

Influence of microwave radiation on relaxation processes in silicon carbide

Yu.Yu. Bacherikov, V.Yu. Goroneskul, O.Yo. Gudymenko, V.P. Kladko, O.F. Kolomys, I.M. Krishchenko, O.B. Okhrimenko*, V.V. Strelchuk

V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41, prospect Nauky, 03680 Kyiv, Ukraine

*E-mail: olga@isp.kiev.ua

Abstract. The methods of optical absorption spectroscopy and high-resolution diffractometry have been used to study the influence of microwaves on characteristics of crystalline SiC. Being based on the X-ray analysis data, optical transmission, photoluminescence, and photoluminescence excitation spectra, it has been shown that the microwave treatment leads to a change in the gradient of internal mechanical stresses and an increase in the migration capability of dislocations and, as a result, to redistribution of recombination centers in the sample.

Keywords: microwave radiation, relaxation processes, silicon carbide, optical absorption spectroscopy, high-resolution diffractometry.

<https://doi.org/10.15407/spqeo23.02.175>

PACS 61.05.cp, 78.20.Ci, 78.55.-m, 78.70.Gq

Manuscript received 04.03.20; revised version received 14.04.20; accepted for publication 10.06.20; published online 12.06.20.

1. Introduction

To reduce the concentration of defect states at the oxide-semiconductor interface, additional external treatments, such as temperature annealing, γ -irradiation, and microwave (MW) processing, are often used. For example, the effect of increasing the transmission coefficient in the SiO₂/SiC and TiO₂(Gd₂O₃, Er₂O₃)/SiC structures after microwave exposure was observed in the works [1–3]. In [4, 5], to explain the changes in optical properties of this type structures, a model of non-thermal interaction of MW with oxide film – semiconductor structures was proposed. According to this model, MW treatment increases the migration capability of dislocations, which in its turn leads to redistribution of the centers responsible for emission and absorption in the oxide film – silicon carbide structures.

In this work, we studied the effect of MW irradiation on redistribution of impurity-defect states in crystalline 6H-SiC.

2. Samples and research methods

A comparative analysis of the optical absorption spectra, X-ray diffraction, photoluminescence (PL), and photoluminescence excitation spectra of crystalline *n*-type silicon carbide (polytype 6H-SiC), grown using the Lely method with the concentration of free electrons

$\sim 10^{18} \text{ cm}^{-3}$, before and after short-term non-thermal exposure to microwave radiation has been carried out.

MW processing was performed in the operation chamber of a magnetron with the frequency $f = 2.45 \text{ GHz}$, specific power 0.04 W/cm^3 . The MW annealing time was 5 s.

The PL spectra were recorded using SDL-2 (СДЛІ-2) setup within the range 400...800 nm. To excite the PL spectra, we used emission of the nitrogen laser ($\lambda_{\text{exc}} = 337 \text{ nm}$). The transmission spectra within the range 300...900 nm were measured using an SF-26 (СФ-26) spectrophotometer. A SIRSh-200 (СИРШ-200) spectral lamp was used as a source of a continuous spectrum to obtain transmission spectra. For additional quality control of the sample, Raman spectra were used. Micro-Raman spectra of the samples were obtained at room temperature in the backscattering geometry by using T64000 spectrometer (Horiba Jobin Yvon) with a confocal microscope and a CCD cooled detector. The Raman spectra were excited using an Ar-Kr laser ($\lambda_{\text{exc}} = 488.0 \text{ nm}$). In Raman studies, the laser beam was focused into a beam with the diameter $< 1 \mu\text{m}$. The accuracy of determining the frequency position of phonon lines was 0.15 cm^{-1} . All the optical measurements were carried out at room temperature. X-ray measurements were performed using PANalytical X-Pert PRO MRD XL high-precision diffractometer (PANalytical B.V., Almelo, the Netherlands) with characteristic radiation $\text{CuK}_{\alpha 1} = 1.54056 \text{ \AA}$.

