**p-n junction on high-pressure-high-temperature grown single crystal diamond: UV-emission spectra and electrical properties**

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**Abstract.** Semiconductor p⁺-p-n structure has been created on synthetic single crystal IIb type diamond grown by high pressure temperature gradient method and doped with boron at growth process. 250 µm thick (001) cut plate was ion implanted by B, As and P at (1 – 1.3)·10¹⁶ cm⁻². Electroluminescence spectra were investigated at different values of electrical voltage and current in regular and S-part of the current-voltage characteristics. Strong exciton recombination emission was observed at the current density up to 60 A*cm⁻². The spectrum transforms at transition from regular conductivity to electrical avalanche breakdown regime. Simultaneously a set of sharp EL lines appears in the range of 327-652 nm on the A-band background. They tentatively attributed to superlumensence effect.

1. Introduction

Diamond is a wide band gap semiconductor with 5.49 eV forbidden indirect gap. There are no intrinsic charge carriers in pure diamond, but doping provides p- and n-type diamonds with various activation energy of holes and electrons. At doping level up to ~ 10¹⁷ cm⁻³ diamond has extremely high heat conductivity and mobility of charge carriers. Diamond possesses outstanding mechanical and optical properties. It is very promising material for electronics and optoelectronic.

Thought studies of natural and doped semiconductor diamonds have been started more than 40 years ago, the most extensively this area began to explore during the last 10 years with the development of methods of growth of synthetic single crystal diamonds with controlled chemical content. The main methods of single crystal growth are the temperature gradient method under pressure [1, 2] and the method of chemical vapor deposition (CVD) [3]. There is a set of different techniques applying these methods. The advantage of the first type method is an opportunity to grow large (10 carats and more) bulk single crystals, very pure IIa type and doped with boron acceptor impurity (IIb type) or nitrogen donor impurity (Ib type) at broad range of concentrations. Microwave plasma assisted CVD method (MPCVD) provides growth of high quality single crystal diamonds: bulk and films, but it requires substrate single crystal diamonds grown by the first method. Thus combination of both these methods is the best for producing layered diamond structures for electronics and optoelectronics.

Besides direct doping at a growth process, ion implantation is a strong tool of additional doping with various chemical elements at a depth down to about several microns. Actually the first p-n
junctions in natural diamonds have been made by ion implantation method and their electrical properties and optical emission in visible range investigated [4, 5]. It was found, that the electroluminescence (EL) spectra are similar to X-ray photoluminescence (PL) ones and the internal quantum yield attains ~ 4×10⁻² per couple of recombinating charge carriers. The maximum of EL and PL spectra was in 420-530 nm attributed to nitrogen impurity luminescence centers (LC) and lattice defects. The maximum electrical current of about 20 mA and rectification ratio of ~ 10⁷ have been obtained in a p-i-n structure made by ion implantation of natural diamond [5]. But besides strong PL and EL in visible range, holes and electrons injection in diamond provides quite strong exciton recombination band with the photon energy close to indirect band gap value: 5.27 eV [6-10]. The exciton binding energy is about 80 meV in diamond, that is why UV emission band can be observed at high temperatures.

Besides making UV diodes, producing diamond UV lasers is a very attractive task. To obtain coherent emission at excitonic UV band one must attain high density of excitons to get exciton liquid condensation effect [11]. In a near UV and visible EL band 300-600 nm one must provide inverse occupation of metastable energetic levels associated with impurities in forbidden gap. Both these tasks can be solved by high density of electrical current with injection of holes and electrons. In this work we made p⁺-p-n⁻ structure on synthetic single crystal diamond implanted by B, As and P and investigated their electrical properties and EL spectra at high current density.

2. Experimental
We grew boron-doped IIb single crystal diamond by the temperature gradient method [1, 2] and cut 250 µm thick (001) plate with maximum sizes 3×5 mm² (Figure 1).

