Supporting information

Isotropic Atomic Layer Etching of GaN using SF_6 plasma and $Al(CH_3)_3$

Stoichiometry and XRD of starting films

The GaN stoichiometry of the films as prepared by ALD can be seen in Figure S.1, obtained from a XPS depth profile. The surface of the film is Ga-deficient compared to the bulk, likely due to the oxidation of the surface. Toward the bulk of the film, the stoichiometry returns toward that expected of GaN, i.e 1:1. The small N deficiency in the bulk is likely due to the preferentially sputtering of N during the depth profile measurement.

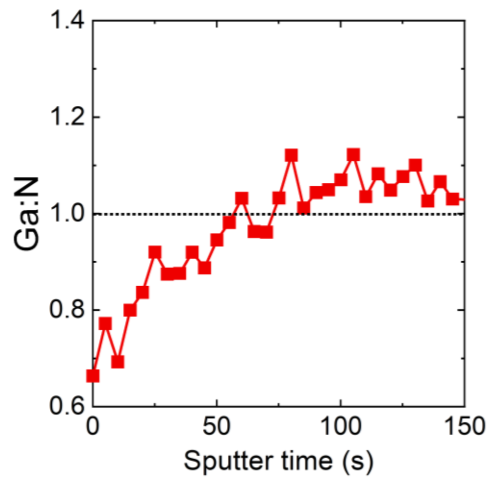

Figure S.1: Ga:N ratio obtained from XPS. The initial surface layer is O-rich and Ga-deficient, with the film transitioning into more stoichiometric GaN in the bulk.

XRD analysis was performed to show that the starting film was crystalline in nature. There is a clear peak at 34.5 ° indicative of (002) GaN as shown in Figure S.2.

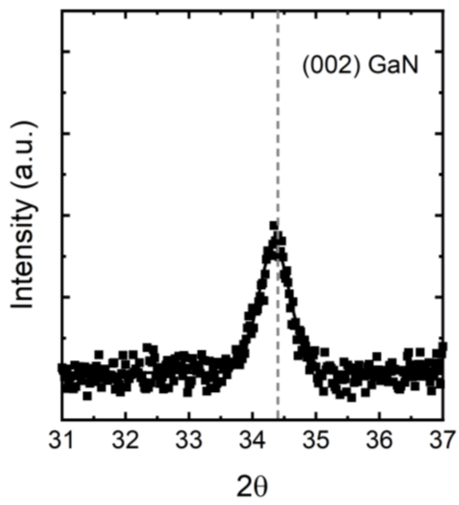

Figure S.2: XRD scan for GaN films used in this work. A peak at the GaN (002) position is observed which is expected for GaN ALD films.

Etched thickness as function of ALE cycles

Figure S.3 shows the etched thickness of the as-prepared GaN films as a function of ALE cycles at 300 °C using the standard process outlined in the main text. The EPC is determined by performing a straight line fit, yielding a value of 0.39 ± 0.02 nm/cycle, in agreement with the value from the saturation curves of 0.40 ± 0.02 nm/cycle.

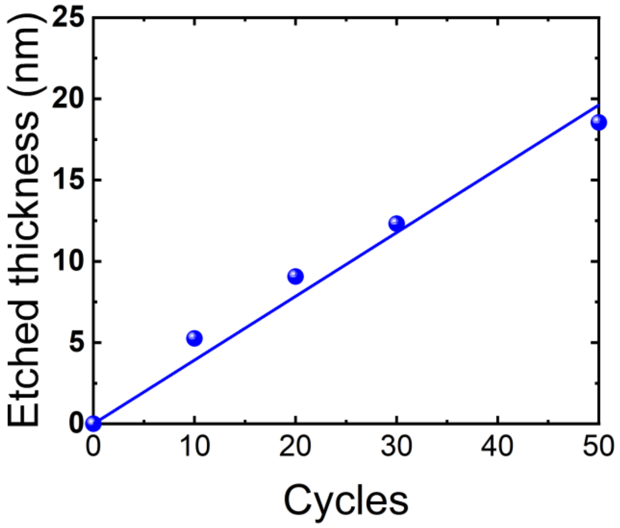

Figure S.3. Etched thickness as a function of ALE cycles at 300 °C, each data point is a separate sample.

