Atomic layer deposition of aluminum phosphate using AlMe3, PO(OMe)3 and O2 plasma: film growth and surface reactions

Citation for published version (APA):

Document license:
CC BY-NC-ND

DOI:
10.1021/acs.jpcc.0c00301

Document status and date:
Published: 05/03/2020

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.
• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.
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 (AlPₓOᵧ) thin films were deposited by atomic layer deposition (ALD) between 25 and 300 °C using supercycles consisting of (i) PO(OMe)₃ 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 AlPₓOᵧ ALD studies using H₂O and O₂ 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 PO(OMe)₃: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 PO(OMe)₃: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 (AlPₓOᵧ) 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 AlPₓOᵧ 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-called 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-C₄H₉OH 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. 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 POₓ 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 POₓ 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 an 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 Al₉PO₃. (see Table 1). Moreover, in this way a fair comparison could be made to already existing Al₉PO₃ 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 POₓ:Al₂O₃ cycle ratio, the growth per supercycle is found to saturate at 1.78 Å. Compared to Al₉PO₃ ALD studies using a 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 (~Al₉POₓ Oₓ) compared to 0.2 in literature reports. The phosphorus content can be further increased by increasing the number of POₓ cycles or substrate temperature. When using a deposition temperature of 150 °C, only 2 POₓ 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 POₓ:Al₂O₃ cycle recipe (Al₉POₓ Oₓ) as well as the 3:1 POₓ: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 gases, which is an advantage.

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

<table>
<thead>
<tr>
<th>Al source</th>
<th>P source</th>
<th>P source coreactant</th>
<th>T sub (°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>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/C₂H₅OH</td>
<td>PO₃/O₃/PO(OMe)₃</td>
<td>450–500</td>
<td>1:30–1:5</td>
<td>1.3/1.1₄</td>
<td>0.04–1.4</td>
<td>9</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>–</td>
<td>PO(OMe)₃</td>
<td>150–400</td>
<td>1:1</td>
<td>1.4–2.4₅</td>
<td>0.4–0.6</td>
<td>17</td>
</tr>
<tr>
<td>AlMe₃</td>
<td>H₂O</td>
<td>P(OMe)₃</td>
<td>150</td>
<td>5:1–20:1</td>
<td>1.7₆</td>
<td>0.2–0.8</td>
<td>12</td>
</tr>
<tr>
<td>AlMe₃</td>
<td>–</td>
<td>PO(OR)₃</td>
<td>250</td>
<td>1:1</td>
<td>1.4₇</td>
<td>0.2–0.3₈</td>
<td>11</td>
</tr>
<tr>
<td>AlMe₃</td>
<td>–</td>
<td>PO(OMe)₃ plasma</td>
<td>320</td>
<td>1:1</td>
<td>3.7₉</td>
<td>1.8–2.₅</td>
<td>18</td>
</tr>
<tr>
<td>AlMe₃</td>
<td>O₂ plasma</td>
<td>PO(OMe)₃ plasma</td>
<td>25–300</td>
<td>1:10:1:1</td>
<td>1.8–4.6₁₀</td>
<td>0.5–1.₉</td>
<td>this work</td>
</tr>
</tbody>
</table>

The GPSC refers to the growth per Al₉PO₃ 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. GCSP measured by profilometry, GPSC measured by photoelectron spectroscopy. GPSC measured by transmission 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.

2. EXPERIMENTAL SECTION

The Al₉PO₃ 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). Al₉PO₃ films were deposited by combining cycles of Al₂O₃ and POₓ. A constant oxygen flow through the ICP gate valve was adopted since it did not lead to any Al₂O₃ or POₓ growth. For POₓ cycles consisting of exposures to PO(OMe)₃ (97%, Sigma-Aldrich) and to an O₂ feed 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 pod and supply line were heated to 70 and 90 °C respectively to prevent precursor condensation. The
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 Al₂O₃ films appeared to be transparent within the measured range. The dispersion relationship for the films was well-described by the Cauchy formula (n(λ) = A + B/λ² − C/λ⁴).

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 Al₂O₃ 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°.
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) 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 mbar. The measurements were performed without the use of a hold step 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 AlₓOᵧ cycle (the growth per cycle is much higher for the AlₓOᵧ cycle compared to the PO₃ 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 AlMe₃ 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 AlMe₃. However, film growth was also proven for AlMe₃ in combination with PO(OEt)₃ without the use of coreactants, 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 AlMe₃.

