High-pressure synthesis and characterization of superconducting boron-doped diamond

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Abstract

Microcrystalline powders of boron-doped diamond were produced in the C–H–B system under a pressure of 8 GPa and at a temperature of more than 2000 K. The presence of boron in the C–B–H system was shown to decrease the temperature-pressure parameters for diamond synthesis compared with those for the binary C–H system (naphthalene). A decrease in the parameters for synthesis in the system with boron may be due to the formation of graphite with less perfect crystal structure during an intermediate stage of diamond formation. Superconducting diamond microcrystals are synthesized in the C–H–B system with boron content of about 5–10 at% in a mixture with naphthalene. Superconductivity below 3.5 K in boron-doped diamond powder is detected in AC magnetic susceptibility measurements.

Keywords: Diamond; Boron; Doping; Synthesis; Superconductivity; Pressure

1. Introduction

The doping of diamond with boron leads to the appearance of p-type conductivity in diamond. With increasing concentration of boron, the electrical conductivity of diamond acquires a metallic character at room temperature [1], and at temperatures of 1–9 K, a transition of diamond to the superconducting state is observed [2–4]. Superconductivity has been discovered in B-doped polycrystalline diamonds synthesized under high pressures and temperatures conditions [2] and in B-doped diamond films [3,4] grown under metastable conditions. Results obtained on monocrystalline samples synthesized in the region of thermodynamic stability of diamond allow refinement of physical properties of diamond and of specific features of boron incorporation into its lattice. In this case, the preparation of diamond in nonmetallic growth media provides the possibility for reducing the influence of metallic impurities on physical properties of diamond. The necessity for synthesis of diamond crystals in nonmetallic media stems from observed variations in the low-temperature behavior of the resistivity of monocrystalline diamond samples obtained in metallic melts under high pressure [1] and, as well, in diamond films [2]. Crystals doped in metal-containing media display a “metallic” temperature dependence of their resistivity to lower (30–50 K) temperatures than in the case of diamond films (200–250 K). The synthesis and doping of diamond with boron in the nonmetallic B–C–H system was achieved previously under high pressures and temperatures [5]; however, specific details of the diamond synthesis and the electrophysical properties of diamond in that case have not been studied. The parameters of the synthesis also have not been accurately determined.

The goal of this paper is to study specific details of the synthesis and structure of diamond crystals doped with boron in the C–H–B system as well as to investigate the
behavior of the magnetic susceptibility of samples at low temperatures.

2. Methods

Experiments were carried out using a toroid-type high-pressure chamber [6] with a reaction volume of about 30 mm$^3$. The procedure for temperature determination is very important for experiments performed under pressure and temperatures above 2000 K. In our experiments, temperature was determined from earlier measurements of the dependence of temperature in the high-pressure chamber on electric power supplied to a heater. The temperature of incongruent melting of SiC [7] was used as a reference point. At this temperature, upon heating, silicon carbide decomposes into a solution of carbon in liquid silicon and graphite. For the synthesis of monocrystalline diamond, carbon, hydrogen, and boron were introduced into the reaction zone of the high-pressure chamber (surrounded with graphite) in the form of homogeneous mixtures of naphthalene C$_{10}$H$_8$ and orthocarborane C$_2$B$_{10}$H$_{12}$, close in their physicochemical properties, or naphthalene with amorphous boron. The boron content with respect to carbon, B/(B+C) in the initial mixture for the diamond synthesis varied from 0.065 to 10 at%. The content of impurities, such as metals, silicon, etc. in the initial mixtures was no more than 0.01 mass%. The reactants were subjected to pressure of 8–9 GPa and then heated to the specified temperature. The hold-up time at constant $P$ and $T$ was 10–60 s. After the synthesis, diamond crystals were boiled for an extended period in perchloric acid (HClO$_4$) and etched in hydrofluoric acid (HF) to remove graphite and accompanying substances. Diamond samples treated in acids contained less than 0.2 mass% of metallic impurities.

