

Enhancing GaN Self Separation in HVPE by Use of Molybdenum

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We prepared 2"-GaN wafers as templates for a self separation process which is happening during cooldown after growing thick layers of GaN in our hydride vapor phase epitaxy (HVPE) reactor. Our templates process starts with GaN grown by metalorganic vapor phase epitaxy (MOVPE) directly on sapphire. These GaN layers are getting masked with 200nm of SiN that is structured by means of optical lithography. These masks are subsequently overgrown with a thin GaN layer by MOVPE. When overgrowing these templates with thick layers of GaN in HVPE, several problems occur. Because of GaN nucleation on the wafer side, the top layer is clamped to the sapphire substrate. This hinders separation during cooldown. Moreover mis-shaped material is growing at the wafer edge in very long growth runs. Both problems can be addressed by using molybdenum to locally influence the V-III ratio during growth.

1. Introduction

Becoming a more and more common material, galliumnitride (GaN) still suffers from the lack of suitable substrates. This leads to the need for heteroepitaxy in mid and low price applications. Although homoepitaxy is used for producing blue lasers, available GaN substrates are much too costly for growing LEDs and transistors. To achieve affordable homoepitaxial substrates, great efforts have been made in the field of ammonothermal growth [1]. Yet thick layers grown by HVPE are still a good candidate to provide GaN wafers for future industrial processes. Although being under research for some time, producing such layers is still not a trivial task. Differences in the thermal expansion coefficients of GaN and sapphire result in big layer curvatures and the large mismatch in lattice constants leads to strain and defects in the GaN layer. In order to cope with these problems, several methods have been developed to remove the GaN layer from the substrate such as laser-lift-off (LLO) [2], mechanical polishing [3] or growth on etchable substrates like GaAs [4] and ZnO [5]. Our approach is to use the difference in thermal expansion coefficients to get a self separation of layer and substrate during cooldown. With our self fabricated MOVPE templates we create weak interlayers which define a breaking point for the separation at a predetermined position. In the last years our institute has developed a standardized procedure to create suitable templates [6].

Unfortunately overgrowing these templates in HVPE seldom leads to wholly intact 2" self separated layers. While the separation layer seems to work very well in the center of the wafer, we still get small pieces of separated material at the wafer edges. The origin of

this effect can be found in the nucleation of GaN on the wafer side. Growth on the wafer sidewall results in a clamping of the top layer (Fig. 1) which prevents the top layer to separate from the substrate. The adhesion of the surplus material seems to be greater than the layer stability, leading to a burst of the separating layer.



Fig. 1: Clamping top layer.

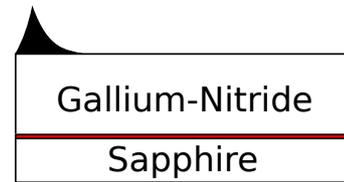


Fig. 2: Polycrystalline edge.

Another unwanted growth effect occurs alongside the wafer edge because of the horizontal design of our reactor. With the ammonia feed horizontally and GaCl being provided by a showerhead we get very high V-III ratios at the upstream wafer edge. GaN formed in long growth runs in this special zone possesses inferior properties such as many hexagonal pits and crystallites (Fig. 2). This effect reduces the usable area of the resulting pseudo substrate.

By simply covering the wafer edge with a metallic ring, the nucleation on the wafer sidewall can be prevented. From earlier experiments we know that molybdenum has the seldom ability to survive HVPE process conditions. Additionally some publications indicate that molybdenum could be able to bind ammonia by turning to molybdenum-nitride [7] thus lowering the V-III ratio in its vicinity. Therefore we studied the possibility of reducing parasitic edge effects by applying a molybdenum ring during growth.

2. Application of a Massive Molybdenum Ring to Prevent Growth on the Wafer Sidewalls

In the first attempt we used a wide ring of molybdenum which covers the whole rotation disc around the wafer (Fig. 3). By this approach the rotation disc is also protected against degradation due to parasitic nucleations on the disc, levering out pieces of quartz during cooldown after long growth runs.

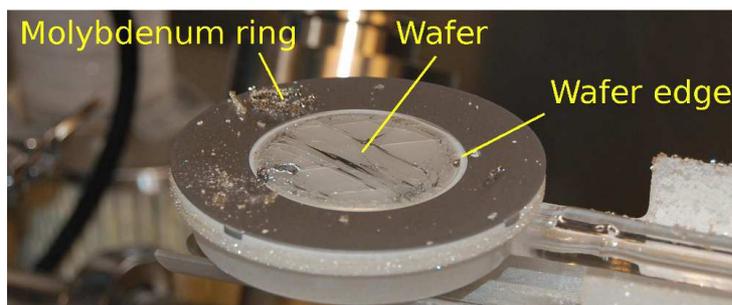


Fig. 3: First try with a completely covered rotation disc.

