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Electrical properties of the high quality boron-doped synthetic single-crystal diamonds grown by the temperature gradient method ☆

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A B S T R A C T

Temperature dependencies of the resistivity and the Hall coefficient in high-quality boron-doped synthetic single crystal diamonds grown by the high-pressure-high-temperature (HPHT) method with different boron contents have been investigated. The concentration of acceptors was varied in the range of 2×10^{15} to 3×10^{17} cm^{-3} in (001) cut plates by a change of boron content in a growth mixture in a range from 0.0004 to 0.04 atomic percent. A special sample preparation has been used for precise measurements. Thin rectangular plates with uniform boron content and without linear and planar structure defects have been laser cut after X-ray topography and UV-luminescence mapping. The donor and acceptor concentrations in each sample have been calculated from the Hall effect data and capacitance–voltage characteristics. The concentrations correlate with the boron content in a growth mixture. Minimum donor to acceptor compensation ratio slightly below 1% was observed at 0.002 at.% boron content in a growth mixture, while it increased at an increase and decrease of boron amount. Samples grown at such boron concentration had maximum carrier mobility. It was 2200 cm^2 / ($V \times s$) at $T = 300$ K and 7200 cm^2 / ($V \times s$) at $T = 180$ K. The phonon scattering of holes dominates in the entire temperature range of 180–800 K, while the scattering by point defects such as neutral and ionized impurity atoms is insignificant. Due to a perfect crystal quality and lattice scattering mechanism bulk diamond crystals grown from the mixture containing 0.0005 to 0.002 at.% of boron may serve as reference semiconductor materials.

1. Introduction

Synthetic single crystal diamonds are promising component in various high-tech devices. Crystals with perfect crystallographic structure and minimum non-controlled impurities are required. High-purity diamond single crystals classified as IIa-type are the most in demand in X-ray optics [1], in Raman lasers [2] and as a Bragg mirror in free-electron lasers [3]. Doped with acceptor and donor atoms semiconductor diamond single crystals are of greatest interest for high-power and high-frequency electronics. Now the only dopant available for bulk diamond with good controllability is boron. The boron-doped single crystals which are classified as a type IIb were studied most extensively [4]. The conventional methods of IIb-type single crystal diamonds growth are high-pressure-high-temperature (HPHT) method [5] and the chemical vapor deposition (CVD) method. HPHT method provides growth of bulk crystals, while the CVD-method [6] is used for homoepitaxial growth of single crystal films on single crystal substrates of high purity [7]. The crystal quality of films depends on the quality of substrate; thus we were focused on the growth of high-quality bulk single crystal IIb-type diamonds by the HPHT method and the study of their electrical properties. Previously we have grown a series of heavily boron-doped diamond single crystals and investigated their electrical properties [8]. The heavily-doped crystals contain many point, linear and planar defects that are unfavorable for producing high performance electronic devices. Only the systematic study of lightly boron-doped crystals reveals the paths for making high-quality diamonds for electronics.

2. Experimental methods

In this work we have grown a series of seven diamond crystals with boron content in the growth mixture (Fe–C–Al–B) in the range from 0.0004 to 0.04 atomic percent (cuboctahedral habitus crystals). The crystals were grown at a pressure of 5.5 GPa and a temperature of about 1700 K by the temperature gradient method on the seed [9,10]. A set of (001) plates with a thickness of approximately 150 microns was cut by a laser. The heavily boron-doped sample was studied for comparison. It was grown in the growth mixture with 0.71 at.% and had octahedral habitus without central cubic growth sector. The plates were polished on both sides and chemically etched to remove metal and organic surface contaminants.

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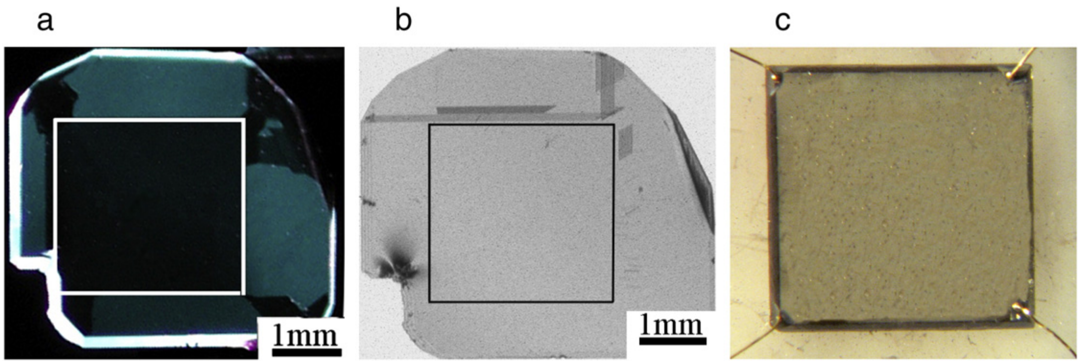

Fig. 1. Photoluminescence (a), and X-ray topography (b) maps of diamond plate cutting schemes for making rectangular homogeneous sample without extended defects for Hall effect measurements (c).

