3C-6H transformation in heated cubic silicon carbide 3C-SiC

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Abstract. Results of the research on the photoluminescence study of the 3C-6H-SiC phase transformation are presented. 3C-SiC crystals with in grown 3C-6H transformation and pure perfect 3C-SiC crystals grown by the Tairov-Tsvetkov method without a polytypes joint after high temperature annealing were investigated. Fine structure at the energy of E = 2.73, 2.79 eV, E = 2.588 eV, and E = 2.48 eV that appeared after annealing was described. The role of stacking faults in the process of structure transformation was investigated.

1. Introduction

Silicon carbide crystallizes in different structures. This behavior was discovered about 100 years ago (in 1912) and called polytypism. More than 200 SiC polytypes were investigated [1], the numerous growth technologies were used [2, 3], a lot of high-power, high frequency, high-temperature and radiation-resistant devices with excellent performance were made. However, the control of polytype in substrates and in the devices is an open question and a great challenge.

The SiC polytypes can be described by different stacking of Si-C layers perpendicular to the direction of the closed-packed plane {111} in cubic or {0001} in hexagonal SiC. The stacking sequences of the two close-packed lattices are fcc: ABCABC hcp: ABABAB. The agglomeration of vacancies on the {111} planes removes parts of {111} plane and produces a stacking fault because the stacking sequence of ABCABCA has changed to the faulty sequence of ABCABABC.

Burgers vectors of these dislocations are $\mathbf{b} = \pm a/6\{112\}$ and these types of two-dimensional defects are called Shockley partial dislocations. The disc of vacancies is bordered by an edge dislocation. Shockley partials are "slipping" dislocations. The disk of agglomerated interstitials creates the stacking sequences of ABCABACABCA. Burgers vectors of these dislocations are $\mathbf{b} = \pm a/3(111)$ and these types of two-dimensional defects are called Frank partial dislocation. Frank partials are "sitting" dislocations [4].

The dislocation activity taking place during plastic deformation is mediated by partial dislocations being nucleated and absorbed at grain boundaries [5].

The generation of stacking faults defects in the device active region causes degradation of SiC devices during long-time operation or during heating of the substrate or devices [6-13]. Therefore, power device degradation takes place due to phase transformations in SiC devices. The study of the phase transformation 3C-6H-SiC showed that multilayer polytypes were formed during this transformation.

So, it is clear that the investigation of the phase transformation is very important for the development of SiC technology, which is used in the automotive, space and environmental industry. This paper presents the results of the research on photoluminescence study of 3C-6H-SiC phase transformation.

2. Experiment

The solid-state phase transformations can be studied in highly doped SiC crystals [6, 14, 15] and in the pure single crystals. The strong donor-acceptor pair (DAP) photoluminescence takes place in the highly doped SiC crystals [6, 14] and the fine structure of PL associated with phase transformation can not be seen.

In this paper very pure high-quality vapor grown 3C-SiC crystals (grown by the sublimation method) was investigated. Platy 3C-SiC crystals contain growth pyramids. Different sides of this pyramid have different resistance due to different impurity concentration and defect content [16]. Very high-quality special one pyramid side 3C-SiC crystals containing heterostructures of SiC-polytypes, namely, the cubic polytypic 3C-SiC and hexagonal polytypic 6H-SiC in grown (3C-6H-SiC grown hetero-structures) were investigated as original structures, and after high temperature heating.

2.1. 3C-SiC crystals with as grown 3C-6H transformation

Pure high-quality light-yellow 3C-SiC single crystals grown by the sublimation method [17] with natural heterostructure 3C-6H-SiC (cubic to hexagonal) were investigated. Non-compensated impurity nitrogen concentration was about $(N_D - N_A) = 10^{17}\,\text{cm}^{-3}$, N_D was about $5 \times 10^{17}\,\text{cm}^{-3}$. Three different areas were identified by colors in crystals: light-yellow area for 3C-SiC, light-grey area for intermediate joint 3C-6H polytypes and non-colored or light-green area for 6H-SiC.

Photoluminescence was not found in the crystals at room temperature (300 K) or at liquid nitrogen temperature (77 K). Three different photoluminescence spectra were observed at liquid helium temperature (4.2 K): for the 3C-SiC area, for the intermediate joint 3C-6H-SiC area and for the 6H-SiC area. The low temperature photoluminescence (LTPL) spectra of the crystal with the natural polytypes joint 3C-6H SiC at the different photoluminescence excitation are shown in Fig. 1. Energy of 2.681 eV is not enough for excitement of 3C-SiC exciton luminescence.

