Atomic Layer Deposition of Aluminum Phosphate Using AlMe₃, PO(OMe)₃, and O₂ Plasma: Film Growth and Surface Reactions

N. Hornsveld, W. M. M. Kessels, and M. Creatore

ABSTRACT: High purity, uniform, and conformal aluminum phosphate (AlP₂O₇) thin films were deposited by atomic layer deposition (ALD) between 25 and 300 °C using supercycles consisting of (i) PO(OMe)₂ dosing combined with O₂ plasma exposure and (ii) AlMe₃ dosing followed by O₂ plasma exposure. In situ spectroscopic ellipsometry and mass spectrometry were applied to demonstrate the ALD self-limiting behavior and to gain insight into the surface reactions during the precursor and coreactant exposures, respectively. Compared to earlier reported AlP₂O₇ ALD studies using H₂O and O₃ as coreactants or without using coreactants, the use of an oxygen plasma generally leads to higher growth per cycle values and promotes phosphorus incorporation in the film. Specifically, when using a 1:1 PO₂:Al₂O₃ cycle ratio and a substrate temperature of 150 °C, the growth per supercycle is found to be 1.8 Å. The [P]:[Al] atomic ratio for this process is approximately 0.5 (∼AlP₀.₅O₂.₉) and can be tailored by changing the ratio between the two cycles or the substrate temperature. In literature reports where the same aluminum precursor was used, the [P]:[Al] atomic ratio was limited to 0.2 or a very high number of phosphorus cycles was needed in order to increase the phosphorus content. Instead, we demonstrate deposition of films with a composition close to AlPO₃ by using a 2:1 PO₂:Al₂O₃ cycle ratio. The limited incorporation of P in the film is suspected to derive from the steric hindrance of the relatively bulky phosphorus precursor. Mass spectrometry suggests that the PO(OMe)₃ precursor chemisorbs on the surface without the release of reaction products into the gas phase, whereas Al(Me)₃ already undergoes methyl ligand abstraction upon chemisorption.

1. INTRODUCTION

Aluminum phosphate (AlP₂O₇) thin films have been explored for a wide variety of applications such as catalyst support, electrode coating to improve both safety and cycle performance of lithium ion battery cathodes, thin film dielectric, and oxidation resistant coating for carbonaceous materials. Film uniformity and conformality are highly relevant for the practical application of aluminum phosphate, especially when deposition on 3D structures is required. The latter case applies, for example, to the field of 3D Li-ion batteries where AlPO₃ is used to coat cathode particles, or in the case of oxidation resistant coatings on fibers or carbon nanotubes. In addition, the ability to tune the composition has been shown to play a critical role for aluminum phosphate thin films. The stoichiometry of the films determines film properties such as catalytic activity, permittivity, leakage current and breakdown fields, and (thermal) stability.

Atomic layer deposition (ALD) is a powerful technique to meet the above-mentioned requirements in thin film deposition. ALD is based on sequential and self-limiting half-reactions between precursors and coreactants with the surface leading to exceptional conformality and thickness control. For multicomponent oxides, the composition of the films and other related film properties, can be tuned by adjusting the number of ALD cycles for each oxide, in a so-defined ALD supercycle.

So far, several studies on the synthesis of aluminum phosphate by ALD have been published. The results and most important process details have been summarized in Table 1. In earlier studies, aluminum phosphate films were deposited using AlCl₃ or Al(OPr)₃ together with P₂O₅ or PO(OMe)₃ precursors and H₂O or t-C₄H₈OH coreactants at fairly high deposition temperatures (450–500 °C). A wide compositional range could be obtained. Yet for some applications, specifically when using temperature sensitive substrates, a high substrate temperature may be unsuitable (see, e.g., ref 12). Moreover, the usage of chlorides (AlCl₃) might be undesirable in some cases, because it may lead to Cl impurities in the deposited films and can cause corrosion of the process chamber. More recently, a process using the chlorine free precursor AlMe₃, a deposition temperature down to 150 °C, and a controllable stoichiometry were demonstrated. Also, ALD without the use of a coreactant after the precursors exposures was reported. Despite these advantages, it has been shown difficult to incorporate a sufficiently large atomic content of phosphorus in the film for the processes where...
ALMe₃ was used. For the reported ALD process using H₂O after ALMe₃ and O₃ after P(OMe)₃,¹² or without the use of coreactants,¹¹ the [P]:[Al] atomic ratio was limited to 0.2. A very high number of PO₃ cycles (>20) was needed to increase the phosphorus content in the films to 0.8.¹¹,¹² This is likely to be caused by steric hindrance of the phosphorus precursor. Moreover, the use of a high amount of PO₃ cycles considerably extends the cycle time of the process. In a more recent study, it was shown that the use of PO(OMe)₃ plasma polymerization greatly increases the reactivity of PO(OMe)₃ precursor, therefore increasing the phosphorus content in the film.¹⁸ For films deposited at 320 °C, the phosphorus atomic content was found to be almost twice as much as the aluminum content. This process is however not strictly ALD, since saturation of the plasma polymerization step was not shown and for deposition temperatures below 320 °C, continuous and unsaturated growth occurred.

