Conference materials
UDC 548.528
DOI: https://doi.org/10.18721/JPM.153.130

Semipolar GaN layers on nanostructured silicon: technology and properties

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Abstract: This paper proposes a method for synthesis of hexagonal GaN on Si(100) and Si(113) substrates, where nanostructures with an element size less than 100 nm are formed on the surface. It has been established that the method of gas-phase epitaxy from metalorganic compounds in a hydrogen atmosphere on such substrates makes it possible to form semipolar layers of GaN(10-11) and GaN(11-22) with a minimum half-width of the X-ray diffraction swing curve of about 30 arcmin. It is shown that during the formation of a semipolar AlN layer at the initial stage of epitaxy, a corrugated surface is formed on NP-Si(100) from the semipolar planes AlN(10-11) and AlN(10-1-1) with counter-directional *c* axes. Then, during the growth of the GaN layer, a transition is made from the symmetrical state of the semipolar GaN(10-11) and GaN(10-1-1) planes to an asymmetric state with the orientation of the *c* axis of the GaN(10-11) layer. That transition is apparently determined by the difference in the values of the surface energy of GaN during epitaxy on the corrugated surface.

Keywords: semipolar gallium nitride, nano-patterned Si substrate, surface energy

Funding: The study was supported by a Russian Foundation for Basic Research grant no. 20-08-00096.

Citation: Bessolov V. N., Konenkova E. V., Rodin S. N., Semipolar GaN layers on nanostructured silicon: technology and properties, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 15 (3.1) (2022) 179–184. DOI: https://doi.org/10.18721/JPM.153.130

Материалы конференции
УДК 548.528
DOI: https://doi.org/10.18721/JPM.153.130

Полуполярные слои GaN на наноструктурированном кремнии: технология и свойства

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Аннотация. Предложен метод синтеза гексагонального GaN на подложках Si(100) и Si(113), на поверхности которой сформирована наноструктура с размером элементов меньше 100 нм. Установлено, что метод газофазной эпитаксии из металлоорганических соединений в атмосфере водорода на таких подложках позволяет сформировать полуполярные слои GaN(10-11) и GaN(11-22) при минимальной полуширине рентгенодифракционной кривой качания около 30 arcmin. Показано, что в процессе образования слоя полуполярного AlN на начальной стадии эпитаксии на NP-Si(100) формируется гофрированная поверхность из полуполярных плоскостей AlN(10-11) и AlN(10-1-1) с противонаправленными «c»-осями. Затем в процессе роста GaN слоя осуществляется переход из симметричного состояния полуполярных GaN(10-11) и

GaN(10-1-1) плоскостей в асимметричное состояние с ориентацией «с»-оси слоя GaN(10-11), причем переход , по видимому, определяется различием величин поверхностной энергии GaN при эпитаксии на гофрированной поверхности.

Ключевые слова: полуполярный нитрид галлия, наноструктурированная кремниевая подложка, поверхностная энергия

Финансирование: Работа выполнена при поддержке гранта РФФИ 00096-08-20.

Ссылка при цитировании: Бессолов В. Н., Коненкова Е. В., Родин С. Н. Полуполярные слои GaN на наноструктурированном кремнии: технология и свойства // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2022. Т. 15. № 3.1. С. 179–184. DOI: https://doi.org/10.18721/JPM.153.130

Introduction

Gallium nitride is an attractive material for various electronic and optoelectronic applications. An important physical property of III-nitrides with a hexagonal crystal structure is that in the heterostructures of these compounds, layers in the direction along the *c* axis are characterized by the presence of piezoelectric polarization, which leads to an internal electric field, to the spatial separation of electrons and holes in quantum wells and a decrease in their radiative recombination (quantum-dimensional Stark effect) [1]. The Stark effect increases the recombination of charge carriers and negatively affects the injection of carriers [2], which significantly reduces the parameters of optoelectronic and electronic devices.

As a solution to these problems related to polarization, using non-polar and semipolar orientations of GaN has been proposed [3]. Currently, attempts are made to synthesize semipolar gallium and aluminum nitrides on micro [4] and nanostructured Si(100) [5] and Si(113) [6] substrates, in which it is proposed to use an inclined face of Si(111) for synthesis. The known methods for creating semipolar layers of GaN(1011) and GaN(1122) on silicon involve microstructured substrates Si(100) and Si(113), respectively, with a one-sided (111)-face in an array of microchannels [7, 8].

