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SEMIPOLAR GALLIUM NITRIDE ON SILICON: TECHNOLOGY AND PROPERTIES

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Abstract. This review represents the last achievements in synthesis of epitaxial layers of gallium nitride (GaN) on silicon (Si) substrate. The basic physical, crystallography and physical-chemical properties of semipolar gallium nitride are described. The possible use of semipolar gallium nitride in production of devices for opto- and microelectronics is discussed. The methods of synthesis of semipolar GaN layers are considered with an emphasis on their advantages and drawbacks. Considerable attention is given to the original method of synthesis of semipolar GaN on planar Si(100), Si(210) substrates with interlayers of SiC and AlN. It is based upon the synthesis of thin SiC-layers on the surface Si(100) or Si(210) using the new method of atom substitution. Such an approach makes possible the epitaxial layers of the semipolar GaN to be synthesized on the Si substrate with deflection of the layer from the Si(100) plane by an angle ~ 55° and with a half-width of the X-ray diffraction rocking curve of GaN(1-101) of the order ω_0~20'.

1. INTRODUCTION

Nitrides of the third group, which exhibit some unique properties, have been the subject of much investigation over many years. Beginning in 60[th] of last century, the researchers directed a major effort toward the development of synthesis of epitaxial layers and single crystals of GaN. Along with developing of the synthesis methods, the properties of epitaxial layers GaN have been studied. The main problem which retards the progress in developing of technology of the GaN-layers and crystals was the absence of appropriate substrates for synthesis of nitride crystals. The review [1] deals with the synthesis of GaN, however the synthesis of semipolar GaN is not considered since the considerable study to this subject has only been given last years. Actually, the instruments for optoelectronics are in general constructed on the basis of structures of gallium nitride which are grown in direction parallel to the *c*-axis of a hexagonal GaN crystal (polar structures). The use of polar structures for producing of the quantum-well (QW) III-nitride optoelectronic instruments leads to the Stark effect. This effect is due to the strong piezoelectric polarization in polar structures [2]. The piezoelectric polarization is absent in semipolar structures, and this fact opens bright opportunities for developing devices of new generation on the basis of semipolar (Al,Ga,In)N structures.

Semipolar structures of GaN contain the semipolar plane on their surface. Some of the possible semipolar planes in the crystalline cell of the hexagonal GaN crystal are shown in Fig. 1. The

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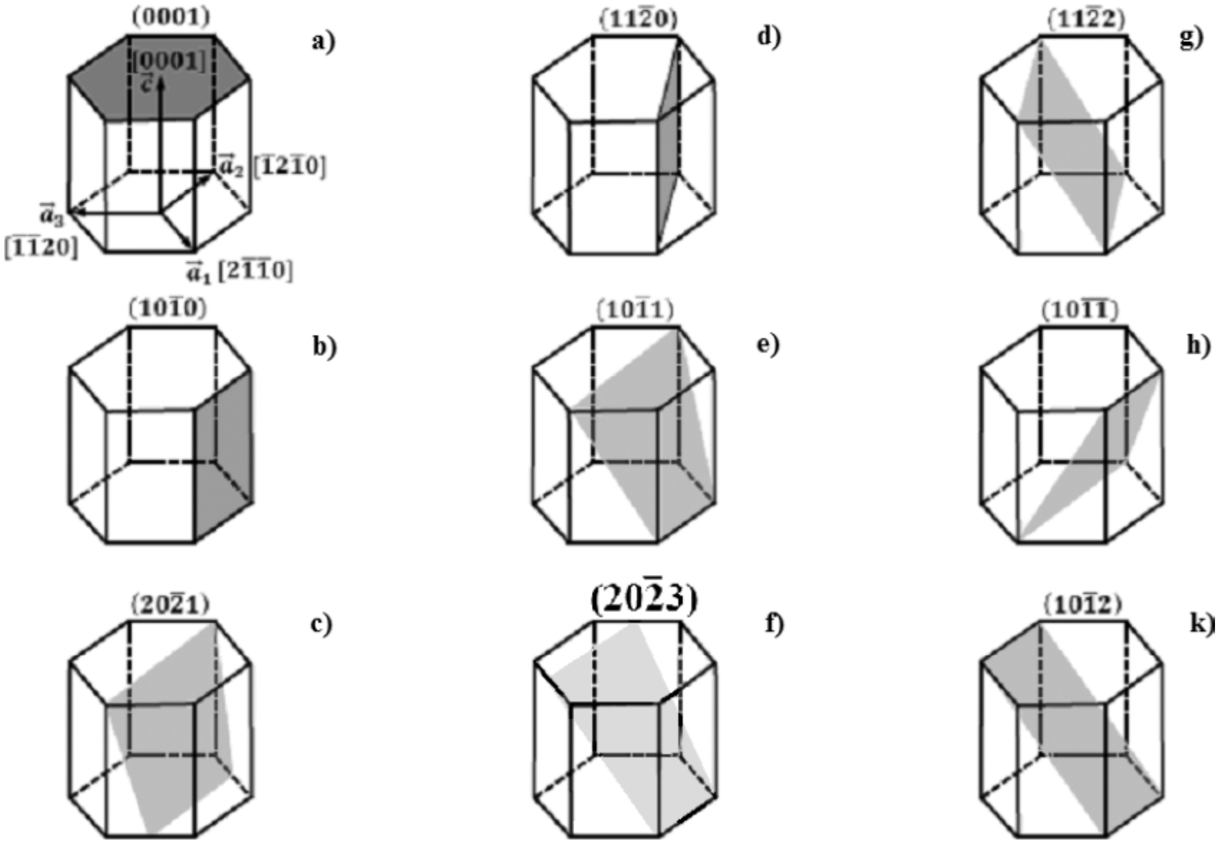


Fig. 1. Different polar (a), non-polar (b), semipolar (c-k) planes in the wurtzite-like crystal of III-nitrides.

values of angles between the semipolar planes and the *c*-axis are given in Table 1.

Table 1. Angles of deflection from the *c*-axis for the different semipolar planes.

Angle	GaN/c-plane	Literature
(10-11) $tg\vartheta = \frac{2c}{\sqrt{3}a}$	61.9°	[3]
(10-12) $tg\vartheta = \frac{c}{\sqrt{3}a}$	43.19°	[4]
(10-13) $tg\vartheta = \frac{c}{2\sqrt{3}a}$	32°	[5]
(11-21) $tg\vartheta = \frac{2c}{a}$	72.91°	[4]
(11-22) $tg\vartheta = \frac{c}{a}$	58.41°	[6]
(11-23) $tg\vartheta = \frac{2c}{3a}$	47.31°	[4]
(20-21) $tg\vartheta = \frac{4c}{\sqrt{3}a}$	75,09°	[4]

In the last two decades all main producers of the instruments on the basis of semiconductors III-nitrides are engaged in the epitaxial growth of the volume gallium nitride. Many companies perform a thorough investigation to develop the technology of synthesis of quasi-substrates for the growth of semipolar GaN. For instance, the Ammono company is under way to develop the ammono-thermal method, and the MTI Corporation institutes - the methods of the chloride-hydride gaseous-phase (HVPE) synthesis of semipolar GaN on the sapphire substrate. At the present time these methods are still rather expensive for commercial production of light-emitting-diodes (LED) and laser structures. The cost reduction is the problem of prime importance in the LED industry, and is of particular value for the use of light-emitting diodes for domestic consumption. The producers of LED's are making efforts to obtain the LED gallium-nitride structures on large-sized substrates. This tendency is conditioned by the fact that the production cost of the LED-chip on a substrate of larger size is significantly lower than that of the similar chip on a substrate of smaller size. At present the producers of LED's are trying to use substrates of size up to 12 in. [7]. The sapphire and carbide silicon substrates of such a di-

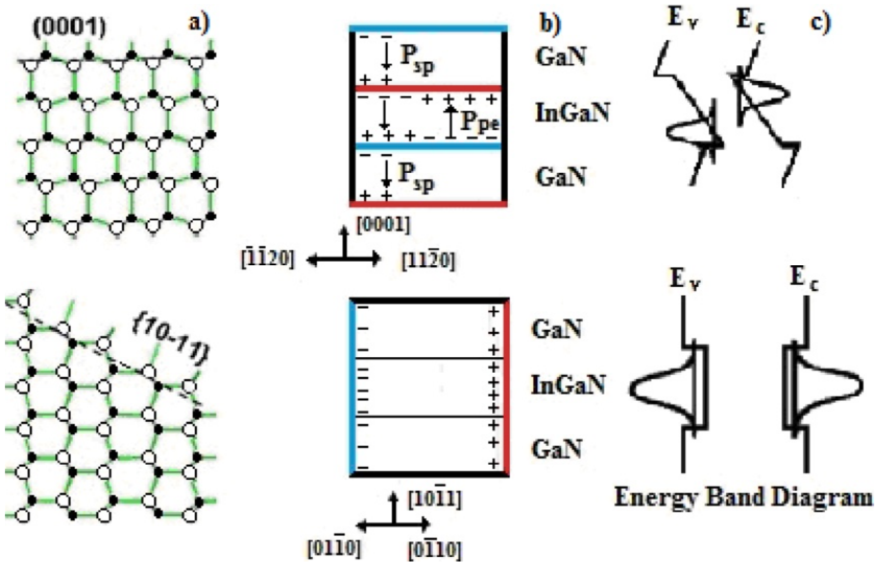


Fig. 2. Schematic sketch of the surfaces GaN(0001) and GaN(10-11), directions of the polarization vector and zone QW-diagrams for the polar and semipolar structures InGaN/GaN. (a) the section of the polar and semipolar structure InGaN/GaN; (b) polarization in the polar and semipolar structures InGaN/GaN; (c) QW-zone diagrams for the polar and semipolar structures.

ameter are not presently produced. Moreover, even though they were produced, the cost would be extremely high. Namely the silicon substrate is therefore one of the most promising substrates for synthesis of structures on the basis of gallium nitride. The use of low-cost silicon substrates of larger size for producing quasi-substrates from semipolar gallium nitride is an attractive way for the cost reduction of laser structures.

2. SPONTANEOUS AND PIEZOELECTRIC POLARIZATION IN HEXAGONAL III-NITRIDE STRUCTURES

The hexagonal layers of III-nitrides are usually synthesized on the plane (0001) of a sapphire substrate. In this case, on each from the two surfaces of the layer of III-nitride, in the course of synthesis there are formed polarization charges. This gives rise an internal electric field in the layer, which has the strong effect on the optical and electrical properties of semiconductors of this kind. Charges on surfaces of semiconductors, as far as it is known, are induced by both spontaneous and piezoelectric polarization. The latter effect is due to the mechanical stresses which arise inside the material. Polarity of an internal electric field depends on the kind of deformation and on the direction of synthesis of crystals, which can occur either from the side on which the gallium atoms come, or from the side on which the nitrogen atoms do (Fig. 2). Mechanical deformation of the epitaxial layer may be caused by its tension or compression.

