Separation of Ga-polar GaN layer from Si substrate by wet chemical etching

K Yu Shubina, T N Berezovskaya, D V Mokhov, A M Mizerov and E V Nikitina

Nanoelectronics Lab, St. Petersburg Academic University, Khlopina 8/3, 194021 St. Petersburg, Russia

Abstract. In this work the effects of H₃PO₄:CH₃COOH:HNO₃:HF etching solution taken with different concentrations to the Ga-polar GaN/SiₓNᵧ/Si(111) epitaxial structures is investigated. Possibility of at least partial separation of Ga-polar GaN film from the silicon substrate without any GaN surface morphology changes by the selected etchants is demonstrated. The etching process mechanism is shown. Resistivity of the photoresist mask to etchants used in the experiments is found.

1. Introduction

Wide bandgap semiconductor materials AₓN and their alloys have a set of unique electrical, optical and mechanical properties, which are important in modern optoelectronics, high power electronics and microelectromechanical systems (MEMS) industry. Since natural substrates for AₓN materials are very expensive, silicon carbide (SiC), sapphire (c-Al₂O₃) and silicon (Si(111)) substrates are used for epitaxial growth of III-nitrides.

One of the key technological problems of GaN synthesis on silicon substrates is 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. Not the least important problem is interdiffusion of Si and Ga atoms under growth conditions, which are typical for molecular-beam epitaxy (MBE). Therefore, the local etching of Si(111) substrate is possible with macroscopic voids formation during the growth process [1]. One way to overcome these problems is forming a thin SiₓNᵧ layer on the Si(111) substrate surface before GaN epitaxial growth [2].

Crystallographic polarity is an essential feature of nitride semiconductor materials with wurtzite crystal structure. Polarity affects the growth kinetics, chemical, structural, optical and electrical properties of heterostructures [3]. N-polar AₓN films are chemically active, while metal-polar layers, which are used more often, are known to be almost chemically inert. Thus the post-growth treatment of metal-polar nitrides by wet chemical etching is challenging. But it can be an advantage for MEMS production. Sacrificial layers are always used to from MEMS. This step can be skipped when etching of the substrate by solution to which the nitride layer is resistant.

2. Experimental details

In this work the experiments for investigation the effects of H₃PO₄:CH₃COOH:HNO₃:HF etching solution, taken with different concentrations, to the GaN/SiₓNᵧ/Si(111) epitaxial structures were carried out. The aim of the experiments was at least partial separation of GaN epitaxial layer from the Si(111) substrate. The Ga-polar GaN films of 0.6-0.8 mkm thickness were obtained by plasma assisted
molecular beam epitaxy (PA-MBE) on Veeco Gen 200 MBE system equipped with RF plasma source. The layers were grown on the semi-insulating (R > 10 kΩ cm) Si(111) substrates, which were cleaned according to the Shiraki method \[4\]. Before the growth, the Si(111) substrates were annealed at $T_{\text{sub}} = 850 \degree$C and then nitridated in the growth chamber using different nitridation temperatures and times. Thin Si$_x$N$_y$ layer, formed during the nitridation process, was used as a buffer layer.

To identify crystallographic polarity of the samples obtained the express-technique was developed (patent application №2016144845 15.11.2016). The meaning of developed technique is the observation of the surface morphology modifications as a result of anisotropic wet chemical etching by hot aqueous KOH solution in case of N-face structure, while surface and thickness of Ga-face material remain unchanged. Checking for surface morphology changes was carried out using scanning electron microscope 25 Supra Zeiss.

To investigate the effects of selected $\text{H}_3\text{PO}_4$:$\text{CH}_3\text{COOH}$:$\text{HNO}_3$:$\text{HF}$ (5:1:1:1) and $\text{H}_3\text{PO}_4$:$\text{CH}_3\text{COOH}$:$\text{HNO}_3$:$\text{HF}$ (5:1:3:0.33) etchants, Ga-polar sample, were immersed in these solutions at room temperature without heating and auxiliary illumination. The duration of etching process was 40-150 s.

