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Synthesis of superconducting boron-doped diamond compacts with high elastic moduli and thermal stability

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ABSTRACT

Polycrystalline bulk compacts (3.5–4.0 mm in diameter and 2.5 mm in height) of superconducting boron-doped diamond with high elastic moduli have been synthesized from mixtures of graphite and boron carbide at pressures 8–9 GPa and temperature of 2500 K. We show that graphite-to-diamond transformation in the presence of liquid boron–carbon growth medium leads to formation of polycrystalline diamond matrix at B_4C concentration in the initial mixture ranging from 3.5 to 5%. Resistive transition of the samples to the superconducting state starts at 4 K and ends at 2.2 K. The thermal conductivity of the samples slightly increases in the temperature range of 230 to 400 K, and at room temperature it is as low as ~0.4 W/cm K. The boron-doped diamond demonstrates very high oxidation resistance up to 1200 K, and can be used as electrical structural material that can be exploited at elevated temperatures in air.

1. Introduction

Diamond is generally known as an electrical insulator. Being heavily-doped with boron, diamond begins to show metallic properties at room temperatures and becomes superconducting at temperatures of liquid helium [1,2]. The critical boron-concentration for the metal-to-insulator transition, $\sim 5 \times 10^{20}\ \mathrm{cm}^{-3}$, was found to coincide with that necessary to induce superconductivity in diamond [3]. In practical terms, conductive boron-doped diamond films are considered as an alternative to traditional carbon electrodes providing wide potential window of water stability, low background current, chemical and mechanical stability [4]. The B-doped diamond electrodes can be used in electroanalysis, electrosynthesis and water treatment [5]. Boron-doped diamond was successfully tested as a heating element in a high-pressure cell [6] at pressures over 10 GPa and temperatures above 3200 K, when traditional heater materials such as Re and $LaCrO_3$ cannot survive. Discovery of superconductivity in B-doped diamond has opened new possibilities to exploit outstanding mechanical properties and chemical stability of diamond combined with its superconductivity. The superconducting diamond films turn out to be an excellent candidate for fabricating monolithic superconducting circuits involving high frequency nanomechanical system with very high quality factor [7]. Micrometer scale superconducting quantum interference device made of B-doped diamond film able to operate at field as high as 4 T independent of the field direction can find application for ultra-sensitive motion detection of diamond-based nanomechanical systems [8]. Synthesis of heavily boron-doped diamond bulk samples (compacts) with a desired shape and high mechanical properties would further expand the applications of this material. In particular, the compacts are of interest for fabrication of superconducting contacts with high wear resistance, superconducting high-pressure cells, diamond tips for scanning tunneling microscopy, miniature heating elements and cells for electroanalysis.

Here we report on high-pressure and high-temperature (HPHT) synthesis of superconducting boron-doped diamond compacts with dimensions of 4 mm in diameter and 2.5 mm in height with very high elastic moduli and resistance to oxidation. In many cases, practical application of conductive diamond requires knowledge of its thermal conductivity. Using bulk samples of B-doped polycrystalline diamond we investigate the temperature dependent thermal conductivity of superconducting diamond for the first time.

2. Materials and methods

The synthesis of the samples was carried out at pressures 8–9 GPa and temperature of about 2500 K using a toroid-type high-pressure chamber. For the synthesis, graphite (99.9999%, MGOSC, Russia) and boron carbide (99.4%, metals basis, Alfa Aesar) with grain size less

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than 20 μm were used as starting materials. The powdered reagents were mixed in a mixer (Jasper mortar and pestle) for 15 min and then placed into the graphite crucible-heater of high-pressure cell [9]. Under pressure, total duration of the heat treatment was about 10 s. After the treatment, samples were quenched under pressure to room temperature by switching of the electric power. The temperature after switching off the electric power dropped from 2500 to 700 K for about 3–5 s, this gives the estimate of 360–600 K/min for the quench rate. The recovered samples were cylinders 3.5–4.0 mm in diameter and 2.5 mm in height (Fig. 1). In the samples synthesized, metal-basis impurities were not detected by energy-dispersive X-ray analysis, which means that the concentration of any impurity element in the reaction system (or in samples) was below 0.1 mass%.

For measurement of transport properties the samples were thinned to a thickness h of 0.3 mm. Thermal conductivity k of the plates was determined by laser flash technique [10] modified to directly measure the thermal diffusivity D not only at room temperature, but also in the temperature range from 150 to 420 K. In the study, the sample was mounted in the cryostat vacuumized to 10^{-3} Torr; the thermal wave was generated on the front sample side by the laser shot ($\lambda = 1.06$ μm, 10 ns), while the temperature rise kinetics $T(t)$ on the rear side was traced by a fast semiconductor IR detector. We determined D by fitting experimental $T(t)$ curves to the model ones assuming heat spread is one-dimensional, as the thickness was an order of magnitude lower than the sample diameter, and the heating laser radiation completely covered the front surface of the diamond disk. Taking into account that the convection losses on the cylindrical surface of the disk are reduced by providing the measurements in vacuum, the radial heat flow in the sample was negligible. To improve the accuracy in the evaluation of thermal diffusivity the kinetics T(t) was averaged over 100 laser pulses to reduce the noise. Since the D value derived from the kinetics $T(t)$ scales with the sample thickness as $D \sim h^2$, also the surface roughness contributes to the error in D. In our case the roughness R_a for the thinned sample has been at the level of 1 μm, leading to the error in D less than 1%. Then, the thermal conductivity was calculated as $k = D\rho C$, were ρ and $C(T)$ are the mass density and heat capacity of the compact, respectively, taking into account those values for the components (diamond and small fraction of B_4C).

