Factors Affecting the Electrical Properties of Polycrystalline Diamond Films: Impact on Electron Emission and Electrochemical Reactions

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Boron-doped diamond electrodes have attracted considerable interest in recent years, due to their excellent electrochemical properties (1). Chemical vapor deposited (CVD) diamond is quite versatile as an electrode. The material can be used in electroanalysis to provide low detection limits for analytes with superb precision and stability, for high-current density electrolysis (1-10 A/cm^2) in aggressive solution environments without any microstructural or morphological degradation, as a corrosion-resistant electrocatalyst support, and as an optically transparent electrode (OTE) for spectroelectrochemical measurements (1). This advanced electrode provides researchers with a material that meets the requirements for a wide range of applications. In terms of signal transduction *via* electroanalytical measurements, diamond generally provides significant improvements over conventional carbon electrodes (e.g., sp^2 carbon), in terms of linear dynamic range, limit of detection, response precision, and response stability. Broader application of this new electrode has been limited by the fact that there has been no commercial source for the material. This situation has recently changed, as there are now at least four commercial units marketing electrically conducting diamond thin-film electrodes (2). Importantly, the cost is not exorbitantly expensive, as is commonly perceived.

Boron-doped diamond is also being investigated as a possible thermionic emitter (3). Thermionic emission provides a means of direct thermal-to-electrical energy conversion. There are several parallels between electron transfer across a solid-liquid interface and electron emission across a solid-vacuum interface. Certainly, in both cases, the homogeneity of the electrical properties in the bulk and at the surface of the material, as well as the uniformity of the surface work function are critical issues.

Boron-doped, polycrystalline diamond is without a doubt a “complex” material. First, the material possesses grains and grain boundaries, which impact the electronic as well as the structural properties. Second, it is well known that polycrystalline diamond is not homogeneously doped with boron. For example, the {111} growth sectors incorporate about 10x more dopant that do the {100} sectors (4). Third, in addition to boron’s influence on the electronic properties of the material, other factors such as lattice hydrogen, adventitious nitrogen, etc. are also important. Fourth, the polycrystalline material possesses localized stress gradients across the grain and grain boundary regions. Finally, polycrystalline films can contain multiple structural and chemical defects that influence the material properties.

Several factors influence the electrical conduction within diamond and the transfer of charge across the solid-liquid or solid-vacuum interface. For example, in electrochemistry, the diamond thin-film electrode response (i.e., electrode reaction kinetics) are controlled by the (i) potential-dependent density of electronic states, which is affected by the doping type, level, and distribution, (ii) surface chemistry, (iii) morphology and microstructure, (iv) defect density, (v) non-diamond carbon impurity content, and (vi) electric double layer structure. *The extent to which any of these factors affects the electrode response very much depends on the reaction mechanism for the particular redox system.*

This paper will discuss the spatial uniformity of the electrical properties and surface work function of polycrystalline, boron-doped diamond as studied by electrochemical methods, thermionic emission energy distributions, scanning electrochemical microscopy, scanning Kelvin probe measurements, and conductivity probe AFM. Specifically, the effect of the boron-doping level and the surface chemistry will be explored. Additional characterization data will include Hall measurements of the carrier concentration and mobility as a function of the doping level, boron nuclear reaction analysis measurements to determine the boron-doping level, and x-ray photoelectron spectroscopy measurements to learn about the surface chemistry.

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