Synergy

To determine at which point the transition between the high etch rate and low etch rate occurred in the synergy plot, it is useful to plot the EPC and etched thickness as a function of cycles. For the first 25 cycles only SF_6 plasma is dosed, for the next 25 cycles only TMA is dosed. After cycle 50 full ALE cycles are performed with both SF_6 plasma and TMA in each cycle.

After an initial high EPC in the first SF_6 plasma only cycle the EPC is zero for the remaining SF_6 plasma pulses, confirming that SF_6 plasma does not continuously etch GaN. A non-zero EPC for the first pulse is likely due to removal of adventitious carbon or changes in the optical properties of the film during the SF_6 plasma pulse. When switching to TMA only pulses after cycle 25 there is an EPC of 0.32 nm/cycle for the first pulse, removing roughly one ALE cycle worth of material. For the remaining TMA only pulses the EPC returns to 0 nm/cycle. When the full ALE cycles start at cycle 50, there is an initially high EPC, which decreases as the number of cycles increase. Around cycle 70, after ~10 nm of etching, the EPC stabilizes at 0.31 nm/cycle, after which a linear increase in etched thickness is observed.

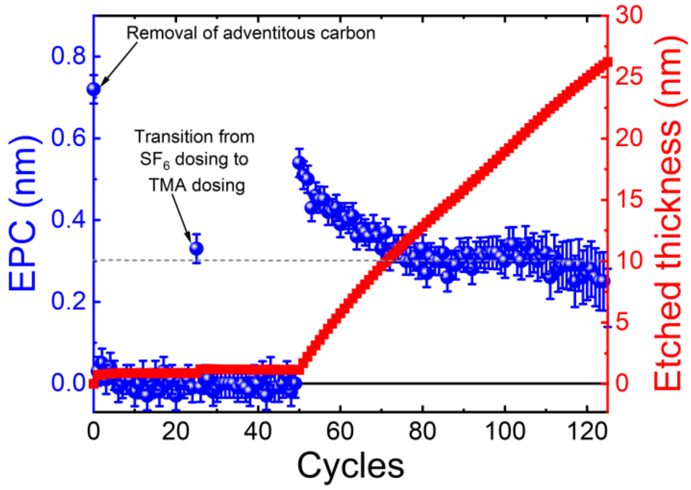

Figure S.4: Plot of the EPC as a function of cycles, determined from Figure 4 of the main text. The first 25 cycles only SF_6 plasma is dosed, then 25 cycles of only TMA. Finally, 75 full ALE cycles are performed where both SF_6 plasma and TMA are dosed each cycle.

Selectivity

Selectivity of the ALE process was tested using the standard recipe for GaN ALE at 150 °C outlined in the main text. Film thicknesses for all samples were measured before and after 30 ALE cycles using ex-situ spectroscopic ellipsometry. The GaN film thickness was also monitored in-situ. For GaN 9.5 nm of etching occurred giving an EPC of 0.32 nm/cycle, while no etching was observed for the Al_2O_3 or HfO_2 film. A slight increase in Al_2O_3 film thickness was observed which is either due to a small amount of AlF_3 ALD, or the volume expansion due to fluorination of the Al_2O_3 which has been observed previously.[1] For HfO_2 no significant change in thickness was observed.

Table S1: Film thicknesses before and after 30 ALE cycles at 150 °C.

Material	Thickness before (nm)	Thickness after 30 ALE cycles at 150 °C (nm)	EPC (± 0.02 nm/cycle)
GaN	41.2	31.7	0.32
Al_2O_3	27.4	27.8	-0.01
HfO_2	22.3	22.2	0.00

Power spectral density

Power spectral density (PSD) plots are also shown for the different etch depths in Figure S.5, highlighting that most the smoothing occurs at the smaller feature scales.

