Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Atomic Layer Deposition of LiF using $LiN(SiMe_3)_2$ and SF_6 plasma

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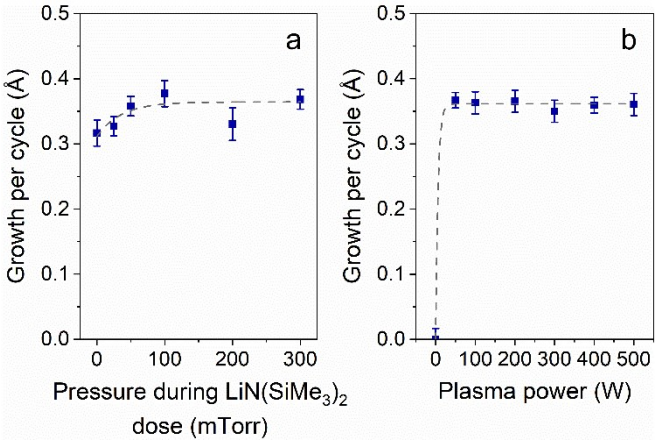

Fig. S1: Growth per cycle obtained by *in situ* SE as a function of (a) pressure during $LiN(SiMe_3)_2$ dose and (b) SF_6 plasma power for ALD of LiF obtained at 150 °C. The precursor dose time was set to 6 s and the plasma exposure time was set to 1 s. The plasma power was set to 300 W when the pressure during $LiN(SiMe_3)_2$ dose was varied and the pressure during $LiN(SiMe_3)_2$ dose was set to 50 mTorr when the plasma power was varied. The dotted lines serves as a guide to the eye.

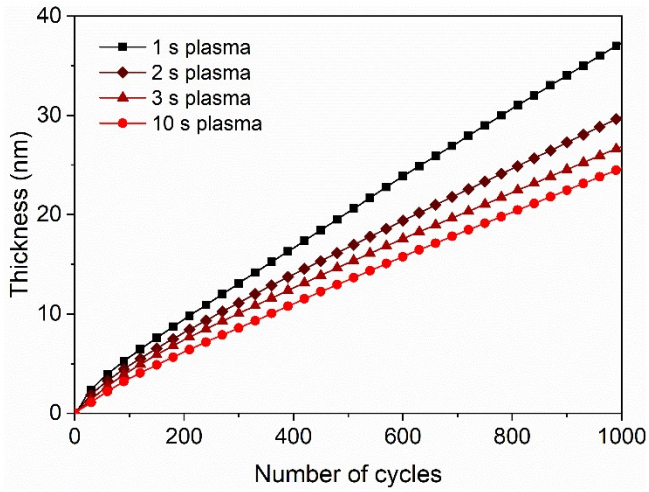

Fig. S2: Film thickness as a function of cycle number for different plasma exposure times measured by *in situ* SE. The dosing time of the $LiN(SiMe_3)_2$ precursor was set to 6 s.

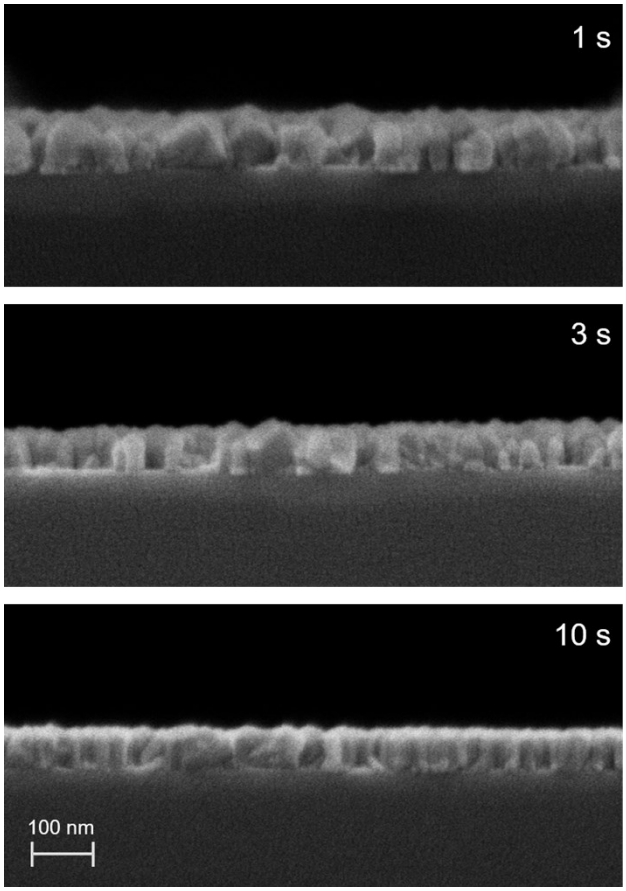

Fig. S3: High resolution SEM images showing the cross-section of LiF films deposited on Si using 2200 cycles and a 1 s, 3 s and 10 s SF_6 plasma exposure, respectively. The scale bar applies to all images.