Laser energy of 3.283 eV excites linear nitrogen exciton spectra in cubic SiC. The series of peaks at (4800–5700) Å gives evidence that the shot-wavelength part of the spectrum is at the energy level which is more than the exciton band gap E_{gx} 3C-SiC (2.349 eV). This can be explained by formation of the structures with bigger E_g than cubic SiC, namely hexagonal SiC.
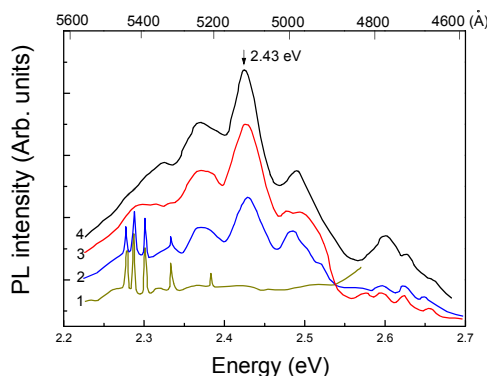

Fig. 1. Low temperature photoluminescence (LTPL) spectra (4.6 K) of 3C-6H-SiC polytypes joint at photoluminescence excitement: *1* – 2.681, *2* – 2.915, *3* – 3.109, *4* – 3.283 eV.

At the phase transformation 6H-3C SiC [14] maximums at the (4800–5700) Å have been reported as the "disorder area" due to the formation of multilayer polytypes.

The area of 4500–4800 Å is usual associated with DAP luminescence in hexagonal SiC. Linear high-resolution spectra are related to the nitrogen bound excitons in 3C-SiC [18] (area of photo-luminescence excitement covers 3C-SiC part of crystal).

The grey intermittent area between light yellow cubic SiC 3C-SiC and uncolored hexagonal 6H-SiC emits at 4800–5600 Å. The yellow part of the crystal has linear structure of nitrogen bound exciton complexes with non-phonons line O (E_{gx} = 2.379 eV). Divacancies centers spectra with non-phonon line at A (E = 1.975 eV) is absent.

The spectra of the yellow part of the SiC-crystal with natural polytypes joint are recorded at 4.2 K at the maximum intensiveness of exciton luminescence and at the maximum intensiveness of the light radiation 5100 Å. The linear structure of the nitrogen bound exciton certifies the highest quality of the pure cubic part of this crystal with in grown joint polytypes defects.

The LTPL spectra at different temperatures (4.5, 7, 10 and 15 K) from the polytypes 3C-6H joint area at the same energy of exciting light shown that the extinction of luminescence occurs with rising temperature. The photoluminescence disappears at 77 K. In the LTPL spectra at 4.3 and 30 K of the uncolored 6H-SiC part of the crystal with joint polytypes the luminescence at (4500–4800 Å) are interpreted as the usual donor-acceptor spectra (DAP) of 6H-SiC. The extinction of luminescence from the hexagonal part and the flaming up of luminescence of the cubic part takes place.

2.2. 3C-SiC crystals with in grown 3C-6H transformation after high temperature annealing

Crystals with natural polytypes joints were annealed for one hour at the temperature of 2000 °C in argon atmosphere. The structure changed after annealing (Photo 1a) and reflexes from hexagonal polytypes can be clearly seen on Laye-patterns (Photo 1a). It means that phase transformation of 3C-6H-SiC occurs. The LTPL spectra changed also. Maximum at E = 1.97 eV (non-phonon line) appeared. Vacancies center (silicon vacancies) can be responsible for this radiation (W.J. Choyke) [1, 2]. It means that vacancies generation in 3C-SiC was observed after annealing of 3C-SiC crystals and phase transformation similar to the 3C-6H-SiC transformation occurs [6, 14].

Short wavelength luminescence ($E > E_{g3C-SiC}$) in the area of (2.5–2.8) eV was activated. Maximal changes were observed in the area of the natural phase transformation namely in the area of the natural polytypes joint. These changes in LTPL spectra after annealing are shown in Fig. 2. The LTPL spectra were registered from the different parts of the crystals with grown polytypes joint. Curve 1 corresponds to the 6H-

SiC area, curve 2 corresponds to the structure with one-dimension disorder on the boundary between hexagonal and cubic polytypes, curve 3 corresponds to the 3C-SiC part of crystal.

The LTPL ($T = 4.3$ K) spectra of 3C-SiC crystal with natural polytypes joint after annealing for one hour at $T = 2000$ ºC (from α-phase – curve 1 and from transition area β→α –curve 2) are shown in Fig. 3. Phonon replicas (TA, TO, LA and LO) of exciton (O) are indicated.

