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Comparative studies of the properties of thick GaN layers with different types of crystal structure grown on a ceramic substrate

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The results of a comparative study of the properties of quasi-bulk GaN with different types of structure are presented. An orientation dependence of the introduction of an unintentionally introduced donor impurity of oxygen which determines the value of the concentration of free electrons in the grown material is discussed.

Keywords: Gallium nitride, ceramic substrate, texture, polycrystal, Raman spectroscopy.

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Gallium nitride (GaN) and solid solutions based on it play an important role in various applications of modern electronics and photonics. Currently, due to the lack of native GaN substrates, active search is being carried out for alternative possibilities for obtaining substrate material. Thus, contrary to the prevailing representations that only a single-crystal material can serve as a substrate for the growth of GaN, it was showed that device-quality nitride layers can be grown on plates made of polycrystalline diamond and composite substrates based on it, as well as on ceramic substrates [1–3]. We previously reported that millimeter-thick, free-released GaN plates can be produced using ceramic substrates. It was found that the grown material is a semiconductor of *n*-type of conductivity, the thermophysical, mechanical and optical properties of which correspond to the properties of GaN obtained by traditional methods of volumetric growth [4,5]. X-ray diffraction analysis showed that, depending on the nucleation conditions, the structure of the grown material is either an ordered wurtzite texture or a polycrystal formed by GaN blocks of various orientations [6,7]. This paper presents the results of a comparative study of the electronic properties of grown GaN layers with the indicated types of crystal structure.

GaN plates up to 3 mm thick were produced by the chloride-hydride method (HVPE) on boron nitride (BN) substrates. It was shown that the process of GaN nucleation on ceramics occurs with the participation of the liquid phase of gallium melt. The type of GaN structure being formed is determined by the nature of the melt spreading on the surface of the BN substrate [7]. In the case when the liquid phase forms a continuous film, GaN texture is formed, oriented in the direction [0001], i.e. perpendicular to the base plane (0001). As the material thickness increases, GaN texture blocks form coherent boundaries (Figure 1, *a*–*b*). In the case when gallium is segregated in the form of droplets, a polycrystalline structure is formed (Figure 1, *c*–*d*). The polycrystalline structure nucleates on the surface of discrete droplets of Ga melt in the form of lamellar crystallites GaN and is formed as a result of their lateral growth in the base plane (0001).

The distribution of the main chemical components and impurities in GaN with different types of structure was studied using the Auger electron spectroscopy (AES) method. AES profiles were obtained by sputtering the material using Ar ion beam with a density of $2\,\text{mA/cm}^2$. The depth of the studied area was $1\,\mu$m. Comparative studies using micro-Raman spectroscopy (Raman scattering spectroscopy, RSS) in backscattering geometry were carried out using a *LabRAM HR Evo UV-VIS-NIR-Open* spectrometer (manufactured by *Horiba*, France). Nd:YAG laser beam (532 nm) was focused into a spot with a diameter of $1\,\mu$m through the lens of a confocal microscope *Olympus* (NA = 0.9) 100×.

Studies of the elemental composition showed that in sample with a texture structure, the ratio of the main components corresponds to the stoichiometric composition of GaN (Ga = 49.7%; N = 49.72%), the content of unintentionally introduced impurities, in particular, carbon and oxygen is: O = 0.18%; C = 0.4%. In sample with polycrystalline structure a change in the ratio of the main components and increase in the percentage of impurities are observed (Figure 2, *a*). In the studied volume of the sample at depth of 100–300 nanometers from the surface, the following values were determined: Ga = 53.5–55.7%; N = 27.8–31.44%; O = 12.6–9.78%; C = 5.3–2.8%. From the nature of the obtained AES profiles it follows that in the bulk of the material the oxygen admixture replaces nitrogen atoms.

In the RSS spectra of the studied samples, lines allowed by the selection rules and related to phonons of symmetry E_2(low) and E_2(high) were observed. The spectrum of the sample with crystalline texture structure (not shown) contained a forbidden symmetry line A_1(TO) with relatively low intensity. From the analysis of this spectrum it follows