Table S1: Thicknesses and refractive index values on various locations of a 200 mm wafer with a 90 nm LiF film prepared using a plasma exposure time of 1 s. The centre of the wafer is defined as (0,0). In the first row the typical error is given for the thickness and refractive index.

Position		Thickness (nm)	Refractive index n at 633 nm
x (mm)	y (mm)		
-100	0	92.0 ± 0.5	1.375 ± 0.005
-50	0	89.5	1.370
0	0	90.0	1.375
50	0	85.5	1.375
100	0	80.0	1.375
0	100	85.0	1.375
0	50	88.5	1.380
0	-50	87.0	1.370
0	-100	85.5	1.370

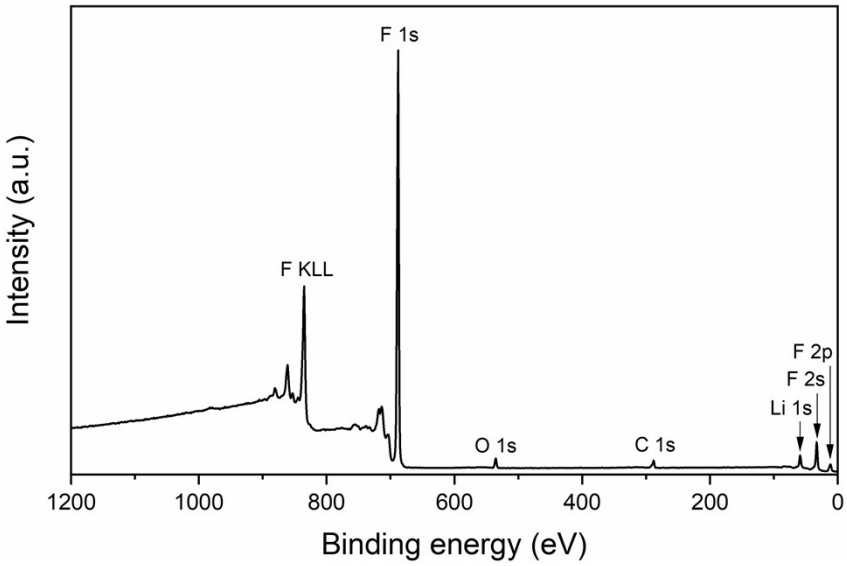

Fig. S4: XPS survey spectrum of a lithium fluoride film grown at 150 °C using 1 s plasma exposure. The spectra for 3 s and 10 s plasma exposure are very similar and therefore not shown.

Table S2: Stoichiometry of LiF films deposited at 150 °C using different plasma exposure times.

Sample	F/Li	C (at%)	O (at%)	H (at%)
1 s plasma duration				
XPS surface	0.80	9.0 ± 0.5	4.5 ± 0.5	-
XPS depth profiling	0.81	0.5 ± 0.5	0.5 ± 0.5	-
RBS/ERD	0.78	0.8 ± 0.1	1.1 ± 0.1	0.9 ± 0.1
3 s plasma duration				
XPS surface	0.80	6.0 ± 0.5	4.0 ± 0.5	-
XPS depth profiling	0.82	0.5 ± 0.5	0.5 ± 0.5	-
RBS/ERD	0.83	0.9 ± 0.1	1.1 ± 0.1	0.8 ± 0.1
10 s plasma duration				
XPS surface	0.80	6.5 ± 0.5	7.0 ± 0.5	-
XPS depth profiling	0.80	0.5 ± 0.5	0.5 ± 0.5	-
RBS/ERD	0.75	1.3 ± 0.1	0.9 ± 0.1	0.7 ± 0.1

