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GaN nano-ceramics were analyzed using transmission electron microscopy (TEM), showing that these ceramics are characterized by highly disoriented grains of the linear size of 100–150 nm. These GaN ceramics were used as substrates for GaN epitaxy in standard MOVPE conditions. For the comparison, MOVPE GaN layers on silicon substrates were grown using similar conditions. It is shown that MOVPE growth of GaN layers is highly anisotropic for both cases. However, the disorientation of the highly mismatched GaN layer on silicon is different from that characterizing GaN layer deposited on the ceramic substrate. In the latter case the disorientation is much higher, and three dimensional in nature, causing creation of polycrystalline structure having large number of the dislocations. In the case of the GaN layer grown on the silicon substrate the principal disorientation is due to rotation around c-axis, causing creation of mosaic structure of edge dislocations. Additionally, it is shown that the typical grain size in AlN nucleation layer on Si is smaller, of order of 20 nm. These two factors contribute to pronounced differences in later stage of the growth of GaN layer on the ceramic. Due to high growth anisotropy an appropriately thick GaN layer can, eventually, develop flat surfaces suitable for construction of optoelectronic and electronic structures. As shown by the TEM data, this can be achieved only at the cost of creation of the relatively large density of dislocations and stacking faults. The latter defects were not observed for the GaN growth on Si substrates.

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1 Introduction

Heteroepitaxial GaN layers have been grown on many foreign substrates such as sapphire [1], silicon carbide [2] or silicon [3-5] for both optoelectronic and electronic applications. The success of the MOVPE epitaxy was discussed over many years, but the microscopic mechanism of the growth of low temperature buffer layer, and subsequent annealing and high temperature epitaxy is not well understood. It is generally recognized that successful nitride heteroepitaxy proceeds *via* several common stages: nitridation of the substrate (sapphire, SiC, silicon, etc), growth of the low temperature buffer layer, annealing, growth of many independent nuclei, coalescence of the nuclei in the later stage, and finally, growth of the flat layer with the reduced density of dislocations. The mechanism of the GaN growth has also been investigated. Despite many efforts, the microscopic mechanism of island creation, dominant growth of selected grains, their coalescence, and the strain reduction *via* creation of dislocations have been only partially elucidated. Generally, the GaN growth is strongly correlated with underlying substrates, while the lattice and thermal mismatch related strain is relaxed by generation of high density of dislocations.

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Recently, a new approach to GaN heteroepitaxy was developed. GaN layers are grown on totally different structures ranging from silica quartz [6-8], the group I metals, e.g. silver [9], or refractory metals, such as W, Mo, Ta and Nb [10]. The two techniques were used: by plasma-assisted MBE (PA MBE) and MOVPE. In case of the deposition of GaN layers by PA MBE, the growth was carried out at very low temperature, about 400°C [10]. Initially the 3nm thick GaN buffer layer was grown. In case of MOVPE the deposition method was closer to the standard GaN epitaxy; the temperature was within 550 to 700°C range. Afterwards, the GaN growth was continued at the temperatures, typical either for PBE MBE (650–830°C) and MOVE (1000°C) techniques. Several physical properties of these GaN layers were investigated and critically assessed. It was shown that GaN layers grown by PA MBE on metal substrates were, in general, more rough than those deposited on silica substrate [10]. Unfortunately, these conclusions were not convincing as the authors stated that the metal substrates were more rough initially, which could affect the morphology of the grown GaN layers [10]. Similarly, the GaN layers, grown on silica substrate have considerable variation of the morphology, depending on the temperature of the growth of the buffer layers [8]. This variation of the morphology may be typical also for more standard sapphire substrates.

Recently, the new GaN nano-ceramic substrates were developed and used [11-14]. To some extent, these new substrates are located between the sapphire, SiC or Si substrates allowing for the lattice oriented growth and the silica glass, leading to uncorrelated growth of the GaN grains. Therefore they offer a unique possibility to investigate the MOVPE growth of GaN layers originated on various crystallographic orientations in nano-scale. This is the subject of this work, mostly based on transmission electron microscope (TEM) investigations. We compare these data with those collected for the growth of GaN layers on silicon substrates.

