External impacts on SiC nanostructures in pure and lightly doped silicon carbide crystals

S.I. Vlaskina[1,2], G.N. Mishinova[3], V.I. Vlaskin[4], V.E. Rodionov[2], G.S. Svechnikov[2]
[1]*Yeoju Institute of Technology (Yeoju University),*
338 Sejong-ro, Yeoju-eup, Yeoju-gun, Gyeonggi-do, 469-705 Korea
[2]*V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine,*
41, prospect Nauky, 03028 Kyiv, Ukraine; e-mail: businkaa@mail.ru
[3]*Taras Shevchenko Kyiv National University,*
64, Volodymyrs'ka str., 01033 Kyiv, Ukraine
[4]*Sensartech, 2540 Lobelia Dr., Oxnard, 93036 California, USA*

Abstract. Influence of plastic deformation and high-temperature annealing ($T = 2100$ °C, $t = 1$ h) on SiC crystals with grown polytypic junctions demonstrating SF and DL spectra have been presented. SF-i and DL-i type luminescence are inherent to SiC crystals with distortions of the structure related with availability of packing defects that lead to one-dimensional disordering (along the *c*-axis). They are a most expressed in doped crystals with original growth defects. DL luminescence appears in pure crystals at plastic deformation and in doped crystals at a hydrostatic pressure. It enhances at the high temperature annealing, too.

Keywords: silicon carbide, phase transition, 3C-6H polytype, luminescence.

1. Introduction

Silicon carbide is a prototype material for polytypism. SiC is a binary compound that has a large number of possible configurations. Continuous improvement of crystal growth techniques is related with understanding the nature of defects in crystalline materials. Defects exist in as-grown crystals and are also formed during device processing stages [1-7]. Defects can be annealed at high temperature [8], can transform into complexes. A special attention is devoted to defects when studying polytypism in the case of SiC [9, 10]. Relatively little is known about point defects in different polytypes of SiC crystals. Therefore, investigation of SiC by using combination of different techniques [11-20], like X-ray combined with photoluminescence, is one of nowadays state-of-the-art topics. The aim of this work is to provide more deep understanding the role of defects in SiC polypype formation. Phase transitions in silicon carbide crystals have been studied in a series of our papers [21-27]: in heavily doped with nitrogen 6H-SiC polytypes [9, 22], in pure (non-doped) perfect cubic 3C-SiC crystals [24], 3C-6H-SiC polytype junctions in pure crystals [24], in perfect non-doped [25] crystals 6H-SiC without defects and with polytype junctions, and in the lightly doped crystals of hexagonal SiC polytypes [26, 27] as well as in current heated SiC crystals [28].

In this work, influence of external impacts, namely: high temperature annealing, bending and irradiation on phase transformations and stacking faults (SF) created during phase transitions as well as deep level (DL) defects have been investigated.

2. Experimental

Low temperature photoluminescence (LTPL) spectra were registered using the ДФС-12 spectrometer with the photodetector ФЭУ-79. To register excitation spectra of photoluminescence, the МДР-2 spectrometer was applied in addition. As sources for excitation of luminescence, a mercury ultrahigh pressure lamp СВДШ-1000 with the УФ-2 filter, and also a xenon lamp ДКсШ-1000 were used. Sometimes, spectra were excited by lasers – nitrogen ЛГИ-21 – 337 nm (3.68 eV) or helium-cadmium ЛГ-70 – 441.6 nm (2.807 eV).

The selected samples of α-SiC crystals were placed either into nitrogen, or helium cryostats.

The photoluminescence spectra were measured using the samples mounted inside a liquid helium or nitrogen cryostat, which provided temperature ranging from 4.2 to 330 K.

The Laue method was applied for structure investigations of the SiC samples. The electron and diffraction methods allow to trace changes of such parameter of the crystal structure as symmetry. Besides, in some cases for an assessment of structural condition of the allocated blocks, the method of transmission electron microscopy (magnification ×15 000) was used. To obtain the pictures of a side surface of the crystal under initial growth conditions, we used the metallographic method.

3. Results and discussion

Table 1 [27] shows LTPL spectra according to structural imperfection and the impurity concentration in α-SiC crystals. Structurally perfect 6H-SiC crystals (or perfect blocks of the crystal that coherently coalesce with disordering the layers) show a typical spectrum of nitrogen-bound exciton complexes together with the linear ABC-spectrum related to Ti (δ-0 − a), and emission spectra of the donor-acceptor pairs.
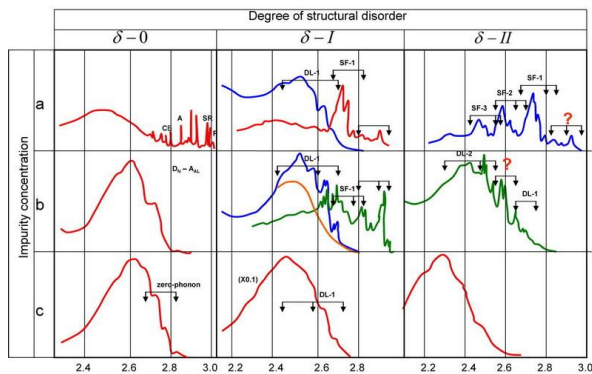