In this work, we report on a new process to synthesize aluminum phosphate thin films using plasma-assisted ALD in which O₂ plasma is applied after each precursor step. It is generally known that with plasma-assisted ALD a high reactivity is delivered to the surface by the plasma species, and therefore, less thermal budget is required at the substrate to drive the ALD surface chemistry than in the case of thermal ALD. PO(OMe)₃ and ALMe₃ were used as precursors as it was proven in different studies these lead to successful deposition of AlPO₃. (see Table 1). Moreover, in this way a fair comparison could be made to already existing AlPO₃ ALD studies. We demonstrated ALD growth occurring for a wide temperature range of 25–300 °C. ALD saturation behavior and the ability to tune film composition were extensively studied. When using a 1:1 PO₃:Al₂O₃ cycle ratio, the growth per supercycle is found to saturate at 1.78 Å. Compared to AlPO₃ ALD studies using an ALMe₃ precursor in combination with H₂O and O₃,¹² or without the use of coreactants,¹¹ the use of an oxygen plasma increased the ability to incorporate phosphorus in the film. The [P]:[Al] atomic ratio for the saturated process at 150 °C is approximately 0.5 (~AlPO₃:O₃) compared to 0.2 in literature reports. The phosphorus content can be further increased by increasing the number of PO₃ cycles or substrate temperature. When using a deposition temperature of 150 °C, only 2 PO₃ cycles per Al₂O₃ cycle were needed to achieve a stoichiometry close to AlPO₄. This work addresses also the film properties as attained when processing the 1:1 PO₃:Al₂O₃ cycle recipe (AlPO₃:O₃) as well as the 3:1 PO₃:Al₂O₃ cycle recipe (slightly phosphorus rich AlPO₄). For both processes, highly uniform, conformal films could be obtained over large 200 mm substrates and over high aspect ratios. Mass spectrometry data suggests that the phosphorus precursor remains intact upon chemisorption, which limits the incorporation of phosphorus atoms. ALMe₃ on the other hand, has been shown to release the ligands in the form of CH₄ groups upon chemisorption. This is in line with literature studies of ALD Al₂O₃ without PO₃.¹⁹

**Table 1. Overview of Process Details Collected from Earlier Work on ALD of Aluminum Phosphate**

<table>
<thead>
<tr>
<th>Al source</th>
<th>coreactant</th>
<th>P source</th>
<th>coreactant</th>
<th>Tsub (°C)</th>
<th>P:Al cycle ratio</th>
<th>GPSC (Å)</th>
<th>[P]:[Al] ratio</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl₃</td>
<td>H₂O</td>
<td>PO₃/O₃/PO(OMe)₃</td>
<td>H₂O</td>
<td>500</td>
<td>1:60–1:5</td>
<td>N.A.</td>
<td>0.06–1.3</td>
<td>16</td>
</tr>
<tr>
<td>AlCl₃/Al(O’Pr)₃</td>
<td>H₂O/C₆H₆OH</td>
<td>PO₃</td>
<td>H₂O/C₆H₆OH</td>
<td>450–500</td>
<td>1:30–1:5</td>
<td>1.3/1.1²</td>
<td>0.04–1.4</td>
<td>9</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>PO(OMe)₃</td>
<td>–</td>
<td>–</td>
<td>150–400</td>
<td>1:1</td>
<td>1.4–2.4³</td>
<td>0.4–0.6</td>
<td>17</td>
</tr>
<tr>
<td>AlMe₃</td>
<td>H₂O</td>
<td>P(OMe)₃</td>
<td>O₂</td>
<td>150</td>
<td>5:1–20:1</td>
<td>1.7⁴</td>
<td>0.2–0.8</td>
<td>12</td>
</tr>
<tr>
<td>AlMe₃</td>
<td>PO(OEt)₃</td>
<td>–</td>
<td>–</td>
<td>250</td>
<td>1:1</td>
<td>1.4⁴</td>
<td>0.2–0.3⁵</td>
<td>11</td>
</tr>
<tr>
<td>AlMe₃</td>
<td>–</td>
<td>PO(OMe)₃ plasma</td>
<td>O₂ plasma</td>
<td>320</td>
<td>1:1</td>
<td>3.7⁵</td>
<td>1.8⁵</td>
<td>12</td>
</tr>
<tr>
<td>AlMe₃</td>
<td>O₂ plasma</td>
<td>PO(OMe)₃</td>
<td>O₂ plasma</td>
<td>25–300</td>
<td>1:1–10:1</td>
<td>1.8–4.6⁶</td>
<td>0.5–1.8⁷⁸</td>
<td>this work</td>
</tr>
</tbody>
</table>

The GPSC refers to the growth per AlPO₃ supercycle which depends on the amount of phosphorus and aluminum cycles and temperature used, specified in the columns to the left. The same holds for the range of deposited [P]:[Al] atomic ratio. *GPSC measured by profilometry, †GPSC measured by photodetector, ‡GPSC measured by electron microscopy, §GPSC measured by spectroscopic ellipsometry. ‖Film composition determined by Rutherford backscattering spectrometry and/or elastic recoil detection. ‡‡Film composition determined by energy-dispersive X-ray spectroscopy. ‡§Film composition determined by solid-state nuclear magnetic resonance. ‡‖Film composition determined by X-ray photoelectron spectroscopy.

### 2. EXPERIMENTAL SECTION

The AlPO₃ thin films were prepared using a FlexAL ALD reactor of Oxford Instruments. The reactor is equipped with an inductively coupled plasma (ICP) source and has a rotary and turbo molecular pumping unit such that it can reach a base pressure of <10⁻⁶ Torr by overnight pumping. The pump unit as well as the ICP source are connected to the deposition chamber through gate valves.

