Supplemental information for: "Role of the precursor's stability for ALD lithium-containing films"
Nicolas Massoni et al., abstract submitted for an AF1 symposium talk.

The main objective of this study is to provide an understanding of the LiPON film growth. So far, no growth mechanism with both precursors employed simultaneously was proposed in the literature. As a basis, the knowledge of the precursors characteristics is fundamental. We have focused on the precursors behavior at different locations of the process, either under their powdery or vapor states.

The precursors were first characterized as a powder at room temperature, before being placed in the heating canisters located close to the ALD tool. The XRD patterns of fresh precursors were collected. For both precursors, existing PDF cards were found in PDF5 database. However the DEPA one reported only reflections but no lattice, nor atomic positions [1]. Within a collaboration with the "Institut des Materiaux de Nantes", a possible structure was recently found and is currently under confirmation by Rietveld modelization. We will be able to publish it, once confirmed. And a the current PDF card will be updated with the complete description in the database.

The melting points and evaporation onsets of the fresh precursors were checked by thermal analysis. No significant deviation from literature was evidenced. The same analysis was done with aged precursors, i.e. after being kept several days heated in the canisters. Only the DEPA exhibited a significant difference between fresh (or as supplied) and aged precursors (Figure 1).

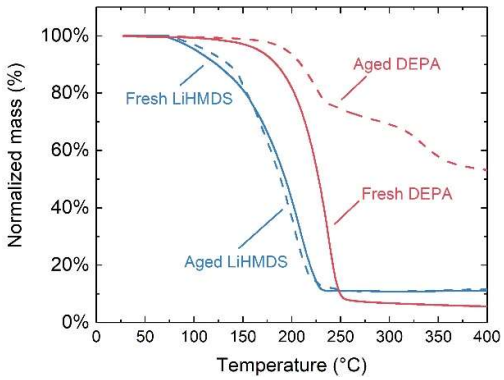

Figure 1. Mass loss as a function of the temperature for fresh

The NMR ^{31}P and FTIR data of fresh vs. aged DEPA have confirmed a structural difference that could explain the thermal analysis differences (Figure 2).

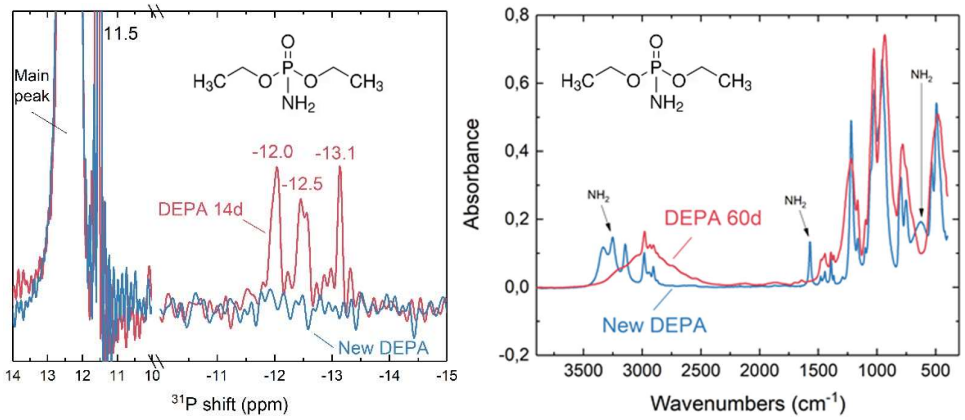

Figure 2. ^{31}P liquid-state NMR (left) and FTIR data (right) of fresh and aged DEPA (14 and 60 days)

It is already confirmed that the P-NH_2 bond was impacted. Starting from the solved structure of fresh DEPA, the refinement of the aged DEPA structure from its XRD pattern, correlated with these analyses, will be made. And a more detailed description of the degradation of the aged DEPA will be provided. New NMR measurements are currently under progress with 35 days-aged DEPA. Structure modifications will be determined and compared to the 14 days-aged DEPA.

Under their vapor state, the PY-GCMS of fresh precursors has brought valuable information, already reported in the abstract. The same analyses of aged precursors are under progress. Hence, the impact of aged precursors on the vapor composition will be evaluated. To complete the study, a mass spectrometer will be plugged to the machine by the end of February to characterize the by-products. Hence, the possible fragments adsorbed on the wafer could be described. With these information, a possible growth mechanism will be proposed.

The outcome of the study is a comprehension of the impact of the precursor ageing on the LiPON film properties, such as GPC, stoichiometry and conductivity. Considering all the results already achieved and the upcoming one, a scientific article is planned to share with the ALD scientific community.

References

[1] PDF00-018-1629