A study of the GaN/Si(111) epitaxial structures grown by PA MBE via coalescence overgrowth of GaN nanocolumns

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Abstract. The GaN/Si(111) epitaxial structures were synthesized by coalescence overgrowth of GaN nanocolumns using the plasma-assisted molecular beam epitaxy (PA-MBE) technique. Such epitaxial structures can be used as a buffer layer for obtaining high quality GaN epilayers. Structural, electrical and chemical properties of these samples were studied. It was demonstrated that KOH etching of the grown GaN/Si(111) samples results in the separation of the GaN epilayer from the substrate.

1. Introduction
The wide-bandgap semiconductor gallium nitride has unique electrical, optical, mechanical, and other properties, which are important for optoelectronics, high-power and high frequency electronics [1]. Moreover, one of the main advantages of GaN is its extremely high thermal and chemical stability. Thus, it can be a promising material for microelectromechanical systems (MEMS) and devices, which can be used in harsh environments [2]. However, there is a well-known problem for further development of nitride technology associated with the lack of low-cost native substrates. For this reason, commercially viable GaN-on-Si epitaxial structures are attracting more and more attention.

At the same time, there are several fundamental challenges for heteroepitaxy of high quality III-N layers on silicon substrates due to the large lattice mismatch (16.9 % for GaN/Si(111)) and the large difference in their thermal expansion coefficients as well as growth peculiarities of polar III-N materials on non-polar Si(111) substrates [3]. Furthermore, there is a problem of Ga and Si interdiffusion that leads to unintentional doping of GaN layers and silicon [4]. One more problem limiting the direct growth of GaN on silicon substrates is meltback etching, which occurs due to the high solubility of silicon in gallium under growth conditions typical for molecular beam epitaxy (MBE) or metalorganic chemical vapor deposition (MOCVD) [5]. Thus, the crystalline quality of the GaN epilayers grown on silicon is not good enough, and their surface is quite rough. One of the promising approaches to improve the crystalline quality of GaN grown on Si(111) substrates can be the use of GaN layers, the morphology of which is changing from nanocolumnar to 2D during GaN growth.

Here we report on the results of the studies of GaN/Si(111) structures synthesized by coalescence overgrowth of GaN nanocolumns using the PA-MBE technique.
2. Experimental details
The GaN/Si(111) samples were obtained using a Veeco GEN200 MBE system equipped with a radio frequency (RF, 13.56 MHz) plasma source. GaN was grown on semi-insulating ($R > 10000 \text{ Ohm}\cdot\text{cm}$) silicon substrates, which were prepared according to the modified Shiraki method [6]. Before the growth, the Si(111) substrates were annealed for 15 min at $T_{\text{sub}} = 900 ^\circ \text{C}$ in order to remove the protective SiO$_2$ layer. The growth procedure began with the deposition of several ($\sim 5$) Ga monolayers on the silicon surface. Then, an array of GaN nanocolumns was formed on the substrate surface under N-rich conditions (flux ratio $F_{\text{Ga}}/F_N \sim 0.4$) at $T_{\text{sub}} = 600 ^\circ \text{C}$. To ensure the coalescence of GaN nanocolumns, the temperature was gradually increased up to $T_{\text{sub}} = 730 ^\circ \text{C}$, and the Ga flux was increased up to the ratio $F_{\text{Ga}}/F_N \sim 6$.

After growth, the samples were studied via scanning electron microscopy (SEM), profilometry, and Hall measurements. The crystallographic polarity of GaN, as well as the possibility separating GaN from substrates, were studied through experiments on KOH chemical etching.

3. Results and discussion

3.1. Morphology studies
The morphology of the grown samples was studied using a Supra 25 Zeiss SEM. A characteristic image of the obtained GaN/Si(111) structures is presented in figure 1.

![Figure 1. SEM image of the GaN/Si(111) epitaxial structure.](image)

As can be seen, first, an array of GaN nanocolumns of about 100 nm height was formed. The SEM studies have shown that the described changes in the growth conditions ensured coalescence of GaN nanocolumns. An increase in the Ga-flux up to Ga-rich conditions allowed obtaining continuous GaN epitaxial layers. The average thickness of the synthesized GaN was about 800 nm according to electron microscopy data. Surface roughness was measured using an AmBios XP-1 profilometer. The characteristic value of the root mean square (RMS) roughness was about $R_q = 5.2$ nm. Thus, it is shown, that the coalescence overgrowth can indeed be used to obtain sufficiently smooth and continuous GaN layers. Moreover, it should be noted that no meltback etching was observed.

3.2. Electrical properties
Next, the electrical properties of the samples were investigated by Hall effect measurements based on the four-probe Van der Pauw method using an Ecopia HMS-3000 measurement system. It was found that although all samples were grown undoped, the GaN epitaxial layers have n-type conductivity with
a carrier concentration \( n \sim 2.0 \times 10^{19} \text{ cm}^{-3} \). It is well known that undoped AlN and GaN films demonstrate n-type conductivity. Despite the fact that this phenomenon has been studied for a long time, there is still no consensus in the scientific community as to what type of structural defects or impurities make the main contribution to the n-type conductivity in undoped GaN and AlN epilayers [7]. In our case, such high values of the carrier concentration can be due to unintentional doping via Ga and Si interdiffusion, as it was mentioned above.