The internal electric field in the layers with quantum wells, which arises in the polar structures GaN/InGaN/GaN separates the electrons and holes. Such a separation decreases the probability of radiative recombination. This effect is most evident in structures whose thickness of the active InGaN-layers exceeds 100 Å. In order to reduce the influence of this effect, researchers form very thin active layers of thickness commonly in the range from 20 to 30 Å.

The influence of strong electric fields which are caused by polarization effects may be reduced by increasing the concentration of free charge-carriers. For this purpose, either the active areas should be doped or the injection current should be increased. These actions provide screening of internal electric fields, resulting, however, in a shift of a radiation maximum, which is observed in LED's, made on the basis of InGaN, with increasing of the injection current.

It was shown that when the deflection angle of the surfaces of the GaN/InGaN/GaN structure containing a quantum well of thickness 3 nm from the *c*–axis, increases, the sign of polarization of charge-carriers may change [8]. Note that the change of the polarization sign is associated with the percentage of In in InGaN. For instance, in order for the polarization sign to be changed in the structure GaN/InGaN/GaN containing the semipolar planes (11-22), the percentage of indium in the solid solution of

InGaN must be 25-30% [8]. It was proved that the change of the polarization sign in the InGaN/GaN-structures with quantum wells depends on the orientation of the semipolar plane, indium content in InGaN-layer and concentration of the charge-carriers in a quantum well [9,10]. For semipolar layers the polarization in the direction perpendicular to the layer surface decreases and becomes zero in the case of the non-polar layer (Fig. 2). However, at the same time as the polarization field decreases, the mismatching of the crystalline lattices between the layer and the substrate increases. The mismatching of the crystalline lattices results in the formation of stacking faults in the hexagonal lattice, which has negative effect on the light-emission properties of crystals. In order to obtain the necessary characteristics of devices operating on the semipolar InGaN/GaN- structures, the densities of stacking faults in them must be lower than that for the same devices operating on the polar InGaN/GaN- structures [4]. Thus, it is necessary to find out the compromise between a decrease of the polarization field directed along the normal to the surface of the sample, and an increase of the number of stacking faults. The authors of papers [3,11] proposed the technique which makes possible to avoid this problem and synthesize the layers of semipolar GaN. For this purpose, they specifically etched the substrate so that the layer of GaN be synthesized at a certain tilt to the surface of the substrate. As a result of this synthesis procedure, in the course of growth the layers of GaN are closed into the homogeneous semipolar GaN- layer.

3. OPTICAL PROPERTIES OF SEMIPOLAR InGaN/GaN-STRUCTURES SYNTHESIZED ON SILICON SUBSTRATE

The first light-emitting diode (LED) on the basis of GaN-structure on Si-substrate has been synthesized with the use of MBE-method by IBM-company. This diode emitted light in ultra-violet range [12], though it contained a high density of faults in the double hetero-structure GaN/AlGaN [12]. Tran *et al.* [13] were the first who reported on obtaining of GaN-structures on Si by the MOVPE-method. Here they have come against the basic problem of formation of cracks in a GaN-layer on Si-substrates. It became apparent that namely this problem will be the decisive factor hampering the proceeding of synthesis of nitride structures on silicon substrates.

One of the evident solutions of this problem was to use of intermediate layers, and thus reduce elastic stresses between a GaN-layer and a Si-substrate. The authors of work [14], for example, formed the intermediate layers of AlGaN/AlN between the GaN-layer and the Si-substrate, while the authors of [15] produced the intermediate low-temperature (LT) AlN-layers. Using the MOCVD method, they managed to synthesize without cracks the GaN-layers of thickness larger than 1 μm on Si. Later on, the single-crystalline LED-hetero-structures on silicon were synthesized on the basis of the AlN/GaN/AlGaN transition layers [16-22]. In recent years the BridgeLux [7,23] and Osram [24] companies announced the production of LED's of power exceeding 600 mW at current 350 mA. These data were obtained for the chip in which the absorbing surface of the silicon substrate has been removed. One can state that there are no any principal restrictions on producing of the GaN LED's on Si.

At present researchers are pursuing the intensive theoretical [25] and experimental [26] studies of properties of LED-structures synthesized on the basis of nonpolar and semipolar epitaxial GaN-layers. It was demonstrated that the internal quantum efficiency of InGaN/GaN LED's synthesized on the nonpolar m-GaN [27] and semipolar GaN(11-22) [28] planes is essentially higher than that of the similar diodes synthesized on the polar plane of GaN(0001)-crystal. This effect was also observed in the process of growth of nonpolar LED's on silicon substrates [29].

The authors of work [30] obtained the LED InGaN/GaN-structure on the basis of semipolar (1-101)-gallium nitride synthesized on silicon and compared the quantum efficiency of a current of this structure with that of the LED structure grown on polar GaN. It is clearly seen that with increasing density of the current through the structure, the efficiency of the LED on the basis of semipolar GaN is higher than on the basis of polar GaN.

The present review focuses on the semipolar gallium nitride hetero-structures synthesized on silicon substrates. The properties of semipolar structures on the basis of GaN, synthesized on the sapphire substrates are thoroughly considered in reviews [11,31] and aren't touched upon in later sections.

Several different ideas were advanced for the synthesis of semipolar-GaN on Si substrate. In the early stage of investigations the researchers came up with the idea of the use of the LT buffer AlN-layer in which the crystalline seeds of ALN would organize the synthesis of semipolar GaN [32,33]. However, the studies of the synthesis mechanism with the use of LT seeds of AlN have revealed the serious problems which was the synthesis of semipolar GaN in various chaotic directions, resulting in the low crystallography indexes of semipolar GaN. At a later time there was proposed the idea of using the faces of silicon substrate itself in the synthesis of semipolar GaN. Thus, for synthesis of semipolar (1-101)GaN, the mask of SiO_2 with 2 μm-fringes and 1 μm-window is firstly deposited on Si(001)-substrate, then the substrate is subjected to a slow etching to the depth of 1μm that to form the Si(111) faces. Then one of the Si(111) faces is closed by SiO_2, and on the other (-1-1-1)Si-face, using the MOVPE-method, the intermediate AlN-layer of thickness of about 70 nm is synthesized with the subsequent layer of semipolar GaN [34-38]. With the help of such a method of synthesis of semipolar (1-101) GaN, the LED InGaN/GaN structures may be produced on (001)Si [39]. It was shown that if the surface of the Si(112) substrate is prepared by this strategy, then the qualitative m-GaN layers can be synthesized by MOCVD method [29]. With the help of the X-ray diffraction method it was found that the crystallographic deflection of the (0002)AlN plane occurs on the boundary with the silicon substrate [40]. It was discovered that the preliminary carbonization of the (001) Si-surface, tilted by 4° from the direction <001>, also leads to the growth of semipolar orientation of GaN. The MOVPE method was used to synthesize the GaN layer of 2 μm-thickness with (10-12) orientation on the preliminary carbonated Si(001) surface [41]. In this case the authors neither deposited the mask nor purposely etched the Si-surface. The study of luminescence properties of semipolar GaN synthesized on Si substrate has shown that the inclusion of small donors (Si) or (O) does not invoke the negative consequences for the GaN layer [42].

The study of structural characteristics of InGaN QW on GaN(1-101)/Si(001) has shown that along the plane [1-10-2] there occurs the relaxation of elastic stresses through formation of dislocations [43]. In this case the internal quantum efficiency of stimulated radiation of laser structures InGaN/GaN on the basis of semipolar GaN(1-101) on Si(001) turned out to be compatible with the efficiency of radiation from analogous laser structures synthesized on sapphire substrate [44]. From the analysis of the published data on parameters of LED structures and laser structures it follows that for constructing of lasers on the basis of GaN on Si, the semipolar-GaN substrates (Table 2) are preferred over the sapphire substrates.

Recently, for synthesis of semipolar GaN the authors of paper [47] proposed to use the planar substrates of silicon with surfaces (112) and (113). For the same purpose it was also proposed to use graphen [48]. In order to improve the characteristics of GaN-layers the combination of methods HVPE and MBE is sometimes used [49]. Notice that the semipolar gallium nitride on silicon substrate is in general synthesized by MOCVD method, at the same time the synthesis of thick layers of

Table 2. Some characteristics of LED (GaN/Si) structures and of laser structures (semipolar-GaN/semipolar substrate).

Chip size	Wavelength	Output power	Forward Voltage	Reference
LED Lateral devices (unpackaged)				
300×300 μm	455 nm	*W*=0.152 mW*I*=20 mA	*V*=4.5 V *I*=20 mA	[16]
500×500 μm	455 nm	*W* =0.5 mW*I*=20 mA*W* =1 mW *I*=45 mA	*V*=3.5 V *I*= 20 mA	[7]
Vertical devices				
1mm×1mm	Blue	*W*=634 mW *I*=350 mA	*V*=3.15 V*I*= 350 mA	[24]
1.4mm×1.4mm	438 nm	*W*=485 mW *I*=350 mA	*V*=3.2 V *I*= 350 mA	[22]
1.1mm×1.1mm	Blue	W=614 mW I=350 mA	V=3.1 V I= 350 mA	[23]

Semipolar GaN laser diodes			
GaN plane	Threshold current density	Wavelength	Reference
Ga(1100)/GaN(1100)	7.5 kA/cm^2	405.5 nm	[45]
GaN(20-21)/GaN(20-21)	15.7 kA/cm^2	384 nm	[46]

semipolar and nonpolar gallium nitride on the sapphire nitride is successfully conducted by chloride vapor-phase epitaxy (HVPE) [31].

4. SYNTHESIS OF SEMIPOLAR GaN ON Si-SUBSTRATE

4.1. Technology of HVPE of AlN-GaN layers on Si-substrate

The HVPE is commonly used to produce the thick (>100 μm) layers of gallium nitride. Review [1] presents the basic chemical and physical features of the growth of AlN- and GaN-layers by method of HVPE. Analysis has shown that the equilibrium partial pressure of a gas GaCl is significantly higher than that of the gas $AlCl_3$, therefore the synthesis of AlN is much more complicated than the synthesis of GaN. Notice that the synthesis reactions of GaN and AlN are carried out in the gas-carrier: hydrogen, nitrogen, argon. As a gas carrier, hydrogen is neither a precursor nor a product of the synthesis reaction of AlN [1]. According to thermodynamics [1], hydrogen can affect only on the intermediate stages of formation of gas $AlCl_3$, whereas on the reaction of synthesis of GaN hydrogen must have a pronounced effect, since it is a product of this reaction itself. In this connection it would be reasonable to use argon or nitrogen as a gas-carrier in synthesis of AlN, however in this case the purity of a gas-carrier is of a great importance. As known, at present, the attained purification of hydrogen is much higher than for any other gas-carrier appropriate for the growth of films. This factor is of a paramount importance, and it should be taken into account in obtaining of buffer AlN-layers of high quality.

In works [50,51] the HVPE was used to grow the structures GaN/AlN/Si, including the semipolar structures GaN/AlN/Si [51]. The growth of the AlN-layer was produced on the preliminary purified Si(100)-substrates which were rotated with frequency 60 revolutions per minute in a hydrogen flow. The relation of flows was H_2/NH_3 = 2:1, the epitaxy temperature of the AlN-layer varied in the range 900-1100 °C, and temperature of the layer GaN was equal to 1050 °C.

