TEM investigation of microstructure of semipolar GaN layers grown on nano-patterned Si(001) substrates

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Abstract. The synthesis of III-nitride binary compounds on commercial standard (001) silicon wafers by vapour-phase epitaxy is one of the promising directions for III-nitride technology development. However, the difference between crystal symmetry of Si(001) and wurzite (0001) surface structures is challenge that hinders the development. A use of silicon substrates with nano-patterned surface is one of the solutions to the problem. In this paper we present a transmission electron microscopy study of polar and semipolar GaN layers grown by halide vapour-phase epitaxy and metalorganic vapour-phase epitaxy on nano-patterned silicon (001) substrate. Crystallographic orientation relationships between the silicon substrate and GaN layers is identified. For GaN layers grown by metalorganic vapour-phase epitaxy an effect of SiC buffer layer synthesized by original growth method on their microstructure and surface morphology is under consideration.

1. Introduction
GaN and its alloys are direct band gap semiconductors, what promotes their widespread dissemination in optoelectronics. In recent years, GaN has become the basic material of optoelectronic in the short wavelength region. High-efficiency UV and blue light emitting diodes [1], [2] and laser diodes [3] have been fabricated on the base of GaN. At the same time, special properties of these materials afford application in high-power and high-frequency devices.

The growth of the GaN based structures is basically carried out by heteroepitaxy on foreign substrates, such as Al$_2$O$_3$(0001), SiC(001) and Si(111). The most common methods are growth by metalorganic vapour-phase epitaxy (MOVPE) and halide vapour-phase epitaxy (HVPE). The use of foreign substrates results in the generation of defects such as threading dislocations (TDs), stacking falls (SFs) and grain boundaries (GBs) in the grown heterostructures due to a lattice mismatch and a difference in thermal expansion coefficients between an epitaxial layer and a substrate. These defects considerably reduce device lifetime and performance, and in order to improve their quality – buffer layers or templates are applied.

At the same time, the synthesis of III-nitride binary compounds on silicon wafers with standard (001) orientation by vapour-phase epitaxy seems attractive in view of the possible integration of GaN-based devices with silicon technology. However, the difference between crystal symmetry of Si(001) and wurzite (0001) surface structures is challenge hindered the integration (Si(100) one has four-fold symmetry while GaN(0001) one has six-fold symmetry).

According to [4] there are a few probable alignments on singular Si(001) surface at nucleation stage during GaN or AlN growth: two rotational alignments of polar grains rotated relative to each other by
30° in the lateral plane and four equivalent alignments of semipolar GaN grains with the r-plane (01 12) oriented parallel to the surface. These conditions do not facilitate the single crystal growth and leads to the formation of polycrystalline films with very rough surfaces. What encourages the search for ways to facilitate growth of one particular crystalline orientation.

Further by the same group of authors in [5] were proposed approaches to realize the synthesis of both polar and semipolar orientations separately, varying the growth conditions. Semipolar layers with one orientation of {01 12} could be realized by using silicon misoriented substrates with vicinal surface, but integration with silicon technology requires the use of oriented Si(001) substrates.

Recently for the growth of semipolar GaN layers it was suggested to use patterned Si(001) [6], [7] or nano-patterned silicon substrate (NP-Si(001)) [8]. In this case the nucleation takes place on specific set of {111} facets primary prepared on Si(001) substrate.

This paper presents the results of a transmission electron microscopy (TEM) study of polar and semipolar GaN layers grown on the NP-Si(001) substrates by HVPE and MOVPE respectively. The NP-Si(100) substrates contain the V-shaped grooves on which surface the SiC layer were synthesized by topochemical atom substitution. Crystallographic orientation relationships between the primary NP-Si(100) substrate and GaN layers are identified. A comparison between microstructures of GaN layers grown by MOVPE on NP-Si(001) with and without use of a SiC buffer layer is carried out.

