Materials Physics and Mechanics 21 (2014) 71-77 Received: June 15, 2014

SEMIPOLAR GaN ON Si(001): THE ROLE OF SiC BUFFER LAYER SYNTHESIZED BY METHOD OF SUBSTRATE ATOM SUBSTITUTION

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Abstract. The new HVPE method has been developed for synthesis of semipolar gallium nitride on the substrate of Si(100) deviated on 2°-7° from the direction <100>. The method is based upon the formation of two buffer layers. First, the thin buffer layer (20-30nm) of SiC is formed, which is grown using the technology of substitution of part of silicon atoms in substrate of Si by carbon atoms, then the layer of AlN is deposited on this surface. It has been shown that the misorientation of Si substrate from the direction <100> and formation of the thin SiC layer permit to form the epitaxial layers of semipolar gallium nitride. The polar axis "c" of wurtzite crystal appeared to be deflected by 55° from the plane (100) of Si substrate. The obtained films of semipolar GaN had a half-width of the rocking curve FWHM of the order of ω_θ ~24'. The thickness of GaN films was in the limits of 10-14 microns. The structure GaN/AlN/SiC/Si(100) formed during this process exhibited a bending of a cylindrical form. The formation of this bending is explained by anisotropy of the deformation of semipolar GaN on silicon.

1. Introduction

Epitaxial structures based upon semipolar GaN play important role in development of light diodes [1] and laser diodes [2]. Semipolar GaN structure can reduce or eliminate the polarization-induced quantum confined Stark effect [3] responsible for wavelength blueshift and limited radiative efficiency [4]. Among various materials such as (Al_2O_3, SiC, Si) namely the silicon is the most attractive substrate for such a light emitted structures. This high merit is attributed to the opportunity of using of large size substrates (up to 300 mm) in diameter, comparatively low cost, high electric and thermal conductivity, however the large difference in the constants of crystalline lattices and Coefficients of the Thermal Expansion (CTE) between GaN and Si leads to the appearance of the cracks during the epitaxial growth of thick GaN layers on the silicon substrates [5]. To suppress the chemical reactions between the silicon substrate and the gaseous phase containing the components necessary for formation of GaN layer the thin buffer layer of AlN is used [6]. During recent years the significant number of papers have been published on the growth of thin (~ 1 micron) GaN layers in semipolar directions by the method of Metal Organic Vapor Phase Epitaxy (MOVPE) on the substrates of Si(113) [7], Si(100) [8,9] and Si(112) [10]. The papers [8] and [11] describe the formation of the light diode and laser structures on the "template" of (1-101) GaN/Si(100) by MOVPE

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method. The method of Hydride Vapor Phase Epitaxy (HVPE) unlike the MOVPE method provides the higher growth velocity and is used at the growth of the semipolar thick > 100 micron GaN layers on the substrate of r-Al_2O_3, for obtaining the free-standing GaN wafers [12]. The use of "in-situ" removal of Si substrate [13] is the additional argument in the favor of application of HVPE for both obtaining the GaN wafers and growing the semipolar GaN on the substrate Si(210) [14].

The given paper describes new approach to the synthesis of the semipolar GaN on the misoriented substrate Si(100) by the combination of recently developed method of solid phase epitaxy (known also as the" Method of the Substrate Substitution") with the HVPE of AlN and GaN layers on such a carbid-silicon "template".

2. Synthesis method

The semipolar layers of GaN were synthesized by combination of two consequent techniques: at the first stage the 30-100 nm SiC layer has been formed by the method of solid phase epitaxy [15-17], then using HVPE method the buffer layer of AlN with thickness about 300 – 1000 nm has been formed and, eventually, the main layer of GaN with the thickness of about 2-15 microns was grown. The temperature of the SiC formation was 1270° C, synthesis of buffer layer of AlN was carried out at 1080°C and the main synthesis of GaN occurred at 1050°C. The synthesis of layers was carried out on the substrates of Si(100) with thickness of 300 microns and with different values of the surface misorientation (2°, 4°, 7°) in the direction <011>. Hydrogen was used as carrier gas.