Our results will be also compared with the results reported by Nyk et al. [15]. These authors used Ga_2O_3 powder reaction with ammonia to obtain the nano-crystalline GaN powder. The powder was then purified and cold-pressed to obtain large area GaN substrates. Other details of the substrate preparation could be found in [15]. Both MOVPE and HVPE GaN layers were grown on these substrates by Nyk et al., who reported the structural and optical properties of these GaN layers [15]. In the present work we will compare the nano-structure of our GaN layers obtained on silicon and GaN sintered substrates with those obtained by Nyk et al. on cold-pressed GaN substrates.

2 Experimental

Nanocrystalline GaN powder used for sintering was synthesized by pyrolysis of the gallium imide precursor [11-13]. The GaN nanopowder were obtained by anaerobic imide route using the pyrolysis temperature was 900°C for 6 h [11-13]. Then the GaN nanopowder was sintered for 10 min in a high pressure torroid cell at 900°C and at the pressure 6 GPa [14]. As the result, GaN nano-crystalline ceramic substrate was obtained, which was prepared to epitaxy by standard cleaning and annealing in MOVPE reactor in ammonia flow at normal pressure at 900°C for about 10 min. Afterwards, GaN layer of about 2-µm thickness was grown by low pressure metalorganic vapor phase epitaxy (MOVPE). No buffer layer was deposited.

For comparison, GaN heterostructure 1-µm thick was grown by low pressure MOVPE (LP MOVPE) at 1170°C on (111)-oriented silicon substrate. The substrate was heated before growth in H_2 ambient at high temperature. After cooling down to 850°C, 30-nm thick AlN nucleation layer was deposited at reactor pressure of 50 mbar. The V/III ratio during growth of AlN nucleation layer was 4000. Nucleation layer was first heated up and then GaN film was deposited at reactor pressure 50 mbar and temperature 1170°C (V/III ratio 1200).

Transmission electron microscopy (TEM) was used to study of the structure of the GaN layers grown on nano-crystalline GaN, and on silicon substrates. TEM observations were performed on a JEOL JEM 3010 electron microscope operating at an accelerating voltage of 300 kV. Cross-sectional and plan view pictures were taken from samples that were prepared by a standard method of mechanical pre-thinning, followed by Ar ion milling.

3 Results and discussion

X-ray diffraction measurements showed the initial GaN nanopowder average grain size close to 120 nm. The X-ray results proved the existence of highly defected hexagonal wurtzite GaN structure. During sintering, the average grain size was about the same: in the typical sintered sample, the average grain size was 100–150 nm.

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The grains had random orientations, and no strong correlation of the grain orientation in the sintered sample was observed. Large size diffraction showed the polycrystalline character of the GaN nano-substrate. The structure of the substrate is presented in figure 1a.

