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Mass Spectrometry Study of Li$_2$CO$_3$ Film Growth by Thermal and Plasma-Assisted Atomic Layer Deposition

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ABSTRACT: Quadrupole mass spectrometry was carried out to detect and identify the reaction products during atomic layer deposition (ALD) of lithium carbonate (Li$_2$CO$_3$). We examined gas phase species for thermal ALD using a LiO$^+$Bu precursor together with H$_2$O and CO$_2$ and plasma-assisted ALD using the same lithium precursor combined with an O$_2$ plasma. For both processes it was concluded that in the first half-cycle the LiO$^+$Bu chemisorbs on the surface by an association reaction of the complete precursor whereas in the second half-cycle the organic ligand is abstracted as tert-butanol. The differences between the two processes lie mainly in the formation of CO$_2$ and H$_2$O reaction byproducts in the second half-cycle when an O$_2$ plasma is used as coreactant instead of H$_2$O. The generation of CO$_2$ supports the fact that it is possible to deposit Li$_2$CO$_3$ films directly by plasma-assisted ALD. Instead, in the case of thermal ALD, an additional CO$_2$ dose step is required to deposit Li$_2$CO$_3$ and suppress LiOH or Li$_2$O formation. The reaction with CO$_2$ appears to be reversible at higher deposition temperatures ($T \geq 250$ °C) and by using extended plasma exposure times, and therefore the composition of the plasma-assisted ALD films can be varied between Li$_2$CO$_3$ and Li$_2$O.

1. INTRODUCTION

Lithium carbonate is the most widely studied model system in atomic layer deposition (ALD) of Li compounds. 1–3 Specifically, it is considered an essential step for incorporating Li into multicomponent ALD electrode and electrolyte materials. Furthermore, it is an electrochemically stable, pure ionic conductor on its own and therefore interesting as protective coating/electron barrier on electrode materials. Several studies have investigated the stoichiometry of atomic layer deposited Li$_2$CO$_3$ as well as LiOH and Li$_2$O by, e.g., time-of-flight secondary ion mass spectrometry (ToF-SIMS) or X-ray photoelectron spectroscopy (XPS). 4–7 From these studies it is known that if an ALD process is employed with two half-cycles using a lithium precursor and H$_2$O, either LiOH or Li$_2$O is formed depending on the deposition temperature. Li$_2$CO$_3$ can be deposited by adding an extra CO$_2$ subcycle to the ALD process. In our previous work, we found that if an O$_2$ plasma is used as coreactant instead of H$_2$O and CO$_2$, the stoichiometry of the films can be varied between Li$_2$CO$_3$ and Li$_2$O, with deposition temperature playing an important role. 8

Cavanagh et al. postulated a reaction scheme for LiOH and Li$_2$CO$_3$ thermal ALD and used a quartz crystal microbalance (QCM) to strengthen their hypothesis based on the measured mass gains and losses during different steps of the ALD process. 8 It was proposed that in the first ALD subcycle, LiO$^+$Bu precursor chemically adsorbs on the surface and remains intact. In the second subcycle LiOH is formed upon H$_2$O exposure, releasing tert-butanol as reaction product. In the last process step CO$_2$ is dosed, resulting in a Li$_2$CO$_3$ film and releasing H$_2$O as reaction byproduct. The mass changes obtained by QCM were close to the values calculated using the molecular mass ratios of the reaction products following from the proposed reactions. So far, the reaction products during the ALD process have not been experimentally confirmed by direct measurements. Moreover, reaction mechanism studies for the plasma-assisted ALD process are still lacking, and it is not known what the differences between plasma-assisted and thermal ALD are in terms of surface reactions. Thermal ALD processes are generally exploiting ligand exchange reactions, where the ligands of the metal precursor are eliminated by bonding to the Lewis acid groups, most commonly hydrogen, provided by the nonmetal coreactant. ALD processes using oxygen, oxygen plasma, or ozone as coreactant typically involve a different chemistry often leading to combustion reactions. 9 With plasma-assisted ALD, a high reactivity is delivered to the deposition surface by the plasma species, and therefore less thermal energy is required at the substrate to drive the ALD surface chemistry. 10 In previous studies we found that the use of plasma species as reactants for the Li$_2$CO$_3$ process allows for deposition at temperatures as low as 50 °C, higher growth per cycle values, and shorter cycle times due to the possibility to deposit Li$_2$CO$_3$ with less process steps. 7

