Electronic Supplementary Information

Table S1: Deposition temperatures (Td), atomic O/Al ratios, proportion of aluminum coordinated units, chemical shift distribution (ΔCS), and standard deviation of the EFG tensor elements' distribution (¯(C_Q)) for the three CVD techniques. Values for evaporation-CVD (e-CVD) ATI are from [1].

e-CVD ATI										
T_d (°C)	O/Al	AlO_6 (at.%)	AlO_5 (at.%)	AlO_4 (at.%)	ΔCS AlO_6 (ppm)	ΔCS AlO_5 (ppm)	ΔCS AlO_4 (ppm)	C_Q AlO_6 (MHz)	C_Q AlO_5 (MHz)	C_Q AlO_4 (MHz)
360	2.00	26.2	40.9	32.9	7.6	9.2	10.2	6.3	8.1	6.3
420	1.68	11.5	42.9	45.6	8.5	10.7	11.6	6.0	8.8	6.0
480	1.52	4.6	41 .8	53.6	10.1	11.6	14.6	6.0	9.2	6.0
550	1.50	7.5	39.2	53.3	10.2	12.2	15.0	7.3	9.2	7.3
600	1.50	15.9	37.6	46.5	9.0	11.0	13.3	5.8	9.1	5.8
700	1.49	59.2	12.2	28.6	9.3	9.5	11.6	5.8	8.5	5.8

DLI-CVD ATI										
T_d (°C)	O/Al	AlO_6 (at.%)	AlO_5 (at.%)	AlO_4 (at.%)	ΔCS AlO_6 (ppm)	ΔCS AlO_5 (ppm)	ΔCS AlO_4 (ppm)	C_Q AlO_6 (MHz)	C_Q AlO_5 (MHz)	C_Q AlO_4 (MHz)
300	-	34.3	33.5	32.2	7.0	8.5	10.0	5.7	6.8	8.7
360	2.12	22.1	40.5	37.4	7.6	9.6	11.0	5.9	7.8	9.6
420	1.80	20.5	41.7	37.8	7.2	9.5	10.5	5.8	8.3	10.3
490	1.54	14.7	39.7	45.6	8.2	11.4	12.8	5.3	8.8	11.0
560	1.57	17.5	39.1	43.4	8.8	11.8	13.5	5.5	8.8	10.6
600	1.56	-	-	-	-	-	-	-	-	-

DLI-CVD DMAI H_2O										
T_d (°C)	O/Al	AlO_6 (at.%)	AlO_5 (at.%)	AlO_4 (at.%)	ΔCS AlO_6 (ppm)	ΔCS AlO_5 (ppm)	ΔCS AlO_4 (ppm)	C_Q AlO_6 (MHz)	C_Q AlO_5 (MHz)	C_Q AlO_4 (MHz)
150	1.81	12.9	44.5	42.6	9.0	10.0	11.0	5.6	7.3	9.4
200	1.67	10.1	45.6	44.3	9.5	11.5	12.5	6.3	7.7	9.7
250	1.53	6.1	45.4	48.5	9.6	11.5	13.2	6.0	8.1	10.1
300	1.50	5.7	44.3	50.0	10.5	12.5	13.5	6.1	8.0	10.2
350	1.51	6.5	45.7	47.8	9.9	12.7	13.9	6.7	8.3	10.2
400	1.53	6.8	47.1	46.1	10.1	13.1	14.9	6.5	8.5	9.5
450	1.53	7.2	46.8	46.0	9.7	13.2	14.9	5.6	8.5	9.7