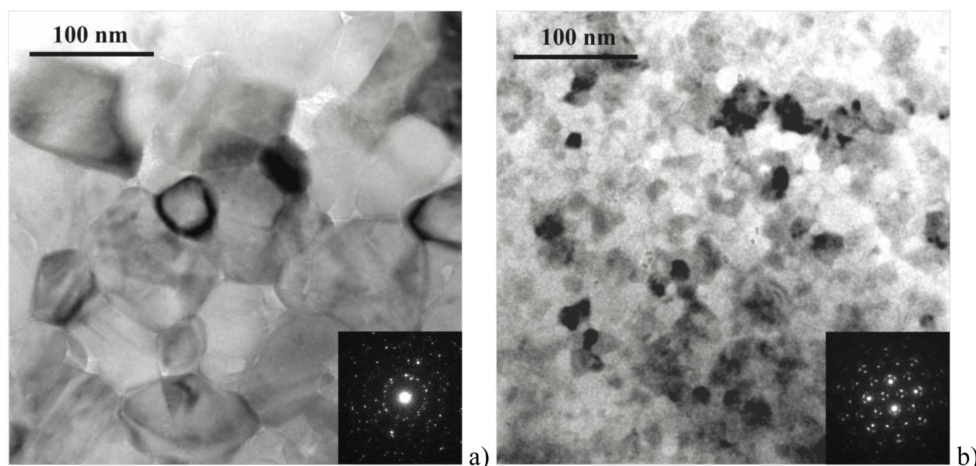

Fig. 1 Plan-view TEM images comparing the size of the GaN crystallites in (a) GaN ceramic substrate and (b) GaN layer grown on AlN nucleation layer deposited on Si substrate. Inserts in the right bottom corners show diffraction patterns.

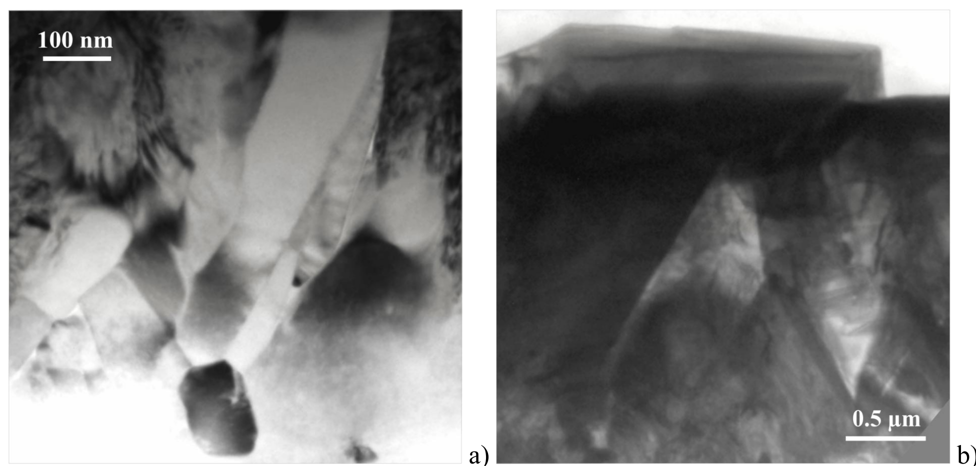

Fig. 2 Cross-section TEM images showing (a) growth of GaN crystals on sintered GaN nano-substrate and (b) surface of GaN epitaxial layer, created by coalescence of several large crystallites.

Figure 1b shows the test GaN layer deposited on silicon substrate. The picture presents a 30-nm thick AlN nucleation layer, and a very thin GaN layer grown on top of the AlN layer. These initial GaN grains, about 20 nm in size, are relatively highly misoriented in the *c*-plane, as shown in figure 1b. The diffraction pattern demonstrates that the GaN grain misorientation is due to rotation around the *c*-axis, i.e. it preserves the overall orientation of the layer, i.e. $(0001)_{GaN/AlN} \parallel (111)_{Si}$. The average rotation angle reaches 12 arc deg. It is still not clear whether the angle depends on the growth technique or the growth conditions.

Subsequent growth of GaN growth occurs on the initial GaN grains that have different size and orientation for these two substrate types. The difference in the growth is, therefore, determined by the difference between the GaN nucleation layers. In the case of the GaN layer deposited on sintered substrate, the GaN grew on relatively large GaN crystallites of about 100 nm in size. These grains are severely disoriented. The fastest growth is observed for the grains having exposed (0001) or $\{10\bar{1}0\}$ surface orientations. A shown in figure 2, the favorably oriented crystallites grow in the columnar manner gradually increasing their size and finally contacting the other grains. This leads to coalescence of the crystallites for the layer of about ½ micron thick. Subsequently, the layer grows uniformly. In the reported experiments, 2-μm thick, uniform GaN layers were

