Boron-rich inclusions and boron distribution in HPHT polycrystalline superconducting diamond

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ABSTRACT

Polycrystalline boron-doped superconducting diamond, synthesized at high pressure and high temperature (HPHT) via a reaction of a single piece of crystalline boron with monolithic graphite, has been investigated by analytical transmission electron microscopy. The local boron distribution and boron environment have been studied by a combination of (scanning) transmission electron microscopy ((S)TEM) and spatially resolved electron energy-loss spectroscopy (EELS). High resolution TEM imaging and EELS elemental mapping have established, for the first time, the presence of largely crystalline diamond–diamond grain boundaries within the material and have evidenced the presence of substitutional boron dopants within individual diamond grains. Confirmation of the presence of substitutional B dopants has been obtained through comparison of acquired boron K-edge EELS fine structures with known references. This confirmation is important to understand the origin of superconductivity in polycrystalline B-doped diamond. In addition to the substitutional boron doping, boron-rich inclusions and triple-points, both amorphous and crystalline, with chemical compositions close to boron carbide \(B_4C\), are evidenced.

1. Introduction

Boron doping of diamond leads to p-type conductivity, and heavy doping leads to a semi-metallic and even a superconducting behavior at low temperatures [1]. Incorporation of boron atoms into the diamond lattice at high pressure high temperature synthesis conditions leads to an accumulation of local stress and strain, which prevents the synthesis of heavily boron-doped diamond in single crystal form [2]. For example, the grain size of heavily boron-doped polycrystalline diamond synthesized in the B–C growth system at high pressures usually does not exceed several microns [3]. In this type of polycrystalline diamond samples, inclusions of the boron–carbon growth medium can be present at the diamond grain boundaries as well as inside grains themselves. An example of this was demonstrated in work by Dubrovinskaia et al. [4], where detection of amorphous boron-rich material at the diamond grain boundaries in a sample synthesized from a mixture of boron carbide (\(\sim 8\%\)) and graphite at a pressure of 20 GPa and a temperature 2300 K, led to the conclusion that

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the diamond grains were isolated from each other by this amorphous material. This idea led to an alternative explanation of superconductivity in boron-doped diamond, namely that of superconductivity limited to the amorphous boron-rich impurity phase in between the B–diamond grains. In principle, mixing reagents (boron carbide and graphite), as a strategy for the preparation of boron-doped diamond, naturally favors the formation of inclusion on diamond grain boundaries. In practice, however, the microstructure of isolated polycrystalline diamond grains is very difficult to resolve, as the formation of a new diamond nucleus on an existing diamond surface (heterogeneous nucleation) is more favorable than growth in the medium itself (homogeneous nucleation). The same authors also pointed out the formation of a diamond matrix with isolated boron-rich inclusions in a polycrystalline sample, synthesized from graphite-like material BC$_3$ [5]. The P-T-parameters for the synthesis were the same as in Ref. [4] and the inclusions were dielectric boron carbide (B$_6$C) phase with slightly smaller lattice parameters $a = 5.582 \text{ Å}$ and $c = 12.013 \text{ Å}$ (normal lattice parameters for carbon-saturated boron carbide B$_6$C are $a = 5.5991 \text{ Å}$ and $c = 12.074 \text{ Å}$) [6]. Inclusions of a tetragonal phase B$_6$C$_3$ have also been evidenced [7] in samples that were synthesized from mixtures of boron carbide (~8%) and graphite at higher temperatures (2500–2700 K) [4]. It is well known that boron in all its modifications, as well as the boron compounds with carbon, does not demonstrate metallic properties or superconductivity at ambient pressure. At the same time, as evidenced by the quoted literature, the mechanism for the formation of heavily boron-doped polycrystalline diamond and boron-doping of diamond remains debatable, leaving space for the advancement of new scenarios of superconductivity in boron-doped diamond. In this context, it has become very important to study the structure of grain boundaries in polycrystalline superconducting diamond obtained in the B–C system at high pressures.

