Materials Physics and Mechanics 44 (2020) 1-7 Received: January 9, 2020

ON CRACKING IN THICK GAN LAYERS GROWN ON SAPPHIRE SUBSTRATES

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Abstract. Self-organization mechanisms promoting elimination of cracks in thick GaN layers grown on sapphire substrates are considered on the basis of the experimental results on the fabrication of the layers by Hydride Vapor-Phase Epitaxy on MOCVD-grown GaN/Al_2O_3 templates. The obtained data support the supposition on the closure of tensile stress-related cracks via diffusion processes and demonstrate the strong contribution of bulk diffusion in addition to surface diffusion discussed earlier.

Keywords: GaN, defects, cracking, Hydride vapor phase epitaxy

1. Introduction

Currently, development of III-nitride epitaxial technology is aimed at the achievement of the best possible quality of the material. Despite numerous efforts to commercialize III-nitride homoepitaxy, most of the epitaxial structures for GaN-based devices are still grown on foreign substrates, mainly on sapphire [1]. Sapphire (0001)Al_2O_3 substrates are known to be highly mismatched to GaN layers in respect to both lattice parameter (14%) and thermal expansion coefficient (30%). It is known that the increase in thickness of heteroepitaxially grown GaN layers provides the decrease in threading dislocation (TD) density, and this improves crystalline perfection [2]. At the same time, growth of thick layers often leads to cracking in both the substrate and the layer due to thermally-induced stress caused by aforementioned mismatches. When relaxation mechanisms are not taken into account, calculations predict that the compressive stress in GaN is reduced by over two orders of magnitude under cooling if the film thickness is increased to 1 mm. Thus, the tensile stress in sapphire substrate is increased by over two orders of magnitude [3]. Stress calculations for GaN/Al_2O_3 with consideration of relaxation mechanisms were performed in Ref. [4]. Three mechanisms of relaxation accompanied with the formation of structural defects were proposed for different film thicknesses: (*i*) pure lattice deformation for films with thicknesses <4 µm, (*ii*) enhancement of the density of interface defects such as "microcracks" and/or dislocations (4-20 µm), and (*iii*) generation of "macrocracks" in sapphire (>20 µm). Macrocracks that develop in GaN/(0001)Al_2O_3 structures are the cause of the mechanical failure of the entire wafer during post-growth cool-down (an example is shown in Fig. 1(a)).

Yet the failure does not necessarily occur in all cases. For instance, as was shown for Metal-Organic Chemical-Vapor Deposition (MOCVD) of GaN, cracking could be observed for 13 µm-thick layers, but did not necessarily appear in the layers with the thickness of 30 µm [5]. This phenomenon was treated in detail by Etzkorn and Clarke [6]. They have

http://dx.doi.org/10.18720/MPM.4412020_1

shown that in sufficiently thick GaN layers grown on sapphire substrates, a particular net of buried cracks, which do not extend to either bottom or top of the film, is formed. Etzkorn and Clarke argued that this cracking pattern could not be produced under compression. Their general conclusion was that cracking resulted from tensile stress, which was generated during the growth when a certain critical thickness of the film was reached. This supposition was supported by the results of some experimental and theoretical studies (see, e.g., [7-9]). For the explanation of crack elimination phenomenon, Etzkorn and Clarke considered several possible scenarios involving diffusion-type processes or non-diffusion crack retraction [6]. Later, Liu et al. [7], who demonstrated formation and healing of buried cracks in thick GaN layers grown by Hydride Vapor-Phase Epitaxy (HVPE), suggested that the lateral overgrowth was the predominating process. In this paper, we will discuss our experimental results on fabrication of thick GaN layers with HVPE using MOCVD-grown templates. Our results are indicative of the dominance of diffusion (both bulk and surface) mechanism of the crack closure during the growth.