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obtained. As shown in figure 2b, the layer contains large density of structural defects, including dislocations and stacking faults. The structural results obtained in this work are compatible with the x-ray diffraction results obtained by Nyk et al. [15]. However, the preparation of these two substrates was different. Nyke et al. [15] used cold-pressed substrates while ours were sintered under very high pressure and temperature. Therefore, we believe that the properties of the layers are typical for this type of substrates and do not depend on the choice of the growth parameters. Thick layers are flat due to highly anisotropic growth of GaN in the directions parallel and perpendicular to the *c*-axis.

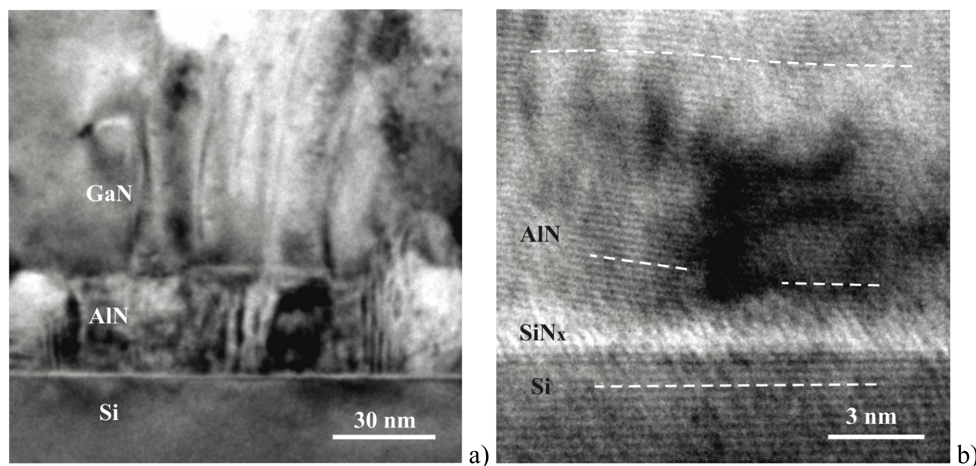

Fig. 3 (a) Cross-section TEM images of the growth of GaN layer on the AlN nucleation layer; (b) HRTEM image of the Si/AlN interface with the amorphous SiN_x intermediate layer.

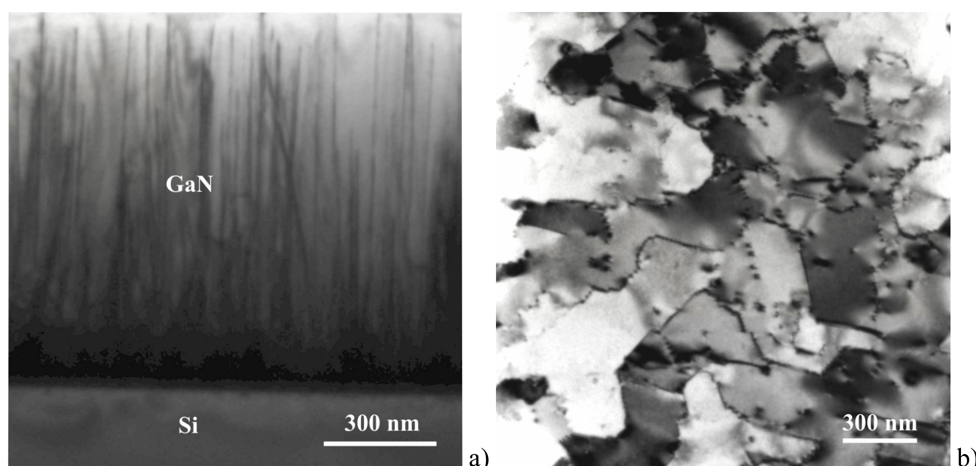

Fig. 4 (a) TEM images of GaN layer grown on Si substrate: cross-section and (b) plan-view. Plan-view image shows well-developed mosaic structure.