Recently, global and local superconductivity measurements performed on HPHT B-doped diamond, synthesized in the B–C system, demonstrated the granular nature of superconductivity in B-doped HPHT diamond. These experiments indicate that the tetrahedrally coordinated boron atoms present in individual diamond grains indeed do cause superconductivity, and not the B-rich grain boundaries or B–C inclusions [8]. In this case B-doped polycrystalline diamond was synthesized via the reaction of a single piece of crystalline boron with monolithic graphite at 8–9 GPa and about 2500 K [9]. In the synthesis method, carbon from a graphite source dissolved in a boron-rich melt and precipitated as diamond on the once-formed diamond surface, which produces polycrystalline diamond with an overall concentration of boron in the samples at a level of approximately 3%. In contrast to the synthesis of diamond from mixtures of reagents, the formation of boron-rich inclusions at grain boundaries of the polycrystalline diamond should be suppressed. Structural information is very important for the understanding of the mechanism of polycrystalline diamond growth, the boron doping mechanism and the origin of superconductivity in boron-doped diamond. This study will be undertaken in the current contribution.

In this work, superconducting HPHT B-doped diamond synthesized from a single piece of crystalline boron and graphite is investigated using a combination of electron diffraction (ED), bright-field and high resolution TEM (BF-TEM/HRTEM), (high-angle) annular dark-field scanning electron microscopy [(HA)ADF-STEM] and spatially resolved EELS, in order to definitively determine the local boron distribution and the boron-containing phases present in the sample.

2. Experimental

Synthesis of the boron-doped polycrystalline diamond was carried out under high pressure and high temperature conditions. A graphite bar ($^{12}$C 99%, C 99.999%) with boron ($^{10}$B 96 at.%, B 99.9% crystalline, Alfa Aesar) embedded in the center was packed in a HPHT cell. Under a pressure of 8–9 GPa, the cell was heated by passing an electric current through the graphite bar. As soon as the temperature inside the bar reached the temperature (~2500 K) of the eutectic melt in the B–C system, diamond formation took place at the boron–graphite interface, as shown in Fig. 1. After synthesis, the sample was crushed into coarse pieces to gain access to the central part of the material, and was subsequently acid treated to remove any non-diamond contamination. The total concentration of boron in the polycrystalline diamond was estimated at a level of 3% [8].

An electron transparent sample for TEM was prepared by ion milling in a Balzers Ar$^+$ ion mill, starting with a 12 kV beam for initial sample thinning, continuing with a 5 kV beam and finishing with a 2 kV beam for final polishing. The initial thinning stage took significantly longer than a conventional sample (approximately 1 week of thinning time at 12 kV). Conventional BF/HR-TEM imaging and electron diffraction experiments were carried out on a JEOL 3000F microscope, operated at 300 kV.

All scanning transmission electron microscopy and spectroscopy experiments were performed on a Titan “cubed” microscope, fitted with aberration corrector for the probe-forming lens and a GIF Quantum energy filter for spectroscopy, operated at 120 kV to minimize knock-on damage in the diamond sample. The convergence semi-angle $\alpha$ for STEM was 21 mrad, the inner acceptance semi-angle $\beta$ for ADF imaging was 27 mrad and for HAADF imaging it was 85 mrad. The collection semi-angle $\beta$ for EELS was 36 mrad. All spectra were acquired at an energy dispersion of 0.25 eV per pixel and an energy resolution of approximately 1.2 eV. The boron and carbon maps were generated by plotting the intensity under the background-subtracted K-edge of B and C at each pixel using a 50 eV energy window. Quantification of the EELS data was performed using Hartree-Slater cross-sections in Gatan Digital Micrograph.

3. Results and discussion

Fig. 2 shows two ADF-STEM images of the polycrystalline boron-doped diamond sample, indicating that the sample consists of densely-packed micrometer-size diamond grains. The diamond nature of the material was confirmed by electron diffraction (example inset in Fig. 2(i)) and carbon K-edge electron energy-loss near-edge fine structure (ELNES) investigation, which will be discussed later. All the grains are well
distinguishable and separated by sharp grain boundaries, which clearly demonstrate the polycrystalline nature of the diamond.

