The effects of GaN nanocolumn arrays and thin Si$_x$N$_y$ buffer layers on the morphology of GaN layers grown by plasma-assisted molecular beam epitaxy on Si(111) substrates

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Abstract. The effects of GaN nanocolumn arrays and a thin Si$_x$N$_y$ layer, used as buffer layers, on the morphology of GaN epitaxial layers are investigated. Two types of samples with different buffer layers were synthesized by PA-MBE. The morphology of the samples was characterized by SEM. The crystalline quality of the samples was assessed by XRD. The possibility of synthesis of continuous crystalline GaN layers on Si(111) substrates without the addition of other materials such as aluminum nitride was demonstrated.

1. Introduction
A$^3$N wide bandgap semiconductor materials and their ternary alloys have a set of unique electrical, optical and mechanical properties, which are important in modern optoelectronics, high power electronics, and microelectromechanical systems (MEMS). Since natural substrates for A$^3$N materials are very expensive, silicon carbide (SiC), sapphire ($c$-Al$_2$O$_3$) and silicon (Si(111)) substrates are used for epitaxial growth of III-nitrides.

One of the key technological problems in GaN synthesis on silicon substrates is the dramatic lattice mismatch (16.9\%) between GaN and Si(111). Moreover, there is a large difference in their thermal expansion coefficients. These two factors lead to relaxation of elastic strain through the formation of misfit dislocations at the GaN/Si interface. Another important problem is interdiffusion of Si and Ga atoms under growth conditions that are typical for molecular-beam epitaxy (MBE). Therefore, the local etching of a Si(111) substrate is possible with the formation of macroscopic voids during the growth process [1]. Different buffer and transitional layers are used to solve the problems mentioned above. In particular, these are GaN nanocolumn arrays and thin Si$_x$N$_y$ layers formed on the surface of Si(111) substrates immediately before planar GaN epitaxial growth [2, 3].

2. Experimental details
In this work, the use of GaN nanocolumn arrays and thin Si$_x$N$_y$ layers as transition or buffer layers for the synthesis of planar epitaxial GaN layers on Si(111) substrates was investigated. The samples of GaN/3D-GaN/Si(111) and GaN/Si$_x$N$_y$/Si(111) epitaxial structures were grown by PA-MBE in a Veeco Gen 200 MBE system equipped with a Veeco UNI-Bulb™ RF plasma source. The thickness of planar GaN epitaxial layers was (0.6 - 1.0) $\mu$m. The synthesis of epitaxial layers was carried out on semi-insulating ($R > 10$ k$\Omega$cm) Si(111) substrates, which were cleaned according to the Shiraki method [4].

The samples of the first type are epitaxial structures with GaN nanocolumn arrays (3D-GaN), which were used as a buffer layer to reduce the dislocation density in the planar GaN layer. To test the
procedure of catalyst-free synthesis of GaN nanocolumn arrays (the same procedure was used in [5]), a sample consisting of GaN nanocolumn arrays formed on a Si(111) substrate was grown. SEM images of the cross-section and the surface of this sample are shown in figure 1. The height of individual nanocolumns in the array was about 300 nm. After selection of the growth conditions that allow obtaining catalyst-free GaN nanocolumns on Si(111) substrates, the samples with GaN nanocolumn arrays as a buffer layer were grown.

![Figure 1](image1.png)

**Figure 1.** SEM images of the 3D-GaN/Si(111) sample with GaN nanocolumn arrays: cross-section (a) and surface morphology (b).

The samples of the second type are epitaxial structures with a thin Si$_x$N$_y$ layer, which was used as a buffer layer. The thin Si$_x$N$_y$ layer was formed during nitridation of a Si(111) substrate in the flux of atomic nitrogen. It is assumed that the use of thin homogeneous continuous Si$_x$N$_y$ layers allows to avoid the mutual diffusion of Ga and Si atoms, as well as the local etching of the silicon substrate with the formation of macroscopic voids on the GaN/Si(111) interface.

