

## Atomic Layer Etching

### Room Regency Ballroom A-C - Session ALE2-MoA

#### ALE of Compound Semiconductors

**Moderators:** David Boris, U.S. Naval Research Laboratory, Ishii Yohei, Hitachi High Technologies

4:00pm **ALE2-MoA-11 Developments of Atomic Layer Etch Processes and their Applications in Fabricating III-V Compound Semiconductor Devices**, *Xu Li, Y Fu, S Cho, D Hemakumara, K Floros, D Moran, I Thayne*, University of Glasgow, UK

**INVITED**

In recent years, atomic layer etch (ALE) to precisely remove very thin layers of materials using sequential self-limiting reactions has attracted extensive attention in semiconductor processing. Our work has indicated that ALE processes have versatile potential in the fabrication of III-V compound semiconductor devices, a number of which will be discussed in this presentation. One example is the use of an ALE process for precise control of the threshold voltage of GaN-based power transistors. This enables both normally off and normally on devices to be realised on the same wafer, which is vital for the realisation of an integrated cascode transistor (Fig 2). Another application example is the realisation of III-As and III-Sb nanowires and finfets for low power logic applications using a lateral ALE process to minimize the wire diameter and fin width. A further example is using a lateral ALE process to selectively etch gate metal stacks to form nanometer scale T-gates required for low noise for RF devices (Fig 3). This has been achieved using Si industry compatible subtractive processes and without the need for complicated resist stacks.

In our ALE processes, Cl<sub>2</sub>, HBr, and SF<sub>6</sub> have been used as the reactive gases for surface modification, with the details depending on the etched materials and target applications. The etching chemistries are based on the formation of self-limited Ga, In, Al, and Sb halides in the case of III-V materials or Mo, W and Pt in the case of T-gate metal stacks. The modified surfaces are then removed using an Ar plasma formed with optimized RF and/or ICP power. The impact of all ALE process parameters on etch induced electrical damage has been an important aspect of our work (Fig 4)

To gain insight into the etching mechanisms, in-situ surface analyses have been carried out using Auger spectrometry and XPS techniques. The ALE processes and surface analyses which will be described in this presentation are carried out in a cluster tool from Oxford Instrument Plasma Technology, which includes an ICP etching chamber with repeat loop function and a Scienta Omicron NanoSAM surface analysis tool with Auger spectrometer and XPS (Fig 1). The clustered arrangement enables samples to be subjected to plasma processing and then transferred, under vacuum, into the analysis chamber. This flexibility enables each step of the ALE cycle to be evaluated (Figs 5&6).

4:30pm **ALE2-MoA-13 GaN and Ga<sub>2</sub>O<sub>3</sub> Thermal Atomic Layer Etching Using Sequential Surface Reactions**, *N Johnson, Y Lee, Steven M. George*, University of Colorado - Boulder

Atomic layer etching (ALE) of GaN and Ga<sub>2</sub>O<sub>3</sub> is important for the fabrication of power electronics devices. Thermal ALE of GaN and Ga<sub>2</sub>O<sub>3</sub> was performed using sequential, self-limiting surface reactions. The thermal ALE was accomplished using fluorination and ligand-exchange reactions. XeF<sub>2</sub> and HF were used as the fluorination reactants. BCl<sub>3</sub> was the main metal precursor for ligand-exchange. Ga<sub>2</sub>O<sub>3</sub> was also etched using Al(CH<sub>3</sub>)<sub>3</sub>, AlCl(CH<sub>3</sub>)<sub>2</sub>, TiCl<sub>4</sub> or Ga(N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub> as the metal precursors for ligand-exchange.

Crystalline GaN samples prepared using MOCVD techniques were etched with sequential XeF<sub>2</sub> and BCl<sub>3</sub> exposures. GaN etch rates varied from 0.18 to 0.72 Å/cycle at temperatures from 170 to 300°C, respectively (see Supplemental Figure 1). Because the GaN etch rates were self-limiting versus BCl<sub>3</sub> exposure and BCl<sub>3</sub> pressure, the GaN etching mechanism is believed to involve XeF<sub>2</sub> fluorination of GaN to GaF<sub>3</sub> and then ligand-exchange between BCl<sub>3</sub> and GaF<sub>3</sub> to yield volatile BCl<sub>w</sub>F<sub>x</sub> and GaF<sub>y</sub>Cl<sub>z</sub> species. GaN fluorination using a NF<sub>3</sub> plasma was also successful for etching crystalline GaN at 250°C.

