

# Chlorine-Based ICP Etching for Improving the Luminance Efficiency in Nitride LEDs

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## Abstract

In this research, formation of fine cone-shaped patterns called PSS (Patterned Sapphire Substrate), and reverse-taper etching of GaN sidewalls were carried out using chlorine-based ICP-RIE (Inductively Coupled Plasma - Reactive Ion Etching) in order to improve the external luminance efficiency of GaN-LED (Gallium Nitride - Light Emitting Diodes). Dry etching systems with a special ICP coil called SSTC (Symmetrically Shielded Tornado Coil) [1] are suited for the formation of PSS, and by controlling parameters such as the flow rates of  $\text{Cl}_2$ ,  $\text{BCl}_3$ , and Ar, process pressure, ICP RF power, and bias electrode RF power, a cone profile with a curved surface can be formed without forming micro trenches. Also it was confirmed that an etching rate of 100 nm/min, and a selectivity of 1.3 over photo resist (PR) were achieved. Furthermore, reverse-taper etching of GaN was carried out with the same system, and smooth,  $70^\circ$  sidewalls were obtained employing a Ni mask.

## INTRODUCTION

In order to improve luminance efficiency of GaN- LEDs epitaxially grown on sapphire, crystal quality improvement, internal quantum efficiency improvements through device structure changes, and external quantum efficiency improvements through light extraction innovation, are required.

ELO (Epitaxial Layer Overgrowth) is a common method for improving crystal quality, epitaxial structure improvement is effective for increasing internal luminance efficiency and reflection on the epitaxial layer/sapphire interface and sidewalls is effective for improving light extraction.

PSS is used for light reflection on the epitaxial layer/sapphire interface, by means of concave-convex nano-patterning on sapphire substrates. This patterning aims to gather light towards the light extraction plane by scattering and diffraction of light on the bottom plane of the LED device, leading to improvement in the external

luminance efficiency. PSS is not only effective for more efficient light extraction but also helps with improvement of the GaN crystal quality.

However, the sapphire substrate is very hard, chemically resistant, and is therefore very difficult to process. To form fine cone-shape patterns on the substrate, the plasma etching method is very effective, but it is accompanied by several problems such as a low etching rate, poor mask selectivity, and substrate heating. In this work, by using the SAMCO model RIE-330iPC ICP-RIE system with the internally developed SSTC ICP source [1], with a proprietary heat resistant processing of the photo resist (PR) mask, these inherently difficult problems in forming PSS were solved.

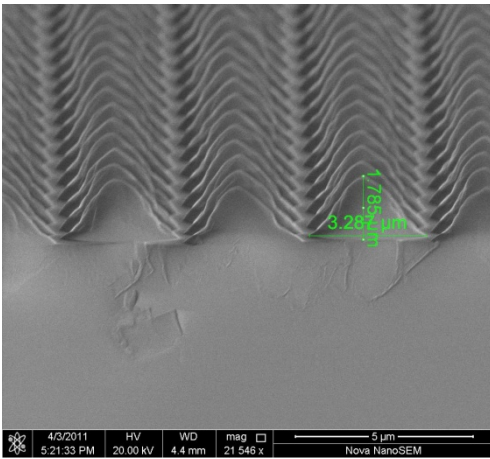
Regarding light reflection on the sidewalls of LED devices, there is a way of etching the GaN sidewall that results in a reverse-taper shape, which improves the external luminance efficiency by preventing light escaping via the sidewalls. This sidewall taper also can be produced using ICP-RIE. Here we explain the details of the research.

## EXPERIMENTAL DETAILS

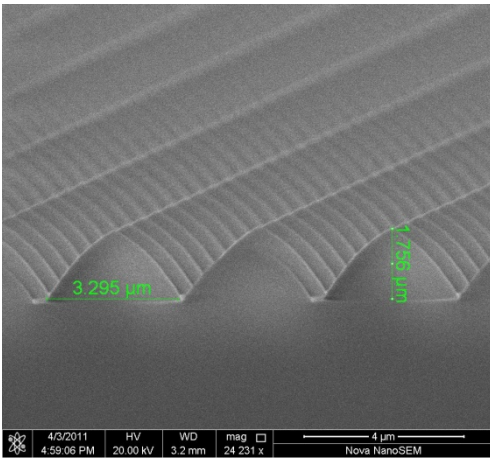
The PSS etching carried out in our research was performed on SAMCO's RIE-330iPC system fitted with SAMCO's internally developed SSTC ICP source with 13.56 MHz ICP power at 2 kW and 13.56 MHz bias power at 1 kW. Based on a chlorine chemistry, additive gases such as  $\text{BCl}_3$ , Ar, and  $\text{CHF}_3$  were used. The bias substrate electrode was equipped with an ESC (electrostatic chuck) and its temperature was kept constant at RT (Room Temperature) using a water medium, and the clamped wafer tray temperature was equilibrated to the ESC using backside helium. Process parameters such as the flow rates of  $\text{BCl}_3$ , Ar, and  $\text{CHF}_3$ , process pressure, and the ICP and bias RF powers were controlled and the feature profile, sapphire etching rates, and selectivity over PR was measured using a SEM. UV curing and hard baking of the PR was carried out to increase its heat resistance.

