

Reaction mechanism of the $\text{Me}_3\text{AuPMe}_3$ and H_2 plasma PEALD process - Supporting Information

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NMR-data

NMR measurements were performed on both types of precursor that were used for the ALD experiments. The obtained results for the $\text{Me}_3\text{AuPMe}_3$ liquid is shown in Figure 1a, the spectrum confirms that the $\text{Me}_3\text{AuPMe}_3$ liquid has a purity of 95%, with <5% of MeAuPMe_3 . The NMR results for the $(\text{CD}_3)_3\text{AuPMe}_3$ liquid (Figure 1b) show that the used precursor liquid has a purity of at least 95% and a deuteration of more than 99%.

Varying the plasma exposure

In-situ RAIRS experiments show that the CH_3 groups and PMe_3 groups are removed from the surface by the H_2 plasma exposures. This was verified by *in-vacuo* XPS measurements, showing that a H_2 plasma exposure of 10 seconds is sufficient to remove the contaminating

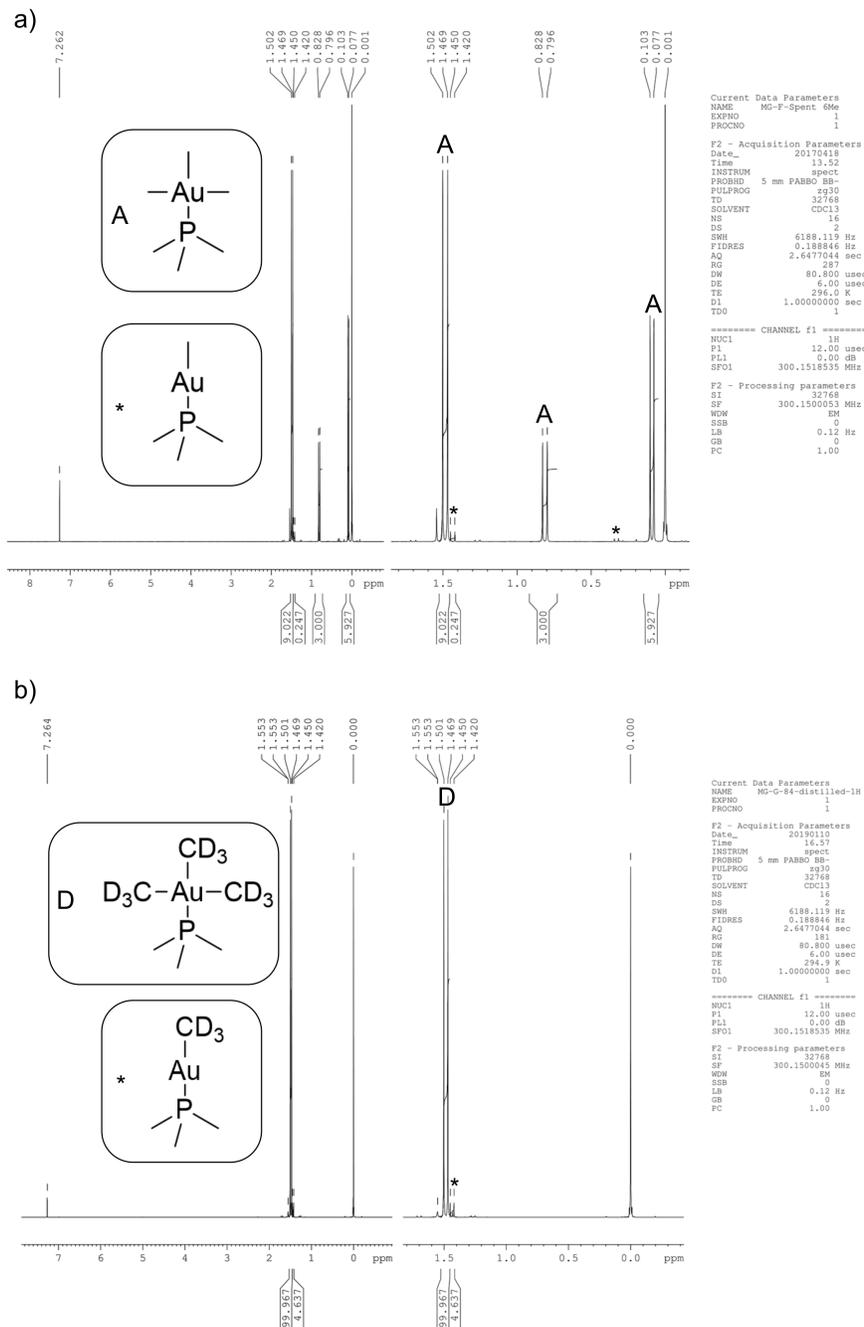


Figure 1: NMR spectra of the used precursor liquids. a) spectrum of $\text{Me}_3\text{AuPMe}_3$, indicating that the liquid has only a minor component of MeAuPMe_3 ($<5\%$). b) spectrum showing a pure $(\text{CD}_3)_3\text{AuPMe}_3$ ($<5\%$, $\text{CD}_3\text{AuPMe}_3$), with at least $>99\%$ deuteration.

surface groups. Beside this, we also performed *ex-situ* XPS measurements on three ALD gold samples, deposited using different plasma exposure lengths. These samples were deposited on silicon oxide substrates at a substrate temperature of 90°C, with saturating precursor exposures. The C1s and P2p peaks for these samples are displayed in Figure 2. The samples were measured after air-exposure (top panel) and after removing the surface contamination by argon sputtering (bottom panel).

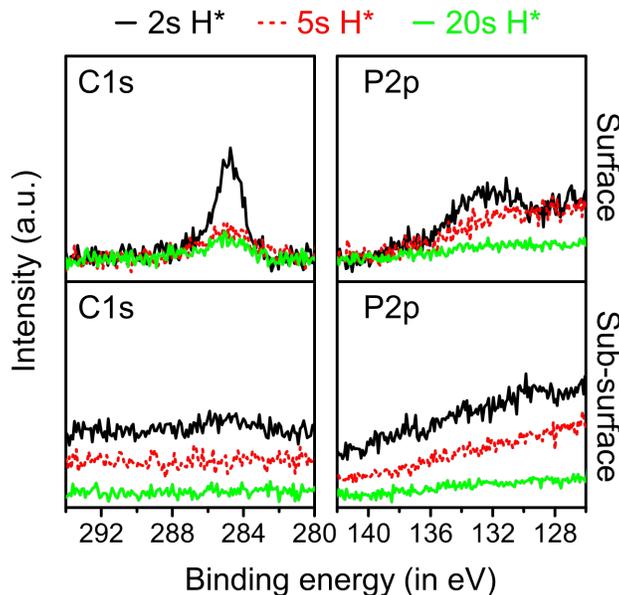