Ga<sub>2</sub>O<sub>3</sub> samples deposited using ALD techniques were etched with sequential HF and BCl<sub>3</sub> exposures. Ga<sub>2</sub>O<sub>3</sub> etch rates varied from 0.59 to 1.35 Å/cycle at temperatures from 150 to 200°C, respectively. The Ga<sub>2</sub>O<sub>3</sub> etch rates were self-limiting versus HF and BCl<sub>3</sub> exposure. Ga<sub>2</sub>O<sub>3</sub> ALE was also performed using HF for fluorination and a variety of metal precursors for ligand-exchange. Ga<sub>2</sub>O<sub>3</sub> etch rates at 250°C were 0.2, 0.8, 1.1 and 1.2

Å/cycle for Ga(N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>, TiCl<sub>4</sub>, Al(CH<sub>3</sub>)<sub>3</sub> and AlCl(CH<sub>3</sub>)<sub>2</sub> as the metal precursors, respectively (see Supplemental Figure 2). The wide range of metal precursors that can etch Ga<sub>2</sub>O<sub>3</sub> argues that the ligand-exchange reaction with GaF<sub>3</sub> is facile

4:45pm **ALE2-MoA-14 Selective GaN Etching Process using Self-limiting Cyclic Approach for Power Device Applications**, *Frédéric Le Roux, N Posseme, P Burtin, S Barnola, A Torres*, Univ. Grenoble Alpes, CEA, LETI, France

Formation of the two-dimensional electron gas (2DEG) in AlGaN/GaN heterostructures is the key-point for successful development of GaN-based power-electronics such as High Electron Mobility Transistors (HEMT) and diodes. Plasma-etching steps are considered as critical in fabrication for such devices. Indeed standard chlorine plasma<sup>1</sup> can lead to surface roughness degradation<sup>2</sup> and surface state modifications (non-stoichiometric layers, surface potential modifications and dangling bonds)<sup>3-5</sup>. This is why Atomic Layer Etching (ALE) and Digital Etching (DE) are developed to limit the material degradations and to have a better etch depth control<sup>6</sup>. The aim of this study is first to evaluate a self-limited GaN etching process using DE for power devices. This DE consists in two steps. First an O<sub>2</sub> plasma oxidizes the GaN surface. Then, the oxidized layer is removed using BCl<sub>3</sub> plasma selectively to the non-oxidized GaN.

Experiments have been carried out on 200mm wafer using the following stack: GaN (80 or 20nm)/Al<sub>0.22</sub>Ga<sub>0.78</sub>N (24nm)/AlN (<1nm)/GaN (1,8µm)/buffer layers/Si substrate.

The development and optimization of the DE process will be presented. The etch mechanism of the self-limited process has first been understood thanks to XPS analyses performed on blanket wafers. It will be demonstrated that the O<sub>2</sub> plasma oxidizes the surface until a saturation level, which enable the self-limitation. Then the BCl<sub>3</sub> plasma removes the oxidized film selectively to the non-oxidized GaN film. This selectivity has been explained by the deposition of B<sub>x</sub>Cl<sub>y</sub> layer on non-oxidized GaN. Small amount of boron oxide by-products is also detected at on the surface after the DE.

Then DE O<sub>2</sub>/BCl<sub>3</sub> cyclic process has been compared to standard chlorine based plasma. It will be shown that the roughness and the uniformity are similar for both processes, while the cyclic process present better performances in term of electrical and material degradation. The benefit of the self-limited GaN etching process has finally been validated on patterned wafers for power device integration.

In the second part of this study, the first results of a Cl<sub>2</sub>/Ar ALE process for GaN etching will be presented and compared to the DE O<sub>2</sub>/BCl<sub>3</sub> cyclic process.

1. Pearton, S. J. *et al.J. Appl. Phys.***86**, 1–78 (1999).
2. Li, X. *et al.J. Semicond.***39**, (2018).
3. Eddy, C. R. *et al.J. Electron. Mater.***28**, 314–318 (1999).
4. Pearton, S. J. *Appl. Surf. Sci.***117–118**, 597–604 (1997).
5. Tripathy, S. *et al.J. Vac. Sci. Tech. Part Vac. Surf. Films***19**, 2522–2532 (2001).
6. Kanarik, K. J. *et al.J. Vac. Sci. Tech. Vac. Surf. Films***33**, (2015).