## RESULTS AND DISCUSSION

A photo resist mask is used for the formation of the PSS. The highest process temperature of photo resist in general is around 120°C, but high RF power is required for the etching of sapphire that is a difficult material to dry etch. With high RF power, and the accompanying ion bombardment, heat from the plasma to the substrate increases, and the PR mask deforms (or burns) due to the increased substrate temperature as is shown in Figure 1, making it impossible to obtain a well defined cone-shaped profile.



(a) PSS fabricated using standard photo resist



(b) PSS fabricated following processing of the resist for increased heat resistance.

Figure 1. Comparison of PSS formation following resist processing for increased heat resistance.

There are two ways to prevent this heat-induced problem: (i) directly cool the sapphire substrates to keep the PR mask below its deformation temperature, and (ii) increase maximum processing temperature of the PR mask.

“Direct cooling” of the sapphire substrate is carried out using mechanical or electrostatic clamping. A one-wafer per batch system will suffer from low throughput, and a multiple-wafers-per batch system with direct wafer cooling would have a very complicated wafer clamping mechanism.

In contrast to wafer direct wafer cooling, a tray-transfer type system will have a simpler mechanism, but without the ability of cooling each wafer, “PR burning” will result. To prevent this problem, surface hardening of the PR by UV curing and inner hardening by high temperature baking was carried out. As shown in Figure 1(b), the UV and thermal processed PR mask did not burn and an excellent PSS profile was obtained.

It is critical to control the PSS profile and the important profile factors are the feature height, width, taper angle, bottom profile, top profile, and taper profile. Without optimizing these factors, an “air gap” can be generated during the GaN epitaxial process (see Figure 2(b)), leading to an increase in the crystal imperfections, or causing the epitaxial layer quality to become degraded, leading to a decline in the internal quantum efficiency.

Furthermore, with disordered cone-shape profiles, scattering and diffraction of light will not take place as designed and this will lead to degraded external quantum efficiency. In addition, as shown in Figure 2(a), in the case of a “two-step” profile, differences in the crystal growth direction increase the probability of imperfections occurring around the top of the profile. Precise PSS profile control is required to suppress these problems.

It is crucial to control the etch selectivity of the sapphire over the photo resist mask in order to control the height of cone-shape. As shown in Figure 3(a), if the selectivity over the mask decreases, the cone-shape height also decreases and the top of the profile turns round. If the selectivity increases, the cone-shape height increases and the top becomes more pointed.

All the etching parameters, for example, the ICP RF power, bias RF power, pressure, and gas flow rates, influence the selectivity control, but if these parameters were changed, it could also result in a lower sapphire etch rate or micro trenches. Therefore, it was decided instead to add  $\text{CHF}_3$  to the etchant gas mixture in order to improve the etch selectivity of sapphire over the PR mask without changing the other process parameters.