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In this work, a quadrupole mass spectrometry (QMS) study was carried out to detect and identify the reaction products during ALD of Li$_2$CO$_3$. QMS gives direct insight into the gas species present in the chamber and can therefore give useful information on the surface reactions. The influence of temperature and plasma exposure time was also investigated. Li$_2$CO$_3$ films were deposited by thermal ALD using a LiO$_2$Bu precursor combined with H$_2$O and CO$_2$ and by plasma-assisted ALD using LiO$_2$Bu together with an O$_2$ plasma. By investigation of the thermal ALD process, previously proposed reaction mechanisms were experimentally confirmed, and knowledge on QMS of lithium materials was obtained, useful for understanding the more complex plasma-assisted ALD process. Knowledge on the reaction products can provide new insights which can be useful for preparing better quality ALD films for lithium ion battery applications.

## 2. EXPERIMENTAL SECTION

The ALD processes presented in this work were carried out using the thermal and remote plasma ALD reactor FlexAL of Oxford Instruments. The reactor is equipped with an inductively coupled plasma source, and it has a turbo and rotary molecular pump such that it can reach a base pressure of $<10^{-6}$ Torr by overnight pumping. For thermal ALD, the cycle consists of the exposure of the substrate to LiO$_2$Bu lithium precursor (97%, Sigma-Aldrich), H$_2$O gas, and CO$_2$ gas, respectively. The plasma-assisted ALD process consists of a combination of exposure of the substrate to the same lithium precursor and to an O$_2$-fed plasma generated with a plasma power of 100 W. The lithium precursor is bubbled from a precursor pod with argon. To reduce possible clogging, the lithium line is equipped with a stainless steel VCR face seal fitting including a silver-plated gasket with 20 μm pores.

The precursor dosing steps are alternated by argon purging steps. The purge time is kept at 6 s for consistency and to clearly separate the process steps. The table and wall temperature were kept at 150 and 120 °C, respectively, unless specified differently. The processing pressure was in the range of 7–200 mTorr and is specified in the time-resolved measurement section. All the ALD process parameters are summarized in Table 1. More details are presented in earlier work.

A Pfeiffer Vacuum mass spectrometer with a mass-to-charge ($m/z$) range of 100 atomic mass units (amu) was connected to the deposition chamber through a pipeline and a 150 μm diameter pinhole. The system is equipped with a Channeltron detector, and the energy of the electrons in the ionizer was set to 70 eV. The pressure in the QMS was maintained below $10^{-6}$ Torr using differential pumping with a turbomolecular pump. Prior to every measurement, the reactor was conditioned with a Li$_2$CO$_3$ film, and the background signal of the reactor was measured as a reference.

The QMS used measures only stable neutral species which are then ionized in the mass spectrometer. To learn about the species present in the reactor during processing, first the total $m/z$ range was measured. The measuring time per atomic mass unit (amu) was set to 200 ms. Only $m/z$ values of 0–60 are plotted in the same figure for comparison. In addition, a measurement without injection of gas at a reactor pressure in the range of $10^{-6}$ Torr is shown. This allows one to discern between precursor species, the Ar signal, and the background signal. Peaks are found at $m/z = 15$ from CH$_3^+$, 31 most likely from CH$_3$O+, 41 from C$_2$H$_5^+$ or C$_2$H$_3^+$, 43 from C$_3$H$_7$O$^+$ or C$_3$H$_5^+$, 57 from C$_4$H$_9$O$^+$ or C$_4$H$_7^+$, and 59 amu from C$_4$H$_9$O$^+$. The cracking pattern of LiO$_2$Bu is very similar to the one of tert-butanol from the NIST database except that the peak distribution is slightly different. However, this discrepancy could also be due to instrumental differences in sensitivity of the mass spectrometers used.