Recently, it has been proposed to use both inclined faces of Si(111) and Si(1-1-1) nanostructures for synthesis on Si(100) and Si(113). (Fig.1, *a*). This work is dedicated to developing a technology of semipolar GaN(10-11) and GaN(11-22) layers on V-shaped and U-shaped nanostructured Si(100) and Si(113) substrates, respectively, with element sizes less than 100 nm.

The nanomask was formed according to the technology described in [9].

a) *b*)

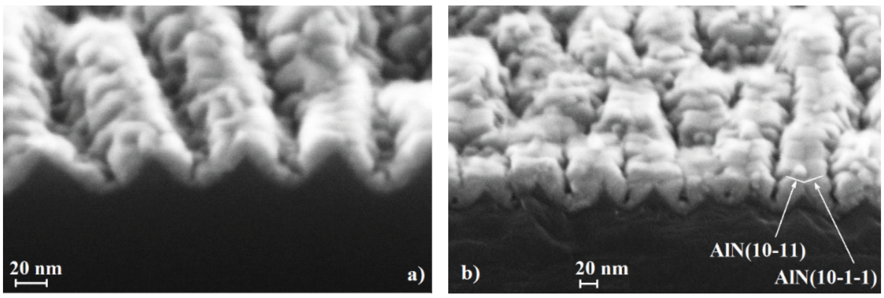

Fig. 1. SEM images of the AlN/NP-Si(100) structure: at the initial stage of growth (*a*), during the formation of a solid layer (*b*)

Materials and Methods

The GaN layers on NP-Si(100) substrates were grown by MOCVD on a modified EpiQuip installation with a horizontal reactor and an induction-heated graphite substrate holder at temperature 1030 °C [5]. Hydrogen was used as the carrier gas, and ammonia, trimethylgallium and trimethylaluminum were employed as precursors. The structures consisted of an AlN layer ~20-40-nm thick and a GaN layer ~1-μm thick. The structural characteristics of the GaN layers were determined by X-ray diffraction, scanning electron microscopy and atomic force microscopy.

A thin AlN layer is formed on the Si(111) and Si(1-1-1) faces at the initial stage of AlN growth on the NP-Si(100) substrate (Fig.1, *a*). A corrugated surface is formed from AlN(10-11) and AlN(10-1-1) layers during further epitaxy (Fig. 1, *b*).

Then the growth of continuous GaN layers on NP-Si(100) occurs in the semipolar direction, as evidenced by the typical nature of the surface morphology (Fig. 2, *a*, *b*) and a minimum half-width of the XRD GaN(10-11) swing curve of about ω_θ = 30 arcmin.

a) *b*)

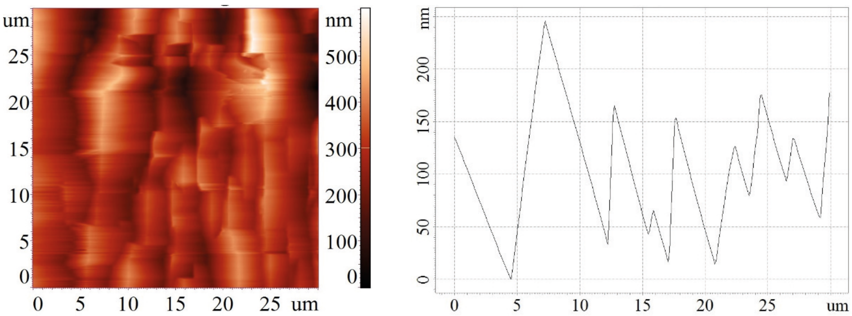

Fig. 2. AFM image and surface profile of the GaN(10-11)/AlN/NP-Si(100) structure

A buffer layer of AlN with a thickness of 20 nm was grown on all structures during epitaxy of AlN and then GaN on NP-Si(113) substrates (Fig. 3, *a*), then either an island layer of GaN(11-22) with dimensions of ~0.05–0.2 μm (Fig. 3, *b*) or a solid layer was grown on the buffer layer thickness ~0.6–1 μm GaN(11-22) (Fig. 4, *a*, *b*). X-ray diffraction analysis showed that the solid layers have a half-width of the X-ray diffraction curve ω_θ ~ 30 arcmin of the semipolar GaN(11-22).