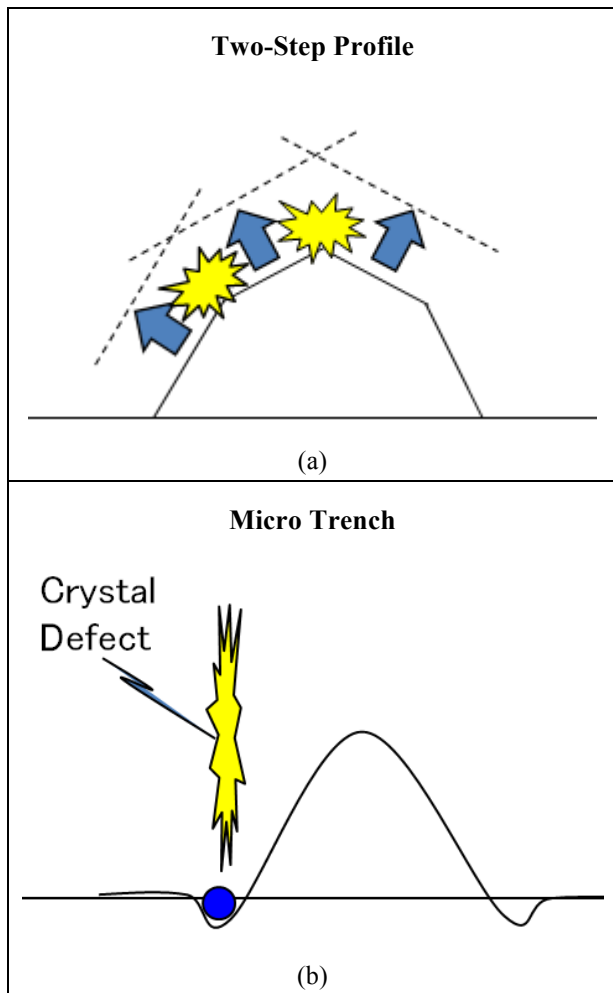
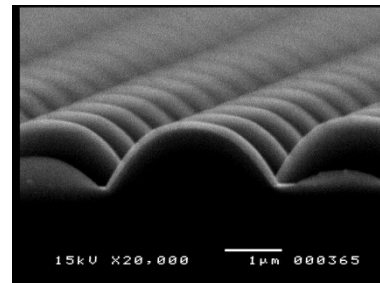


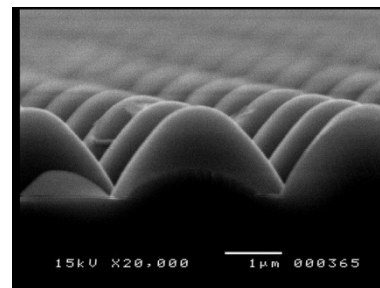
Figure 2. PSS shape and crystal defects. PSS profiles that produce epitaxial defects: (a) Two-step profile causes differences in the crystal growth direction, increasing the probability of imperfections around the top of the profile. (b) Micro-trenches on the fringe of the dot cause an “air gap” to form during crystal growth, increasing the probability of imperfections above the trench.

As shown in Figure 4, by employing  $\text{CHF}_3$  it was possible to improve the sapphire to PR selectivity without decreasing the sapphire etching rate. CH polymer is formed and functions as a protective film when  $\text{CHF}_3$  is added to the etchant gas mixture. This polymer film is also formed on the sapphire surface, but the thin film reacts with the oxygen supplied from the sapphire structure and is removed from the sapphire surface. Thus, with the improvement of the PR heat resistance and of the sapphire to PR selectivity by adding  $\text{CHF}_3$  gas, an etching rate of more than 100 nm/min, and the formation of cone-shape profiles were both achieved.

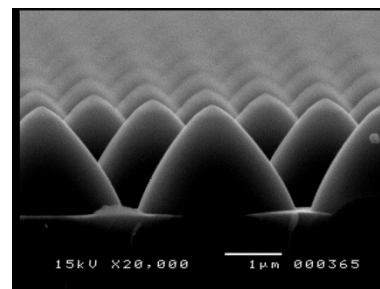
The reverse taper formation of the GaN sidewall during etching employs  $\text{Cl}_2$  and Ar gases. In order for the GaN etching to proceed in the lateral direction, the pressure was set to a relatively high 7 Pa, and the bias power was set to the lowest power at which etching would continue (~50W).



(a) Selectivity 0.7



(b) Selectivity 1.0



(c) Selectivity 1.3

Figure 3. Changes in resist mask selectivity result in changes in PSS shape and height

Figure 5(a) shows that when the ICP RF power is low, lateral etching is weak and a step is formed on the sidewall. Increasing the ICP power to 800W (Figure 5(b)) results in removal of the step, and results in a virtually straight reverse-tapered sidewall, in this case around  $70^\circ$ . Because the angle varies depending on the GaN crystal plane, control beyond this cannot be achieved. The GaN etching rate was 140nm/min when using a Ni mask, which is the preferred mask material. Because of lateral mask erosion,  $\text{SiO}_2$  masks do not allow formation of a reverse taper profile as dramatic as can be achieved with Ni masks.

## CONCLUSIONS

Using ICP-RIE etching based on chlorine chemistry, optimal cone-shaped patterns were formed on sapphire substrates and reverse taper etching of GaN was carried out. By processing the resist mask for higher temperature resistance, an excellent PSS profile was obtained using the simpler tray processing method. Formation of a 70° reverse taper sidewall profile was achieved by optimizing parameters for the GaN reverse taper etching using a Ni mask. Future challenges include finer patterning of the PSS and concave-convex nano-patterning of the GaN surface.