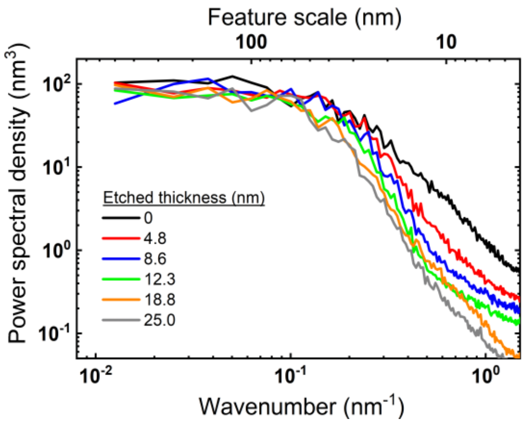

Figure S.5: Power spectral density for the GaN film etched to different depths, highlighting that the majority of smoothing occurs at the smaller length scales comparable to the total etch thickness.

XPS depth profiles

XPS depth profiles were measured for the different etch depths, as well as for the starting GaN film as shown in Figure S.6. The depth profiles also illustrate that the film is being etched as the Si2p3 peak starts to appear sooner as the number of ALE cycles is increased.

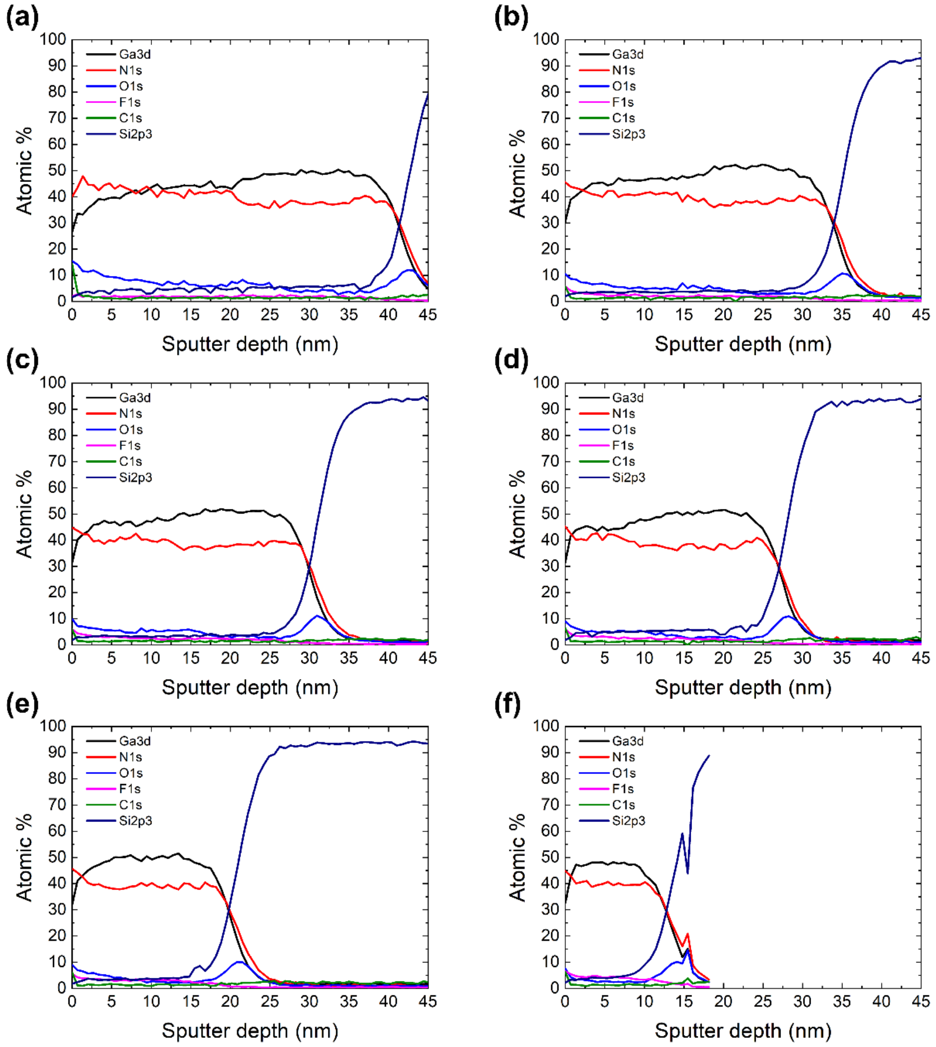

Figure S.6: XPS depth profile for the different number of ALE cycles (a) starting film, (b) 10, (c) 20, (d) 30, (e) 50 and (f) 75. Fewer scans are shown for figure (f) as the GaN film was significantly thinned such that the Si peak appeared earlier.