Figure 1 presents a schematic overview of the developed process (see section 3.1). AlPO₃ films were deposited by combining cycles of Al₂O₃ and PO₃. A constant oxygen flow through the ICP gate valve was adopted since it did not lead to any Al₂O₃ or PO₃ growth. For PO₃ cycles consisting of exposures to PO(OMe)₃ (97%, Sigma-Aldrich) and to an O₂ fed plasma are adopted, with Ar purge steps in between. The PO(OMe)₃ precursor was kept in a stainless steel container and introduced into the chamber by vapor draw. The PO(OMe)₃ precursor and supply line were heated to 70 and 90 °C respectively to prevent precursor condensation. The

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**Figure 1.** Schematic of the pulsing sequence of the ALD supercycle for deposition of AlPO₃. The duration of the ALMe₃ dose step is 50 ms. The reactor pressure is also indicated in the uppermost row.
pressure was set to 200 mTorr during the PO(OMe)3 dose step by slightly closing the gate valve connected to the turbo pump. Also a hold step was used. In this way the surface is exposed to more PO(OMe)3 and for a longer period of time. Moreover, a stabilization step of 1 s was used to ensure the gas flow and pressure stabilized at 200 mTorr. For stabilization of the plasma, the reactor was filled with oxygen prior to switching on the power supply. The plasma power was set at 100 W for the POx cycle. The Al2O3 cycle consists of alternating exposures to AlMe3 (>99%, Sigma-Aldrich) and O2-fed plasma with purge steps in between. The AlMe3 precursor was also kept in a stainless steel container and introduced into the chamber by vapor draw. For the AlMe3 precursor pod and supply line temperatures of 30 and 60 °C were used, respectively. The plasma power for the Al2O3 cycle was set to 200 W.

One ALD supercycle consists of n POx cycles and 1 Al2O3 cycle. Depositions were carried out on Si substrates with native oxide for standard characterization and on substrates with wurtzite (WZ) InP nanowire arrays for conformality studies. These substrates are placed on a 200 mm carrier wafer. The deposition table temperature was set between 25 and 300 °C. The reactor wall is maintained at a temperature of 120 °C, except for the deposition at 25, 50, or 100 °C, where the reactor wall is kept at 25, 50, or 100 °C, respectively. The actual substrate temperature might be slightly lower for table set point temperatures >120 °C since it is unlikely that the substrate could reach exactly the same temperature as the table due to a reduced thermal contact in vacuum.

The film thickness and dielectric function were monitored in situ by spectroscopic ellipsometry (SE) with a J. A. Woollam, Inc. M-2000F (245-1000 nm) system and ex situ using variable angle spectroscopic ellipsometry (VASE) with a J. A. Woollam, Inc. M-2000D (190-1000 nm) system. Ex situ measurements were performed from 60−80° with steps of 5°. POx as well as AlPOx films appeared to be transparent within the measured range. The dispersion relationship for the films was well-described by the Cauchy formula \( n(\lambda) = A + B/\lambda^2 - C/\lambda^4 \).

Transmission electron microscopy (TEM) was used to probe the thickness of the films along individual InP nanowires. The wires had a length of ∼1.5 µm and a hexagonal cross-section with an average diameter of ∼180 nm and were arranged in a square array with a 500 nm pitch. Energy dispersive X-ray spectroscopy (EDX) was used to probe the chemical composition along the InP nanowires. The combination of TEM and EDX gives insight into the conformality of the AlPOx films.

Elastic recoil detection (ERD) and Rutherford backscattering spectroscopy (RBS) were carried out to determine the composition and mass density of the films. The hydrogen profiles were determined by ERD using a 2 MeV He+ beam impinging on the sample under 15° glancing incidence and 30° recoil angle. RBS is performed in channeling mode, to reduce the background under the C and O features, using the same beam and with detectors at scattering angles of 170° and 105°.

Figure 2. Growth per supercycle (GPSC) obtained by SE (red circles) and the [P]:[Al] atomic ratio measured by XPS (blue circles) as a function of precursor dosing or coreactant exposure time. In parts a and b, the results are presented for PO(OMe)3 dose and O2 plasma exposure after PO(OMe)3, respectively. Parts a and b also show data for different pressure and plasma power settings, respectively. In parts c and d, the results of AlMe3 dose and O2 plasma exposure after AlMe3 are presented. The lines serve as a guide to the eye. All samples were deposited using a deposition temperature of 150 °C.
X-ray photoelectron spectroscopy (XPS) spectra were recorded by a Thermo Scientific K-alpha+ system using monochromatic Al Kα X-rays. The spot size of the beam was 400 μm and the base pressure of the system was 10^-8 mbar. The measurements were performed without the use of depth profiling, and it was found that these results are consistent with the RBS/ERD results. It is therefore expected that they are representative for the bulk part of the films. The crystallinity of the AlPₓOᵧ layers was investigated using a Philips X’Pert MPD diffractometer equipped with a Cu Kα source (1.54 Å radiation).

A Pfeiffer Vacuum mass spectrometer with a mass-to-charge (m/z) ratio 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 an AlPₓOᵧ film and the background signal of the reactor was measured as a reference. The measuring time per atomic mass unit (amu) was set to 200 ms. For the time-resolved measurements, the selected m/z values were tracked per channel using a dwell time of 50 ms. The QMS data of at least 10 ALD cycles were monitored to verify that steady-state values were achieved. The measurement procedure has been reported more extensively in our previous mass spectrometry work.²⁰

### 3. RESULTS AND DISCUSSION

#### 3.1. ALD Process Optimization

**3.1.1. Saturation Behavior.** As mentioned before, the plasma-assisted ALD process of AlPₓOᵧ consists of POₓ and Al₂O₃ cycles. The plasma-assisted ALD process of Al₂O₃ is well-known from literature and its saturation behavior has been extensively investigated.²¹,²² On the contrary, ALD of POₓ growth no ALD saturation could be achieved.²³ The same behavior was found in our studies (see Figure S1). In addition, it was found that the growth per cycle of the film increases with increasing cycle number, i.e., the thickness of the film, also shown in Figure S1 of the Supporting Information. Furthermore, the POₓ films showed high reactivity upon air exposure and therefore the stoichiometry of the films could not be determined by *ex situ* analysis (e.g., XPS).