The UV-luminescence method was used to obtain a map of growth sectors distribution in diamond plates (Fig. 1a). The crystallographically defect-free areas of plates were visualized by the X-ray topography (Fig. 1b). Finally combining X-ray topography and UV-luminescence data rectangular shape plates within a single growth sector (with uniform impurities content) and without linear and planar structure defects were cut for electrical measurements. The typical sizes of samples were $2.5 \times 2.5 \times 0.15$ mm^3. The Ti–Pt–Au ohmic contacts were made in the corners of the plates by magnetron sputtering and annealing at $T = 1000$ K (Fig. 1c).

The electrical resistivity, the density of the free charge carriers and their Hall mobility were tested by the Hall effect method using the Van-der-Paw technique in the temperature range from 77 to 800 K employing the LakeShore Cryotronics^{TM} 7708 Hall Measurement System.

The uncompensated acceptor concentration (N_A–N_D) and the uniformity of doping on the area of the plates were additionally tested by measuring the capacitance–voltage characteristics. It was implemented using Keithley 4200-SCS measuring system with a DC bias from 0 to 15 V at frequencies of 10–100 kHz. For these measurements we made 9 round Schottky contacts (platinum) of the 400 μm diameter at one side of plates and a full area ohmic contact on the opposite one. The N_A–N_D value was determined from the dependence of capacitance versus DC bias in the depletion mode of Schottky contact [11].

3. Experimental results and discussion

To prove the effect of inhomogeneity and extended defects in specimens on the results of electrical measurements we investigated the temperature dependencies of electrical resistivity $\rho(T)$, the Hall mobility $\mu_H(T)$ and the Hall density of holes $p_H(T)$ on the unshaped (Fig. 1a,b) and the rectangular cut plate (Fig. 1c) which was cut from diamond crystal grown in the mixture with 0.006 at.% boron. While the resistivity curve did not change after the final cut we found dramatic difference in the Hall effect data at $T < 300$ K when unshaped plate and rectangular cut after the selection of homogeneous area free of extended defects were measured. The results are shown in Fig. 2. One can see strong drop of the carrier mobility and a deviation from the activation law in their density at low temperatures measured on the unshaped plate.

Such differences occur due to inhomogeneous acceptor and donor concentrations in different growth sectors in unshaped plate. Also the extended structure defects affect the carriers scattering. So in the case of measuring unshaped plates a simple analysis of the Hall effect data is incorrect due to a complex conductivity mechanism. This is evidently indicated that the true material parameters can be obtained from the Hall effect data only by measuring the properly cut samples. Further we studied only specially cut rectangular shape plates. The temperature dependencies of the electrical resistivity and the Hall mobility of holes in diamond samples with different boron content in the growth mixture are shown in Fig. 3.

We determined the actual concentration of acceptors (N_A, boron) and compensating donors (N_D, nitrogen) by the regression analysis of the temperature dependencies of Hall effect data using the least squares method. Varying N_A and N_D parameters of the theoretical model of conductivity, we achieved the minimum total deviation from the experimental curve in the whole temperature range.

To compute the theoretical concentration of the free charge carriers we used the Fermi distribution for electrons and holes and the

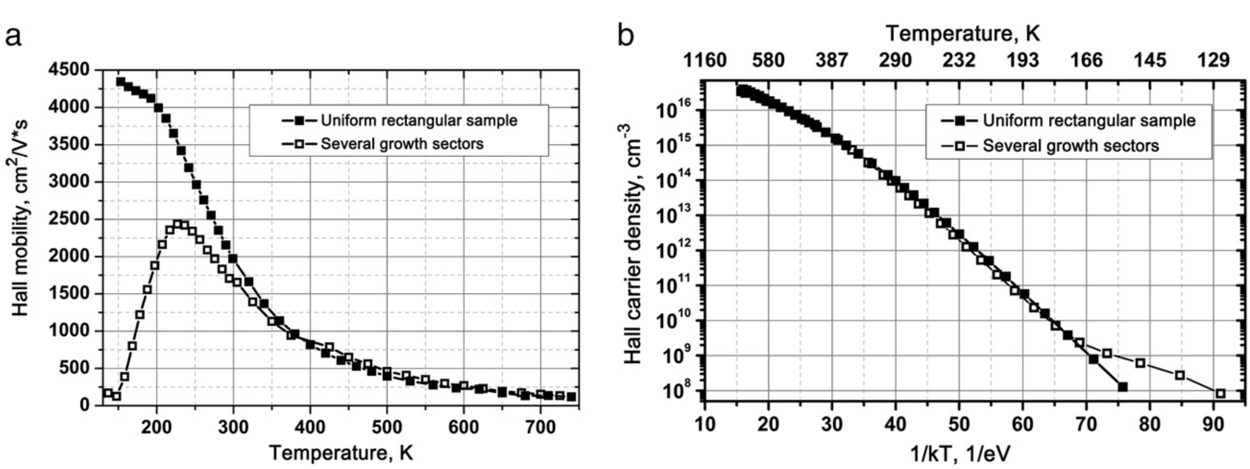

Fig. 2. Hall mobility (a) and the density of holes (b) temperature dependencies measured on unshaped (empty squares) and rectangular cut diamond plates without extended defects (full squares).