Metal-assisted photoenhanced wet chemical etching of GaN epitaxial layers

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Abstract. In our work we successfully achieved selective removal of GaN epitaxial layer from the Si(111) substrate by photoenhanced wet chemical etching in K₂S₂O₈:KOH solution. Ti, Ni, Ti/Au, Cr/Au metal films were tested as etch masks. In case of thin Ti and Ni films the etch rate was quite low and metals were slightly dissolved. The use of mask containing Au film (noble metal) increased etch rate for 2-4 times. As a result, GaN was selectively removed from the substrate and highly anisotropic etch profile was formed.

1. Introduction
The wide-bandgap semiconductor material GaN has a number of unique properties, which are important for the manufacturing of modern opto- and nanoelectronics devices, and microelectromechanical systems (MEMS). However, natural substrates for GaN are currently very expensive, and silicon carbide (SiC), sapphire (c-Al₂O₃) and silicon (Si(111)) substrates are typically used for epitaxial growth of GaN. The most commercially attractive is low-cost GaN-on-Si technology.

It is well-known that crystallographic polarity is an essential feature of the wurtzite GaN, which affects structural, optical and electrical properties of the material [1]. It should be noted that GaN epitaxial films which are grown along [0001] direction (or Ga-polar films) are the most chemical resistant (figure 1).

![Figure 1. Schematic view of wurtzite GaN lattice exhibiting the polarity along the c-axis.](image)
Due to its extremely high thermal and chemical stability, GaN is very promising material for MEMS applications in harsh environments [2]. Thus, GaN-on-Si technology becomes more promising for MEMS industry. On the other hand, GaN durability makes postgrowth processing with traditional wet chemical etching challenging. For a long time, the etching of GaN was possible only by reactive ion etching (RIE) or inductively coupled plasma (ICP) etching [3]. However, the development of wet chemical etching techniques for nitrides goes on. Stimulation of chemical reactions with auxiliary illumination, current transmission and metals as catalysts, made possible wet chemical etching of GaN [4–5]. In this work we elaborated the technique for the complete removal of GaN epitaxial layers from silicon substrate by selective wet chemical etching.

2. Samples
The GaN/Si(111) samples were obtained by plasma assisted molecular beam epitaxy (PA-MBE) on Veeco Gen 200 MBE system equipped with RF plasma source. GaN epitaxial films 0.6–0.8 μm thickness were grown on the high-resistance (R > 10 kOhm) silicon substrates with (111) crystallographic orientation. Preliminarily Si(111) substrates were chemically cleaned according to Shiraki method [5]. Before the start of growth process, clean Si(111) substrates were annealed in the growth chamber at 1000 °C and then nitridated in the growth chamber. Formed by nitridation on the substrate surface, thin SiₓNᵧ layer was used as a buffer layer. Crystallographic polarity of the samples was identified by previously developed technique (patent application №2016144845 15.11.2016), based on wet chemical etching of GaN surface by hot aqueous KOH solution. All the samples demonstrated Ga-polarity. SEM images of Ga-polar sample before and after etching in hot KOH solution are demonstrated in figure 2.

![SEM images](image.png)

Figure 2. SEM image of Ga-polar GaN/SiₓNᵧ/Si(111) sample before (a) and after etching in hot aqueous KOH solution (b). Formation of hexagonal etch pits is a result of defect-selective etching of GaN layer.

3. Experimental details
As it was mentioned above, great chemical stability of Ga-polar GaN films makes traditional approaches to wet chemical etching inapplicable. At first, we tried to use photoenhanced wet chemical etching method. The etching solution contained potassium persulfate and potassium hydroxide (K₂S₂O₈:KOH) mixture. To induce the hole generation, necessary for the etching process, Xe lamp light source was used. The samples, coated with photoresist mask, were immersed in etching solution at room temperature. Unfortunately, the etching rate was extremely low. Moreover, we found that photoresist mask could be damaged by the etchant after 1 hour of etching. Thus, we decided to use metal mask. Samples with Ti, Ni, Ti/Au, Cr/Au mask were prepared. Metal films were formed by e-beam vacuum deposition on BOC Edwards AUTO 500 vacuum coating system. The etching procedure
was similar to the one mentioned above. After etching, the surface of the samples was examined with contact profilometer Ambios XP-1 and scanning electron microscope Supra 25 Zeiss.