3. Experimental results and discussion

The quality of the initial crystalline 6H-SiC was additionally controlled using Raman spectroscopy. Fig. 1 shows the Raman spectra inherent to various points of the sample.

As can be seen from Fig. 1, in the Raman spectrum we observed the phonon bands characteristic for 6H-SiC: the intense ones with the frequencies 145 and 150 cm^{-1} (FTA modes), 767 and 789 cm^{-1} (FTO modes), 96 cm^{-1} (FLO mode) and the weak ones with the frequencies 236, 241, 266 cm^{-1} (FTA modes), 797 cm^{-1} (FTO mode), 504, 514 cm^{-1} (FLA modes), 965, 889 cm^{-1} (FLO modes) [6]. In addition, as can be seen from Fig. 1, observed is a coincidence of Raman spectra recorded in various points of the sample, which indicates the structural homogeneity of the studied material, and the absence of impurities of other SiC polytypes.

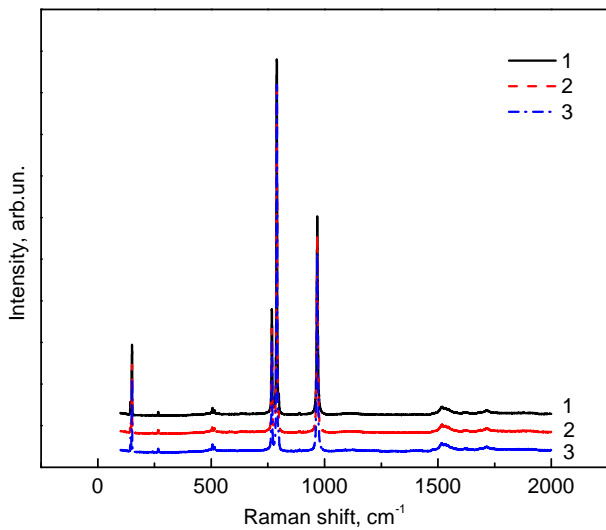


Fig. 1. Raman spectra of the sample in various points.

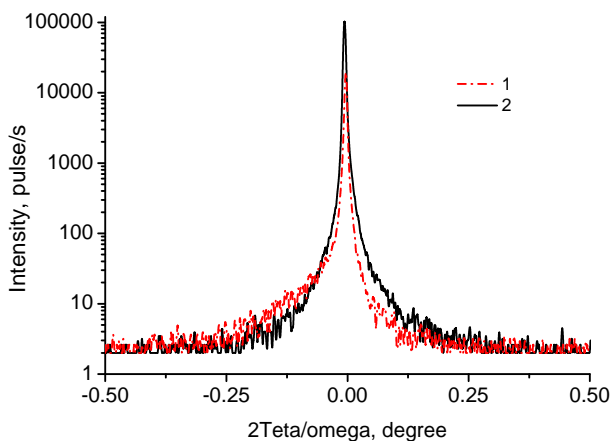


Fig. 2. Experimental 2θ - ω scans near the (111) reflection: 1 – initial SiC sample, 2 – after microwave processing.

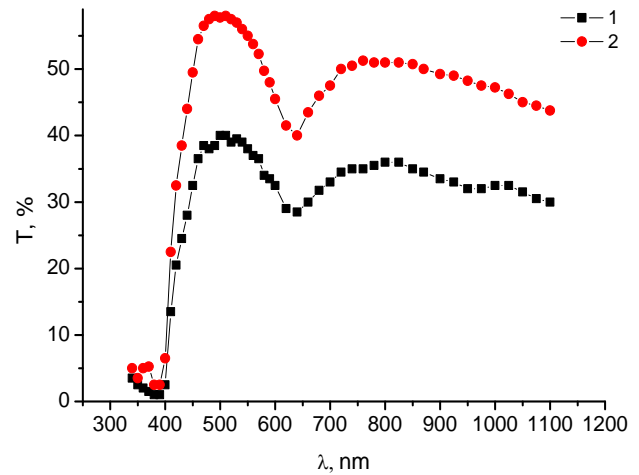


Fig. 3. Optical transmission spectra of 6H-SiC before (1) and after (2) microwave processing.