DLI-CVD DMAI O_2													
T_d (°C)	O/Al	AlO_6 (at.%)	AlO_5 (at.%)	AlO_4 (at.%)	$Al(O,C)_4$ (at.%)	ΔCS AlO_6 (ppm)	ΔCS AlO_5 (ppm)	ΔCS AlO_4 (ppm)	ΔCS $Al(O,C)_4$ (ppm)	C_Q AlO_6 (MHz)	C_Q AlO_5 (MHz)	C_Q AlO_4 (MHz)	C_Q $Al(O,C)_4$ (MHz)
500	1.48	5.1	45.5	49.3	0.0	11.5	14.1	14.7		6.0	8.3	9.9	
600	1.25	6.6	36.2	47.0	10.2	11.4	13.5	15.3	16.7	6.8	8.2	10.0	13.5
700	1.10	8.4	22.0	39.8	29.8	12.2	13.6	15.2	16.7	5.2	8.1	10.0	14.0

[1] V. Sarou-Kanian, A. N. Gleizes, P. Florian, D. Samelor, D. Massiot and C. Vahlas, *J. Phys. Chem. C*, 2013, **117**, 21965-21971.

Figure S1: SEM cross-sections of alumina films deposited onto Si substrates using (a) evaporated ATI in N_2 at 520 °C, and DLI CVD of (b) ATI at 480 °C, (c) DMAI at 200 °C in the presence of H_2O and (d) DMAI at 600 °C in the presence of O_2.