2. Experimental Section
Three samples: one GaN/AlN/SiC/NP-Si(001) grown by HVPE and two GaN/AlN/SiC/NP-Si(001) and GaN/AlN/NP-Si(001) grown by MOVPE have been investigated by TEM.

2.1. Nano-patterned silicon substrate
A dense array of the V-shaped nanogrooves with a period about 90 nm and a groove depth about 70 nm was formed using the wave-ordered structure (WOS) technology [9] followed by (wet- or plasma-chemical) etching of Si(100) substrate. The silicon substrates with miscut angle less than 0.1° were used. Note that the WOS-nanomask (periodic SiN nanostripes) itself has an asymmetric structure, since oblique SiN nanostripes occur on (111) facet and do not occur on (111) facet of the nano-groove.

2.2. Si/SiC template
The thin layer of cubic silicon carbide with a thickness about 100 nm on silicon substrate was synthesized by topochemical atom substitution [10]. In this method the SiC layer is a product of chemical reaction between crystalline silicon and carbon monoxide:

\[ 2\text{Si}^{(cr)} + \text{CO}^{(v)} \rightarrow \text{SiC}^{(cr)} + \text{SiO}^{(v)} \uparrow. \]  

This leads to the formation of a system of voids in the surface region of silicon substrate. The thickness of the defective layer in the substrate reaches 3 μm. According to [11], the volume of pores must be approximately equal to the that of grown silicon carbide. In the electron micrograph, the total volume of voids seems to be somewhat greater. This system of voids should decrease elastic stresses at the interface that are caused by lattice mismatch and a difference in the coefficients of thermal expansion of the substrate and deposited layer.

Earlier a successful use of such Si/SiC templates had already been demonstrated for growth of polar AlN, GaN by MOCVD [12] on Si(111) and semipolar GaN by HVPE [13] on Si(001) misoriented substrates with miscut angle 4-7° along [110] direction.

2.3. GaN Growth
The growth of polar AlN and GaN layers by HVPE was carried out at 1080°C and 1050°C in growth zone respectively. Hydrogen was used as a carrier gas at a ratio of component fluxes H2:NH3 = 2:1. The growth of semipolar GaN layers on NP-Si(001) and SiC/NP-Si(001) substrates by MOCVD was carried out in a modified EpiQuip setup equipped with a horizontal reactor and inductively heated graphite
substrate holder, covered with AlN. At first, an approximately 20 nm thick AlN seed layers were grown. Subsequently, the thick undoped GaN layers with the thickness of about 1 μm were grown at 1025°C. Hydrogen was used as a carrier gas, whereas ammonia, trimethylgallium, and trimethylaluminum were used as precursors. The NP-Si(100) substrates were subjected to a standard cleaning procedure used for the MOCVD method including etching with an aqueous solution of the hydrofluoric acid.

2.4. TEM study
The TEM study of the microstructure, surface morphology and orientation relationships of GaN layers on NP-Si(001) substrate was carried out using a Philips EM420 electron microscope operated at 100 kV. Samples were prepared using a conventional cross-sectional and plane-view TEM specimen preparation technique, including cutting and a tripod polishing followed by a low-angle Ar⁺ ion milling with energies ranging from 4 to 1 keV.

3. Experimental Results
Cross-sections in two mutually perpendicular directions of each sample were prepared for the TEM study. To facilitate the handling of the data denote the direction along and perpendicular to nano-grooves as [110] and [1 10] respectively.

