Physics of the Solid State, 2023, Vol. 65, No. 12

Structure and recombination properties of twin boundaries in κ-phase of gallium oxide

© O.F. Vyvenko[1], A.S. Bondarenko[1], E.V. Ubyivovk[1], S.V. Shapenkov[1,2],
A.I. Pechnikov[2], V.I. Nikolaev[2], S.I. Stepanov[2]

[1]St. Petersburg State University,
St. Petersburg, Russia
[2] Ioffe Institute,
St. Petersburg, Russia
E-mail: vyvenko@gmail.com

Received May 18, 2023
Revised September 7, 2023
Accepted October 30, 2023

Recent studies of the structure of the metastable hexagonal ε-phase of gallium oxide have established that it consists of oriented nanodomains of the orthorhombic κ-phase. In this work we demonstrate that when the κ-phase of gallium oxide is produced by epitaxial growth on gallium nitride, its hexagonal-prismatic microcrystals consist of rotary domains with built-in extended antiphase boundaries. It was found that domain and antiphase boundaries are characterized by reduced luminescence intensity.

Keywords: gallium oxide, κ-Ga_2O_3, domains, recombination, TEM.

DOI: 10.61011/PSS.2023.12.57677.5241k

1. Introduction

In recent years, gallium oxide acquired rapidly growing interest due to the prospects for its wide application in power and high-voltage electronics, as well as in optoelectronics, in particular, for the creation of photodetectors „blind“ for solar radiation [1]. It can be crystallized in 5 polymorphous modifications. Most studies on gallium oxide were carried out on monoclinic β-Ga_2O_3 due to its thermal stability and the possibility of obtaining large single crystals. However, the low symmetric beta-phase monoclinic lattice is poorly compatible with available industrial substrates, and the tendency to crack at cleavage planes limits its use in applications.

On the other hand, the metastable $\kappa(\varepsilon)$-phase combines well with trinitrides and silicon carbide, and its important distinguishing property is the extraordinary high spontaneous polarization, which provides the possibility of creating quantum wells with a high two-dimensional electron density [2]. According to the latest transmission electron microscopy (TEM) data [3] κ-phase is orthorhombic ($Pna2_1$), and its as-grown layers consist of a set of rotational domains that form a pseudohexagonal structure (ε-Ga $_2O_3$). The atomic structure of domain boundaries and other defects in the crystal structure, as well as the nature and degree of their influence on the electronic properties of the material remain poorly studied. This article will present the first results of studying the structure and luminescence of individual microcrystallites of κ-Ga_2O_3.

2. Experimental

In this paper intergrown or individual microcrystallites of κ-Ga_2O_3 were studied, they have the shape of hexagonal prisms up to $0.8\,\mu$m thick. They were obtained by chloride-hydride vapor phase epitaxy (HVPE) on hexagonal gallium nitride (2h-GaN) with (0001) basal plane orientation. A detailed description of the method of their growth, data from X-ray diffraction analysis and studies of luminescent properties at the macro level can be found elsewhere [4].

The luminescent properties of κ-Ga_2O_3 microcrystallites were studied in scanning electron microscope (SEM) Zeiss Supra 40 VP in the cathodoluminescence (CL) mode at accelerating voltage of 10 kV and at room temperature. For a more detailed study of the structure of microcrystallites and the spatial distribution of luminescence intensity, a lamella of planar orientation (i.e. (001) for κ-Ga_2O_3 and (0001) for GaN) with minimum thickness of gallium nitride supporting substrate was cut using a focused ion beam of Zeiss Auriga dual-beam station. The structure of microcrystallites was studied using scanning transmission electron microscopy (STEM) on Zeiss Libra 200FE at accelerating voltage of 200 kV at room temperature.

