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Nanostructures in lightly doped silicon carbide crystals with polytypic defects

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Abstract. In this work, photoluminescence spectra of lightly doped SiC crystals with in-grown original defects are reported. Undoped SiC single crystals with the impurity concentration of $N_D - N_A \sim (2\ldots8)\cdot10^{16}$ cm^{-3}, $N_A \sim (2\ldots8)\cdot10^{17}$ cm^{-3}, and $N_D - N_A \sim (1\ldots5)\cdot10^{17}$ cm^{-3}, $N_D \leq 1\cdot10^{18}$ cm^{-3} were investigated. The analysis of absorption, excitation and low temperature photoluminescence spectra suggests formation of a new micro-phase during the growth process and appearance of the deep-level (DL) spectra. The complex spectra of the crystals can be decomposed into the so-called DL$_i$ (i = 1, 2, 3, 4) spectra. The appearance of the DL$_i$ spectrum is associated with formation of new nano-phases. Data of photoluminescence, excitation and absorption spectra show the uniformity of different DL$_i$ spectra. Structurally, the general complexity of the DL$_i$ spectra correlated with the degree of disorder of the crystal and was connected with one-dimensional disorder, the same as in the case of the stacking fault (SF$_i$) spectra. The DL$_i$ spectra differ from SF$_i$ spectra and have other principles of construction and behavior. The DL$_i$ spectra are placed on a broad donor-acceptor pairs emission band in crystals with higher concentrations of non-compensated impurities. The excitation spectra for the DL$_i$ and SF$_i$ spectra coincide and indicate formation of nanostructures $14H_1\langle4334\rangle$, $10H_2\langle55\rangle$, $14H_2\langle77\rangle$, $8H\langle44\rangle$.

Keywords: silicon carbide, polytype, stacking fault, photoluminescence spectra, nanostructure.

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1. Introduction

Silicon carbide (SiC) is material widely used in several industrial applications such as high power electronics, light emitting diodes, as well as in researches such as photo-voltaic and quantum technologies. Silicon carbide exists as several different polytypes according to the stacking sequence of SiC atomic double layers in the crystal lattice. Great advances were reported in growing a single crystalline polytype by controlled sublimation and chemical vapor deposition [1–3]. Polytypic transformation in SiC was investigated by many authors [4–19].

The phase transformation in highly doped by nitrogen 6H – SiC crystal and the mechanism of solid-phase transition through formation of multilayer polytypes has been studied [5, 14]. Syntax coalescence becomes a very important characteristic of α-polytype SiC crystals – the intergrowth of two or more polytypes

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when not only the major axis *c* but also the axis *a* coincide in the hexagonal structures. It happens because of the "layer-by-layer" crystal growth and the existence of different types of errors in the layers sequence (SF) along the axis *c*. The layers with in-grown one dimensional disorder in the original α-SiC crystals are called D-layers. D-layers have a clear crisp coalescence boundary with the neighboring blocks of the structurally perfect 6H – SiC along the (0001) plane.

However, single crystals with multiple nucleations also exist. The interaction of the growth fronts produces incoherent boundaries (the so-called "mosaic"). In this case, all kinds of in-grown dislocations and properties of "border inconsistencies" play a crucial role. To stabilize the appropriate polytype structure, it is essential to consider the influence of different factors: thermodynamic, kinetic, impurity, and dislocation nucleation mechanisms. Any fluctuation of the stabilization parameters can lead to errors in structure formation. It also contributes to a very small stacking fault energy in silicon carbide (2–9 mJ/m^2).

Photoluminescence (PL) is one of the most widely used experimental techniques for the physical characterization of semiconductors. The complex research of the low temperature photoluminescence (LTPL) spectra under different conditions of registration and at various temperatures is one among the most widely used experimental techniques for the physical characterization of the crystals [3, 6, 17]. The simultanious control of the phase state and structural imperfactions showed defect formation as a result of polytypes reorganization in the process of crystal growth.