Figure 2: *Ex-situ* XPS spectra for the C1s and P2p peaks of three ALD deposited gold samples using different plasma exposures. The depositions were carried out on silicon oxide substrates at 90°C, using saturating $\text{Me}_3\text{AuPMe}_3$ exposures. Air-exposed samples are displayed in the top panel, while the bottom panel show the same samples after 100s of argon sputtering.

On the air-exposed samples, there is a clear P2p peak present for the sample with a plasma exposure of 2 seconds, while for the longer exposures this peak is not clearly present and remains below the detection limit. After removing the top-layer by argon sputtering there is no clear presence of phosphorous for the longer plasma exposures and there is a small remnant visible of the P2p peak, around 130 eV, for the shortest plasma exposure. For the carbon peak (C1s) there is also a clear difference on the air-exposed surface for the shortest plasma exposure and the other two samples. The 5 s and 20 s plasma exposed

samples have a comparable C1s peak, which can be attributed to adventitious carbon from exposure to the atmosphere. For the 2 s plasma exposed sample the C1s peak is significantly larger compared to the other samples. While there will be a contribution of adventitious carbon for all three samples, the air-exposure for all three samples was similar. The most likely origin of this additional carbon is from the CH₃ groups of the PMe₃ ligand. A lower GPC is observed for shorter plasma exposures, indicating that something is prohibiting the chemisorption of additional precursor molecules during the precursor exposure, causing the lower GPC. From the *ex-situ* XPS measurements it is to be expected that there are still PMe₃ ligands present on the surface for shorter plasma exposures, which occupy possible chemisorption sites, reducing the amount of gold atoms that can be deposited during each Me₃AuPMe₃ exposure.

