**Abstract.** The luminescence spectra of SiC crystals and films with grain boundaries (GB) on the atomic level were observed. The GB spectra are associated with luminescence centers localized in areas of specific structural abnormalities in the crystal, without no reference to the one-dimensional layer-disordering. The zero-phonon part of GB spectra is always within the same energy range (2.890…2.945 eV) and does not fit in the dependence of its position in the energy scale on the percent of hexagonality as in the case of stacking faults (SF) and deep level (DL) spectra. The zero-phonon part 2.945…2.890 eV with a fine structure is better observed in crystals with the centers of origin growth of crystal, if \( N_D - N_A \approx (2…8) \times 10^{16} \text{ cm}^{-3} \), \( N_D \approx (2…7) \times 10^{17} \text{ cm}^{-3} \). The edge phonons of the Brillouin zone TA-46 meV, LA-77 meV, TO-95 meV and LO-104 meV are involved in development of the GB spectrum. This spectrum may occur simultaneously with the DL and SF ones. The GB spectra also occur after high temperature processing the \( \beta \)-phase (in the 3C-SiC) with appearance of the \( \alpha \)-phase. The temperature range of observation is 4.2…40 K. There is synchronous thermal quenching of all elements in the fine structure. The thermal activation energy of quenching is \( E_a \approx 7 \text{ meV} \).

**Keywords:** silicon carbide, nanocrystalline film, luminescence, grain boundaries.

Manuscript received 03.05.17; revised version received 01.08.17; accepted for publication 06.09.17; published online 09.10.17.

1. Introduction

Silicon carbide is a wide bandgap indirect semiconductor with variety of polytypes. Experimental results and theoretical calculations showed that the luminescence of different polytypes strongly influenced by defects [1-3]. The luminescence spectra [4, 5] of SiC crystals and films with stacking faults (SF) in high-purity SiC [2] and with deep level (DL) [6-9] in lightly doped SiC reflect formation of intermediate metastable phases during 3C-\( \leftrightarrow \)6H transitions. SF and DL spectra hand-in-hand follow the structure transformations.

Grain boundaries in silicon carbide produced by sublimation were examined using high resolution transmission electron microscope (HRTEM) [6]. 6H-SiC polytype boundary parallel to (0001) and 6H/15R hetero-polytype boundary with a thickness on the atomic level were observed. But luminescence of these defects was not investigated. Therefore, it is very important to investigate the grain boundaries (GB) by using optical methods.

Nowadays, since SiC thin films and crystals are widely used to fabricate devices, it is essential to understand properties of grain boundaries that can decrease the efficiency of these devices.

The purpose of this work is to decode the structure of low-temperature luminescence spectra in SiC crystals and in films with GB.
2. Experimental results and discussion

We studied low temperature spectra by using techniques described early [7]. For this experiment, we selected lumpy, blocky SiC crystals and crystals with steps of growth. The same type of spectra (GB) was observed, if crystals had block’s disorientation in a basal plane (not only along the c axis). GB spectra are shown in Fig. 1 for the case when blocks have a common axis c, but were disoriented in the basal plane. Such GB spectrum is not observed in the thin plate-like crystals (not lumpy, not blocky crystals).

The low temperature photoluminescence spectrum of the SiC crystal which has blocks disoriented in the basal plane (concentration \( N_D - N_A \sim 3 \times 10^{16} \text{ cm}^{-3} \), sample \( \text{N2}_{\text{DL}} \)) with GB spectrum at 4.2 ° K is shown in Fig. 1.

Thus, after detection of SF\(_{i}\) and DL\(_{i}\) spectra and their careful investigations [10-12], we found another new spectrum, which zero-phonon line had been allocated at 2.890...2.945 eV (the so-called GB spectrum) (Fig. 1). This spectrum, like to the cases of SF\(_{i}\) and DL\(_{i}\) spectra, clearly shows the fine structure. The GB spectrum was observed only in pure crystals, when the concentration of non-compensated impurities was \( N_D - N_A \sim (2...9) \times 10^{16} \text{ cm}^{-3} \).

Fig. 2 shows the zero-phonon structure of the GB spectrum for different crystals of DL\(_{i}\) (Fig. 2a) and SF\(_{i}\) series (Fig. 2b). It can be seen that GB spectrum is very structured (see inset in Fig. 2a, where one segment equals 1 meV). The slit width (equal to 0.5 meV) yields to the detailed spectrum fractures and allowed to see the fine structure. In the particular case (sample N14\(_{DL}\)), the nature of GB spectrum is maximally manifested. The inset (Fig. 2a) shows an enlarged part of the zero-phonon part of the spectrum. GB spectrum was observed only in pure crystals, when the concentration of non-compensated impurities was \( N_D - N_A \sim (2...9) \times 10^{16} \text{ cm}^{-3} \).

