Study of frequency dispersion of capacitance-voltage characteristics of boron-doped diamond Schottky diodes

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Abstract. A single-crystal diamond doped with boron was studied in this work. For electrical measurements an array of Schottky contacts and a large Ohmic contact were fabricated. The capacitance-voltage (C-V) characteristics of the sample were obtained experimentally in wide temperature range and modeled. At high temperature (445 K) the slope of the C-V characteristics does not depend on the test signal frequency. The calculated concentration of free charge carriers is the same for all frequencies within the experimental error and approximately corresponds to the total boron concentration. At low temperatures (235 K), there is a significant difference in capacitances measured at different frequencies, the calculated concentration varies from 5·10¹⁷ cm⁻³ to 5·10¹⁵ cm⁻³ in the available frequency range. The reasons for the frequency dispersion of capacitance-voltage characteristics of boron-doped diamond diodes are discussed.

1. Introduction
The development of the Arctic territories is an important strategic issue for Russia and other countries. In 2019 the MOSAiC expedition was launched aimed at fundamental investigation of the Arctic region. Scientist from a number of countries worked together during more than a year and obtained a lot of new data [1,2]. Unlike the usual laboratory research, the field study in such harsh and distant conditions consumes a lot of resources: food, energy, man-hours. All these restrictions decrease the number of possible expeditions, yet offer a perfect testing platform for new methods of increasing energy efficiency.

Many complex problems should be solved before these polar territories will be carefully explored [3,4]. This cannot be achieved without using of novel technologies. One of the main issues for any distant explorations is the energy supply, and here one can find 2 key directions: energy saving devices, capable of working in harsh environment, and energy storage system in distributed generation networks [5–7]. Diamond, being a material with ultimate electrical, mechanical and thermal properties can find its application in the extreme conditions of the Far North. It is known, that one of the easiest and prospective energy saving method is to change basic material for power devices from ubiquitous Si to wide bandgap one (SiC, GaN and diamond). Efficiency of that change can save up to 38.6% per year for SiC [8]. Also, this power sources can be smaller and lighter which is important in case of limited space on icebreaker. We can foresee that diamond will reduce size of such energy supplies and be able to reduce energy consumption even comparing with SiC ones, thanks to its wide bandgap. Diamond can be a basis of energy storage system of the new generation [9] providing reliable operation for a grid-tied power generation system and improving the energy quality.

Nowadays diamond growth and doping technologies are of high level [10–13], yet a lot of tasks are still unsolved during production of boron-doped diamond devices. Diamond, in contrast to “classical”
semiconductor materials (Si, GaAs) has a deep impurity level. It leads to low ionization degree of boron dopant (less than 0.1%). This results in a dependence of capacitance-voltage characteristics on frequency in some temperature range. This study is devoted to investigation of frequency dispersion of capacitance-voltage characteristics in boron-doped diamond Schottky diodes.

2. Materials and methods

Chemical vapor deposition (CVD) single-crystal diamond, grown on high pressure high temperature (HPHT) substrate was investigated in this work. Thickness of the CVD layer was 2.5 μm, it was heavily doped by boron during growth (boron concentration 1.4·10¹⁹ cm⁻³ obtained by SIMS method). For electrical measurements the small rectifying Schottky contacts and a large Ohmic Pt contact were fabricated by magnetron sputtering at 70°C and 300°C, respectively (Fig. 1b). Diameter of the Schottky circular contacts were 420 μm.

The sample was 3x3x0.5 mm, an array of 25 Schottky diodes was obtained on its front surface. All these diodes were investigated at direct and alternated current at room temperature. Contact points with acceptable current-voltage and capacitance-voltage (C-V) characteristics were then studied more thoroughly.

![Diagram of the sample with formed diode structures](image)

Figure 1. Diamond sample with formed diode structures: (a) – layers scheme; (b) – photo of the sample (from above).

For electrical investigations computer-controlled complex for admittance spectroscopy were used. The complex includes cryogenic probe station with optical probe positioning Janis CCR 10, Agilent E4980A RLC-meter, two temperature controllers LakeShore 336 and 331, and Pfeiffer vacuum post. The experimental setup allows one to conduct measurements within wide temperature range of 20-475 K and wide test signal frequency sweep from 20 Hz to 2 MHz [14].

This work was mainly focused on analyzing the capacitance-voltage characteristics of sample. For a bulk doped p-type semiconductor with Schottky barrier the relationship between capacitance and voltage is expressed by [15]:

\[
C \equiv \frac{\partial Q_{nc}}{\partial V} = S \left[ \frac{\varepsilon \varepsilon_0 e N_A}{2 (V_b - V - kT / q)} \right]^{-1}
\]

(1)

where \( N_A \) is the acceptor concentration (in this case is the boron impurity concentration), \( V_b \) is the Schottky barrier height, \( S \) is the Schottky contact area. The observed concentration of free charge carriers is the derivative of the capacitance with respect to voltage:

\[
p = 2 \left[ \varepsilon \varepsilon_0 e S^2 \frac{d}{dV} \left( \frac{1}{C^2} \right) \right]^{-1}
\]

(2)
3. Results and discussion

The C-V characteristics of the sample were recorded at different frequencies of the test signal (from 1 kHz to 1 MHz) in the whole temperature range achieved by the setup. However, at temperatures below 235 K, the registered capacitance was less than the resolution of the LCR meter due to the small area of the contacts. This circumstance limited the range of temperatures available in the experiment to that from 235 K to 445 K.