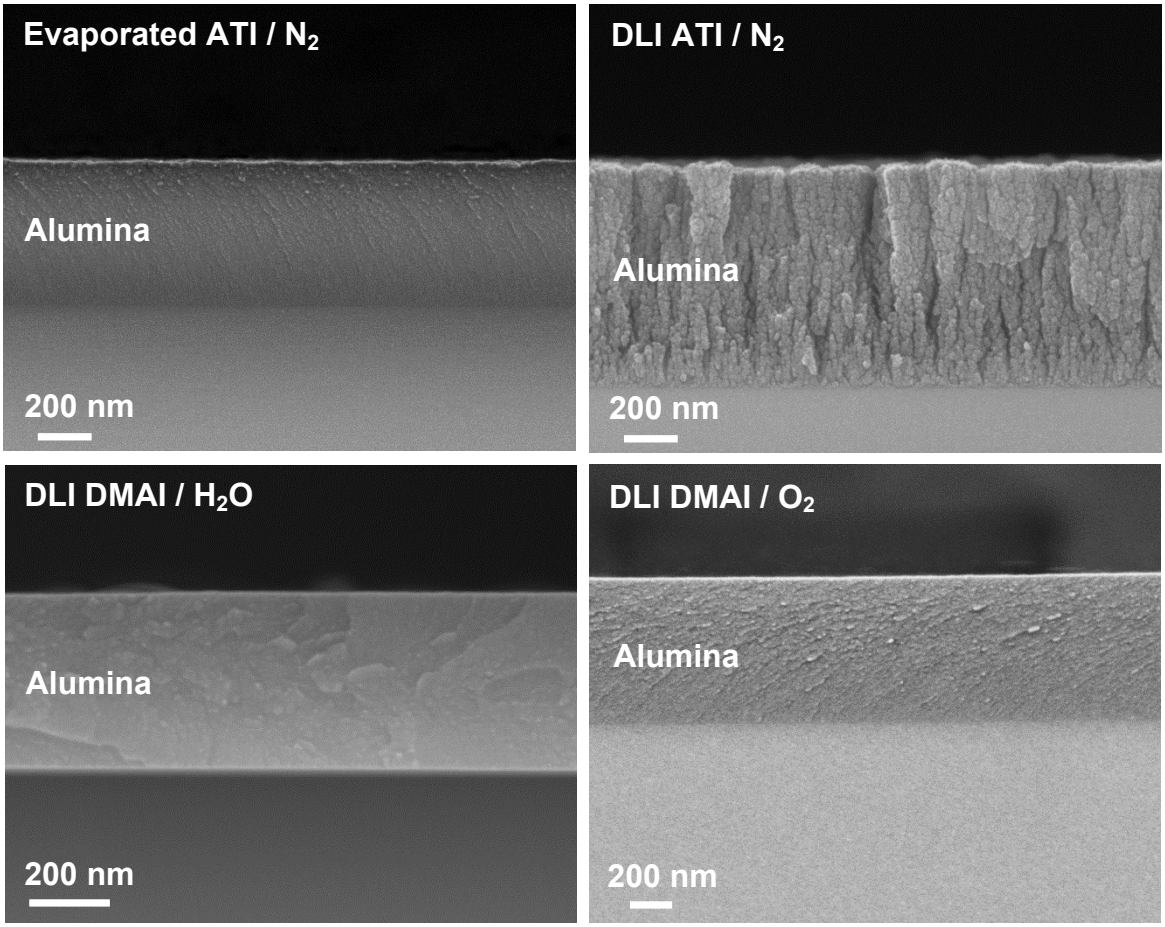
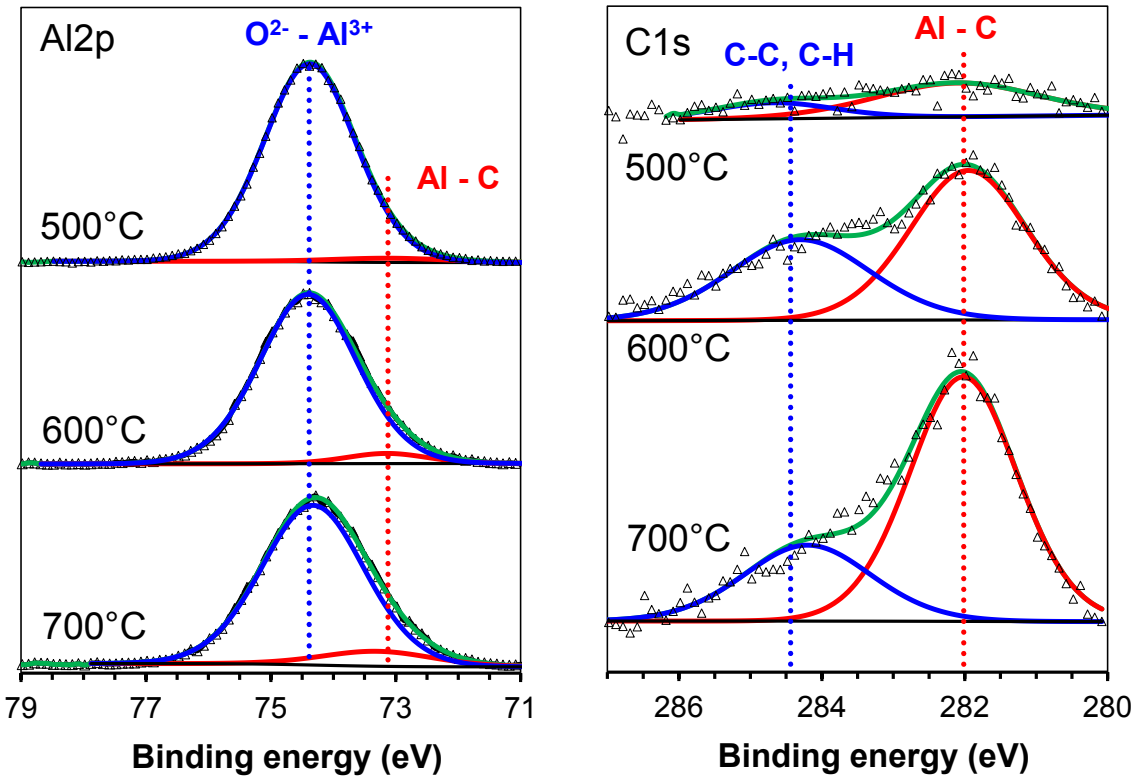