The commonly used procedure for the growth of the semipolar layers of GaN (1-101) [7] is the following one: the surface of Si(100) is disguizing and subjected to chemical etching. The etching agent is chosen in such a way that the velocity of the etching would be depended on the directions of crystallographic axes. At this etching method it is possible to obtain the planes of Si(111) with the slope of 55° to the plane of Si (100). Namely these planes are used for the growing of GaN (1-101) [7]. According to the method proposed in the works [15-17] the epitaxial SiC is formed by the substitution of part of Si atoms in substrate by C atoms. This process is featured by the formation of the intermediate phase of silicon vacancies – atoms of carbon in silicon substrate. One of peculiarities of this method is formation of dilatation elastic dipoles (vacancy Si – atom C). Namely due to the formation of such kind of dipoles the elastic energy releasing at the standard growing methods of SiC on Si may come to relaxation [18]. As a result the dilatation dipoles "vacancy Si –atom C" are formed at the treatment of the surface Si by carbon monoxide (CO). If we decline the plane Si (100) at 1-10° from the direction <100> towards to <011> direction and then heat it up to temperatures above 600° C, the plane (100) of silicon, according to the thermodynamical considerations, will acquire the step-wise shape. The upper lying and lower lying surfaces will be the planes (100), and the steps will be confined by the planes (011). As it is well known the silicon lattice along the direction <011> is the most friable, which is inherently connected with the main crystallographic peculiarities of the Si lattice. The molecules of CO are rushing perpendicular to the steps along this direction inside the Si and part of the (011) Si is transforming into the (111) SiC step, having the angle with the plane (100) equals 55°.

3. Experimental details

During epitaxy of AlN and GaN layers by the HVPE on the surface 3C-SiC(001), there occurs synthesis of semipolar GaN that will emerge on monocrystalline faces of the 3C-SiC(111) layer of a thickness of about 50 nm (Fig. 1).

The structures GaN/AlN/SiC/Si(100) have been studied by the methods of x-ray diffractometry (RD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic-force spectroscopy (AFM).

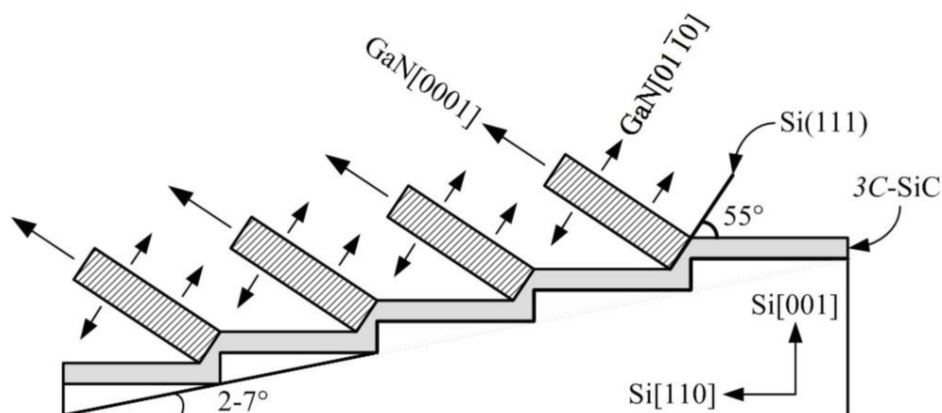

Fig. 1. Scheme of the process of synthesis of semipolar GaN on the 3C-SiC(111) quasi surface.

The XRD results indicate the presence of homogeneously ordered GaN layers with the layer deviation from the polar position of the *c* axis of the wurtzite crystal by an angle of 42° for the substrate Si(001) with a disorientation of 7°. Analysis of the electron diffraction pattern (Fig. 2) recorded at the interface of the heterostructure GaN/AlN/3C-SiC/Si(001) showed that the polar axis *c* of gallium nitride was parallel to the direction [111] of the silicon substrate; i.e., the layer deviation from the polar position of the *c* axis of wurtzite crystal was about 55° without taking into account the substrate disorientation (Fig. 2a).