The obtained C-V characteristics of diamond demonstrate the presence of fundamental features of this wide-gap material when performing electrical measurements of concentration distribution (Fig. 2 a). At high temperatures (445 K), the slope of the \(1/C^2-V\) dependence is the same for all frequencies. So it can be assumed that at this temperature all impurity is ionized in the applied field.

At low temperature of 235 K, a significantly different behaviour of capacitance is observed at different frequencies (Fig. 2 b). The change in the slope of the \(1/C^2-V\) dependence is due to the presence of a deep level in the sample, the emission rate from which is comparable to the available frequency range at 235 K. Thus, at frequencies greater than 10 kHz, the reverse emission rate from the trap to the valence band is higher than the frequency of the test signal, as a consequence, a smaller fraction of the impurity can be ionized with increasing frequency. The phenomenon of frequency dispersion of C-V characteristics in diamond was first noticed at room temperature by Glover in 1973 [3].

To describe the data obtained, consider the equivalent circuit of the Schottky diode in Fig. 2c. In general case, the equivalent circuit of a Schottky diode is a series-parallel circuit consisting of a barrier capacitance \(C_b\), shunting its differential resistance of the space charge region \(R_d\) and a series-connected resistance \(R_S\), which includes bulk resistance and dissipative loss in the presence of a deep level. During electrical measurements, the RLC meter reduces the full equivalent circuit to parallel or series, so that the differential capacitance measured by the instrument is a complex function of applied voltage, frequency, temperature, emission rate, concentration.

![C-V characteristics at 445 K (a) and 235 K (b) for various test signal frequencies, dashed line shows modelling results; Equivalent circuit of a Schottky diode (c).](image_url)
At high temperatures, the bulk resistance is small, which means that the registered capacitance is the barrier capacitance of the junction, distorted by leakage currents. At 445 K, the bulk resistance and the parallel resistance $R_d$ are small. Small values of $R_d$ result in leakage currents in-phase with the applied voltage, which distorts the C-V measurements. The occurrence of high leakage currents at high temperatures is caused by generation-recombination processes in the space-charge region, as well as by the device structure, which assumes significant leakage currents along the surface.

For low-temperature (235 K) measurements, distortions of the C-V characteristics and high cut-off voltages (15 V for 50 kHz) are due to a significant role of the bulk resistance. This resistance is the part of $R_s$ where a significant portion of the applied voltage drops. At high frequencies, $R_s$ increases with increasing frequency, which leads to different slopes of C-V characteristics. In order to obtain concentration dependences at different temperatures, we used expression (2), Fig. 3.

Figure 3. Frequency dependence of the registered concentration of free charge carriers calculated by expression (2) for different temperatures. Dashed line - modelling, points - experimental data.

The concentration $p=4\cdot10^{18}$ cm$^{-3}$ calculated for 445 K is the same for all frequencies within the experimental error, Fig. 3. This concentration approximately corresponds to the total boron concentration estimated using SIMS (including the electrically inactive one), taking into account the compensation by the background nitrogen impurity.

For 235 K in the low-frequency region (1-10 kHz), the measured concentration of free charge carriers is $5\cdot10^{17}$ cm$^{-3}$. Correct measurement of high-frequency concentrations at low temperatures requires additional measurements with a larger contact area, due to the limited resolution of the LCR meter.

In [16], the authors observed similar distortions when measuring the capacitance of Schottky diodes based on 4H-SiC, and proposed methods for correcting these artefacts. In particular, a method was proposed for choosing an equivalent circuit for the LCR meter, as well as expression (3) for modelling concentration characteristics:

$$N(T, f, E_A) = N_A^- + \frac{N_A^+ - N_A^-}{1 + \left(\frac{\omega}{e_p}\right)^2}$$

where $N_A^-$ is the impurity concentration of acceptors ionized at a given temperature without applied field, $N_A^+$ is the total concentration of impurities in the sample, $e_p$ is the emission rate of charge carriers (holes) from a deep level into the valence band. After analyzing the expression, one can see that at high frequencies ($\omega >>> e_p$) the observed concentration is determined exclusively by temperature-ionized charge carriers, since at this frequency the applied voltage does not have time to ionize the deep level.
At low frequencies ($\omega << \epsilon_p$) the observed concentration is determined exclusively by the doping concentration.

Simulation of the concentration-frequency dependence was carried out in the Matlab environment, the results of which are shown in Fig. 3 by dashed lines. The difference in the experimentally obtained low-frequency concentration and that simulated at low temperatures is due to the contribution of parasitic resistances.

4. Conclusions

In this work, a Schottky diode based on boron-doped single-crystal diamond was investigated by means of admittance spectroscopy. It is shown that at high temperature (445 K) the slopes of C-V characteristics do not depend on frequency, and the calculated concentration corresponds to the total concentration of boron impurity. At low temperatures, the frequency dispersion of the observed concentration of free charge carriers was in the range from 10 kHz to 1 MHz. The observed frequency dispersion of the apparent concentration was described using both circuitry and physical models. The significant variation in C-V characteristics of boron-doped diamond Schottky diode as a function of temperature and frequency is a unique feature of this wide band gap material associated with the presence of a deep boron level. This phenomenon requires further precision consideration, since frequency dispersion of capacitance can significantly limit the field of application of a device based on a single crystal diamond.

5. References

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