Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2024

Supporting information for:

Surface chemistry in atomic layer deposition of AlN thin films from $Al(CH_3)_3$ and NH_3 studied by mass spectrometry

Pamburayi Mpofu[1], Houyem Hafdi[1], Pentti Niiranen[1], Jonas Lauridsen[2], Oscar Alm[2], Tommy Larsson[2], Henrik Pedersen[1*]

[1] Department of Physics, Chemistry and Biology, Linköping University, SE-581 83, Linköping, Sweden

[2] Seco Tools AB, SE-737 82, Fagersta, Sweden

*Corresponding author: henrik.pedersen@liu.se

Stoichiometry of deposited films

Elemental composition of the deposited films was measured by XPS. The measurements show close to 1:1 Al:N stoichiometry for both processes, with ± 5% error bar. Table S1 summarizes the elemental composition from XPS after 600 s of sputter cleaning.

Table S1: *Overview of optimized process parameters and film stoichiometry from XPS.*

Process	TMA pulse time (s)	NH_3 pulse time (s)	Deposition temperature (°C)	Al (at.%)	N (at.%)	O (at.%)	C (at.%)	Al:N ratio
TMA plasma	0.1	12	300	49.5	47.6	1.2	1.7	1:0.96
	0.1	12	400	47.9	44.6	4.1	3.4	1:0.93
TMA thermal	0.1	18	350	47.5	45.3	4.4	2.8	1:0.95
	0.1	18	400	48.6	44.4	3.6	3.4	1:0.91

Verification of Al-N bonding in the film was also done using XPS. Characteristic peaks of Al-N at 74.1 eV in Al 2p core level spectra can be seen in Fig. S1, for plasma ALD (Fig. S1a) and thermal ALD (Fig. S1b).[1] An additional peak, assigned to metallic Al can be seen at 72.8 eV (plasma) and 72.5 eV (thermal),[2] which are attributed to ion induced sputtering effects when sputtering the XPS.[3]

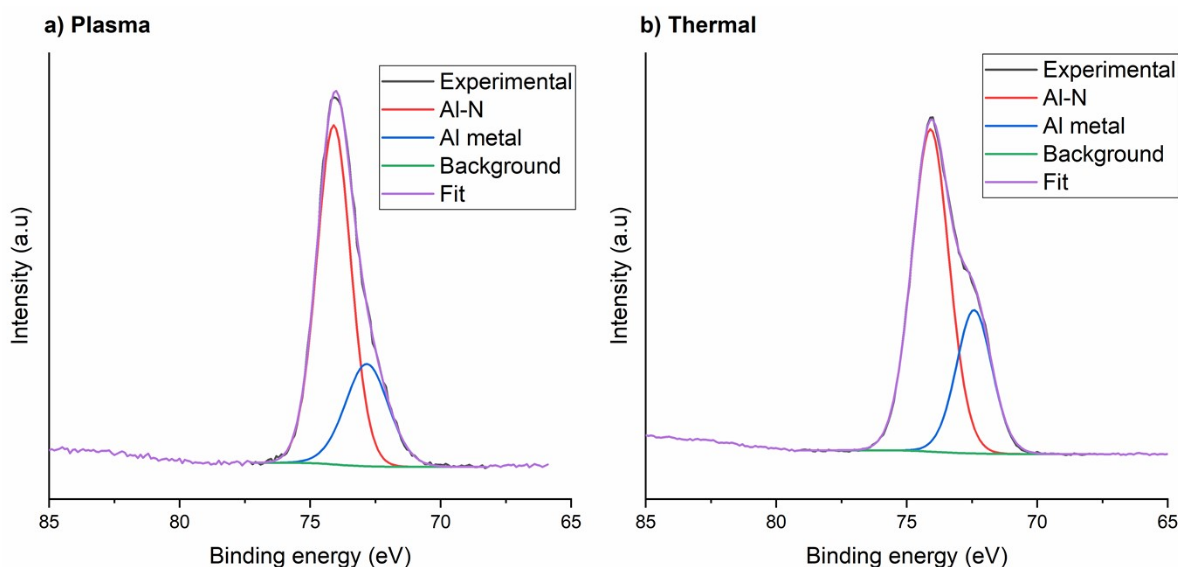

Figure S1: *High resolution XPS of Al 2p core level spectra for the plasma process (a) deposited at 300 °C and thermal process (b) deposited at 350 °C.*