2. Experimental technique

The initial substrates were 2" (0001)Al_2O_3 wafers with 3.2 to 4.6 µm-thick GaN layers grown by MOCVD on low-temperature GaN buffer layers. Thick (100-1500 µm) epitaxial layers were grown in a home-made horizontal HVPE reactor at the atmospheric pressure. The growth temperature was 1050 ^{0}C. Argon with 99.997% purity was used as a carrier gas, while metallic Ga (99.9999%) and gaseous NH_3 (99.999%) were used as Ga and N sources, respectively. Gallium was chlorined with gaseous HCl with 99.999% purity. It appeared that HVPE-grown layers with thicknesses exceeding 400 µm were not necessarily destructed during the cool-down from the growth temperature to the room temperature. An example of the appearance of a 1000 µm–thick HVPE layer is shown in Fig. 1(b), where it is seen that the whole structure is undamaged and retains its integrity.

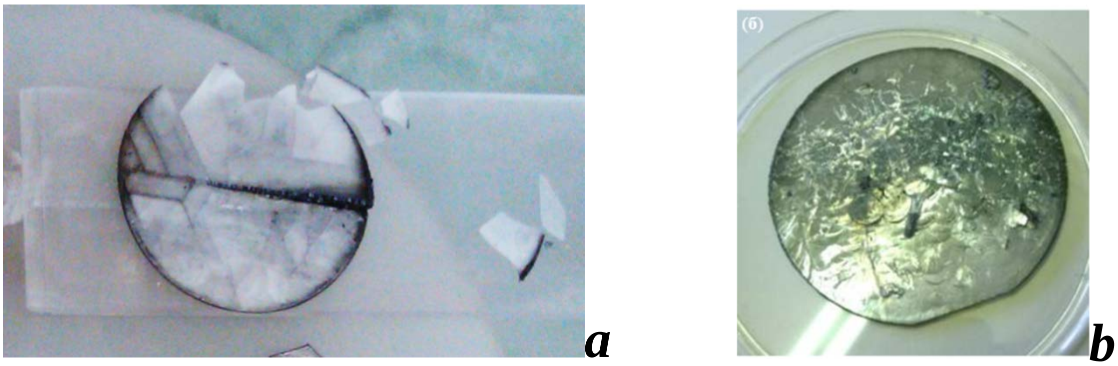
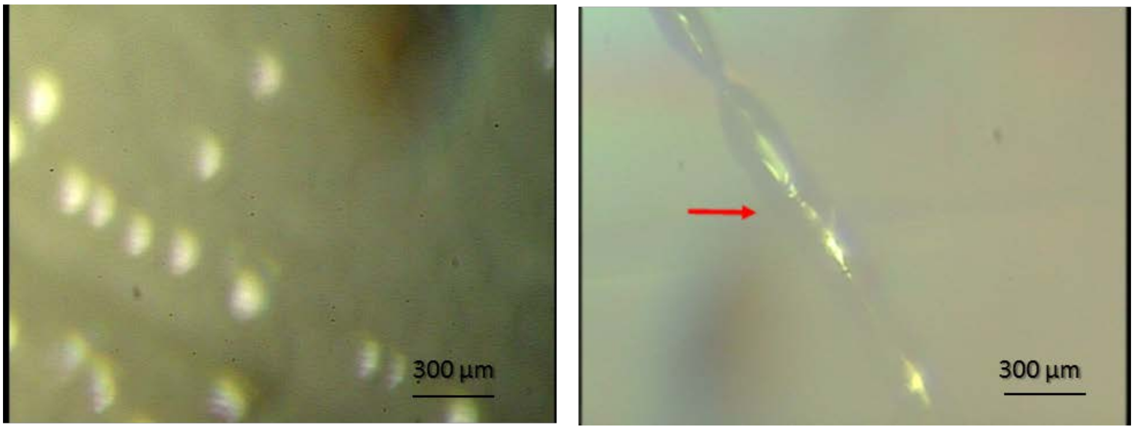


Fig. 1. Optical photographs of thick GaN layers grown by HVPE on templates prepared with MOCVD: *a*, a layer with thickness <100 µm, this sample experienced destruction right on the growth pedestal after cooling down to the room temperature; *b*, a layer with thickness of 1000 µm, which retained its integrity. The diameter of both wafers is 50.8 mm

3. Experimental results

Optical microscopy study was performed with various focus depths from the surface to the bulk of the material (down to approx. 200 µm). The studies revealed the presence of a set of crack nets located at a considerable distance from the HVPE layer/substrate interface. The nets were arranged one above another in the bulk of the layer with crack density decreasing towards the surface. Figures 2 and 3 show the specifics of crack propagation. Figure 2(a) shows an image obtained with the maximum focus depth. The observed area does not contain any cracks. Figure 2(b) shows the image obtained with the minimum focus depth, which allowed for observing a buried crack (indicated by arrow) that did not intersect the surface.