This first try already had the desired effect of preventing nucleation on the wafer side. Additionally no growth took place in a 1 mm broad ring at the wafer edge. As a third effect the wafer cracked during growth and the cracks filled with metallic gallium. This usually happens when the V-III ratio is extremely low. As the recipe has not been altered compared to previous growth runs, these facts indicate that the large molybdenum surface has taken ammonia from the process, a lot more than originally intended.

To decrease this effect we started using smaller molybdenum rings. We tried rings with a width of 4 mm and 2.5 mm. The latter one is the smallest considered to be mechanically stable in our HVPE process. With these smaller rings we were able to grow 300 μm thick, crackfree samples, which is the largest thickness being stable at room temperature. These samples still have a growth-free ring along the edge and thus are guaranteed to prevent clamping. However, growth with no clamping and covering the full 2" wafer would be preferred. This can be achieved by increasing the ammonia flow by 50%. Unfortunately this change in the flow pattern increases the current thickness inhomogeneity compared to our standard process (Fig. 5). To prevent this, further optimization will be necessary.

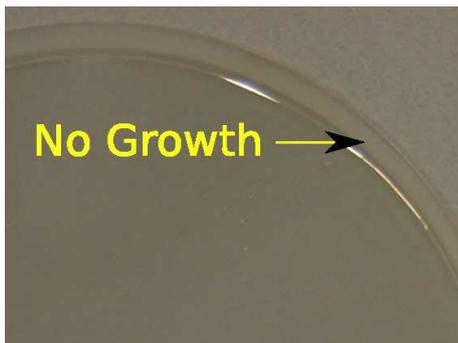


Fig. 4: Standard sample with Mo ring.

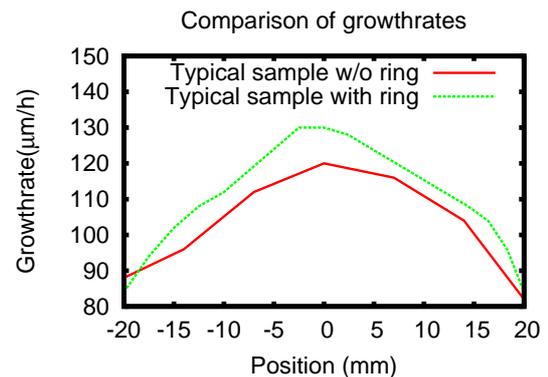


Fig. 5: Standard growth without and growth with mo-ring and additional ammonia.

Next we applied this new growth process to our self separation templates. Unfortunately the self separation didn't work with the molybdenum being applied already from the start of the HVPE growth. The ring seems to alter the growth conditions in a way that the weakened interlayer isn't able to develop properly which normally happens in the first few micrometers of HVPE growth. As a consequence we started HVPE growth without the molybdenum ring and applied the ring in a second, longer growth step resulting in the intended wafer thickness. This procedure however requires cooling down after the first growth step and a reconditioning of the reactor. This two step process makes the HVPE growth long and complicated.

Figs. 6 and 7 show a comparison of two self separation samples, one grown with and one without help of a molybdenum ring. Both samples have been grown on the same type of template. In both cases the growth has been designed as two-step growth with reactor reconditioning for a better comparison. The only difference in the recipe is the higher ammonia flow in the growth with molybdenum ring to compensate the effect of the ring on the V-III ratio. Although thickness homogeneity of the sample grown with



Fig. 6: Separated layer without ring.



Fig. 7: Separated layer with ring.

ring is worse than of the sample grown without molybdenum ring, the sample with ring has broken into considerably fewer pieces. Especially the size of the parts belonging to the layer edge is significantly larger. Thus the molybdenum ring is a great improvement towards separating whole 2" wafers. It can also be noticed that no mis-shaped material has grown along the wafer edge.

3. Application of a Sputtered Molybdenum Ring to Prevent Growth on the Wafer Edge

As seen in chapter 2, a massive molybdenum ring stable enough to withstand HVPE process conditions has some negative effects on GaN growth in general. To gain better control of the effect, we sputtered a thin layer of molybdenum on top of the MOVPE template and structured it by means of optical lithography and lift-off so that only a very small ring along the wafer edge was left (Fig. 8). The thickness of the sputtered molybdenum amounts to 150 nm in the first experiments.

