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U.S. NAVAL RESEARCH LABORATORY

# Surface Science Studies of GaN Substrates Subjected to Plasma-Assisted Atomic Layer Processes

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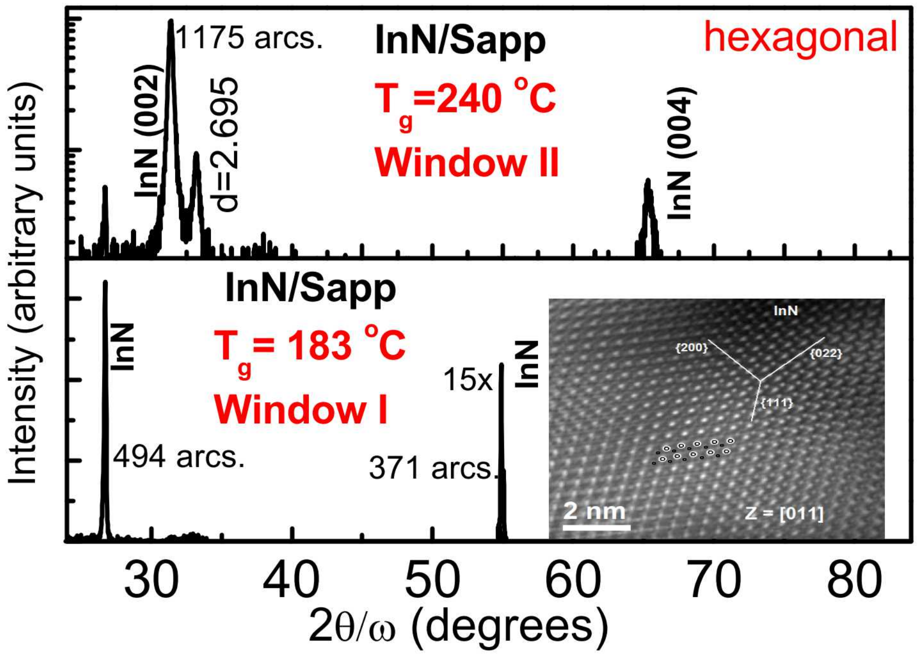
NRL, ESTD

# Motivation

## Current prospects

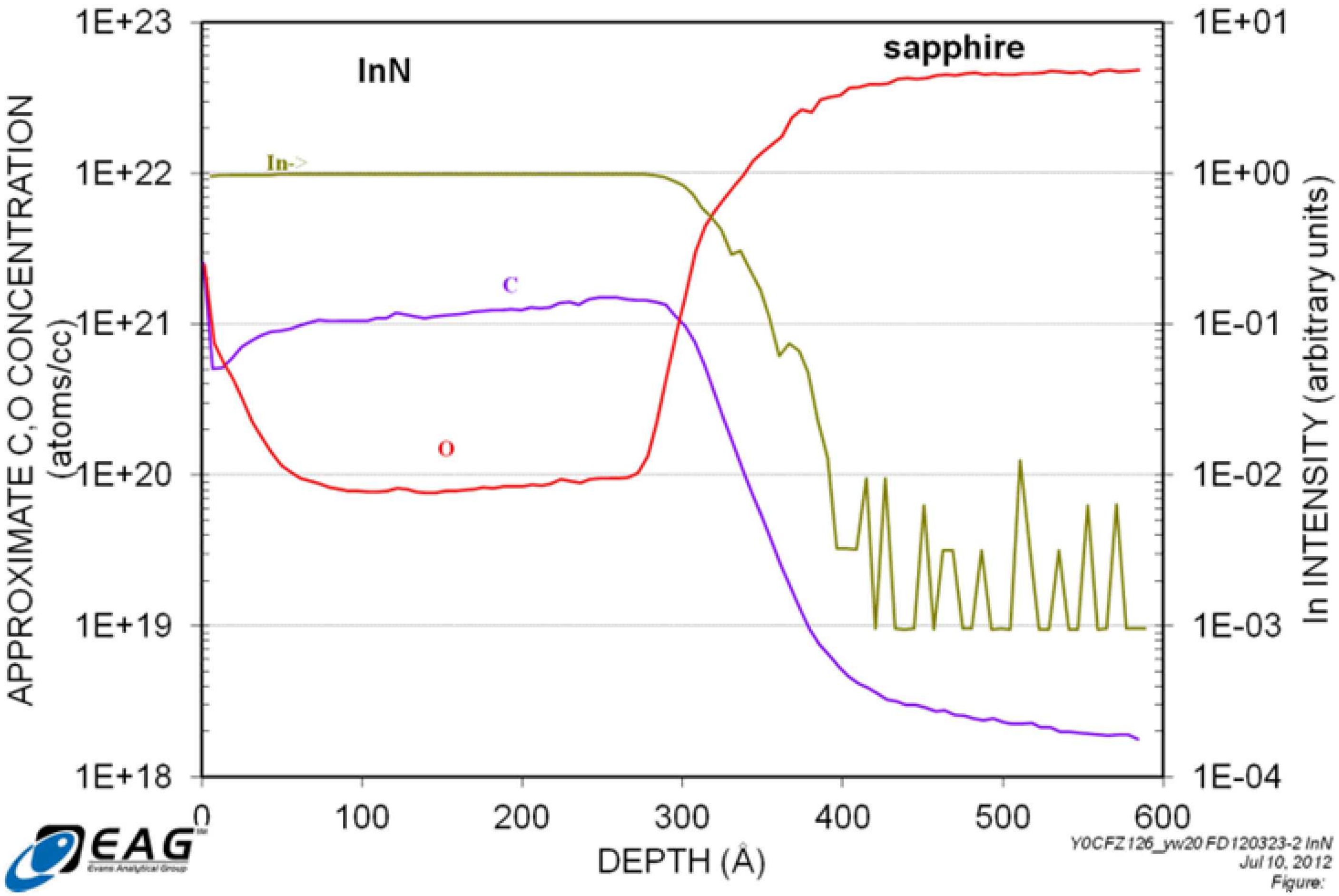
- Plasma Assisted-ALE is one of the best methods to grow epitaxial materials at low temperature [1,2]
- We have reported ALEp of InN and two growth windows for cubic and hexagonal phases [1]
  - Two different phases of ALEp InN
    - For $T_g$ = 183˚C: cubic phase (Window I)
    - For $T_g$ =240˚C: hexagonal phase (Window II)




