

Recent progress in understanding the electrochemical behavior of the oxidized boron-doped diamond electrode surface

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Boron-doped diamond (BDD) thin films have recently come to be considered as being among the most ideal electrode materials for electroanalysis and electrolysis. For BDD films prepared by use of the microwave plasma-assisted chemical vapor deposition (MPCVD) method, the as-deposited surfaces are hydrogen-terminated. These surfaces, however, can be oxidized while being used as anodes, i.e., at relatively high potentials, and in the process, the physical and electrochemical properties can be modified.

One of the consequences of the electrochemical oxidation is that the as-deposited hydrogen termination converts to oxygen termination. The physical properties are quite different: hydrogen-terminated diamond surfaces exhibit hydrophobicity and high electrical conductivity, whereas oxygen-terminated diamond surfaces exhibit hydrophilicity and very low conductivity. Furthermore, the electrochemical properties, e.g., the electron-transfer behavior for some compounds, have also been reported to be greatly affected by anodic and oxygen-plasma treatment of BDD electrode surfaces.

An important aspect of the oxidation of the diamond surfaces is the presence of oxygen-containing surface functional groups. Because the direction and magnitude of surface dipoles is different for hydrogen- and oxygen-terminated surfaces, the hydrophilic-hydrophobic properties as well as the electron-transfer properties for ions and polar molecules are expected to be quite different. It has also been argued that changes in surface functional groups can cause great changes in surface conductivity, but it has also been argued that the latter are caused by changes in the amounts of hydrogen present in a shallow surface film region.

The mechanisms underlying the differences in the surface conductivities for the hydrogen- and oxygen-terminated BDD surfaces remain controversial. Understanding these mechanisms is important for the further development of applications that utilize the surface properties of diamond, including electronic devices, as well as electrochemical ones such as electroanalytical techniques and electrolytic processes.

In the first part of the present work, the electrochemical properties of several types of diamond electrodes, including polycrystalline and homoepitaxial films, that underwent anodic treatment were examined with the electrochemical impedance spectroscopic (EIS) technique, as well as with capacitance-potential measurements. From an analysis of the Bode plots, it was found that an additional capacitance element, which is

apparent in the relatively high frequency range, was generated on the polycrystalline and (100) homoepitaxial diamond electrodes after anodic treatment. This capacitive element can be characterized as being non-faradaic, because it has negligible dependence on the applied potential. Acceptor densities and depth profiles were calculated from the Mott-Schottky plots, and the acceptor densities in the near-surface region of the anodically-treated surfaces were found to be extremely low [1]. These results indicate that passive layers were generated on the diamond surfaces by the anodic treatment. The capacitance-potential behavior was also consistent with a model consisting of a semiconductor with a passive surface film. The passive film is proposed to arise as a result of the removal of hydrogen acting as an acceptor in the subsurface region, leaving hydrogen that is paired essentially quantitatively with the boron dopant, effectively neutralizing it.

In the second part of this work, the electrochemical behavior of several different types of redox-active species, both ionic and neutral types, were compared for the polycrystalline BDD films [2]. For some anionic reactants, there is an inhibition of the electron transfer for the anodically oxidized surface compared with the as-deposited surface, and there is also an acceleration of the electron transfer for the anodically oxidized surface for some cationic reactants. These results can be explained by interactions of the ionic charges with the dipoles on the two types of diamond surfaces. However, there are also marked differences in behavior even for neutral species. For example, there is a large inhibition in the oxidation of ascorbic acid for the anodically oxidized surface, whereas there is a negligible change in the ease of oxidation of dopamine. In order to explain the interaction of these two surfaces with neutral reactants, we have speculated that dipole-dipole interactions are important. Therefore, we have calculated the dipole moments using density functional theory with allowance for the presence of an aqueous environment. Although we found that such interactions are indeed important in the present work, we found that the “zeroth-order” model, in which the dipole of the reactant causes it to be oriented unfavorably for ET to the diamond surface, is inadequate. Therefore, it appears to be necessary to consider the electron transfer as a process involving the whole system, including molecule and diamond surface. In doing this, specifically using molecular orbital calculations involving small diamond clusters (ca. 60-80 atoms), we have found differences in the degree of matching of the orbital energies of the two types of diamond surfaces with those of the ascorbic acid molecule.

The overall picture of the oxidized BDD electrode surface is one in which there is a strong surface dipole, due to the presence of C-O functional groups such as carbonyl and ether groups, on top of a very poorly conducting thin (tens of nm) passive film. The effect of the surface dipoles appears to be particularly influential when the surface passive film is highly insulating.

References

1. D. A. Tryk, K. Tsunozaki, T. N. Rao, A. Fujishima, *Diamond Relat. Mater.*, **10**, 1804 (2001).
2. D. A. Tryk, H. Tachibana, S. Funyu, H. Inoue, T. Fukazawa, H. Notsu, E. Popa, T. Kondo, A. Fujishima, submitted to *Diamond Relat. Mater.*