The results of the saturation behavior of the AlPₓOᵧ supercycle are presented in Figure 2. This figure shows the saturation of the growth per supercycle as well as the [P]:[Al] ratio for a substrate temperature of 150 °C. The [P]:[Al] ratio gives an indication on the phosphorus incorporation in the films. The overall stoichiometry will be discussed in section 3.3. In Figure 2a, the saturation behavior of the PO(OMe)₃ precursor is shown. First, the growth per supercycle and composition were determined for a lower reactor pressure of 20 mTorr and without the use of a hold step after the PO(OMe)₃ dose (diamond symbols). As observed from the graph, both do not saturate. By using a hold step, the GPC and phosphorus content increased because the sample surface was exposed to precursor molecules for a longer period of time (square symbols). When a higher set pressure was adopted during PO(OMe)₃ exposure, the gate valve connected to the turbo pump was further closed, leading to a higher partial pressure of PO(OMe)₃ (triangle symbols). As shown by the circular symbols, the phosphorus content and growth per supercycle increased by using a pressure of 200 mTorr and a hold step of 4 s after PO(OMe)₃ dose. As a side effect the dosage of the phosphorus precursor is more efficient, since a shorter phosphorus precursor dosing time is needed to achieve the same phosphorus content in the films. It seems that the growth per supercycle saturates faster than the [P]:[Al] ratio. A possible explanation is that the growth per supercycle is mostly determined by the Al₂O₃ cycle (the growth per cycle is much higher for the Al₂O₃ cycle compared to the POₓ cycle), whereas the [P]:[Al] ratio is determined by both cycles. Since our main goal was to increase the film phosphorus content, we focus here on the saturation of the [P]:[Al] ratio. This is achieved for 500 ms PO(OMe)₃ dose and therefore chosen as the standard PO(OMe)₃ dose time. The [P]:[Al] ratio for the saturated process is then 0.5 and the growth per supercycle is equal to 1.78 Å.

Figure 2b depicts the saturation behavior of the O₂ plasma after the PO(OMe)₃ dose step. The growth per supercycle and [P]:[Al] ratio both saturate at approximately 5 s plasma exposure. It can be observed that without the use of plasma after the PO(OMe)₃ exposure there was still film growth, however much lower (1.2 Å/supercycle) and also the [P]:[Al] ratio was relatively high (~0.8) compared to the saturated values obtained for the PO(OMe)₃ dose. The [P]:[Al] ratio decreased when the plasma exposure time was increased. This suggests that if longer plasma exposure times are used, the surface is more reactive to the AlMeₓ molecules in the following process step and therefore more aluminum will be incorporated. The oxygen plasma is expected to convert the methoxy groups of the PO(OMe)₃ molecule into —OH and/or —O surface species. These surface species have been shown promote the chemisorption of AlMeₓ.²⁹ However, film growth was also proven for AlMeₓ in combination with PO(OEt)₃ without the use of coreactants,¹¹ and PO(OMe)₃ and PO(OEt)₃ are very similar. Most certainly the presence of —OH or —O surface species increase the reactivity a lot; however, the removal of the methoxy-groups seems not to be necessary for chemisorption of AlMeₓ.

The saturation behavior of the AlMeₓ dose step is shown in Figure 2c. As expected, the growth per supercycle as well as the [P]:[Al] ratio saturate quickly for this highly volatile and reactive precursor. The standard AlMeₓ dose time was chosen to be 50 ms.

As was the case for the POₓ cycle, there was still film growth without the use of plasma after AlMeₓ (see Figure 2d). This observation suggests that reactions between AlMeₓ and PO(OMe)₃ can occur: PO(OMe)₃ is likely to behave as Lewis base because of the oxygen lone pairs in the phosphate unit, while the surface adsorbed AlMeₓ serves as Lewis acid.²⁴,²⁵ However, the growth per supercycle decreased, and [P]:[Al] ratio was much lower (0.13) when the plasma step was eliminated from the recipe. In addition, compared to previously reported literature data for a 1:1 cycle ratio process where AlMeₓ in combination with different coreactants were used (see Table 1), the phosphorus content is much higher for our plasma-based process. The oxygen plasma presumably not only removes the organic ligands, but also enhances the reaction of the layer with a metal organic precursor to form a metal phosphate. Interestingly, the surface reactions already saturate when the O₂ plasma exposure time is greater than 0.5 s. The *in situ* SE measurement only measures the middle of the sample, and it was observed in previous work on plasma-
assisted ALD of Al$_2$O$_3$ that film uniformity is improved for longer plasma exposures compared to the saturation time.$^{21}$ This is related to the fact that growth rate is usually slightly higher in the center where the flux of plasma species is highest. Therefore, the standard value for the O$_2$ plasma exposure time after AlMe$_3$ was chosen to be 3 s such that a better uniformity of the films can be expected. Film uniformity and also conformality of the films will be discussed in section 3.2.