For the time-resolved measurements, the selected $m/z$ values were tracked per channel using a dwell time (or integration time) of 50 ms. The QMS data of at least 10 ALD cycles were monitored to verify that steady-state values were achieved. Moreover, all measurements were repeated at least three times to verify reproducibility. The pressure in the system was monitored to distinguish pressure-related fluctuations in the signal from variations in the gas composition unrelated to the pressure changes. This allows for distinguishing the signals originating from species potentially involved in the reactions. Also, to distinguish reaction products from other species in the chamber, reference measurements were carried out. In the reference measurements one or more of the reagents are excluded from the standard ALD sequence. A similar procedure was used by Knoops et al. for ALD of TaN$_x$.

### Table 1. ALD Process Parameters Used for the Measurements

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<tr>
<td>Ar purge times</td>
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For the thermal ALD process, the LiO$_2$Bu precursor is combined with H$_2$O and CO$_2$ gas steps, respectively. The cracking patterns for H$_2$O and CO$_2$ gas dose together with the background signal of the reactor are shown in Figure S1 in the Supporting Information. Peaks originating from H$_2$O$, H^+$, OH$^+$, and O$^+$ can be recognized in the mass spectrum of H$_2$O. The pattern of CO$_2$ predominantly consists of CO$_2^+$, CO$^+$, and...
C⁺ species, as expected. In the plasma-assisted ALD process of Li₂CO₃, the H₂O and CO₂ gas are replaced by an O₂ plasma. During the O₂ plasma exposure step, mainly O⁺ and O₂⁺ species are identified in the cracking pattern as shown in Figure S2 in the Supporting Information.

3.2. Time-Resolved Measurements for Thermal ALD Li₂CO₃. To obtain information on the reaction products formed during the thermal ALD process, time-resolved mass spectrometry was carried out. From the ionization patterns shown in the previous section, it was concluded that the LiO'Bu precursor can be tracked by following m/z = 15 and 59. H₂O and CO₂ can be tracked by following m/z values 18 and 44, respectively. Hence we started the investigations by tracking the changes in ion current for m/z = 15, 18, 44, and 59. The results for other common m/z values will be discussed later in this section.

In Figure 2, the time-resolved QMS data are plotted for one ALD cycle of Li₂CO₃. The graph is divided into several sections representing the different ALD process steps (i.e., LiO'Bu, H₂O, and CO₂ dosing, respectively), which are alternated by Ar purging. In addition to the standard ALD recipe, also the curves are plotted for conditions when only one or two of the reagents are used in the recipe. In this way it is possible to distinguish the reaction products from other species present in the reactor. In every plot four different curves are shown, corresponding to the following recipes: the standard recipe, the recipe with only LiO'Bu and H₂O (corresponding to the ALD process of LiOH), the recipe with only H₂O, and the recipe with only CO₂.

Before discussing the trends of the different fragments, we report on the variation in pressure according to the different recipes. In Figure 2g, the pressure curves are plotted. The pressure during the lithium precursor dose was around 7 mTorr. During the Ar purge step, Ar gas was injected from a different line, and the pressure increases and stays constant around 12 mTorr, as observed from the graph. In the first second of the following subcycle the automated pressure control (APC) gate valve is closed to promote the distribution of H₂O in the chamber and limit the exposure time necessary to saturate the reaction with a dosing time of 50 ms. In this way also the purge time is kept relatively short. The Ar flow is stopped, and therefore the pressure decreases. When H₂O is dosed, the pressure reaches 20 mTorr. During the CO₂ dose step, another small pressure drop is observed due to a slight delay of the CO₂ flow caused by the geometry of the gas dosing system. When the CO₂ reaches the chamber, the pressure increases to about 200 mTorr. Note that the pressure curves are plotted on a logarithmic scale for clarity, since the pressure during the CO₂ dosing was relatively high compared to the pressure when dosing other reagents.

In the first ALD subcycle the LiO'Bu precursor is introduced in the chamber. During this subcycle hardly any change in the signals is observed. However, on a much smaller ion current scale it is possible to observe a slight signal increase at all the m/z values related to the precursor (e.g., 15, 31, 41, and 59 amu). This is shown in the inset of Figure 2f. The intensity of this signal is much lower compared to the signal obtained in the next subcycle, as will be discussed later. This suggests that the increase originates from dissociation of residual, unreacted LiO'Bu molecules in the mass spectrometer or negligible abstraction of tert-butanol during the LiO'Bu surface reaction.
As addressed in the Introduction, it was postulated by Cavanagh et al. that LiO'But molecularly absorbs on the sample surface. The current QMS data is in line with this postulation because the signal at m/z = 59 is definitely negligible with respect to the signal obtained in the next subcycle. The LiO'But most likely chemisorbs on the sample surface with an association reaction of the complete precursor. In such an association reaction, the precursor remains intact when it chemically adsorbs without the release of reaction products into the gas phase.