Liquid gallium and aluminum were used as a source of the III-group element. The metal was transported into a deposition zone with the help of gaseous hydrogen chloride. Ammonia was used as a source of nitrogen, and hydrogen as a gas-carrier. In order to remove the silicon surface faults the peroxide-ammonia and peroxide-acid treatments were combined. Before the peroxide-ammonia treatment the substrates were degreased by boiling in organic solvents. Then the substrates were boiled for 20 minutes in a solution NH_3:H_2O_2:H_2O (1:2:5). After washing in deionized water the peroxide-acid treatment was carried out. The etching of the substrates was made in a solution HCl:H_2O_2:H_2O (1:2:5) in a crystal glass for 20 minutes. After that, the substrates were washed in deionized water. In order to remove the film of silicon oxide from the surface of Si-substrate, the etching of the plates was carried out in a solution of hydrofluoric acid HF:H_2O (1:5) for 2 minutes. After washing in deionized water and drying in vapors of isoprophilen alcohol, the substrates were charged in a reactor.

4.2. Synthesis of semipolar-GaN on Si(100)

The epitaxial growth of gallium nitride on silicon substrate at high temperatures presents some difficulties since silicon chemically reacts with gallium [52]. Because of this, the thin buffer AlN-layer is firstly deposited on Si. In the process of epitaxy which is carried out by the MOCVD method on substrates of Si(111) and Si(100), this layer takes in general an orientation (0001) [53]. Then the GaN is deposited on the substrate. In work [51] the structures GaN/AlN/Si(100) were grown by HVPE method. In this case the AlN-layer was grown at temperature 950 °C, and the layer GaN at temperature 1050 °C, relatively.

It is known, that in the synthesis of AlN-layers by HVPE on substrate Si(100) at growth temperature of T=950 °C which is rather low for the epitaxy of nitride compounds, the structure of the layer becomes less ordered. Along with this, the sizes of blocks constituting the film increase. This fact is a consequence of the low velocity of formation of incipient seeds. After incipience, the seeds of a next phase are growing in conditions close to the equilibrium. The velocity of their growth is not high, however, new small centers of crystallization don't appear. The surface of AlN-layer acquires an appearance of faced blocks consisting of nanocrystals with planes of type *c*-AlN(111), *h*-AlN (1102), *h*-AlN(1012), *h*-AlN(1013) and so on (Fig. 3). The similar approach was used in work [33] for the synthesis of low temperature AlN-layer by MOCVD method. The authors of paper [54] pointed out that in the process of the magnetron sputtering of aluminum nitride on a silicon substrate the layer of semipolar orientation AlN(10-13) can be formed.

In study [51] the synthesis of GaN was carried out at high temperature of epitaxy (T=1050 °C). At

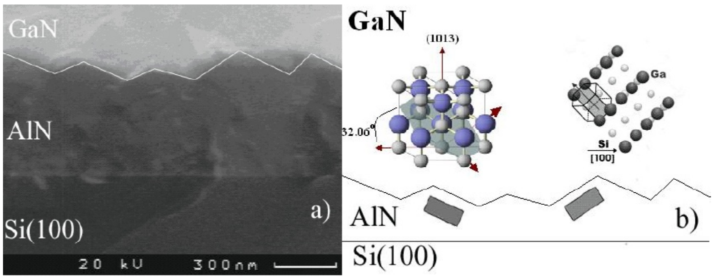


Fig. 3. Growth of the semipolar GaN-film on silicon substrate. (a)- SEM image of the cleavage of the GaN/AlN/Si(100)-structure; (b) schematic drawing of the growing of semipolar GaN.

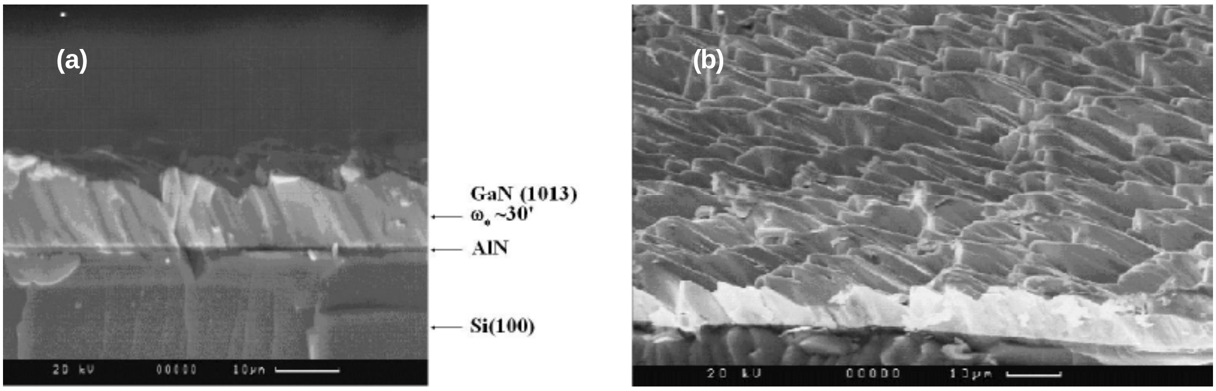


Fig. 4. The SEM microphotograph of the semipolar structure GaN/AlN/Si(100); (a) –image of the cleavage; (b) – image of the surface of the layer.

such a temperature of synthesis by HVPE method the GaN-layers of hexagonal modification are commonly formed [55]. In a given case, the faced blocked surface of the AlN(111)-layer was present on the Si-surface (Fig. 3a). This layer had a significant effect on the structure of the GaN-layer, which finally resulted in formation of semipolar GaN (Fig. 3b). The x-ray diffraction studies have shown that in this case there was formed the epitaxial layer of hexagonal structure GaN. The tilt of surfaces (0001) to the surface of the substrate was ~ 20°-25°. We suppose that the plane of this layer may correspond either to orientation of the face GaN(10-13) or to orientation of GaN(10-14). By our opinion, the intensity of X-ray peaks and the image of the layer cleavage in SEM (Fig. 4a) are unambiguously point to the growth of GaN of a given orientation. A half-width of the rocking curve of the skew-symmetrical reflections (0004) of the GaN-layer was equal to ω_q = 30 arcmin. From the SEM microphotograph of the surfaces of GaN-layers (Fig. 4b) we can see that the layer has the characteristic multilayer structure. The structure of semipolar GaN (10-13) synthesized on Si-substrate in work [51], in its crystallography parameters, was much like the semipolar GaN grown on the sapphire substrate (m-Al_2O_3) by HVPE method [56]. As shown in work [51], the angle between the experimentally grown plane GaN(10-13) and the plane GaN(0002) is approximately 25°. This value of the angle between the planes GaN(10-13) and GaN(0002) is less than the tabulated value ~ 32°. We suggest that this discrepancy is associated with a disorientation of blocks of the film when the buffer AlN-layer is forming. This suggestion is proved by the fact that the similar orientation of the blocks of the AlN-layer was observed by the authors of work [32] in the course of synthesis of buffer AlN-layers on the Si(111)-substrate by MOCVD method.

The photoluminescence of GaN was measured at temperature 77K. Studies have shown that in all spectra there were observed well distinguishable luminescence bands with maximums $h\nu_{max}$ = 3.47 eV, 3.27 eV, and 3.18 eV. These data are presented in Fig. 5. From comparison of these spectra with the spectra of semipolar GaN, synthesized on the sapphire substrate by HVPE method [31], one can asserts that they are in good qualitative agreement. In the photoluminescence spectra the bands with a maximum $h\nu_{max}$ = 3.47 eV are related to the peaks of excitons, while the bands with maximums $h\nu_{max}$ = 3.27 eV and $h\nu_{max}$ = 3.18 eV were prescribed to the donor-acceptor recombination [31]. It is evident that in the case of GaN on Si these luminescence bands can also be explained by analogous recombination mechanisms.

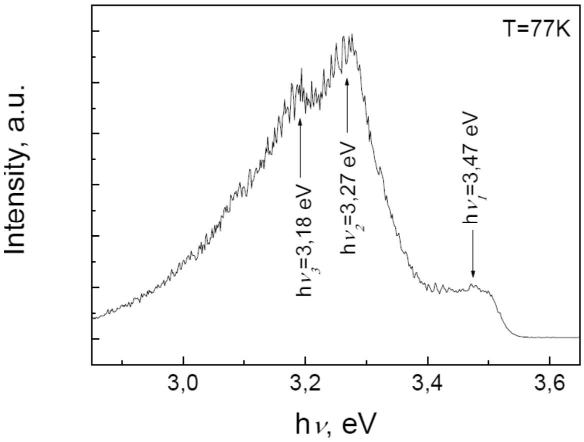


Fig. 5. Luminescence spectrum of semipolar GaN at 77K, synthesized on Si(100).

Thus, the results unambiguously have shown that using AlN as a buffer gas it is possible to synthesize the epitaxial layers of semipolar gallium nitride on Si(100) substrate by HVPE method. For the best of GaN-layers the half-width of the rocking curve of X-ray diffraction was ω_0(0004) = 30 arcmin.

5. SYNTHESIS OF SEMIPOLAR GaN ON TEMPLATE SiC/Si

5.1. The substitution method – a new type of epitaxy of SiC on Si

In works [57,58] generalized in reviews [59,60], there was discovered and developed an essentially new method of synthesis of thin epitaxial films of SiC on Si. On the basis of this method there was worked out the semi-industrial technology for the production of substrates of single-crystalline silicon nanocarbide on silicon wafers of diameter 3 - 6 in. The developed method for producing films of silicon carbide on silicon differs fundamentally from all others existing methods and technologies which are used at present for the growth of single crystals, films and nano-structures. This method is based on the substitution of part of atoms inside a silicon substrate by carbon atoms. For this purpose the carbon atom is preliminary introduced into the interstitial position of the silicon lattice, while the neighboring silicon atom is removed, which results in producing the silicon vacancy. In this case in the near-surface area of the silicon lattice there appears an ensemble of the dilatation dipoles which are the stable complexes consisting of elastically attracting centers of dilatation, i.e. of the carbon atom in an interstitial position and of the silicon vacancy. The energy of elastic interaction between the point faults depending on their crystallography disposition in silicon was studied in [58]. The synthesis of elastic dipoles of this type occurs due to the chemical reaction between silicon and carbon monoxide. It was shown that for the silicon crystal the most favorable displacement of the dilatation dipole is position perpendicular to the plane (111). In this case practically the whole dilatation elastic energy relaxes exclusively by virtue of dipoles, resulting in a high quality of the silicon carbide films. The orientation of the film is conditioned by an “old” crystalline structure of the original matrix of Si, and not only by the surface of the substrate, as it is usually realized in traditional techniques of growing the films. Upon completion of the chemical transformation, the mechanical dipoles, which have performed their function, decompose into the fault-free silicon carbide film and pores lying under its surface. The temperature and pressure are chosen so, that the nucleation of SiC-seeds can occur concurrently and with equal velocity.

