Separation of AlN layers from silicon substrates by KOH etching

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Abstract. In this work, the AlN/Si(111) epitaxial structures grown consistently by plasma assisted molecular beam epitaxy (PA MBE) and hydride vapour phase epitaxy (HVPE) methods were studied. The PA MBE AlN buffer layers were synthesized via coalescence overgrowth of self-catalyzed AlN nanocolumns on Si(111) substrates and were used as templates for further HVPE growth of thick AlN layer. It was shown that described approaches can be used to obtain AlN layers with sufficiently smooth morphology. It was found that HVPE AlN inherited crystallographic polarity of the AlN layer grown by PA MBE. It was demonstrated that the etching of such AlN/Si(111) epitaxial structures results in partial separation of the AlN epilayers from the Si(111) substrate and allows to form suspended structures. Moreover, the avoidance of surface damage and backside overetching was achieved by use thin Cr film as surface protective coating and by increasing the layer thickness accordingly.

1. Introduction

Due to expansion of the semiconductor electronics application area, as well as the growing requirements for compactness, energy efficiency and performance of electronic devices, it becomes necessary to update the component base of modern electronics. Up to date, III-N semiconductors are one of the most promising materials for solving this problem [1]. These materials have unique optical and electrical properties [2]. In addition, they have extremely high thermal and chemical stability [3, 4]. Therefore, the development of III-N materials technology is especially important for the creation of devices operating in harsh environments.

Despite the obvious advantages of using III-N semiconductors for creating new electronic devices, there are still problems that hinder the rapid development and implementation of nitride-based electronics in everyday life. The first and the main obstacle is the lack of low-cost native III-N substrates. Therefore, heteroepitaxy of nitrides on silicon substrates is of increased interest.

At the same time, heteroepitaxy of high quality III-N layers on silicon substrates is quite challenging due to the several reasons. Large lattice mismatch (16.9 % for GaN/Si(111) and 19 % for AlN/Si(111)) leads to the high density of dislocations, and the difference in the thermal expansion coefficients of the materials increases the risk of epitaxial structures cracking. Moreover, there are several growth peculiarities of polar III-N materials on non-polar Si(111) substrates [5]. Furthermore, Al, Ga and Si interdiffusion can cause unintentional doping of III-N layers and silicon substrate [6, 7].
It is well-known, that AlN can be used as a buffer layer for heteroepitaxy of GaN on silicon to solve some of the problems above. However, it is reported that it may have quite rough surface morphology and poor crystalline quality [8]. One of the promising approaches to improve the crystalline quality of III-N-based heterostructures grown on Si(111) substrates can be formation of GaN and AlN epitaxial layers using coalescence overgrowth of GaN and AlN nanocolumns respectively [9].

In our previous work [10], it was shown that etching of such structures in a KOH solution can lead to the gradual separation of AlN layers from the substrate. At the same time, several damage of the sample surface was observed. In addition, a possibility of overetching of the AlN layer backside was found. This work is a continuation of research on the separation of AlN layers from the substrate by KOH etching.

2. Samples and experimental details

The AlN/Si(111) samples were synthesized consistently by PA MBE and then by HVPE method (see figure 1).

First, the AlN films with nanocolumnar seed layers were grown on the semi-insulating ($R > 10000 \ \Omega \cdot \text{cm}$) Si(111) substrates using Veeco Gen 200 MBE system. The pre-epitaxial preparation of the substrates was carried out according to the modified Shiraki method [12]. Before the growth, the Si(111) substrates were annealed for 30 min at $T = 850 \ ^\circ\text{C}$ in order to remove SiO$_2$ layer. The growth procedure was similar to the described in papers [10, 11]. The obtained by PA MBE AlN/Si(111) samples were used as templates for HVPE growth of thick AlN layer. At the first stage of the process, the growth zone was heated up to $T = 1080 \ ^\circ\text{C}$, then the PA MBE template was moved from the cold zone into the growth zone and annealed in an Ar atmosphere for $t = 10 \ \text{min}$. After annealing, AlN layers were grown on the AlN/Si (111) templates. Aluminium chloride and ammonia were used as reagents. High purity Ar was used as a transport gas. The parameters of the growth flows are arranged as follows: total argon flow $V_{Ar} = 4 \ \text{l/min}$, ammonia flow $V_{NH_3} = 1 \ \text{l/min}$, aluminum chloride flow $V_{HCl(Al)} = 200 \ \text{ml/min}$. The growth time was $t = 5 \ \text{min}$.

Both types obtained samples were studied via scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis. The identification of the crystallographic polarity of the AlN epilayers, as well as the separation process of AlN from Si(111) substrates, were carried out using chemical etching in KOH:H$_2$O (1:5) solution. To avoid surface damage during the AlN separation by etching in KOH, the Cr mask was formed on the sample surface by e-beam evaporation using BOC Edwards AUTO 500 vacuum coating system.
3. Results and discussion

3.1. Morphology studies

Characteristic SEM images of the two types obtained AlN/Si(111) structures are presented in figure 2. As it can be clearly seen in figure 2(a), AlN nanocolumn coalescence allowed the formation of the continuous AlN epitaxial layer, as it was shown previously [10].