5:00pm **ALE2-MoA-15 ALE of GaN (0001) by Sequential Oxidation and H<sub>2</sub>/N<sub>2</sub> Plasma**, *Kevin Hatch, D Messina, H Fu, K Fu, X Wang, M Hao, Y Zhao, R Nemanich*, Arizona State University

Atomic layer etching of GaN may be used to reduce the high surface defect concentrations produced during inductively coupled plasma (ICP) etching and other processing methods. We have demonstrated a new method for plasma enhanced atomic layer etching (PEALE) of GaN (0001) using sequential surface modification by remote O<sub>2</sub> plasma, followed by removal of the surface oxide through H<sub>2</sub>/N<sub>2</sub> plasma etching. The efficacy of etching the surface oxide via H<sub>2</sub>/N<sub>2</sub> plasma exposure was confirmed by deposition and removal of several nm of plasma enhanced atomic layer deposited (PEALD) Ga<sub>2</sub>O<sub>3</sub> epilayers on GaN. The composition of the H<sub>2</sub>/N<sub>2</sub> plasma was investigated, and a H<sub>2</sub>:N<sub>2</sub> volumetric flow ratio of 2:1 was found to produce sufficient etch rates at 500°C. An etch per cycle (EPC) of 2 nm was achieved and is attributed to the oxidation rate of GaN. This PEALE process was performed on “as-grown” unintentionally doped GaN (UID-GaN) deposited on a GaN substrate by metalorganic chemical vapor deposition (MOCVD), which also underwent Ar/Cl<sub>2</sub>/BCl<sub>3</sub> ICP etching prior to the PEALE process. Application of several PEALE cycles resulted in improved surface stoichiometry, which was attributed to removal of Ga-rich layers created during ICP etching. After the PEALE process the N:Ga ratio increased from 0.5 to 0.8, and the surface roughness improved from R<sub>RMS</sub> = 0.3 nm to R<sub>RMS</sub>

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= 0.2 nm, as measured by AFM. This ALE process has been performed on ICP etched samples prior to regrowth and the I-V characteristics have been measured, showing improved voltage breakdown observed.

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**5:15pm ALE2-MoA-16 Comparative Study of Two Atomic Layer Etching Processes for GaN, Cédric Mannequin, C You, University of Tsukuba, Japan; G Jacopin, T Chevolleau, C Durand, University Grenoble-Alpes, France; C Vallée, LTM-UGA, France; C Dussarat, T Teramoto, Air Liquide Laboratories, Japan; H Mariette, University Grenoble-Alpes, France; K Akimoto, M Sasaki, University of Tsukuba, Japan; E Gheeraert, University Grenoble-Alpes, France**

Drastic reduction of defect density after etching in nitride semiconductor-based devices becomes a pressing requirement to improve further device performances. Defects introduced by etching process during the formation of the recess gate at AlGaIn/GaN or during the fabrication process of GaN displays based on  $\mu$ -Light Emission Diodes are the main sources issues of devices reliability degradation. Atomic Layer Etching (ALE) processes relying on two times separated half reactions: adsorption step and activation step are of great interests for solving these issues.

In this work, we propose a comparative study of two ALE processes for undoped *c*-oriented Ga-polar GaN, relying both on Cl<sub>2</sub>-based plasma for the absorption step but using two different gases for the activation step. The two ALE processes were developed in an Inductively Coupled Plasma etcher (RIE-200IP from SAMCO). In-situ Optical Emission Spectroscopy (OES) was used to monitor gas dissociation for the adsorption, activation and purge steps, allowing identification of active species. Additionally, OES monitoring were used to calibrate Cl<sub>2</sub> dosing time and purging time to ensure complete separation of the Cl<sub>2</sub> dissociation by-products and the gas used for the activation step. The ICP source power (RF<sub>source</sub>) and pressure for the adsorption step were varied in the 5–120 W range and 0.65–2 Pa range, respectively. For set adsorption step conditions, the self-bias (V<sub>DC</sub>) of the activation step was varied in the range of 11–40 V by changing the ICP Bias power (RF<sub>bias</sub>). For each condition, the Etching rate Per Cycle (EPC) was estimated from the etched depth of GaN submitted to 200 ALE cycles using Scanning Electron Microscopy images and reported as a function of V<sub>DC</sub> (from the activation step).

