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## **Silicon carbide phase transition in as-grown 3C-6H polytypes junction**

**S.I. Vlaskina<sup>1,2</sup>, G.N. Mishinova<sup>3</sup>, V.I. Vlaskin<sup>4</sup>, G.S. Svechnikov<sup>1</sup>, V.E. Rodionov<sup>1</sup>, S.W. Lee<sup>5</sup>**

<sup>1</sup>*Institute of Semiconductor Physics, National Academy of Science of Ukraine  
45, prospect Nauky, 03028 Kyiv, Ukraine; e-mail: businkaa@mail.ru*

<sup>2</sup>*Yeoju Institute of Technology, 200 Myeongseong-ro, Gyeonggi-do, 469-705 Korea*

<sup>3</sup>*Taras Shevchenko Kyiv National University, 64, Volodymyrska str., 03033 Kyiv, Ukraine*

<sup>4</sup>*Sensartech, 2540 Lobelia Dr., Oxnard, 93036 California, USA; e-mail: vladys@sensartech.com*

<sup>5</sup>*Physics Department, Dongguk University, Pildong 3-26, Chung-ku, Seoul, Korea*

**Abstract.** Perfect pure (concentration of donors  $\sim 10^{16} \text{ cm}^{-3}$ ) single crystals with joint polytypes (hexagonal-cubic) or heterojunction investigated using low temperature (4.2 K and 77 K) photoluminescence. Phase transformation started exactly from lamella between polytypes.  $\beta \rightarrow \alpha$  (3C-6H) SiC transformation distributes from lamella as from nuclear. Photoluminescence spectra are similar to the spectrum demonstrated by pure perfect 3C-SiC crystal in the field of mechanical deformation. In the zone of joint polytypes and zone of the plastic deformation in perfect 3C-SiC crystal after bending, the same stacking faults are localized. Luminescence in the disordered  $\alpha$ -zone as a result of phase transformation is represented by a set of intensely pronounced stacking fault spectra. These spectra reside on more or less intense background band, which are emission of the donor-acceptor pairs in SiC. Excitation luminescence spectra confirm appearance of stacking faults which are responsible for metastable intermediate micro- and nano-SiC structures. Solid-phase transformations  $\beta \rightarrow \alpha$  are related with the same intermediate metastable microstructure that take place in the transformation  $\alpha \rightarrow \beta$ .

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

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### **1. Introduction**

Silicon carbide is material for fabrication of electronic devices. Occurrence of polytypism can scatter charge carriers and act as a region with a high density of recombination centers. In most experiments dealing with polytypism, SiC phase transformation has been reported as a result of high-temperature annealing [1-4] or deformation [5-8].

Recently considerable attention is paid to materials with metastable structures at the micro- and nanolevels. These materials have been successfully used for creation

of unusual structural and functional properties, as well as combinations of properties. To obtain these metastable materials, there applied are plastic deformation of crystals, irradiation, rapid condensation of vapors (gas) [9-11].

Spectroscopic diagnostics is an effective method for studying the mechanism of interfacial rearrangements, which allows monitoring of these processes at the level of the energy states of the crystal [12].

In this work, we used low-temperature spectroscopy to investigate SiC phase transition in silicon carbide heterojunctions both as-grown and occurring under deformation.

## 2. Experiment

Crystals with joint polytypes (hexagonal-cubic) or heterojunction were specially selected. Noncompensated donor's concentration was  $\sim 10^{16} \text{ cm}^{-3}$ . The cubic part of crystals was yellow 3C-SiC, hexagonal part of crystal was light green (6H-SiC), intermediate lamella between 3C-SiC and 6H-SiC was grey.

Low-temperature photoluminescence (LTPL) spectra ( $T=4.2 \text{ K}$ ) of yellow (3C-SiC) part of SiC crystal with natural polytypes joint recorded at maximum of exciton luminescence (curve 1) and recorded at maximum of 5100 Å radiation (curve 2) is shown in Fig. 1.

High resolution spectra give evidence of recombination of excitons bound to nitrogen donors at the cubic and hexagonal sites (PRS-spectra) and phonon replicas [9, 10]. Such spectra exist in very pure SiC crystals ( $N_D - N_A \sim 10^{16} \text{ cm}^{-3}$ ) only. At temperatures higher than 18 K, PRS-spectra disappears (Fig. 2).