In the next subcycle H2O is dosed, and large signals at m/z = 15, 18, and 59 are detected instantly. The signals are now much larger as compared to the first subcycle, which suggests the presence of surface reactions. After dosing, the APC is kept closed for 4 s meaning the reactor is not being pumped and therefore the signals only decrease very slowly. The increase for m/z = 59 indicates that a precursor fragment was released during this subcycle, since this is the main peak of the LiO'But cracking pattern. This is supported by the increase in ion current for m/z = 31 and 41 amu, as shown in the Supporting Information (Figure S3). The presence of these mass values also indicates that the precursor ligand is most likely released in the form of tert-butanol since 31, 41, and 59 amu are the three major peaks in the tert-butanol mass spectrum.

H2O is difficult to pump, and in the purge step after H2O dose, it seems as if not all the H2O is removed from the chamber. However, it was shown in our previous work that the purge times are sufficient to suppress a significant CVD contribution to film growth. As mentioned in the Introduction, it is known from previous studies that H2O dosing initiates the reaction toward LiOH. LiOH is hygroscopic and can easily adsorb H2O and form a hydrate. The hygroscopic character is reversible, and H2O can desorb from the LiOH-hydrate during the purge times, which might be the reason for the slow decay of the signal during the purge step.

In the third subcycle, CO2 was introduced in the chamber, and the reaction toward Li2CO3 takes place. As observed from Figure 2b, it is established that H2O is a reaction byproduct. Moreover, no precursor-related reaction products were observed.

Based on these observations, a reaction sequence during Li2CO3 thermal ALD can be proposed. Our reaction mechanism is in line with findings from literature and therefore confirms earlier data. In summary, in the first subcycle the LiO'But precursor chemically adsorbs without the significant release of reaction products into the gas phase (eq 1). In the second subcycle LiOH is formed upon H2O dosing, and the ligand is released in the form of tert-butanol (eq 2).

\[
\text{LOC(CH}_3\text{)}_3\text{H(g)} \rightarrow \text{LiOC(CH}_3\text{)}_3\text{H(ads)} \quad (1)
\]

\[
\text{LiOC(CH}_3\text{)}_3\text{H(ads)} + \text{H}_2\text{O(g)} \rightarrow \text{LiOH(ads)} + \text{HOC(CH}_3\text{)}_3\text{H(g)} \quad (2)
\]

\[
\text{LiOH- LiOH(ads)} + \text{CO}_2\text{(g)} \rightarrow \text{Li}_2\text{CO}_3\text{(ads)} + \text{H}_2\text{O(g)} \quad (3)
\]

The first two equations also describe the binary reaction of LiOH ALD. In our previous studies we showed that the introduction of CO2 in the chamber initiates the reaction toward Li2CO3. As preliminary conclusion, we have demonstrated that upon CO2 dosing, H2O was released in the gas phase and is therefore a reaction byproduct, according to eq 3.

3.3. Time-Resolved Measurements for Plasma-Assisted ALD Li2CO3. The plasma-assisted ALD process of Li2CO3 consists of two half-cycles: in the first half-cycle the lithium precursor is dosed in the chamber, and in the second half-cycle the O2 plasma is ignited (see Figure 3).
dissociation of unreacted LiO\(^{18}\)Bu molecules in the mass spectrometer. During the Ar purge, the signal decreases slowly again. The H\(_2\)O (m/z = 18) and CO\(_2\) (m/z = 44) levels are not altered when LiO\(^{18}\)Bu is injected into the chamber. Similar to the thermal ALD process, also for plasma-assisted ALD no significant release of reaction products into the gas phase was observed in the first subcycle. Therefore, it is expected that the precursor chemisorbs by an association reaction as well.