As discussed above, other authors [4] reported that the diamond grains in their superconducting HPHT boron-doped polycrystalline state were completely isolated from each other by layers of a boron-rich amorphous phase, leading to the conclusion that this phase was responsible for the superconducting transition. Bearing this statement in mind, higher magnification (HA)ADF-STEM and HR-TEM images were recorded, as shown in Fig. 3, to expose the details of the grain junctions and boundaries in our sample.

The ADF-STEM images (Fig. 3(a) and (b)) do not show the presence of impurity-phases at the diamond grain boundaries. However, triangular shaped non-diamond inclusions were detected at some of the grain triple points. The material present at the triple points appears to be amorphous, as deduced from the lack of diffraction contrast in the ADF-STEM (Fig. 3(b)) images. The HAADF-STEM image (inset Fig. 3(a)) displays a strong contrast difference between the phase(s) present at the triple points (indicated by the black triangles) and the diamond material. HAADF-STEM imaging is also known as Z-contrast imaging, as the image intensity is both mass-thickness sensitive and directly proportional to \( Z^{1.7} \) [10,11]. The low contrast at the triple-junctions suggests either a lower local density or the presence of lighter constituting atomic species in these regions, namely B \((Z = 5)\) instead of C \((Z = 6)\). As mainly incoherently scattered electrons contribute to the HAADF-STEM image formation, diffraction contrast is minimized under these imaging conditions and the sharp grain boundaries visible in the ADF-STEM image are not so apparent (see demonstrative comparison between Fig. 3(a), being ADF-STEM with diffraction contrast and the inset (a) being HAADF-STEM with Z-contrast).

The high resolution TEM image in Fig. 3(c) displays a triple-point (TP) region together with a direct diamond–diamond grain boundary. From the lack of fringes in the triple-point area, it is clear that the material within the triple points is amorphous. This is however not the case for the boundary between the two diamond grains; both grains remain crystalline up to the boundary. In other words: the diamond/diamond grain boundaries in the material show a minimal amorphous presence. Therefore, our study does not confirm the formation of a continuous boron-rich amorphous phase isolating diamond grains from each other in polycrystalline...
superconducting diamond. These findings corroborate with conclusions in recent work by Zhang et al. [8] that superconductivity in polycrystalline diamond has a granular character and coincides with the substitutional heavy boron doping in diamond grains.

To verify the presence of boron in the grain junction regions and probe the chemical nature of the boron at these sites, EELS spectra were acquired from the large and small triangular pockets in Fig. 3(a) and (b), as well as from a typical diamond grain area. The boron and carbon K-edge EELS spectra acquired from the large triple-junction in Fig. 3(b) are shown in Fig. 4 (black spectrum). Both the boron K-edge and the carbon K-edge ELNES show typical features of boron carbide $\text{B}_4\text{C}$ [12,13]. A quantification of the B:C ratio in this region yields a ratio of $\sim 47 \pm 2$ at.% boron and $\sim 53 \pm 2$ at.% carbon, corresponding to the formula $\text{B}_3\text{C}$. However, the B K-edge fine structure is identical to literature references for the B K-edge in $\text{B}_4\text{C}$, while the carbon K-edge significantly differs from the C fine structure of $\text{B}_4\text{C}$ [13]. This can be either explained as a partial boron carbide phase formed within the probed area or, more likely, as a mixture within the probed area of the amorphous boron carbide $\text{B}_4\text{C}$ and the diamond phase.

