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Peculiarities of photoluminescence spectra behavior in SiC crystals and films during phase transformations

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Abstract. Peculiarities of photoluminescence spectra behavior in SiC crystals and thin films with in-grown defects during phase transformations have been studied. On the deep-level(DL)-spectra, as an example, their characteristics and behavior were investigated. It has been shown that all DL spectra have the same logic of construction and demonstrate identical behavior of the thin structure elements.

Keywords: photoluminescence spectra, SiC crystals and thin films, phase transformations, in-grown defects.

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1. Introduction

Due to improvement in SiC crystal growth techniques and experimental methods many semiconductor material-related problems have been solved. However, there are still a number of problems related with polytypism and defects in wide-band gap semiconductors such as SiC. Different polytypes and defects can already be found in grown crystals and films, but they also can be formed during device processing steps, for instance, annealing at high temperatures. A large variety of defects exists in SiC because of the binary compound nature and polytypism. Study of defects in SiC is very complicated. One can find a lot of papers related to these problems.

Optics of defects in SiC crystals and single crystalline films 4H-SiC was described in [1-3]. Silicon

carbide nanostructures and Si-SiC core-shell nanowires as well as SiC nanotubes of high crystalline quality were described in [4]. The potential application of these nano-objects with regards to their eventual integration in biology and electronics is highly attractive.

Polytypism and one-dimensional disorder in silicon carbide using synchrotron edge topography were studied in [5]. The results of spectral studying the defects in very pure SiC crystals and single crystalline films 4H-SiC were described in [6]. The photoluminescence research of the phase transition 6H-3C-SiC with and without joint polytypes was presented in [7]. Low temperature photoluminescence changes of the transition phase in SiC crystals were represented with the stacking fault spectra within the temperature range 4.2...35 K. The stacking fault spectra that indicate metastable formation of nanostructures in the SiC crystals (14H₁(4334),

10H₂(55), 14H₂(77)) were studied in the work [8]. Defects in the lightly doped SiC crystal with grown defects of structure were studied in [9-11].

The deep-level (DL) spectra manifested itself the most clearly, emphatically and intensively in the case when strong diffuse scattering effects are present in the Laue diffraction pattern [11-14], after intercalation of the multilayer polytypes and layers with the disorder structure (single axis disorder), in SiC crystals and films with the impurity concentration of $N_D - N_A \sim (2...8) \cdot 10^{16} \text{ cm}^{-3}$, $N_A \sim (2...7) \cdot 10^{17} \text{ cm}^{-3}$.

A linear spectrum (with phonon part) at 4.2 K is located on the wide band with the maximum in the green-yellow region, which starts to dominate at 77 K and remains up to the 160...170 K, when the DL spectrum winks out [9, 11, 12, 14].

The appearance of the thin-linear structure in DL spectra requires at least a certain minimum concentration of impurities ($N_D - N_A$), as well as expressed (in concentration and in behavior) deformations of the crystalline structure (DL₁).

An increase in the degree of deformations – deviations from the determinate growth to the multilayer and mosaic crystal types, appearance of several growth centers leads to the complexity of the whole spectrum, emergence of set of the DL spectra with the same behavior in the corresponding registration conditions. The DL spectra as well as the corresponding SF spectra [8] are related with their crystalline matrixes and shifts in the common energy scale.

It is convenient to demonstrate all general characteristics of the DL spectra by using the example of the most common DL₁ spectrum. Observation of this fine linear structure ($T = 4.2 \text{ K}$) allowed to determine the exact boundaries of the zero-phonon part of the DL spectrum and confirm the complex internal logic of the composition of this zero-phonon part (DL-I(X) and DL-II(Y)). Existence of the fine linear structure allowed to track individual behavior of each element of this structure vs. temperature.

However, although for the SF spectra many parameters have been determined (thermal activation energy of quench, peculiarities of the spectra at the different intensity and polarization of excitation light, intensity in quench vs. delay time [8]), there was a lack of such information for the DL spectra.

In this paper, we intend to fill this gap and provide more understanding the SiC defects.

