Electrochemical Properties of Ar^+ Sputtered Polycrystalline Diamond Electrodes with Smoothed Surfaces

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The initial rough, faceted surfaces of boron-doped conductive polycrystalline diamond electrodes were smoothed by Ar^+ ion sputtering at very low energy (50 eV). A lower background current was measured at the modified electrodes with a mirror-like appearance than at the initial polycrystalline electrodes. The electrochemical responses to several redox systems also showed a morphological-dependence in some cases. Here, we discuss the electrochemical properties of the diamond electrodes with the smoothed surfaces from the point of view of a novel electrode material.

Boron-doped polycrystalline diamond thin films have emerged as attractive new electrode materials because of their unique electrochemical properties.[1–4] Because these properties make diamond a promising electrode material for electro-analysis, several reports have appeared on its use for the detection of several types of biochemical species or environmental pollutant.[5–7]

We have focused on the surface-modification of diamond electrodes in order to improve their electrochemical properties. Surface-modification at the atomic level is a well-known phenomenon, in that the electrochemical properties of electrodes are found to be quite sensitive to the chemical termination on the surface. For example, the electrochemical responses to several different redox systems for oxygen-terminated diamond electrodes and hydrogen-terminated diamond electrodes are remarkably different.[8] Moreover, hybrid electrodes, such as metal-modified diamond electrodes, have been prepared by electrochemical deposition methods[9,10] or ion-implantation methods[11] to realize novel multifunctional electrodes.

In the present work, we have focused on the effects of surface morphology. We have previously reported that the initial rough surface of polycrystalline boron-doped diamond (BDD) could be smoothed very easily by using a radio-frequency glow discharge optical emission spectroscopy (rf-GDOES) technique.[12] Here, we have studied the differences in the electrochemical properties between 'rough surface' and 'smoothed surface' diamond electrodes.

Polycrystalline BDD electrodes were deposited onto Si substrates using a microwave plasma-assisted chemical vapor deposition system. The detailed procedures for the preparation were described elsewhere.[4] After the diamond was deposited it was sputtered using a GDOES instrument at an Ar pressure of 0.51 Torr by applying an rf power of 40 W at 13.56 MHz. The values of the gas pressure and the applied power relate to the plasma per se. The surface of the diamond became mirror-like in appearance. The smoothed surfaces of the polycrystalline diamond films were characterized by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Electrochemical measurements were carried out in a single-compartment cell. An Ag/AgCl electrode was used as the reference electrode and a Pt wire was used as the counter electrode. Current-potential curves were recorded using a potentiostat. The electrochemical properties were studied by using both hydrogen-terminated and oxygen-terminated electrodes. Although the as-deposited diamond electrodes were terminated with hydrogen, we could oxidize the electrodes so that they became oxygen-terminated by employing anodic oxidation, i.e., +3.0 V for 30 min.

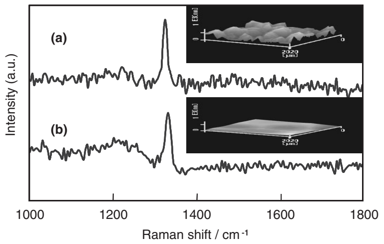

Figure 1. AFM images and Raman spectra of BDD electrode surface (a) before and (b) after Ar^+ sputtering.

Figure 1 shows AFM images and their corresponding Raman spectra for samples before and after sputtering. Over the area that we examined, the maximum peak-to-valley heights were 1.49 μm and 267 nm, respectively for the two types of surface, while the average surface roughness values were 238 and 30 nm, respectively. The Raman spectra of both samples before and after sputtering exhibited sharp peaks for the sp^3 carbon-related band at 1331 cm^{-1}. This shows that the diamond retained the sp^3-carbon structure even after sputtering with the Ar^+ ions.

XPS spectrum for the sputtered BDD shows a clear Ar $2p_{1/2}$ peak at 250.6 eV, which indicates the presence of argon on the diamond surface (not shown). Because argon atoms are physically adsorbed at the surface, it showed less surface conductivity. In order to remove the argon atoms from the surface and to increase the surface conductivity, the sample was annealed at 800 °C in an H_2 ambient. The Ar $2p_{1/2}$ peak disappeared and the surface conductivity was recovered after annealing, which indicates that the surface was H-terminated. After the anodic oxidation, a sharp O 1s peak and an O KLL Auger peak clearly appeared in the XPS spectrum (not shown); the calculated O/C ratio of the O-terminated diamond was 0.23, while the calculated O/C ratio of the H-terminated diamond was 0.021. Therefore, it can be confirmed that the surface became O-terminated.

