Micro-Structural Heterogeneity for Electrochemical Activity at Polycrystalline Diamond Thin Films Observed by Electrogenerated Chemiluminescence Imaging

K. Honda, T. Noda
Department of Chemistry and Earth Sciences, Faculty of Science, Yamaguchi University, 1677-1 Yoshida, Yamaguchi-shi, Yamaguchi 753-8512, Japan

A. Fujishima
Kanagawa Advanced Science and Technology (KAST), 3-2-1, Sakado, Takastu-ku, Kawasaki-shi, Kanagawa, 213-0012, Japan

Recently, numerous studies have been reported on the electroanalytical applications of diamond that is ideal electrode material for electrochemical detection of biological species. The highly sensitive and selective detection using the electrogenerated chemiluminescence (ECL) is a promising analytical method to improve the selectivity for the detection of specific compounds, and to make use of the superiority of the diamond electrode without the requirement of modification.(1) In this study, to make the reactivity for the ECL reaction at polycrystalline diamond surface and the mechanism of the ECL process of the $Ru(bpy)_3^{+2}$ – tripropylamine (TPrA) system clear, the visualization of active site using ECL imaging analysis was carried out.

The ECL images were observed using the microscope that was attached to the electrochemical cell under the objective lens. Figure 1 shows the ECL images at the as-deposited diamond surface observed at ca. 2.0 V vs. Ag/AgCl. The spatial distribution for ECL intensity indicates that the electrochemical reactivity at polycrystalline diamond electrode was microscopically heterogeneous. In the ECL images, the squire-shaped region exhibited extremely lower ECL intensities and these regions correspond to the (100)-oriented growth sectors. On the other hand, Fig 1-B shows that the ECL for the (111) sector exhibits homogeneous emission. The dependence of the ratio of the intensity at each face and the average on the applied potential was examined. The ratio for the (111) sector was almost constant at any potential. However, for (100) surface, the ratio increased linearly with increasing in the potential, indicating that the conductivity for (100)-oriented microcrystalline is remarkably lower than that for other types of oriented microcrystallite, and the low reactivity of (100) surface was compensated by applied potential because of the low conductivity of this surface.

Micro-Raman imaging was used to investigate the microcrystallite-based heterogeneity for the conductivity at the boron-doped polycrystalline diamond. Fig. 2 shows the Raman intensity maps for the diamond line (approx. 1332 cm^{-1}) at the as-deposited surface including the (100) and (111) growth sectors. It is known that the intensity of the diamond line decreased with increasing in the boron-doping level at diamond macrocrystallite. In Fig.2, the raman intensity also shows the heterogeneity and the Raman intensity at the (100)-oriented microcrystallite is approximately 8 times higher than that at (111), suggesting that the boron doping level at (100)-oriented microcrystallite was ca. 1/8 of (111).

As a result, it was confirmed that heavily doped polycrystalline diamond films contains mocrocrystals with different boron doped level, i. e., semiconductor and semi-metallic diamond microcrystal. Therefore, this micro-structural heterogeneity for boron concentration results in the heterogeneity for the electrochemical reactivity at the boron-doped polycrystalline diamond.

1. K Honda, M. Yoshimura, T. N. Rao, and A. Fujishima, *J. Phys. Chem. B.*, 107, 1653 (**2003**).

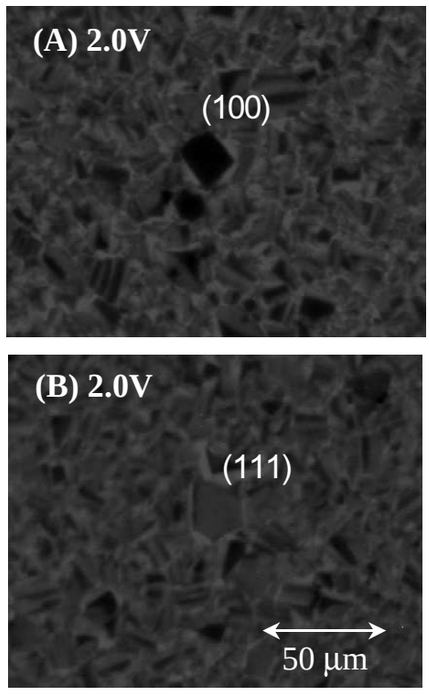

Figure 1. Images during the ECL emission at as-deposited diamond.

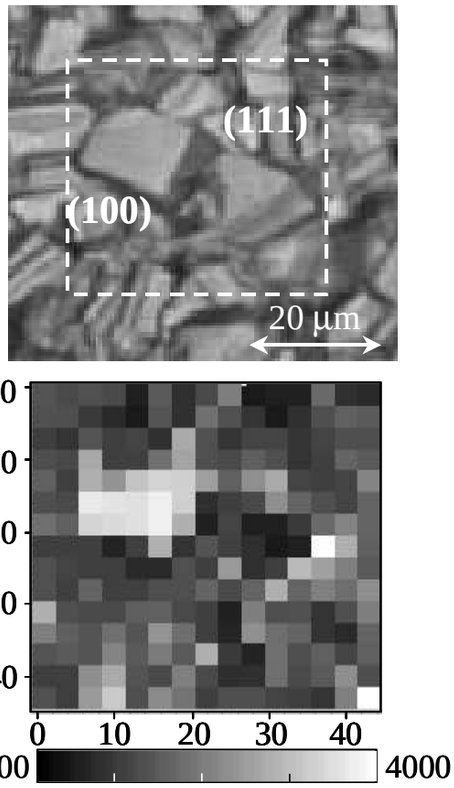

Figure 2. Spectral maps of probed area of as-deposited diamond