One of the most important properties of nano-SiC synthesized by an atom substitution method is the unique possibility of producing of semipolar layers of hexagonal crystals and, particularly, of semipolar epitaxial GaN-layers. We mentioned above that to produce the more perfect in structure layers of semipolar-GaN on Si, the surface Si(100) is masked and treated in a chemical etching substance. In this case there is a possibility to obtain the planes Si(111) with a tilt 55° to the plane Si(100). These are precisely the planes on which GaN(1-101) is grown. When using the substitution method [57-60], the formation of the longitudinal wedge-shaped bump of silicon carbide occurs in a natural way. In order to form the Si-surface with SiC-layer obtained by an atom substitution method the substrates masking the surface aren’t used as also aren’t the chemical etching substances. If one use the face of surface Si (100), which is tilted out of the direction <100> by 2°-10° to the direction <011>, and then heat this surface above 600 °C, then the plane (100) of silicon, according to thermodynamics, will be coated by steps. The planes which are at the top and at the bottom are the planes (100), and the steps will be bounded by planes (011). Along directions <011> the silicon lattice is most “loose”, which is due to the specific crystallographic structure of Si- lattice. Along this direction, according to studies [58-60], the CO-molecules move inward of Si, perpendicular to the steps. The Si-surface is saturated by CO, and the interaction of Si with CO occurs with formation of dipoles “silicon-vacancy-carbon atom-silicon matrix”. Since the elastic attraction between the silicon vacancy and carbon

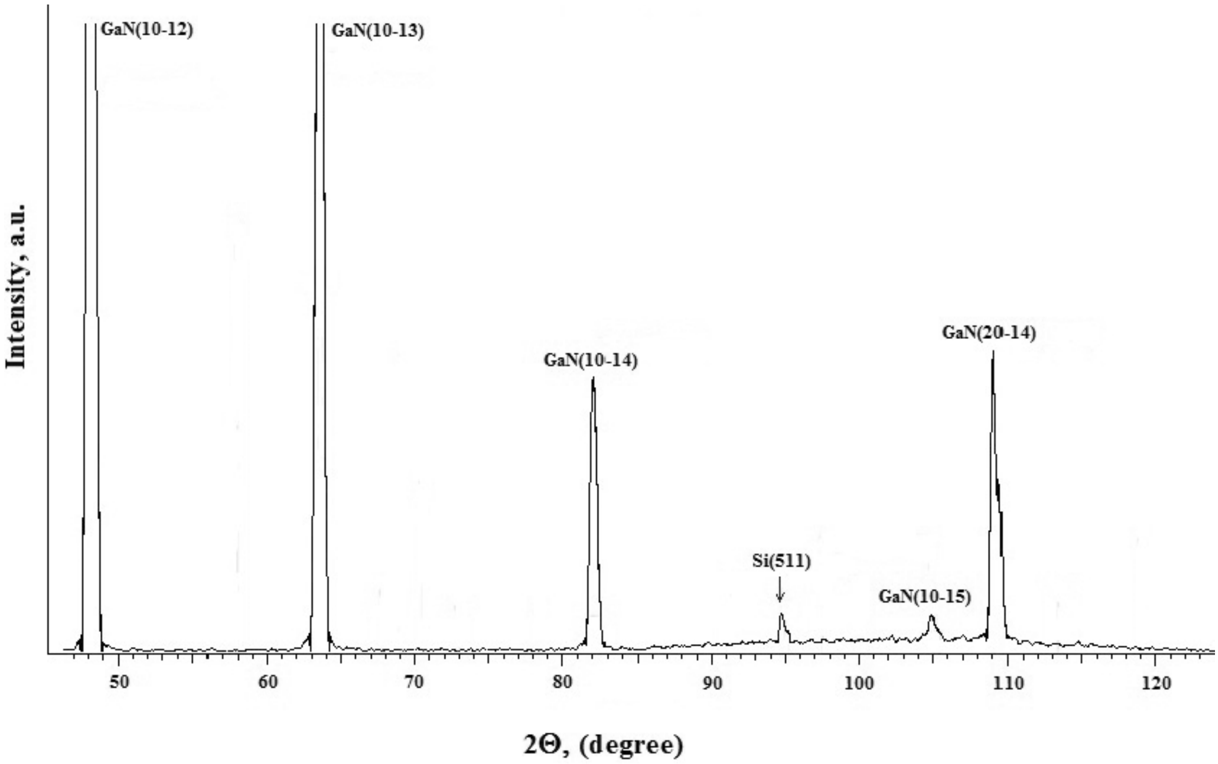


Fig. 6. X-ray diffragram of semipolar GaN-layer grown on SiC/Si(210) [61,62].

atom in the silicon matrix is maximum along the direction <011>, part of the step (011) of Si just turns into the face (111) of SiC. As known, an angle between the planes (111) and (100) in a cubic crystal with a diamond lattice is ~55°. As a result, the longitudinal wedge-shaped bump of silicon carbide is formed. It has a tip extending over the platform of the step, and a tilted face which reaches the platform lying at the bottom of the step, giving the tilt angle of ~55°. In general case, the surface Si(100) will consist of a set of parallel steps which appear as triangular prisms (lateral faces of small pyramids) [60]. Notice that since the symmetry of such prisms is inherent in both cubic and hexagonal crystals, it follows that the symmetry is not degenerated. This means that on these surfaces can grow crystals with a cubic symmetry as well as with hexagonal. And not the orientation of the substrate will be a decisive factor (what is rather important) but the thermodynamic conditions such as the temperature and density of falling fluxes of the components from which the layer grows. If under given conditions the hexagonal modification is stable, then namely it will grow, and if the cubic structure is stable, then the latter will. This opens up fresh opportunities for growing of hexagonal semipolar crystals. It has been just this method which was firstly realized in works [61,62]. The authors synthesized the epitaxial layer of semipolar-GaN on the surface Si (210) [61,62], and the semipolar GaN-layer on the surface (001) Si [63]. In both cases the role of a buffer layer was played by SiC-layer synthesized by an atom substitution method.

5.2. Synthesis of semipolar-GaN on SiC/Si (210)

At first, on the surface (210) of Si-substrate, using the atom substitution method [57-60], there was formed the SiC-layer. Further on, the substrate Si(210) with SiC-layer was prepared for the growth of AlN and GaN, according to the technique described in Section 4.1. Then with the use of the HVPE method, the thin layer of hexagonal aluminum nitride (~100 nm) has been grown. The growth of this compound was carried out at temperature 950 °C. Thereafter, the GaN-layer of thickness ~10 μm has been grown on the surface of AlN-film. The growth of the GaN-layer was carried out at temperature 1050 °C. Thus, the conditions for synthesis of nitride compounds were precisely the same as they were for the synthesis of AlN and GaN on the substrate of Si (001) not containing the buffer layer of SiC [51]. We described these conditions of the growth in Section 4.1. Hydrogen served as a gas–carrier.

The X-ray studies of GaN-layers grown on AlN/3C-SiC/Si(210) gave the following results [61,62].

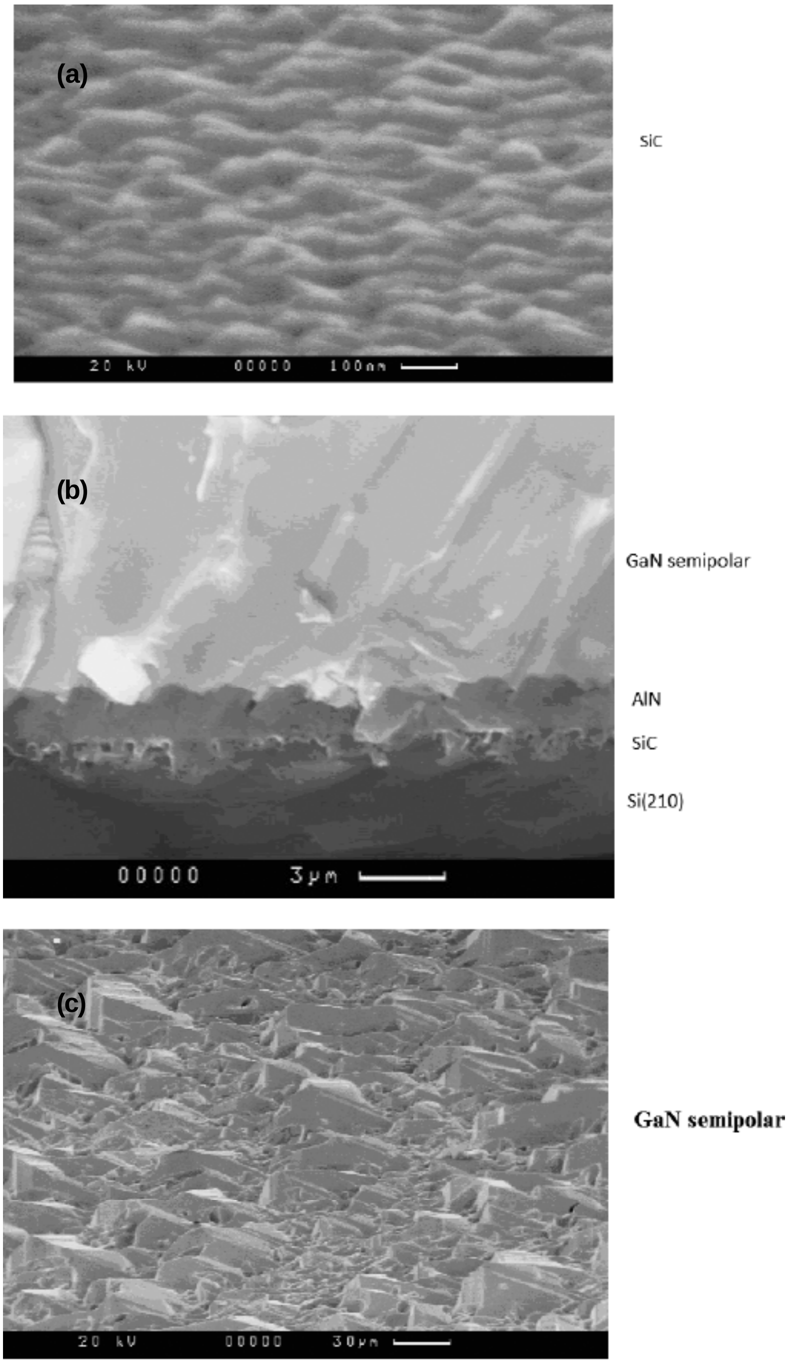


Fig. 7. The SEM images of the original Si (210)-surface with SiC layer (a); the image of the cleavage (b) and of the surface (c) of GaN-layer synthesized on SiC/Si(210).