4. Results and discussion
Since the rate of photoenhanced wet chemical etching for GaN epitaxial layers is extremely low, the chemical resistance of the mask is very important to avoid unintentional etching. As a result of the experiments it was found that the use metal films allows to avoid fast damage of mask by etchant. However, not all masks appear to be resistant to $K_2S_2O_8$ : KOH solution. In figure 3 surface of Ga-polar sample with Ti mask with 70 nm thickness on the initial stage of etching is demonstrated.

![Figure 3. SEM image of the surface of GaN/Si(111) sample, partially coated with Ti mask after etching in $K_2S_2O_8$ : KOH solution. Slight etching of Ti mask (right half) is observed.](image)

It is obvious that during the etching process thin Ti film is gradually etched by $K_2S_2O_8$ : KOH solution. So it turns out that the etching rate of thin Ti mask is higher than etching rate of GaN epitaxial layer. It leads to the emergence of local etching points in the area protected with Ti mask. Moreover, it reduces the etching rate of unprotected GaN area. Thus, we can assume that Ti is not a suitable mask material for the etching of GaN in $K_2S_2O_8$ : KOH solution. It is worth to note that similar behavior was observed for Ni mask. However, in case of Ti mask with 1 mkm thickness, no local points of etching were found in protected area, but the etch rate of GaN was still extremely low.

Surprisingly, completely different results were obtained with the masks, containing Au film. In this case, etching rate of GaN increased in 2-4 times. Our results, obtained with noble metal (Au) are consistent with work [7]. It confirms the assumption of Bardwell et al. [8] that a noble metal working as a cathode increases the reaction rate, acting as a catalyst, on the surface of which a radical ion $SO_4^{2-}$ forms from the persulphate ion $S_2O_8^{2-}$. These radicals are by-products of photolysis of $K_2S_2O_8$ under light with wavelength 310 nm or smaller. As a result, higher etching rate allowed to insure complete removal of GaN from the Si(111) substrate surface (see figure 4). It is worth to note that highly anisotropic etch profile was formed. In addition, no local etching points were observed in the protected area of GaN epitaxial layer. Finally, figure 4 demonstrates that the silicon substrate is not damaged. Thus, we have successfully ensured the etch selectivity to silicon.

Some material residues are clearly visible in figure 4a. It turned difficult to remove them from the substrate surface. Later studies have shown that these were residues of Si$_x$N$_y$ layer, which was formed during the nitridation of Si(111) substrate.
Figure 4. SEM image of Ga-polar GaN/Si$_x$N$_y$/Si(111) sample after etching in K$_2$S$_2$O$_8$:KOH. (a) Some material residues are observed, (b) highly anisotropic etch profile is formed.

5. Conclusion

In our experiments we successfully achieved selective removal of GaN epitaxial layer from the Si(111) substrate by photoenhanced wet chemical etching in K$_2$S$_2$O$_8$:KOH solution with auxiliary illumination by Xe lamp. We tried to use Ti, Ni, Ti/Au, Cr/Au metal films as etch masks. In case of Ti and Ni masks the etch rate was lower and metals were slightly dissolved and that significantly inhibited the etch process. In case of use Au film (noble metal) the etch rate was 2-4 times higher. Finally, highly anisotropic etch profile was formed. Thus, the relatively cheap method for anisotropic etching of GaN layer was elaborated. At the same time, the rate of metal-assisted photoenhanced wet chemical etching of GaN is quite low compared with RIE rate.

Acknowledgments

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