![Figure 1. Picture of diamond plate with marked areas of implantation with As and P ions. Black spot in the central part is a growth defect.](image1)

One plane of the plate was implanted by B and the opposite one – by As and P according to Figure 2. Central part of the plate contains growth defect and this area was not implanted by donor atoms. The implantation conditions are shown in Table 1.

| Depth, µm | Impurity | Implantation energy, keV | Doze, cm⁻²  |
|-----------|----------|--------------------------|------------|
| 0,5       | As⁺      | 180                      | 1·10¹⁶     |
| 1,1       | P⁺       | 180                      | 1·10¹⁶     |
| 3,5       | B⁺       | 100                      | 1,3·10¹⁶   |
After implantation crystal was annealed at 600°C for 6 hours in argon gas flow. Electrical contacts have been made by silver conducting paste. The crystal was attached to massive heat sink copper plate by the same silver conducting paste. The IR absorption spectrum of implanted crystal was measured using Thermo Nicolet Nexus FT-IR spectrometer. The spectrum of the studied sample has typical for boron-doped diamonds absorption peak at 1282 cm\(^{-1}\) and absorption tail at wavenumbers above 2700 cm\(^{-1}\). 3 additional absorption peaks at 2455, 2799 and 2926 cm\(^{-1}\) indicate absorption on implanted donor atoms. The estimated acceptor concentration is \(\sim 10^{16}\) cm\(^{-3}\).

Fig.3 shows current-voltage \((I-V)\) characteristics in both donor-implanted areas. At direct current values above \(\sim 0.2\) A \(I-V\)-characteristics sharply became \(S\)-type with significant drop in voltage at limited current. The temperature of the sample increased rapidly and this part of \(I-V\)-characteristics was not measured correctly and not presented in the plots. The minimal electrical resistance was 70 and 425 Ω at two different points in P-doped area and 50 Ω in As-doped area. The maximal electrical power was 25 and 17 W in P-doped area and 12.5W in As-doped area respectively. The maximum current density was estimated 60 A*cm\(^{-2}\) according to the area of electrical contacts and visible crossection of the light-emitting area. The rectification ratio was relatively low: just about \(10^2\) at ± 40 V in a regular part of \(I-V\)-characteristics at As and P-doped areas.

![Figure 3. \(I-V\) characteristics of \(p^+-p-n\) structures in As-and P implanted areas in linear (left) and semilogarithmic (right) scale.](image)

Bright optical emission was observed at direct current in both implanted areas. EL spectra at different values of voltage and electrical current are presented in Fig. 4. EL spectra were measured using TRIAX 552 spectrometer.

As seen in Fig. 4 spectra in both As and P-doped areas contain typical for diamonds broad luminescence \(A\) band in 350-650 nm wavelengths with a maximum at about 500 nm. This band is attributed to lattice defects and nitrogen luminescence centers. The intensity of excitonic bands at 230-250 nm in As-doped area of the structure is relatively low – about 3 orders of magnitude less than the intensity of visible \(A\) band. Unlike As, P-doping provides quite strong UV excitonic luminescence with the maximum intensity just about 30% of the \(A\) band. Such a high UV yield was observed at the regime of high current density in the \(S\)-part of \(I-V\)-characteristics. The ratio was about 5-10% in a regular part of \(I-V\)-characteristics. Taking into account, that the integral intensity of EL at high electrical current regime is much stronger than at medium values, we note that the obtained maximal integral excitonic intensity is really strong. But the most interesting result is an evident transformation of EL spectra observed at high current density with respect to medium current regime (Fig. 4 right). Particularly interesting is transformation of excitonic bands and appearance of sharp EL bands in whole range from 250 to 650 nm.

![Figure 4. EL spectra in both As and P-doped areas.](image)
Figure 4. Semilogarithmic plots of EL spectra at different values of voltage and current in $p^+-p-n$ structures in As-implanted area (left) and P-implanted area with higher electrical resistance (right).

There are two very intensive lines at 327,3 nm and 337,4 nm. The Gauss line fitting revealed a fine structure of the bands. The BHWHA (band halfwidth at a half of amplitude) of Gauss peaks is in the range of 7-20 meV, that is significantly less than $kT = 25 - 50$ eV for the temperature range 300 – 600 K. We assume that these narrow bands arise due to superluminescence effect at electron transitions from P energetic level (0.6 eV below the conduction band) directly to boron acceptor level (0.37 eV above the valence band) or via intermediate nitrogen donor level (1.6 eV below the conduction band). The sublevels associated with defects have place, thus a set of lines appear in the 3.5-4.5 eV range.

3. Conclusion

We investigated peculiarities of UV and visible optical emission of $p^+-p-n$ structure on ion implanted diamond at high electrical current density for the first time. Strong exciton recombination UV emission was observed accompanied with a change in spectra at transition from regular to $S$-part of current-voltage characteristics of this semiconductor structure. In addition a set of sharp light emission bands appeared in a broad range from 327 to 650 nm. The strongest of them are double peak at 327,3 and 337,4 nm. They may arise due to superluminescence effect.

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