The film of gallium nitride is hexagonal. In the process of the epitaxial growth the GaN-layer is crystallized in the form of blocks resembling a “layering pie” and consisting of parallel “scales”. The crystallographic orientation of the planes of the blocks varied from GaN(10-15), through GaN(10-14) and GaN(10-13), to GaN(10-12) (Fig. 6). The half-width of the rocking curve of the skew-symmetrical reflection (1124) of the GaN-layer was ω_q = 25 arcmin. In the process of growing of the layer, there occurs an inclination of growing blocks (10-12) of hexagonal GaN-crystal from the plane Si(001) by an angle ~ 43°.

Fig. 7 shows the SEM images of the original surface Si(210) with the SiC-layer (Fig. 7a); the image of the cleavage (Fig. 7b) and the image of the surface of the GaN-layer synthesized on SiC/Si(210) (Fig. 7c). As seen from these images, the GaN-layer has a characteristic semipolar structure of the surface, which is similar to the structure synthesized by authors of work [56].

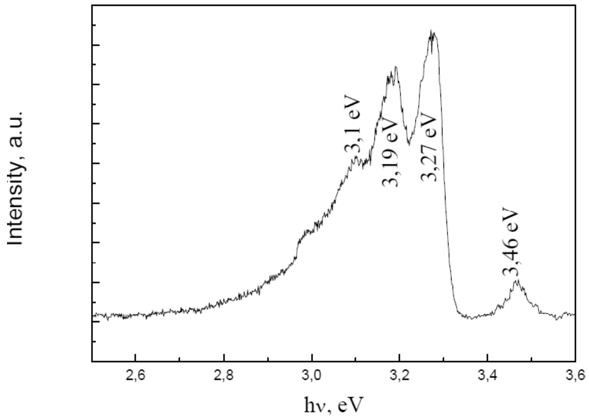


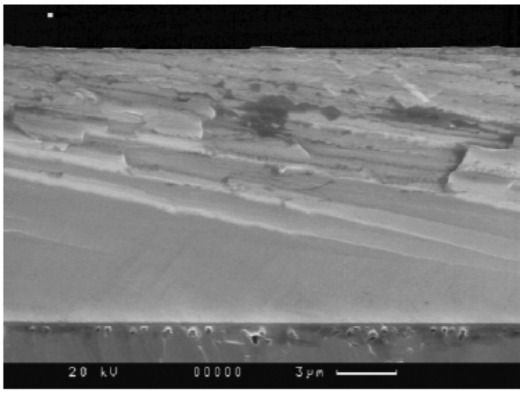
Fig. 8. The photoluminescence spectrum of GaN semipolar at 77K, synthesized on Si(210).

The photoluminescence spectrum of GaN synthesized on SiC/Si(210) are shown in Fig. 8. There are clearly observed the luminescence bands with maximums $h\nu_{max}$ = 3.46, 3.27, 3.19, and 3.1eV (Fig. 8). Such bands are also observed in the synthesis of GaN semipolar on the sapphire substrate with the use of the HVPE method. We described above the reasons of their occurrence. However, in a given case, there appears the additional small peak with energy $h\nu_{max}$=3.1 eV (see Fig. 8). We suggest that it could be due to the presence of the cubic modification c-GaN. Authors of work [64] have found the analogous peak in the c-GaN/3C-SiC structures doped by carbon. Cubic gallium nitride can be present on the faces of the 3C-SiC(100) layer at initial stage of growth, as was observed by authors of paper [41].

5.3. Synthesis of GaN-semipolar on SiC/Si(100)

As in the case of the surface of Si(210), authors of work [63] synthesized the SiC-layer on the surface Si(100) by the substitution method of atoms [57-60]. The synthesis of layers was carried out on the substrates Si(100) of thickness 300 μm with different disorientations of the surface (2°,4°,7°) in direction <011>. The SiC layers were synthesized at temperature 1270 °C. The thickness of any SiC film was about 30 nm. Thereafter, the AlN-layer of thickness 300-1000 nm was synthesized on the surface of SiC-films by HVPE method. Further, on the surface of the AlN-layer the basic GaN-layers of thickness 2-15 μm were synthesized (Fig. 9).

The structures GaN/AlN/SiC/Si(001) were investigated with the use of the X-ray diffractometry, the scanning electron microscopy, the transmission electron and atomic-force microscopy. The results of X-ray diffractometry point to the presence of the equally ordered GaN-layers whose deflection angle from the *c*-axis polar position of a wurtzit crystal is about 42° for the substrate Si(001) with disorientation 7°. Analysis of the microelectronogram (Fig. 10a) taken from the area of interface of GaN/AlN/3C-SiC/Si(001) heterostructure have shown that the polar *c*-axis of gallium nitride is parallel to direction [111] of the silicon substrate, i.e. the deflection of the layer from the polar position of the *c*-axis of a wurtzit crystal is about 55° without regard for disorientation of the substrate (Fig. 10a). The image of the structure obtained by the method of high-resolution tunnel transmission electron microscopy (TEM) have shown that the angles between the normal to the substrate and the normal to the lines of stacking faults, which are as a rule present in the direction [0001]GaN, are 48° and 51° for the structures synthesized on the substrates with disorientation 7° and 4°, respectfully (Fig. 10b). These results agree with the results obtained from the microelectronogram. Based on the results of the X-ray diffractometry and on microelectronograms, one can state that the combined technology of the solid-phase epitaxy of *3C*-SiC and the HVPE of GaN on

a)


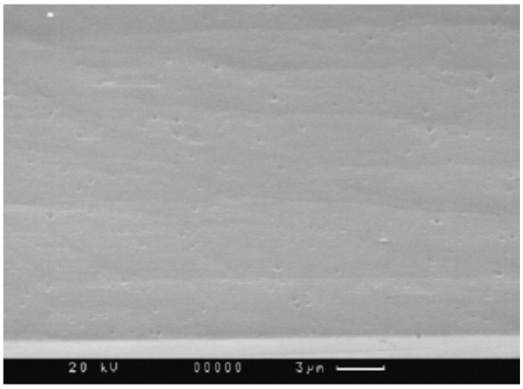
b)


Fig. 9. The SEM images of the cleavage (a) and of the surface (b) of GaN-layer synthesized on AlN/SiC/Si(100).

a) b)

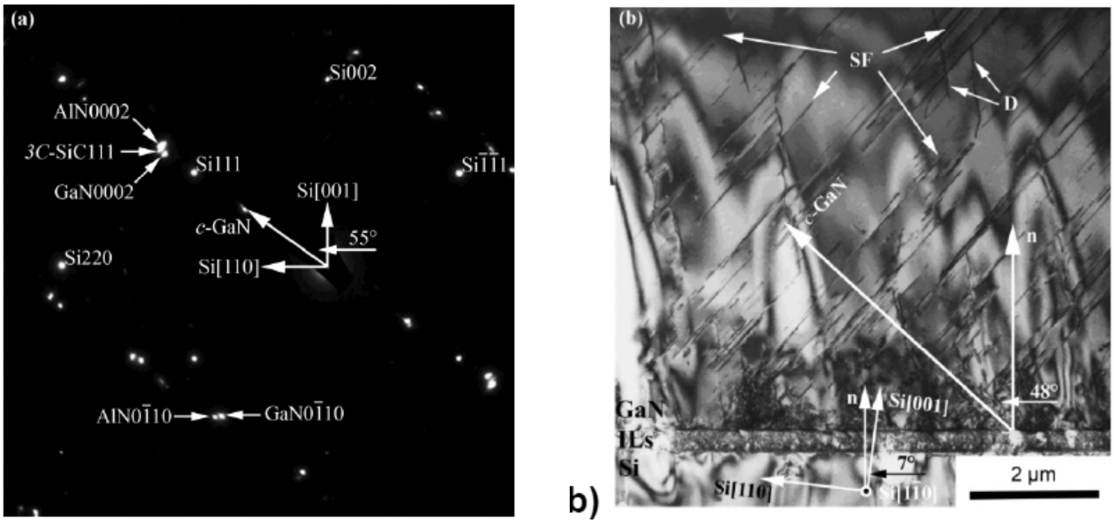


Fig. 10. Microelectronogram (a) and TEM image (b) of GaN/AlN/*3C*-SiC/Si(001) heterostructure. Arrows mark the stacking faults (SF) arising in direction [0001] of gallium nitride, the dislocations (D) and the intermediate layers of AlN and 3C-SiC (ILs).

the disoriented substrate Si(100) makes possible the synthesis of GaN(10-12)- semipolar or GaN(1-101)- semipolar.

The GaN/AlN/SiC/Si(100) structures, according to the X-ray-diffraction analysis, had a bending of cylindrical character. The radii of curvature *R* of bendings were measured for all films in two mutually perpendicular directions R_a,<2-110> and $R_ñ$,<1-101>, relatively (see Table 3). Measurements of radii have shown that the film was most strongly curved only in one of the directions, and, depending on the thickness of the GaN-layer, the most significant changes of radii occurred in direction <11-23>. It turned out that the thicker is the GaN-layer, the more is the difference between bendings in directions <11-20> and <11-23>. The X-ray measurements have also shown that the half-widths of the X-ray diffraction rocking curves (FWHM) for the reflection (1-101)GaN, for all heterostructures with different disorientations of the surface (2°, 4°, 7°) are practically the same and are about ω_0 ~ 20-24 arcmin.

When the SEM-image of the surface GaN/AlN/SiC/Si(001) is compared with the data obtained in studies [31,47], it is apparent that the surface and the cleavage of the surface have the characteristic structure of semipolar GaN .

Fig. 11 presents the AFM images of the surface of GaN-layer. It is clear that in direction <2-110> there appear cracks in the layer (Fig. 11a), and in direction <1-101> there are no cracks (Fig. 11b). In direction <1-01> the roughness of the layer is about 80 nm, which is significantly less than in direction <2-110> (Fig. 11).

The photoluminescence spectra from the samples of GaN semipolar were made at temperature 77K and 300K. At temperature 77K in the photoluminescence spectra of GaN-layers there was observed a band with maximum h_{max} = 3.454 eV, (FWHM=51 MeV), while at temperature 300K a band with maximum h_{max} = 3.39 eV, (FWHM=96 MeV). The latter may be interpreted as a recombination band of an exciton coupled on an acceptor [55] (Fig. 12). A small width of the exciton band unambiguously proves a high quality of the GaN-semipolar layer.

Table 3. Dependences of the radii of curvature on the thickness.

thickness t_{GaN} μm	disorientation Si $_{(001)}$	Experiment R_a, m <11-20>	Model R_c, m <11-23>	R_a, m <11-20>	R_c, m <11-23>
~2	2°	-1.6	-1.8	-2.74	-3.96
10	4°	-0.4	-1.6	-0.54	-0.79
14	7°	-0.25	-1.4	-0.39	-0.56

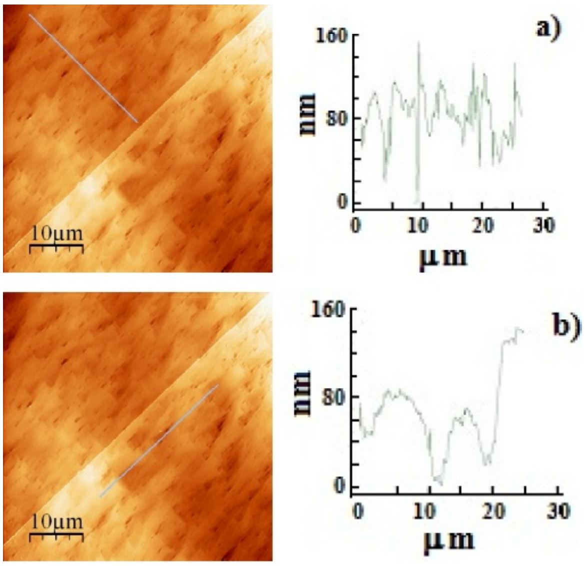


Fig. 11. The AFM image of the surface of GaN-layer in the GaN/AlN/SiC/Si(001) heterostructure, and the profiles of distribution of the surface irregularity in different directions: (a) – direction <2-110> ; (b) – direction <1-101>.