In the case of the first activation gas, we report an ALE mode with an EPC of 0.276 nm, corresponding to 1.3 monolayer (ML) of the GaN wurtzite structure in the *c*-direction. For this first activation gas, a constant EPC were observed for V<sub>DC</sub> in the 15–17 V range consistent with ALE process. For higher V<sub>DC</sub>, the EPC continuously increase with V<sub>DC</sub>. For the second activation gas, we report an ALE mode presenting an EPC of 0.567 nm corresponding to 2 ML. A constant EPC for V<sub>DC</sub> in the 16–22 V range were observed. From Atomic Force Microscopy observations of 500 x 500 nm<sup>2</sup>, we report significant decrease of the Rms roughness from 0.18 nm for as-deposited GaN surface to 0.07 nm after ALE processing.

Finally, we will discuss and tentatively propose mechanisms to explain the significant differences observed between our two ALE approaches.

**5:30pm ALE2-MoA-17 Chlorinated Surface Layer of GaN in Quasi Atomic Layer Etching of Cyclic Processes of Chlorine Adsorption and Ion Irradiation, Masaki Hasegawa, T Tsutsumi, Nagoya University, Japan; A Tanide, SCREEN Holdings Co., Ltd.; H Kondo, M Sekine, K Ishikawa, M Hori, Nagoya University, Japan**

In fabrication of the next-generation power electronic devices of gallium nitride (GaN), an atomic layer etching (ALE) technique with cyclic processes of ion irradiation and Cl adsorption steps has been attracted for reduction of plasma induced damage. To control the ALE of GaN, we have studied the chlorinated surface layer of GaN at each Ar and Cl reaction step using the beam experiments with *in situ* X-ray photoelectron spectroscopy (XPS).[1,2]

Samples were GaN films grown on sapphire substrate by Hydride Vapor Phase Epitaxy (HVPE) method. Prior to the beam experiments, native oxide on GaN surface was removed by wet cleaning (5% HF) and Ar ion sputter. The as-cleaned surface was exposed by Cl radicals with a dosage of 10<sup>19</sup> cm<sup>-2</sup> generated in Cl<sub>2</sub> gas (flow rate 0.5 sccm) plasma by application of RF power of 400 W. Next, Ar ions with a dosage of 10<sup>16</sup> cm<sup>-2</sup> and the accelerating voltage of 100 V or 200 V. The one cycle consisted of these Ar ion irradiation and Cl radical exposure. To stabilize the GaN surface, five cyclic processes were carried out. Then, the GaN surface at each step was analyzed by angle-resolved XPS with take-off-angles of 20, 30, 40, 60, and 90 degrees with respect to the wafer plane. Depth profiles were analyzed by the maximum entropy method.

The Ar ion bombardments change the GaN surface to Ga-rich. Subsequently, as the ion-bombarded Ga-rich surface exposes to the Cl adsorption step, the surface stoichiometry recovers to high N/Ga ratio, resulting to form Ga chlorides as a volatile. The depth profiles obtained from XPS data after the 7th Cl radical exposure were compared with the different Ar ion energies. In the depth profiles of Cl concentration after Cl radical exposure after irradiation with 100-eV-ion (a) and 200-eV-ion (b), the Cl amount and penetration with a depth of approximately 2 nm during the Cl radical exposure were in details observed quantitatively. In the Ar ion bombardments, the formation of non-bonded Ga (dangling bond) and disordered structure was dominated by the ion energies. The resultant etching depth per cycle and the surface stoichiometry were depended on the non-bonded Ga amounts that resulted to desorb Ga chlorides during the Cl radical exposure. This indicates that the surface chlorination layer determined the ALE-properties of real layer-by-layer etching and self-limiting reaction. Not only the ion energy but also the chlorination layer depths should be taken account for the ALE cyclic processes.

[1] T. Takeuchi et al., J. Phys. D: Appl. Phys. 46, 102001 (2013).

[2] Y. Zhang et al., J. Vac. Sci. Technol. A 35, 060606 (2017).

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