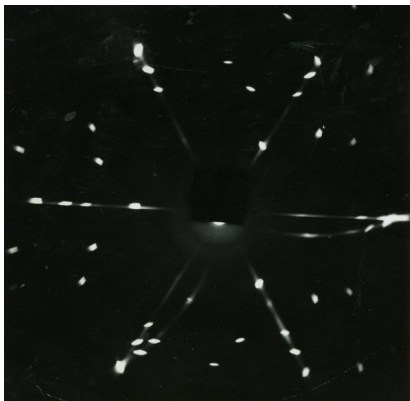
LTPL spectra of light-green (6H-SiC,  $E_{gx} = 3.024 \text{ eV}$  at 4.2 K) part of SiC crystal with natural polytypes joint recorded at 4.2 K and 30 K are shown in Fig. 3. At high-resolution spectra at 4.2 K recorded nitrogen-bound exciton PRS-complexes. Exciton complexes at 3.008 eV (P), 2.993 eV (R), 2.995 eV (S) shows a very low level of impurities in SiC crystal with joint polytypes transformation.

Thermal quenching of luminescence from the hexagonal part of SiC crystal and buildup of luminescence from the cubic part of SiC crystal takes place.

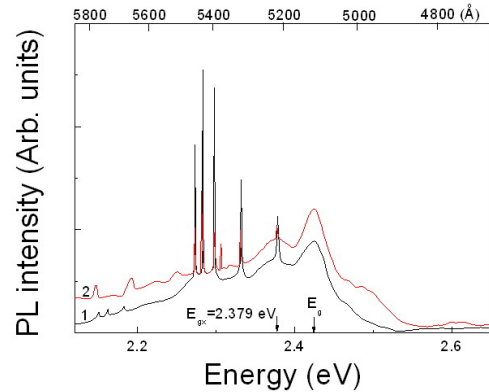
Laue pattern of this heterojunction in crystal with joint as-grown polytypes is shown in Photo 1.

The area between the yellow (3C-SiC) part and light-green (6H-SiC) was grey and belongs to the area of disorder like that already described in [2].

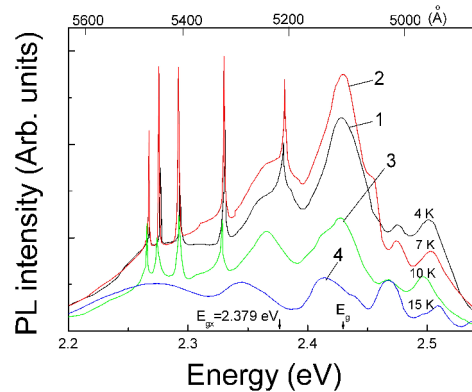
Phase transformation started exactly from this lamella between polytypes.  $\beta \rightarrow \alpha$  (3C-6H) SiC transformation distributes from lamella as from nuclear, and this distribution changes a color of some crystal area.



**Photo 1.** Laue pattern of SiC crystal with joint as-grown polytype (3C-6H) transformation.



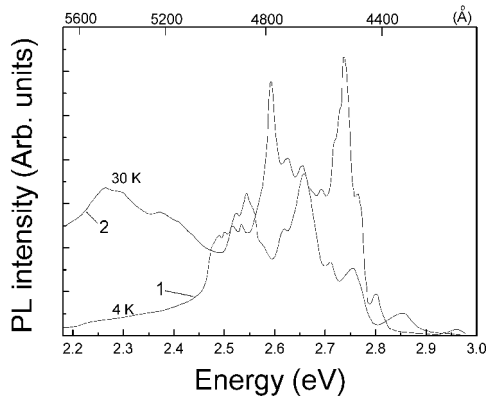
**Fig. 1.** LTPL spectra (4.2 K) of yellow (3C-SiC) part SiC crystal with as-grown polytype joint recorded: 1 – at the maximum of exciton luminescence; 2 – at the maximum of 510-nm radiation.



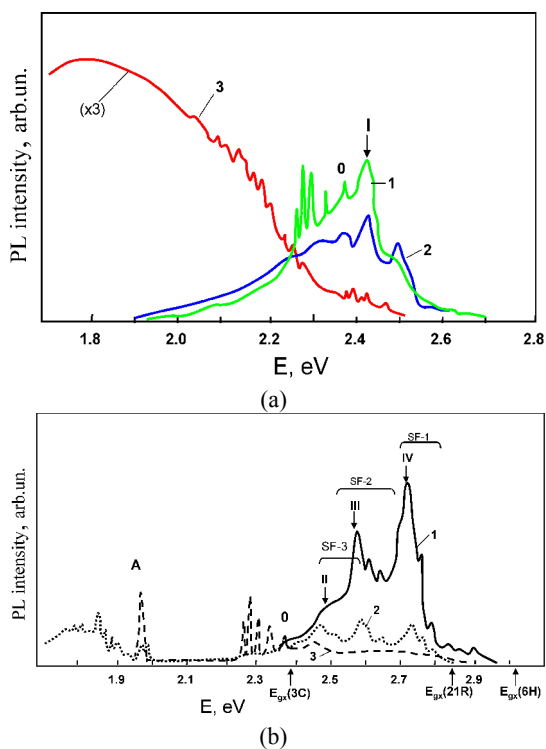
**Fig. 2.** LTPL spectra at different temperatures (from polytypes joint area) at the same energy of exciting light: 1 –  $T = 4.5 \text{ K}$  (black), 2 – 7 K (red), 3 – 10 K (green), 4 – 15 K (blue).