- Still don't understand nucleation and growth mechanism
- Moving to GaN substrates for better lattice match

[1] Nepal *et al.*, *Cryst. Growth and Des.*, **13**, 1485 (2013)
[2] Nepal et al., *Appl. Phys. Lett.* **103**, 082110 (2013).

# Contamination Issues




- plagued by 1000x too much carbon and oxygen by semiconductor purity standards

# Experimental Procedure

## Surface Preparation

- Ex situ cleaning (wet chemical): Acetone & Isopropanol & DI, Then: $UV/O_3$ +HF
- In situ cleaning (Ga Flash Off Atomic Layer Process (GFO ALP), Plasma)

## ALP Ga Flash Off

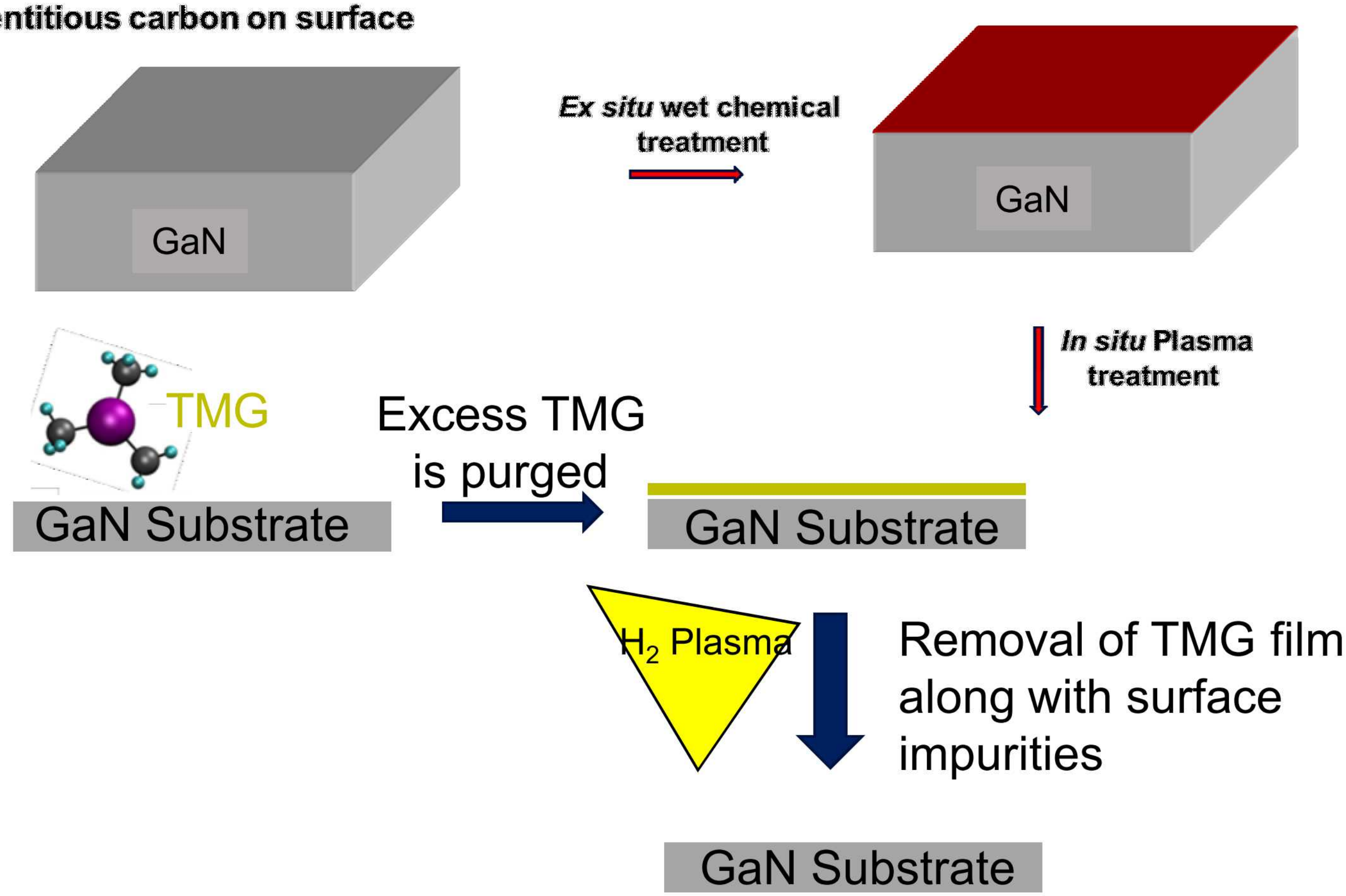
- TMG pulse : 60 ms
- Purge: 10 s
- $Ar/H_2$ plasma pulse : 21 s
- Purge : 19 s