a) *b*)

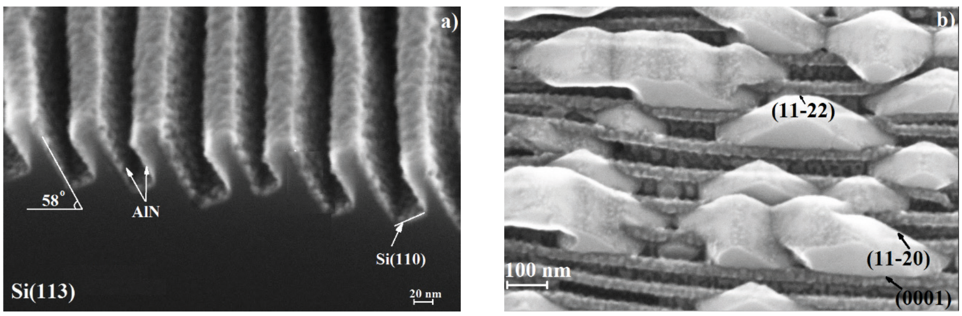

Fig. 3. SEM-images of AlN/ NP-Si(113) structure (a), GaN/AlN/NP-Si(113) for a solid layer formed (*b*)

It can be seen that the AlN layer completely and uniformly covers the NP-Si(113) surface (Fig. 2). The formation of a GaN layer on an NP-Si(113) substrate covered with a buffer AlN layer occurs by an island mechanism on the open faces of Si(111) nanochannels (Fig. 3, *a*). The shape of the crystals of the GaN island layer indicates the presence of (0001), (11-20) and (11-22) faces (Fig. 3, *b*). It can be seen that the island GaN(11-22) layer is given by the direction of the Si(111) plane and tends to form a continuous layer at thicknesses of about 1 mm (Fig. 4).

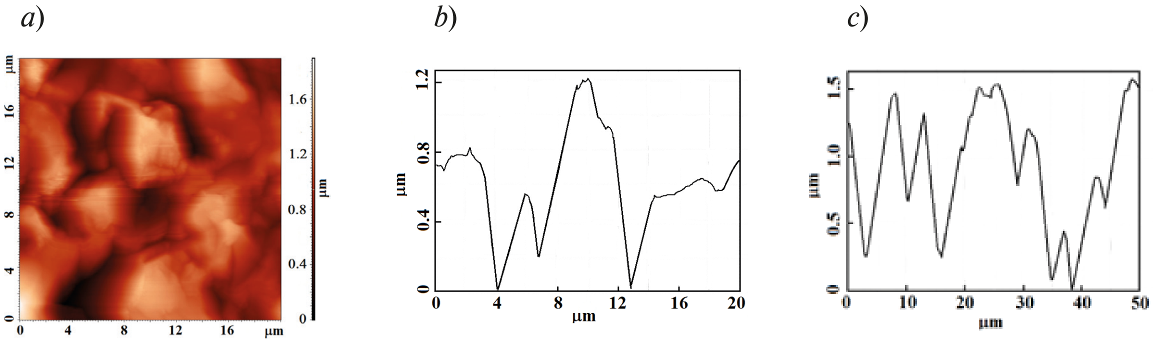

Fig. 4. AFM image (*a*) and surface profiles of the GaN(11-22)/AlN/NP-Si(113) structure in the direction along (*b*) and perpendicular (*c*) to the nanochannel

The surface of the GaN(10-11) and GaN(11-22) layers differs according to atomic force microscopy data (Figs. 2, 4). The surface of the GaN(10-11) layer shows blocks of semipolar gallium nitride elongated along the grooves with a surface inhomogeneity of 150-200 nm (Fig. 2, *b*), and the surface of the GaN(11-22) layer shows rectangular almost square blocks, between which dips of up to 1.3 microns are observed (Fig. 4, *b*). The aspect ratio (the ratio of height to width dimensions) of the blocks is 0,03 for GaN(10-11) and 0,15 for Ga(11-22). (Figs. 2, *b*, 4, *b*).