2.3. Pure 3C-SiC crystals after high temperature annealing

Pure perfect 3C-SiC crystals (grown by Tairov-Tsvetkov method) without the polytypes joint were annealed, too, and structural and spectroscopic changes were also observed. Reflexes from hexagonal polytypes appeared on Laye-patterns (Photo 1b). It means that phase transformation in pure perfect 3C-SiC occurs too after annealing.
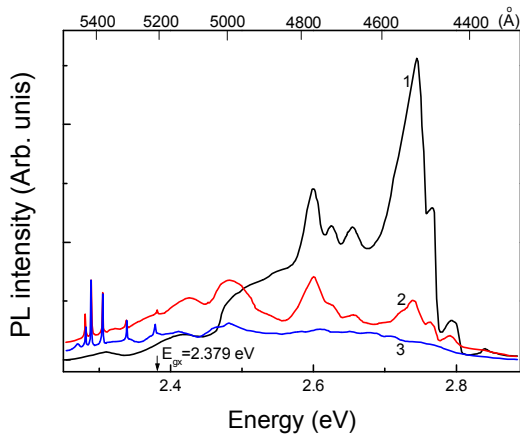

Fig. 2. LTPL spectra registered from the different parts of 3C-SiC crystal with grown polytypes joint after annealing for 1 hour at 2000 ºC. *1* – 6H-SiC area, *2* – the structure with one-dimension disorder on the boundary between hexagonal and cubic polytypes, *3* – 3C-SiC part of the crystal at the interface.
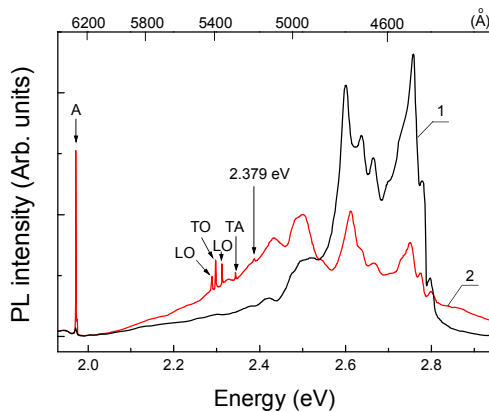

Fig. 3. LTPL spectra ($T = 4.3$ K) of 3C-SiC crystal with natural polytypes joint after annealing for one hour at $T = 2000$ ºC. *1* – from α-phase, *2* – from transition β→α area.
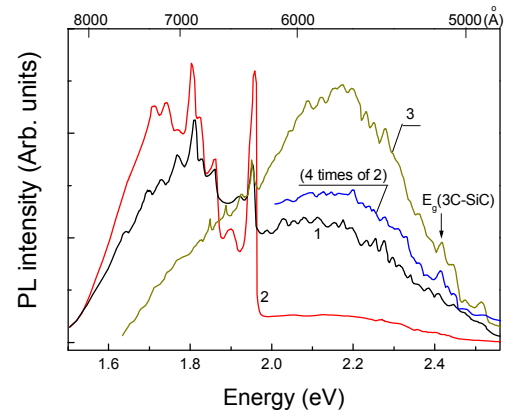

Fig. 4. LTPL spectra of pure perfect crystals after annealing. *1* – after annealing during 1 hour, $T = 2000$ ºC; *2* – after annealing during 6 hour, $T = 2000$ ºC; *3* – after annealing during 10 hour, at $T = 2000$ ºC.

Pure perfect 3C-SiC crystals demonstrated LTPL at 4.2 K usual for 3C-SiC, nitrogen-exciton complexes. The pure 3C-SiC crystal did not have PL at 77 K. After annealing for 1, 6 and 10 hours at $T = 2000$ ºC LTPL at 77 K appeared (the same as in case of the crystals with joint 3C-6H SiC transformation). The LTPL spectra of pure perfect crystals after annealing are shown in Fig. 4 at 77 K. It is clear that the lines at $E = 1.97$ eV and 1.8 eV (divacancies lines) appear at the beginning of annealing (when crystals are annealed for 1 hour). Later, the spectra is shift to a short-wave length area and emission appears at $E > E_{g\,3C-SiC}$, namely at (2.4–3.0) eV.

So, if short-wave length luminescence was activated in crystal with the natural 3C-6H-SiC joint after annealing at the area of transformation for 1 hour, the same result takes place in perfect crystals after annealing for 6-10 hours.

And line-spectra due to the divacancies centers with non-phonon line A ($E = 1.975$ eV) appear only after long time annealing for 6-10 hours (in crystal with the natural 3C-6H-SiC joint after annealing at the area of transformation for 1 hour).

The LTPL spectra from polytypes joint area of crystal with the in grown 3C-6H-SiC polytypes joint combined with luminescence spectra of excitation before and after annealing for 1 hour, $T = 2000$ ºC are shown in Fig. 5. It is clear that fine structure appears at the energies $E = 2.73$; 2.79 eV, $E = 2.588$ eV, and $E = 2.48$ eV. Fine structure was not detected in the crystal before annealing.