The structural perfection of the samples can be estimated by measuring 2θ - ω scans for symmetric (111) reflections by using the high-resolution diffractometry. Fig. 2 shows 2θ - ω scans near the (111) reflection before and after microwave processing the 6H-SiC samples. As can be seen from Fig. 2, the presence of additional diffuse scattering in the region of smaller angles (curve 1) in the 2θ - ω scan for the initial 6H-SiC sample indicates tensile strain in the lattice of this sample, which can be caused by the presence of defects in the form of vacancy type complexes in the samples. 2θ - ω scans of the sample after processing (curve 2) have a symmetrical shape, which may indicate dissolution of the complexes of these defects or appearance of new ones with the opposite sign of deformation (interstitial type). It is likely that processing led to removal of tensile strains in the crystal, probably due to the motion of dislocations and redistribution of defect complexes.

Fig. 3 shows the optical transmission spectra of 6H-SiC sample before and after microwave processing.

As can be seen from Fig. 3, the transmission spectrum of the initial sample is a typical transmission spectrum of crystalline 6H-SiC doped with nitrogen impurities [7, 8]. The absorption band observed in the spectral range close to 630 nm is associated with the presence of nitrogen impurities, as it is indicated in the literature [7, 8]. Short-term exposure with MW radiation leads to an increase in transmittance within the whole observed interval without changing the shape of the spectrum.

The increase in the transmission of samples after MW processing is most likely caused by the following: under the influence of MW radiation, the fields of internal mechanical strains are redistributed, as evidenced by the data of X-ray analysis (Fig. 2), and the number of internal interfaces caused by motion of dislocation walls in the bulk of silicon carbide, which can result in the decrease in losses of light scattering inside the sample.

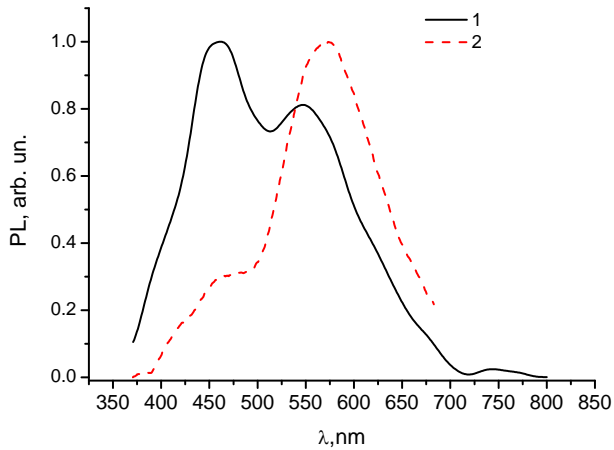


Fig. 4. Photoluminescence spectra of 6H-SiC normalized to the maximum of the band before (1) and after (2) microwave processing.

Fig. 4 shows the normalized photoluminescence spectra for 6H-SiC before and after MW processing.

As can be seen from Fig. 4, two broad luminescence bands with the peaks close to 540 and 460 nm are observed in the PL spectrum of both the initial and microwave-treated 6H-SiC. The band in the range near 460 nm in the PL spectra of silicon carbide is associated with the presence of luminescence centers caused by intrinsic defects [9] or by violation of the stoichiometry of silicon carbide crystals [10], as it is mentioned in the literature. The authors of [11–13] correlate the PL bands within the range 400...600 nm with recombination of donor-acceptor pairs of the type *i*-center – nitrogen or admixture (nitrogen) – defect.

It should be noted that PL radiation excited with $\lambda_{exc} = 337$ nm penetrates into silicon carbide to the depth close to 100 nm. Therefore, the presented PL spectra are primarily due to radiative recombination in the near-surface region containing a number of defects typical for it. First of all, these are defects that arise due to the distortion of the periodic potential of the crystal lattice and breaking the chemical bonds of atoms at the surface, as well as local surface imperfections of type of structural defects, impurities and their complexes. Appearance of a short-wave wing of the PL band with the peak around 460 nm (Fig. 4, curve 1) can be explained exactly by the radiative recombination in the centers formed with the participation of surface defects.