3. Results and discussion

In Figure 1, a the solid line with dots shows the cathodoluminescence spectrum of the massive part of the sample, in which gallium oxide microcrystallites grow together into a continuous layer. In this case, the excitation of electron-hole pairs predominantly occurs in κ-Ga_2O_3 layer, and the contribution of the luminescence of the GaN substrate to the recorded signal is suppressed. This is clearly seen from the decomposition of the spectrum presented in Figure 1, a into components, where the position and shape of the spectral bands shown by dashed lines were obtained from a pure GaN substrate and correspond to the GaN interband transition (~ 3.47 eV), luminescence of its extended defects

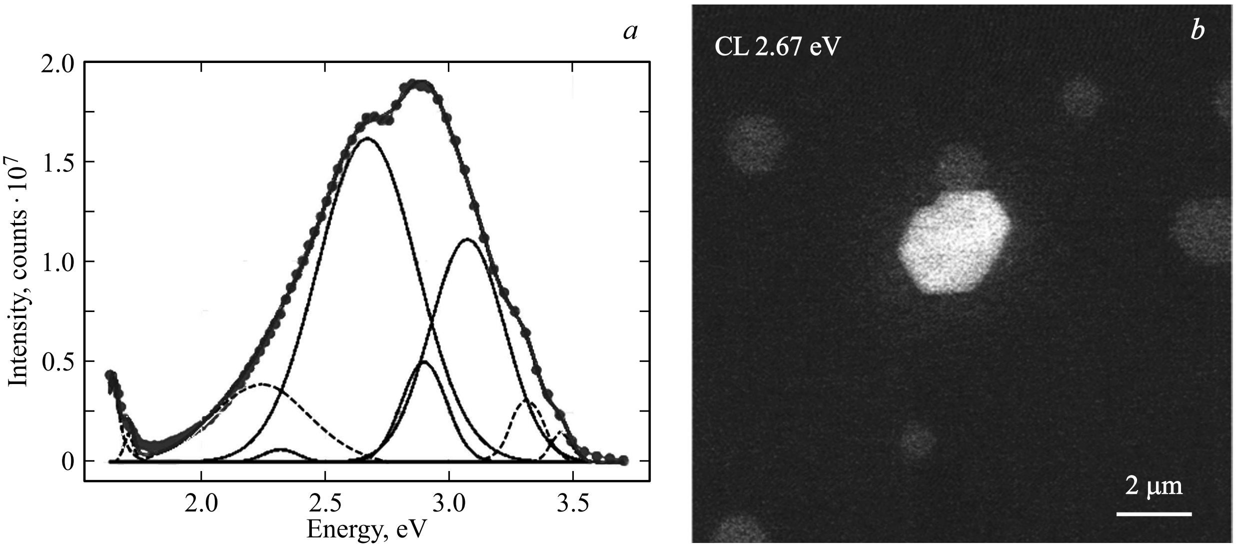

Figure 1. (a) — decomposition of the cathodoluminescence spectrum of layer κ-Ga$_2$O$_3$ to components; (b) — monochromatic cathodoluminescence map at photon energy 2.67 eV of a series of microcrystallites κ-Ga$_2$O$_3$ on GaN.

($\sim 3.1 - 3.35$ eV) [5] and yellow luminescence of GaN (~ 2.18 eV) [6].

The components of the luminescence spectrum κ-Ga$_2$O$_3$ are highlighted in Figure 1, a by solid lines. The spectral position of their maxima agrees well with the previously reported data for the $\kappa(\varepsilon)$-phase Ga$_2$O$_3$: ~ 2.32 eV, ~ 2.67 eV, ~ 2.93 eV and ~ 3.10 eV. In a recent paper by Hidouri et al. [8] the spectral bands of luminescence in $\kappa(\varepsilon)$-phase of gallium oxide in the energy range 1.5–3.4 eV were attributed to ensembles of point defects, presumably, gallium vacancies, hydrogen impurities and their complexes. According to the assumption made, such ensembles have different sizes and are unevenly distributed in the epitaxial layer, and the spatial unevenness of their distribution can be associated with the predominant formation of ensembles of point defects near the domain boundaries that make up the pseudomorphic structure of $\kappa(\varepsilon)$-phase.