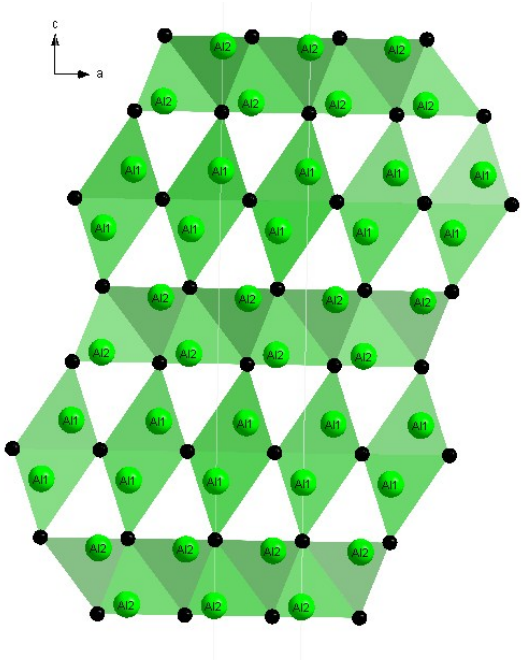
Figure S2: High resolution Al2p and C1s X-ray photoelectron spectra of DLI DMAI+O_2 alumina thin films deposited from 500 to 700°C. The decomposition of the spectra into the assigned chemical species is shown for each core level.



The Al2p signal clearly show the presence of intensity at the locations expected for Al^{3+} in an O^{2-} environment with Al2p binding energy of about 74.4 eV and O1s binding energy near 531.5 eV [1,2]. Moreover, the signals observed at about 73.2 eV in Al2p and near 282.0 eV in C1s can be attributed to aluminum oxycarbides or aluminum carbides. The Al2p binding energy of aluminum (oxy)carbide is lower than that measured for Al_2O_3 since C is less electronegative (more electropositive) than O, hence Al in aluminum carbide is more effectively reduced and measured at a lower binding energy. Similarly, the C1s binding energy of the carbide is significantly more negative than that of adventitious C-C bonds as Al is more electropositive than C.

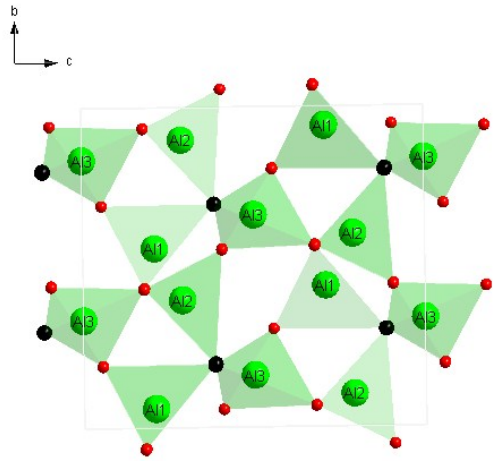
[1] L. Baggetto, C. Charvillat, J. Esvan, Y. Thébault, D. Samélor, H. Vergnes, B. Caussat, A. Gleizes and C. Vahlas, *Chem. Vap. Dep.*, 2015, **21**, 343-351.
[2] L. Baggetto, J. Esvan, C. Charvillat, D. Samélor, H. Vergnes, B. Caussat, A. Gleizes and C. Vahlas, *Physica Status Solidi C*, 2015, **12**, 989-995.

Figure S3: Crystal structures and NMR parameters (C_Q and η_Q) of Al_4C_3 and Al_4O_4C calculated from DFT. Green, black and red balls correspond respectively to aluminum, carbon and oxygen in the structure.



Al_4C_3			
Site	δ_{iso} (ppm)	C_Q AlC_4 (MHz)	η_Q
Al-1	98.52	14.66	0.00
Al-2	112.02	16.34	0.00

From T. M. Gesing and W. Jeitschko, *Z. Naturforsch. B*, 1995, **50**, 196-200.



Al_4O_4C			
Site	δ_{iso} (ppm)	C_Q AlO_3C (MHz)	η_Q
Al-1	114.18	18.78	0.41
Al-2	101.45	10.64	0.03
Al-3	97.47	11.14	0.23

From G. A. Jeffrey and M. Slaughter, *Acta Crystallogr.*, 1963, **16**, 177-184.