MW processing leads to redistribution of the centers of radiative recombination in 6H-SiC. So, after this processing, there is an increase in the intensity of the PL band with the peak near 540 nm relative to that with the peak close to 460 nm, as well as a significant decrease in the photoluminescence in the short-wave range.

Moreover, a decrease in the relative intensity of the short-wave wing of photoluminescence, as well as the PL band caused by intrinsic defects in silicon carbide correlates with an increase in the transmission of the 6H-SiC sample due to microwave exposure (Figs 3 and 4).

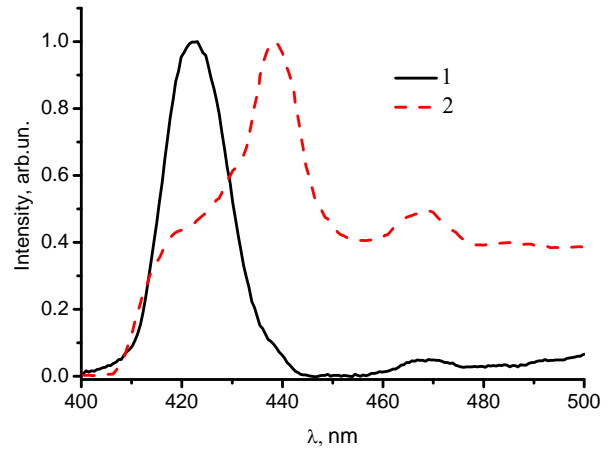


Fig. 5. Luminescence excitation spectra of 6H-SiC normalized to the maximum of the band before (1) and after (2) microwave processing.

Fig. 5 shows the normalized luminescence excitation spectra of 6H-SiC for the PL band with the peak near 560 nm before and after MW processing.

As can be seen from Fig. 5, in the luminescence excitation spectrum of the initial SiC, the intense band with the peak at 425 nm and the very weak band with the peak at 467 nm are observed (Fig. 5, curve 1). After MW processing, in the luminescence excitation spectrum of 6H-SiC, the additional band with the peak near 435 nm appears (Fig. 5, curve 2). The bands in luminescence excitation spectrum within the range 420...440 nm can be associated with the absorption bands of 2.98 eV (416 nm) and 2.85 eV (435 nm) observed in [8], which are related with nitrogen. In this case, the 2.98 eV band is the near-edge absorption band caused by photoionization of nitrogen with transition of electrons to the absolute minimum of the conduction band [8]. Probably, absorption in the centers formed with participation of surface defects also contributes to this band. The 2.85 eV (435 nm) band is caused by photoionization of nitrogen at the *h*- and *2k*-positions to the high located minimum of the conduction band [8]. In [8], it was also suggested that the absorption band of ~ 2.85 eV consists of two overlapping components that have approximately equal intensities as a consequence of forbidden transitions.

Motion of dislocations caused by MW irradiation [5] results in fluctuations in the heterogeneity of the distribution of dopants and defects both at the surface and in the bulk of SiC, which, in turn, leads to a change in the nature of the inter-impurity interaction between the absorption centers. In addition, appearance or disappearance of structural defects due to microwave processing should be accompanied by a change in the symmetry of the nearest environment of individual nitrogen atoms, which entails redistribution of the intensities inherent to individual bands composing the band of luminescence excitation spectrum within the range 420...440 nm.

4. Conclusions

Thus, the increase in the transmission of crystalline 6H-SiC after MW processing can be caused by a change in the gradient of internal mechanical strains due to interaction of MW radiation and dislocations, which leads to a decrease of the losses in light scattering by dislocations inside the sample. In addition, interaction of MW radiation with dislocations can lead to their redistribution. As a result of migration of dislocations and their interaction with impurities and defects of the crystal lattice, there appear additional centers that can manifest themselves as centers of radiative and non-radiative electron-hole recombination [14, 15], which is pronounced in redistribution of the intensity of the PL bands.