3.1. Polar GaN layer grown by HVPE on NP-Si(001)
The analysis of TEM images (see figure 1 (a)) of the polar GaN layer grown by HVPE on NP-Si(001)/SiC template prepared in cross-section geometry shows that the one is relatively uniform in thickness and has smooth surface. Assuming that direction [110] of silicon substrate is chosen along the nano-grooves (see figure 1 (b)) and [1 10] direction is perpendicular, we get that [1 100] direction of GaN is parallel to the nano-grooves and [1 1 2 0] is perpendicular. The analysis of selective area electron diffraction (SAED) pattern taken at the interface revealed the following orientation relationships: $(002)_{\text{Si}} \parallel (002)_{\text{SiC}} \parallel (0002)_{\text{AlN}} \parallel (0002)_{\text{GaN}}$, $(2 \bar{2} 0)_{\text{Si}} \parallel (2 \bar{2} 0)_{\text{SiC}} \parallel (1 \bar{1} 2 0)_{\text{AlN}} \parallel (1 \bar{1} 2 0)_{\text{GaN}}$ and $(2 \bar{2} 0)_{\text{Si}} \parallel (2 \bar{2} 0)_{\text{SiC}} \parallel (2 \bar{2} 0 0)_{\text{AlN}} (2 \bar{2} 0 0)_{\text{GaN}}$.

Figure 1. (a) – dark field cross-sectional TEM image of the polar GaN layer taken using 0002 reflection; (b) – bright field cross-sectional TEM image of NP-Si(001)/3C-SiC interface. The Si[110] and GaN[1 1 0 0] zone axes are depicted.

According to the plane-view TEM-images it was found that layer consists of misoriented grains with low-angle GBs formed by TDs. Analysis of SAED pattern taken along [0001] direction identified that grains are rotated relative to each other around the c-axis by angle ~1°.

3.2. Semipolar GaN layer grown by MOVPE on NP-Si(001) without use of the SiC buffer layer
The TEM study of the semipolar GaN layer grown by MOVPE on NP-Si(001) without SiC buffer layer prepared in cross-section geometry shows that the layer is heterogeneous in thickness and has rough
surface (see figure 2). The analysis of cross-sectional TEM images and SAED patterns shows that layer is polycrystalline and consists of the grains with one preferential orientation. The following orientation relationships are identified: $[\bar{1}10]_\text{Si} \parallel [\bar{2}110]_\text{GaN}$ and angle between $[1\bar{1}1]_\text{Si}$ and $[0001]_\text{GaN}$ directions $\sim 4.5^\circ$, as shown in inset of figure 2 (a). The crystallographic tilting indicates a significant influence of surface morphology on epitaxy process of GaN films.

3.3. Semipolar GaN layer grown by MOVPE on NP-Si(001) with use of the SiC buffer layer

The TEM study of the semipolar GaN layer grown by MOVPE on NP-Si(001) with SiC buffer layer prepared in cross-section geometry shows that the layer is heterogeneous in thickness and has rough surface as it is shown in figure 3. The analysis of cross-sectional TEM images and SAED patterns shows that layer is polycrystalline and consists of the grains with one preferential orientation. The following orientation relationships are identified: $[\bar{1}10]_\text{Si} \parallel [\bar{2}110]_\text{GaN}$ and $[\bar{1}1\bar{1}]_\text{Si} \parallel [0001]_\text{GaN}$. This orientation corresponds to the nano-structure on the silicon substrate.

The preferential orientation GaN layer grown on NP-Si(001)/SiC template different from the orientation of the layer grown without SiC buffer layer. It means, that thickness and morphology of SiC layer terminated the role of substrate nano-patterning. Also as can be seen from comparison of figures 2 (a) and 3 (a) in case of the GaN growth on NP-Si(001)/SiC template the density of basal SFs is of an order of magnitude greater than in case of the growth on NP-Si(001).
4. Conclusions
The TEM study of the polar GaN layer grown by HVPE on NP-Si(001)/SiC template prepared in cross-section geometry shows that the layer is relatively uniform in thickness and has smooth surface. Assuming that direction $\overline{1}$$T$$10$ of silicon substrate is directed along the nanogrooves and $\overline{1}$$T$$10$ direction is perpendicular, we get that $\overline{1}$$T$$00$ direction of GaN is parallel to the nanogrooves and $[1120]$ is perpendicular. The following orientation relationships are revealed: $(002)_{\text{Si}}$ || $(0002)_{\text{GaN}}$, $\overline{2}$$\overline{2}$$0$_{\text{Si}}$ || $(12\overline{2}0)_{\text{GaN}}$ and $\overline{2}$$\overline{2}$$0$_{\text{Si}}$ || $(2\overline{2}00)_{\text{GaN}}$. According to the plane-view TEM-images it was found that layer consists of misoriented grains with low-angle GBs. Analysis of SAED pattern taken along $[0001]$ direction shows that grains are rotated relative to each other around the $c$-axis by angle $\sim 1^\circ$.