3. Results and discussions

The cubic polytype β-SiC becomes unstable at the temperature of $T > 1500$ ºC and β→α transformation begins. Close-packed layers (111) shift and an increase in numbers and area of spreading of stacking faults are observed like α→β transformation [19]. The stacking faults spread in volume uniformly after annealing.
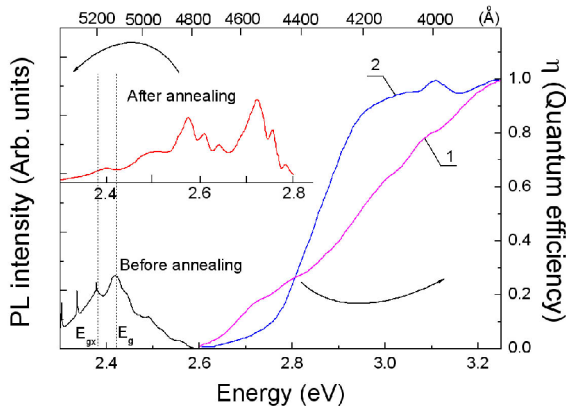
Fig. 5. LTPL spectra from polytypes joint area (of the crystal with as grown 3C-6H-SiC polytypes joint) combined with spectra of luminescence excitation (η): *1* – before annealing, *2* – after annealing during 1 hour (*T* = 2100 ºC).

Before annealing   After annealing

a

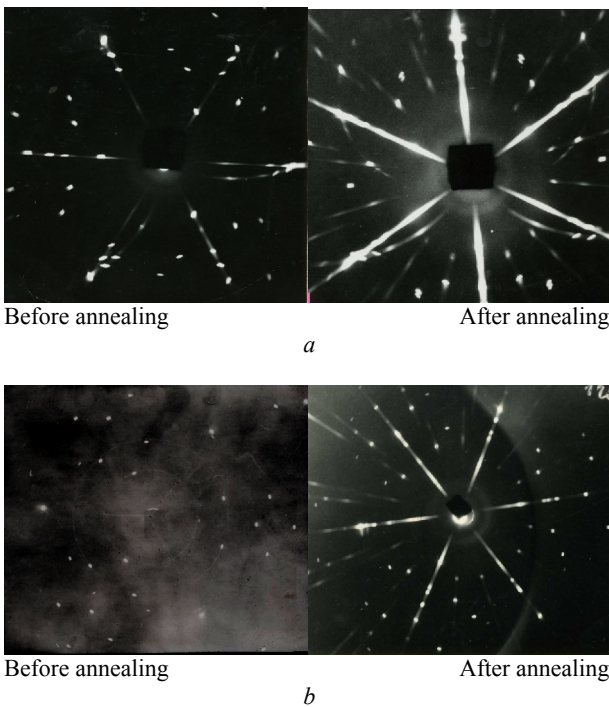Before annealing   After annealing

b

Photo 1. a) X-ray diffraction pattern of 3C-SiC with joint polytypes 3C-6H-SiC (as grown before annealing and after annealing during 1 hour at the temperature 2100 ºC); b) X-ray diffraction pattern of pure perfect 3C-SiC (as grown before annealing and after annealing for 10 hours at temperature 2000 ºC).

β→α transformation starts from natural polytypic joint 3C-6H-SiC exactly as from seeds. This process spreads onto some sectors with changing of crystal's color (Fig. 1).

Vacancies are generated in β-SiC during high temperature annealing. Short-wavelength luminescence at the area of $E > E_{gx3C}$ is activated in the transmission zone on the boundaries of β→α phases transformation. The disorder spectra very similar to the luminescence

spectra described in [6] are pitched on a more-or-less intensive line of DAP radiation.

The pure perfect 3C-SiC grown by the Tairov-Tsvetkov method crystals without the polytypes joint should be annealed for a longer time (*t* = 6-10 hours) for the same β→α transformation and for the same spectra appearance.

It is clear that decoding of these spectra should give the answer to the question about β→α transformation on the atomic scale.

4. Conclusion

3C-SiC crystals with in grown 3C-6H transformation and pure perfect 3C-SiC crystals grown by the Tairov-Tsvetkov method without the polytypes joint after high temperature annealing were investigated.

At the first stage vacancies were generated (line A at *E* = 1.973 eV appeared). Some indicated linear spectra (2.38–2.47 eV) on the DAP background were observed. These spectra were very intensive in the zone of β→α transformation and gave evidence about disordering processes in cubic SiC. Pure perfect 3C-SiC crystals should be annealed for a longer time (*t* = 6-10 hours) for the same β→α transformation and for the same spectra appearance. Stacking faults play the main role in the process of structure transformation.

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