The obtained data completely confirm the assumption made in [4, 5] about the resonance nature of interaction of microwave radiation with dislocations, which leads to a change in the number and configuration of dislocations and, accordingly, to redistribution of recombination centers in the sample.

References

1. Bacherikov Yu.Yu., Konakova R.V., Kocherov A.N. *et al.* Effect of microwave annealing on silicon dioxide/silicon carbide structures. *Techn. Phys.* 2003. **48**. P. 598–601. <https://doi.org/10.1134/1576474>.
2. Effect of microwave annealing on silicon dioxide/silicon carbide structures. *Techn. Phys.* 2003. **48**. P. 598–601. <https://doi.org/10.1134/S106378420702017X>.
3. Bacherikov Yu.Yu., Konakova R.V., Milenin V.V. *et al.* Changes in characteristics of gadolinium, titanium, and erbium oxide films on the SiC surface under microwave treatment. *Semiconductors*. 2008. **42**, No 7. P. 868–872. <https://doi.org/10.1134/S1063782608070191>.
4. Okhrimenko O.B. A model for non-thermal action of microwave radiation on oxide film/semiconductor structures. *Semiconductor Physics, Quantum Electronics and Optoelectronics*. 2014. **17**, No 3. P. 227–231. <https://doi.org/10.15407/spqeo17.03.227>.
5. Okhrimenko O.B. Phenomenological model of athermal interaction of microwave radiation with the structures wide-gap semiconductor – oxide film. *Semiconductor Physics, Quantum Electronics & Optoelectronics*. 2015. **18**. P. 452–455. <https://doi.org/10.15407/spqeo18.04.452>.
6. Nakashima S. and Harima H. Raman investigation of SiC polytypes. *phys. status solidi (a)*. 1997. **162**. P. 39–64. [https://doi.org/10.1002/1521-396X\(199707\)162:1<39::AID-PSSA39>3.0.CO;2-L](https://doi.org/10.1002/1521-396X(199707)162:1<39::AID-PSSA39>3.0.CO;2-L).
7. Gorban' I.S., Skirda A.S. Photoionization spectra of impurity centers in α -SiC(6H) under high temperatures. *Ukrainskii fizich. zhurnal*. 1981. **26**, No 2. P. 228–232 (in Russian).
8. Gorban' I.S., Krokhmal' A.P. The impurity optical absorption and conduction band structure in 6H-SiC. *Semiconductors*. 2001. **35**. P. 1242–1248. <https://doi.org/10.1134/1.1418064>.
9. Makarov V.V. Luminescent and optical properties of silicon carbide irradiated with fast neutrons. *Fizika tverdogo tela*. 1971. **13**, No 8. P. 2357–2362 (in Russian).
10. Levin V.I., Tairov Yu.M., Tsvetkov V.F. Silicon carbide luminescence and its relation with variances of stoichiometry. *Fizika i tekhnika poluprovodnikov*. 1984. **18**, No 7. P. 1194–1198 (in Russian).
11. Shi-Yi Zhuo, Xue-Chao Liu, Ting-Xiang Xu *et al.* Strong correlation between B-Al-N doping concentration fluctuation and photoluminescence effects of *f*-SiC. *AIP Adv.* 2018. **8**. P. 075130. <https://doi.org/10.1063/1.5044492>.
12. Shi-Yi Zhuo, Xue-Chao Liu, Wei Huang *et al.* Photoluminescence properties of N and B codoped fluorescent 4H-SiC and 6H-SiC. *AIP Adv.* 2018. **8**. P. 125001. <https://doi.org/10.1063/1.5053996>.
13. Satoshi Kamiyama, Motoaki Iwaya, Tetsuya Takeuchi *et al.* Fluorescent SiC and its application to white light-emitting diodes. *J. Semicond.* 2011. **32**. P. 013004. <https://doi.org/10.1088/1674-4926/32/1/013004>.
14. Zaluzhnyi A.G. *Dislocations in Crystals, Their Motion and Elastic Properties*. Moscow, Publ. House “Moscow Engineering Physics Institute”, 1990 (in Russian).
15. Mataré H.F. *Defect Electronics in Semiconductors*. Wiley-Intersci., N-Y–London–Sydney–Toronto, 1971.