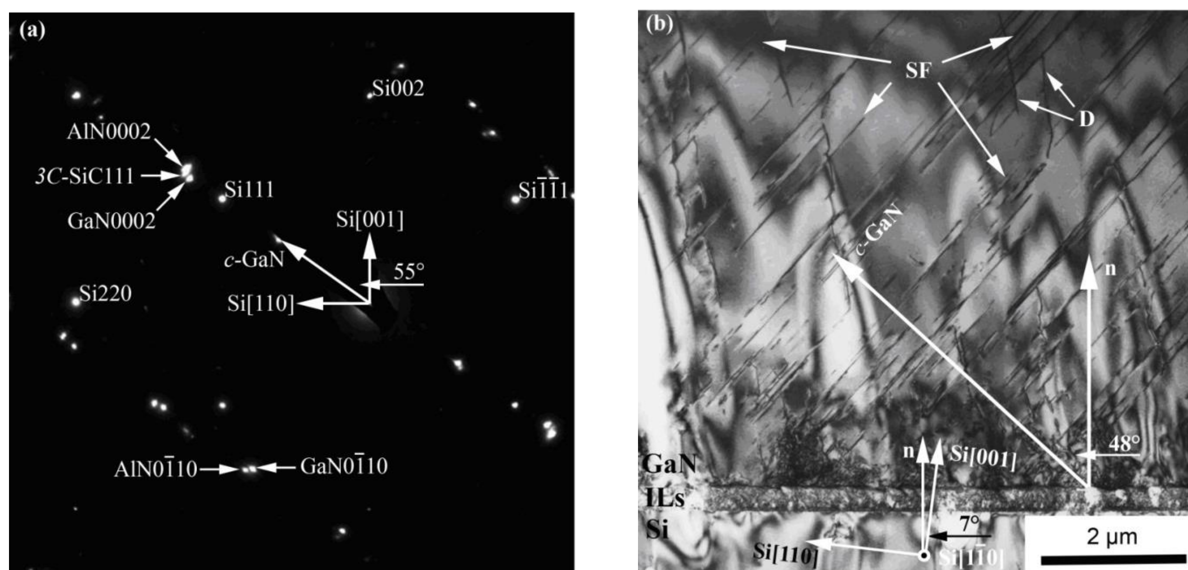

Fig. 2. (a) Electron diffraction pattern and (b) TEM image of the heterostructure of GaN/AlN/3C-SiC/Si(001). Arrows in the gallium nitride layer indicate stacking faults (SF), dislocations (D), and intermediate layers (IL) of AlN and 3C-SiC.

TEM image of the structure showed that the angle between the normal to the substrate and the perpendicular direction to lines of the stacking faults in the direction [0001] GaN was 48° and 51° for structures synthesized on substrates with cutoff angles 7° and 4°, respectively (Fig. 2b), which is in agreement with the microelectron diffraction pattern analysis results. The sum of the XRD and TEM results enables one to assume that the combined technology of solid-

phase epitaxy of 3C-SiC and HVPE of GaN on the off-cut Si(001) substrate enables one to synthesize the semipolar GaN (10-12), GaN(1-101).

The aggregation of the results obtained by the RD and TEM allows for conclusion that the combined technology of solid-phase epitaxy of SiC with HVPE of GAN on the misoriented substrate of Si(100) opens the opportunity to synthesize by HVPE method the semipolar epitaxial films of GaN without the use of lithographic masks and chemical etching agents. The comparison of the experimental data with crystallographic parameters for semipolar GaN crystals shows that the proposed method is appropriate for synthesis of thick layers GaN (1-101) or GaN(10-12) on Si(001) because the angle between GaN(10-11) and c-plane is 61,9° and the angle between GaN(10-12) and c-plane is 43,2° [19, 20].