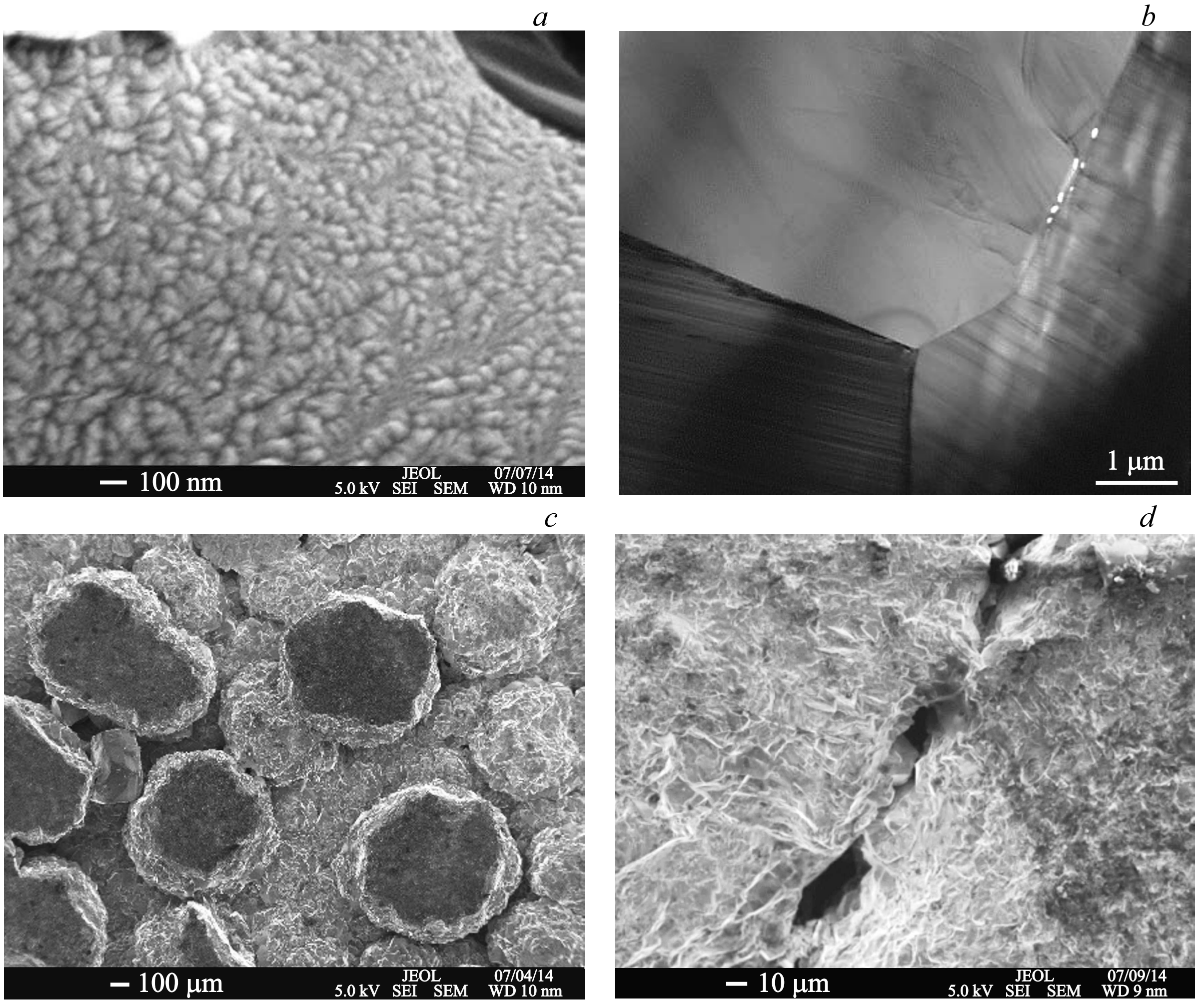

Figure 1. Stages of formation of two types of GaN structure: (*a*) SEM image of the initial stage of texture formation on GA melt layer; (*b*) TEM image of interblock texture boundaries in sample 1.5 mm thick. SEM images of polycrystalline structure: (*c*) stage of formation of individual blocks on melt droplets; (*d*) image of interblock boundaries. The zoom scales in SEM images correspond to: (*a*) — 100 nm; (*c*) — 100 μm; (*d*) — 10 μm.

that the predominant orientation of the texture blocks coincides with the direction of the hexagonal axis *c* [5].