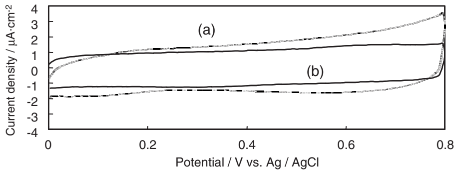

Figure 2. CVs for 0.1 M H_2SO_4 at BDD electrodes (a) before and (b) after Ar^+ sputtering. Potential sweep rate: $100\,mVs^{-1}$.

Firstly, we measured CV for a 0.1 M H_2SO_4 solution at both of the BDD electrodes before and after sputtering. The background current was lower for the smoothed electrode than it was for the initial polycrystalline electrode (Figure 2). Determination by AFM gave a surface area of $1.21\,cm^2$ for the polycrystalline electrode and $1.04\,cm^2$ for the smoothed electrode for each $1\,cm^2$ of Si substrate.

Next, we studied the electrochemical responses for several redox couples. The morphological changes in the surface did not appear to cause a notable change except the experimental errors in the electrochemical behavior when the H-terminated BDD electrode was used.

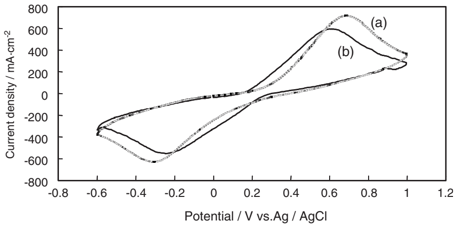

Figure 3. CVs for 1 mM $K_3Fe(CN)_6$ at BDD electrodes (a) before and (b) after Ar^+ sputtering.

Table 1. Comparison of anodic-cathodic peak potential separations for several redox species at diamond electodes before and after Ar^+ sputtering

	Δ Ep/mV (H-termination)		Δ Ep/mV (O-termination)	
	before	after	before	after
$Ru(NH_3)Cl_3$	140	140	206	206
$Fe(ClO_4)_2{\cdot}6H_2O$	972	811	682	672
K_3IrCl_6	348	296	**530**	**331**
$K_4Fe(CN)_6$	170	169	**540**	**320**

On the other hand, the electrochemical responses for several redox couples changed when the electrodes were O-terminated. Figure 3 shows CVs in a 0.1 M Na_2SO_4 solution containing 1 mM $K_3Fe(CN)_6$ before and after sputtering. A 540 mV anodic-cathodic peak separation was observed in the CV for the electrode before sputtering, and a small peak separation (320 mV) was obtained for the electrode after sputtering. This fact indicates an increase in the heterogeneous electron transfer rate constant at the electrode with the smoothed surface compared to the electrode with the rough surface. An increase in the apparent electron transfer rate constant due to the sputtering was also observed for the $InCr^{2-/3-}$. The results of the electrochemical measurements are summarized in Table 1.

However, we never observed any changes for $Ru(NH_3)_6{}^{2+/3+}$ and $Fe^{3+/2+}$ at the smoothed surface. As described above, it is known that the electrochemical properties of diamond electrodes are quite sensitive to the surface termination.[11] That is, a negative surface-charge density due to oxygen termination may affect the potential at the reaction plane. As a result, the negative charge of the carboxyl group can act as a repulsive site with respect to a redox species with a negative charge.

When we measured the electrochemical responses by using as-grown electrodes under the same conditions including the surface terminated species, such differences (bold in Table 1) could not be observed. This indicates that the observed differences of electrochemical response must be explained as the morphological dependences as follows. When the surface is rough and has an O-terminated surface, there are more repulsive sites with a carboxyl group for redox species with a negative charge because of the three-dimensional roughness. The ruggedness of the surface was decreased by sputtering, so the amount of surface oxygen decreased in parallel. Indeed, the surface roughness of the electrode before sputtering (Ra = 238 nm) was 8 times greater than it was after sputtering (Ra = 30 nm). This was consistent with the results of the electrochemical measurements.

We conclude that an O-terminated smoothed surface only accelerates the apparent electron-transfer rate constant for redox species with a negative charge. The present work offers new insights into how the surface morphology of polycrystalline diamond electrodes can affect the electrochemical properties. Also, diamond electrodes with a smoothed surface may not only be useful for electrochemical applications, but also for the study of basic electrochemical properties.

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