Crystallinity of deposited films

The crystallinity of the deposited AlN films was investigated using θ-2θ XRD. Fig. S2 shows that all three peaks for both the plasma and thermal processes which are in good agreement with the (100), (002), and (101) peaks of wurtzitic AlN (ICSD no. 01-070-0354). The films are thus suggested to be polycrystalline with no preferred orientation or texture.

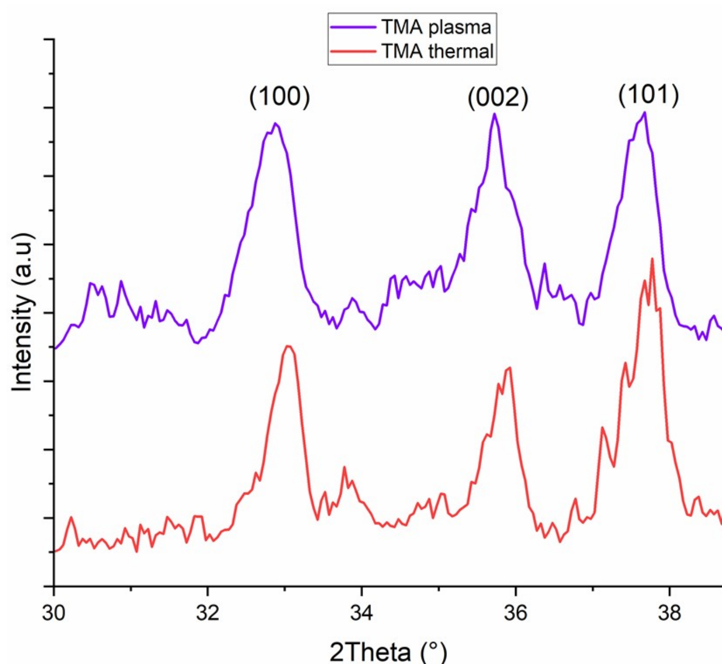

Figure S2: *X-ray diffraction patterns of plasma and thermal processes deposited at 300 and 350 °C respectively.*