Fig. 4a (curve 1) shows the luminescence spectrum ( $T = 4.2 \text{ K}$ ) of the lamella (area between 6H- and 3C-SiC in the crystal ( $N_{2\beta}$ ) with natural polytype's joint. The weakened line spectrum of the PL associated with nitrogen-exciton complexes in cubic crystals. Very similar spectrum demonstrates pure perfect 3C-SiC crystal (sample  $N_{9\beta}$ ) in the field of mechanical deformation. Sample  $N_{9\beta}$  has undergone plastic deformation (Fig. 4a, curve 2). It means that the deformation twins and stacking faults play a major role in the restructuring of cubic SiC and transition in hexagonal SiC. A feature of these spectra is the fact that their characteristic short-wave part is in the region of energies higher than 3C-SiC band gap ( $E > E_{gx}^{3C}$ ). It indicates formation of high-energy structures in comparison with the cubic phase, namely, hexagonal phase.

At  $T > 77 \text{ K}$ , this luminescence is quenched. Another broadband spectrum (lightly structured) is recorded (Fig. 4a, curve 3). And this spectrum has a characteristic line-like structure in the energy region  $E > E_{gx}^{3C}$ , too.



**Fig. 3.** LTPL spectra of 6H-SiC part in 3C-SiC with joint polytypes at different temperatures:  $T = 4.3$  K (1),  $T = 30$  K (2).



**Fig. 4.** Low-temperature photoluminescence spectra of SiC cubic crystals.

(a) Spectra of structural defected cubic crystals with as-grown joint polytypes (sample N2 $\beta$ ) and very pure 3C-SiC crystal after strong plastic deformation (sample N9 $\beta$ ): 1 – spectrum in the lamella of the growth zone of phase transition with stacking faults (sample N2 $\beta$ ) at  $T = 4.2$  K; 2 – photoluminescence ( $T = 4.2$  K) in the zone of maximum deformation (deformation by bending at  $T = 2100$  °C during  $t = 30$  min) (sample N9 $\beta$ ); 3 – photoluminescence (77 K) spectrum in the same zone of maximum plastic deformation (same zone as for the curve 2).

(b) Photoluminescence (4.2 K) spectra of the crystal with natural joint polytypes (sample N2 $\beta$ ) after high-temperature annealing at  $T = 2000$  °C during  $t = 1$  hour: 1 – PL spectrum in the zone, which underwent phase transformation  $\beta \rightarrow \alpha$  (crystal color changes in the crystal from yellow to grey); 2 – PL spectra in the area of boundary  $\beta \rightarrow \alpha$  transition; 3 – PL spectrum of the yellow part of crystal that was not subjected virtually to the phase transformation.

After annealing the crystal with natural phase transformation (sample N2 $\beta$ ) at  $T = 2000$  °C during  $t = 1$  hour, there observed are changes in crystal structure and photoluminescence spectra [4]. Laue patterns show transformation  $3C \rightarrow 6H$ . Phase 6H-SiC appears and diffuse effects associated with stacking faults appear, too. At  $T > 1500$  °C,  $\beta$ -SiC becomes unstable, the transition  $\beta \rightarrow \alpha$  begins, during which close-packed layers (111) are shifted. The number of stacking faults is increased. The area of stacking faults distribution is increased, too. Stacking faults are evenly distributed inside the volume after the phase annealing of  $\beta$ -SiC. But stacking faults are sharply localized only in the zone of plastic deformation in perfect 3C-SiC crystal after bending.

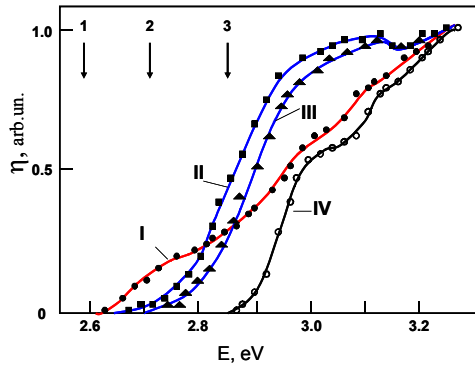
For better understanding the process of phase transformation, photoluminescence spectra of the crystal with natural joint polytypes (sample N2 $\beta$ ) after high-temperature annealing were measured (Fig. 4b). The part of a cubic crystal, almost did not undergo significant structural changes, while the other indicates the phase transformation, which is precisely the boundary zone of lamellae. Fig. 4b shows the photoluminescence spectra ( $T = 4.2$  K) related to these different parts of the crystal.