## Substrates:

- Bulk GaN

**Why surface cleaning? Oxygen in lattice at surface, adventitious carbon on surface**

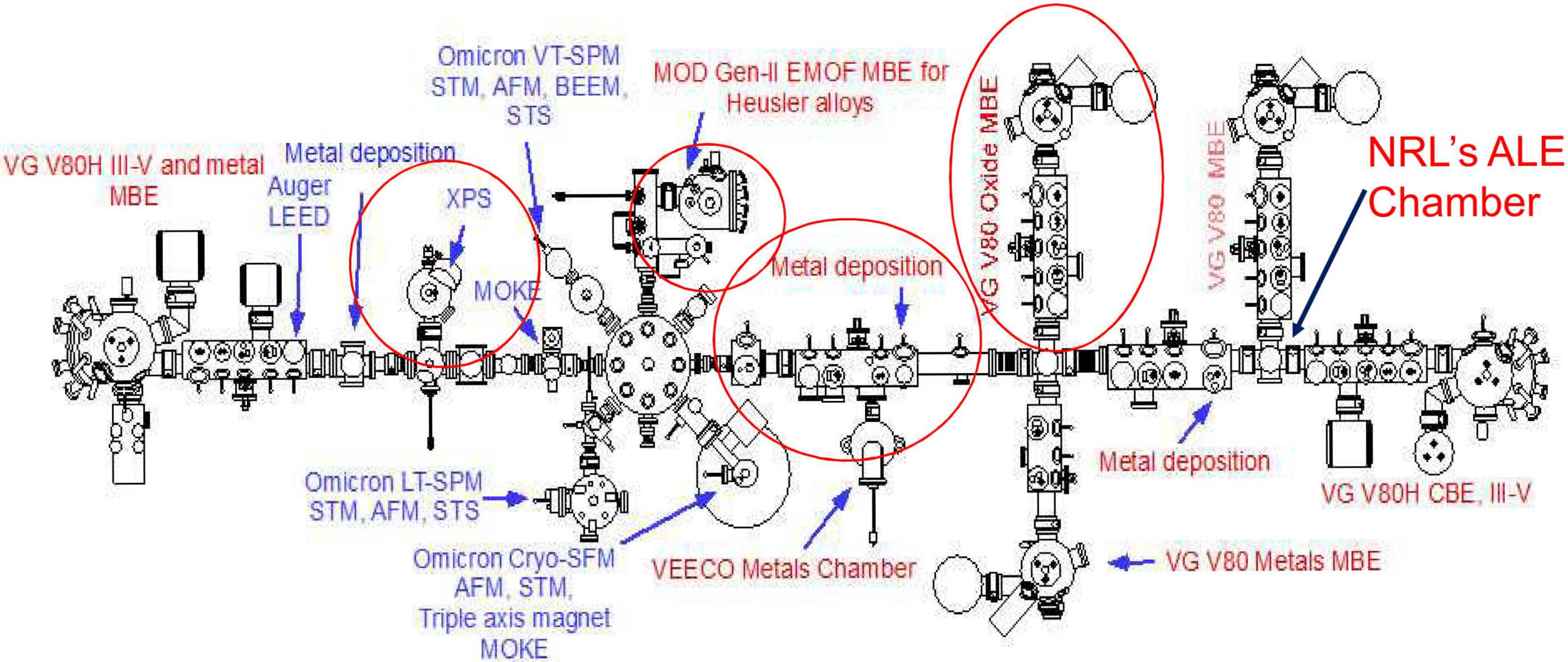
**Process flow for epitaxial growth**



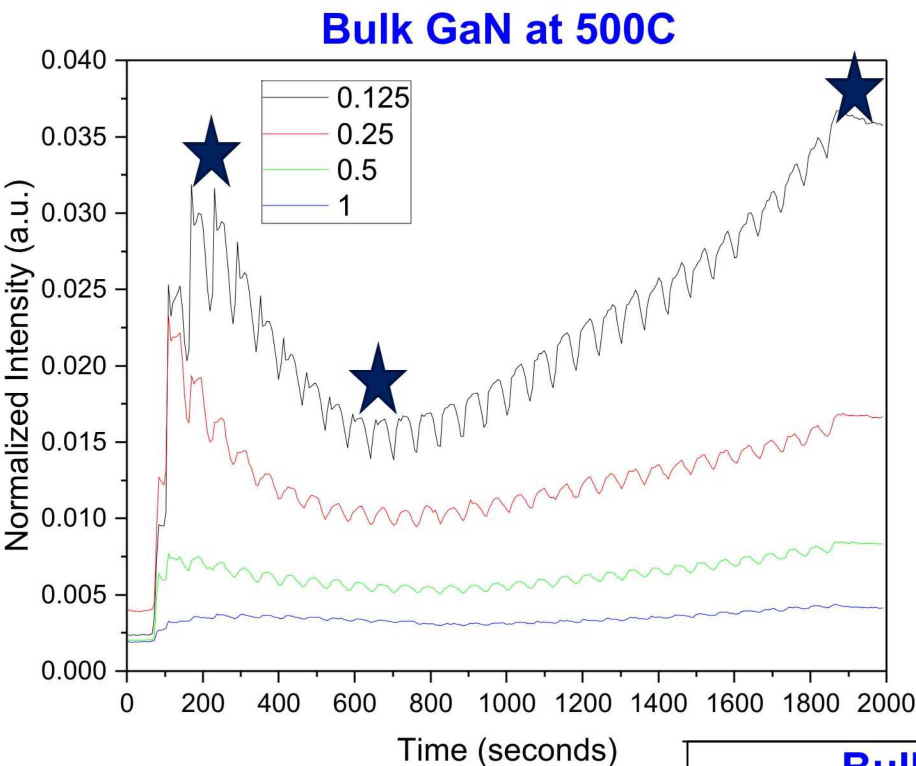


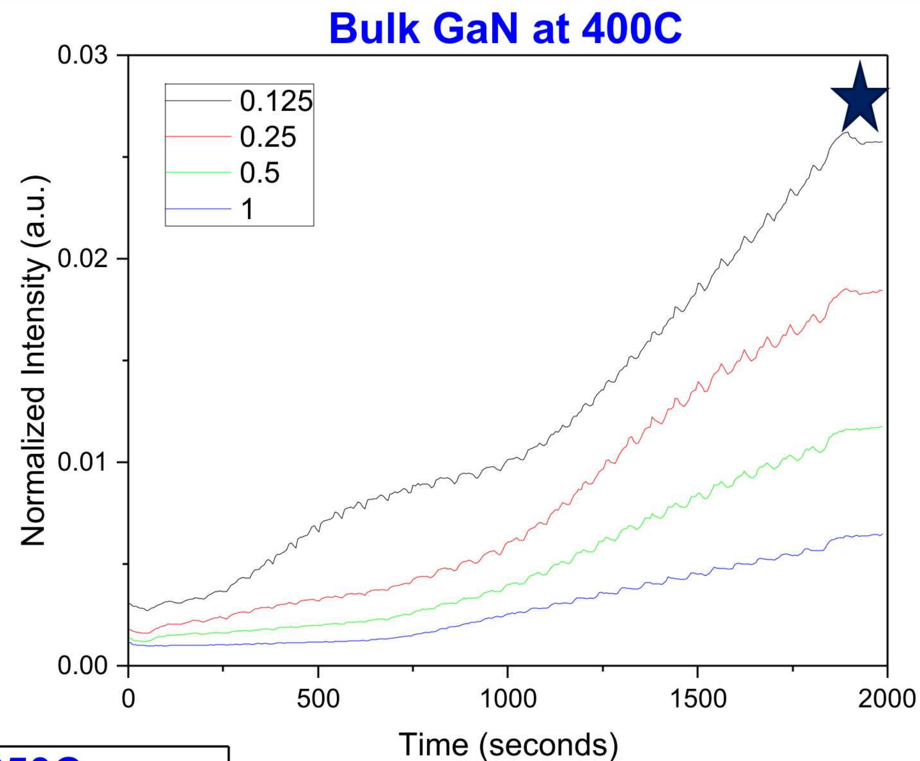

S. Rosenberg, et. al., J. Vac. Sci. Technol. A 37, 020908 (2019), doi: 10.1116/1.5080380
S. Rosenberg, et. al., J. Vac. Sci. Technol. A 37, 020908 (2019), doi: 10.1116/1.5080090