As was reported in our earlier work, no surface reaction takes place when O\(_2\) gas is introduced in the chamber without ignition of plasma.\(^7\) This is confirmed by the mass spectrometry data in Figure 3. If we only use LiO\(^{18}\)Bu and O\(_2\) gas, the curve follows the same trend as when there is no lithium precursor (as indicated by the blue and red line). However, if the plasma is switched on, we observe a large signal increase for all the masses shown in Figure 3. The increased ion current for m/z = 15, 31, 41, and 59 amu during the plasma step indicates a reaction of the precursor ligand. In addition, volatile byproducts such as CO\(_2\) and H\(_2\)O were detected (Figure 3b and Figure 3e), attributed to the combustion of the absorbed ligand by O radicals.\(^{15,16}\) By comparing our measured CO\(_2\) cracking pattern shown in Supporting Information Figure S2 (parent ion at m/z = 44: 100% and at m/z = 28: ± 25% of normalized peak height) to the measurements shown in Figure 3, it can be concluded that also CO is present in the deposition chamber during the O\(_2\) plasma step. As observed from the time-resolved measurements, the CO\(^+\) signal (Figure 3c) has a comparable intensity during the plasma exposure step as the CO\(_2\)^{+} signal (Figure 3e). The origin of CO could either be through incomplete combustion of the ligands or through dissociation of CO\(_2\) in the plasma. Although the signals are decreasing, the detection of H\(_2\)O, CO\(_2\), and CO continues for the whole plasma duration. Moreover, the presence of high signals at m/z = 15 (CH\(_3\)^{+}), 29 (CHO^+, shown in Supporting Information Figure S4) and 30 (most likely CH\(_2\)O^+) during the O\(_2\) plasma exposure step suggests additional surface reactions. The peaks are similar in height with respect to the fragments of tert-butanol, different from the thermal ALD process, where m/z = 15 is relatively small and m/z = 29 and m/z = 30 are much smaller. Therefore, it is expected that other surface reactions occur, for which only a fraction of the precursor is converted to combustion byproducts.

Another finding concerns the deposition of Li\(_2\)CO\(_3\) directly using the plasma-assisted ALD route.\(^7\) We have shown in Figure 3 that a high amount of CO\(_2\) is formed during the O\(_2\) plasma exposure step. Therefore, it is expected that a secondary reaction by CO\(_2\) could be initiated during the O\(_2\) plasma exposure step. As observed from the time-resolved measurements, the CO\(^+\) signal (Figure 3c) has a comparable intensity during the plasma exposure step as the CO\(_2\)^{+} signal (Figure 3e). The origin of CO could either be through incomplete combustion of the ligands or through dissociation of CO\(_2\) in the plasma. Although the signals are decreasing, the detection of H\(_2\)O, CO\(_2\), and CO continues for the whole plasma duration. Moreover, the presence of high signals at m/z = 15 (CH\(_3\)^{+}), 29 (CHO^+, shown in Supporting Information Figure S4) and 30 (most likely CH\(_2\)O^+) during the O\(_2\) plasma exposure step suggests additional surface reactions. The peaks are similar in height with respect to the fragments of tert-butanol, different from the thermal ALD process, where m/z = 15 is relatively small and m/z = 29 and m/z = 30 are much smaller. Therefore, it is expected that other surface reactions occur, for which only a fraction of the precursor is converted to combustion byproducts.

\[
\text{LiOC(CH}_3\text{)}_3\text{(ad)} + O^\text{(g)} \\
\rightarrow \text{LiOH(ad)} + \text{HOC(CH}_3\text{)}_3\text{(g)} \\
+ \text{combustion byproducts [CO}_2\text{(g)} + \text{CO(g)} + \text{H}_2\text{O(g)}}
\]

\[
\text{(4)}
\]

\[
\text{2LiOH(ad) + CO}_2\text{(g)} \rightarrow \text{Li}_2\text{CO}_3\text{(i)} + \text{H}_2\text{O(g)}
\]

\[
\text{(5)}
\]