a ***b***

Fig. 2. Optical photographs of a thick HVPE-grown GaN layer taken with various focus depths of the microscope: *a*, maximum focus depth; *b*, minimum focus depth. An arrow in image (*b*) points to a buried crack

Images presented in Fig. 3 show the evolution of the microstructure of buried cracks within the bulk of the material. Moving the focus from the layer/substrate interface along the growth direction, a heavily cracked region was detected. This can be seen in Fig. 3(a), where a net of cracks with irregular shape is seen with weaker contrast (marked with white arrows). Also, cracks with good contrast with lower density are seen above them (marked with a red arrow). Important features of the defect pattern here are spheroid-like voids formed along the crack trajectory as well as spherical micropores located in the immediate vicinity of the cracks (Fig. 3(b,c)). The upper portion of the GaN bulk is shown in Fig. 3(d). This image demonstrates that all the underlying cracks are completely closed and only micropores exist above them (as seen in the lower left side of the image).

Transmission Electron Microscopy (TEM) studies were performed with the use of Philips EM–420 (accelerating voltage 80 kV, resolution 5 Å) and Jeol JEM–2100F (accelerating voltage 200 kV, resolution 2 Å) microscopes. Specimens for TEM studies were prepared using standard procedures of mechanical thinning and subsequent etching with Ar^+ ions with energy 3 to 4 keV. According to TEM data, the crack-free surface layer in the investigated sample had a thickness of 10 to 15 µm with TD density as low as 4×10^7 cm^{-2}. TEM results also confirmed the existence of both voids (Fig. 4(a)) and micropores (Fig. 4(b)) in the bulk of the studied layer. The TEM study also showed that the process of evolution of the shape of buried cracks via formation of voids was accompanied by changes in the trajectories of TDs, so dislocations got deviated from their typical path along the direction of the growth. Figure 4(a) shows a TEM image of a cross-section of the layer, where one can see a buried void and a dislocation that changed its direction near the surface of the void. The change of the direction of dislocation propagation can be indicative of the existence of diffusion processes leading to dislocation motion [10].

For accessing the quality of the GaN material, we used Raman and PL techniques. Horiba Jobin-Yvon T64000 Raman spectrometer (France) was used in these studies. Raman signal was excited with YAG:Nd laser (excitation wavelength λ=532 nm). The results of Raman spectroscopy performed in backscattering geometry at 300 K revealed low residual strain value in the studied sample. In Raman spectra (not shown), three allowed lines related to phonons of E_2(low), E_2(high) and A_1(LO) symmetry were observed. The Raman shift and full-width at half-maximum (FWHM) of the E_2(high) line equaled 567.5 cm^{-1} and 2.1 cm^{-1}, respectively, and these values were close to those typical of non-deformed GaN (567.8 cm^{-1} and 1.9 cm^{-1}, respectively [11,12]). According to the Raman shift of A_1(LO) phonon line (733.7 cm^{-1}), free electron concentration in the sample equaled (5-6)×10^{16} cm^{-3}.

Low-temperature (*T*=10 K) PL spectrum of the layer (not shown) was dominated by excitonic lines (bound exciton, BE, peaks) and their LO phonon replicas. The high quality of the material was confirmed by the absence of strong "yellow" PL line (with peak at ~2.2 eV), which can be often observed in GaN luminescence spectra [13]. This was indicative of low concentration of point defects that are responsible for the appearance of this line. There was no indication of the presence of other ‘defect’ lines, such as ‘green’ (with peak at ~2.4 eV) and blue (with peak at ~2.9 eV) lines that are typical of HVPE-grown GaN even with relatively high purity [14] either. High-resolution PL spectrum revealed a number of narrow excitonic bands, which were also indicative of the high quality of the material [15].