D.F. Storm et al. / Journal of Crystal Growth 456 (2016) 121–132

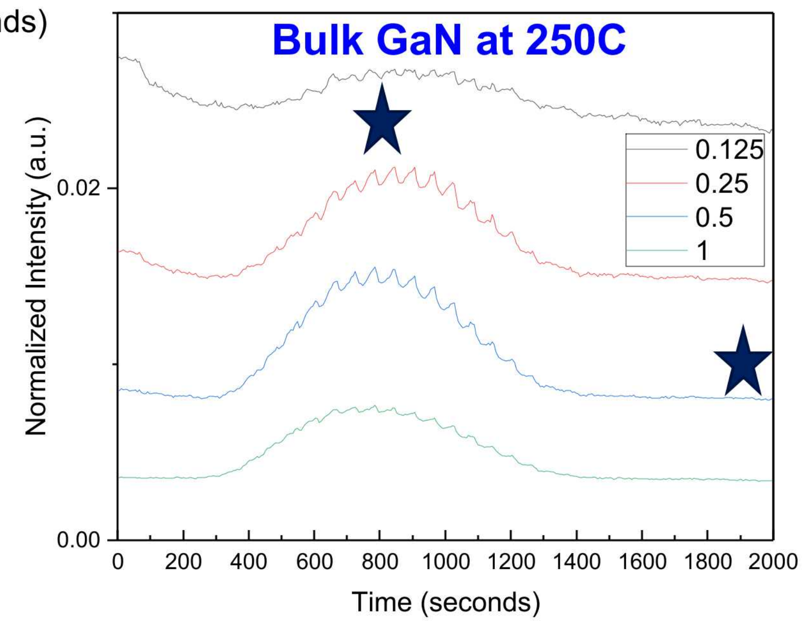
# UCSB Chamber Set Up



# GISAXS of ALP Ga Flash Off at Different Temperatures



# XPS Analysis

| Temperature | GFO ALP Cycles | $O/O_0$ |
|---|---|---|
| 250 | 12 | 0.956775 |
| 250 | 30 | 0.881354 |
| 400 | 30 | 1.083015 |
| 500 | 3 | 1.424906 |
| 500 | 10 | 0.71398 |
| 500 | 30 | 1.047371 |
| 500 | 10-Hydrogen only | 0.784837 |
| 500 | 10-anneal | 1.444746 |