From the results in parts b and d of Figure 2, we can conclude that the implementation of an O$_2$ plasma greatly improves the surface reactivity of both precursors in the following process step. The plasma exposure time after AlMe$_3$ saturates much faster than the plasma exposure time after PO(OMe)$_3$. This could be related to a more efficient combustion and/or differences in reaction upon AlMe$_3$ and PO(OMe)$_3$ precursor adsorption. In the standard recipe an O$_2$ plasma power of 100 W was used for the PO$_x$ cycle compared to 200 W for the Al$_2$O$_3$ cycle. To exclude that the saturation is a function of the number of PO$_x$ cycles used in the recipe. The [P]:[Al] ratio increased rapidly to almost 1 by only increasing the number of PO$_x$ cycles to 2, corresponding to a stoichiometry close to AlPO$_4$ (see section 3.3 for the film oxygen content). Upon further increasing the number of PO$_x$ cycles, the [P]:[Al] ratio kept slightly increasing. The growth per supercycle also increases with number of PO$_x$ cycles, but does not follow the same trend. The phosphorus content in the films could be further increased for a number of PO$_x$ cycles $n > 10$. As mentioned before, PO$_x$ alone is unstable when exposed to air. For AlP$_x$O$_y$ we found an upper limit in terms of P incorporation in the film, which is stable in air. The AlP$_x$O$_y$ films are stable when [P]:[Al] $\leq 3.3$. In the next sections we will focus on the 1:1 as well as the 3:1 PO$_x$;Al$_2$O$_3$ cycle ratio process as highlighted in Figure 3. The 3:1 cycle ratio is especially interesting, because it leads to a slightly phosphorus-rich aluminum orthophosphate (AlPO$_4$) stoichiometry.

3.1.3. Exploring the Temperature Window. The film thickness and growth rate of the process were investigated for an extended range of deposition temperatures. Figure S2 shows the thickness evolution as a function of the number of ALD cycles for temperatures between 25 and 300 °C. The growth curve is linear for the whole temperature range. In Figure 4, the temperature dependence of the growth per supercycle plotted for processes using a 1:1 as well as a 3:1 PO$_x$;Al$_2$O$_3$ cycle ratio. For both cases, the growth per supercycle decreases with an increase from room temperature up to 300 °C. This was expected since the growth rates for the processes of PO$_x$ (Figure S1) and Al$_2$O$_3$ separately also decrease with increasing temperature.$^{21,22}$ Furthermore, it can be observed that the slope for both cycle ratios decreases for temperatures ≥150 °C. This might be related to differences in the table temperature set point and the actual substrate temperature for table temperatures >120 °C (maximum wall temperature). As mentioned before, it is unlikely that the substrate could reach exactly the same temperature as the table due to a reduced thermal contact in vacuum. Finally, it should be noted that the results obtained from SE agree well with those from RBS and ERD analysis: the amount of deposited atoms (open symbols) scales with the growth per supercycle in terms of thickness (closed symbols).

Figure 3. Growth per supercycle (circles) and [P]:[Al] atomic ratio (squares) as a function of number of PO$_x$ cycles for the AlP$_x$O$_y$ process at a deposition temperature of 150 °C. The dashed lines serve as a guide to the eye.

Figure 4. Growth per supercycle as a function of substrate temperature for AlP$_x$O$_y$ processes using a 1:1 (squares) and 3:1 (circles) PO$_x$;Al$_2$O$_3$ cycle ratio. The dashed lines serve as a guide to the eye. The growth per supercycle is obtained from spectroscopic ellipsometry (in Å, closed symbols) and a combination of RBS and ERD (in at.-nm$^{-2}$, open symbols).

3.2. Film Uniformity and Conformality. The uniformity and conformality were investigated to further demonstrate the ALD behavior of the AlP$_x$O$_y$ process. Film thickness and refractive index nonuniformity were determined using SE-mapping of films deposited on a 200 mm wafer using a 1:1 and 3:1 cycle ratio (see Figure 5 and Figure S3). The nonuniformity (standard deviation, 1 sigma) of the thickness
and refractive index for the 1:1 process were determined to be 1.4% and 0.4%, respectively. For the 3:1 process this was 1.9% and 0.2%, respectively. This points out to good uniformity for both processes. As observed from Figure 5a, a slight thickness gradient is visible, which could be related to the position of the injection of the precursors. The refractive index (Figure 5b) is lower at the spots where a higher thickness is observed. It is therefore more likely that the gradient is related to the flux of PO(O Me)3 than AlMe3 molecules, since for a higher phosphorus content the refractive index will be lower. For the 3:1 process, a similar gradient in the film thickness is observed (Figure S3a). However, this gradient was not observed in the contour plot of the refractive index (Figure S3b). This is probably related to the fact that three POx cycles are deposited for every Al2O3 cycle, and therefore, variations in the phosphorus content and thus the refractive index are below the sensitivity of the measurement.

The conformality of the 3:1 cycle process was studied by depositing on a InP nanowire array. The nanowires were separated and analyzed using TEM and EDX. Figure 6a shows a top-down and tilted SEM image of the nanowire array. Parts b–d of Figure 6 clearly show a conformal, ~23 nm thick aluminum phosphate film along the full length of a nanowire. The ratio between the thickness at the bottom and the top of the nanowire was determined to be >0.9. The EDX mappings in Figure S4 show the presence of indium and phosphorus inside the wire and AlPO4 on top. The aluminum, phosphorus, and oxygen contents were uniformly distributed over the wires. The combination of TEM and EDX results indicate conformal deposition of AlP2Oy films on 3D structures.

3.3. Chemical, Physical, and Optical Properties. 3.3.1. Stoichiometry. In section 3.1, we focused on the [P]:[Al] ratio in connection with the saturation behavior. In this part an in depth study is carried out on the overall stoichiometry of the films, including the presence of impurities and also verifying temperature dependence. The chemical composition of the deposited films was studied by ex situ XPS and a combination of RBS and ERD. 50 nm thick films were deposited using a 1:1 or 3:1 POx:Al2O3 cycle ratio. Carbon traces (~3%) were detected at the surface; sputtering of the surface led to less than ~1% carbon in the bulk of the layer. This is shown in the survey spectra measured by XPS in Figure S5. Next to carbon, oxygen, phosphorus, and aluminum were detected, as expected. In Figure 7, XPS measurements of AlP2Oy films grown at 150 °C are presented showing the (a) Al 2p, (b) P 2p, (c) O 1s, and (d) C 1s core level spectra. The spectra were measured without sputtering, since it was found that these results are consistent with the RBS/ERD results shown hereafter. The binding energy scale was calibrated by using the C 1s adventitious carbon peak at 284.8 eV. The binding energy values are in agreement with those expected for aluminum phosphate reported in literature.27,28 Specifically, the Al 2p, P 2p, and O 1s peaks of the 3:1 process are located at the position expected for a AlPO4 film. The Al 2p and O 1s peak deconvolution could not be performed since the expected peak positions for AlPO4 and Al2O3 are close to each other and the peaks are very narrow.
symmetric. The obtained stoichiometry for the 1:1 cycle process is calculated to be Al0.5PO3.4 and for the 3:1 process Al1.1PO4.8.