The characteristics of the obtained samples were studied by scanning electron microscopy (SEM) and X-ray diffractometry (XRD). The surface morphology was checked using a Zeiss Supra25 scanning electron microscope. A DRON-8 multifunctional diffractometer was used for X-ray diffractometry experiments.

### 3. Results and discussion

As a result of the work, two types of samples were obtained (GaN/3D-GaN/Si(111) and GaN/Si$_x$N$_y$/Si(111) epitaxial structures).

The SEM micrograph of the sample with GaN nanocolumn array, used as a buffer layer, is shown in figure 2. The height of individual nanocolumns reaches 0.2 μm. On the cross-section a gradual coalescence of GaN nanocolumns into a continuous GaN layer is clearly visible. The surface morphology of the obtained epitaxial layer has a mosaic structure, which is characteristic for GaN epitaxial layers grown on silicon substrates. Thus, as a result of using 3D-GaN buffer layer, continuous crystalline GaN epitaxial layer was obtained on Si(111) substrate with no additional materials used.

In figure 3, the cross-sectional SEM images of GaN/SixNy/Si(111) epitaxial structures are shown. The sample shown in figure 3(a) was obtained with 60 min nitridation, while the duration of the nitridation process for the sample shown in figure 3(b) was 30 min.
Figure 2. SEM cross-sectional image of the GaN/3D-GaN/Si(111) sample containing GaN nanocolumn array as a buffer layer.

Figure 3(a) shows a continuous GaN epitaxial layer (60 min nitridation of a Si(111) substrate), while the structure of the GaN layer in figure 3(b) is coalesced co-directional GaN blocks (30 min nitridation). Thus, according to [6], the duration of the nitridation process affects the homogeneity and continuity of Si$_3$N$_x$, and hence the morphology of the GaN epitaxial layer.

(a)  
(b)

Figure 3. Cross-sectional SEM images of the GaN/Si$_3$N$_x$/Si(111) samples grown with nitridation of a Si(111) substrate for 60 min (a) and 30 min (b).

To assess the presence of stresses in GaN layers grown on Si(111) substrates with a thin Si$_3$N$_x$ layer and arrays of GaN nanocolumns as buffer layers, the samples were examined by X-ray diffractometry. Figure 4 shows the XRD rocking curves for the samples of both types. It can be seen from figure 4 that the position of the peaks corresponding to GaN ($2\theta_{\text{GaN}} \approx 34.75^\circ$) and the broadening of the rocking curves do not vary significantly depending on the buffer layer used. Thus, the use of GaN nanocolumn arrays and a thin Si$_3$N$_x$ layer as a buffer layer allows growing GaN epitaxial layers on Si(111) substrates that are approximately equal in the crystalline quality. The presence of the defects (dislocations) in the epitaxial GaN layer, as well as its mosaic structure, contribute to the broadening of the rocking curve. The difference in the intensity of the peaks corresponding to GaN directly corresponds to the difference in the thickness of GaN layers.
It is worth noting that for the sample with 30 min nitridation, the local etching of a Si(111) substrate was observed. For the samples obtained with 60 min nitridation and GaN nanocolumn arrays as a buffer layer, no cases of local etching were detected. Moreover, according to the results of measurements based on the Hall effect, the use of 3D-GaN and thin Si$_x$N$_y$ buffer layers does not prevent the mutual diffusion of Si and Ga atoms, thus providing unintentional doping.

4. Conclusion
In this work, the effects of GaN nanocolumn arrays and a thin Si$_x$N$_y$ layer, used as buffer layers, on the morphology of GaN epitaxial layers are investigated. The samples of GaN/3D-GaN/Si(111) and GaN/Si$_x$N$_y$/Si(111) epitaxial structures were obtained. The possibility of synthesis of continuous crystalline GaN layers on Si(111) substrates without the use of additional materials such as aluminum nitride was demonstrated. However, neither type of buffer layer makes it possible to avoid the mutual diffusion of Si and Ga atoms with unintentional doping. Moreover, there is a probability of local etching of a Si(111) substrate when using a thin Si$_x$N$_y$ buffer layer.

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