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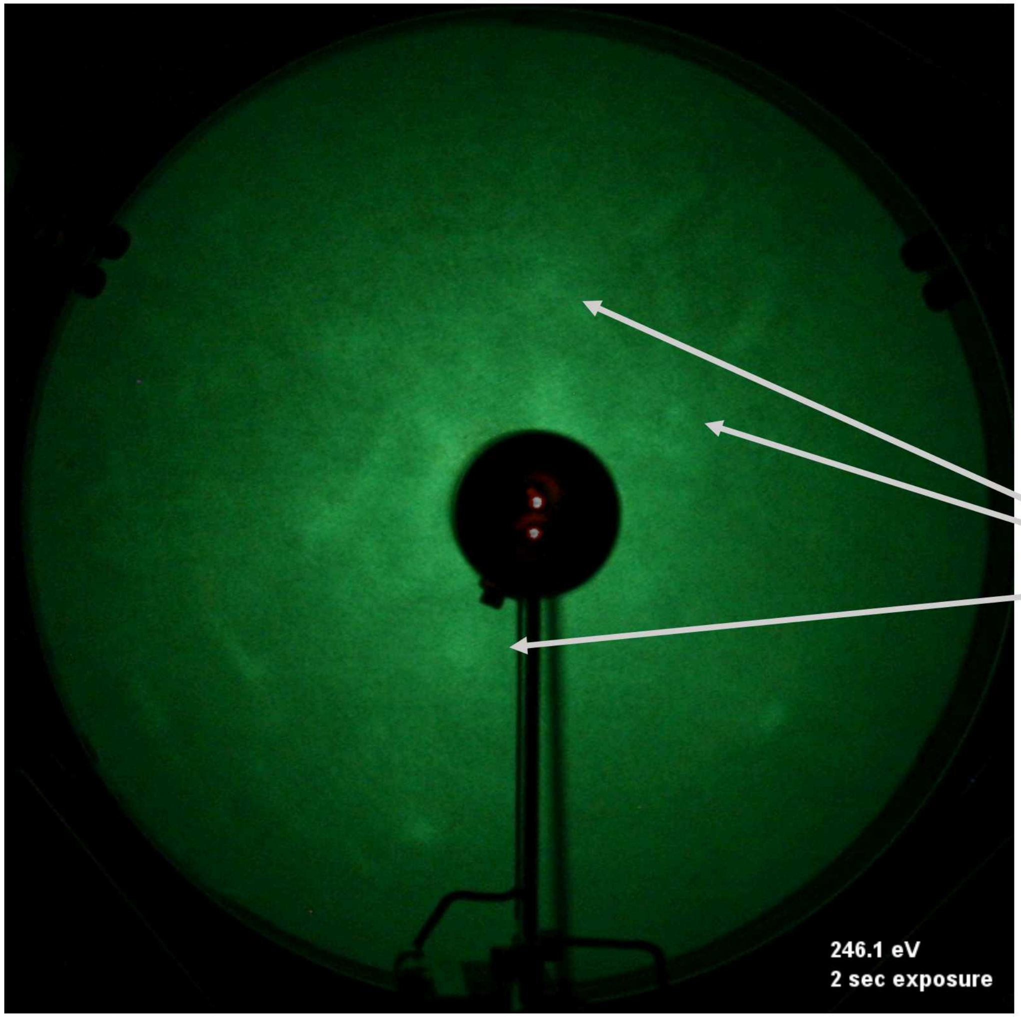
# LEED: As Received