The saturation behavior of the AlMe₃ 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 AlMe₃ dose time was chosen to be 50 ms.

As was the case for the PO₃ cycle, there was still film growth without the use of plasma after AlMe₃ (see Figure 2d). This observation suggests that reactions between AlMe₃ 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 AlMe₃ serves as Lewis acid. 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 AlMe₃ 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 Al2O3 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 O2 plasma exposure time after AlMe3 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 O2 plasma greatly improves the surface reactivity of both precursors in the following process step. The plasma exposure time after AlMe3 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 AlMe3 and PO(OMe)3 precursor adsorption. In the standard recipe an O2 plasma power of 100 W was used for the POx cycle compared to 200 W for the Al2O3 cycle. To exclude that the saturation is due to a higher plasma power, which slightly increases the ion flux and slightly reduces the ion energy,26 also 200 W was tested for the POx cycle (red open symbols), whereby all other settings remained unchanged. However, this does not influence the saturation time.

Overall, it is observed that the growth per supercycle saturates at 1.78 Å. Interestingly, this is approximately the sum of the growth per cycle of the plasma-assisted Al2O3 process which is 1.30 Å,22 and the growth per cycle for POx on Si with native oxide which is determined to be 0.5 ± 0.1 Å over the first 100 cycles (see Figure S1). The [P]:[Al] ratio for the saturated process is 0.5.

3.1.2. Tuning the Phosphorus Content. As discussed in previous paragraph, there is a limit to the incorporation of phosphorus ([P]:[Al] ratio of 0.5) when AlPOx films are deposited at 150 °C using the 1:1 PO2:Al2O3 cycle ratio. The film composition can be tuned by varying the number of POx cycles while the number of Al2O3 cycles is kept constant. Figure 3 shows the growth per supercycle and [P]:[Al] ratio as a function of the number of POx cycles used in the recipe. The [P]:[Al] ratio increased rapidly to almost 1 by only increasing the number of POx cycles to 2, corresponding to a stoichiometry close to AlPO4 (see section 3.3 for the film oxygen content). Upon further increasing the number of POx cycles, the [P]:[Al] ratio kept slightly increasing. The growth per supercycle also increases with number of POx cycles, but does not follow the same trend. The phosphorus content in the films could be further increased for a number of POx cycles n > 10. As mentioned before, POx alone is unstable when exposed to air. For AlPOx, we found an upper limit in terms of P incorporation in the film, which is stable in air. The AlPOx films are stable when [P]:[Al] ≤ 3.3. In the next sections we will focus on the 1:1 as well as the 3:1 PO2:Al2O3 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 (AlPO4) 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 is plotted for processes using a 1:1 as well as a 3:1 PO2:Al2O3 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 POx (Figure S1) and Al2O3 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 POx cycles for the AlPOx 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 AlPOx processes using a 1:1 (squares) and 3:1 (circles) PO2:Al2O3 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).
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(OMe)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 PO₃ 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 AlPₓOᵧ 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 PO₃: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 AlPₓOᵧ 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
The obtained stoichiometry for the 1:1 cycle process is calculated to be Al$_{0.5}$PO$_{3.4}$ and for the 3:1 process Al$_{1.1}$PO$_{4.8}$.

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 $^\circ$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 AlP$_x$O$_y$ 1:1 process is compared to the AlP$_x$O$_y$ 3:1 process and an Al$_2$O$_3$ plasma ALD reference. For the AlP$_x$O$_y$ processes, we refer to the number of atoms per supercycle whereas Al$_2$O$_3$ consists of only one ALD cycle. The dashed lines serve as a guide to the eye.

Figure 7. (a) 30$^\circ$ tilt SEM images of an as-grown WZ InP nanowire array. (b) Bright-field TEM image of a single nanowire with an AlP$_x$O$_y$ film prepared using a 3:1 cycle ratio. (c and d) Bright-field TEM images taken around the (c) top and (d) center of the same nanowire.

Figure 8. Number of Al, P O and H atoms deposited per nm$^2$ per (super)cycle as a function of deposition temperature measured by RBS and ERD. The AlP$_x$O$_y$ 1:1 process is compared to the AlP$_x$O$_y$ 3:1 process and an Al$_2$O$_3$ plasma ALD reference. For the AlP$_x$O$_y$ processes, we refer to the number of atoms per supercycle whereas Al$_2$O$_3$ consists of only one ALD cycle. The dashed lines serve as a guide to the eye.

