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

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Abstract. The AlN/Si(111) epitaxial structures were synthesized by coalescence overgrowth of AlN nanocolumns using PA MBE technique. Such epitaxial structures can be used as a buffer layer for obtaining high quality AlN and GaN layers. Structural, electrical and chemical properties of these samples were studied. For the first time it was demonstrated that the etching of the obtained type of AlN/Si(111) structures in KOH can become a promising method for obtaining high quality free-standing AlN and GaN.

1. Introduction
Wide bandgap semiconductors, especially III-N compounds, are one of the most prospective materials for the development of modern electronics. III-nitrides have unique electrical, optical and mechanical properties, which are of importance for optoelectronics, high-power and high frequency electronics and microelectromechanical system (MEMS) industry [1]. Among III-N materials, AlN has the largest band gap (6.2 eV). Since it is direct-bandgap semiconductor, AlN is a promising material for deep-ultraviolet light sources [2]. Moreover, it has attracted a huge attention due to its giant piezoelectric properties, which are important for surface and bulk acoustic wave devices [3]. However, there is well-known problem for further development of nitride electronics connected with the lack of natural substrates. Since AlN and GaN substrates are very expensive, low-cost AlN-on-Si epitaxial structures are attracting more and more attention.

On the other hand, one of the key technological problems of A3N heteroepitaxy on silicon substrates is large lattice mismatch (16.9 % for GaN/Si(111) and 19% for AlN/Si(111)), and large difference in their thermal expansion coefficients. Nonetheless, it is well-known, that AlN is often used as a buffer layer for heteroepitaxy of GaN on silicon. However, it is reported, that the crystalline quality of AlN buffer layer is not good enough, and its surface is quite rough [4]. One of the promising approaches to improve the crystalline quality of AlN grown on Si(111) substrates can be use of AlN nanocolumn arrays as a seed layers.

Here we report on the results of the studies of AlN/Si(111) structures synthesized by coalescence overgrowth of AlN nanocolumns using plasma-assisted molecular beam epitaxy (PA MBE) technique.

2. Experimental details and results
The AlN/Si(111) samples were obtained by PA-MBE using Veeco Gen 200 MBE system equipped with RF (13.56 MHz) plasma source. The growth procedure was similar to the described in paper [5]. AlN was grown on the semi-insulating (R > 10000 Ohm•cm) silicon substrates with (111) crystallographic orientation. Silicon substrates were prepared according to modified Shiraki method [6]. Before the growth, the Si(111) substrates were annealed for 30 min at T_sub = 850 °C in order to remove SiO_2 layer. The growth procedure began with the deposition of several Al monolayers onto the...
silicon surface to prevent Si$_x$N$_y$ formation. Then, an array of AlN nanocolumns was formed on the substrate surface under Al-rich conditions (flux ratio F$_{Al}$/F$_{N}$ ~ 1.7) at $T_{sub} = 850$ °C. In order to provide the coalescence of AlN nanocolumns the temperature was decreased down to $T_{sub} = 750$ °C and the Al flux was decreased down to the ratio F$_{Al}$/F$_{N}$ ~1.3.

The morphology of the samples grown was studied using scanning electron microscope (SEM) Supra 25 Zeiss. As it can be seen in figure 1, first, an array of AlN nanocolumns about 200 nm height was formed.

![Figure 1](image1.png)

**Figure 1.** SEM image of AlN/Si(111) epitaxial structure.

Moreover, it is evident in the micrograph that described changes in growth parameters led to the AlN nanocolumn coalescence that allowed the formation of the continuous AlN epitaxial layer about 300 nm thick. The samples obtained have quite smooth surface morphology with RMS roughness of 6.2 nm. Thus it is shown, that indeed the coalescence overgrowth can be used to obtain quite smooth AlN layers.

Crystallographic polarity of the AlN epitaxial layers was identified by wet chemical etching in 40 °C KOH solution for 5 min. It was found, that all the samples are Al-polar, because after etching the surface of the AlN layer remained unchanged at the defect-free area (see figure 2).

![Figure 2](image2.png)

**Figure 2.** SEM image of the surface of AlN/Si(111) epitaxial structures after etching in KOH solution for t=1, 2.5, and 5 min.

It can be seen that with the increase of etching time at the area with some «scales» and other defects of the surface the etch pits are formed. With further increase of the etching time, it can lead to the penetration of the etchant deep into the AlN structure and its etching from the inside. At the same time, it was found that AlN nanocolumns were etched in accordance with their crystallographic orientation, and the pyramid-like structures were formed (see figure 3).
Figure 3. SEM image of AlN/Si(111) epitaxial structure after etching in KOH solution for t=1, 2.5, and 5 min.

It can be seen that with an increase in the etching time, it becomes possible to achieve a gradual separation of the AlN layer from the substrate. It is known that there are some attempts to separate GaN and AlN layers for the substrates using pre-growth modified by wet etching GaN buffer layer [7], or porous SiC layer [8]. In this work for the first time it is demonstrated, that the etching of AlN/Si(111) epitaxial structures with a nanocolumnar seed layer can also be promising method to obtain free-standing AlN layers, which could be used as a substrates for A3N epitaxial growth.

However after 10 min etching in KOH, the AlN layer was partially destroyed at the edge of the sample (see figure 4).

Figure 4. SEM image of AlN/Si(111) epitaxial structure after etching in KOH solution for 10 min.

To prevent such damage of the AlN layer, it may be necessary to use a protective coating, such as thin metal films. In addition, the thickness of the continuous AlN layer should be increased in order to avoid overetching on the backside. It can be noticed that some residuals of the bases of the etched nanocolumnar structure remained on the Si (111) surface. Such formations are also observed during the etching of thin layers of Ga-polar GaN grown on Si (111) substrates [9]. Presumably, the crystal structure of such grains can be different from a wurtzite, including a polycrystalline, since AlN was grown on the mismatched Si (111) substrates. To clarify this issue, additional studies are required.

Furthermore, the electrical properties of the samples were investigated by Hall effect measurements based on four-probe Van der Pauw method using Ecopia HMS-3000 measurement system. It was found that despite all samples were grown undoped, AlN epitaxial layers have n-type conductivity with a carrier concentration $n \approx 2.1 \times 10^{18}$ cm$^{-3}$. It can be due to the presence of deep-level defects [10].
3. Conclusion
In this work the results of the studies of AlN layers grown on silicon substrates are presented. AlN/Si(111) epitaxial structures were synthesized using PA MBE technique via coalescence overgrowth of the nanocolumnar seed layer. It is shown that indeed the coalescence overgrowth approach can be used to obtain quite smooth AlN layers. Such design of the AlN epitaxial layers can be used as a buffer layer for synthesis of high quality AlN and GaN layers on silicon substrates. Structural, electrical and chemical properties of the obtained AlN/Si(111) structures were studied. It is shown that AlN epitaxial layers have n-type conductivity with a carrier concentration $n \sim 2.1 \times 10^{18} \text{ cm}^{-3}$. The crystallographic polarity of the samples was identified by wet etching in KOH solution and all the samples are Al-polar. Moreover, during the etching experiments for the first time it is demonstrated that the etching of the obtained type of AlN/Si(111) structures in KOH can become a promising method for obtaining high quality free-standing AlN and GaN. However, to avoid some damage and backside overetching it is necessary to use some protective coating and to increase the layer thickness.

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