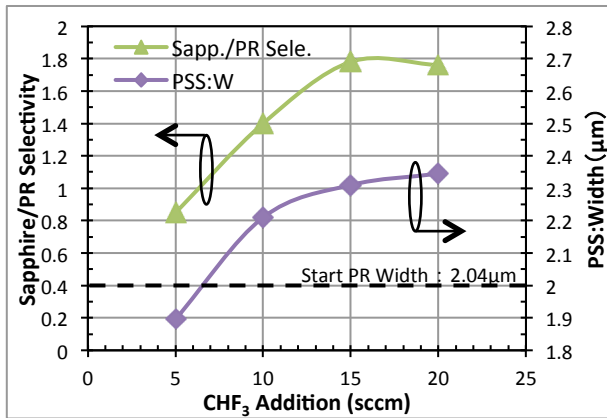


Figure 4. By adding CHF<sub>3</sub> to the etchant mix, the sapphire to resist selectivity can be improved and the PSS height and shape can be controlled. The addition CHF<sub>3</sub> forms a CH polymer that functions as a protective film. The polymer film is also formed on the sapphire surface, but the film reacts with oxygen generated from sapphire and is quickly removed from the surface. By this mechanism the sapphire etching rate does not decrease and yet the etch selectivity can be improved.

## ACKNOWLEDGEMENTS

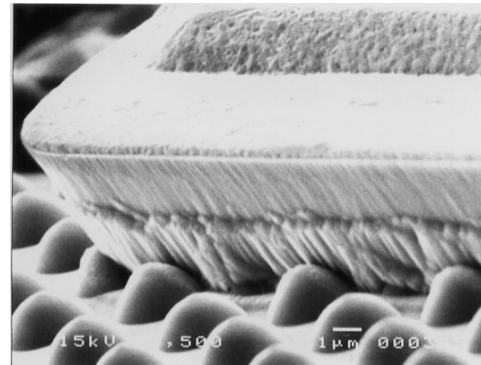
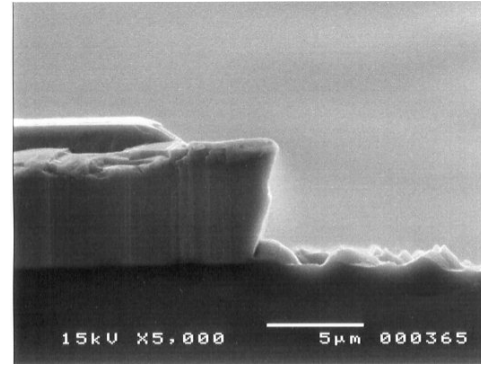
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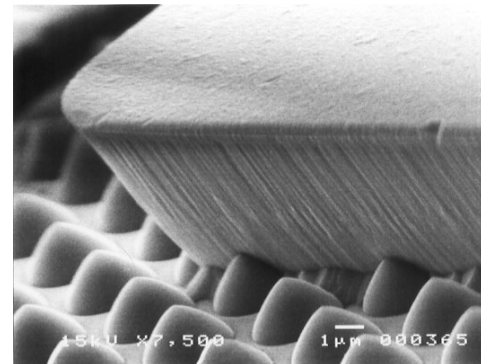
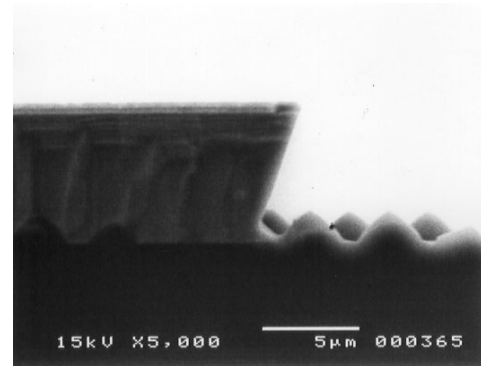
[1]S.Nakagami ,H.Nakano,T.Tatsuta, M.Sawai and O.Tsuji: 18th International Symposium on Plasma Chemistry, 32P-72, August 26-31(2007), Kyoto University, Japan

## ACRONYMS

LED: Light Emitting Diode  
 PSS: Patterned Sapphire Substrate  
 SEM: Scanning Electron Microscope  
 SSTC: Symmetrically Shielded Tornado Coil



(a) ICP=500W



(b) ICP=800W

Figure 5. GaN-LED reverse taper etching. Increasing the ICP power results in a flat and smooth reverse taper profile. Etching angle was 70° and is dependent on the GaN crystal plane.