Structures GaN/AlN/SiC/Si(100) according to the results of RD analysis exhibited the cylinder-like bending. But the measurements of the curvature radii R in two mutually perpendicular directions R_a,<11-20> and R_c,<11-23> have shown the significant changes depending on the GaN layer thickness only in one direction (table I). The values of half-widths of x-ray diffraction rocking curves (FWHM) for reflex (1-101) in GaN layers for all structures practically didn't differ from each other and had the values of ω_θ ~ 20-24 arcmin. The Fig.3 shows the AFM image of the surface of GaN layer and the profiles of surface inhomogeneity distribution in directions <11-23> (a) and <11-20> (b), respectively.

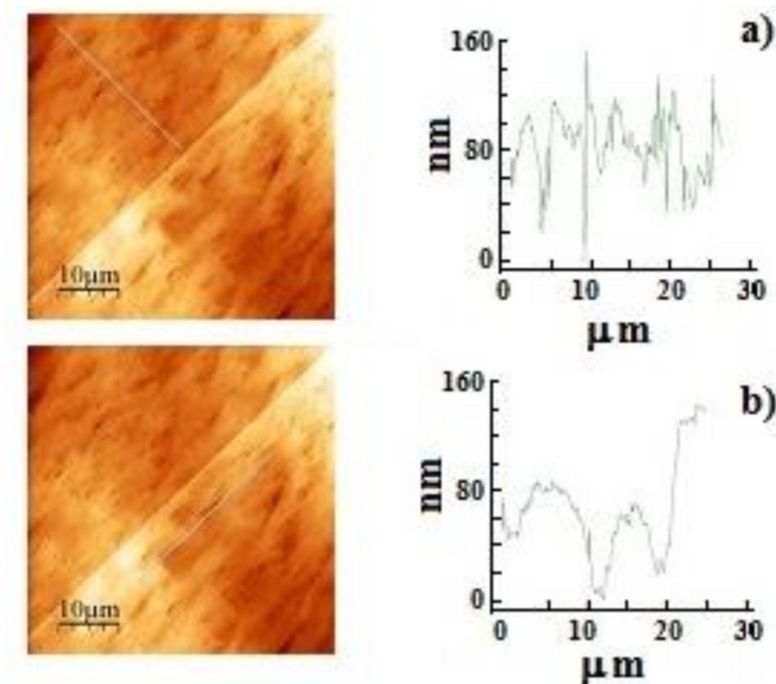

Fig. 3. AFM image of the surface of GaN layer and the profiles of surface inhomogeneity distribution in directions <11-23> (a) and <11-20> (b), respectively.

This figure shows that the roughness of the layer is at about 80 nm in the direction <11-23> that is significantly less than in the direction <11-20>. These results prove strong morphological anisotropy during growth of semipolar GaN layer.

4. Discussion

Since the experimental data permit to suggest unambiguously, that the structures GaN/AlN/SiC/Si(100) have the concave bending of cylindrical shape. On our opinion, the concave bending of the surface is connected with the difference of the coefficients of thermal expansion for silicon and gallium nitride and the anisotropy of the deformation of the

structure GaN(1-101)/AlN/SiC/Si(011) seems to related with the difference of the coefficients of thermal expansion along the directions “a”-<11-20> and “c”-<11-23> of the wurtzite semipolar crystal of gallium nitride. In fact, the values of CTE in the lattice of gallium nitride in the direction of axes “c” and “a” are different at the room temperature (α_c GaN ~ $3.52\cdot10^{-6}$ 1/K, α_a GaN ~ $3.93\cdot10^{-6}$ 1/K [21]). They differ also from the CTE of silicon equals α_{Si} ~ $2.6\cdot10^{-6}$ 1/K [5].

As known, at the cooling of the structures of polar gallium nitride, synthesized on the silicon substrate the layer of gallium nitride is in the state of isotropic compression because the CTE of GaN for lattice “a” is higher than CTE of Si. With the increase of the thickness of the GaN layer the curvature radius of the structure bending is reducing. Let us assume that the contribution of thin interlayers of SiC and AlN in the bending of the structure GaN/AlN/SiC/Si(100) is insignificant. From here follows, that at the cooling of the layer of semipolar gallium nitride on the silicon substrate from the temperature of epitaxy down to room temperature the bending of the structure GaN/Si will be determined only by difference in CTE between GaN and Si. The CTE for lattices GaN and Si differ not only along the direction “a” of GaN lattice, but also along the direction “c” of the lattice GaN and Si (Fig.4).