Monochromatic map of a free-standing κ-Ga$_2$O$_3$ microcrystallite on GaN substrate at the emission energy of 2.67 eV, as the most intense luminescence component of κ-Ga$_2$O$_3$, is shown in Figure 1, b. The GaN substrate does not luminesce with this energy, and only the microcrystallite prisms of κ-Ga$_2$O$_3$ give a bright contrast in the image. Note, that even a single prismatic microcrystallite is characterized by all intense components of the luminescence spectrum of κ-Ga$_2$O$_3$ presented in Figure 1, a (monochromatic maps at other photon energies are not shown for brevity). In other words, defects in its crystal structure fully characterize the luminescent properties of κ-Ga$_2$O$_3$ layer produced by heteroepitaxially on gallium nitride substrate.

On the prepared lamella, the STEM method revealed the features of the domain structure of an individual microcrystallite κ-Ga$_2$O$_3$. Figure 2, a shows a bright-field STEM image (BF-STEM), where 6 domains of approximately the same size with linear boundaries between them can be distinguished, two of which are most clearly visible due to the selected diffraction conditions. Thus, the prism center acts as a 6th order axis of symmetry, which is also manifested in the symmetry of reflexes when studying such crystals using various X-ray diffraction methods [3,4]. Besides, multiple linear contrasts parallel to each other are observed inside the domains, the directions of contrasts correspond to the directions of antiphase boundaries found in nanocrystalline κ-Ga$_2$O$_3$ [3]. They are elongated from the center to the top of the hexagon and form angles of 30° with the boundaries of each of the domains.

In the previous paper of our group [4], it was noted that the centers of microcrystallite prisms predominantly coincide with the position of the exit of the grown-in GaN dislocations on the surface. It can be supposed that the growth of gallium oxide microcrystallites starts with the formation of structurally imperfect nuclei near the dislocation exits, where the GaN crystal structure experiences the greatest deformations, and during their subsequent lateral growth the mechanical stresses at the interface with the substrate are partially compensated by the formation of antiphase boundaries.

The panchromatic cathodoluminescence map shown in Figure 2, b is recorded on the same lamella as shown in Figure 2, a. It demonstrates that the luminescence intensity near domain boundaries and large antiphase boundaries is reduced, which indicates their increased recombination activity. This fact corresponds to Hidouri et al. [8] supposition about the possible segregation of recombination centers near domain boundaries in κ-Ga$_2$O$_3$. At the same time, as can be seen from Figure 2, a, not all domain and antiphase boundaries exhibit increased recombination, which can be explained by the variability of their own atomic and electronic structure, which determine the nature of the recombination activity. As it was demonstrated,

