

Direct Proof for Electrochemical Substitution of Surface Hydrogen of Boron-doped Diamond Electrode by TOF-ESD Method

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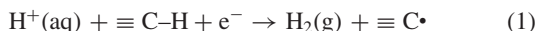
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The substitution of surface hydrogen on boron (B)-doped diamond electrodes during electrochemical hydrogen evolution was confirmed using TOF-ESD method. The results show that surface-H(D) was substituted by D(H) as a result of the reduction of $D^+(H^+)$ in solution during the electrochemical hydrogen evolution at the B-doped diamond.

Boron (B)-doped diamond (BDD) thin film has been recently recognized as an attractive electrode material in aqueous solutions.^{1,2} The electrochemical characteristics are strongly affected by the surface composition. It is known that the O-terminated BDD surface has been formed and the electrochemical properties of the surface are significantly changed after anodic polarization around the oxygen evolution potential.^{3–6} The hydrogen evolution reaction (HER) may also affect the surface termination of BDD. The mechanism of HER has been studied in detail using a wide variety of metal electrodes. At a metal electrode, HER is known to proceed via intermediate hydrogen atoms (H_{ads}), directly adsorbed on the metal surfaces. The diamond surface, however, is already H-terminated and the question is whether the terminal hydrogen may or may not take part in the HER. The mechanism for HER at the BDD electrode has not been experimentally clarified, but was treated quantum chemically.⁷ The proposed mechanism⁷ expects the formation of the carbon radical at the surface as:



where $\equiv C\cdot$ denotes surface dangling bond of diamond and then, the substitution of the surface-H by H^+ in the solution side should be possible. On the other hand, if $\equiv C-H$ works like a metal, then it is not substituted.

The highly sensitive detection of the hydrogen at the BDD surfaces is essential to clarify the HER mechanism. Ueda and co-workers have developed a scanning time-of-flight type electron-stimulated desorption (TOF-ESD) system to detect the 2-D hydrogen distribution at solid surfaces with a spatial resolution of 1 μm , called a "protoscope."^{8,9} In the present study, the substitution of the terminal H(D) on BDD by H(D)ER was confirmed using an ex situ TOF-ESD method.⁸

The details of the growth of the polycrystalline BDD thin films using a high pressure microwave plasma-assisted chemical vapor deposition system have been previously reported.^{3,4,6} The substrate was a conducting n-Si(111) ($<0.01 \Omega cm$) and heavily doped BDD films were used in the present study. The cathodic H(D)ER treatment at the BDD surface was carried out using a

conventional three-electrode configuration with a platinum counter and an Ag/AgCl reference electrodes. The electrode potential was held at $-2.5 V$ in 0.1 M H_2SO_4/H_2O or 0.1 M D_2SO_4/D_2O for 30 min. The TOF-ESD measurement was carried out in the "protoscope" analyzer. Details of the "protoscope" were previously reported.^{8,9} In the present study, the off-axis electron(e^-) gun (LEED gun) was mainly used for the TOF-ESD measurements in the submillimeter scale. The other pencil-type e-gun, which is normally used for FE-SEM imaging, was used for the TOF-ESD measurement in the submicrometer scale. In the TOF spectrum, desorbed species, i.e., H^+ and O^+ , appear as a function of flight time in μs . To avoid the effects of adsorbed water and contamination, all the spectra were measured at the surfaces after heat treatment in the "protoscope" chamber up to 500 $^\circ C$, which was sufficiently below the decomposition temperature for H- or O-terminations at the BDD.¹⁰

Figure 1a and 1b show the change in the TOF spectra measured on an as-grown BDD electrode surface (a) with and, (b) without the DER treatment in the 0.1 M D_2SO_4/D_2O solution. The start point of the flight time of the ion was noted as position, P, which indicates the photon signal generated by the primary electron irradiation. Both the desorption peaks of H^+ and O^+ species were clearly observed. The presence of oxygen at the as-deposited BDD surface was also confirmed by XPS measurement.⁶ The yield of H^+ was apparently decreased by the DER treatment in the deuterated solution, indicating the substitution of the H-termination by D. However, the yields of the O^+ species

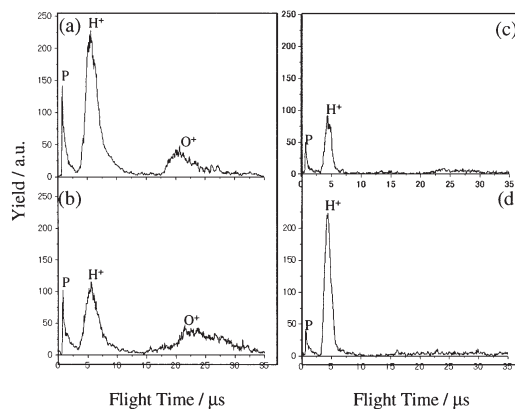


Figure 1. TOF spectra ($V_s = 0 V$) measured at an as-deposited diamond film (a) before and (b) after cathodic polarization in 0.1 M D_2SO_4/D_2O solution at $-2.5 V$ for 30 min and TOF spectra ($V_s = 4 V$) measured at a predeuterated diamond film (c) before and (d) after cathodic polarization in 0.1 M H_2SO_4/H_2O solution at $-2.5 V$ for 30 min.