The Al2p peak was also examined for the films etched at different temperatures to evaluate whether there was any contamination of the film from the etch precursor. Figure S.7 shows the individual Al2p peaks used to determine the peak binding energy and peak area in Figure 11 of the main text. The Al2p peak diminishes and shifts to lower binding energy as the temperature at which ALE is performed is increased. The higher temperature promotes ALE of the GaN films and diminishes the AlF_3 ALD reaction which is also possible with the chemistry used here. Some Al is still visible at high temperatures, with a bonding energy characteristic of Al-O rather than Al-F. This is likely due to the final exposure of the ALE process being TMA. Any excess TMA is thus free to adsorb on the GaN surface. When transferred to the XPS in ambient this adsorbed TMA is oxidized. Al contamination could likely be avoided by using trimethylgallium as an alternative source of methyl groups, which has been shown to be effective for ALE of Ga_2O_3.[2]

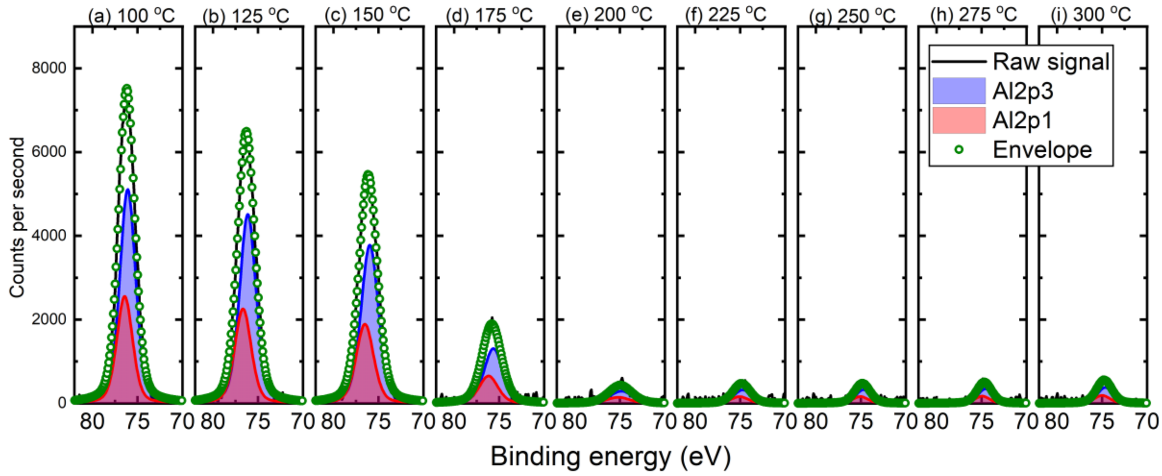

Figure S.7: Al2p peak for GaN films post ALE at (a) 100 °C, (b) 125 °C, (c) 150 °C, (d) 175 °C, (e) 200 °C, (f) 225 °C, (g) 250 °C, (h) 275 °C and (i) 300 °C. Appearance of a clear Al peak in the 100 °C spectra as well as a film thickness increase from spectroscopic ellipsometry indicates the growth of an AlF_x film at this temperature. The Al2p peak decreases with increasing temperature, and remains roughly constant above 200 °C. A small Al2p peak is still observed at the higher temperatures as the final dose of the ALE cycles is TMA.

CIF files used

GaN and GaF CIF files were obtained from the materials project database. For GaN mp-804 was used and for GaF mp-588. The unit cells and atomic positions were then optimized with the settings described in the main text.

References

[1] N.J. Chittock, M.F.J. Vos, T. Faraz, W.M.M. (Erwin) Kessels, H.C.M. Knoops, and A.J.M. Mackus, "Isotropic plasma atomic layer etching of Al_2O_3 using a fluorine containing plasma and $Al(CH_3)_3$," Appl Phys Lett **117**(16), 162107 (2020).

[2] K.A. Hatch, D.C. Messina, and R.J. Nemanich, "Plasma enhanced atomic layer deposition and atomic layer etching of gallium oxide using trimethylgallium," Journal of Vacuum Science & Technology A **40**(4), 042603 (2022).