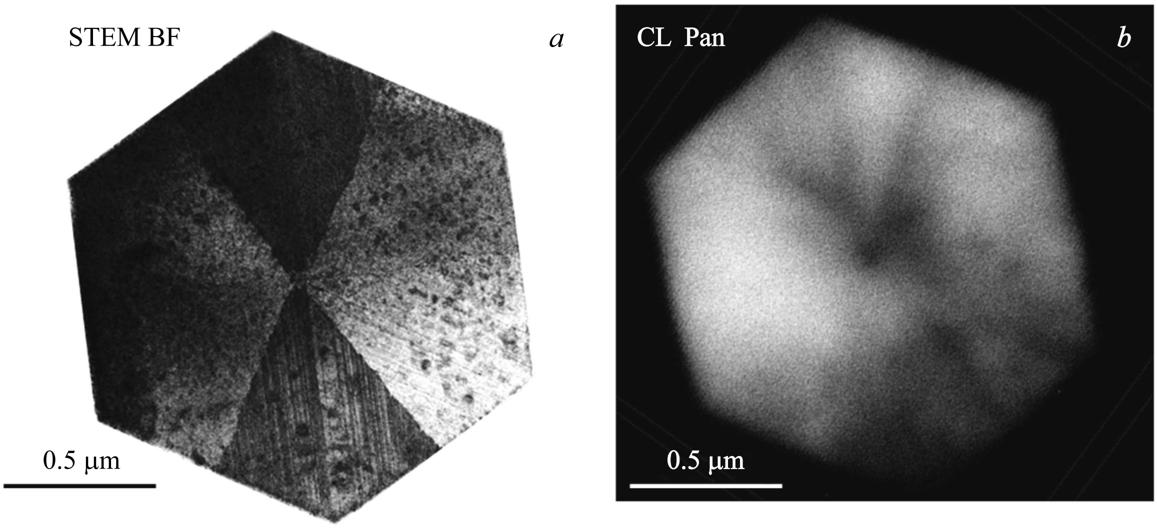

Figure 2. Microgram STEM-BF (*a*) and cathodoluminescence map in panchromatic mode (*b*) for individual microcrystallite κ-Ga_2O_3 (identically oriented).

for example, in CdS [9], twin boundaries themselves can be sources of luminescence without the need for the participation of clusters of point defects. Therefore, the observed decrease in the cathodoluminescence signal along the domain boundaries cannot serve as confirmation of the Hidouri et al model on the nature of radiative transitions in κ-Ga_2O_3.

4. Conclusion

The results of a study of the structure and recombination properties of microcrystallites of κ-phase gallium oxide grown epitaxially on the basal plane of hexagonal GaN are presented. Microcrystallites have the shape of regular or irregular hexagonal prisms and consist of rotational domains of six orientations, each of which contains parallel sets of extended and rectilinear antiphase boundaries. A local decrease in luminescence intensity along domain and antiphase boundaries was discovered, which is the first demonstration of their influence on the recombination properties of gallium oxide.

Funding

The study was supported by the Russian Science Foundation grant No. 23-23-00202, https://rscf.ru/project/23-23-00202. Experimental results were obtained using the equipment of the Interdisciplinary Resource Center for „Nanotechnology“ of St. Petersburg State University.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] S.I. Stepanov, V.I. Nikolaev, V.E. Bougrov, A.E. Romanov. Rev. Adv. Mater. Sci. **44**, 63 (2016).

[2] E.B. Yakimov, A.Y. Polyakov, V.I. Nikolaev, A.I. Pechnikov, M.P. Scheglov, E.E. Yakimov, S.J. Pearton. Nanomater. **13**, *7*, 1214 (2023).

[3] I. Cora, F. Mezzadri, F. Boschi, M. Bosi, M. Čaplovičová, G. Calestani, I. Dódony, B. Péecza . R. Fornari. Cryst. Eng. Commun **19**, *11*, 1509 (2017).

[4] S. Shapenkov, O. Vyvenko, V. Nikolaev, S. Stepanov, A. Pechnikov, M. Scheglov, G. Varygin. Phys. Status Solidi B **259**, *2*, 2100331 (2022).

[5] S. Shapenkov, O. Vyvenko, E. Ubyivovk, V. Mikhailovskii. J. Appl. Phys. **131**, *12*, 125707 (2022).

[6] M.A. Reshchikov H. Morkoç. J. Appl. Phys. **97**, *6*, 061301 (2005).

[7] V. Montedoro, A. Torres, S. Dadgostar, J. Jimenez, M. Bosi, A. Parisini. Mater. Sci. Eng. B **264**, 114918 (2021).

[8] T. Hidouri, A. Parisini, S. Dadgostar, J. Jimenez, R. Fornari. J. Phys. D **55**, *29*, 295103 (2022).

[9] P.Q. Zhao, S.J. Xiong, X.L. Wu, P.K. Chu. Appl. Phys. Lett. **100**, *17*, 171911 (2012).

Translated by I.Mazurov