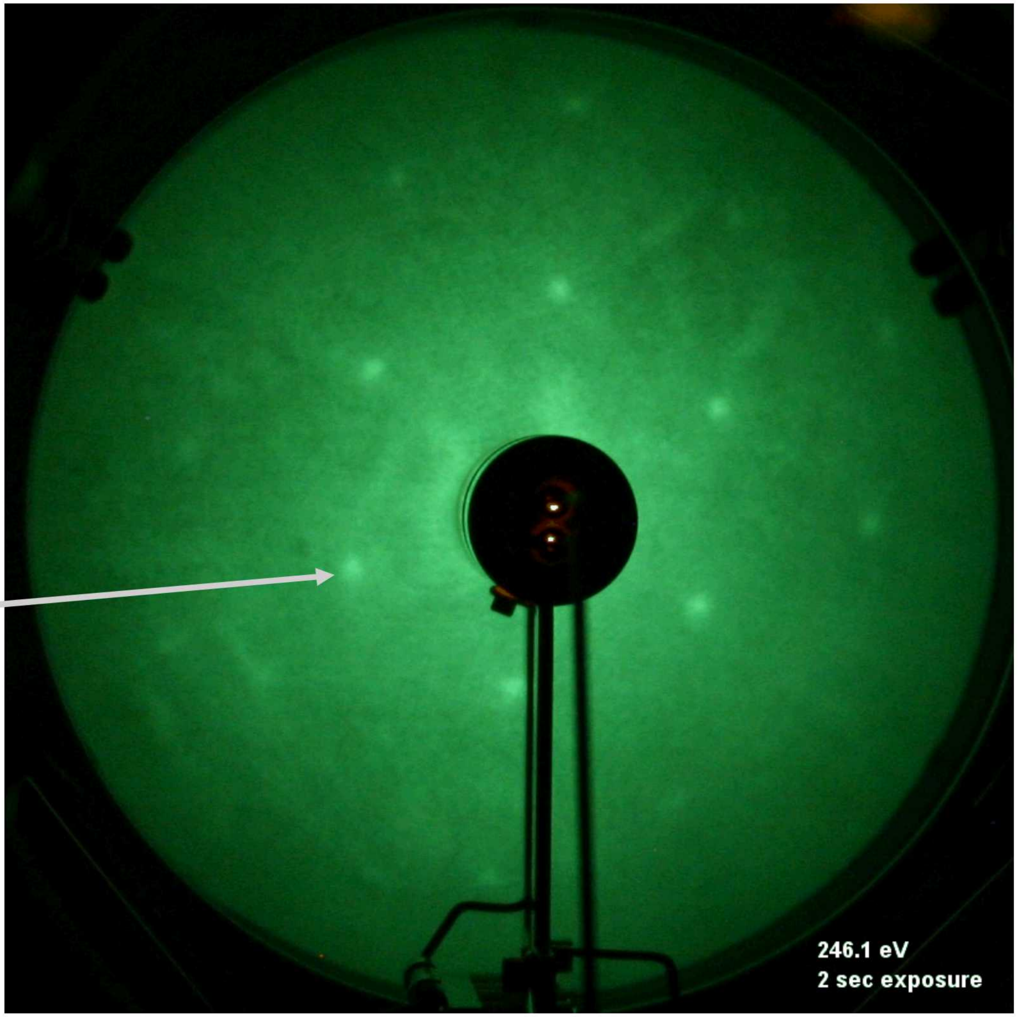



Faint spots- in the shape of a hexagon.

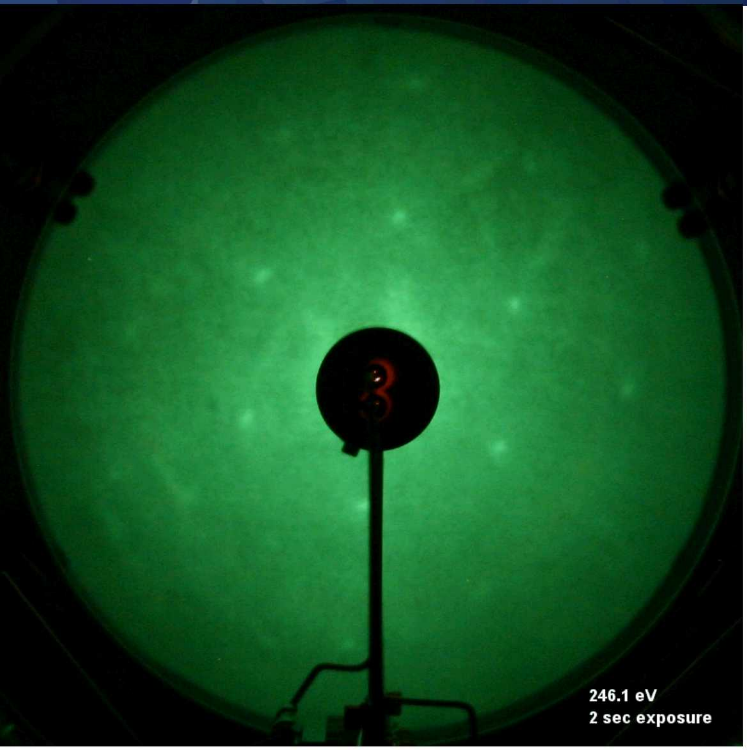
# LEED: After Ex-Situ Cleaning

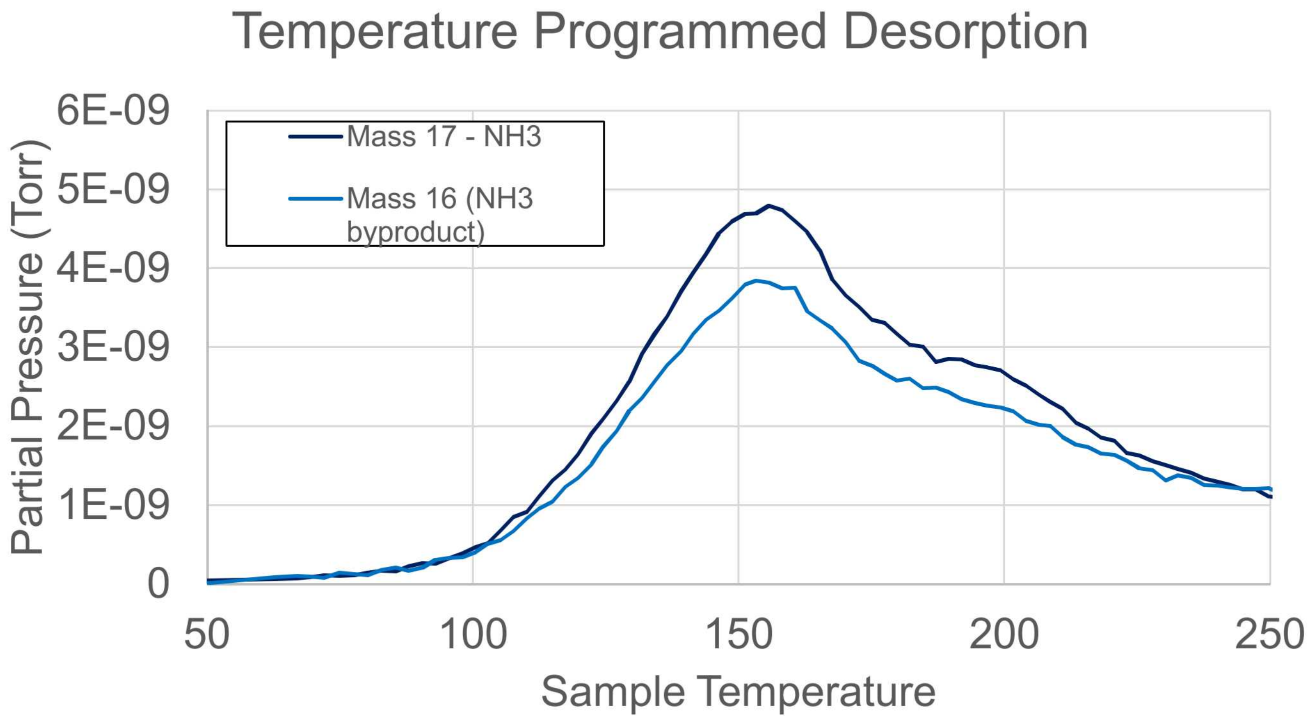
**<u>Ex-Situ Cleaning</u>**:
5 min Swirl:
Acetone,
Isopropanol
DI water
Dry with Nitrogen
Then:
10 min UV/Ozone treatment
1 min concentrated HF etch

