Novel approach for III-N on Si (111) templates fabrication by low-temperature PA MBE using porous Si layer

Zolotukhin D*, Seredin P1, Lenshin A1, Goloshchapov D1,3, Mizerov A2
1Voronezh State University, Universitetskaya pl. 1, Voronezh, 394018, Russia
2St. Petersburg Academic University, Khlopina 8/3, 194021 St. Petersburg, Russia
3Voronezh State Technical University, Voronezh, Russia

Abstract. We report on successful growth of GaN nanorods by low-temperature plasma-assisted molecular beam epitaxy on a Si(111) substrate with and without preformed thin porous Si layer (por-Si). The deposited GaN initially forms islands which act as a seed for the wires. Porous structure of the por-Si layer helps to control nucleation islands sizes and achieve homogeneous distribution of the nanorods diameters. In addition 850 nm-thick crack-free GaN layer was formed on Si(111) substrate with preformed por-Si layer.

1. Introduction
For decades, there have been numerous attempts to solve a well-known problem of III-nitride material family, i.e., defects and dislocations due to a lack of proper substrates. Nanorods have attracted much interest in recent time because of their potential for the fabrication of electronic and optoelectronic devices [1-3]. Moreover, nanorods properties and presence of large free surface helps to suppress propagation of the threading dislocations and stress generation [4] arising from lattice and thermal expansion coefficient mismatches (17% and 54% for GaN on Si(111), respectively [5]). Conventionally nanorods are formed by using complex approaches such as selective growth, Vapor-Liquid-Solid (VLS) technique, etc. [6]. However, these approaches involve the usage of complex technological processes, which significantly increased the cost of the resulting device. The solutions for this problem can be the use of cheap compliant Si substrates with a por-Si layer. Self-organized array of nanopores in a por-Si layer leads to the formation of GaN nucleation islands with the same sizes, which in turn leads to the formation of nanorods with the same diameters.

In this paper we report on fabrication of self-organized nanorods with the same diameters on a compliant Si-substrate by a low temperature plasma-assisted MBE (LT PA MBE). In addition 850 nm thick crack-free GaN/por-Si/Si(111) template was formed to demonstrate a possibility of tensile stress generation suppression using a por-Si layer.

2. Experimental
All Si substrates were pre-treated using the Shiraki method [7]. Then a 20 nm-thick por-Si layer was formed on several substrates using the original method of selective etching. After that all the substrates were annealed at 820°C for an hour until the 7×7 surface reconstruction was observed by RHEED. All growth processes were performed by using Veeco Gen 200 PA MBE setup. For comparison nanorods were grown at the one growth process on conventional Si(111) substrate and substrate with a por-Si layer (sample a and b, respectively) without nitridation step. LT GaN nanorods were formed at
$F_{Ga}=F_{N}=0.1 \mu m/h$ flux ratio and the substrate temperature of $T_s=400^\circ C$. Prior to sample growth, the Si(111) substrate with a por-Si layer underwent a high-temperature ($T_s=850^\circ C$) nitridation step for one hour at nitrogen plasma source forward power of 500 W and reflected power 0 Wr, with a nitrogen flow rate of 3.7 sccm. After that the 10-nm-thick GaN buffer layer was grown at $T_s=650^\circ C$ and $F_{Ga}/F_{N}=1$. Then 840 nm of HT GaN was formed at higher values of $T_s=700^\circ C$ and $F_{Ga}=0.6 \mu m/h$ (at fixed $F_N=0.1 \mu m/h$). RHEED was used for in situ control of the surface morphology of the layers. The surface morphology also was investigated ex situ by an atomic force microscope (AFM) scanning electron microscopy (SEM) and optical microscope (OM).

3. Results

Cross section SEM images of all heterostructures (Figure 1) illustrate rather planar morphology for all the interfaces. One can also observe a more pronounced nanocolumnar structure in case of sample b.

![Figure 1](image1.png)

Figure 1 Cross-section SEM images of the GaN/Si(111) (left) and GaN/por-Si/Si (right) nanorods.

In addition, SEM image of GaN/por-Si/Si heterostructure revealed an increase in the distances between nanorods as well as in homogeneity of the distribution of their diameters.