Nucleation data

In-situ transmission FTIR measurements were used to study the nucleation stage of the Me₃AuPMe₃ - H₂ plasma ALD process. For this a silicon substrate (with native oxide) was used and was heated to 90°C during the ALD deposition. The sample could be mounted on the substrate holder with different incidence angles of the IR beam, with respect to the surface normal of the sample. Experiments were performed in which the IR beam had an incidence angle of 0° and 75° with respect to the surface normal. Difference spectra for ALD cycle 1; 20, and 40 of both experiments are displayed in Figure 3. At an incidence angle of 0° (Figure 3a) it is not possible to identify any of the expected absorption peaks from the precursor, while at an incidence angle of 75° (Figure 3b) there are clearly changes in absorption present after the first precursor exposure. And after 20 ALD cycles the difference spectra start to resemble the steady state case of the process. The displayed spectra of Figure 3b are scaled down to compensate for the increase in measured surface area due to the larger incidence angle.

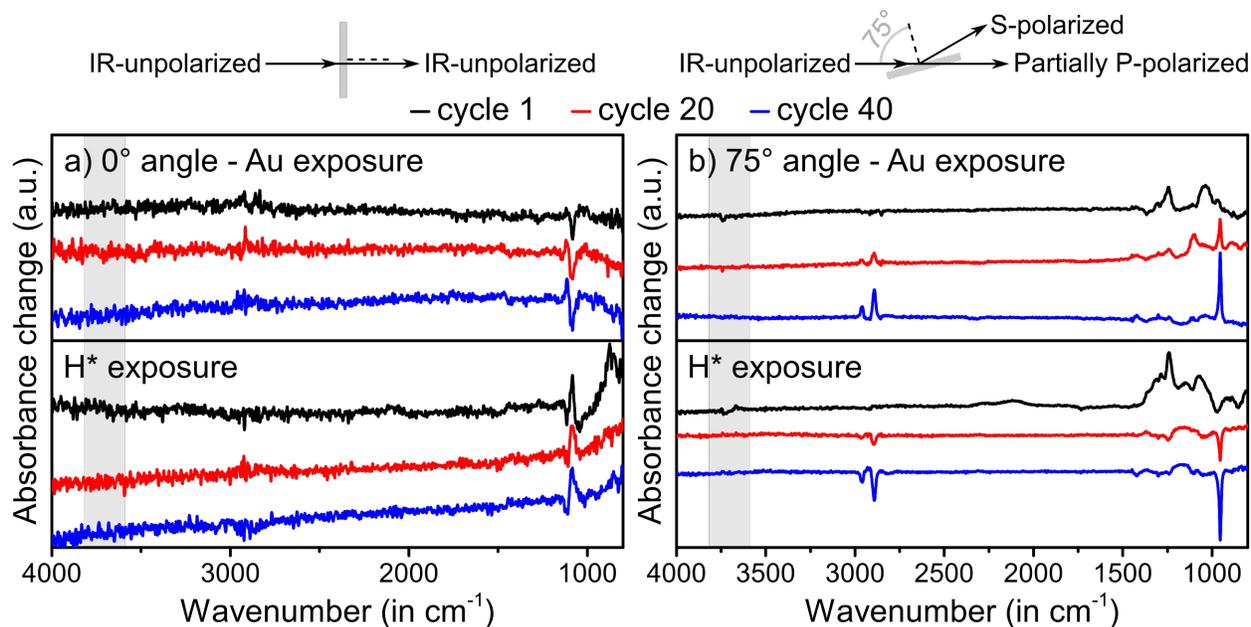


Figure 3: Transmission infrared difference spectra for the precursor and co-reactant exposures for ALD cycles 1, 20, and 40. The spectra were measured after each exposure during the gold ALD deposition and was performed at a substrate temperature of 90°C . The grey box marks the OH stretching region. a) Sample mounted with its surface normal parallel to the incident IR beam. b) Sample mounted with the surface normal angled at 75° with respect to the incident IR beam. The spectra were scaled down by a factor of 3,86 to correct for increase in measured surface area. The geometry of the incident IR beam and the substrate is drawn above the figure for both cases. The dash black line represents the surface normal of the sample.