Photoluminescence of a slightly structurally changed part of the crystal is related with nitrogen-exciton complexes, and the famous line spectrum is associated with di-vacancy centers in 3C-SiC with the zero-phonon line A ( $E = 1.97$  eV). Also, there is a weak broad background band, extending far into the short-wave region (Fig. 4b, curve 3). Vacancies are generated in cubic SiC crystals during high temperature annealing. Short-wave photoluminescence is activated in the region  $E > E_{gx}^{3C}$  (Fig. 4b, curve 2) in the transition zone – at the border of  $\beta \rightarrow \alpha$  phase.

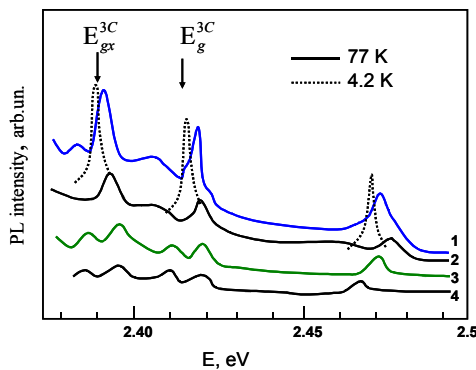
Finally, the luminescence inherent to the disordered  $\alpha$ -zone as a result of phase transformation is represented by a set of intensely pronounced stacking fault spectra SF (Fig. 4b, curve 1). Stacking fault spectra reside on more or less intense background band, which is the emission of the donor-acceptor pairs of 6H-SiC (Fig. 4b, curve 1). This fact is confirmed by the corresponding excitation spectra of luminescence in  $\beta$ -SiC (Fig. 5).

Thus, in the case of solid-phase transformations  $\beta \rightarrow \alpha$  formed by the same intermediate metastable microstructure as in transformation  $\alpha \rightarrow \beta$ .  $\beta$ -SiC crystals with no visible structural defects in the initial state of growth require a much longer high-temperature annealing ( $t = 6 \dots 10$  hours) of  $\beta$ -SiC for phase transformation [4, 12].

Line-like luminescence within the energy range 2.38 to 2.47 eV is the most intense in the area of  $\beta \rightarrow \alpha$  phase transformation, as well as at the phase boundaries and their embryos. It can be associated with formation of clusters of defects in {111} plane, belonging to intrinsic silicon in annealed  $\beta$ -SiC). These spectra are observed within the range of annealing temperatures 1900...2100 °C, where the solid-phase transformations take place.



**Fig. 5.** Photoluminescence excitation spectra ( $T = 4.2$  K) that match the specified positions of the PL spectra in Figs 4a and 4b. The arrows (marked 1, 2, 3) are long-wave edge of excitation spectra, which coincide with the short-wave values of: 1 – SF – 1, 2 – SF – 2, 3 – SF – 3.



**Fig. 6.** The short-wave part of the photoluminescence spectrum ( $T = 77$  K) of cubic SiC as-grown crystals with stacking faults and emerged after the external impact on the crystals. This line structure is preceded to exciton band gap in cubic crystals  $E > E_{gx}^{3C}$  (located in the high-energy region). 1, 2 – spectra of the pure perfect defectless 3C-SiC crystals after high temperature annealing at  $T = 2000$  °C for 10 hours (sample N1 $\beta$ ) and 6 hours (sample N10 $\beta$ ); 3 – PL spectrum of the as-grown crystal with polytype joint (sample N2 $\beta$ ) (see also this spectrum in Fig. 4a, curve 3); 4 – PL spectrum of the pure perfect 3C-SiC crystal (sample N9 $\beta$ ) after the strong plastic deformation at  $T = 2100$  °C, for  $t = 30$  min).

The fine structure is shown in Fig. 6. At  $T = 77$  K (look also Fig. 4a, curve 3), the halfwidth of lines 3...5 meV and at 4.2 K lines are narrowed down to 2 meV and shifted to longer wavelengths by 2 meV.

This spectrum is more intense in samples with a long-term high-temperature annealing. In crystals with the as-grown polytype's joint or in crystals after plastic deformation spectrum is less intense, and the fine structure is smeared (broadened) possibly due to stress fields.

The position of long-wave elements in this fine structure at 4.2 K coincides exactly with that of the exciton and the true band gap  $\beta$ -SiC at  $T = 4.2$  K (2.39 eV and 2.418 eV). Then, the most high-energy structure of 2.47 meV is caused by appearance and buildup of the hexagonal directions in the cubic crystal structure.

### 3. Conclusion

Low-temperature photoluminescence of crystals  $\beta$ -SiC with joint polytypes transformation shows the same spectra as those inherent to pure  $\beta$ -SiC crystals after plastic deformation or after high temperature annealing. This type of spectra is indicative of formation of intermediate (3C-6H) metastable micro- and nanostructures by involving the stacking faults.

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