In crystals with the impurity concentration \( N_D - N_A > 3 \times 10^{16} \text{ cm}^{-3} \) and \( N_D > 10^{18} \text{ cm}^{-3} \) (Fig. 3), GB spectra was not seen since refers to shallow levels of luminescence centers, like to SF\(_{i}\) spectrum. GB range can be observed simultaneously with those of SF\(_{i}\) and DL\(_{i}\) spectrum in impurity conditions (a) and (b) – Table (Fig. 3).

So, in case of GB spectra (similar to the case of DL\(_{i}\) and SF\(_{i}\)) the fine structure has allowed to define the boundaries of the zero-phonon part of the spectrum. GB have a line structure with the same density, stockade, which were observed in [11]. It indicates that the GB spectra represent incoherent boundaries. The GB spectra reflect locations of two matrices docking (the side mosaic’s docking). Literally, it’s non-compliance of the border (border inconsistencies in films). The rest part of the spectrum is described by involving phonon replicas at the edge of the Brillouin zone TA-46, LA-77, TO-95 and LO-104 meV, like to the other shallow centers (as in SF\(_{i}\)). But, unlike SF\(_{i}\) spectra, availability of non-phonon part here (in GB) in explicit manifestation indicates luminescence center locality rather than ply, extended character inherent to SF\(_{i}\) centers.

The temperature range of existence of the GB center (4.2...40 K) is similar to the shallow SF\(_{i}\)-centers.

The dependence of the GB spectra appearance (Fig. 3) on the degree of structural disorder \( \delta-I, \delta-II \) is sometimes observed and sometimes is not observed. Therefore, we can say that the dependence on the degree of structural disorder is not fixed.
Fig. 2. The zero-phonon structure of the GB spectrum for different crystals: a) DL₁ series for samples with $N_{D}-N_{A}$ ~ (2…8)$\times$10^{16} cm⁻³, $N_{A}$~ (2…7)$\times$10^{17} cm⁻³. The inset shows an enlarged part of the zero-phonon GB spectrum (photoluminescence (PL) and phosphorescence (PS), $\tau$ = 3 ms) for the sample N₂DL with $N_{D}-N_{A}$ ~ 2$\times$10^{16} cm⁻³ and for the sample N₄DL with $N_{D}-N_{A}$ ~ 8$\times$10^{16} cm⁻³ from two polar faces of the crystal (0001) and (0001). The line 1 describes photoluminescence of the other side of the crystal (lumpy), where there is a spiral, stage; 2 – PL of the mirror part of the crystal. b) SFi series for most pure samples with $N_{D}-N_{A}$ ~ (4…9)$\times$10^{16} cm⁻³, $N_{A}$ < (1…3)$\times$10^{16} cm⁻³. c) GB spectrum (I) before plastic deformation (PD) and (2) after plastic deformation (PD) combined with (3) calculated the zero-phonon part of the SFi spectrum [6].

Fig. 3. Low-temperature photoluminescence spectra according to the structural imperfection and impurity concentration in SiC crystals and films. Zero-phonon parts: SF₁ ~ 2.855…2.793 eV, DL₁ ~ 2.730…2.625 eV, GB ~ 2.945…2.890 eV. a) Pure SiC crystals and films with non-compensated concentration $N_{D}-N_{A}$ ~ (4…9)$\times$10^{16} cm⁻³, $N_{A}$ ~ (1…3)$\times$10^{17} cm⁻³; b) lightly doped samples with $N_{D}-N_{A}$ ~ (2…8)$\times$10^{16} cm⁻³, $N_{D}$ ~ (2…7)$\times$10^{17} cm⁻³; c) doped samples with $N_{D}-N_{A}$ > 3$\times$10^{17} cm⁻³, $N_{D}$ > 10^{19} cm⁻³.
The impurity concentration in the crystal affects the appearance and manifestation of the GB spectrum. If the impurity concentration is low in pure samples (Fig. 3a), the fine structure in the GB spectrum is generally observed, but it is weakly pronounced. With impurity concentration increase (Fig. 3b), the GB spectrum is more pronounced, and there is a clear expression of the fine structure in the spectrum. In the heavily doped crystals, the GB range is not observed (Fig. 3c).

Thus, GB spectra can be observed simultaneously with the SFᵢ and DLᵢ spectra in the case of pure and lightly doped crystals (a) and (b) in Fig. 3. In the heavily doped crystals (Fig. 3c), GB spectra are not observed.

The zero-phonon spectrum part of GB is located at the energy of 2.95...2.89 eV and has the most pronounced line structure in the case of lightly doped crystals (Fig. 3b). The maximum resolution of the fine structure in the spectra of GB is defined as $\Delta H = 0.5$ meV (equal to half-width of the fine-structure elements).

The GB spectrum is shown through interaction with edge phonons TA-46, LA-77, TO-95, LO-104 meV within the temperature range (4.2...40 K). As the temperature increases, synchronous thermal decay of all elements of the fine structure is observed. The thermal activation energy of extinguishing is equal to $E_a^T = 7$ meV.