The EELS spectrum acquired from inside a thin diamond grain are also displayed in Fig. 4 (blue line). Both the boron and carbon K-edge fine structures show distinctly different signatures compared to the spectra acquired from the pocket area. The boron K-edge spectrum from the diamond grain is characterized by a low intensity pre-peak at 189.0 eV and three resolved peaks A, B, C at 196.5, 202.0 and 209.5 eV, while the B fine structure from the...
The boron-rich phase at the triple point is dominated by a sharp pre-peak at 196.5 eV and a broad peak. The boron K-edge is known to be coordination sensitive [14,15], meaning that we have a different local coordination of the probed boron atoms in both areas. Quantification of the B concentration from this spectrum yields a value of 3.5 at.% B, which is similar to the B content in CVD grown superconducting NCD diamond films [16]. The small 1s \( \pi^{*} \) feature at 285 eV has its origin in the presence of amorphous carbon, a result of sample preparation [8].

In order to gain insight into the boron coordination in the HPHT diamond grains, a known reference for tetrahedrally coordinated B in pristine CVD-grown NCD (nanocrystalline diamond) diamond is plotted together with the acquired data in Fig. 5. The B K-edge fine structure from the HPHT diamond grain region is highly similar to that of B in CVD diamond, confirming that boron is tetrahedrally embedded in the diamond grains in our HPHT sample [17,18].

Although most of the diamond grains in the polycrystalline diamond appear to be of uniform composition, a few grains contain boron-rich inclusions. Fig. 6(a) shows one of these inclusions inside a single diamond grain. Typically these inclusions are one to several hundreds of nm in diameter. The material is crystalline \( \text{B}_4\text{C} \), as evidenced by the electron diffraction pattern in Fig. 6(b). The ADF-STEM image shown in Fig. 6(c) demonstrates the presence of another inclusion inside an individual diamond grain. A STEM-EELS experiment was performed in order to confirm the chemical composition inside this grain. Fig. 6(d) and (e) display the boron and carbon elemental distribution inside the investigated area. The boron map clearly evidences a boron-rich inclusion embedded inside the diamond grain, and the carbon map confirms a lower content of carbon inside the inclusion. The EELS spectrum acquired from the inclusion area (Fig. 6(g)) shows a typical boron and carbon fine structure of boron carbide and quantification analysis yields 72 ± 6 at.% boron and 28 ± 6 at.% carbon in the inclusion.

The absence of a gradient distribution of carbon and boron around the boron-rich inclusions in our polycrystalline diamond (Fig. 6(e) and (f)) excludes the possibility of a boron “exsolution” from boron-doped diamond upon quenching under pressure as the formation mechanism of these inclusions. The results rather suggest that the inclusions were trapped during the polycrystalline diamond growth. In addition, the formation of singular boron-rich inclusions of up to 0.4 \( \mu \)m in size cannot be explained by the precipitation of boron from boron-doped diamond upon quenching for 2–5 s. The precipitation would mean a carbon and boron diffusion in opposite directions, which is very slow in diamond. It was reported, for instance, that carbon diffusion in diamond is on a scale much less than \( \sim 32 \) nm at 2600 K for 0.5–20 h under pressure of 7.7 GPa [19]; diffusion of boron in diamond was not detected at temperatures as high as 1900 K [20]. The precipitation mechanism for the formation of boron-rich inclusions in boron-doped polycrystalline diamond upon cooling is therefore not realistic.

### 4. Conclusions

Polycrystalline boron-doped superconducting diamond, synthesized at high pressure and high temperature (HPHT) via a reaction of a single piece of crystalline boron with monolithic graphite, has been investigated by analytical transmission electron microscopy. High resolution TEM imaging and EELS elemental mapping evidence the presence of largely crystalline diamond–diamond grain boundaries within the material and confirm the presence of substitutional boron dopants within individual diamond grains through comparison of the acquired boron K-edge EELS fine structures with known references for substitutional boron in diamond. In
addition to this substitutional boron doping mechanism, the presence of isolated boron-rich inclusions and triple points, both amorphous and crystalline in nature with a chemical composition close to boron carbide $\text{B}_4\text{C}$, is evidenced. Our study suggests that these boron-rich inclusions are trapped during the growth of polycrystalline diamond.

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