Table 2. Properties of 50 nm AlP$_x$O$_y$ Films Fabricated Using 1:1 and 3:1 Cycle Ratios at 25, 150, and 300 $^\circ$C

<table>
<thead>
<tr>
<th>cycle ratio</th>
<th>$T_{\text{sub}}$ ($^\circ$C)</th>
<th>stoichiometry</th>
<th>[H] (at. %)</th>
<th>mass density (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>25</td>
<td>AlP$<em>{1.0}$O$</em>{3.0}$</td>
<td>9.4 ± 1.2</td>
<td>2.3 ± 0.1</td>
</tr>
<tr>
<td>1:1</td>
<td>150</td>
<td>AlP$<em>{5.4}$O$</em>{2.95}$</td>
<td>4.7</td>
<td>2.3</td>
</tr>
<tr>
<td>1:1</td>
<td>300</td>
<td>AlP$<em>{1.3}$O$</em>{3.33}$</td>
<td>2.6</td>
<td>2.1</td>
</tr>
<tr>
<td>3:1</td>
<td>25</td>
<td>AlP$<em>{1.5}$O$</em>{3.57}$</td>
<td>6.6</td>
<td>2.1</td>
</tr>
<tr>
<td>3:1</td>
<td>150</td>
<td>AlP$<em>{1.8}$O$</em>{4.11}$</td>
<td>3.3</td>
<td>2.1</td>
</tr>
<tr>
<td>3:1</td>
<td>300</td>
<td>AlP$<em>{1.9}$O$</em>{4.30}$</td>
<td>2.5</td>
<td>2.1</td>
</tr>
</tbody>
</table>

$^a$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.
atoms is equal for the AlP$_x$O$_y$ 1:1 cycle process and the Al$_2$O$_3$ process, and does not increase when the number of PO$_x$ cycles is increased to 3 (Figure 8d). This suggests that the incorporation of hydrogen is mostly dependent on the Al$_2$O$_3$ cycle, which is similar for these processes.

For the AlP$_x$O$_y$ 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 AlP$_x$O$_y$ 1:3 process and also the growth rate for the PO$_x$ ALD are temperature dependent (Figure S1). This suggests that the amount of PO(OMe)$_3$ adsorbed on an Al$_2$O$_3$ substrate shows no clear temperature dependence, although PO(OMe)$_3$ adsorption on PO$_x$ 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 Al$_2$O$_3$ 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 AlP$_x$O$_y$ 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 Al$_2$O$_3$ films is found to be ∼ 2.8 g cm$^{-3}$.

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 Al$_2$O$_3$ 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).

Therefore, the obtained mass density for our ALD AlP$_x$O$_y$ 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 AlP$_x$O$_y$ films can be crystallized using a heat treatment of the as deposited films.

### 3.3.3. Optical Properties.

The optical constants of the AlP$_x$O$_y$ 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 PO$_x$:Al$_2$O$_3$ 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 AlP$_x$O$_y$ films, which vary from 1.47 to 1.53.

Moreover, the refractive index for Al$_2$O$_3$ ALD films is reported to be 1.64 ± 0.02 (at 100 °C), also in line with this hypothesis. 14

![Figure 9. Refractive index versus $[P]/[Al]$ ratio for films deposited using substrate temperatures from 25 to 300 °C and an 1:1 cycle ratio. The refractive index and $[P]/[Al]$ ratio were determined from SE and XPS analysis, respectively. The dashed line serves as a guide to the eye. The inset shows refractive index of films from 190–1000 nm determined by ex situ VASE for films deposited at 150 °C using a 1:1 and 3:1 cycle ratio.](https://dx.doi.org/10.1021/acs.jpcc.0c00301)

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 AlP$_x$O$_y$ 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 O$_2$ 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 AlMe$_3$ precursors can be tracked by following for example $m/z$ = 15 (CH$_4^+$), 79 (PO$_3^+$), and 57 (Al(CH$_3$)$_2^+$). Oxygen can be tracked by following $m/z$ = 16 (O$^+$) which overlaps with CH$_4$ or $m/z$ = 32 (O$^+$) which overlaps with CH$_3$OH. The typical combustion byproducts H$_2$O and CO can be tracked following $m/z$ = 18 (H$_2$O$^+$) and 44 (CO$_2^+$) amu, respectively.

