\approx 111\,\mu A$). However, the current responses are also very low in comparison with that of the Pt bulk. It is probably because the position of Pt particle at the near diamond surface caused a remarkably protective nature for the anodic dissolution of Pt particle. The depth distribution of platinum ions deduced from TRIM computer code (750 keV, 5×10^{14} platinum $\mathrm{cm^{-2}}$) is estimated in the range of 80–140 nm. The low current responses were also observed at glucose oxidation by using Ni- and Cu-implanted BDD which were much smaller compared to those at their related metal bulks.[5,7] However, with its very low background current, Pt-implanted BDD exhibited enhanced signal-to-background current ratio (S/B) to be ≈ 3.8 times higher than Pt-metal. This behavior is usually known to reflect the lower detection limit of electrode.

Stability of both electrodes was also observed. The oxidation currents, obtained for 10 mM H_2O_2 in 0.1 M PBS, decreased $\approx 13.5\%$ and $\approx 52\%$ after 10 repetitive cycles at Pt-implanted BDD and Pt metal, respectively. These results indicate that the adsorption at Pt-implanted BDD surface is less. Furthermore, peak potential at Pt metal shifted to 1.0 V after the 10th cycle indicates strong adsorption occurred at Pt-metal. Hall et al. proposed that the adsorption mechanism of H_2O_2 at Pt electrode is due to the strong binding between H_2O_2 and Pt, which inhibited further oxidation process of H_2O_2.[8]

However, potential shift is also observed at Pt-implanted BDD electrodes. While at Pt bulk the peak potential shifted to more negative potential, at Pt-implanted BDD it shifted to more positive potential ($\Delta E = \approx 0.05\,\mathrm{V}$). The probable reason is due to effect of increasing of O-termination part at BDD surface during the cycles. As it is already known, at O-termination BDD oxidation peak potentials generally shifted to more positive potentials.[9]

The aim of this letter is to present the advantage of metal implantation method for fabrication of metal-modified BDD electrodes for electroanalytical purposes. The notable point is the higher S/B ratio of Pt-implanted BDD in comparison to that of Pt metal electrode, beside the stability of signal current due to less adsorption of H_2O_2 on electrode surface. Furthermore, stability of the small size metal particles at the near surface of BDD results in the possibility for cleaning process of the electrode, as already reported by sonication.[5] This shows much advantage of the implantation method for metal modification at the inert surface of BDD, as it is reported that metal electro-deposition at BDD electrode detached easily by cycling.[10]

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science and technology (MEXT) of the Japanese Government.

References

1 P. F. Luo and T. Kuwana, *Anal. Chem.*, **66**, 2779 (1994).
2 I. G. Casella, E. Desimoni, and T. R. I. Cataldi, *Anal. Chim. Acta*, **248**, 117 (1991).
3 T. Yano, D. A. Tryk, K. Hashimoto, and A. Fujishima, *J. Electrochem. Soc.*, **145**, 1870 (1998).
4 R. Uchikado, T. N. Rao, D. A. Tryk, and A. Fujishima, *Chem. Lett.*, **2001**, 144.
5 K. Ohnishi, Y. Einaga, H. Notsu, C. Terashima, S.-G. Park, and A. Fujishima, *Electrochem. Solid-State Lett.*, **5**, D1 (2002).
6 T. A. Ivandini, R. Sato, Y. Makide, A. Fujishima, and Y. Einaga, *Diamond Relat. Mater.*, in press.
7 J. F. Prins, *Semicond. Sci. Technol.*, **18**, S27 (2003).
8 S. B. Hall, E. Khuldaish, and A. L. Hart, *Electrochim. Acta*, **43**, 579 (1998).
9 I. Yagi, H. Notsu, T. Kondo, D. A. Tryk, and A. Fujishima, *J. Electroanal. Chem.*, **473**, 173 (1999).
10 F. Montilla, E. Morallon, I. Duo, Ch. Comninellis, and J. L. Vazquez, *Electrochim. Acta*, **48**, 3891 (2003).