### 3.3. Crystallographic polarity

It is well known that crystallographic polarity is an essential feature of wurtzite GaN, which affects the structural, optical and electrical properties of the material [8]. As it was mentioned above, GaN has high chemical stability and, in particular, Ga-polar GaN is the most resistant to aggressive environments. Therefore, it is important to know and control the polarity of the GaN layers.

The crystallographic polarity of the obtained GaN epitaxial layers was identified by wet chemical etching in 70 °C KOH solution (KOH:H\(_2\)O = 1:5) for \( t = 5 \text{ min} \) [9]. It was found, that all the samples are Ga-polar because after etching the height of the GaN layers and its surface remained unchanged in the defect-free area (see figure 2).

![Figure 2. SEM images of the surface (a) and cross-section (b) of the GaN/Si(111) epitaxial structures after etching in KOH solution for \( t = 5 \text{ min} \).](image)

It can be seen that multiple etch pits were formed on the sample surface. A possible reason for their appearance is defect-selective etching. There are some structural defects typically present in the GaN epitaxial layer: dislocations [10], nanotubes [11], or inversion domains [12]. At the same time, it was found that GaN nanocolumns were slightly etched in accordance with their crystallographic orientation, and the gaps between them widened and increased in height. Therefore, the etching of the samples was continued.

### 3.4. Separation of GaN epilayers by wet chemical etching in KOH

It is known that attempts are being made to chemically separate GaN and AlN layers from the substrates using a pregrown and modified by wet etching GaN buffer layer [13] or porous SiC layer [14]. Spontaneous mechanical peeling of GaN layers grown on GaN nanocolumns was also observed [15, 16]. In this work, wet chemical etching of the grown GaN/Si(111) epitaxial structures was used for this purpose.

To study the etching of the obtained structures, the duration of the process was increased up to 30 min and then to 60 min. After each step, the samples were examined using SEM (see figure 3).
As can be seen, the crystallographic etching occurs in the area of the array of GaN nanocolumns. KOH solution can penetrate to the GaN/Si(111) interface through the gaps between individual nanocolumns. As a result, a characteristic pyramidal relief is formed. It is obvious that with an increase in the etching time, it becomes possible to achieve a gradual separation of the GaN layer from the substrate.

However, it was found that the GaN surface suffers from prolonged etching in hot KOH solution (see figure 4).

To prevent such damage to the GaN layer, it may be necessary to use a protective coating, such as thin metal films or, for example, Si₃N₄. In addition, the thickness of the continuous GaN layer should be increased to avoid overetching on the backside.

It should be noted that, in addition to etching GaN, the silicon substrate was also etched with KOH solution (see figure 5).
Figure 5. Cross-section SEM images of the GaN/Si(111) epitaxial structure after etching in KOH for \( t = 60 \) min: (a) the macroscopic cavity formed by etching of the silicon substrate, (b) the backside morphology of the GaN layer in the cavity area.

Etching of silicon with KOH at the GaN/Si(111) interface resulted in the formation of multiple cavities of various lengths \( (l = 0.5 – 80 \) μm). Unfortunately, it was not possible to trace the regularities of the formation of such voids. At the same time, with the formation of cavities, the areas of suspended GaN were formed.

Thus, it was demonstrated for the first time, that the etching of GaN/Si(111) epitaxial structures with a nanocolumnar seed layer in KOH during 60 min results in partial separation of the GaN epilayer from the Si(111) substrate. Therefore, the described method is also promising to obtain freestanding GaN layers, which can be used as native substrates for A\(^3\)N epitaxial growth.

4. Conclusion
In this work, the GaN/Si(111) epitaxial structures were studied. GaN/Si(111) samples were synthesized using the PA MBE technique via coalescence overgrowth of self-catalyzed GaN nanocolumns. Structural, electrical and chemical properties of the obtained GaN/Si(111) structures were studied. It is shown that the coalescence overgrowth approach can indeed be used to obtain sufficiently smooth GaN layers and to avoid meltback etching. This design of the GaN epilayers can be used as a buffer layer for the synthesis of high quality GaN layers on silicon substrates. It was found that the synthesized GaN epitaxial layers have n-type conductivity with a carrier concentration \( n \sim 2.0 \times 10^{19} \) cm\(^{-3}\). The crystallographic polarity of the samples was identified by wet etching in KOH solution, and it was shown that all the samples are Ga-polar. Moreover, it was demonstrated for the first time that the etching of GaN/Si(111) epitaxial structures with a nanocolumnar seed layer in KOH during 60 min results in partial separation of the GaN epilayer from the Si(111) substrate. Thus, the described method can also be promising to obtain free-standing GaN layers which can be used as native substrates for A\(^3\)N epitaxial growth. However, to avoid surface damage and backside overetching, it is necessary to use some protective coating and increase the layer thickness accordingly.

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