The stoichiometry, atomic percentage of hydrogen and calculated mass density obtained by a combination of RBS and ERD are presented in Table 2. These measurements are generally accurate within ±1% and can therefore be used to confirm the previously presented XPS data. The atomic percentages and stoichiometry from XPS for deposition temperatures between 25 and 300 °C are presented in Table S1. The [P]:[Al] ratio measured by RBS and ERD is in line with the ratio measured by XPS. Carbon was found only at the top surface of the films and always below 1.2 at. %, also in line with the XPS results. Without the application of sputtering, the amount of oxygen and carbon measured by XPS was slightly higher compared to the RBS and ERD measurements. This is attributed to the excess of carbon and oxygen present on the surface after air exposure as XPS only measures first few nanometers of the film. The use of higher substrate temperatures limits the incorporation of hydrogen impurities.

In Figure 8, the amount of atoms deposited on a square nanometer per (super)cycle are reported, measured by a combination of RBS and ERD. The AlP0.4 process using a 1:1 cycle ratio is compared to the AlP0.4 process using a 3:1 cycle ratio and an Al2O3 plasma ALD reference. When the 3:1 cycle ratio was used instead of the 1:1 cycle ratio, the amount of incorporated phosphorus and oxygen atoms increased, as expected. The increase in amount of phosphorus atoms does not scale linearly with the amount of PO cycles used. This is in line with the trend observed for the [P]:[Al] ratio as a function of PO cycles shown in Figure 3. On the basis of the RBS/ERD data for the 3:1 recipe at 150 °C, 2.94 P atoms per square nanometer are incorporated every supercycle. The surface density in AlPO4 units per cm² can be calculated via $\rho \cdot N \cdot (\frac{2}{3})$, where $\rho$ is the mass density and $\mu$ is the molecular mass of AlPO4, and $N$ is Avogadro’s number. Given the fact that one monolayer of aluminum orthophosphate contains roughly 5.4 AlPO4 units, and therefore also 5.4 P atoms, per square nanometer, in each supercycle, approximately half a monolayer of AlPO4 is deposited.

Figure 8. Number of Al, P O and H atoms deposited per nm² per (super)cycle as a function of deposition temperature measured by RBS and ERD. The AlP0.4 1:1 process is compared to the AlP0.4 3:1 process and an Al2O3 plasma ALD reference. For the AlP0.4 processes, we refer to the number of atoms per supercycle whereas Al2O3 consists of only one ALD cycle. The dashed lines serve as a guide to the eye.

### Table 2. Properties of 50 nm AlP0.4 Films Fabricated Using 1:1 and 3:1 Cycle Ratios at 25, 150, and 300 °C

<table>
<thead>
<tr>
<th>cycle ratio</th>
<th>T sub (°C)</th>
<th>stoichiometry</th>
<th>[H] (at. %)</th>
<th>mass density (g cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1 25</td>
<td>AlP0.4O3.08</td>
<td>9.4 ± 1.2</td>
<td>2.3 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>1:1 150</td>
<td>AlP0.4O2.95</td>
<td>4.7</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>1:1 300</td>
<td>AlP0.4O2.33</td>
<td>2.6</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>3:1 25</td>
<td>AlP1.3O3.37</td>
<td>6.6</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>3:1 150</td>
<td>AlP1.3O3.11</td>
<td>3.3</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>3:1 300</td>
<td>AlP1.3O3.00</td>
<td>2.5</td>
<td>2.1</td>
<td></td>
</tr>
</tbody>
</table>

The stoichiometry was calculated from a combination of RBS and ERD measurements. The mass density was calculated by combining RBS, ERD, and SE results. In the first row the typical error is given for a certain parameter.
Phosphorus atoms for the AlPₓO₃ process and the Al₂O₃ process, and does not increase when the number of PO₃ cycles is increased to 3 (Figure 8d). This suggests that the incorporation of hydrogen is mostly dependent on the Al₂O₃ cycle, which is similar for these processes.

For the AlPₓO₃ 1:1 process, approximately the same number of phosphorus atoms are deposited per supercycle for different temperatures (Figure 8b). However, the number of deposited phosphorus atoms for the AlPₓO₃ 1:3 process and also the growth rate for the PO₃ ALD are temperature dependent (Figure S1). This suggests that the amount of PO(OMe)₃ adsorbed on an Al₂O₃ substrate shows no clear temperature dependence, although PO(OMe)₃ adsorption on PO₃ does. The data in Figure 8b also suggest that the decrease in phosphorus content in the films for increased temperatures reported in Table 2 is mostly related to the decrease in number of incorporated aluminum atoms. This (in addition to the contribution of the lower reactor wall temperature) could also explain why the decrease in growth per supercycle is less for higher deposition temperatures compared to lower temperatures for the 1:1 cycle (Figure 3). As the deposition of Al atoms decreases with temperature, deposition of P atoms becomes more important; however, since phosphorus adsorption after an Al₂O₃ cycle is not temperature dependent, the effect on the growth rate is much less.