Investigated in the paper [5] have been defects in heavily doped with nitrogen single crystals by using photoluminescence. However, correspondence between the PL spectra and mechanism of phase transformation has not been investigated. The nature of the PL spectra depends on the concentration of impurities. Spectroscopy of defects in pure perfect crystal SiC has already been described in the works of Refs. [6, 16, 20–22].

In this report, LTPL studies of lightly doped α-SiC single crystals have been presented. This work is the continuation of the spectroscopic diagnosis of defects created by the unstable growth conditions in lightly doped α-SiC single crystals.

2. Experimental

The method of optical spectroscopy LTFL was used in this work, as it is very sensitive to structural changes.

The group of single crystalline α-SiC crystals grown by using Lely's (Tairov's) method [3] was selected for the research. Undoped SiC single crystals with the impurity concentration of $N_D - N_A \sim (2\ldots8)\cdot10^{16}$ cm^{-3}, $N_A \sim (2\ldots8)\cdot10^{17}$ cm^{-3}, and $N_D - N_A \sim (1\ldots5)\cdot10^{17}$ cm^{-3}, $N_D \le 1\cdot10^{18}$ cm^{-3} were investigated. In perfect 6H – SiC crystals, the donor impurity (N) and the acceptor impurity (Al) in low-temperature recombination show well-known blue radiation of donor-acceptor pairs (DAP). This type of recombination usually dominates [3].

We selected samples with LTPL (77 K) in the turquoise green spectrum area. We will call these samples deep level (DL) samples. The turquoise green luminescence was observed within the whole crystal volume as well as only in some parts of the crystal. For example, in the block from one side of the (0001) SiC crystal, the DL luminescence was observed while the other part of the crystal produced the DAP (6H – SiC) luminescence. These blocks were separated from the rest of the crystal by using layer-by-layer polishing and were selected for further structural analysis.

The X-ray (Laue's method) and electron diffraction methods were used to detect symmetrical and layering parameters of the crystals. Moreover, in some cases, to analyze structural peculiarities of the allocated blocks, the transmission electron microscopy technique (TEM) (×15 000) was used. The metallographic method was used for evaluating the crystal face surface in the starting growth state.

LTPL spectra were registered by the ДФС-12 spectrograph with the photodetector (ФЭУ-79). In photoluminescence (PL) experiments, a nitrogen ЛГИ-21, λ = 337 nm (3.68 eV) or helium-cadmium ЛГ-70, λ = 441.6 nm (2.807 eV) laser, respectively, were used. Also, a mercury ultrahigh pressure lamp СВДШ-1000 with УФ-2 filter and xenon lamp ДКСШ-1000 were used.

The PL spectra were measured using the samples contained in a liquid helium or nitrogen cryostat, which provided temperatures ranging from 1.5 to 330 K.

3. Results and discussions

SF related luminescence dominates in pure SiC crystals [22]. After full extinction of the SF_i luminescence described in [23] at the temperature of 35-40 K, a weak (in its intensity) and wide background band of radiation remained. This luminescence was more or less clearly pronounced and had a rich structure depending on the features and degree of the one-dimensional disorder of the samples.

The spectra of this type (DL_i) differ from SF_i spectra and have other principles of construction and behavior. The DL_i spectra are localized on the background of the broad DAP spectral band of crystals with higher concentrations of non-compensated impurities. Originally, these spectra were found and investigated in defective crystals (1_{DL}, 2_{DL} samples in Fig. 1) with a higher concentration of the main impurity. In these samples, the DL spectrum was much more intensive, whereas the SF spectrum (which was also present) even at 4.2 K was poorly pronounced, or practically was not fixed.

The dependence of the intensity of the DL_i spectra on the impurity concentration is shown in Fig. 1.

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Fig. 2 shows absorption spectra of DL_i samples. Samples with DL_1 spectra have a more or less pronounced sharp absorption edge (typical for 6H – SiC crystals) that transforms into a long-wave smooth tail, testifying to the existence of absorption in the transparency region of this phase. There are no evidence that this absorption is related with the impurity concentration ($N_D - N_A \sim (3…8) \cdot 10^{16}$ cm^{-3}) in the samples.