Fig. 1. LTPL spectra according to the structural imperfection and impurity concentration in α-SiC crystals. a) Pure SiC crystals and films with non-compensated concentration $N_D − N_A \sim (4...9) \cdot 10^{16}$ cm^{-3}, $N_A \sim (1...3) \cdot 10^{16}$ cm^{-3}; b) lightly doped samples with $N_D − N_A \sim (2...8) \cdot 10^{16}$ cm^{-3}, $N_D \sim (2...7) \cdot 10^{17}$ cm^{-3}; c) doped samples with $N_D − N_A > 3 \cdot 10^{17}$ cm^{-3}, $N_D > \sim 1 \cdot 10^{19}$ cm^{-3}.

The typical for this paper spectra are those of (δ-I – a), (δ-II – a) described in [25, 27] for SF-samples as well as (δ-I – b), (δ-II – b) [26, 27] for DL-samples.

The peculiarity of the photoluminescence spectra related to the zones of disorder depends on the impurity concentration in the matrix as the whole (perhaps there is a relation with a change in the Fermi level). In pure SF (i = 1, 2, 3, …) samples (version a) at low temperature, the SF-i spectra are dominant, while the intensity of the DL-i spectra is very low.

On the contrary, in the doped samples the DL-i spectra are dominant and located on a broad donor-acceptor pair emission band, while SF-i spectra are barely visible (b) or practically invisible (c) (Table 1). The spectrum DL-I is placed on a broad structure bandless background. Table 1 shows LTPL spectra according to the structural imperfection and impurity concentration in α-SiC crystals [27].
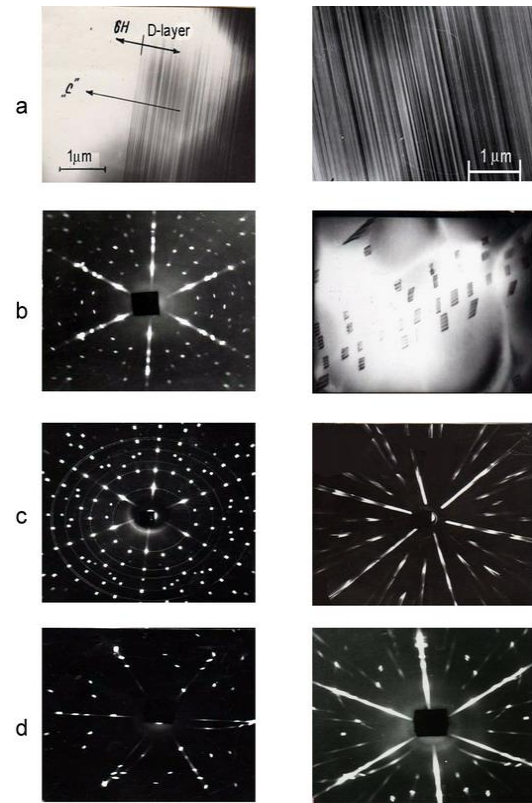

Fig. 2. Laue diffraction pattern of grown one-dimensional disordered D-layers in α-SiC for SiC crystals demonstrated SF. a) Sample 6SF (concentration $N_D − N_A \sim 6 \cdot 10^{16}$ cm^{-3} [25-27], transmission electronic microscopy (TEM) pattern (magnification ×15 000) of the boundary 6H-SiC – D-layer (on the left) and D-layer (right). b) Sample 5SF (concentration: $N_D − N_A \sim 3 \cdot 10^{16}$ cm^{-3}) [25-27] with grown structural defects (left) forming the range with SF in 6H-SiC and TEM (pattern with formations of SF in 6H-SiC after plastic deformation growth defects (left) forming the range with SF in 6H-SiC after plastic deformation (right)). c) Sample 1SF (concentration $N_D − N_A \sim 2 \cdot 10^{16}$ cm^{-3}) [25-27] before (left) and after plastic deformation (right). d) Sample 2SF (concentration $N_D − N_A \sim 3 \cdot 10^{16}$ cm^{-3}) [23, 24, 27] initially with SF before (left) and after annealing ($T = 2100$ °C, $t = 1$ h) (right).

The Laue diffraction pattern (Fig. 2) of grown one-dimensional disordered D-layers in α-SiC crystals with SF show different diffuse effects (δ-I and δ-II) giving evidence of structure disordering.

(δ-I) These effects origin is related with emergence of new nodes in the reciprocal lattice of the crystal. New reflections appear on the main lines of Laue patterns and in their surroundings. There is a selective blurring of the base reflexes (6H), appearance of the radial bridges – the strips which connect them. Sometimes there is a radial segmentation of reflexes, which indicates the disorientation between the layers-blocks of the crystal parallel to the basal plane.

