Structure of GaN grown from vapour phase on a seeded layer of gallium melt formed on a boron nitride ceramic substrate

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Abstract. In this study, two empirical models for the growth of millimetre-thick GaN material with either highly ordered textured or polycrystalline structure on a ceramic substrate by Hydride Vapour Phase Epitaxy (HVPE) are considered. It is suggested that the specific type of the structure of GaN is determined at the nucleation stage and depends on the character of the wetting of the surface of the substrate by the liquid gallium melt.

1. Introduction
Since the beginning of the “nitride revolution” in the field of optoelectronics and solid-state lighting, real progress in improving the quality of nitride epitaxy has been expected from the achievements in the production of GaN substrates. However, the existing technologies for the synthesis of single crystals of gallium nitride are still technologies with a high level of complexity, and the resulting material is extremely expensive. The dimensions of the wafers obtained from bulk ingots are still far from meeting the needs of the mass production of devices. The development of alternative cost-effective approaches to the synthesis of bulk material, or a material with properties very similar to those of bulk GaN, providing controlled growth, high purity, stoichiometric composition and type of crystal structure of the resulting products is an urgent task. In particular, realization of the formation of self-orienting films of gallium nitride and bulk crystals on alternative substrates utilizing the idea of synthesis by direct reaction of gallium melt with ammonia or molecular nitrogen is of great interest in nitride technologies. Despite the numerous studies that were carried out, there is still no complete understanding of the processes responsible for the formation of such materials. It has been shown that controlled nucleation is an important tool for controlling the microstructure of materials grown in the form of flakes and microcrystals [1,2]. In this work, the mechanisms of the growth of thick gallium nitride slabs by vapour phase deposition on a ceramic substrate are considered. In particular, two mechanisms of the formation of bulk GaN material with different types of structures are analyzed. In our previous studies, correlation of optical properties with specifics of structure of the material was established with microcathodoluminescence, photoluminescence and Raman scattering studies [3]. It was shown that intrinsic defects in textured GaN, namely basal stacking faults [4], are responsible for strong blue emission at the room temperature and for narrow exciton-related UV luminescence band at the cryogenic temperature. At the present level of the development of the growth technique, this already means that this GaN material is a promising material for the new boosting technologies of non-classical solid-state photon emitters self-assembled within the host crystalline matrix.
2. Experimental
Large-area few-millimetre-thick slabs were obtained by the deposition of gallium nitride on boron nitride ceramic plate in Hydride Vapour Phase–Epitaxy (HVPE) setup with a horizontal reactor. The working gases were inert carrier gas argon, 99.997% pure; ammonia (NH₃), 99.997% pure, and gaseous hydrogen chloride (HCl, 99.999% pure) [5]. It was shown that the slab material was a semiconductor with n-type conductivity with thermal and mechanical properties very similar to those of single-crystal GaN produced by conventional bulk growth techniques. X-ray diffractometry (XRD) and transmission electron microscopy studies showed that the material represented either a highly ordered wurtzite GaN[0001] texture or had a polycrystalline structure [6].

3. Results and discussion
Results of microscopic and compositional studies of interface region showed that at the stage of the nucleation of GaN there was no epitaxial interaction between the BN ceramic substrate and the grown material due to the formation of a gallium-based liquid phase on the surface of the ceramics. The absence of such interaction ensures free separation of the grown GaN from the substrate after the end of the growth process. Along with that, there is a significant difference between the process of nucleation of GaN on the BN substrate used and that on traditional semiconducting or sapphire wafers. Material growth occurs under conditions of high gallium supersaturation of the growth zone, which is supported by the presence of an additional Ga source in the form of liquid phase. The liquid phase of the gallium melt is formed as a result of the segregation of gallium delivered to the surface of the ceramic substrate from the primary source, gaseous gallium chloride. In Ref. [7], the results of estimates of the values of contact angles for non-reaction systems "liquid metal - covalent ceramics" for 288 different variants including boron nitride are presented. According to that study, normally, liquid metals do not wet the surface of covalent ceramics due to the high surface tension: in particular, the contact angle between the liquid Ga droplet and the BN is 153 °. In this case, mutual adhesion is provided by weak van der Waals forces through the interactions of the Ga liquid phase and the surface of the substrate. Also, it is known for certain that the ratio of the main components in the mixture of working gases plays an important role in the formation of the structure of nitride compounds. In the case of the growth by the vapour–liquid–solid (VLS) mechanism, this is especially critical, since the composition of the gas mixture above the metal liquid phase determines the final type of morphology of the material. Under conditions of high saturation of the vapour phase with respect to gallium and under the condition of using a non-wettable substrate, the Ga melt forms droplets and remains in this form throughout the entire growth process [8]. Along with that, it is shown that nitrogen atoms or ions dissolved in the liquid phase of gallium contribute to its spreading. At the particular level of nitrogen supersaturation of the vapour phase, it is possible to obtain wetting liquid Ga layers up to 2 monolayers in thickness, on which planar continuous layers of nitride materials can be grown [9].