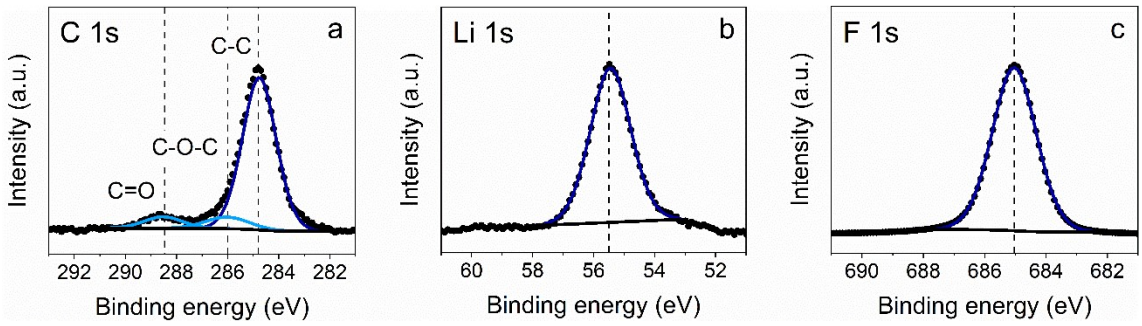

Fig. S5: (a) C 1s, (b) Li 1s, and (c) F 1s spectra of a 40 nm thick lithium fluoride film grown at 150 °C using 1 s plasma exposure time after storage in atmosphere for one month. The measured data (black dotted lines) and fitted peaks (blue lines) are reported. Carbon is detected only at the surface of the films.