5.4. Structural characteristics of epitaxial GaN-layers on silicon: the effect of buffer layers

The microstructure of GaN-layers on SiC/Si was studied by the TEM method. The cross-sections of Si(011) were prepared by a cleavage and the subsequent mechanical polishing with the aid of etching by Ar+ ions.

Studies by TEM method have shown that the layers of gallium nitride consist of separate blocks of different orientation (Fig. 13) The size of blocks varies from 0.1 to 10 m. The blocks have faults whose density ranges from 2×10^5 to 3×10^6 cm^{-2}. Fig. 14 presents the typical areas of the diffraction structure taken from the samples shown in Fig. 13.

Most of GaN blocks exhibit the wurtzite structure and are parallel to [21-10]GaN.

From Figs. 14-16 follows that the orientation of the *c*-axis of most wurtzite GaN blocks is along the

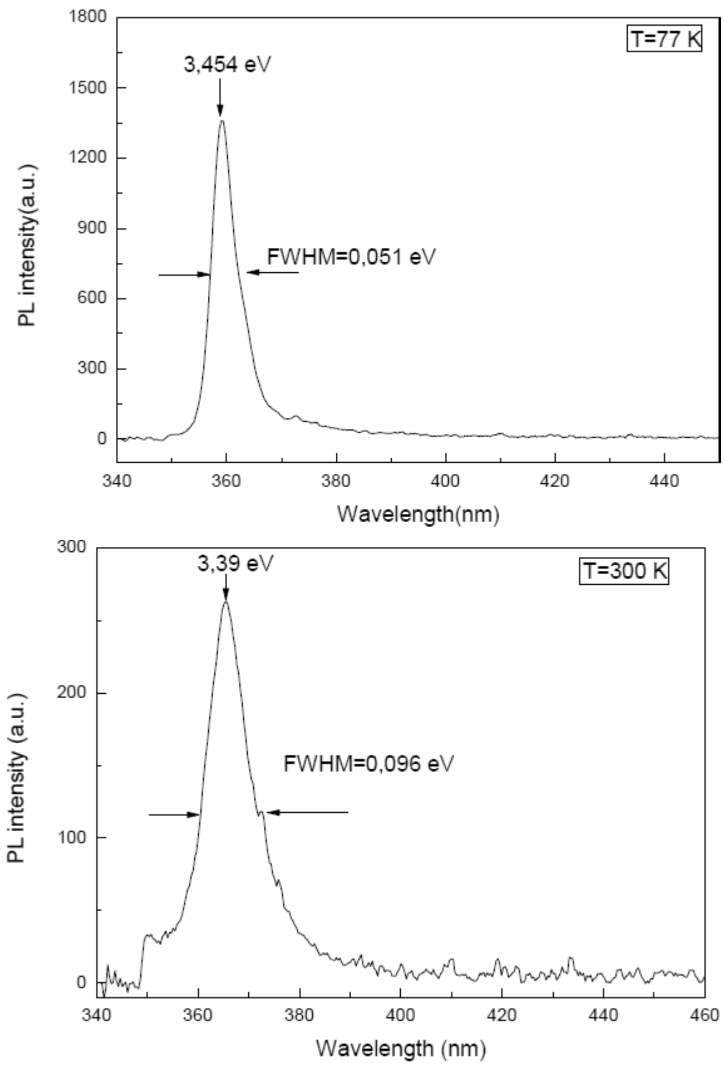


Fig. 12. The photoluminescence spectra of GaN/AlN/SiC/Si(100): a - 77K, b - 300K.

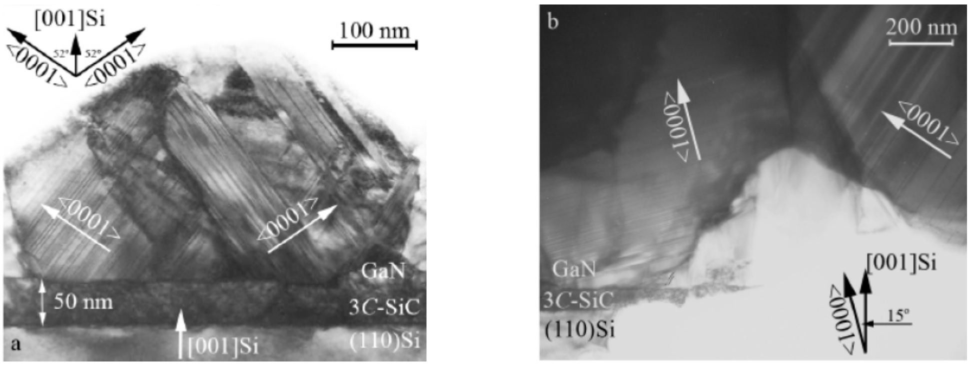


Fig. 13. Cross-sectional TEM images of different areas of GaN/SiC/(001)Si heterostructure.

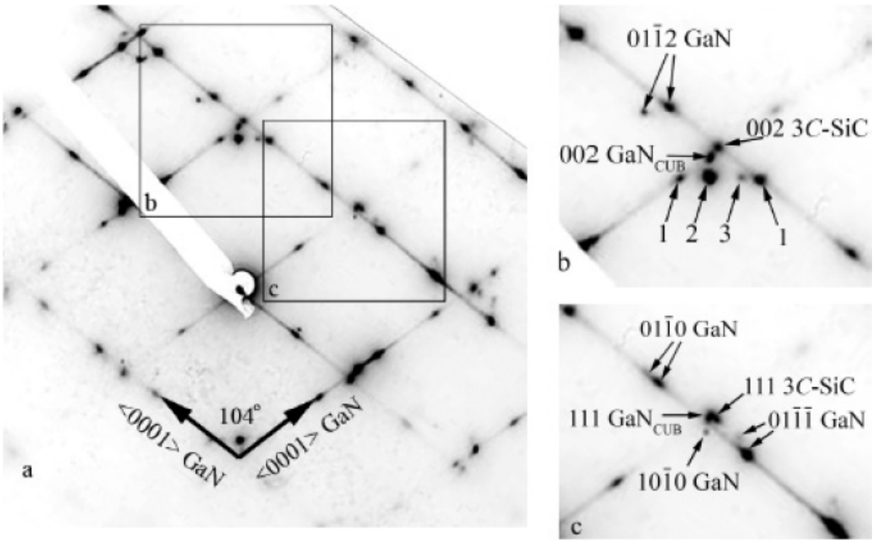


Fig. 14. a: DP taken from the area shown in Fig. 4a; b, c: magnified photo of the DP outlined in Fig. 13. In Fig. 14b the diffraction spots 1 and 3 correspond to wurtzite grains with common *a*-axis. *C*-axis of the grain giving the diffraction spot 1 is parallel to <111>Si.

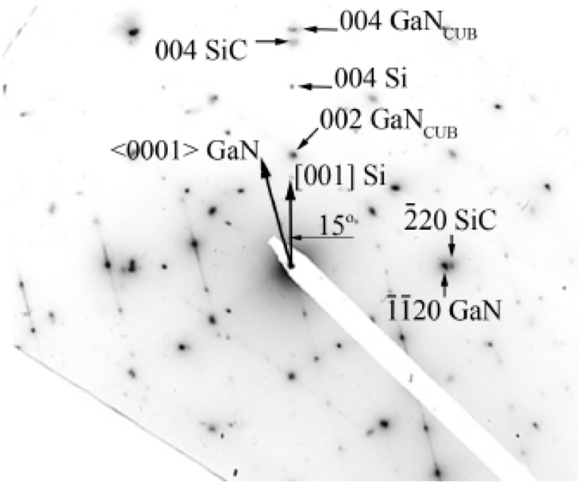


Fig. 15. DP recorded from the area represented in Fig. 13b.

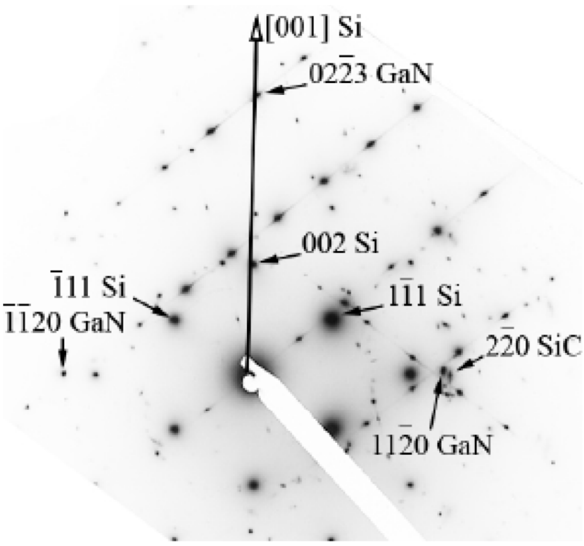


Fig. 16. DP recorded from the interface area.

direction <111> of the substrate. The *c*-axis deflects from the normal to the surface by an angle 52°. It means that the majority of the GaN blocks are oriented along the semipolar direction of the hexagonal lattice, as they do in [39].

We determined the Miller indexes of the interface planes by the electron diffraction method. The reflection marked in fig.16 indicate onto direction [0223]. The planes (02-23)GaN and (001)Si coincide. If we take into account that the [2110] direction of the layer coincides with the direction [110] of the substrate, then the following epitaxial relations must hold: (02-23)GaN || (001)3C-Si || (001)Si and [2110]GaN || [110]3C-SiC || [110]Si. A mismatch between the lattices of GaN and 3C-SiC is equal to 3.5% in the [110] SiC direction and 10% in [110] direction. It means that there must exist also the GaN blocks with a tilt of *c*-axis from the normal to the surface by an angle 52° around [110] SiC. It is proved by the presence of direction [11-20] on the diffraction pattern outlined in Fig. 15. All possible orientations of GaN blocks in the figure can be obtained by turning through 45° around [001]3C-SiC-axis. The *c*-axis of a few blocks deflects by 15° from the normal to the surface (Fig. 15). Analogously, it was found that for these blocks: (0117)GaN||(001)3C-Si||(001)Si and [2110]GaN||[110]3C-SiC || [110]Si. According to the results of [37], it was suggested that the thin GaN-layer, which can arise above the cubic buffer layer, starts to grow on facets {111}, and only thereafter the wurtzite GaN-layer grows on facets {111} of the hexagonal GaN-layer. There is a certain tilt between the plane of the hexagonal GaN-layer and the 3C-SiC plane (Figs. 14 and 15). This tilt is due to the difference in the lattice constants of the hexagonal GaN-layer and the buffer 3C-SiC layer.