Arrhenius plots

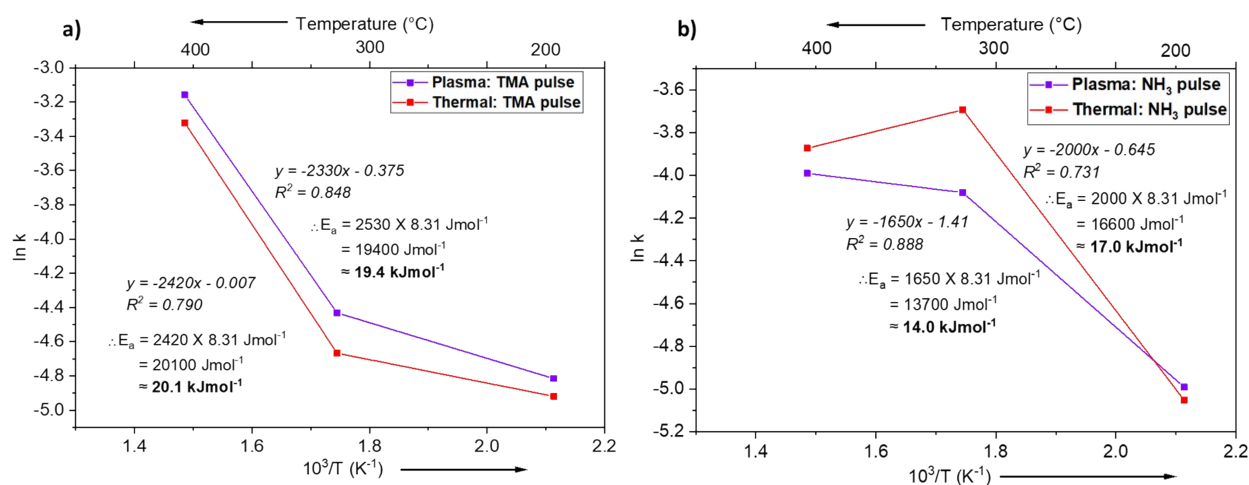

Figure S3. *Arrhenius plots used to approximate the activation energies for the methane evolution during TMA pulses (a) and NH_3 pulses (b).*

Nucleation delays

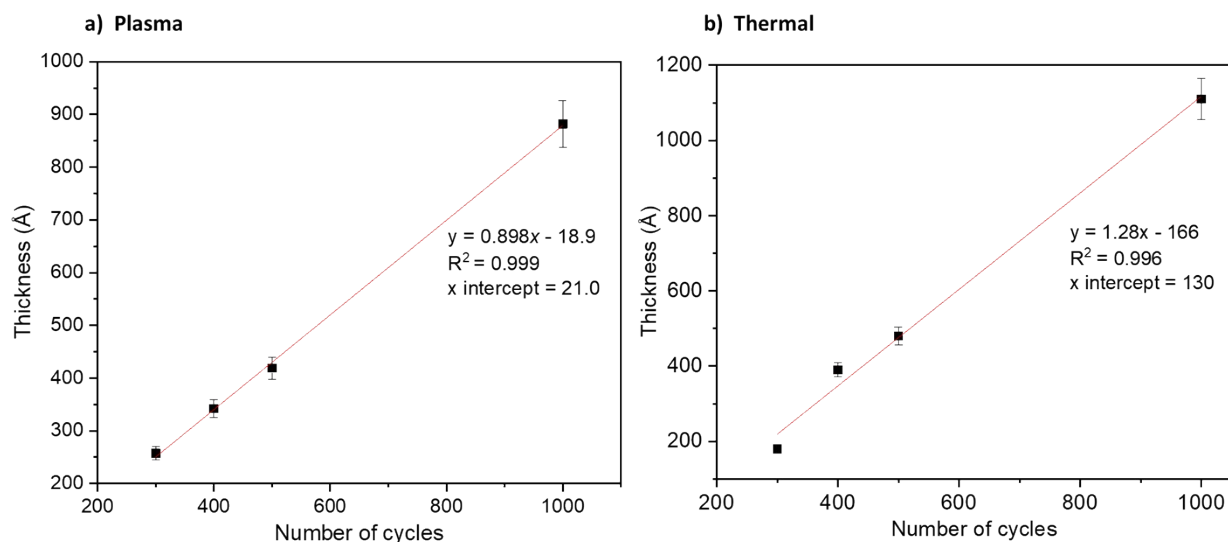

Figure S4: *Nucleation delays between plasma (a) and thermal (b) processes showing that 21 and 130 ALD cycles (x-intercept values) are needed, respectively, for nucleation and film growth to begin.*

References

(1) Jose, F.; Ramaseshan, R.; Dash, S.; Bera, S.; Tyagi, A. K.; Raj, B. Response of Magnetron Sputtered AlN Films to Controlled Atmosphere Annealing. *J. Phys. D. Appl. Phys.* **2010**, *43*, 075304.

(2) Hoque, E.; Derose, J. A.; Kulik, G.; Hoffmann, P.; Mathieu, H. J.; Bhushan, B. Alkylphosphonate Modified Aluminum Oxide Surfaces. *J. Phys. Chem. B* **2006**, *110*, 10855–10861.

(3) Xie, F. Y.; Gong, L.; Liu, X.; Tao, Y. T.; Zhang, W. H.; Chen, S. H.; Meng, H.; Chen, J. XPS Studies on Surface Reduction of Tungsten Oxide Nanowire Film by Ar + Bombardment. *J. Electron Spectros. Relat. Phenomena* **2012**, *185*, 112–118.