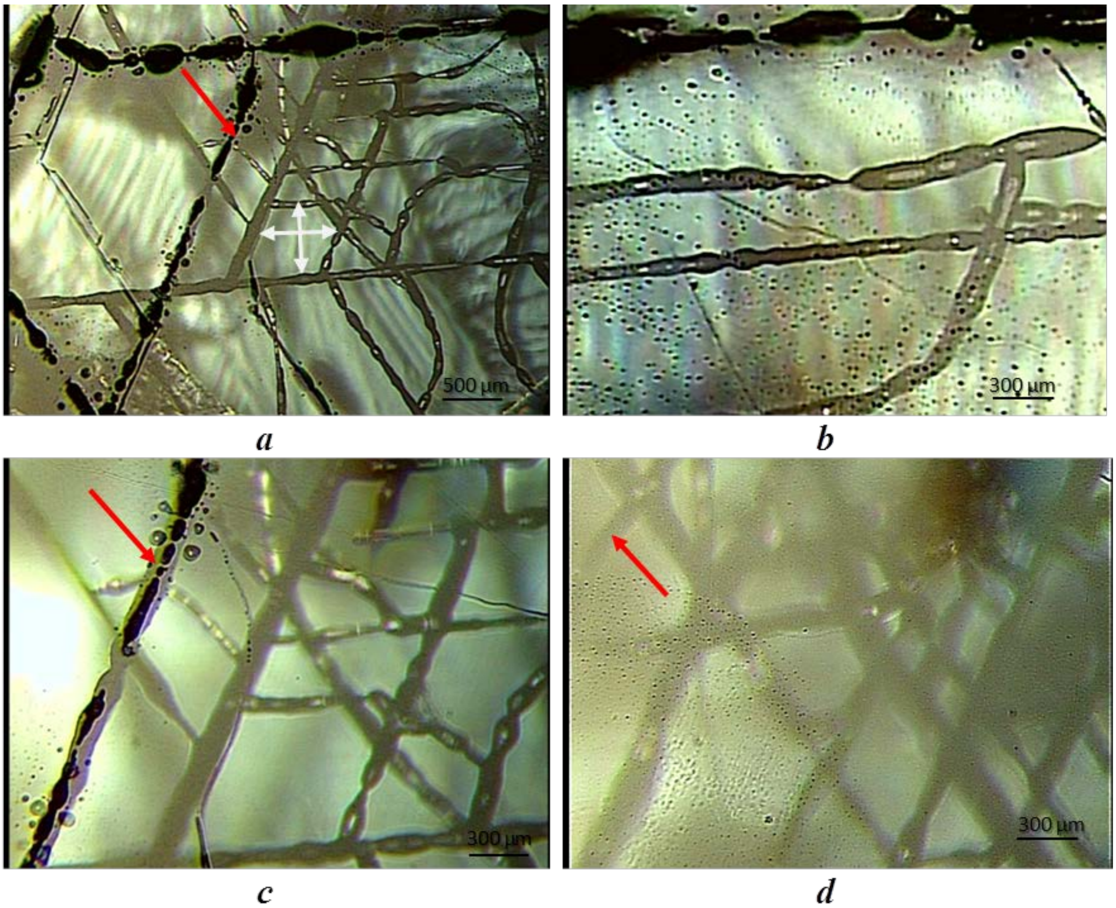


Fig. 3. Optical microscopy images illustrating reduction of crack density during HVPE of the 650 µm-thick GaN layer: *a*, deeply buried cracks; *b*, spherical micropores located in the vicinity of the cracks; *c*, partly closed crack propagated in the overlying section; *d*, the third (upper) section that does not contain cracks. Red arrows in images (*a*), (*c*), and (*d*) show the same crack, which allows for following its propagation, changes in its shape and its complete closure