The semipolar GaN layers have been grown by MOVPE on NP-Si(001) substrate with and without use of the SiC buffer layer. The layers are heterogeneous in thickness and have rough surface. Both layers are polycrystalline and consist of the grains with one preferential orientation.

For GaN film grown right on patterned silicon substrate without the use of the SiC buffer layer the following orientation relationships for grains are identified: $[\overline{1}10]_{\text{Si}}$ || $(2\overline{2}1)_{\text{GaN}}$ and $[111]_{\text{Si}}$ almost parallel with $(0001)_{\text{GaN}}$ while for one grown with use of the SiC buffer layer have been found that $[\overline{1}$$T$$00]_{\text{Si}}$ || $(2\overline{2}1)_{\text{GaN}}$ and $[\overline{1}11]_{\text{Si}}$ || $(0001)_{\text{GaN}}$. It means that thickness and morphology of SiC layer terminate the role of substrate nano-patternning and preferential orientation in the second case can be connected with initial substrate miscut. The use of SiC buffer layer allows to get GaN grains by MOCVD with $[\overline{1}11]_{\text{Si}}$ || $(0001)_{\text{GaN}}$ orientation but leads to higher SF density. It was found that the surface consists mainly of the $\{10\overline{1}1\}$ and $(0001)$ facets.

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References
[1] Nakamura S, Senoh M, Iwasa N and Nagahama S, 1995 Appl. Phys. Lett. 67(13) 1868–1870
[2] Kinoshita A, Hirayama H, Ainoya M, Aoyagi Y and Hirata A, 2000 Appl. Phys. Lett. 77(2) 175
[3] Nakamura S, Senoh M, Nagahama S, Iwasa N, Yamada T, Matsushita T, Kiyoku H and Sugimoto Y, 1996 Jpn. J. Appl. Phys. 35 L217–20
[4] Schulze F, Dadgar A, Biasing J and Krost A, 2004 J. Cryst. Growth 272 496–499
[5] Schulze F, Dadgar A, Bläsing J and Krost A, 2004 Appl. Phys. Lett. 84(23) 4747–4749
[6] Izyumskaya N et al., 2013 J. Appl. Phys. 114(11) 35021–9
[7] Reuters B, Strate J, Hahn H, Finken M, Wille A, Heuken M, Kalisch H and Vescan A, 2014 J. Cryst. Growth 391 33–40
[8] Bessolov V et al., 2019 Phys. Status Solidi Basic Res. 256(2) 1–5
[9] Smirnov V K, Kibalov D S, Orlov O M and Graboshnikov V V, 2003 Nanotechnology 14(7) 709–715
[10] Kukushkin S A and Osipov A V, 2018 IOP Conf. Ser. Mater. Sci. Engin. 387 012044
[11] Kukushkin S A and Osipov A V, 2013 J. Appl. Phys 113 249091–7
[12] Kukushkin S A, Osipov A V, Rozhavskaya M M, Myasoedov A V, Troshkov S I, Lundin V V, Sorokin L M and Tsatsul’nikov A F, 2015 Phys. Solid State 57(9) 1899–1907
[13] Bessolov V N, Konenкова E V, Kukushkin S A, Myasoedov A V, Rodin S N, Osipov A V and Shcheglov M P, 2014 Mater. Phys. Mech. 21(1) 71–77