

DESIGN OF LI-CONTAINING LAYERS WITH LIHMDS

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Lithium-containing layers

Several lithium-containing materials have been deposited with ALD over the past years. Lithium hexamethyl disilazide (LiHMDS) is one of the most promising precursors to deposit lithium-containing films. However, this precursor is known to exhibit dual-source behavior: in some cases, significant amounts of silicon are incorporated in the film due to the silyl groups. On the other hand, sometimes only the lithium component is deposited. For future application of this precursor and its use in ternary and quaternary processes it is important to understand what triggers the dual source behavior of LiHMDS.

Single-source vs. dual-source behavior

We developed a new, simple ALD process to deposit lithium silicate with LiHMDS and O₂* (plasma). Lithium and silicon are both present in the deposited films, so this is an example of **DUAL-SOURCE BEHAVIOR**. Earlier, a similar process was developed with ozone [1, 2]. In contrast, when LiHMDS is combined with trimethylphosphate (TMP), Li₃PO₄ is formed [3]. Here LiHMDS exhibits **SINGLE SOURCE BEHAVIOR**.

To study the mechanisms leading to silicon incorporation, we intermixed the LiHMDS-O₂* process with TMP in an ABC/ACB way. The growth and process chemistry were characterized with in situ ellipsometry and in situ time-resolved full range mass spectrometry, whilst the stoichiometry of the films was obtained from elastic recoil detection (ERD) and x-ray photoelectron spectroscopy (XPS) measurements.

Composition and GPC

Process	T (°C)	nm	GPC (nm)	Si (%)	O (%)	Li (%)	H (%)	P (%)	C (%)
LiHMDS-O ₂ *	150	116.18	0.23	23	53.9	22.6	0.5	-	-
LiHMDS-O ₂ *	300	122.24	0.24	24.2	54.7	20.4	0.72	-	-
LiHMDS-O ₂ *-TMP	300	134.33	0.27	22	58.5	17.3	0.2	2.11	-
LiHMDS-TMP-O ₂ *	300	78.6	0.16	19.2	58.4	18.2	0.53	3.65	-
LiHMDS-TMP	325	49.9	0.08	1.22	47.8	28.8	7.11	10.8	4.18

- The thermal process grows slower than the plasma processes
- LiHMDS-TMP-O₂* grows slower than other plasma processes
- Very little contamination in plasma-enhanced processes
- P contribution from TMP in mixed processes seems negligible, but PO₄ units should be considered.