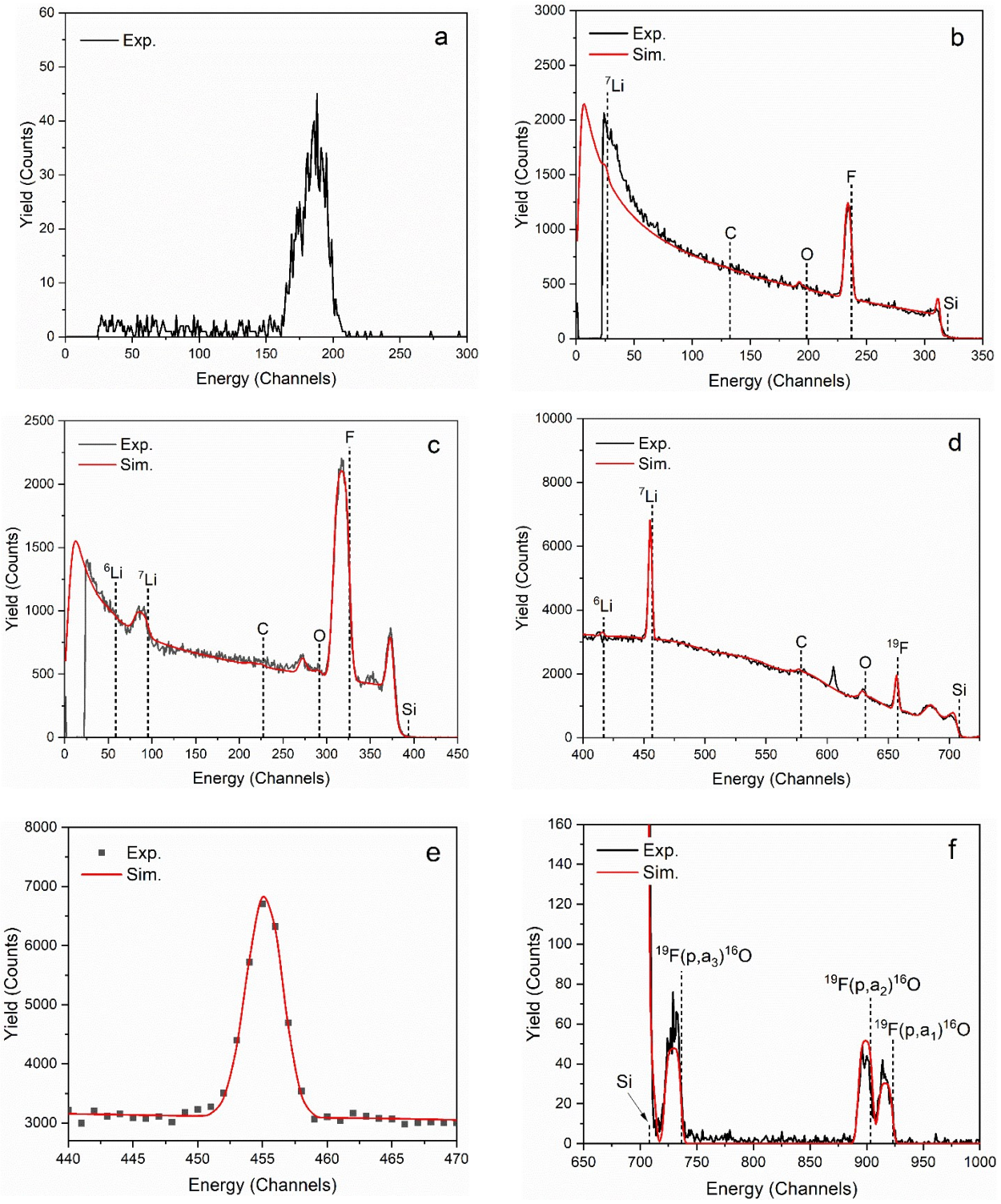

Fig. S6: Spectra from 40 nm LiF deposited at 150 °C using 3 s plasma exposure as measured with (a) Elastic Recoil Detection (ERD), (b, c) Rutherford Backscattering Spectrometry (RBS) at 170° and 107° respectively, and (d to f) Elastic Backscattering Spectrometry (EBS). The experimental spectra are plotted in black and the simulated spectra in red. Figure (e) shows the ^{7}Li peak in detail and (f) zooms in on three peaks originating from nuclear reactions with ^{19}F. The 107° RBS spectrum (c) shows also a significant Li peak which is in agreement with the EBS result. The EBS spectrum shows a peak between the C and O peak which is not simulated. The origin of this peak is unclear although its position is close to the nitrogen surface channel. RBS clearly shows the absence of N in the films. Note that the spectra for 1 s and 10 s plasma exposure are very similar and are therefore not shown.

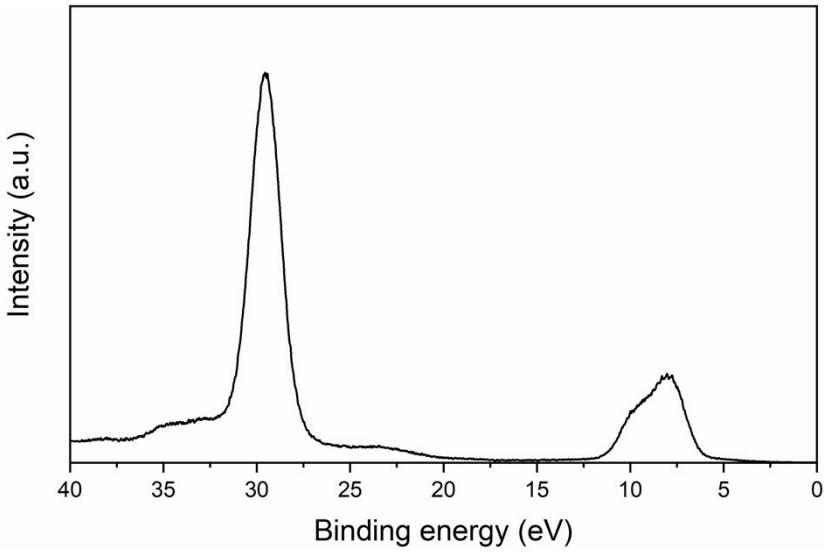

Fig. S7: XPS valance band spectrum of a LiF film grown at 150 °C using 1 s plasma exposure. The spectra for 3 s and 10 s plasma exposure are very similar and therefore not shown.

Table S3: Relevant *m/z* ratios, their assigned ions and their (main) assigned parent molecules.

15	CH_3^+	CH_3F, CH_4
16	CH_4^+	CH_4
17	NH_3^+	NH_3
20	HF^+, Ar^{++}	HF, Ar
31	CF^+	CF_4, CH_xF_y
32	S^+, CHF^+	SF_6, H_2S, CH_xF_y
33	CH_2F^+, HS^+	CH_2F_2, CH_3F, H_2S
34	CH_3F^+, H_2S^+	CH_3F, H_2S
50	CF_2^+	CF_4, CHF_3, CH_2F_2
51	CHF_2^+, SF^+	CH_2F_2, CHF_3, SF_6
52	NF_2^+	NF_3
65.5	$HN(SiMe_2)_2^{2+}$	$LiN(SiMe_3)_2$, $HN(SiMe_3)_2$
69	CF_3^+	CF_4, CHF_3
73	$SiMe_3^+$	$LiN(SiMe_3)_2$, $HN(SiMe_3)_2$, $SiMe_3F$, $SiMe_3H$
77	$SiMe_2F^+$, $LiNSi_2^+$	$SiMe_3F$, $SiMe_2F_2$, $LiN(SiMe_3)_2$
81	$SiMeF_2^+$	$SiMe_2F_2$, $SiMeF_3$
85	SiF_3^+, Me_2SiNCH^+	SiF_4^+, $SiMeF_3^+$, $LiN(SiMe_3)_2$