did not show much change after the cathodic polarization treatment. The stability of the O-termination against the cathodic polarization has already been confirmed by the XPS measurements at preoxidized BDD electrodes.⁶

In Figure 1c and 1d, the results of the comparative experiment, in which the predeuterated sample electrode was HER treated in the 0.1 M H₂SO₄ solution, are shown. The predeuteration treatment was carried out by heating the sample under continuous D₂ flow, resulting in the substitution of almost all the H- and O-terminated BDD surfaces into the D-terminated one, because the temperature of 900 °C, used for the treatment, is known to be higher than the desorption temperature of the H and O species at the BDD surfaces.¹⁰ The sharper H⁺ peaks in Figure 1c and 1d than those in Figure 1a and 1b can be attributed to the specimen bias (Vs) in the TOF-ESD measurement. Although the disappearance of the O⁺ yield in Figure 1c supported the surface substitution by D, the yield of H⁺ was still clearly observed. The subtraction of the background H⁺ yield was quite difficult, because the surface was not prepared under the UHV, and Ar⁺ bombardment/annealing cycles could not be used to keep the surface termination formed under atmospheric pressure or in solution. Also, the desorption of D⁺ can not be detected in the present equipment, since the ESD yield of D⁺ from BDD has been known to be much lower than that of H⁺, although the existence of surface-D was confirmed by a more sensitive TOF-ESD equipment. Thus, only the change in the H⁺ yield can be useful to qualitatively estimate the effects of the cathodic polarization treatment. The increase in H⁺ yield in the HER treated area at the predeuterated surface was really observed, as expected.

In Figure 1, the area, where the cathodic polarization treatment was carried out, was estimated from the detailed map of the TOF spectra at various positions, because the focusing spot of LEED gun was not coincident with that of FE-SEM gun at the sample surface. However, the use of the same e-gun for both SEM and TOF-ESD measurements is possible using FE-SEM gun and favorable for the confirmation of the measurement position. Although the fine structure of the TOF spectra cannot be obtained by the measurement using this e-gun because of the small cross section and the higher incident energy, the 2-D distribution of the H⁺ yield can be sufficiently estimated. The predeuterated BDD surface was prepared and a HER treatment was carried out by dipping the half of the sample surface into the 0.1 M H₂SO₄ solution. After the polarization for 10 min at -2.5 V, the surface was rinsed with milli-Q water and placed in the "protoscope" chamber, then, heated to 500 °C. The TOF-ESD line scan of 128 × 2 points (the scanning area corresponded to 182 × 5.68 μm²) around the positions marked in Figure 2 by FE-SEM-gun was carried out. At each position, the TOF spectrum was obtained and the peak assigned for H⁺ was integrated. The integrated yields were plotted versus the y axis in Figure 2a. At y = 16.5 mm, an extremely large H⁺ yield was observed and was assigned to the H⁺ desorbed from the tungsten electrode, which was placed on the sample edge to hold and heat the sample surface. The H⁺ yields increased around y = 9.0 mm, which corresponded to the boundary between the HER treated and untreated areas. About a 30% increase in the H⁺ yield was estimated by the HER at the predeuterated BDD surface. Although the change in Figure 2a seems smaller as compared with the changes in the H⁺ yield shown in Figure 1, it can

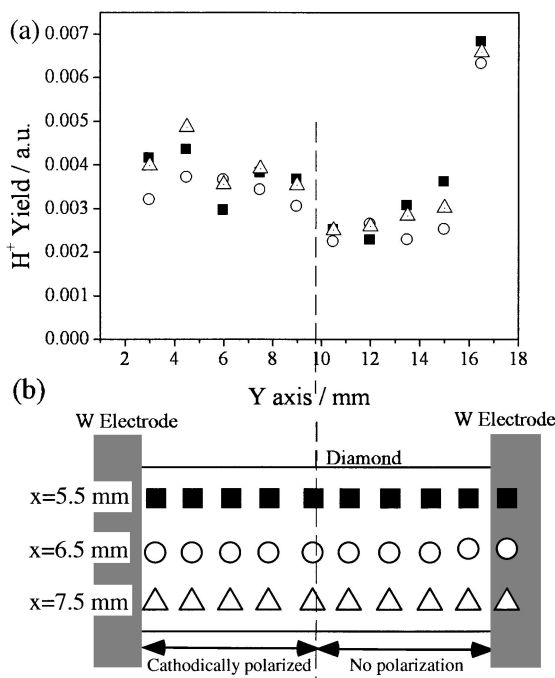


Figure 2. (a) Integrated H⁺ yield profile at various position on the cathodically polarized diamond sample (Vs = 20 V). Half area of the sample was not cathodically polarized, but rinsed by water. The measured positions are illustrated in (b) as those characters.

be explained by the shorter treatment period.

The substitution of the H(D)-termination by the D⁺(H⁺) in the solution at the extreme cathodic potential was confirmed from the above-mentioned results. The HER at the BDD electrode does proceed via the carbon radical formation as shown in Eq 1. However, it is difficult to estimate the surface concentration of the substituted sites because of the lack of the inspected correlation between the obtained H⁺ yield and the surface concentration of the surface-H. The H-absorption in the subsurface or bulk of the BDD¹⁴ may also confuse this problem. Since the surface roughness affects the H⁺ yield, the TOF-ESD measurements at the epitaxially grown BDD films are desired to estimate the kinetics of the substitution of the surface-H.

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