Figure 2, *b* shows a typical RSS spectrum obtained on samples with the polycrystalline structure. The spectrum exhibits two narrow lines that are characteristic of hexagonal GaN (E_2(low) and E_2(high)), as well as two broad bands associated with phonon-plasmon modes PLP$^-$ and PLP$^+$. It is known that the position and width at half maximum of the lines PLP$^-$ and PLP$^+$ can be used to determine the concentration and mobility of free charge carriers: with an increase in the concentration of free electrons, the phonon-plasmon modes shift towards higher frequencies [8,9]. According to the made estimates, in GaN sample with the texture structure the electron concentration corresponded to $\sim 10^{17}\,\mathrm{cm}^{-3}$, in the sample with polycrystalline structure it was noticeably higher and amounted to $\sim 3\cdot 10^{19}\,\mathrm{cm}^{-3}$. Note that in the spectrum, in addition to the main lines characteristic of hexagonal GaN, two additional lines are observed with frequencies ~ 546 and $\sim 648\,\mathrm{cm}^{-1}$ (in Figure 2, *b* they are marked with the asterisk and the arrow, respectively). The line with a maximum at the frequency $\sim 648\,\mathrm{cm}^{-1}$ falls into the spectral region located between transverse (TO) and longitudinal (LO) phonons. It was noted in the paper [10] that the presence of such wide band implies scattering with the participation of phonons with wave vectors $\mathbf{q} \neq 0$. In this paper, two possible processes were used to explain the appearance of this band: forbidden Fröhlich LO-scattering or scattering by electron charge density fluctuations.

It was previously shown that in RSS spectra of bulk GaN crystals with high oxygen content, the appearance of so-called *Q*-modes is observed (at normal pressure at the frequency $\sim 544\,\mathrm{cm}^{-1}$). These modes are vibrational modes of the oxygen donor impurity occupying the positions of nitrogen atoms in the GaN [11] lattice. Taking into account the AES data, it can be assumed that the appearance

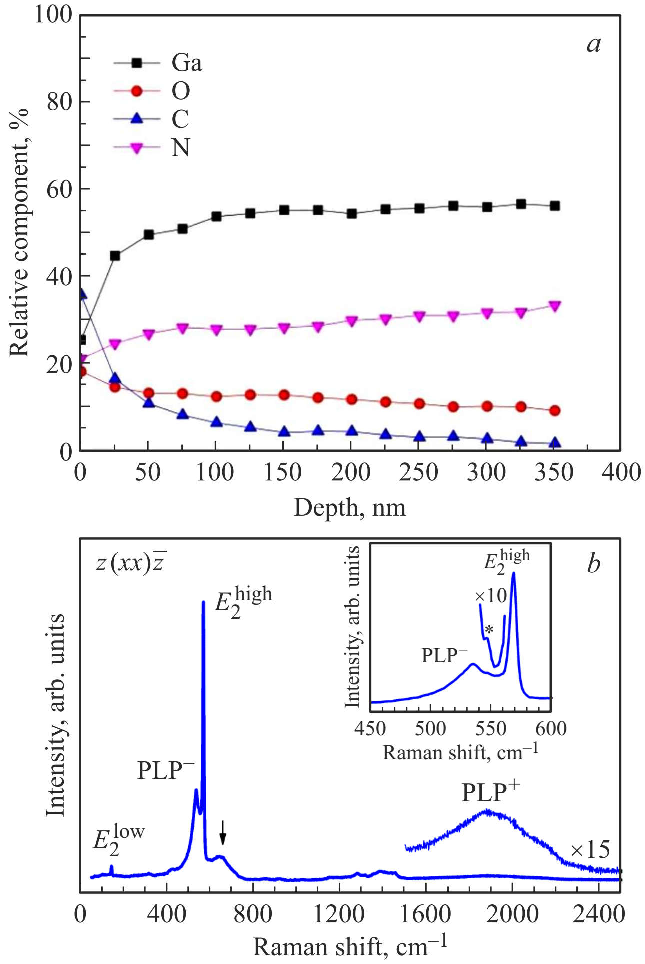

Figure 2. (*a*) OES profile of main components distribution in GaN with a polycrystalline structure; (*b*) RSS spectra of the same sample. The arrow marks the line at the frequency 648 cm^{-1}, the asterisk — at the frequency 546 cm^{-1}.

of the line at frequency of 546 cm^{-1} in the spectrum of polycrystalline sample can also be due to the presence of oxygen impurity.

Thus, the results of a comparative study of the properties of GaN grown on ceramic substrate revealed the interrelated effects of the orientation dependence of the entry into the crystal lattice of unintentionally introduced impurities, and increase in the concentration of free carriers. For the case of polycrystalline structure, which is formed as a result of lateral growth, a more than six times increase in the content of oxygen donor impurity is observed compared to textured material, the blocks of which have predominant orientation parallel to the normal to the substrate surface. The totality of the results obtained correlates with the results of studies [12,13], which also reported a significant increase in the concentration of free carriers in areas of lateral growth of bulk GaN under conditions of ammonothermal synthesis, which, as shown, is associated with an increase in the concentration of oxygen impurity.

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Conflict of interest

The authors declare that they have no conflict of interest.

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