3. Results and discussion

From results of our experiments and published data, we compare in Fig. 1 the tentative regions of diamond formation in the B–C [8], C–H–B, and C–H systems to the calculated graphite–diamond equilibrium line. As follows from analysis of these data, the synthesis of diamond in the binary systems B–C and C–H requires rather high pressures (at least 8 GPa) and temperatures (above 2300 K); whereas, diamond formation in the B–C–H system occurs at lower $P$ and $T$ (the temperature of the synthesis is about 2000–2100 K). Results of X-ray phase analysis of the synthesized diamond powders (with crystal sizes ranging from 1 to 40 μm) are presented in Fig. 2. According to these data, there is no evidence for nondiamond phases in the diamond powders treated in acids. The cubic cell parameter was calculated from the (331) line of diamond and the (533) reflection of silicon, which served as a standard. The absolute error on the cell parameter is estimated to be $3 \times 10^{-5}$ nm. The cell parameter of diamond increases systematically with increasing boron concentration in the initial mixture, as shown in Fig. 3; however, it is obvious that, at larger boron concentrations in the starting materials, boron is less effectively doped into diamond when the doping level approaches the limiting solubility of boron in diamond. Diamond synthesis in the binary B–C system is apparently the limiting case, producing the maximum concentration of boron in diamond. Experiments on diamond synthesis in the B$_4$C–C system near the eutectic melting line of the
mentioned system succeeded in obtaining doped diamond with the maximum cell parameter \((0.3578 \pm 0.0001 \text{ nm})\) and a shift of the characteristic diamond Raman mode \(1332 \text{ cm}^{-1}\) toward lower values by about \(40–45 \text{ cm}^{-1}\). (See Fig. 4). The Raman spectra from the (1 1 1) faces are presented in Fig. 4. The following features of the Raman scattering from crystals synthesized in the region of the thermodynamic stability of diamond should be noted. The reproducibility was observed in spectra for crystals of various sizes taken from the powders synthesized in experiments with identical parameters. Lines characteristic of graphite-like carbon were absent in the spectra. The crystals were transparent for laser radiation with a wavelength of 488 nm, which follows from the appearance of a silicon line in experiments that used a silicon table for samples. The Raman line of diamond at \(1332 \text{ cm}^{-1}\),

![Fig. 3. Cubic cell parameter of diamond, \(a_0\), versus boron atomic concentration, \(B/(C+B)\), in the B–C–H \((C_{10}H_8+B)\) system.](image)

![Fig. 4. Room temperature Raman spectra of diamond samples recorded at a laser wavelength of 488 nm. (a)–(f) Raman spectra taken from (1 1 1) faces of crystals synthesized at various \(B/(C+B)\) ratios in the C–H–B system; (g) Raman spectrum taken from a fracture surface of polycrystalline diamond synthesized in the B4C–C.](image)
characteristic of undoped diamond, shifts toward lower values with increasing boron concentration in the initial mixture, and if the center of the line shifts to 1305 cm\(^{-1}\), asymmetry of the peak increases due to the appearance of a smoothly varying low-frequency component. For the polycrystalline diamond sample with an extremal value of the lattice parameter obtained in the B\(_4\)C–C system, the position of the Raman line of diamond is substantially displaced (by about 10 cm\(^{-1}\)) with respect to that for monocrystalline samples obtained at boron concentrations of 5–10 at\%. The relationship between the characteristic Raman mode frequency of diamond and the cell volume for crystals and polycrystals synthesized in this work is presented in Fig. 5 along with some previously published data. A close to linear relationship is apparent in these data. The maximum observed expansion of the diamond corresponds to a “negative” pressure of about 4.2 GPa applied to undoped diamond, as estimated from the compression isotherm \[9\]. The “negative” pressure in doped diamond with the maximum volume corresponds to the tensile strength of diamond \[10\]. It follows from data shown in Fig. 5 that the deviation of the Raman frequency line for doped diamond toward lower values with respect to corresponding values for an extended lattice of undoped diamond points to softening of optical phonons in doped diamond.