The dependence of the luminescence intensity on the excitation light intensity is expressed as $I_{\text{lum}} = I_{\text{exc}}^\alpha$, $\alpha = 0.7$. (Radiation of high-pressure mercury lamp was used in the range of two orders of magnitude.) There is a differentiated change in the intensity of the fine structure. Namely, the short-wave part of the thin structure decreases quickly.

Luminescence intensity distribution ($I_{\text{lum}}$) on the elements of the fine structure is the same as at $\tau = 3$ ms in the attenuation at $I_{\text{exc}} = 0.004 I_0$. (The energy $E_{\text{exc}}$ is higher than that or equal to 3.05 eV.)

Character of change in the damping (with different delay times $\tau$) in the afterglow in the range of $\tau = 3...15$ ms is $I = I_0 \tau^{-\alpha}$.

Values of $\alpha$ are the same as in the case of DLᵢ, for the same range of $\tau$ [8]. Also, there is a differentiated variation of the fine structure intensity. Namely, the short-wave part falls faster.

Maximal total intensity of the GB spectrum decrease takes place, if excitation light polarization is parallel to the c axis of the crystal. Thus, the luminescence intensity decreases with polarization of the exciting light parallel to the c axis.

Plastic deformation of the crystal (three-point bending) stimulates the appearance of the GB spectrum or strengthening the existed GB spectrum. Plastic deformation of SFᵢ series, having initially GB range, amplifies them or stimulates their appearance. There is redistribution of the intensities in the fine structure in pure crystals (Fig. 3a). Namely, the intensity of the most short-wave part of the spectrum is noticeably reduced. In cubic β-SiC crystals, we observed occurrence of GB spectra after high temperature annealing.

3. Conclusion

By comparing the spectra SFᵢ, DLᵢ and GB in different conditions of registration and after various treatments of the crystal we can make the following conclusions.

1. Behavior of SFᵢ, DLᵢ and GB spectra is different. The zero-phonon part of GB spectrum does not follow restructuring of the crystal. The zero-phonon part of GB spectra does not fit in the dependence of its position in the energy scale on the percent of hexagonally as in the cases of SFᵢ and DLᵢ spectra. GB spectra are always in the same energy range (2.890...2.945 eV). It indicates that the GB spectra are characteristic for the grain boundaries. In the whole, mosaic interphase transformation of the GB spectra reflects the grain, interlayer boundaries in SiC crystals and films. The GB spectra are associated with luminescence centers localized in areas of specific structural abnormalities of the crystal, without no reference to the one-dimensional layer disordering (as SFᵢ and DLᵢ).

2. The GB spectra are the most intense and structurally expressed in crystals of DLᵢ series in samples with a lumpy growth terraces (staggered) from several centers. The GB spectra are observed in crystals with certain structural requirements and the impurity situation $N_D - N_A$ ~ (4...9)·10¹⁶ cm⁻³, $N_A$ ~ (1...3)·10¹⁶ cm⁻³, and especially in lightly doped samples with $N_D - N_A$ ~ (2...8)·10¹⁶ cm⁻³, $N_D$ ~ (2...7)·10¹⁷ cm⁻³. In the case of doped samples with $N_D - N_A$ > 3·10¹⁷ cm⁻³, $N_D$ > 10¹⁹ cm⁻³, the GB spectra are not observed (Fermi level is raised). These spectra may occur simultaneously with the DLᵢ spectra and SFᵢ spectra. GB spectra also occur after high temperature processing of β-phase (in the 3C-SiC), with appearance of the α-phase, but much lower intensity with weak fine structure.

3. There observed is the zero-phonon part 2.945...2.890 eV with a fine structure. The edge phonons of the Brillouin zone TA-46 meV, LA-77 meV, TO-95 meV and LO-104 meV are involved in the development of the GB spectrum. The zero-phonon part 2.945...2.890 eV with a fine structure (in DLᵢ series of crystals) is better pronounced in crystals with the centers of origin growth of crystal with $N_D - N_A$ ~ (2...8)·10¹⁶ cm⁻³, $N_D$ ~ (2...7)·10¹⁷ cm⁻³.

4. The temperature range of observation is 4.2...40 K, i.e. the same as in the case of part SF-II of calculated SFᵢ zero-phonon [6]. There is a synchronous thermal quenching of all elements of the fine structure. The thermal activation energy of quenching is $E_a^T$ ~ 7 meV (it also coincides with the SF-II part of calculated zero-phonon of SFᵢ [6]).

5. Plastic deformation of the crystal (three-point bending) stimulates appearance of GB spectra. Plastic deformation of SFᵢ series crystals, having initially GB range, strengthens the GB spectra. There is redistribution of the intensities in the fine structure. The intensity of the most short-wave part of the spectrum is noticeably reduced.
References