Thus, the *c*-axis of most wurtzite GaN blocks synthesized on SiC/Si substrates is oriented by angle 52° to the surface in relative to normal.

6. THE MODEL OF SYNTHESIS OF GaN SEMIPOLAR ON SiC/Si

In Section 5.1 we describe in details the specific features of the synthesis of SiC on Si by a substitution method of atoms. Namely this peculiarity ensures to synthesize the semipolar gexagonal crystals on silicon coated by a layer of silicon carbide synthesized by method used in [57-60].

For the synthesis of semipolar gallium nitride on a silicon substrate, it is necessary to ensure the following. The difference in parameters of the lattices must be minimal at the temperature of epitaxy. Free energy of formation of the layer in the semipolar direction must be less than the free energy of layer formation in the polar direction. Namely on these principles the idea of synthesis of semipolar GaN-layer is just based. For this purpose, at first, the steps of the disoriented surface Si(100) must be transformed into the quasi-step surface SiC with face (111). This face just determines the direction of the synthesis of the crystal. At second, the difference in lattices of crystals SiC and GaN is provided by putting of the buffer layer AlN on SiC. This hypothesis is proved by the data obtained in investigations of the X-ray diffraction of the GaN/SiC/Si. The data on X-ray diffraction have found the ordered layers of semipolar GaN with surface orientation either (1-101) or (10-12) on the surfaces Si (001) with surface deflection by 2°, 4°, and 7°. The structures GaN/SiC/Si have the cylindrical bend. It follows from measurements of radii *R* of curvature in two mutually perpendicular directions, that the structure is bended most strongly in one of the directions only. Moreover, it turned out that this bend depends significantly on thickness of the GaN-layer. On the cleavage of the surface passing along the plane (1010) of the substrate, the characteristic tooth-like relief is revealed (see Fig. 4). Such a change of the surface morphology in the layers of orientation (1120) is associated with the sophisticated mechanism of growth of layers. By our opinion, the quasi-step surface of the silicon carbide layer stimulates the formation of seeds of the hexagonal semipolar AlN, and further on of GaN with an angle 35-47° with the *c*-axis and the plane SiC(001). Thereafter, the GaN seeds, having the shape of elongated ridges, merge. These seeds are insignificantly disoriented in relative to each other. For this reason, many blocks are formed on the substrate, which, with increasing of the thickness of the layer, widespread absorbing smaller seeds, i.e. their coalescence takes place. Once the seeds are merged, the surface acquires the orientation (1-101) or (10-12). It has the characteristic appearance of many pyramids with the smooth edges and apex, and the parallelogram at the bottom.

The banded relief occurs at intersection of the layer surface by the stacking faults of different kind (basial and prismatic). These defaults are formed near the heterostructure and are due to high density of stacking faults.

The bend of the surface is due to the difference in the coefficients of thermal expansion (CTE) of silicon and gallium nitride. The anisotropic deformation of the structure Si(011)/SiC/AlN/GaN(1-101) is probably associated with the difference of these coefficients along the *a*- and *c*-directions of the wurtzite semipolar crystal of gallium nitride. Actually, at room temperature the coefficients of thermal expansion of GaN-lattice in the direction of the *c*- and *a*-axis are equal to: α_c GaN ~ $3.52\cdot10^{-6}$ 1/K, α_a GaN ~ $3.93\cdot10^{-6}$ 1/K [65], and the CTE of silicon at the same temperature is α_{Si} ~ $2.6\cdot10^{-6}$ 1/K [66].

As known, with cooling of the films of polar gallium nitride synthesized on the silicon substrate, the layer of gallium nitride is in the state of isotropic

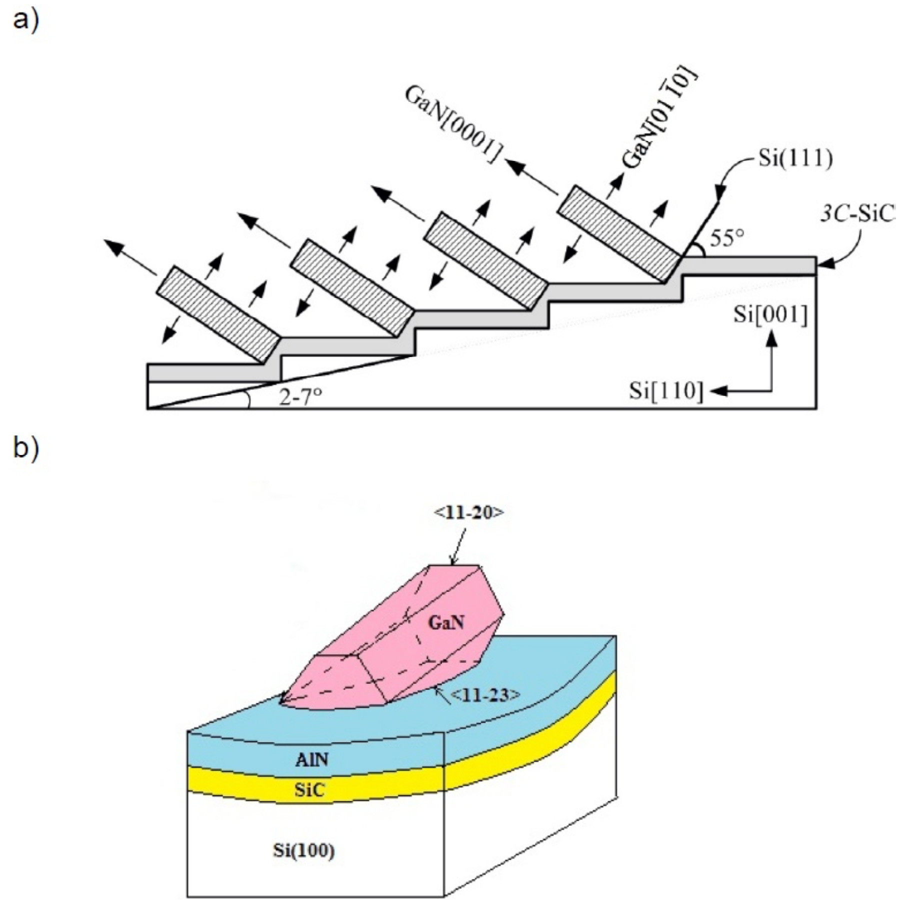


Fig. 17. The process of formation of semipolar GaN on SiC/Si(100); (a)- sequent stages of the synthesis process of semipolar GaN on SiC/Si(100), schematic drawing; (b) – a general appearance of the heterostructure GaN(1-101)/AlN/SiC/Si(100).

compression. It is associated with the fact that CTE of GaN for the lattice "*a*" is larger than the CTE of Si [67]. With increasing of the thickness of the GaN-layer the curvature radius of the structure decreases. We suppose that the thin intermediate layers of ÇÑ-SiC and AlN contribute insignificantly into the bend of the GaN/Si layer. Hence, with cooling of semipolar gallium nitride, synthesized on the silicon substrate, from the epitaxy temperature to room temperature, not only the difference in CTE of the GaN *a*-lattice and Si, but the difference in CTE of the GaN *c*-lattice and Si (Fig. 17b) will make its own contribution. Since the CTE of the lattices "*a*" and "*c*" differ, with cooling of the structure GaN(1-101)/AlN/SiC/Si(100), the anisotropic bend of this layer will occur. Let us estimate the anisotropic bend of semipolar GaN on Si(100)-substrate, using the formula (1) obtained in the [66] Si(100). We will assume that for the GaN the CTE in the semipolar plane is equal to the CTE in the plane (100).

$$\frac{1}{R}=6m\varepsilon\left(\frac{h}{h_2}\right)\left(\frac{1+h}{1+mh\left(4+6h+4h^2\right)+m^2h^4}\right), \quad (1)$$

where: $m = E_1/E_2$, $h = h_1/h_2$;

$\varepsilon = (\alpha_1 - \alpha_2)\Delta T$,

E_1 is Young's modulus of GaN = 210 GPa, E_2 = 165.6 GPa is Young's modulus of Si;

h_1 – thickness of GaN , h_2 – thickness of Si;

α_1-CTEs of the GaN *a*- lattice and GaN *c*- lattice, α_2 – CTEs of Si-lattice;

ΔT – the difference between the temperature at which the bend is calculated and the temperature at which the bend does not occur.

The estimates obtained for the curvature radii of the bend of GaN-layer in direction <21-10> and <1-101> on the Si(100)-substrate are given in Table 3.

7. CONCLUSION

A new method of the synthesis of semipolar layers of gallium nitride on plane substrates Si(210) and Si(100) was proposed and realized by the HVPE technique. The semipolar direction of the synthesis of GaN is conditioned by formation of 3D-pyramidual projections of SiC(111). It was experimentally shown that a combination of an atom substitution method, used in the synthesis of silicon carbide on silicon, and a method of hydride-chloride epitaxy of gallium nitride on a silicon carbide “template” can result in formation of epitaxial layers of semipolar gallium nitride. The angle of X-ray diffraction for GaN(1-101) was ω_0 ~20'. The proposed approach to the synthesis of semipolar gallium nitride on silicon substrate essentially differs from both the methods with using of the low-temperature buffer layer [32] and methods with using of the masked surface with faces Si(111) on the surface Si(100) [34]. This approach could be promising in the production of ‘templates’ for the structures of the gallium-nitride optoelectronics.

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REFERENCES

[1] S.A. Kukushkin, A.V. Osipov, V.N. Bessolov, B.K. Medvedev, V.K. Nevolin and K.A. Tsarik // *Rev.Adv.Mater.Sci*. **17** (2008) 1.

[2] F. Bernardini, V. Fiorentini and D. Vanderbilt // *Phys.Rev. B* **56** (1997) R10024.

[3] Y. Honda, N. Kameshiro, M. Yamaguchi and N. Sawaki // *J. Cryst. Growth* **242** (2002) 82–6.

[4] A. Romanov, E. Young, F. Wu, A. Tyagi, C. Gallinat, S. Nakamura, S. Denbaars and J. Speck // *J. Appl. Phys. 109* (2011) 103522.

[5] B. Ma, D. Jinno, H. Miyake, K. Hiramatsu and H. Harima // *Appl.Phys.Lett.* **100** (2012) 011909.

[6] T. Tanikawa, T. Hikosaka, Y. Honda, M. Yamaguchi and N.Sawaki // *Phys. Status Solidi C* **5** (2008) 2966–8.

[7] D. Zhu, D.J. Wallis and C.J. Humphreys // *Rep.Prog.Phys*. **76** (2013) 106501.

[8] K. Kojama, H. Kamon, M. Funato and Y. Kawakami // *Phys.Stat.Solidi C* **5** (2008) 3038.

