# 応用物理学会学術講演会予稿のタイトル

# Investigation of fluorine-based plasma for Atomic Layer Etching of GaN

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#### 1. Introduction

Atomic Layer Etching (ALE) is a cyclic etching process, aiming to remove one monolayer by cycle, and opens a new path to overcome the challenging issues of GaN etching [1]. Most of the reported plasma assisted ALE of GaN rely on chlorination of GaN surfaces to form GaCl<sub>x</sub> products for the adsorption step and Ar ions irradiation for the activation step. [2-3]. Fluorination of GaN leads to the formation of nonvolatile GaF<sub>x</sub> by-products (boiling point close to 950°C) which could re-inforce the required self-limited feature of the adsorption step. In this work, we propose to investigate the use of CF<sub>4</sub>/O<sub>2</sub>/Ar plasma to achieve fluorination of GaN as the adsorption step, combined with Ar ions irradiation as an activation step.

#### 2. Experiment

A SiO<sub>2</sub> hardmask was deposited and patterned by photolithography into an array of 3  $\mu$ m-diameter holes on top of un-doped *c*-axis oriented GaN grown on a sapphire substrate. ALE processes were developed in an Inductively Coupled Plasma (ICP) etcher (RIE-200iP from SAMCO). For the adsorption step, the feeding gas consisted in CF<sub>4</sub>/O<sub>2</sub>/Ar gas mixture. The ICP source power (RF<sub>source</sub>) and pressure were set at 100 W and 5 mTorr, respectively. No ICP bias power (RF<sub>bias</sub>) was applied during the adsorption step. The activation step relied on a Ar plasma at 5 mTorr. The self-bias voltage (DC bias) during activation was varied in the 12—39 V range by tuning RF<sub>bias</sub> power. For each condition, Etching rate Per Cycle (EPC) was estimated from the etched depth of GaN submitted to 200 ALE cycles, measured from Scanning Electron Microscopy (SEM) images.

#### 3. Results and Discussion

In Figure 1, in the case of  $O_2$  flow rate set at 10 sccm, two distinct regimes are clearly identified. In regime I (DC bias < 26V), EPC decreases with the DC bias voltage. In regime II (DC bias > 26V), EPC increases with DC bias. For a  $O_2$  flow rate of 20sccm, GaN is not etched for low DC bias (DC bias  $\leq 15$  V), By increasing DC bias above 15 V, EPC slightly increases and seems to plateau in the 0.34-0.55 nm range. XPS shows the presence of C and F atoms on surface in the case of 10 sccm  $O_2$ , but O and F are detected in the case of 20 sccm  $O_2$ . We assume that weakly dissociated CF4/O<sub>2</sub>/Ar plasma leads to the deposition of thin  $C_xF_y$  oligomers similarly to the polymer layers formed during the steady-state of Reactive Ion Etching of Si [4-5]. Low energetic Ar ions (regime I) induce de-fluorination of the  $C_xF_y$  oligomers by fragmentation, releasing additional F species readily available for the fluorination of GaN. Subsequent incoming Ar ions either degrade the oligomer layers and activate the underneath GaF<sub>x</sub>, or activate GaF<sub>x</sub> back diffusion back through the thin oligomer. As DC bias further increases, Ar ions degrades the  $C_xF_{y}$ , released F species recombine with sputtered CF<sub>x</sub> to form volatile CF<sub>4</sub>, reducing the available amount of F species for GaN fluorination, leading to a decrease of EPC. At DC bias higher than 26 V (regime II), Ar ions sputter both the oligomers and GaN.

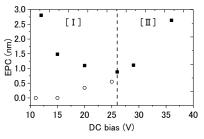


Figure 1. EPC as function of the DC bias during activation step for a  $CF_4/O_2/Ar$  plasma at adsorption with a  $O_2$  flow rate of 10 sccm (back) and 20 sccm (white).

By increasing  $O_2$  flow rate to 20 sccm, drastic change for the EPC is observed. Formation of  $C_xF_y$  is inhibited by the higher concentration of reactive O radicals in the plasma phase favoring the formation of CO and CO<sub>2</sub>, reducing the  $C_xF_y$  ions concentration required for polymerization. The presence of O species in the fluorinated GaN surface leads to a shift in the threshold energy required for efficient Ar ions activation.

#### 4. Conclusion

We have investigated the use of  $CF_4/O_2/Ar$  plasma for the surface modification step in the ALE of GaN. The defluorination of a  $C_xF_y$  layer, formed during adsorption, upon low energetic Ar ions is believed to be responsible for the high observed EPC. We also demonstrate that the O<sub>2</sub> flow rate is a critical parameter to control the fluorination of GaN during adsorption.

### References

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