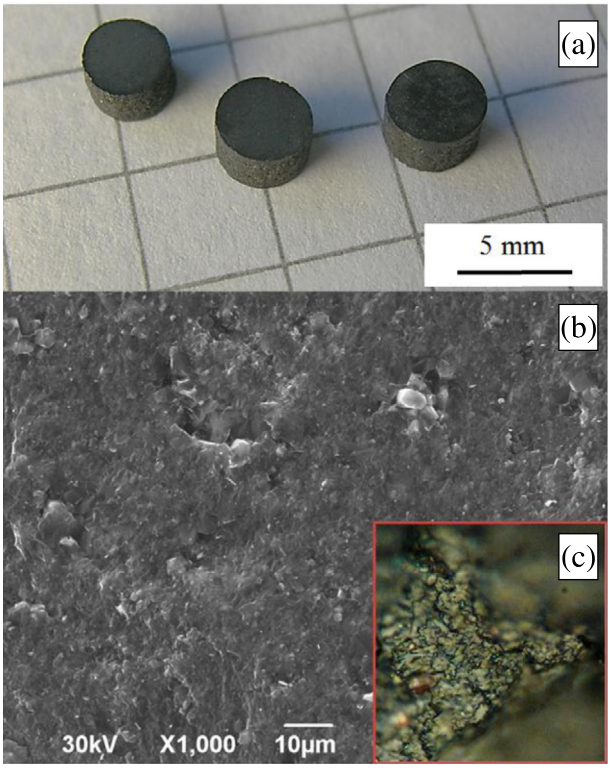

Fig. 1. Compacts of heavily B-doped diamond synthesized from mixtures of graphite with B_4C (a), and microstructure of the compact fracture surface as seen in SEM (b) and optical microscope (c). Amber-yellow inclusions of boron carbide in polycrystalline diamond matrix are identified on the sample surface (c). The scales in image (b) and inset (c) are the same.

Electrical resistivity measurements were performed by using four gold electrodes glued with silver epoxy to the polished sample surface at the circular edge. In resistivity calculations, the geometric factor was the same for all measured samples. For comparison purposes, one of the cylindrical samples was crashed and the electrical measurements were made on the elongated piece with rectangular shape. In this case, two potential contacts were arranged between two current contacts at the surface of this piece. In this contact configuration it was possible to estimate the geometric factor within 20–30% accuracy and we have got the resistivity value close to that measured on circular sample.

Elastic properties were studied by the pulse ultrasound method [11]. The sound velocity was measured at a frequency of 5 MHz for transverse wave and of 10 MHz for longitudinal one, by evaluating the ultrasonic wave travel time through the specimen. The density of the compacts was measured using the Archimedes method of weighing in distilled water.

Phase composition of samples was examined with X-ray diffraction (XRD) analysis using Rigaku Ultima IV diffractometer. The micro-Raman measurements were performed at room temperature in the backscattering configuration using the 488 nm Ar-laser excitation, a TriVista 555 spectrometer and ×100 objective. The laser power was kept at about 0.5 mW. Surface topography on as-received and fractured compacts was examined with scanning electron microscope (SEM) and optical microscopy. Oxidation of the diamond samples, crushed into coarse powders, was studied by differential thermal analysis using the Pyris Diamond Thermogravimetric Analyzer (Perkin Elmer) and thermoanalyzer STA 409 PC Luxx (Netzsch). The studies were carried out in ambient atmosphere at heating rate 10 K/min up to 1720 K, then immediately starting the cooling down the sample.

3. Results and discussion

3.1. Structure and phase composition of the compacts

In the graphite–boron carbide system, graphite transformation into diamond starts above the eutectic melting point of ~2500 K at 8–9 GPa [12]: carbon of graphite phase dissolves in the liquid boron-rich B–C growth medium, and crystallizes in the form of polycrystalline diamond. In the synthesis process, the growth medium is partly captured as inclusions by the growing diamond phase, and about 2 to 4% of boron can enter into the diamond as structural impurity [2,13,14]. Therefore, an excess of B_4C content in the primary powder mixture should be provided, in other words, a critical content of B-rich growth medium in the reaction system should exist, at which the complete graphite-to-diamond transformation takes place. Taking this point into the consideration, the synthesis was performed using mixtures of graphite with different B_4C percentages: 10, 7, 5, 4.5, 3.5 and 2.8 mass%. It was found that excessive B-rich liquid phase is formed during the synthesis from the mixture with 7 and 10% of B_4C. In this case the liquid leaves the sample and interacts with a graphite crucible-heater to form diamond that worsened the synthesis conditions and resulted in the compacts with irregular shape and cracks along the extended boron-rich inclusions. The lower content of 2.8% B_4C in the initial mixture was insufficient for the formation of diamond matrix. With the optimal content of boron carbide in the mixture in the range of 3.5% to 5% it was able to produce solid samples of cylindrical shape with better structural uniformity. Only these optimal compacts were characterized in the present paper. We speculate that if we could prepare more homogeneous mixture of reagents (e.g. with finer