Results and Discussion

At the initial nucleation stage of the epitaxial AlN layer by MOCVD, AlN(10-11) and AlN(10-1-1) planes form on NP-Si(100) substrates. These planes have different surface energies. The values of surface energies known in the literature are given rather averaged and the influence of surface nanostructuring is not taken into account.

The calculated surface energy of ideal AlN and GaN surfaces with polar and semipolar orientations according to [10] shows that these values are less for polar planes than for semipolar (1-101) and (11-22) planes (Table 1).

Data on the surface energy of ideal GaN surfaces with polar and semipolar orientations in a nitrogen-enriched gas atmosphere show that the energy values also depend on the orientation of the face [11].

It can be seen that the surface energy increases depending on the orientation of the GaN surface in the following order: (0001), (11-22), (1-101), (000-1), (11-2-2) and (1-10-1). The corrugated AlN surface leads to the synthesis of GaN(1-101) and GaN(1-10-1) layers [12], which have different surface energies (Table 2). These differences, as well as differences in the properties of the NP-Si(100) substrate [13], can provide different growth rates of GaN faces in different directions, and lead to the formation of a GaN layer in one direction (Fig. 2, *a*, *b*).

Table 1

Surface energy of ideal AlN and GaN surfaces with polar and semipolar orientations

ev/A^2	(0001)	(000-1)	(1-101)	(11-22)	(11-20)
AlN	0.250	0.255	0.261	0.259	0.170
GaN	0.185	0.228	0.193	0.194	0.141

Table 2

Surface energy of the faces of GaN surfaces in an atmosphere enriched with nitrogen atoms [11]

	(0001)	(000-1)	(1-101)	(1-10-1)	(11-22)	(11-2-2)
eV/A^2	0.204	0.234	0.224	0.257	0.221	0.250

The nucleation of the GaN(11-22) layer occurs on the surface of the AlN/Si(111) face, at higher growth rates than AlN (Fig. 1, *b*). First, an island layer is formed (Fig. 3, *a*, *b*) and after the coalescence stage, a continuous layer with a semipolar GaN(11-22) surface is formed (Fig. 4, *a*, *b*). The different character of the profile of the initial NP-Si(100) and NP-Si(113) leads to different morphology of the GaN(10-11) and GaN(11-22) surfaces. The different morphology of the layers, in our opinion, is associated with the formation of GaN(10-11) at a later stage of growth after the synthesis of the corrugated AlN layer, in contrast to the synthesis of GaN(11-22), which occurs directly on a thin AlN layer on the Si(111) face.

The shape of the insular nucleus (Fig. 2, *b*) shows the presence of the planes *c*-GaN, *m*-GaN and GaN(11-22). The orientation of the nanocrystallites in the array is set by the direction of the plane Si(111) of the nanochannels in NP-Si(113).

The thickness of the layer in the direction of growth [0001] and in the direction of formation of the plane (11-22) is about 100 nm (Fig. 3, *b*), which corresponds to the close values of the surface energy of these planes (Table 1).

The larger size of the nucleus (Fig. 3, *b*) and the larger width of the peaks of the ACM image (Fig. 4,*b*) in the direction along the nanochannels than in the direction perpendicular to them clearly indicates the different diffusion length of Ga-L adatoms during the formation of the insular layer. As is known, $L = (D \cdot t)^{1/2}$, where D is the diffusion coefficient of Ga atoms on the surface, and t is the lifetime of the Ga atom on the surface of the nanostructure. The coefficient D depends on the epitaxy temperature, which has been constant throughout the growth, and we believe that D is the same in both directions and, therefore, the influencing factor t remains. When atoms diffuse along the nanochannels, the adatoms on the surface have a larger value t than in the direction perpendicular to the nanochannels. Perhaps this is due to the presence of nanogrooves in the direction perpendicular to the nanochannels, which lead to a violation of surface diffusion and a decrease in t; and, consequently, leads to a shorter period of undulation and a smaller island size in this direction (Fig. 3, *b*).

Conclusion

Thus, it is shown that during the synthesis of GaN(11-22) by MOCVD in a hydrogen atmosphere at the initial stages of growth, the orientation of the layer is set by the direction of the plane of Si(111) nanochannels in NP-Si(113). The detected effect of transition from the symmetric state of semipolar linear AlN(10-11) nanocrystallites with counter-directional *c* axes, which are formed on symmetrical silicon NP-Si(100) nanogrooves of the substrate, to an asymmetric state with a single orientation of the *c* axis GaN(10-11) layer, according to the model, is determined by the difference in surface energy (10-11) and (10-1-1) faces of the GaN layer.