2. Experimental

The method of optical spectroscopy – low-temperature photoluminescence (LTPL) – was used in this work, as it is very sensitive to structural changes. LTPL spectra were registered by the ДФС-12 spectrograph with the photodetector (ФЭУ-79). In photoluminescence (PL) experiments, a nitrogen laser ЛГИ-21 ($\lambda = 337 \text{ nm}$, 3.68 eV), or helium-cadmium laser ЛГ-70 ($\lambda = 441.6 \text{ nm}$, 2.807 eV), respectively, were used. Also,

mercury ultrahigh pressure lamp СВДШ-1000 with УФ-2 filter and xenon lamp ДКСШ-1000 were used. In addition, MDR-2 spectrometer was applied in the case of registering the excitation spectra of PL.

The selected samples of α -SiC crystals were contained in a liquid helium or nitrogen cryostat, which provided the temperatures ranging from 1.5 up to 330 K. The crystals were irradiated, de-energized, then they were taken out from liquid nitrogen and the intensity of FL was measured at the temperature increase. The change in the intensity of exciting light within about two orders was achieved by graded weakening of the exciting beam from a mercury lamp (СВДШ-1000).

The investigated monocrystalline α -SiC crystals, grown using Lely's (Tairov's) method, were N1_{DL} and N9_{DL}. The N1_{DL} sample was characterized by additional obligate nodes in the reciprocal lattice, diffuse bridges between reflexes and other degradation signs. The N9 sample is a "morphological freak". All the above mentioned peculiarities are enhanced by the appearance of new reflexes, and amplification of diffuse (blurring) effects. This type of crystals has clear spirals of growth and steps of surface growth (Fig. 1).

Evolution of the thin-structure elements with temperature for the sample DL₁ (N1_{DL}) up to the temperature 77 K was described in ref. [11]. The thin structure at several temperatures was described in detail:

- nature of intensity variation of individual/separate elements of this thin structure with temperature,
- dependence of shift and half-width of elements of thin structure on temperature.

At the temperature 30 K, the local phonon (LOC 91 meV) disappears, and the thin line structure elements shift towards higher energy, and their broadening stops, and from 60 K the fading of DL-I(X) and DL-II(Y) takes place. The other interval of temperatures (higher than 60 K) is shown in Fig. 2. The full attenuation takes place at higher temperatures.

The temperature dependences of PL suppression for the DL-I(X) and DL-II(Y) components of zero phonon part of a spectra DL₁ (sample N1_{DL}) and DL-II(Y) of DL₂ (sample N9_{DL}) are shown. Curve 1 fades more quickly, has smaller thermal activation energy (0.21 eV) and corresponds to DL-I(X) zero phonon part. Curves 2 and 3 have the same activation energy (0.26 eV) and correspond to DL-II(Y) in different DL_i samples. Curves 1, 2, and 3 are plotted with the background deduction, and curve 4 – without it.

Table. Band gap (optical E_g and exciton E_{gx} , eV) in SiC.

Polytype	E_g	E_{gx}	$\Delta = E_g - E_{gx}$
6H	3.109	3.024	0.085
33R	3.087	3.002	0.085
21R	2.938	2.853	0.085
8H	2.868	2.783	0.085
10H ₂	2.798	2.713	0.085
14H ₂	2.698	2.613	0.085

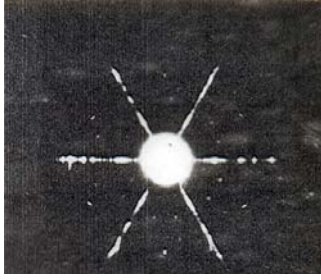


Fig. 1. Laue diffraction pattern of one-dimensional disordered D-layers in a-SiC for SiC crystal (N9 sample).