3.3.2. Mass Density and Crystallinity. The mass density for AlPₓO₃ films deposited using a 1:1 cycle ratio varies between 2.1 and 2.3 g cm⁻³ for deposition temperatures from 300 down to 25 °C (Table 2). The mass density of ALD Al₂O₃ films is found to be ~ 2.8 g cm⁻³.21,22 The incorporation of phosphorus in the film decreases the mass density. The mass density is slightly lower for higher substrate temperatures and this is expected to be related to an increased phosphorus content in the films. Films deposited using a 3:1 cycle ratio have a mass density of ~ 2.1 g cm⁻³ for deposition temperatures between 25 and 300 °C. This is in line with our hypothesis, since the phosphorus content does not vary that much for these samples either. In literature the mass density of P-doped Al₂O₃ ALD films is reported to vary from 2.2 g cm⁻³ ([P]:[Al] = 1:3) to 2.9 g cm⁻³ ([P]:[Al] = 0.1).9,16 Therefore, the obtained mass density for our ALD AlPₓO₃ films lies within the lower limit of these literature values.

The as-deposited aluminum phosphate films were also characterized by XRD and where found to be amorphous for the whole temperature range of 25 to 300 °C (Figure S6). It has been shown that AlPₓO₃ films can be crystallized using a heat treatment of the as deposited films.15

3.3.3. Optical Properties. The optical constants of the AlPₓO₃ films deposited at different temperatures were evaluated using ex situ VASE measurements as shown in Figure 9. The films are transparent over the whole measured range. The inset of Figure 9 shows the refractive indices of films deposited using a 1:1 and 3:1 PO₃/Al₂O₃ cycle ratio as a function of wavelength. The refractive indices follow a Cauchy dispersion relation yielding a value of 1.51 and 1.47 at 589 nm, respectively. From the difference in refractive index it can be concluded that when the P content is increased, the refractive index decreases. Our refractive indexes compares well to values reported in literature of ALD AlPₓO₃ films, which vary from 1.47 to 1.53.17,18 Moreover, the refractive index for Al₂O₃ ALD films is reported to be 1.64 ± 0.02 (at 100 °C), also in line with this hypothesis.14

As observed from Figure 9, the refractive index decreases for higher deposition temperatures. This is expected, since the phosphorus content of the films increases as well. Only the phosphorus content of the sample deposited at 25 °C is higher than expected.

3.4. Surface Reactions. To gain more insight into the deposition process, the reaction products within the AlPₓO₃ 1:1 cycle ratio recipe were analyzed by mass spectrometry. Insights into the surface reactions can help in understanding the limited incorporation of phosphorus in the film. Moreover, it can give insights into the benefits to use the O₂ plasma coreactant. To identify the species present in the reactor, first the spectra during precursor dosing were measured in the range of m/z = 0–100. As observed in Figure S7 in the Supporting Information, the PO(OMe)₃ and AlMe₃ precursors can be tracked by following for example m/z = 15 (CH₃⁺), 79 (PO₃⁺), and 57 (Al(CH₃)₃⁺). Oxygen can be tracked by following m/z = 16 (O⁺) which overlaps with CH₄⁺ or m/z = 32 (O₂⁺) which overlaps with CH₂OH⁺. The typical combustion byproducts HO₂ and CO₂ can be tracked following m/z = 18 (H₂O⁺) and 44 (CO₂⁺) amu, respectively.

Figure 10 depicts the time-resolved QMS data of one ALD cycle of AlPₓO₃ using a 1:1 cycle ratio. In parts a–f of Figure 10, the QMS measurements are reported for m/z = 15, 16, 18, 44, 57, and 79. Additional mass to charge ratios 28 (CO⁺ or C₂H₄⁺), 29 (C₂H₅⁺/CHO⁺), 30 (C₂H₆⁺/CH₂O⁺), 31 (CH₃O⁺/P⁺), 32 (O₂⁺/CH₂OH⁺), and 46 (CH₂O₂⁺ or C₂H₄O⁺) amu are measured and can be found in the Supporting Information, Figure S8. Also the pressure in the system was monitored and is plotted in Figure 10g. The graph is divided into several intervals representing the different ALD process steps: i.e., PO(OMe)₃ dose, O₂ plasma exposure, AlMe₃ dose, and O₂ plasma exposure, alternated by Ar purge steps. Compared to the ALD recipe for AlPₓO₃ described in the first section, all purge steps are now extended to 5 s to clearly separate the process steps facilitating data interpretation. Extended purge times did not influence the process. In addition to the standard ALD recipe, also the curves are plotted for recipes when only one of the precursors combined with an O₂ gas flow are used. Since for these recipes no ALD...
growth occurred, it is possible to distinguish the ALD reaction products from other species present in the reactor, such as precursors, coreactants, and background species. In ALD, we can exclude species originating from fragmentation and ionization occurring in the mass spectrometer. In every plot, three different curves are shown, corresponding to the following recipes: the standard 1:1 recipe, the recipe with only PO(Ome)_3 and O_2, and the recipe with only AlMe_3 and O_2.

The delivery of PO(Ome)_3 in the first subcycle led to an increase in signal for m/z = 15 (CH_4^+) and 79 (PO_3^+) and 18 (H_2O^+ from H_2O), 44 (CO_2^+ from CO_2), 57 (Al(CH_3)_2^+ from AlMe_3), and 79 (PO_3^+ from PO(Ome)_3) The standard ALD recipe (black) is compared to the PO(Ome)_3 + O_2 recipe (red dotted) and AlMe_3 + O_2 recipe (blue dotted). The precursor and coreactant dosing steps are alternated by argon purge steps of 5 s.