Authors and CV



Yuriy Yu. Bacherikov, defended his Doctoral Dissertation in Physics and Mathematics in 2010. Leading scientific collaborator at the V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. Authored over 300 publications, 6 patents, 1 monograph. The area of his scientific interests includes physics and applications of wide-band semiconductor compounds and devices based on them.



Viktor Yu. Goroneskul, Researcher at the Department of Physics of Optoelectronic Devices, V. Lashkaryov Institute of Semiconductor Physics. Authored over 50 publications. The area of his scientific interests includes development of the sensors for monitoring environmental parameters on the basis of optron systems with open optical channel.



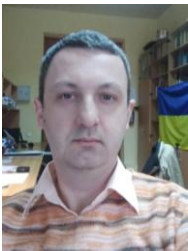
Olexandr Yo. Gudymenko, Ph.D. in Physics and Mathematics, Researcher at the Department of Structural and Elemental Analysis of Materials and Systems at the V. Lashkaryov Institute of Semiconductor Physics. Author of more than 56 publications. His research interests include: solid-state physics, dynamical theory of diffraction of radiation, X-ray optics,

X-ray diffraction analysis of semiconductor crystals, hetero- and nanosystems, XRD analysis materials, X-ray reflectometry of thin films.



Vasyl P. Kladko, Doctor of Sciences (Physics and Mathematics), Corresponding Member of NAS of Ukraine, Head of the Department of Structural and Elemental Analysis of Materials and Systems at the V. Lashkaryov Institute of Semiconductor Physics. Author of more than 300 publications.

His research interests include: solid-state physics, dynamical theory of diffraction of radiation, X-ray optics, X-ray diffraction analysis of semiconductor crystals, hetero- and nanosystems.



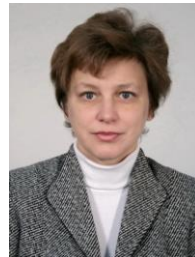
Oleksandr F. Kolomys, born in 1979, defended his Ph.D. dissertation in Physics and Mathematics in 2006. Senior Researcher at the Laboratory of submicron optical spectroscopy, V. Lashkaryov Institute of Semiconductor Physics. Authored over 130 publications, 3 patents, 3 chapters of text-books. The area of his scientific interests includes Raman and lumines-

cent microanalysis of light emitting properties, structure, composition, electronic and phonon excitations in solids, physical and chemical properties of semiconductors, chemicals and nanostructures for modern micro-, nano- and optoelectronics with submicron spatial resolution.



Irina M. Krishchenko, Ph.D. in Physics and Mathematics, Researcher at the Laboratory of Physical and Technical Basics of Optoelectronics, V. Lashkaryov Institute of Semiconductor Physics. Authored over 30 publications. The scientific activity is directed to the study of quantum dots of silicon (germanium) and the effects

of local surface plasmon resonance in porous films with ensembles of Au (Ag) nanoparticles obtained using pulsed laser deposition.



Olga B. Okhrimenko, defended his Doctoral Dissertation in Physics and Mathematics in 2016. Leading scientific collaborator at the V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. Authored over 140 publications, 1 patent, 1 monograph. The area of her scientific interests includes investigation of the patterns

and physical mechanisms of formation and rearrangement of the defect-impurity system of the thin-film dielectric-semiconductor structures, depending on technology of preparation, composition of thin films, additional processing and introduction of buffer layers.



Viktor V. Strelchuk, Professor, Doctor of Sciences in Physics and Mathematics, Head of Optical Submicron Spectroscopy Laboratory at the V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. Field of research: physics of semiconductors, Raman and photoluminescence spectroscopy of semi-

conductors, nanostructures and nanoscale materials. He is the author of more than 100 scientific publications and technical patents.