- Clear 6- fold symmetry.
- First order diffraction spots
- Well-ordered & un-reconstructred surface



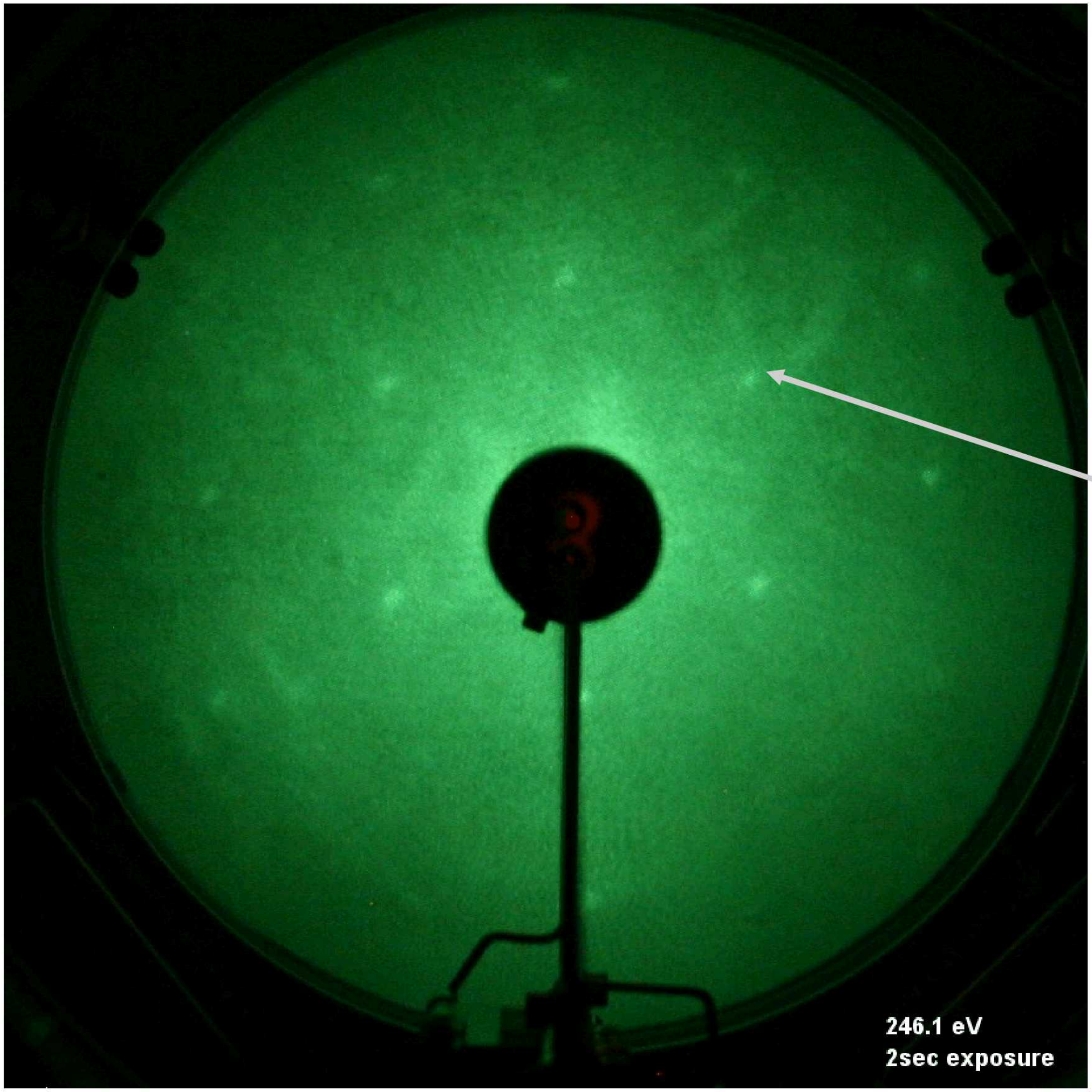
# LEED & TPD of Ex-Situ Cleaned GaN




$NH_3$ is released from the surface as the substrate is heated

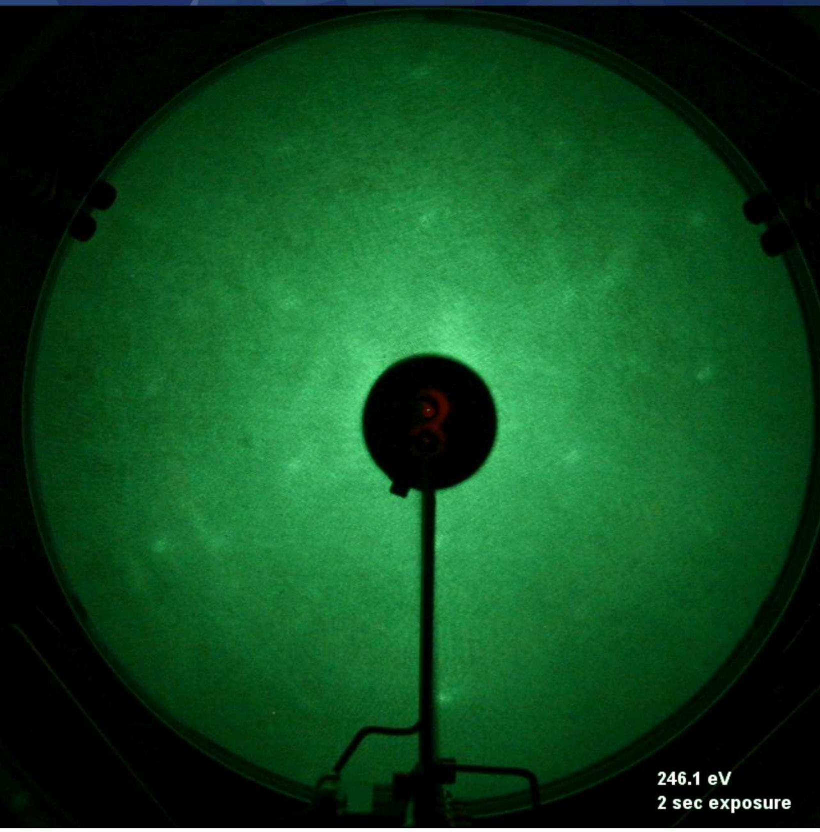
# LEED on GFO ALP GaN

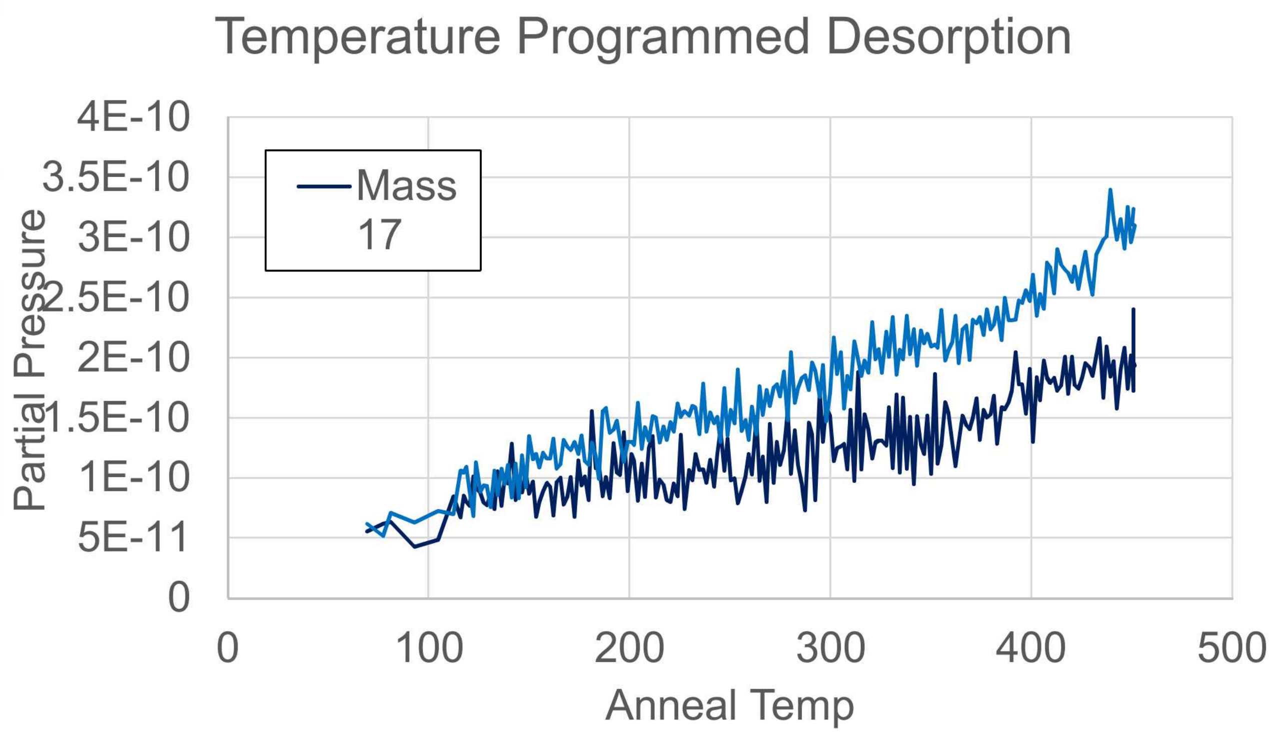



**Ex-situ Cleaned followed by GFO ALP in commercial tool at 500C for 10 cycles.**

- Clear 6- fold symmetry.
- First order diffraction spots
- Well-ordered & un-reconstructred surface
- Same as Ex-situ surface,

# LEED & TPD of GFO ALP Cleaned GaN




No $NH_3$ is released from the surface as the substrate is heated, most likely meaning that all the N has been tied up through the GFO ALP.

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# Summary

- **GFO ALP at 500C for 10 cycles and with hydrogen only for 10 cycles, both show a ~25% reduction in Oxygen on the surface**
- ***Ex-situ GaN surface and GFO ALP GaN surface are both well ordered and unreconstructred***
- ***Ex-situ GaN surface when heated in TPD experiments evolves $NH_3$ from the surface, suggesting that the Nitrogen is not ordered on the surface***
- ***GFO ALP seems to make the GaN surface air stable***
- **In-situ & Ex-situ techniques are capable of developing the optimum Low-Temperature ALP**

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