Returning to the question about conditions for diamond synthesis, it seems most interesting to understand why the appropriate \(T–P\) parameters decrease if boron is added to naphthalene. Using the X-ray phase analysis and Raman spectroscopy, we investigated the products resulting from processing the initial materials at temperatures somewhat lower than those required for diamond formation (Fig. 6). According to X-ray phase analysis, either graphite or graphite with boron carbide appears in these products. According to current notions about diamond synthesis from organics under high pressures and temperatures, graphite formation is an intermediate stage of the process \[11\]. This graphite subsequently serves as a source of carbon during the nucleation and growth in the medium of gaseous products of decomposition. Analysis of the results presented in Fig. 6 obviously shows that the graphite structure, both from X-ray diffraction (by the broadening of diffraction lines) and from Raman spectroscopy, becomes more defective when boron is introduced into the C–H system. If the Raman line at 1580 cm\(^{-1}\) is characteristic of graphite obtained as a result of naphthalene decomposition, the appearance of an intense 1360 cm\(^{-1}\) band (D mode) and weak 1620 cm\(^{-1}\) band (D’ mode) \[12\] in Raman spectra for graphite formed in the presence of boron points to structural disorder in graphite. If boron concentration in the initial mixture exceeds 2.4%, the formation of boron compounds with carbon is apparently possible at elevated temperatures. Thus, the lines, which are with sufficient certainty related to boron carbide, can be understood in the corresponding diffraction patterns and Raman spectra of these samples. However, whether boron carbide is present during conditions of the

![Fig. 6. Raman spectra of samples synthesized in the C–H–B system at 8 GPa and 1900 K (D and D’—bands of lattice disorder in graphite, G—characteristic Raman mode for single crystals of graphite). Inset: Diffraction patterns of the samples (G—graphite).](image-url)
diamond synthesis, remains unclear. It should be noted that the structural changes in graphite are more clearly pronounced in Raman spectroscopy than in X-ray diffraction, which primarily points to disturbances in the short-range order of the structure. At the same time, the broadening of X-ray diffraction lines of graphite obtained in the presence of boron, compared with those for more perfect graphite synthesized from naphthalene, indicates that its crystal perfection decreases. In our opinion, these observations point to the formation of graphite with structural disorder in the system with boron. Such disorder can appreciably soften the $T$–$P$ parameters for diamond synthesis from boron-containing mixtures, taking into account that the formation of perfect graphite is regarded under certain conditions as a process competing with diamond formation [13].

The magnetic susceptibility (AC) of samples as a function of temperature was determined with a miniature inductance coil that was calibrated against a piece of superconducting Pb with a volume close to the volume of samples investigated. The temperature dependence of the magnetic susceptibility is shown in Fig. 7 for the monocrystalline powder of diamond (cell parameter $0.35748 \pm 0.00003$ nm, Raman mode frequency 1300 cm$^{-1}$) and polycrystalline sample (with lattice parameter $0.3578 \pm 0.0001$ nm and Raman mode frequency 1290 cm$^{-1}$). It is clearly seen that the transition to a superconducting state also is observed in the monocrystalline powder; however, the volume of the superconducting phase is equal, according to our estimate, to about a half of the total volume of diamond in the powdered sample. In contrast, the volume of the superconducting phase for the polycrystalline samples is larger than half of its volume. The superconducting transition temperature of the diamond powder also is lower than in its polycrystalline counterpart. This is apparently the result of different structural states of doped diamond in these two samples.

4. Conclusions

Specific features of the synthesis and structure of crystals of diamond doped with boron in the B–C–H system have been studied. An appreciable decrease in the diamond synthesis parameters (both pressure and temperature) is found when boron is doped into the naphthalene system. The formation of imperfect graphite during an intermediate stage of the diamond formation may be responsible for the decrease of $P$, $T$ parameters. The dependence of the characteristic Raman mode frequency of diamond on unit cell volume points to softening of the optical phonon upon boron doping. Superconducting diamond monocrystals have been synthesized with boron contents of 5–10 at% in a mixture with naphthalene.

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