The reaction mechanism was proposed for plasma-assisted ALD of Li\(_2\)CO\(_3\) on the basis of experimental data obtained for a deposition temperature of 150 °C and a plasma exposure time of 3 s. Now the influence of substrate temperature and plasma exposure time will be discussed since it was found in previous work that the stoichiometry of the plasma-assisted ALD process is temperature and plasma exposure dependent.\(^7\) By using a short O\(_2\) exposure time and a substrate temperature of ≤ 200 °C, stoichiometric Li\(_2\)CO\(_3\) was formed. At higher temperatures Li\(_2\)O is formed, and it was proposed that this is further promoted by prolonging the O\(_2\) plasma exposure. However, when changing the temperature we do not observe clear differences from QMS. Likely, this is related to the fact that the QMS will only measure a small part of the reaction products coming from the heated table and substrates surfaces. The reactor wall surface is heated to a maximum of 120 °C only and comprises the largest part of the reactor. All internal surfaces of the reactor (i.e., also the reactor walls) contribute to the reaction since the process window of plasma-assisted ALD extends down to 50 °C. This means that even at high deposition temperatures (T ≥ 250 °C), the largest part of the measured reaction products originates from the formation of Li\(_2\)CO\(_3\) instead of Li\(_2\)O. Another probable reason for the incremental change in QMS signal is the difference in obtained reaction products we expect to see in the reaction is quite small. If we replace Li\(_2\)CO\(_3\) by Li\(_2\)O in eq 5, essentially only the relative amount of CO\(_2\) byproducts would slightly increase.

It was shown in previous studies that a plasma duration of 1 s was already sufficient to obtain stoichiometric Li\(_2\)CO\(_3\), which (partly) shifts toward Li\(_2\)O at elevated temperatures (T ≥ 250 °C). It was postulated that the extended plasma exposure promotes the development of Li\(_2\)O at T ≥ 250 °C, since higher growth rates were observed for longer plasma exposure times and the higher growth rates were typical for LiOH/Li\(_2\)O growth (probably related to the hygroscopic nature of the films).\(^7\) We now take a closer look into the CO\(_2\) combustion byproduct. In Figure 4, QMS data for 15 and 44 amu are plotted for a plasma exposure time of 10 s and table temperature of set point of 300 °C. As observed in the graph, the detection of CO\(_2\) continues for a long time when the plasma duration is extended whereas the CH\(_2\)^{+} signal saturates. CO\(_2\) is formed by the combustion of precursor ligands (eq 4) and expected to be simultaneously used in the reaction toward Li\(_2\)CO\(_3\) (eq 5). Since only 1 s plasma duration is sufficient to obtain Li\(_2\)CO\(_3\) films, we know from Figure 4b that an excess of CO\(_2\) is present. However, the source of precursor ligands (and therefore CO\(_2\)) will eventually be released in the gas phase and pumped away from the reactor. This is confirmed by the graphs in Figure 4a, as the CH\(_2\)^{+} signal (which is directly related to the combustion of precursor ligands) saturates. However, since the detection of CO\(_2\) continues, it is expected that a longer O\(_2\) plasma exposure leads to CO\(_2\) desorption from the Li\(_2\)CO\(_3\) film. This will eventually reduce the CO\(_2\) in
the surface region of the film, which allows for LiOH/Li2O to form.

4. CONCLUSIONS

The reaction mechanism of thermal and plasma-assisted Li2CO3 ALD has been investigated using time-resolved QMS. It was concluded that for both processes the LiO’Bu precursor ligand chemisorbs on the surface with an association rate of the complete precursor. By introduction of the co-reactant in the following subcycle, the organic part is released in the form of tert-butanol. This provides proof for the previously proposed reaction mechanism of thermal ALD LiOH/Li2O. When an O2 plasma is used instead of H2O gas, CO2 gas and plasma excited O2 are released in the form of Li2CO3. The standard ALD recipe (black) is compared to the recipe with only O2 plasma (red) and the recipe with only LiO’Bu and O2 gas (blue). O2(g) and O2(plasma) represent O2 gas and plasma excited O2, respectively. The precursor dosing steps are alternated by argon purge steps of 6 s.

Figure 4. QMS data for a long plasma exposure time of 10 s and substrate temperature of 300 °C following m/z = 15 (CH3+) and m/z = 44 (CO2+). The standard ALD recipe (black) is compared to the recipe with only O2 plasma (red) and the recipe with only LiO’Bu and O2 gas (blue). O2(g) and O2(plasma) represent O2 gas and plasma excited O2, respectively. The precursor dosing steps are alternated by argon purge steps of 6 s.

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