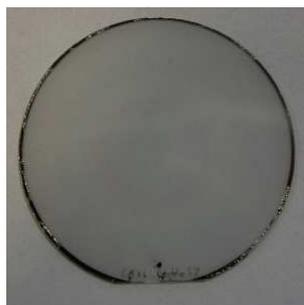


Fig. 8: MOVPE template with sputtered molybdenum ring.

Such templates have been overgrown with 80 μm and 200 μm GaN in HVPE, respectively. For the sample overgrown with 80 μm of HVPE GaN, a distance of about 600 μm width free of GaN can be seen in the SEM picture (Fig. 9, left sample). Growth on the sapphire side however doesn't seem to be affected by the topside ring of molybdenum. For the 200 μm thick sample this distance is covered with polycrystalline material (Fig. 9, right sample). We think that this is caused by a consumption of the sputtered molybdenum

during growth. Molybdenum is converted to molybdenum nitride which is barely stable at process temperatures and thus dissolves or evaporates and is carried to the exhaust by the gas stream.

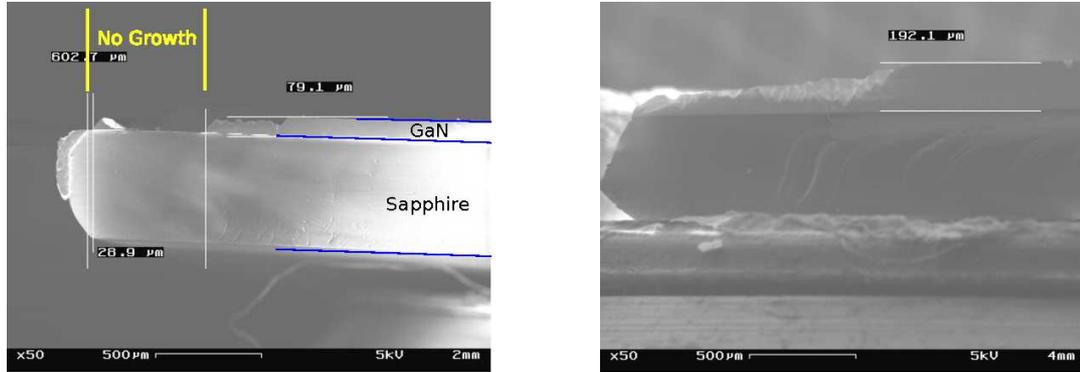


Fig. 9: SEM cross section, 80 μm and 200 μm GaN growth with sputtered molybdenum ring.

The formation of polycrystalline growth can even be seen macroscopically for self separated GaN layers. For most separated pieces this polycrystalline ring has broken off before removal of the sample from the machine, thus posing no obstacle in the separation process. However it still reduces the usable surface of the separated sample. Additionally the effect of the sputtered molybdenum in its present state is not strong enough to prevent the mis-shaped growth along the wafer edge. Next we want to try to deposit thicker molybdenum layers, the problem herein lies in the long deposition times and the poor adhesion of molybdenum to the wafer during lift-off.

4. Conclusion and Outlook

We have shown that molybdenum is most likely influencing the local V-III ratio in ammonia based epitaxy by drawing ammonia from the process. We have used this effect to improve the properties of our self separated GaN layers. However using solid molybdenum rings in combination with our method to produce weakened interlayers result in the necessity to split growth into two steps, making the process quite complex and time-consuming.

When using a thin, sputtered Mo layer instead of a solid Mo ring, no two-step growth is needed and all process parameters can be taken from the standard growth without molybdenum applied. However with the molybdenum being consumed, this method is not as effective as applying a solid Mo ring, in particular for thick layers to be grown. Some area of the 2" wafer is lost to bad growth.

For future investigations one should use solid molybdenum that is only partly exposed to the process environment to take advantage of a stable molybdenum source and having good control over the effect intensity. A possible setup to achieve this would be a modified rotation disc for the HVPE system that can hold a sapphire wafer in a defined position on top of a molybdenum plate or ring.

Acknowledgment

I want to thank I. Argut for preparing the separation templates and doing all lithography connected with the sputtered molybdenum experiments. The help in preparing the solid molybdenum parts by R. Rösch is also gratefully acknowledged. Thanks also go to D. Maier from the Institute of Electron Devices and Circuits for doing the sputtering. This work was financially supported by Freiburger Compound Materials GmbH, Freiberg.

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