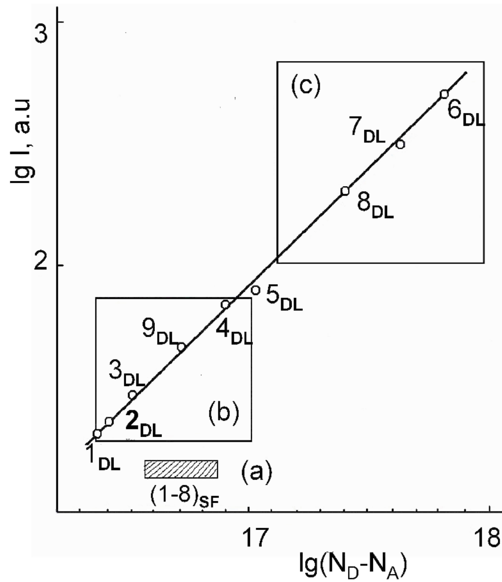

Fig. 1. Intensity of the DL_i spectra (i = 1) (T = 77 K) at 2.4…2.5 V vs. the impurity concentration for different samples (of the SF_i and DL_i series). Shaded area – the SF_i spectra from the ref. [22]. (a) Most pure samples with only SF spectra, $N_D - N_A \sim (4…9)\cdot10^{16}$ cm^{-3}, $(1…5)\cdot10^{16}$ cm^{-3}, $N_D < 1\cdot10^{17}$ cm^{-3}, $N_A \sim (1…3)\cdot10^{16}$ cm^{-3} from the ref. [22]. (b) Pure samples with the SF_i and DL_i series, $N_D - N_A \sim (2…8)\cdot10^{16}$ cm^{-3}, $N_A \sim (2…8)\cdot10^{17}$ cm^{-3}. (c) Samples with only DL_i spectra, $N_D - N_A \sim (2…7)\cdot10^{17}$ cm^{-3}, $N_D < 1\cdot10^{18}$ cm^{-3}.

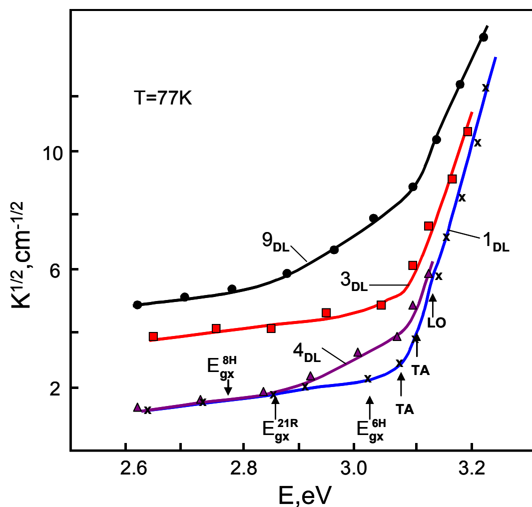

Fig. 2. Absorption spectra of DL samples.

However, the shift to the longwave area and absorption coefficient fully correlate with the degree and character of structural defects in the samples. The absorption area is located far away in the longwave side in relation to the exciton absorption edge (E_{gx}) of 6H – SiC. It rather strongly suggests formation of structures with a higher percentage of cubic α-SiC than 6H – SiC. The peculiarities of the absorption spectra are also in good agreement with those for the DL_i excitation spectra. The absorption at the energy $E < E_{gx}$ 6H – SiC can be attributed to the absorption of the new matrix of micro- or nano-phases, as noted in the analysis/study of the SF_i spectra [22].

The PL spectra (77 K) and corresponding excitation low temperature photoluminescence spectra (ELTPLS) of these DL samples are shown in Fig. 3.