89	SF_3^+	SF_6

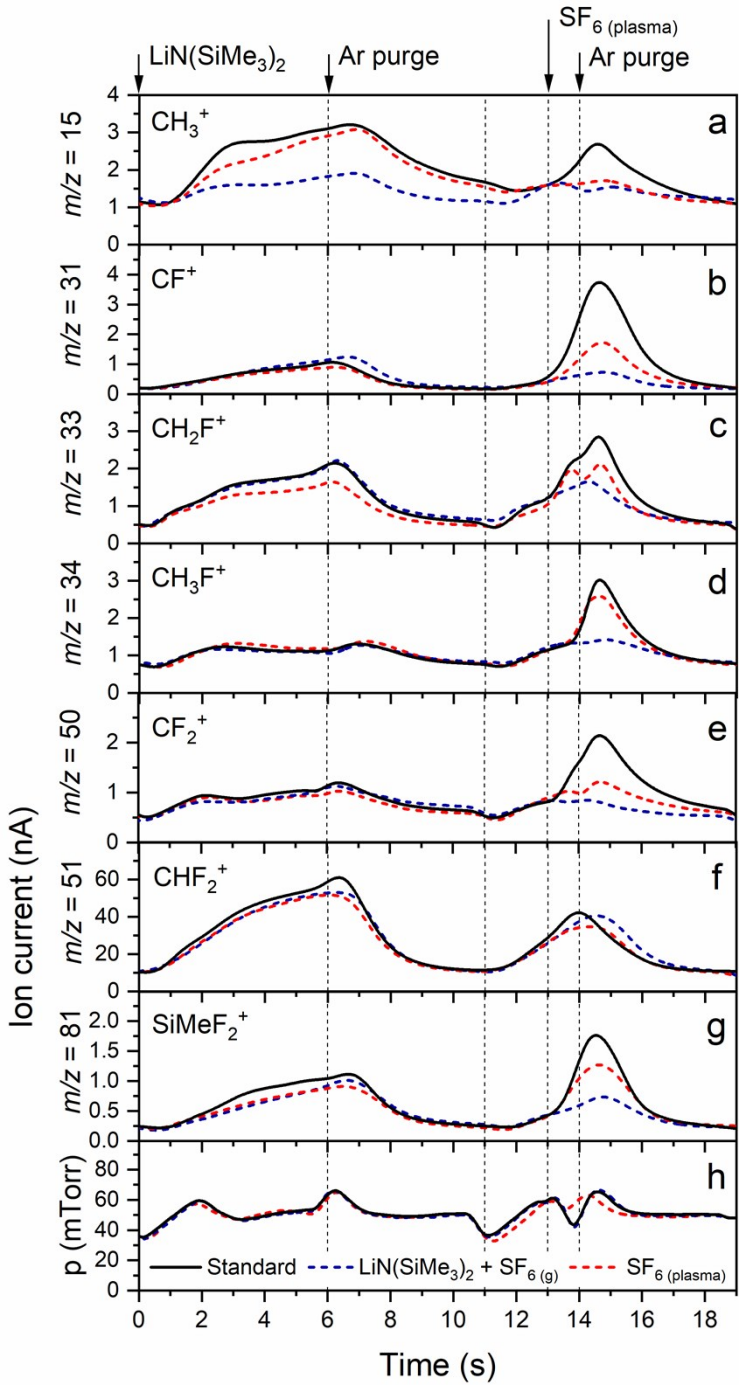

Fig. S8: Time-resolved QMS data of *m/z* = 15, 31, 33, 34, 50, 51, and 81. The standard ALD recipe (black) is compared to the $LiN(SiMe_3)_2$ + SF_6 recipe (blue dotted) and SF_6 plasma recipe (red dotted). The precursor and coreactant dosing steps are alternated by argon purge steps of 5 s.