Considering experimental aspects of GaN growth on BN ceramics, two generalized mechanisms for the growth of gallium nitride with a highly ordered GaN texture and polycrystalline structure are suggested in this work. The probability of the dominance of a certain mechanism is determined by the nature of the spreading of the gallium liquid phase over the ceramic surface. If the liquid phase forms a film, the growth of gallium nitride proceeds according to the «evolutionary selection» mechanism proposed by van der Drift [10]. In the case when gallium segregates in the form of droplets, a polycrystalline structure of GaN is formed according to a mechanism similar to VLS.

In accordance with evolutionary selection rules, the final orientation of the textured materials deposited from the vapour phase is controlled by vertical growth rate of individual crystallites of the starting seeded polycrystalline phase. The preferred crystallographic orientation of the resulted texture of the material is set by the orientation of crystalline blocks with the vertical growth rate close to the maximum. Formation of [0001]–ordered GaN texture material considered in this work occurs in accordance with this classical scheme. It was found that primarily seeded polycrystalline GaN layer is formed on the surface of Ga melt layers spread over the surface of ceramic substrate. Scanning electron microscopy (SEM) image of the surface of the seeded layer is shown in Fig. 1(a). Further
nucleation of texture blocks with multidirectional orientation occurs as a result of secondary nucleation of GaN on the surface of the seeded layer as illustrated in Fig. 1(b). According to the results of XRD studies, with the thickness of the material increasing, the preferred orientation of the blocks becomes that strictly along the hexagonal axis [0001]. The lateral dimension of the blocks increases up to several hundred micrometres with a material thickness of up to 3 mm. Along with that, the structural quality of the material of blocks and inter-block boundaries is improved.

Figure 1. SEM images illustrating: the initial stage of the formation of a polycrystalline seeded GaN layer over a spread film of a gallium melt (a), and the initial stage of the formation of a GaN texture (b)

The main prerequisite for the formation of a polycrystalline GaN structure is that Ga liquid phase does not wet the surface of the BN covalent ceramics and acquires the shape of spheres. Let us note that on the basis of this effect, one of the growth options of VLS mechanism – "droplet epitaxy" was developed for the synthesis of nanostructures [11]. In the experiments in our work, uniform nucleation of GaN crystallites in the form of plates occurred on the curved surface of the liquid Ga droplets. As a result of the lateral growth of crystallites, the spheres grew together, which resulted in the formation of a monolithic material with a polycrystalline structure. Blocks of this structure reach millimetre range in lateral dimensions in comparable range of the thickness of a grown material. Figure 2(a,b) shows SEM images illustrating two different stages of the formation of the polycrystalline GaN structure. Figure 2(a) shows that at the stage of the nucleation, the material is formed in the form of globules covered by plate-like GaN crystallites. As the lateral growth of the crystallites progresses, the globules coalesce (Figure 2(b)) and form a monolithic GaN polycrystalline specimen.

4. Conclusion
One of the features of the formation of the structure of free–standing bulk gallium nitride material with the thickness in the millimetre range grown by vapour deposition on boron nitride ceramic substrate is discussed. As follows from the context of the work, controlled nucleation is an important tool for controlling the microstructure of a material, which determines its functional properties for future applications. It is shown that in the process of the growth of GaN by chloride–hydride growth method a nucleation of GaN on BN ceramics proceeds with Ga liquid phase segregation. On the basis of experimental observations, it is concluded that the type of the formed structure depends on the character of distribution of gallium melt over the surface of the BN substrate. Two different mechanisms of the formation of bulk gallium nitride material with either highly oriented [0001]-texture or polycrystalline structure are considered. As suggested, the probability of the dominance of
the certain mechanism is determined by the conditions under which nucleation at the initial stages of GaN growth occurs.

![Image 1](image1.png) ![Image 2](image2.png)

**Figure 2.** SEM images illustrating: the initial stage of the formation of the GaN plates on the surface of droplets of gallium melt (a), and the following stage of the formation of monolithic GaN polycrystalline specimen (b)

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