Plasma step results in OH/O-Li surface

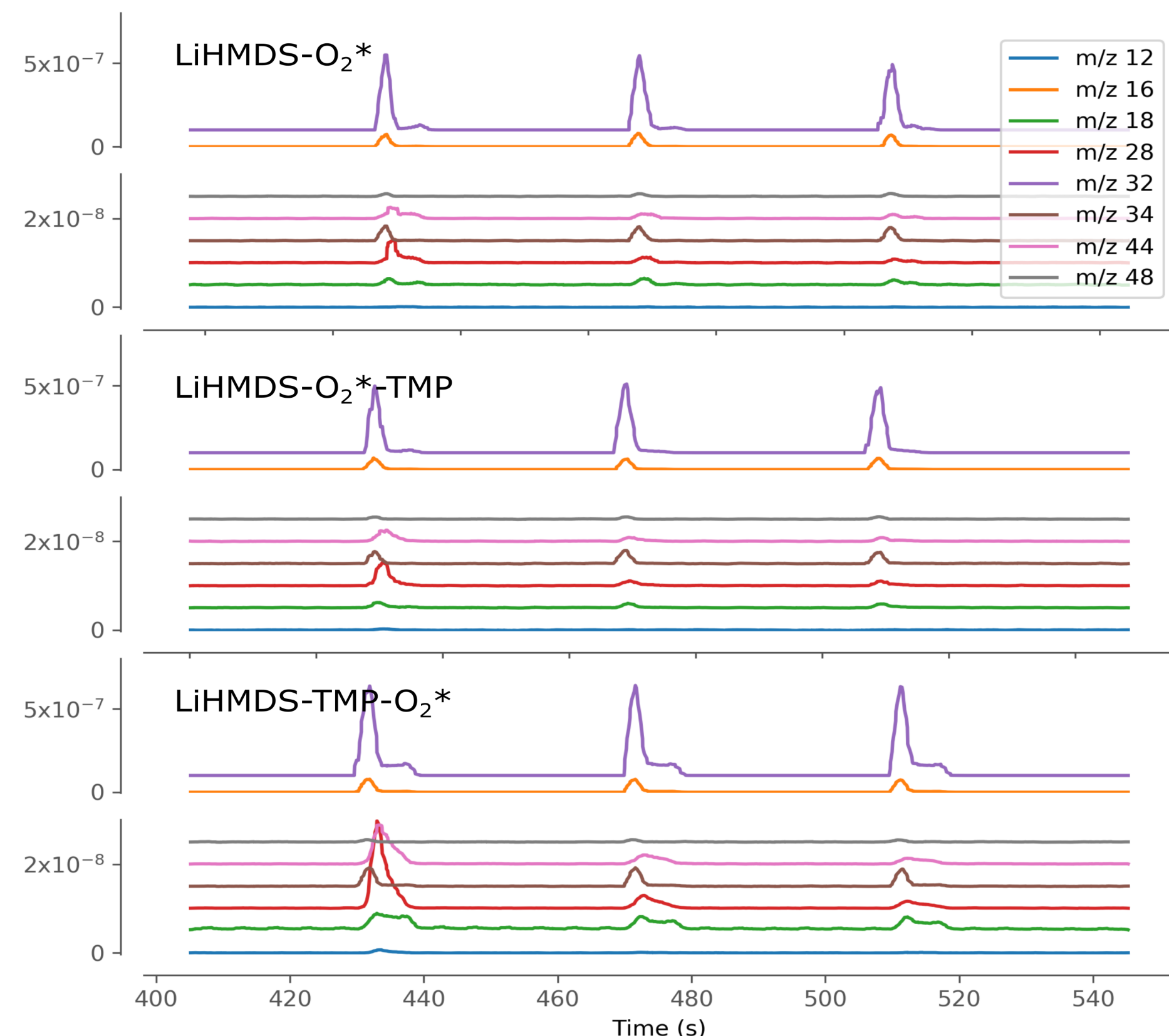


Fig. 1 (above) slices of the time-resolved mass spectra of the oxygen plasma in different processes. Typical combustion products are observed. The shape of the combustion peaks is different because TMP is combusted in the bottom graph. The oxygen plasma creates a mixed OH/O-Li surface.

Mass spectrometry

By combining data from different ALD cycles, we are able to construct a time-resolved spectrum for the full m/z range [4]. By taking horizontal (see above) or vertical slices of these spectra, a full picture of the gas mix in the reactor can be obtained.

We conducted time-resolved, full-range mass spectrometry for all processes. The LiHMDS-TMP process is enabled solely by a dipole-driven, self-saturation physisorption mechanism and features no dissociative component. The LiHMDS-O₂* process features both. This becomes clear by studying the LiHMDS-TMP-O₂* process, where the TMP molecule removes the HMDS groups (and hence the silicon) of the physisorbed LiHMDS.

References

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All identified mechanisms are present in LiHMDS-TMP-O₂*