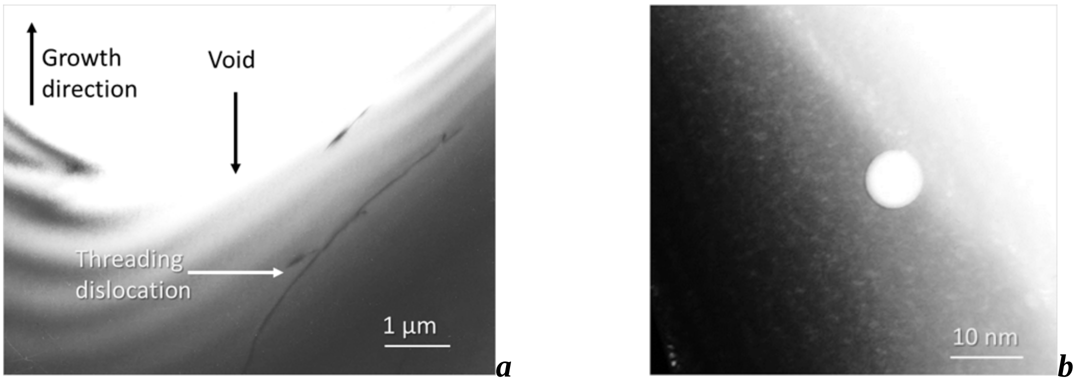


Fig. 4. TEM image of a cross-section of the thick GaN layer with buried cracks, which illustrates the interaction between an inner void and a threading dislocation (*a*), and a spherical micropore located in the immediate vicinity of the void (*b*)

4. Discussion

We shall start the discussion with the established fact that cracks in thick GaN layers originate from the increase of tensile strain during the growth when material reaches a certain critical thickness and that they remain buried in the bulk of the material [6]. Etzkorn and Clarke offered some possible scenarios of the formation of buried cracks. One of them was a diffusion-type process of crack closure. The driving force for this process obviously was the 'desire' of the system to lower the overall stored energy, which resulted in the decrease of the surface area of cracks [6]. We believe that the dominating role of the diffusion mechanism is now supported by our experimental results. On the basis of our data it can be suggested that the observed formation of multi-layered nets of cracks in the bulk of thick GaN layers proceeds according to the following scenario. After the layer reaches the critical thickness, cracks of the first level are formed. Under high temperatures (those of GaN HVPE growth), surface diffusion occurs at the walls of the cracks while bulk diffusion occurs in their vicinity. This leads to the evolution of the shape of the cracks, which proceeds till their continuity is interrupted as a result of the formation of voids along the crack trajectory. Then the cracks break up into a series of voids via a series of pinch-off events [16,17]. It can be suggested that the formation of micropores in the vicinity of the voids results from the subsequent process of void spheroidisation, which completes crack closure. These processes of the formation of cracks and their diffusion-mediated closure at the first level partly relax the strain that was generated during the growth. Thus, newly formed net of second-level cracks have lower density. These cracks undergo similar changes and additionally serve as internal sinks for micropores that had resulted from the first-level crack closure. As a result of this, the cracks of the lower level become fully closed, and the voids of the next level have larger mean diameter as compared to that of the channels of the lower level. With growth strain gradually relaxing, the density of cracks decreases and they all become closed. The remaining micropores, which now have no internal sinks, are absorbed by the free surface, which serve as an external sink, and thus, disappear. This scenario of buried crack evolution is also supported by TEM observation of the dislocation motion. The change in the direction of dislocation propagation could be considered as an extra proof of the existence of intensive diffusion processes, namely, a mass transfer by two counter-fluxes, where vacancies are moving towards the cracks or voids, which serve as powerful internal sinks for them, while atoms are moving towards the dislocation. The first flux defines the changes in the shape of both the crack and voids, while the second flux leads to non-conservative dislocation motion. As growth of the material proceeds further, the crack/void–containing region gets buried in the bulk of GaN and strain-free portion of the material with low TD density is formed above it, as was confirmed by the results of Raman, PL, and TEM studies presented above.

Conclusion

In conclusion, the results of the study of crack elimination in thick GaN layers grown by HVPE on GaN/Al_2O_3 templates prepared with MOCVD showed that non-catastrophic (those not leading to sample destruction) cracks that form during long growth runs appeared to be an important structural element, which encouraged additional relaxation processes in the bulk of thick GaN layers grown on foreign substrates. The suggestion by Etzkorn and Clarke [6], who postulated that changes in the shape of initial buried cracks result from surface diffusion, were complemented with our experimental data that were indicative of the existence of simultaneous processes of bulk diffusion. This provides extra arguments in favor of diffusion mechanisms of crack closure. The diffusion processes obviously reduce free energy and help strain relaxation in the growing thick GaN layers.

Acknowledgment. *Authors acknowledge support from the Ministry of Science and Higher Education of the Russian Federation, goszadanie No. 3.1421.2017/4.6.*

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