Figure 2. Cross-section SEM images of the AlN/Si(111) samples obtained by PA MBE (a) and both PA MBE and HVPE (b).

The growth of AlN by HVPE on the AlN/Si(111) templates synthesized by PA MBE led to the formation of 2.5 µm thick continuous AlN layers (see figure 2(b)).

3.2. XRD analysis

Next, the samples were studied with XRD measurements using DRON-8 X-ray diffractometer. The characteristic XRD curves for both types of obtained samples are shown in figure 3.

Figure 3. XRD curves of the obtained samples.

The obtained XRD curves clearly show the peaks corresponding to Si(111) substrate and the AlN layers. From the position of the AlN (0002) reflex using the Bragg condition:

\[ 2d \sin \theta = n\lambda, \]  

(1)
the lattice constant $c$ of the synthesized AlN layers was calculated, $c_{\text{AlN}} \approx 4.980 \, \text{Å}$. The obtained value is consistent with the reference values ($c_{\text{AlN}} = 4.980 - 4.982 \, \text{Å}$).

3.3. Crystallographic polarity
It is well known that crystallographic polarity is an essential feature of wurtzite III-N materials, which affects their properties [13]. In particular, III-nitrides with metal-face polarity are the most chemically stable. The crystallographic polarity of the obtained by PA MBE and HVPE methods AlN layers was identified using express technique based on wet chemical etching in 40 °C KOH solution (KOH:H$_2$O = 1:5) for $t = 5 \, \text{min}$. It was found, that all the samples are Al-polar because after etching the height of the AlN layers and the surface remained unchanged (see figure 4).

![Figure 4](image1.png)

**Figure 4.** SEM images of the AlN/Si(111) samples grown by PA MBE (a) and both PA MBE and HVPE (b) after etching in KOH KOH:H$_2$O (1:5), $T = 40 \, ^\circ\text{C}$, $t = 5 \, \text{min}$.

Moreover, the experiment showed that HVPE AlN inherited crystallographic polarity of the AlN layer grown by PA MBE in contrast to the N-face AlN layers grown by HVPE on Ga-face GaN/Si(111) PA MBE template, that was shown in our previous work [14]. Besides this, it can be seen in figure 4(b) that not only PA MBE AlN is separating from the substrate, but HVPE AlN tends to separate on the interface HVPE AlN/PA MBE AlN.

3.4. Separation of AlN epilayers by wet chemical etching in KOH
As it was shown in our previous work [10], the approach to separation of AlN layers from Si(111) substrates by KOH etching has two serious disadvantages: surface damage and the risk of backside overetching. In this work, to protect the surface of the AlN epilayers from defect-selective etching, the samples were coated with a 55 nm Cr layer. As it can be seen in figure 5, thin Cr layer indeed allowed to avoid surface damage during the etching in KOH.

![Figure 5](image2.png)

**Figure 5.** SEM images of the AlN/Si(111) structures after etching in KOH KOH:H$_2$O (1:5), $T = 40 \, ^\circ\text{C}$, $t = 10 \, \text{min}$ (a), $T = 70 \, ^\circ\text{C}$, $t = 5 \, \text{min}$ (b).
Moreover, it was found that the Cr film can hold the separated AlN layer and prevent its crumbling (see figure 5(b)). The slight upward curvature of the Cr/AlN layers after its separation could be due to gradient in the strain of the materials in growth direction [15].

AlN layers grown by HVPE also were partially separated from the substrate by KOH etching (see figure 6.)

![Figure 6. SEM images of the HVPE AlN/Si(111) structures after etching in KOH KOH:H₂O (1:5), T = 40 °C, t = 10 min.](image)

The increase of the layer thickness up to 2.5 µm indeed allowed to avoid the backside overetching and the film crumbling during the separation of AlN by KOH etching.

4. Conclusion

In this work, the AlN/Si(111) epitaxial structures grown consistently by PA MBE and HVPE methods were studied. The PA MBE AlN layers were synthesized via coalescence overgrowth of self-catalyzed AlN nanocolumns on Si(111) substrates and were used as templates for HVPE AlN growth. Morphology of the obtained epitaxial structures was studied. It was shown that the described approaches allow obtaining sufficiently smooth AlN layers and the design of the PA MBE AlN epilayers with transition from nanocolumnar to 2D morphology can be used as a buffer layer for the heteroepitaxy of high quality III-N layers on silicon substrates. It was identified by etching in KOH that all the obtained samples have Al-face polarity. The experiment showed that HVPE AlN inherited crystallographic polarity of the AlN layer grown by PA MBE. Moreover, it was demonstrated that the KOH etching of such AlN/Si(111) epitaxial structures results in partial separation of the AlN epilayers from the Si(111) substrate. Moreover, the avoidance of surface damage and backside overetching was achieved by use 55 nm Cr film as surface protective coating and by increasing the layer thickness accordingly. Thus, it is shown that etching in KOH can also be promising method to form suspended structures based on AlN/Si(111) or to obtain free-standing III-N structures.

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