Figure 10. Time-resolved QMS data of m/z = 15 (CH_4^+ from CH_4, PO(Ome)_3, or AlMe_3), 16 (CH_3^+ from CH_4 or O_3^+ from O_2), 18 (H_2O^+ from H_2O), 44 (CO_2^+ from CO_2), 57 (Al(CH_3)_2^+ from AlMe_3), and 79 (PO_3^+ from PO(Ome)_3). The standard ALD recipe (black) is compared to the PO(Ome)_3 + O_2 recipe (red dotted) and AlMe_3 + O_2 recipe (blue dotted). The precursor and coreactant dosing steps are alternated by argon purge steps of 5 s.

Precursor chemisorbs by a dissociation reaction of the complete precursor. In such an association reaction, the precursor remains intact without the release of reaction products into the gas phase. Next, the O_2 plasma is expected to convert the methoxy groups of the PO(Ome)_3 molecule into −OH or =O. As shown in Figure 10, a little amount of CH_3^+ was detected when the O_2 plasma is ignited. In addition, typical combustion byproducts were detected as well, i.e., H_2O and CO_2. Figure S8 in the Supporting Information shows additional formation of C_2H_6, C_3H_8, and CO_2 byproducts. As observed in Figure 2b in section 3.1, the growth per supercycle and the relative aluminum content were enhanced in the presence of and for extended O_2 plasma exposure. This implies that when the hydrocarbon groups are removed by the O_2 plasma, surface groups are created that are prone to reactions with AlMe_3 in the next process step.

During the AlMe_3 dose step the formation of CH_3^+ and CH_4^+ products was observed. For CH_3^+, the difference between the black and blue line is smaller. CH_3^+ most certainly originates from dissociative ionization of CH_4 in the mass spectrometer. CH_4 is one of the classical reaction products observed by ALD of Al_2O_3. A reaction takes place in which methyl ligands (CH_3 and hydroxyl groups on the surface combine and form CH_4. Moreover, it is found that we do not measure any AlMe_3-related peak during AlP_2O_5 standard ALD (see Figure 10e). AlMe_3 dissociates and/or is consumed by surface reactions with the substrate or reactor walls before it reaches the mass spectrometer. This makes sense since it is well-known that AlMe_3 has a high reactivity. In the AlMe_3 + O_2(g) recipe (blue dotted line), the molecules do not react or adsorb and stay intact because the substrate and reactor walls were already completely saturated with AlMe_3. Therefore, we do see a high peak for the AlMe_3 + O_2(g) recipe.

In the last process step, an O_2 plasma is used to remove the remaining methyl ligands by combustion. It was already shown in section 3.1 that without the use of the plasma coreactant the phosphorus content in the film was extremely low, indicating the low reactivity of PO(Ome)_3 with AlMe_3 and necessity for removal of these groups in this process step (see Figure 2d). As shown in Figure 10a and b, CH_3^+ ions are formed, but also the typical combustion products H_2O and CO_2. Figure S8 shows additional formation of C_2H_6 and C_3H_8 byproducts, similar to the combustion of the phosphorus precursor ligands. The formation of H_2O in the plasma could lead to additional (thermal ALD like) reaction pathways, as was the case for Al_2O_3. It was shown in section 3.3 that the [P]:[Al] ratio is only 0.5 when a 1:1 cycle ratio is used. QMS data suggests that, unlike AlMe_3, the relatively bulky phosphorus precursor remains intact upon adsorption and limits the incorporation of phosphorus atoms by steric hindrance. Therefore, it can indeed be expected that the aluminum content of films deposited using the 1:1 cycle process is larger than the phosphorus content. In the AlP_2O_5 paper by Dobbelare et al, AlP_2O_5 films are obtained with an [P]:[Al] atomic ratio of 1.8 using plasma polymerization. In this case the PO(Ome)_3 molecules are partly dissociated in the plasma and therefore steric hindrance is not an issue. However, for our process the limited phosphorus incorporation can be overcome by using >1 PO_3 cycles.
4. CONCLUSIONS

Amorphous aluminum phosphate thin films have been deposited by plasma-assisted ALD using a wide deposition temperature range of 25 to 300 °C. ALD behavior was achieved for every precursor and co-reactant process step and the process resulted in ALD films with excellent uniformity and conformality as demonstrated on 200 mm wafers and nanowires, respectively. It has been shown that the use of an O2 plasma step is beneficial for increasing surface reactivity for the precursor molecules. When using a substrate temperature of 150 °C, the growth per supercycle saturates at ~1.8 Å. The [P]/[Al] atomic ratio for the saturated process is approximately 0.5 (AlPO3.5) and can be tailored by changing the ratio between the Al2O3 and PO4 cycles and/or the substrate temperature. When using 2 PO2 cycles, a composition close to AlPO4 is obtained. The use of higher substrate temperatures reduces the incorporation of hydrogen impurities and the adsorption of aluminum atoms, which, as a result, leads to an increase in the phosphorus content in the film. It is expected that the lower phosphorus limit of the ALD AlPO4 : 1:1 PO2 :Al2O3 cycle ratio process is determined by differences in chemisorption processes of both precursors and steric hindrance of the phosphorus precursor. Regarding this effect, it has been proposed that PO(O)Me3 chemisorbs on the surface without the release of reaction products into the gas phase. Instead, the introduction of AlMe3 results in a release of Al2O3. The two intermediate O2 plasma steps are needed to remove the (remaining) organic ligands of both precursor molecules and introduce surface groups that are prone to reactions with the precursors. Altogether, it has been shown that the use of an O2 plasma can offer advantages to more commonly used thermal ALD processes of AlPO4 and deliver high quality ALD films.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c00301.

Notes

The authors declare no competing financial interest.

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