Acknowledgments

The authors are grateful to Quantum Silicon, LLC (Moscow, Russia) for providing NP-Si(100) substrates, as well to A. V. Smirnov for useful discussions, M. Shcheglov for X-ray structural measurements, and A.V. Solomnikova for AFM measurments.

REFERENCES

1. **Romanov A. E., Baker T. J., Nakamura S., Speck J. S.,** Strain-induced polarization in wurtzite III-nitride semipolar layers, Journal of Applied Physics. 100 (2006) 023522.

2. **Fiorentini V., Bernardini F., Della Sala F., Di Carlo A., Lugli P.,** Effects of macroscopic polarization in III-V nitride multiple quantum wells, Physical Review B 60 (1999) 8849.

3. **Zhang Z.-H., Liu W., Ju Z., Tiam Tan S., Ji Y., Kyaw Z., Zhang X., Wang L., Sun X.W., Volkan Demir H.,** InGaN/GaN multiple-quantum-well light-emitting diodes with a grading InN composition suppressing the Auger recombination, Applied Physics Letters. 104 (2014) 243501.

4. **Honda Y., Kameshiro N., Yamaguchi M., Sawaki N..** Growth of $(1\bar{1}01)$ GaN on a 7-degree off-oriented (0 0 1) Si substrate by selective MOVPE, Journal of Crystal Growth. 242(1) (2002) 82–86.

5. **Bessolov V., Zubkova A., Konenkova E., Konenkov S., Kukushkin S., Orlova T., Rodin S., Rubets V., Kibalov D., Smirnov V.,** Semipolar GaN(10–11) Epitaxial Layer Prepared on Nano-Patterned SiC/Si(100) Template, Physica Status Solidi B. 256(2) (2019) 1800268.

6. **Yu X., Hou Y., Shen S., Bai J., Gong Y., Zhang Y., Wang T.,** Semi-polar (11–22) GaN grown on patterned (113) Si substrate. Physica Status Solidi C. 13(5–6) (2016) 190–194.

7. **Chen G.-T., Chang S.-P., Chyi J.-I., Chang M.-N.,** Growth and characterization of crack-free semipolar {1-101}InGaN/GaN multiple-quantum well on V-grooved (001)Si substrates, Applied Physics Letters. 92(24) (2008) 241904.

8. **Tanikawa T., Hikosaka T., Honda Y., Yamaguchi M., Sawaki N.,** Growth of semi-polar (11-22) GaN on a (113)Si substrate by selective MOVPE, Physica Status Solidi C. 5(9) (2008) 2966–2968.

9. **Smirnov K., Kibalov D.S.,** Wave-Ordered Structure Induced by Nitrogen Ion Beam on Silicon Surface: A Self-Forming Hard Nanomask and Its Applications, In: Proceedings of the 21st International Conference on Ion-Surface Interactions, Yaroslavl, Russia, 22–26 August 2013; Vol. 1 (2013) p.62–66.

10. **Akiyama T., Seta Y., Nakamura K., Ito T.,** Modified approach for calculating individual energies of polar and semipolar surfaces of group-III nitrides, Physical Review Materials. 3 (2019) 023401.

11. **Kawamura T., Akiyama T., Kitamoto A., Imanishi M., Yoshimura M., Mori Y., Morikawa Y, Kangawa Y., Kakimoto K.,** Absolute surface energies of oxygen-adsorbed GaN surfaces, Journal of Crystal Growth. 549 (2020) 125868.

12. **Wang T.,** Topical Review: Development of overgrown semi-polar GaN for high efficiency green/yellow emission, Semiconductor Science and Technology. 31 (2016) 093003.

13. **Bessolov V., Konenkova E., Rodin S., Kibalov D., Smirnov V.,** Formation of semipolar group-III-nitride layers on textured Si(100) substrates with self-forming nanomask, Semiconductors. 55(4) (2021) 471–474.

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Received 18.05.2022. Approved after reviewing 14.06.2022. Accepted 16.06.2022.