3. Results and discussion

3.1. Crystallographic polarity

As a result of the polarity identification experiments, Ga polarity of the samples was confirmed. SEM images of Ga-polar sample surface before and after polarity identification etching are demonstrated in figure 1.

Despite the Ga-polarity, some changes in the surface morphology of the sample (hexagonal etch pits) are clearly visible (see figure 1, b). The primary cause of their appearance can be selective etching of various structural defects present in the GaN epitaxial layer: dislocations \[5\], nanotubes \[6\] or inversion domains \[7\]. However, the morphology of the defect-free areas and the thickness of the epitaxial layer remained unchanged, that indicates the Ga-polarity of the sample.

3.2. GaN epitaxial film separation from the substrate

As a result of the etching in $\text{H}_3\text{PO}_4$:$\text{CH}_3\text{COOH}$:$\text{HNO}_3$:$\text{HF}$ (5:1:1:1) and $\text{H}_3\text{PO}_4$:$\text{CH}_3\text{COOH}$:$\text{HNO}_3$:$\text{HF}$ (5:1:3:0.33) solutions, samples with GaN film, partially separated from the substrate, were obtained. The thickness of the GaN epitaxial layer has not changed. SEM image of the sample after etching is
demonstrated in figure 2. Slight upward curvature of the GaN layer appeared after its separation from the substrate by the etching process. It could be due to gradient in the strain of the material in growth direction [8].

![Figure 2. SEM image of the sample after etching in H₃PO₄:CH₃COOH:HNO₃:HF (5:1:1:1) solution. GaN film is partially separated from the Si substrate.](image)

![Figure 3. SEM cross-sectional image of the sample after etching. The mechanism of the separation process is clearly visible.](image)

The H₃PO₄:CH₃COOH:HNO₃:HF etching solution includes a mixture of nitric and hydrofluoric acids, which is commonly used for silicon etching. Therefore the separation mechanism of the GaN film from the Si₃N₄/Si(111) substrate is based on the silicon etching. However it should be noted that the etching occurs on the GaN/Si interface (see figure 3). Wherein, thin Si₃N₄ layer dissolves completely, as it was confirmed by additional experiments.

The etchant is assumed to react with the interface not only from the side faces of the sample, but also penetrating through the GaN epitaxial layer structural defects. What is more, the etching is not defect-selective and the surface morphology of the GaN epitaxial film remains unchanged (figure 4, a).

![Figure 4. SEM image of Ga-polar GaN/Si₃N₄/Si(111) sample after etching in H₃PO₄:CH₃COOH:HNO₃:HF (5:1:1:1) etching solution. The morphology of GaN epitaxial layer remain unchanged (a). There is no evidence of etching in the area protected by photoresist mask (b).](image)
In the sample areas coated with photoresist, the evidence of etching is not found (figure 4, b) and the photoresist mask is not dissolved. Variations in the composition of the etching solution did not lead to significant changes in the etching process and its results.

4. Conclusion
In this work the effects of etchants H₃PO₄:CH₃COOH:HNO₃:HF (5:1:1:1) and H₃PO₄:CH₃COOH:HNO₃:HF (5:1:3:0.33) to GaN/Si₃N₄/Si(111) Ga-polar epitaxial heterostructures was investigated. As a result, the possibility of at least partial separation of the Ga-polar GaN epitaxial film from the Si(111) substrate without additional lighting and heating was demonstrated. The mechanism of the process based on penetration of the etchant through structural defects of the epitaxial layer to the interface layer/substrate and etching Si₃N₄/Si(111) substrate was shown. It was experimentally established that these etchants do not damage the Ga-polar epitaxial layer and do not change its morphology. Resistance of the photoresist mask to H₃PO₄:CH₃COOH:HNO₃:HF (5:1:1:1) and H₃PO₄:CH₃COOH:HNO₃:HF (5:1:3:0.33) solutions was determined. It was found that results of etching in the etchants mentioned above are not significantly different.

Acknowledgments
The work was done as a part of the state assignment (№ 16.9789.2017/BCh) of the Ministry of Education and Science of the Russian Federation

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