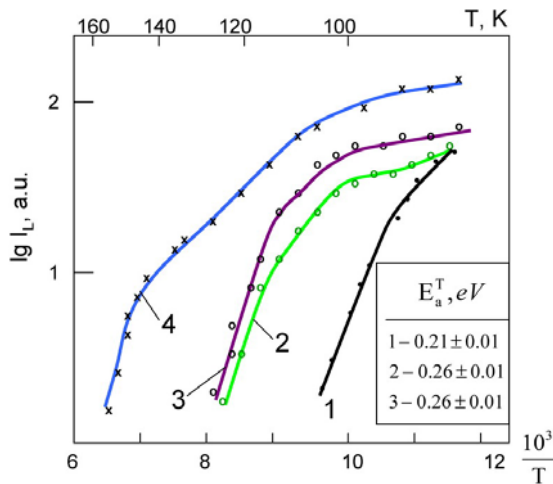


Fig. 2. Temperature dependences of PL suppression for the DL-I(X) and DL-II(Y) components of zero phonon part in the DL₁ spectra (sample N1_{DL}) and DL-II(Y) of DL₂ (sample N9_{DL}). Curves 1, 2, 3 are for zero phonon parts without background, 4 – with background. 1 – excited with 2.696 eV, for DL-I(X), 2 – excited with 2.66 eV, for DL-II(Y), 3 – excited with 2.5 eV, for DL-II(Y), 4 – excited with 2.5 eV, with background.

Thus, the X-component fades at temperature ~105 K with thermal activation energy of $E_{xt} = 0.21 \pm 0.01$ eV. When the temperature reaches 120...125 K, the Y-component fades with $E_{yt} = 0.26 \pm 0.01$ eV. And the course of this attenuation allows to assume the pumping of Y-components intensity in this temperature interval corresponding to the sharp attenuation and disappearance of X-component in the DL spectra.

At the temperature 30 K, local phonon (LOC 91 meV) disappears, and the thin line structure elements shift towards higher energy, and their broadening stops, and from 60 K the fading of DL-I(X) up to 105 K and DL-II(Y) to 125 K takes place. The obtained thermal activation energy probably determines the depth of the ground level in the corresponding electron transition.

Therefore, the most explored and most clearly exhibited in N1_{DL} and N9_{DL} samples DL₁ spectrum with the base motive of building structure (34) (21R-SiC) has two components:

$$DL-I(X) = 2.73 \dots 2.67 \text{ eV};$$

$$DL-II(Y) = 2.685 \dots 2.625 \text{ eV}.$$

The DL-I(X) component exists within the temperature range 4.2...105 K and DL-II(Y) component – within 4.2...125 K. The background is visible up to 160...170 K.

At the temperatures higher than 60 K, the fading occurs as the whole without the shift in the energy scale $E_{av} = 0.26 \pm 0.01$ eV. The difference between the activation energies $\Delta(E_a(Y) - E_a(X)) = (45 \dots 50)$ meV, which is in full agreement with the amount of $\Delta_1 - \Delta_2 = 0.043$ eV, which estimates the energy difference between the levels associated with the ground states X and Y obtained from the PL spectra [11]. This shift between two parts of the DL spectra was accurately determined from the low-temperature photoluminescence spectra [11]. All these changes of intensity X- and Y-components match the features of thermal luminescence of this sample at the low-temperatures 80...130 K.

The spectra of thermostimulated luminescence are shown in Fig. 3.

The crystal was irradiated, de-energized, then it was taken out from liquid nitrogen and, with an increase in temperature, it is shown that the maximum of PL intensity corresponds to the temperature where curves 1-3 in Fig. 2 fade.

Fig. 3 shows the temperature dependence of the quenching components DL₁: DL-I(X) and DL-II(Y) (zero phonon spectrum of the DL₁ (sample N1_{DL}). A thermally stimulated luminescence spectrum is shown for DL₂ spectrum, too (sample N9_{DL}).

Determination of the thermal activation energy was made from the temperature fading of photoluminescence for two groups (DL-I(X) and DL-II(Y)) of zero phonon parts in spectra DL₁ (sample N1_{DL}) and for DL-II(Y) spectra DL₂ (sample N9_{DL}).

The DL spectra of these samples are shown in [11]. It is worth mentioning that the temperature behavior of Y-component of more longwave spectra of DL₃ gives the same value of the thermal activation energy $E_{yt} = 0.26 \pm 0.01$ eV.