The control GaN/Si layer structure is presented in figures 3 and 4. The structure is typical for well controlled GaN growth on foreign substrates using AlN nucleation layer. First amorphous SiN layer, resulting from the initial nitridation of Si (111) surface [16], is obtained. The degree of the crystallinity and the thickness and structure of the layer depends on the technical parameters of the initial stage of the growth. Long nitridation results in the creation of Si_3N_4 crystalline layer, which is harmful for the growth of the buffer. Therefore, this stage should be relatively short and should lead to the creation of a very thin amorphous SiN layer. In our case, the layer was about 1.5–2 nm thick, i.e. it has several atomic layers. This layer relaxes a part of the strain, serves to develop properly the metallic orientation of the buffer, and prevents direct contact of Al and Si, which may lead to the dissolution of Si and creation of mixed Si–Al structure. Therefore, this stage has to be grown in N-rich conditions.

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A typical low-temperature AlN buffer was also grown. It has crystalline structure with relatively high density of threading dislocations originating at the SiN−AlN interface, as shown in figure 3b. As seen from the figure, other defects like stacking faults are not observed. The AlN layer is composed of crystallites of an average size of the about 20−30 nm. This AlN layer nucleates over the amorphous SiN layer which creates considerable misorientation between the AlN grains. These AlN grains also contain a large density of dislocations. Subsequent growth of GaN layer is characterized by a reduced dislocation density. This reduction in the dislocation density occurs at the AlN−GaN interface, as shown in figure 3a. It should be noted that the GaN growth is not fully epitaxial, because GaN layer and AlN buffer are only partially in register.

The final stage of the growth of thick GaN layer on Si substrate occurs without any significant change of the dislocation structure. Basically, being parallel to the growth direction, the dislocations preserve their density. The surface of the layer is again flat due to highly anisotropic growth of GaN. The stacking faults are essentially absent, which is one of the main differences as compared to the GaN layers grown on ceramic substrates.

It should also be noted that the dislocations in the epitaxial layers are not uniformly distributed. As seen from figure 4b, they create a mosaic structure with typical grain size of about 200−500 nm. The mosaic structure is believed to be at least partially determined by the analogous structure of the buffer. The misorientation between grains is relatively large due to their rotation around the *c*-axis by about 0.7−1.2 arc deg. Similar growth of GaN layer on Si (111) substrate was reported by Kaiser et al. [17]. As is shown in figure 4a, the dislocations do not change their distribution during growth as they are parallel to the *c*-axis. From these observations it may be concluded that the mosaic GaN structure is created during the initial stage of the growth of GaN layer on AlN buffer. Therefore, the control of the GaN layer structure should concentrate on the investigation of the nucleation and growth of GaN on AlN buffer.

4 Summary and conclusions

The results obtained in this work may be summarized as follows:

(1) Growth of GaN layer by MOVPE is highly anisotropic and even for large misorientations for GaN substrate can lead to flat surface for thick 1−2-μm layers.

(2) Growth of GaN layer on sintered GaN substrate leads to polycrystalline structure due to high misorientation of large size (about 100 nm) of GaN crystallites in the substrate.

(3) Large size of the GaN grains and their three-dimensional misorientation related to the structure of GaN ceramic substrate leads to creation of a large density of extended defects such as dislocations and stacking faults in the layer. The dislocations may create mosaic structure.

(4) Successful growth of GaN epi-layer requires controlled nitridation of the Si surface and the growth of AlN buffer having small size of grains of about 20 nm.

(5) Small GaN grains of about 20-nm size, relatively highly misoriented with respect to the *c*-plane, lead to the creation mosaic structure of the thick GaN layer grown on the Si(111) substrate. No stacking faults are formed in the thick GaN layers. The mosaic structure of thick GaN/Si layer is related to the underlying structure of the buffer layer.

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