![Figure 2](image2.png)

Figure 2. The lateral sizes distribution histogram obtained from AFM study of por-Si layer (left), GaN/Si(111) layer (centre) and GaN/por-Si/Si(111) layer (right).

The lateral sizes of the distribution histogram obtained from the AFM study of the substrate and samples surfaces (Figure 2) shows that the use of a por-Si layer has a crucial influence on the distribution of the diameters of the nanorods.
Figure 3. Cross-section SEM and OM image of GaN/por-Si/Si(111) heterostructure.

As can be seen from Figure 3, we achieved a flat GaN/Si interface in GaN(850 nm)/por-Si/Si(111) heterostructure without pronounced interaction. Moreover, OM revealed a crack-free surface, which corresponds to a low level of tensile stress at room temperature.

4. Discussion

As shown in Nechayev et. al. paper [8], growth temperature significantly affects on nucleation islands sizes due to increase of surface adatom mobility. The higher surface mobility led to greater average nucleation islands sizes. However, it is necessary to take into account that we are talking only about the average size, while the real distribution of nucleation islands sizes remains fairly chaotic. Lee S et. al. [9] reported that the most energetically favorable crystallographic plane for GaN growth on silicon is the {111} plane. We believe that etching of Si(111) substrate led to similar as described in [10] surface morphology with isotropically distributed etching hillocks. In the case of a thin (20 nm) porous layer, the etching hillocks becomes truncated with {111} plane at the top and roughly same diameter. Thus, GaN was nucleated on the tops of isotropically distributed hillocks with a further increase in grain sizes until nucleation island completely covers the entire surface of the truncated hillock. This fact can account for better uniformity of the distribution of the diameters of the nanorods.

The cross section SEM image of sample c revealed flat GaN-Si interaction which related with Ga-Si phase diagram [11]. A long nitridation step led to Si$_3$N$_4$ layer formation which acts as a mask and prevent Ga-Si interaction was formed on Si(111) substrate surface GaN buffer layer with the thickness of 10 nm in sample c. The stress arising from thermal expansion coefficient difference of $\Delta\alpha_{Si-GaN} = 2.9 \times 10^{-6}$ K$^{-1}$ [12] between GaN and Si can be estimated using formula (1)

$$\sigma_{th} = M_{GaN} \int_{RT}^{T} \Delta\alpha_{Si-GaN} dT$$

where $M_{GaN}$ is the GaN biaxial modulus. Using $M_{GaN} = 478$ GPa [13] and $T_s = 700^\circ$ the tensile stress can be evaluated as $\sigma_{th} = 970$ MPa. As described in [14], for films on substrates with different elastic properties, this critical thickness for channeling steady-state propagation parallel to the interface by cracks that extend to the film-substrate interface is given by the relation (2)

$$h_{critical} = \frac{I}{E} / Z\alpha^2$$
where $\Gamma$ is the fracture resistance of the material, $\overline{E}$ is the plane strain elastic modulus $\overline{E} = E/(1-\nu)$ (using elastic constants from [15] can be evaluated as 379 GPa for GaN), $Z = g(\alpha, \beta) \pi / 2$. If we assume that GaN layer grown is fully unstrained, then using the values listed in [14] and $\sigma_0=970$ MPa, the critical thickness can be evaluated as $h_{\text{critical}}=804$ nm. Nevertheless, the OM study of GaN (850nm)/por-Si/Si(111) heterostructure (Figure 3) revealed crack-free surface, despite a lower calculated critical thickness value. We believe that this excess of the critical thickness is related with stresses relaxation at the por-Si / GaN interface.

Summarizing, by using compliant substrates with a porous Si layer and different PA MBE regimes, we have obtained self-organized array of nanorods with approximately the same diameters as well as a crack-free thick GaN layer on Si(111) substrate. The use of low growth temperature for nanorods growth and Si$_x$N$_{1-x}$ mask layer for GaN layer growth helps to suppress Ga-Si interaction and prevent deterioration of the Si-GaN interface. In addition, we confirmed a positive role of a porous Si layer for relaxation of the tensile stress. Thus, compliant Si(111) substrates with a porous Si layer seems to be suitable for GaN based device fabrication by PA MBE.

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