(δ-II) At such degree of disorder, occurrence of additional diffuse effects takes place, which causes emergence of continuous strips between selective reflections, the intensity of these is comparable with that of the basic reflexes. This is an evidence of an increasing one-dimensional disorder along the hexagonal axis *c*. Namely, the emergence and increase in the intensity of the radial bridge strips connecting the selective reflections in the Laue patterns are determined by emergence and changes in numbers of SF. The SiC multiple-polytypes are also identified as layers.

The most clear, expressive and intense DL spectra appear in the version (δ-II − b). Shown in ref. [26] is the Laue pattern (Fig. 2a) corresponding to the version (δ-I − b) (sample 4_{DL}) and Fig. 2b – to the version (δ-II − b) (sample 9_{DL}).

The line DL spectra (together with their phonon satellites) (4.2 K) are superimposed with a wide background band possessing the maximum in the greenish-yellow range, which becomes dominating at 77 K and remains up to 160…170 K. The intensity of DL spectra vs the impurity concentration has been depicted in ref. [2]. Appearance of the thin line structure in DL spectra requires both the minimum concentration of uncompensated impurity (N_D–N_A), and definitely expressed distortions of crystal structure.

Strengthening the distortions, deviations from natural growth towards multiple layers, or mosaicity of the crystals, emergence of several centers of growth lead to complication of the overall spectrum, i.e., emergence of the whole series of DL-i type spectra with identical behavior in the corresponding conditions of registration. They, as well as the corresponding SF-i spectra, are associated with their crystal matrix and changes in the overall energy scale [27]. It is convenient to demonstrate all main characteristics of DL-i spectra on the DL-1 example (the most often occurring spectra in crystals) [26].

Supervision of thin line structure ($T =$ 4.2 K) allowed to establish exact spectral borders of the zero phonon part in DL spectra, and further being convinced of difficult internal regularities of creation of this zero phonon part of DL-i that (as a whole) is translated by phonons of the central Brillouin zone (LO-120 meV) and by the local phonon (LOC-91 meV), to form a general DL spectrum picture. Availability of this thin structure

allowed to track differentially individual behavior of each element in this structure under different conditions of spectra registration (at temperature changing within the interval 4.2…60 K) to determine the thermal activation energy of quenching and the nature of changes in the intensity in attenuation at different delay and influence of polarization of exciting light.

It is also interesting to identify the effect of plastic deformation on the nature of the SF and DL spectra as well as the effect of a high-temperature annealing.

In pure (with minimal main impurity) 6H-SiC crystals without defects that show a weak blue luminescence (version δ-I − a) under initial conditions, after carrying out considerable extent plastic deformation by bending, this initial luminescence almost disappears, and there remain weak DL-1 luminescence and emission of the divacancy centers (generated by deformation).

Changes in luminescence are not observed after similar deformation in crystals with a higher impurity concentration, which have much more intense initial blue luminescence of donor-acceptor pairs (version δ-I − c). Luminescence changes only after applying a high pressure (40…60 Kbar, $T =$ 2000 °C), namely: intensity of luminescence as a whole considerably falls, there observed is domination of the DL-1 spectra. However, line spectra are not observed. This luminescence in doped crystals appears only after radiation with neutrons ($E \geq$ 3 MeV) at the doses $D =$ $10^{16}…10^{18}$ n·cm^2 and the subsequent annealing ($T =$ 1100 °C, $t =$ 0.5 h). For the crystals with prevailing DL-1 luminescence under initial conditions (version δ-II − c), similar neutron processing also results in emergence and domination of divacancy spectra.

Plastic deformation by bending the crystals (versions δ-II − b and δ-II − c) does not influence the structural part of initial DL spectra and only strengthens a little the wide background band.

High-temperature annealing ($T =$ 2000 °C, $t =$ 1…5 h) leads to the general increase in the DL emission, generally due to the strengthening the wide background band. It is more expressed in crystals with a higher concentration of impurities (by 1.5…2 times). The same annealing of the crystals that do not possess DL luminescence under initial conditions doesn't lead to its emergence.

Thus, the external influences on DL luminescence are qualitatively different in the purest crystals and in impurity crystals.

4. Conclusion

The influence of plastic deformation and high-temperature annealing ($T =$ 2100 °C, $t =$ 1 h) on SiC crystals with SF and DL spectra has been revealed. The SF-i and DL-i types of luminescence are inherent to SiC crystals with distortions of the structure related with availability of packing defects causing one-dimensional disordering (along the *c*-axis). They are a most expressed in doped crystals with original growth defects. DL luminescence

appears in pure crystals at plastic deformation and in doped crystals at a hydrostatic pressure. It is also enhanced at the high temperature annealing.

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