Figure 10 depicts the time-resolved QMS data of one ALD cycle of AlP$_x$O$_y$ 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 C$_2$H$_4^+$), 29 (C$_2$H$_5^+$), 30 (C$_2$H$_6^+$), 31 (CH$_3$O$^+$), 32 (O$^+$), 46 (CH$_3$O$^+$), and 44 (CO$^+$) 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, O$_2$ plasma exposure, AlMe$_3$ dose, and O$_2$ plasma exposure, alternated by Ar purge steps. Compared to the ALD recipe for AlP$_x$O$_y$ 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 O$_2$ 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 addition, 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 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$_3^+$ from CH$_4$, PO(OMe)$_3$, or AlMe$_3$), 16 (CH$_4^+$ from CH$_4$ or O$_2$ from O$_2$), 18 (H$_2$O$^+$ from H$_2$O), 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$_3^+$ from CH$_4$, PO(OMe)$_3$, or AlMe$_3$), 16 (CH$_4^+$ from CH$_4$ or O$_2^+$ from O$_2$), 18 (H$_2$O$^+$ from H$_2$O), 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.

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$_2$O and CO$_2$. Figure S8 in the Supporting Information shows additional formation of C$_2$H$_4$ and C$_2$H$_4$O 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$_4^+$ and CH$_3^+$ 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$_2$O$_3$. 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$_2$O$_5$ 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$_2$ 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$_2$O and CO$_2$. Figure S8 shows additional formation of C$_2$H$_4$ and C$_2$H$_4$O byproducts, similar to the combustion of the phosphorus precursor ligands. The formation of H$_2$O in the plasma could lead to additional (thermal ALD like) reaction pathways, as was the case for Al$_2$O$_3$.

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$_2$O$_5$ film by Dobbelare et al, AlP$_2$O$_5$ 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$_x$ 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 coreactant 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 (AlPO₃O₅) and can be tailored by changing the ratio between the Al₂O₃ and PO₄ cycles and/or the substrate temperature. When using 2 PO₄ 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 AlPO₄ ± 1:1 PO₄: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(OMe)₃ chemisorbs on the surface without the release of reaction products into the gas phase. Instead, the introduction of AlMe₃ results in a release of CH₄ groups in the gas phase, similar to the more commonly used ALD process 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.

In situ thickness measurement for ALD of PO₄ using various deposition temperatures and plasma exposure times, in situ thickness measurements for ALD of AlPO₄ using deposition temperatures from 25 to 300 °C, contour maps of thickness and the refractive index across 200 mm wafers of AlPO₄ films deposited at 150 °C using a 3:1 cycle ratio, HAADF-STEM and EDX mappings of a single WZ InP nanowire array with AlPO₄ film, XPS survey spectra of an AlPO₄ film with and without the use of sputtering, ex situ XPS stoichiometry results for AlPO₄ films deposited using deposition temperatures from 25 to 300 °C, XRD goni scans of ~50 nm thick AlPO₄ films, cracking patterns obtained by mass spectrometry during PO(OMe)₃ and AlMe₃ precursor dose, and time-resolved QMS data of m/z = 28, 29, 30, 31, 32, and 46 (PDF)

AUTHOR INFORMATION

Corresponding Author
N. Hornsveld – Department of Applied Physics, Eindhoven University of Technology 5600 MB Eindhoven, The Netherlands; orcid.org/0000-0002-7121-1572; Email: n.hornsveld@tue.nl

ACKNOWLEDGMENTS

This project is financially supported by ADEM, A green Deal in Energy Materials of the Ministry of Economic Affairs of The Netherlands. The authors gratefully acknowledge Cristian van Helvoirt for technical assistance and Dr. Marcel Verheijen for TEM analysis. Solliance and the Dutch province of Noord-Brabant are acknowledged for funding the TEM facility. Furthermore, Dr. Lachlan Black is acknowledged for initializing the work on PO₄ and Al₂O₃ for scientific discussions as well as for his contribution to the microscopy studies on nanowires. Moreover, the authors would like to thank the Advanced Nanomaterials & Devices group of Prof. Erik Bakkers for providing the substrates with nanowire arrays.

REFERENCES


AUTHOR INFORMATION

W. M. M. Kessels – Department of Applied Physics, Eindhoven University of Technology 5600 MB Eindhoven, The Netherlands; orcid.org/0000-0002-7630-8226

M. Creature – Department of Applied Physics, Eindhoven University of Technology 5600 MB Eindhoven, The Netherlands

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acs.jpcc.0c00301

Notes

The authors declare no competing financial interest.