There is correlation between the energy shift of longwave edges of the excitation low temperature PL spectra and the corresponding DL_i spectra. Consequently, it is possible to eliminate completely shorter wavelength DL_i spectra from the total complex panorama of the DL_i spectra (for example as it is shown for 9_{DL} sample) by choosing suitable photon energy of the exciting radiation. It was done using monochromatic light and various lasers.

Structurally, the total complexity of the DL_i spectra correlated with the degree of disorder of the crystal and was related with peculiarities of defect characteristics performance (as in the case of the SF_i spectra [22]) and, above all, with such its manifestations as one-dimensional disordering. The complex spectrum of the crystals can be decomposed into the so-called DL_i (i = 1, 2, 3, 4) spectra.

As it is shown in Fig. 3, the PL spectra of the 1_{DL} and 8_{DL} samples are represented mainly by only one DL_1 and DL_2 spectra, respectively, while the sample 9_{DL} includes more than one DL_3, DL_4 spectra, which corresponds to an even higher degree of the structural disordering of the crystals.

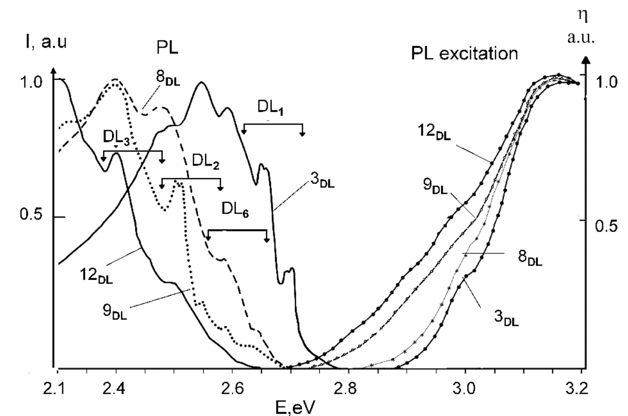

Fig. 3. DL_i spectra (I) and corresponding photoluminescence excitation spectra (η) at T = 77 K. The longwave edge of the photoluminescence excitation spectra for the DL_i and SF_i types is the same ($i = 1 \rightarrow E_{gx}$ (21R), $i = 2 \rightarrow E_{gx}$ ($10H_2$), $i = 3 \rightarrow E_{gx}$ ($14H_2$), ..., $i = 6 \rightarrow E_{gx}$ (8H).

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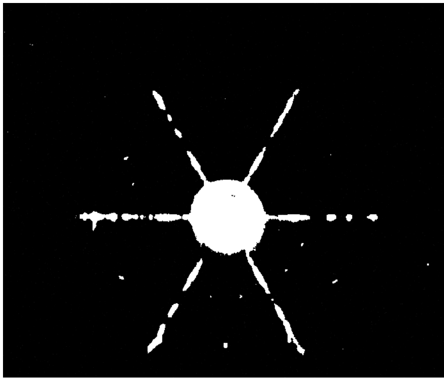
a)



b)

Photo 1. Laue pattern of SiC crystals with DL luminescence spectra: a) sample 4_{DL}, b) sample 9_{DL}.

Comparison of Laue patterns (Photo 1) shows that the crystal 9_{DL} looks like "morphological freak". Following changes in DL-luminescence in this crystal with layer-by-layer grinding of the (0001) face (along the axis *c*), it was possible to trace transformation of the structure during the growth process. The spectrum from the base surface of one of the faces of the crystal in the original state of the sample 9_{DL} is dominated by DL_3 and weaker DL_2 and DL_1 spectra, then with the grinding of the defect layers, DL_2 luminescence was mainly observed, and from the other natural face DL_1 luminescence took place. Thus, the luminescence within one sample reflects distribution of the corresponding luminescence centers during the growth process and indicates the independence of each of the DL_i spectra.

