Electronical and Optical Properties of Semiconductors

Optical Properties of Synthetic Diamond Single Crystals


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Abstract—Synthetic diamond single crystals were grown by the thermal gradient method in a high-pressure apparatus in the presence of solvent catalysts (nickel, iron). Absorption, luminescence, and photoluminescence excitation measurements were performed in order to determine the nature of impurity–defect complexes in both as-grown crystals and crystals treated at high temperature (T = 2000–2200 K) and high pressure (P = 6.0–6.5 GPa). Different luminescence and absorption bands were assigned to impurity centers containing nitrogen and nickel atoms.

1. INTRODUCTION

The combination of unique physical (optical, electrical, thermal, and mechanical) properties and the high radiative and chemical durability of diamond opens up wide possibilities for using this material in instrument making (optical windows, heat removal, ultraviolet and thermal sensors, detectors of ionizing radiation, active media for lasers, optoelectronic devices, and so on). However, the development of this line of research is hindered by the lack of high-quality crystals with the required parameters. In this context, the synthesis of large diamond single crystals with a high-quality structure, based on new processing techniques and complex research into the physical (primarily, optical) properties of the synthesized crystals, is an urgent scientific and engineering problem [1]. In this study, we report new experimental data obtained by studying the absorption, luminescence, and luminescence excitation spectra of synthetic diamonds grown under different conditions and subjected to thermobaric treatment in different modes.

2. EXPERIMENTAL

Diamond single crystals were synthesized by the thermal gradient method in the temperature range 1750–1800 K at pressures of ~(5.4–5.5) GPa in a split-sphere high-pressure apparatus. Single crystals 4–7 mm in diameter were grown in a Ni–Fe–C system. In some cases, a stabilizing thermobaric treatment of crystals was performed at temperatures in the range T = (2000–2200) K and pressures P = (6.0–6.5) GPa for 3–24 h. The initial crystals had a saturated yellow color. The optical properties of diamonds were investigated in a wide temperature range from 78 to 300 K by measuring the absorption in the wavelength range 0.2–25 μm, photoluminescence (PL), and luminescence excitation spectra in the range 0.2–2 μm. Absorption spectra in the range 0.2–3.0 μm were recorded on a Carry 500 UV-VIS-NIR double-beam spectrometer (Varian, United States) and, in the range 1.4–25 μm, on a Protege-460 Fourier spectrometer (Nicolet, United States). Photoluminescence spectra were measured on an MDR-23M monochromator with 600–1200 groove/mm gratings. An FÉU-83 (or FÉU-100) photomultiplier and germanium p–i–n diode, cooled to liquid-nitrogen temperature, were used as detectors of optical signals. A DKSÉL-1000 xenon lamp (power 1000 W) with a set of ultraviolet (UV) light filters served as the light source. When luminescence excitation spectra were recorded, the radiation of the xenon lamp, resolved by the MDR-12 diffraction monochromator, was focused on the sample under study.

3. RESULTS AND DISCUSSION

In our experiments, we recorded a number of strong PL bands, including the electronic–vibrational bands due to residual unintentional impurities (nitrogen, nickel, and so on) and intrinsic structural defects in the synthetic diamond crystals. As an example, Fig. 1 shows the typical PL spectra of as-grown diamond crystals (Figs. 1a, 1b, sample 1811) and crystals subjected to thermobaric high-temperature treatment at T = 2173 K and P = 6.5 GPa for 16 h (Figs. 1c, 1d, sample 2005). As can be seen, the luminescence spectra of the samples under investigation contain a strong wide band A with a maximum in the wavelength range 510–540 nm (the photon energy 2.30–2.45 eV), which is characteristic of growth pyramids on octahedral faces. At room temperature, this band has an extended long-wavelength wing and a half-width of about 370 meV.
When the crystals are cooled to 78 K, an electronic–vibrational band with a leading zero-phonon line $S_3$ at an energy (wavelength) of about 2.496 eV (496.7 nm) arises in the photoluminescence spectra. This line contains characteristic low-energy vibrational replicas at 2.457 eV (504.6 nm), 2.426 eV (511 nm), and 2.391 eV (518 nm). The energies of the corresponding phonons are 40, 70, and 105 meV, which is consistent with the data of [2–5]. The most distinct is the electronic transition involving a quasi-local phonon with an energy of ~40 meV (Fig. 2). The spectra also contain a weaker zero-phonon line at 2.621 eV (473.3 nm), which is due to the same luminescence center. In this case, the initial synthetic diamond crystals have a yellow-green saturated color. The experiments show that thermobaric high-temperature treatment at a pressure of 6.5 GPa and an annealing temperature of ~2173K for 20 h changes the color of synthetic diamonds: they become much lighter, with a characteristic soft green hue. The photoluminescence spectra of such crystals at liquid-nitrogen temperature show a richer quasi-linear structure, which is observed in the high-energy wing of the wide band. Several strong narrow zero-phonon lines are also observed in the luminescence spectra: $S_2(A)$ at ~2.369 eV (523.3 nm), $S_2(B)$ at ~2.535 eV (489.1 nm), $S_2(C)$ at ~2.594 eV (477.8 nm), and a number of weaker components associated with these lines, including vibrational replicas. The lines $A$, $B$, and $C$, observed after thermobaric treatment (see also the fine structure of the spectra in Fig. 2), can be assigned to the optical transitions in the electronic structure of so-called $S_2$ centers [5]. It should be noted that the lines of the $S_2$ group ($A$, $B$, $C$) also manifested themselves with a much lower intensity in the spectra of most of the starting synthetic diamonds under study. High-temperature thermobaric treatment of such samples led to an increase in the intensity of the $S_2$ lines by a factor of 5–10. In general, these experiments showed that thermobaric treatment of diamonds leads to a significant increase in the intensity of both $S_3$ and $S_2$ electronic–vibrational bands. As was noted, an increase in the concentration of corresponding luminescence centers, $S_2$ and $S_3$, facilitates crystal bleach and enhances the luminescence intensity by a factor of 3–5 in comparison with starting samples at the same excitation levels. In our opinion, this fact indicates that annealing of nonradiative recombination centers takes place upon thermobaric treatment and active rearrangement of defects in a crystal matrix, which involves residual process impurities (mainly nitrogen and nickel). Previously, these luminescence centers were found in natural and synthetic diamonds and assigned to Ni atoms in a positively