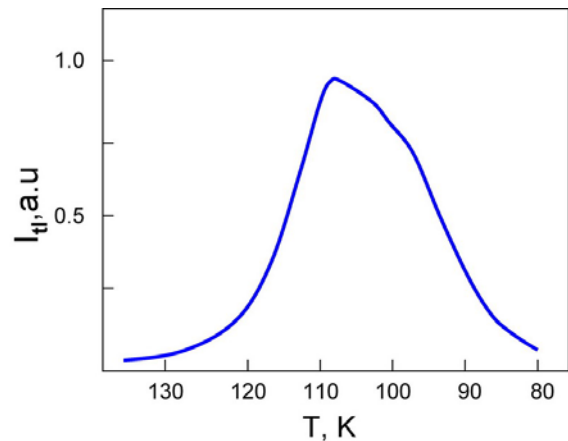


Fig. 3. Thermostimulated luminescence spectra (sample N1_{DL}).

In general, the identical temperature behavior of spectra DL₁, DL₂, and DL₃ etc. testifies to the structural uniformity of the centers responsible for DL luminescence. It is clear that behavior of the DL_i series is absolutely different from behavior of SF_i series [8]. The change of intensity of exciting light within about two orders, reached by gradual weakening of the exciting beam from the mercury lamp CBДIII-1000, reveals a sublinear dependence of the intensity of the DL luminescence, which is $I_L \sim I_{ex}^k$, where $k=0.7...0.9$ (Fig. 4).

However, for the most short-wave structural components of the zero phonon part of the DL spectra at a small intensity of excitation (when the intensity falls dramatically), the character of the dependence comes nearer to the linear one (Fig. 4). Fig. 4 shows the dependence of the intensity of different elements in the spectrum DL₁ fine structure, on the excitation intensity (at $T=77$ K (sample N2_{DL})). For the short-wave region, the fine structure differential intensity for the variation of DL-I(X) and DL-II(Y) spectra equals to 0.7...0.9.

The energy change of the quantum of exciting light was determined by the spectra of photoluminescence. Similar spectra were observed during the reverse phase transformation [7]. The quenching of the DL₁ spectra (phosphorescence) at different time delays ($T = 77$ K) is depicted in Fig. 5.

The attenuation of DL luminescence in a wide time range $t = 10^{-7}...10^{-3}$ s is shown in Fig. 6. The change of radiation intensity corresponds to the regularity of $I = I_0 t^{-\alpha}$.

It is possible to allocate three stages:

(0...0.5) μ s – fast fluorescence attenuation with dropping the luminescence intensity approximately by 1.5-2 orders.

(0.5...150) μ s – this is a stage of phosphorescence characterized by the index number 0.4.

Further (0.15...15 ms) there is faster attenuation related to the elements of structure of zero phonon parts of DL spectra.

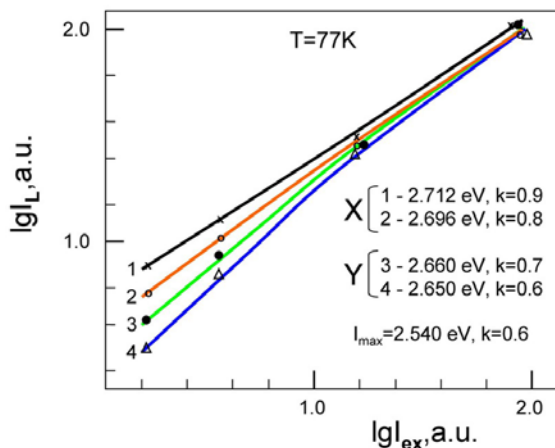


Fig. 4. Dependence of intensity of DL luminescence vs. intensity of exciting light ($T = 77$ K).

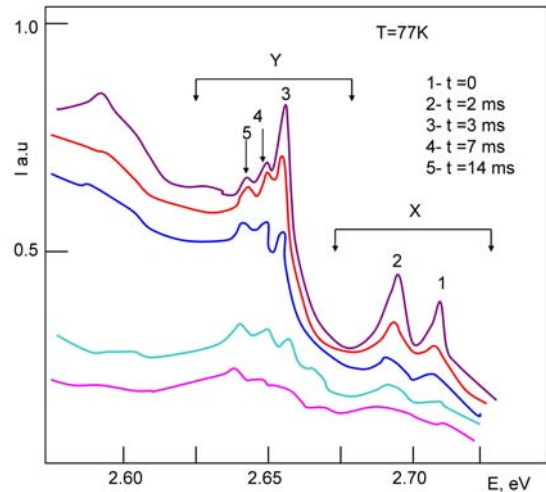


Fig. 5. DL₁ spectra at fading with various temporal delays (phosphorescence) (Sample N2_{DL}). $T = 77$ K.