Comparison of the longwave edge of these samples with the longwave edges of the SF_i type samples (pure crystals) (Fig. 4) [21, 22] shows evidence that the ELTPLS for DL_i type spectra and ELTPLS for SF_i type coincide:

$i = 1 \rightarrow E_{gx}$ ($14H_1$) $\langle 4334 \rangle$,
$i = 2 \rightarrow E_{gx}$ ($10H_2$) $\langle 55 \rangle$,
$i = 3 \rightarrow E_{gx}$ ($14H_2$) $\langle 77 \rangle$,
$i = 4 \rightarrow E_{gx}$ (N/A),
$i = 5 \rightarrow E_{gx}$ (33R) $\langle (3332)_3 \rangle$,
$i = 6 \rightarrow E_{gx}$ (8H) $\langle 44 \rangle$.

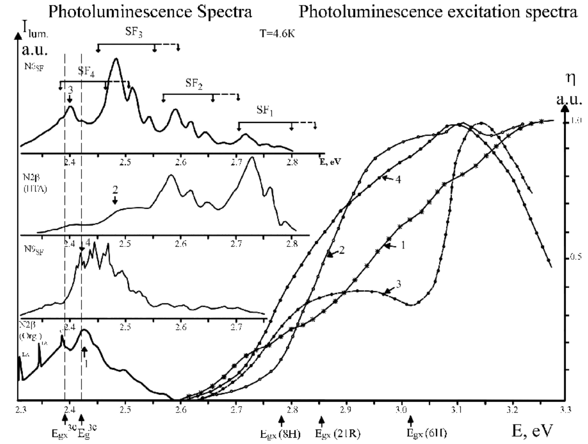


Fig. 4. SF_i spectra and corresponding photoluminescence excitation spectra (ELTFLS) at $T = 4.6$ K. The longwave edge of ELTFLS for DL_i and SF_i types is the same ($i = 1 \rightarrow E_{gx}$ ($14H_1$), $i = 2 \rightarrow E_{gx}$ ($10H_2$), $i = 3 \rightarrow E_{gx}$ ($14H_2$). Arrows (↓,↑) indicate the areas of the PL spectra for which the excitation spectra were recorded.

Thus, the analysis of the excitation spectra of the DL_i luminescence leads to the conclusion that the spectra are in qualitative agreement with the excitation spectrum of ELTPLS luminescence for the appropriate type SF_i (ELTPLS DL_1 → ELTPLS SF_1, ELTPLS DL_2 → ELTPLS SF_2). Consequently, DL luminescence is related to formation of a new micro-phase during the growth, and DL spectra are also indicators of the corresponding motif forming [23] the main phase adjustment.

4. Conclusion

In this work, photoluminescence spectra of lightly doped SiC crystals with in-grown original defects are reported. Undoped SiC single crystals with the impurity concentration of $N_D - N_A \sim (2\ldots8)\cdot10^{16}$ cm^{-3}, $N_A \sim (2\ldots8)\cdot10^{17}$ cm^{-3}, and $N_D - N_A \sim (1\ldots5)\cdot10^{17}$ cm^{-3}, $N_D \leq 1\cdot10^{18}$ cm^{-3} were investigated. The analysis of absorption, excitation and low temperature photoluminescence spectra of lightly doped SiC crystals with in-grown original defects suggests formation of a new micro-phase during the growth process and appearance of the deep-level (DL) spectra. The complex spectra of the crystals can be decomposed into the so-called DL_i (i = 1, 2, 3, 4) spectra. The appearance of the DL_i spectrum is associated with formation of new nano-phases. Data of photoluminescence, excitation and absorption spectra show the uniformity of different DL_i spectra. Structurally, the general complexity of the DL_i spectra correlated with the degree of disorder of the crystal and was connected with one-dimensional disorder, the same as in the case of the stacking fault (SF_i) spectra. The DL_i spectra differ from SF_i spectra and have other principles of construction and behavior.

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The DL_i spectra are placed on a broad donor-acceptor pairs emission band in crystals with higher concentrations of non-compensated impurities. The excitation spectra for the DL_i and SF_i spectra coincide and indicate formation of nanostructures $14H_1\langle 4334\rangle$, $10H_2\langle 55\rangle$, $14H_2\langle 77\rangle$, $8H\langle 44\rangle$.

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