[9] W. Scheibenzuber and U.T. Schwarz // *Phys.Stat.Solidi B* **248** (2011) 647.

[10] L. Schade, U.T. Schwarz, T. Wernicke, J. Rass, S. Ploch, M. Weyers and M. Kneissl // *Appl. Phys. Lett*. **99** (2011) 051103.

[11] F. Scholz // *Semicond. Sci. Technol.* **27** (2012) 024002.

[12] S. Guha and N.A. Bojarczuk // *Appl. Phys. Lett.* **72** (1998) 415.

[13] C.A. Tran, A. Osinski, R.F. Karlicek Jr. and I. Berishev // *Appl. Phys. Lett*. **75** (1999) 1494.

[14] H. Ishikawa, G.-Y. Zhao, N. Nakada, T. Egawa, T. Jimbo and M. Umeno // *Jpn. J. Appl. Phys.* **38 (**1999) L492.

[15] A. Dadgar, J. Blasing, A. Diez, A. Alam, M. Heuken, J. Christen and A. Krost // *Jpn.J.Appl.Phys.* **39** (2000) L1183.

[16] A. Dadgar, M. Poschenrieder, J. Blasing, K. Fehse, A. Diez and A. Krost // *Appl. Phys. Lett.* **80** (2002) 3670.

[17] T. Egwa, T. Moku, H. Ishikawa, K. Ohtsuka and T. Jimbo // *Japan. J. Appl. Phys.* **41** (2002) L663–4.

[18] B.S. Zhang, H. Liang, Y. Wang, Z.H. Feng, K. Ng and K.M. Wand Lau // *J. Cryst. Growth* **298** (2007) 725.

[19] H. Ishikawa, T. Jimbo and T. Egawa // *Phys. Status Solidi* c **5** (2008) 2086.

[20] W.E. Fenwick, N. Li, M. Jamil, T. Xu, A. Melton, S. Wang, H. Yu, A. Valencia, J. Nause, C. Summers and I.T. Ferguson // *Proc. SPIE* **7231** (2009) 723119.

[21] H. Kim *et al.* // *Proc. Natl Acad. Sci.* **108** (2011) 10072.

[22] J.Y. Kim *et al* // Proc. SPIE 8262 (2012) 82621D.

[23] D. Zhu *et al*, http://bridgelux.com/media-center/press-releases/bridgelux-announces-new-breakthrough-in-gan-on-silicontechnology- for-solid-state-lighting.

[24] Osram 2012, http://ledsmagazine.com/news/9/1/19.

[25] J. Bhattacharyya, S. Ghosh and H.T. Grahn // *Phys.Status Solidi B* **246** (2009) 1184.

[26] D. Iida, A. Miura, Y. Okadome, Y. Tsuchiya, T. Kawashima; T. Nagai, M. Iwaya, S. Kamiyama, H. Amano and I. Akasaki // *Phys.Status Solidi A* **204** (2007) 2005.

[27] X. Li, X. Ni, H.Y. Liu, F. Zhang, S. Liu, J. Lee, V. Avrutin, Ü. Özgür, T. Paskova, G. Mulholland, K.R. Evans and H. Morkoç // *Phys.Status Solidi C* **8** (2011) 1560.

[28] Y. Ji, W. Liu, T. Erdem, R. Chen, S. Tiam Tan, Zi-Hui Zhang, Zh. Ju, X. Zhang, H. Sun, X. Wei Sun, Y. Zhao, S.P. DenBaars, S. Nakamura and H. Volkan Demir // *Appl.Phys.Lett* **104** (2014) 143506

[29] X. Ni, J. Lee, M. Wu, X. Li, R. Shimada, Ü. Özgür, A.A. Baski, H. Morkoç, T. Paskova, G. Mulholland and K.R. Evans // *Appl.Phys.Lett.* **95** (2009) 101106.

[30] Ch.-H. Chiu, D.-W. Lin, Ch.-Ch. Lin, Zh.-Y. Li, W.-T. Chang, H.-W. Hsu, H.-Ch. Kuo, T.-Ch. Lu, Sh.-Ch. Wang, W.-T. Liao, T. Tanikawa,

Y. Honda, M. Yamaguchi and N. Sawaki // *Applied Physics Express* **4** (2011) 012105.

[31] A. Strittmatter, J.E. Northrup, N.M. Johnson, M.V. Kisin, P. Spiberg, H. El-Ghoroury, A. Usikov and A. Syrkin *// Phys.Status Solidi B,* **248** (2011) 561.

[32] F. Schulze, J. Bläsing, A. Dadgar and A. Krost //*Appl. Phys. Lett*. **84** (2004); 4747.

[33] F. Schulze, A. Dadgar, J. Bläsing and A. Krost // *Journal of Crystal Growth* **272** (2004) 496.

[34] T. Hikosaka, T. Narita, Y. Honda, M. Yamaguchi and N. Sawaki // *Appl.Phys.Lett*. **84** (2004) 4717.

[35] T. Hikosaka, Y. Honda, M. Yamaguchi and N. Sawaki // *J.Appl.Phys.* **101** (2007) 103513.

[36] T. Hikosaka, T. Tanikawa, Y. Honda, M. Yamaguchi and N. Sawaki // *Physica Status Solidi C* **5** (2008) 2234.

[37] T. Tanikawa, Y. Honda, M. Yamaguchi, H. Amano and N. Sawaki // *Phys.Status Solidi B* **249** (2012) 468.

[38] T. Sugiura, E.-H. Kim, Y. Honda, H. Takagi, T. Tsukamoto, H. Andoh, M. Yamaguchi and N. Sawaki // *Phys.Semicond*. **1399** (2011) 503.

[39] N. Sawaki and Y. Honda // *Science China. Technol. Sciences* **54** (2011) 38.

[40] H.F. Liu, L. Zhang, S.J. Chua, D.Z. Chi // *J. Mater. Sci.* **49** (2014) 3305.

[41] Y. Abe, J. Komiyama, T. Isshiki, S. Suzuki, A. Yoshida, H. Ohishi and H. Nakanishi // *Materials Science Forum* **600-603** (2009) 1281.

[42] N. Izyumskaya, F. Zhang, S. Okur, T. Selden, V. Avrutin, U. Ozgur, S. Metzner, C. Karbaum, F. Bertram, J. Christen and H. Morkoc // *J. Appl. Phys.* **114** (2013) 113502.

[43] Z.H. Wu, T. Tanikawa, T. Murase, Y.-Y. Fang, C.Q. Chen, Y. Honda, M. Yamaguchi, H. Amano and N. Sawaki // *Appl. Phys.Lett.* **98** (2011) 051902.

[44] T. Murase, T. Tanikawa, Y. Honda, M. Yamaguchi and H. Amano // *Physica Status Solidi* C **8** (2011) 2160.

[45] M.C. Schmidt, K.-Ch. Kim, R.M. Farrell, D.F. Feezell, D.A. Cohen, M. Saito, K. Fujito, J.S. Speck, S.P. DenBaars and Sh. Nakamura // *Jpn. J.Appl.Phys.* **4** (2007) L190.

[46] D.A. Haeger *etal*. // *Appl. Phys. Lett.,* **100** (2012) 161107.

[47] R. Ravash, A. Dadgar, F. Bertram, A. Dempewolf, S. Metzner, T. Hempel, J. Christen and A. Krost // *Journal of Crystal Growth* **370** (2013) 288.

[48] P. Gupta, A.A. Rahman, N. Hatui, M.R. Gokhale, M.M. Deshmukh and A. Bhattacharya // *Journal of Crystal Growth* **372** (2013) 105.

[49] A. Moldawer, A. Bhattacharyya, L. Zhou, D.J. Smith and Th.D. Moustakas // *Phys. Stat. Solidi C* **11** (2014) 585.

[50] V.N. Bessolov, V.M. Botnaryuk, Yu.V. Zhilyaev, E.V. Konenkova, N.K. Poletaev, S.D. Raevski, S.N. Rodin, S.L. Smirnov, Sh. Sharofidinov, M.P. Shcheglov, H.S. Park and M. Koike // *Tech.Phys.Lett.* **32** (2006) 674.

[51] V.N. Bessolov, Yu.V. Zhilyaev, E.V. Konenkova, N.K. Poletaev, Sh. Sharofidinov, M.P. Shcheglov //*Technical Physics Letters* **38** (2012) 9.

[52] H. Ishikawa, K. Yamamoto, T. Egawa, T. Soga, T. Jimbo and M. Umeno // *J.Crystal Growth* **189-190** (1998) 178.

[53] S. Joblot, E. Feltin, E. Beraudo, P. Vennéguès, M. Leroux, F. Omnès, M. Laügt and Y. Cordier // *J.Crystal Growth* **280** (2005) 44.

[54] S.B. Jhong *et al*. // *Next-Generation Electronics International Symposium. Kaohsiung. Taiwan.* p.96, (2010).

[55] T.B. Wei, Z.Q. Hu, R.F. Duan, X.C. Wei, J.K. Yang, J.X. Wang, Y.P. Zeng, G.H. Wang and J.M. Li // *Journal of the Electrochemical Society* **157** (2010) H721.

[56] T. Wernicke, S. Ploch, V. Hoffmann, A. Knauer, M. Weyers and M. Kneissl // *Phys.Status Solidi B* **248** (2011) 547.

[57] S.A. Kukushkin and A.V. Osipov // *Phys.Solid State* **50** (2008) 1238.

[58] S.A. Kukushkin and A.V. Osipov // *J.Appl.Phys.* **113** (2013) 4909-1.

[59] S.A. Kukushkin, A.V. Osipov and N.A. Feoktistov// *Phys.Solid State* **56** (2014) 1457.

[60] S.A. Kukushkin and A.V. Osipov // *J. Phys. D:Appl.Phys.* **47** (2014) 31300-1 .

[61] V. Bessolov, E. Konenkova, M. Shcheglov, Sh. Sharofidinov, S. Kukushkin, A. Osipov and V. Nikolaev// *Phys. Status Solidi C* **10** (2013) 433.

[62] V.N. Bessolov, E.V. Konenkova, S.A. Kukushkin, V.I. Nikolaev, A.V. Osipov, Sh. Sharofidinov and M.P. Shcheglov // *Technical Physics Letters* **39** (2013) 274.

[63] V.N. Bessolov, E.V. Konenkova, S.A. Kukushkin, A.V. Mysoedov, A.V. Osipov, S.N. Rodin, M.P. Shcheglov and N.A. Feoktistov// *Technical Physics Letters* **40** (2014) 802.

[64] A. Zado, E. Tschumak, J.W. Gerlach, K. Lischka and D.J. As // *J. Cryst.Growth* **323** (2011) 88.

[65] R.R. Reeber and K. Wang // *Mat.Res.Soc.Symp.* **622** (2000) T6.35.1.

[66] L. Liu, J.H. Edgar // *Mater.Sci.Eng.R*. **37** (2002) 61.

[67] T. Nishiguchi, M. Nakamura, K. Nishiom T. Isshiki and S. Nishino // *Appl.Phys.Lett*. **84** (2004) 3082.