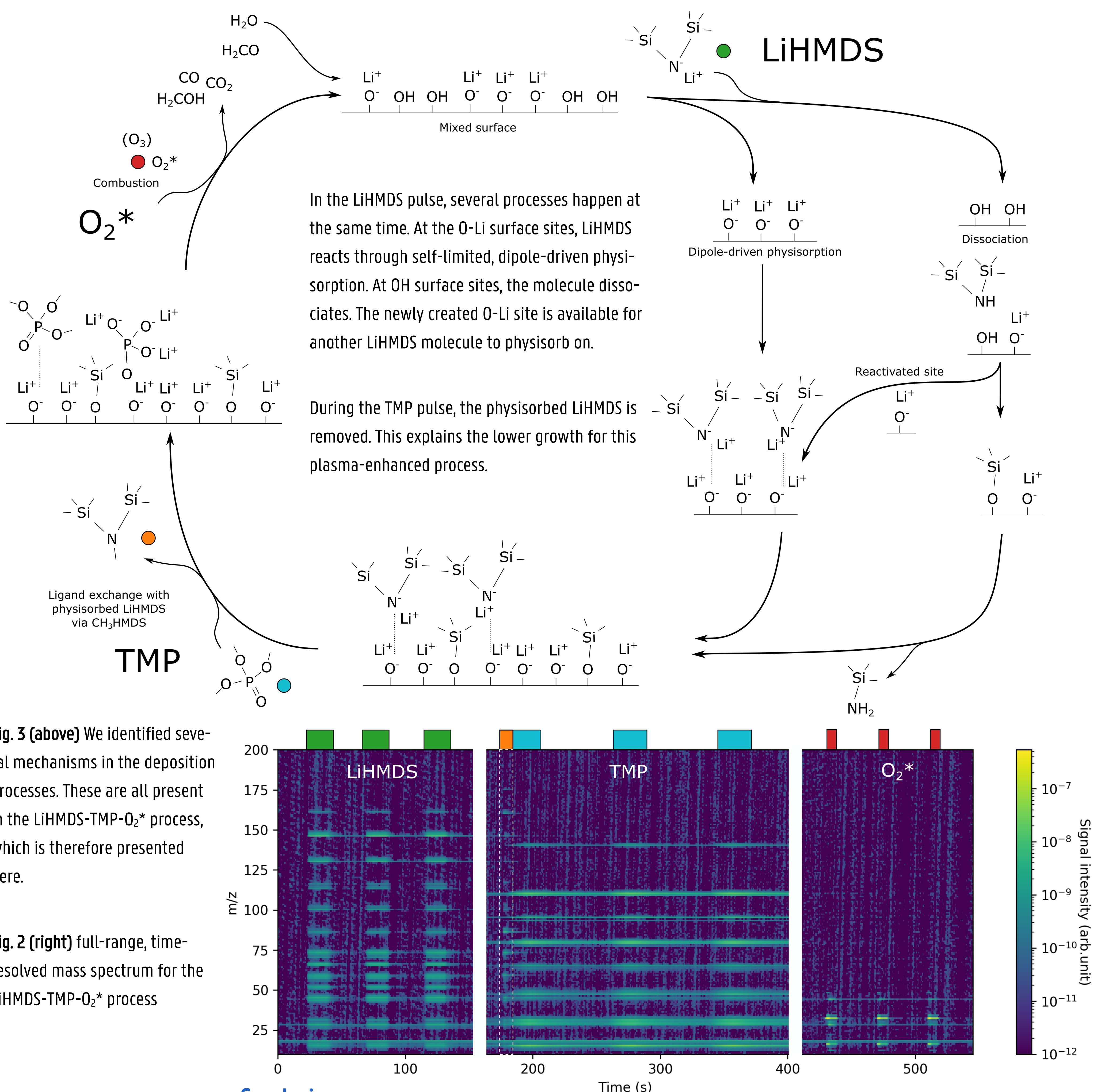


Fig. 3 (above) We identified several mechanisms in the deposition processes. These are all present in the LiHMDS-TMP-O₂* process, which is therefore presented here.

Fig. 2 (right) full-range, time-resolved mass spectrum for the LiHMDS-TMP-O₂* process

Conclusions

By careful study and comparing mixed processes, we were able to distinguish the mechanisms governing LiHMDS adsorption. **The first driver for silicon incorporation is the presence of hydroxyl groups:** they react with LiHMDS creating HMDS as a reaction product. This HMDS will react as well with the hydroxyl groups and acts as a source of silicon. Secondly, whenever lithium-containing films are deposited, **a blanket of physisorbed LiHMDS** will be present after the LiHMDS pulse. If the next precursor pulse fails to remove the HMDS, silicon will be incorporated in the film.

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