# The local structure in heavily boron-doped diamond and the effect this has on its electrochemical properties

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## ARTICLE INFO

## ABSTRACT

Transmission electron microscopy (TEM) coupled with electron energy loss spectroscopy (EELS), and first principles calculations of EEL spectra were utilized to elucidate the relationship between the microscopic structure and the electrochemical properties of heavily boron-doped diamond (h-BDD). The electrochemical properties of h-BDD containing 1 at.% and 3 at.% boron are very different. TEM observations showed that 1 at.% h-BDD consists of small densely packed diamond crystallites, while 3 at.% h-BDD contains small voids and a graphite phase partly along the grain boundaries. The EEL spectrum of the grain interior in 1 at.% h-BDD and comparison of this with a theoretical spectrum shows that the boron atoms are mostly dispersed as single isolated substitutional atoms on diamond lattice sites in the grain interior and that only a small amount of $sp^2$-bonded carbon is present. In contrast, in the grain interior of 3 at.% h-BDD, the boron atoms are mostly associated with nearest neighbor boron pairs, and consequently $sp^2$-bonded carbon is formed. Thus, the local structure has a significant effect on the amount of $sp^2$-bonded carbon. The quite different electrochemical properties of the samples are ascribed to the amount of $sp^2$-bonding arising from the different local structures.

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## 1. Introduction

The unique electrochemical properties of boron-doped diamond make it an attractive electrode material [1—4]. Diamond can be varied from a p-type semiconductor to a metal-like conductor by adjusting the boron doping level. Furthermore, in 2005 Ekimov et al. showed that heavily boron-doped diamond (h-BDD) was superconducting [5]. This finding ignited interest in the electronic structure of boron-doped diamond and consequently many papers on the electronic structure of h-BDD were published in the late 2000s [6—9]. For electrochemical applications, a high boron concentration in diamond is usually preferable owing to the higher conductivity. However, there is dilemma in that heavy boron doping can easily cause non-diamond $sp^2$-bonded carbon

impurities to be incorporated as a more stable phase, since diamond is a thermodynamically metastable form of carbon, even at CVD growth temperatures and pressure. On the other hand, we have previously reported that h-BDD containing $sp^2$-bonded carbon impurities shows interesting characteristics different from the typical properties of standard boron-doped diamond and $sp^2$-bonded carbon materials [10,11]. Such disordered h-BDD electrodes exhibit similar properties to glassy carbon electrodes, which have active properties after anodic treatment, whereas the dimensional stability of h-BDD electrodes are similar to typical diamond electrodes, which are much more durable than glassy carbon electrodes. Carbon materials, such as graphite, have been classically utilized as electrode materials in the electrochemical industry and are nowadays utilized for Li ion batteries and supercapacitors. In comparison with diamond, one of the reasons for the versatility of $sp^2$-bonded carbon material is the moderate durability, which allows it to undergo activation treatment. Therefore, it is expected that new electrochemical applications will be found that make use of the $sp^2$ and $sp^3$-bonded carbon in h-BDD containing non-

diamond carbon impurities. However, the origin of the characteristics of both $sp^2$ and $sp^3$-bonded carbon in disordered h-BDD material is still unclear.

The recent progress in transmission electron microscopy (TEM) techniques, has enabled the local structure of boron in a diamond matrix and that at dislocations in h-BDD to be investigated by atomic resolution imaging and spectroscopy [12–15]. S. Turner at al. have found a distinct difference between the coordination of boron dopants in pristine diamond areas and in defective regions in h-BDD samples using TEM [12]. Meanwhile, the influence of the local structure on the electrochemical properties of h-BDD has only been studied using scanning probe microscopy [16]. In this study, to clarify the relationship between the local structure and the electrochemical properties of h-BDD, TEM and electron energy-loss spectroscopy (EELS) of h-BDD were performed. Further clarification was obtained by carrying out theoretical calculations of the EEL spectra expected from h-BDD. In particular, we focused on the local structure around boron atoms and the non-diamond carbon sites in strongly disordered samples with $sp^2$-bonded carbon impurities.

## 2. Experimental section

**Synthesis of heavily boron-doped diamond**: Polycrystalline h-BDD thin films were grown on Si (100) substrates using a 2.45 GHz microwave plasma chemical vapor deposition (CVD) system equipped with 5 kW microwave plasma reactors (CORNES Technologies Corp., Model AX 5400). In order to enhance the diamond nucleation density, the silicon substrates were pretreated by abrading with diamond powder and were then ultrasonically cleaned in deionized water and isopropyl alcohol. The films were grown under a pressure of 110–120 torr with a total gas flow of 500–550 sccm using hydrogen, acetone and trimethoxyborane. Compared with dopant gases such as diborane and trimethylboron, trimethoxyborane, a volatile liquid, has advantages such as safety and low cost, especially when synthesizing heavily boron-doped diamond. In addition, the combination with acetone, which is a liquid source of carbon, makes it easy to control the doping concentration by controlling the composition of the mixed source. Oxygen atoms contained in the mixture are considered to reduce the growth rate but to improve film quality, since oxygen atoms attack both diamond and non-diamond carbon [17]. Two types of h-BDD films were prepared using different compositions of the carbon and boron sources. The composition of the sources, based on the Raoult's law at 25 °C, was such that the boron-to-carbon (B/C) ratios in the feed gas were 1% or 5%. The amounts of $sp^2$-bonded carbon impurities were also expected to be different for the two different conditions.