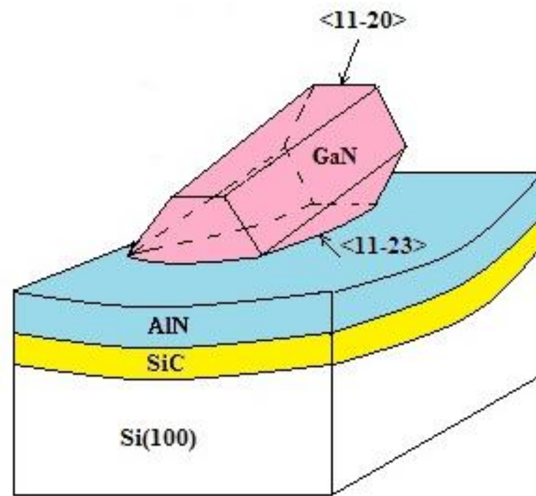

Fig. 4. Schematic drawing of the synthesis of the GaN(1-101)/AlN/SiC/Si(100) structure.

Since the CTE of lattices “a” and “c” are different, the cooling of the film of semipolar gallium nitride on the silicon substrate will lead to the anisotropic bending of the structure GaN/AlN/SiC/Si(100). That to confirm this hypothesis we estimated by formula [22] the anisotropic bending of the semipolar GaN on Si(100) substrate , assuming that CTE of GaN in the semipolar plane will be equal to CTE of GaN in the plane (100).

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

where: $m = \frac{E_1}{E_2}$, $h = \frac{h_1}{h_2}$, $\varepsilon = (\alpha_1 - \alpha_2)\Delta T$,

- E_1 – Young modulus of GaN =210 GPa, E_2 = 165,6 GPa – Young modulus of Si
- h_1- thickness of GaN , h_2 – thickness of Si.
- α_1- CTE of the lattice GaN “a” and “c” respectfully, α_2 – CTE of lattice Si.
- ΔT – Difference between growth and room temperature.

The estimates obtained on the GaN layer bending radii in the directions of <11-23> and <11-20> on the substrate Si(100) are presented in the Table I.

Table 1. Dependences of the radii of curvature of the heterostructure in the direction of disorientation of substrate (R_a) and in the perpendicular direction (R_b) on the GaN layer thickness.

GaN layers Thickness, μm	Disorientation, deg	Experiment	
		R_a, m	R_b, m
~ 2	2	-1,6	-1,8
10	4	-0,4	-1,6
14	7	-0,25	-1,4

It is seen that appearance of anisotropic deformation in the layer of semipolar GaN synthesized on the substrate of Si(100) is in accordance with the hypothesis according to which this deformation is due to two reasons: difference in the thermal expansion coefficients for lattices SiC and lattices GaN, and anisotropy of the coefficients of thermal expansion along the plane of semipolar GaN.

5. Conclusions

Thus, the new approach to the growing of the semipolar layers of gallium nitride by HVPE method on the planar substrate of Si(100) deviated from the plane (100) towards the plane Si(011) has been proposed and implemented. The semipolar direction of the GaN synthesis has been given by the formation of the three-dimensional prisms of SiC covered by the planes (111). The formation of given structures became possible due to development of the method of solid- phase epitaxy of SiC on Si and favorable matching of these films with the properties of AlN and GaN films. As a result of our studies we have grown the layers of GaN on the silicon carbide “template “ with orientation of the surface parallel to planes (10-12) or (1-101) and with value of half-width of x-ray diffraction of FWHM ω_θ~24'. The proposed approach, given in this paper, permits to grow thick layers (>10 micron) of gallium nitride and could be perspective at the formation of “templates” for the structures of gallium nitride based optoelectronics.

Acknowledgment

Authors express their deep gratitude to the Russian Science Foundation (grant No 14 12-01102) for support of this work.

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