Measurements of spectra with temporal delays (t) in the millisecond range show a higher attenuation speed of DL-X as compared to DL-Y, as well as stronger attenuation of the short-wave elements of the structure in each group (Fig. 6). Here, the index number α changes within 0.65...1.0 (Fig. 6 on the right).

At the temperature of 4.2 K and the delays 0.1 μ s...10 ms, the index numbers are $\alpha_1 = 1.5$ (fast attenuation) and $\alpha_2 = 0.4$. At the delays of 3...10 ms, the differential change of the fine structure elements $\alpha = 0.7...0.9$ and short-wave elements in each group of DL-I and DL-II decays faster. This behavior is very similar to that of the photoluminescence vs. the intensity of excitation light.

Here, as in the case of the SF centers [8], one can assume a significant radiative lifetime, which is due to the spatially separated recombining electrons and holes with slightly overlapping wavefunctions.

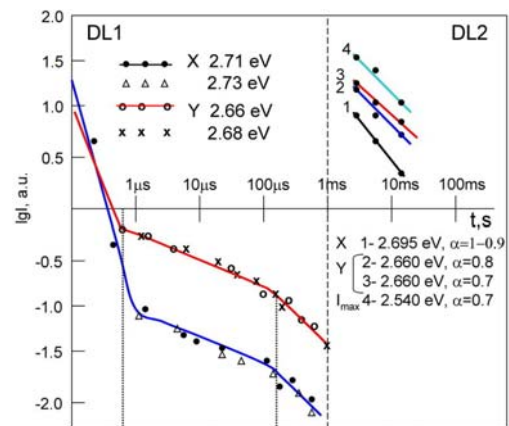


Fig. 6. The law of changes in the intensity of PL in DL1 spectra at different delays in a wide time interval. At 4.2 K sample N1_{DL} (on the left) and at 77 K sample N2_{DL} (on the right).

In the case of intensity of the DL spectrum vs. polarization of exciting light measurements, the selective changes in the intensity of the fine structure inside each group of DL-I and DL-II were observed. The changes are in reverse for E_{ex} parallel and perpendicular to the c -axis.

It is clear that all the samples DL_i show the identical behavior of the thin structure DL-X and DL-Y irrespective of belonging to the DL_1, DL_2 type, etc., such as temperature broadening and a shift in the short-wave area, the differentiated character of attenuation. The broadening of elements and as a whole blurs out the thin structure of DL-X and DL-Y spectra, which is observed with the increase in $N_D - N_A$ from $2.6 \cdot 10^{16} \text{ cm}^{-3}$ to $(5 \dots 7) \cdot 10^{17} \text{ cm}^{-3}$ (even at $T = 4.2 \text{ K}$ (sample N9_{DL})).

The temperature (4.2...77 K) shift of lines as a whole is estimated as 7 meV in comparison with the shift of the certain line in the thin structure which equals ~3 meV in the samples with $N_D - N_A \sim (2 \dots 3) \cdot 10^{16} \text{ cm}^{-3}$.

3. Conclusion

All DL-i spectra have identical construction, namely: every zero phonon part has two structural groups X and Y (DL-X and DL-Y) and their phonon repetitions (as a whole) with the participation of LA and LO phonons and a local phonon (4.2 K).

Behavior of each DL_i spectra is identical under various conditions of registration. The intensity of each element of fine structure (X and Y) changes with temperature (4.2...77 K). The intensity passes through a maximum. The intensity of X and Y components fade. The DL-X fades to ~105 K with the thermal energy of activation equal to 0.21 eV. The DL-Y fades to ~125 K with the thermal energy of activation equal to 0.26 eV.

There is the sublinear law in attenuation within the wide time interval $t = 10^{-6} \dots 10^{-3} \text{ s}$. Speeds of attenuation for the elements of the thin structure at final stages are different. The speeds of attenuation depend on the intensity of the exciting light (sublinear dependence) and are different for the elements of the thin structure.

DL_i spectra are the same as SF_i , which reflects fundamental SiC polytype transformations. But DL_i and SF_i spectra have different nature and characters, even when they follow the nanostructure transformations together.

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