The atomic content of boron in the h-BDD films grown from sources with B/C ratios of 1% and 5% were estimated to be 1 at.% and 3 at.%, respectively, by glow discharge-optical emission spectroscopy (GD-OES) (Fig. S1). Hereinafter, we refer to these h-BDD films as 1 at.% h-BDD and 3 at.% h-BDD.

**Characterization of the h-BDD films**: To estimate the amount of boron in the h-BDD films, glow discharge-optical emission spectroscopy (GD-OES) using a GD-profiler HR (Horiba Jobin Yvon Inc., France) was carried out with reference to a h-BDD film with a known boron concentration measured by secondary ion mass spectroscopy (SIMS). To investigate the carbon bonding structures in the films, Raman spectra were recorded in ambient air at room temperature with an Acton SP2500 (Princeton Instruments) under excitation at 532 nm from a green laser diode. Cyclic voltammetry was conducted with a potentiostat/galvanostat (HZ-5000, Hokuto Denko Corp.) using a single-compartment three-electrode PTFE cell with an Ag/AgCl (saturated KCl) reference electrode and a Pt coiled wire counter electrode. The geometric area of the working

electrode was $0.36 \, cm^2$. The electrical contacts for the electrochemical measurements were made by attaching copper wires to the h-BDD surface with silver paste. The cyclic voltammetry measurements were performed after anodic treatment of the surface, to which 3.0 V vs. Ag/AgCl was applied for 10 min in 0.1 M $HClO_4$.

**TEM sample preparation and TEM-EELS analysis**: TEM samples of the h-BDD films were prepared by a lift-out method using focused ion beam (FIB) equipment (Hitachi MI4000L). The FIB damaged surface layers of the TEM samples were removed by 900 eV Ar ion sputtering using an ion-milling tool (Fischione, NanoMill Model 1040). TEM observations and EELS measurements of the h-BDD specimens were performed using an aberration-corrected TEM (JEOL, JEM-ARM200F) with a cold field-emission gun and an electron energy filter (Gatan, GIF Quantum ERS, Model 966). The TEM was operated at 80 kV to minimize the electron beam damage to the specimens during observation and the EELS measurements. EEL spectra were acquired at an energy dispersion of 0.1 eV/ch and a collection angle of ~50 mrad using an electron probe with a convergence angle of ~20 mrad. The full width at half maximum of the zero loss peak during the EELS measurements was around 0.6 eV. EELS data analysis and quantification with Hartree-Slater cross sections were performed using Gatan digital micrograph software.

**Computational procedure**: The DFT calculations were performed using two different methods. One is the projector-augmented wave (PAW) method as implemented in the VASP code [18–20]. This makes efficient and accurate optimization of the atomic arrangement and evaluation of the total energies. The exchange and correlation terms in the Kohn-Sham equation were taken into account by the generalized gradient approximation (GGA) as formulated by Perdew, Burke and Enzerhof (PBE) [21]. A Monkhorst-Pack k-point grid with a spatial resolution of $0.5 \, Å^{-1}$ was used for all the structures [22]. The kinetic energy cutoff was 500 eV for all calculations. Structural optimization was truncated when the force on all ions became $<2.0 \times 10^{-3}$ eV/Å.

In order for the theoretical EEL spectra to be correct, it is necessary to take into account the correlation between the core-holes and the excited electrons. This can be evaluated in a straightforward way using an all electron method. For this purpose, we employed another theoretical method, i.e., the full-potential linearized augmented plane wave (APW) plus local orbitals technique as implemented in the WIEN2k code [23,24]. The muffin-tin radius, RMT, was set to 0.71 Å for all atoms. The basis set for the APW method was determined by a cutoff energy of 260 eV. The theoretical EEL spectra were calculated using the electric-dipole transitions in the core-hole state. The core-hole effects were fully taken into account in the present calculations by removing one electron from the B 1s orbital of interest and putting one additional electron at the bottom of the conduction band. In order to avoid artificial interactions between core-holes, the supercell sizes were chosen to be more than 200 atoms. Each of the calculated spectra was broadened by a Gaussian function with a full width at half maximum of 1.0 eV. The transition energies were obtained as the difference in electronic energy between the ground and core-hole states.

## 3. Results and discussion

### 3.1. Characterization of the h-BDD films

Fig. 1a shows Raman spectra of the 1 at.% and 3 at.% h-BDD films. The Raman spectrum for the 1 at.% h-BDD film is typical of h-BDD. In the spectrum, the zone-center optical phonon peak for diamond which is normally observed around $1330 \, cm^{-1}$ for intrinsic diamond, has shifted slightly to a lower wavenumber and can be