**ABSTRACT:** Phosphorus oxide (POx) capped by aluminum oxide (Al2O3) has recently been discovered to provide excellent surface passivation of crystalline silicon (c-Si). In this work, insights into the passivation mechanism of POx/Al2O3 stacks are gained through a systematic study of the influence of deposition temperature (Tdep = 100–300 °C) and annealing temperature (Tann = 200–500 °C) on the material and interface properties. It is found that employing lower deposition temperatures enables an improved passivation quality after annealing. Bulk composition, density, and optical properties vary only slightly with deposition temperature, but bonding configurations are found to be sensitive to temperature and correlated with the interface defect density (Dff), which is reduced at lower deposition temperature. The fixed charge density (Qf) is in the range of + (3–9) \times 10^{12} \text{ cm}^{-2} and is not significantly altered by annealing, which indicates that the positively charged entities are generated during deposition. In contrast, Dff decreases by 3 orders of magnitude (~10^{13} to ~10^{10} \text{ eV}^{-1} \text{ cm}^{-2}) upon annealing. This excellent chemical passivation is found to be related to surface passivation provided by hydrogen, and mixing of aluminum into the POx layer, leading to the formation of AlPOx upon annealing.

**KEYWORDS:** silicon, surface passivation, phosphorus oxide, aluminum oxide, interface properties

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**INTRODUCTION**

Passivation of crystalline silicon (c-Si) surfaces is important for various (opto)electronic applications, such as photovoltaics, photonics, and nanoelectronics. Passivation layers, such as SiOx, SiNx, and Al2O3, can be used to suppress the recombination at the silicon surfaces by terminating the Si dangling bonds and thereby lowering the defect concentration, which is known as chemical passivation. Additionally, fixed charges present in the passivation layer or at the interface between the c-Si and the passivation layer can induce band bending in the silicon. This band bending can repel charge carriers and thereby reduce recombination, which is known as field-effect passivation. Excellent passivation of c-Si surfaces can be achieved by a proper combination of chemical and field-effect passivation.

In Figure 1, an overview of c-Si surface passivation schemes is shown in terms of interface defect density (Dff) and fixed charge density (Qf), which are generally used as a measure for chemical and field-effect passivation, respectively. This figure is divided into materials with negative (left) and positive fixed charge density (right) on c-Si. The various passivation schemes span a wide range of Dff and Qf values. A low Dff is always favored to obtain good chemical passivation, while a high Qf is desired to obtain good field-effect passivation. The sign of Qf has to be chosen appropriately (ideally negative for p-type Si and positive for n-type Si surfaces) to avoid an increase in minority carrier concentration at the surface, which can lead to additional recombination losses.

A general trend that appears in Figure 1 is that an increase in magnitude of Qf comes at the expense of an increase in Dff. It is possible that this trend results from defects capturing charge, causing the formation of charged entities. Such an effect has been shown for SiNx where Si dangling bonds present in the SiNx are able to capture electrons and holes, leading to charged defects. However, some materials seem to be less prone to this effect than others. Al2O3 (red squares) for example can reach a combination of low Dff and high negative Qf, which makes Al2O3 the preferred material for the passivation of p-
passivating Si surface passivation, which makes it highly suited for obtaining. We have investigated structural and passivation scheme. However, the passivation mechanism of pulsed-Al2O3 stack using nanosecond laser pulses. The passivation annealing time. It has been shown that self-aligned contact deposition annealing, as well as the e wires46 and it has been found that it can also provide excellent openings with local depositions, an O2 plasma (1 min, 15 mTorr, 200 W) was used to form a thin (~1 nm) SiO2 layer on top of the silicon. Note that other types of SiO2 interlayers, such as the SiO2 which forms during the PO deposition process itself on HF-last Si, or SiO2 resulting from a standard Radio Corporation of America (RCA) clean, have been found to result in very similar passivation quality. Since the passivation quality of the SiO2/PO/Al2O3 stacks does not depend on the type of SiO2 used or on the intentional growth of a SiO2 layer, the stacks are labeled as PO/Al2O3, as the SiO2 layer is usually not explicitly mentioned in such cases.

Postdeposition annealing (PDA) was performed using a Jipelec rapid thermal processing system for all samples, unless stated otherwise. The samples were annealed for 10 min in N2, while the annealing temperature was varied between 200 and 500 °C with 50 °C increments.

Characterization. A Sinton WCT-120TS quasi-steady-state photocurrent (QSSPC) setup was used to assess the passivation quality of the PO/Al2O3 stack. The effective minority carrier lifetime (τeff) values were measured on samples after PDA at an excess carrier density Δn = 10^{15} cm^{-3}, which were then used to calculate the effective surface recombination velocity S_{eff,max} using $S_{eff,max} = \frac{2*W}{\tau_{eff}}$, where W is the wafer thickness. It should be noted that S_{eff,max} presents the upper limit to the surface recombination velocity, because this simplified relation assumes an infinite bulk lifetime.

The layer thicknesses and refractive indices were determined by ex situ spectroscopic ellipsometry (SE) using a J. A. Woollam M-2000D UV–vis ellipsometer (1.25–6.5 eV). These measurements were performed after PDA and the optical properties of the PO/Al2O3 stacks were modeled as a single layer using a Cauchy model in the energy range 1.25–5 eV. The Cauchy model assumes zero absorption, and this assumption was verified using a generalized B-spline model, which revealed that the extinction coefficient k = 0 in the measured energy range.

The atomic composition and atomic density of the films were studied using a combination of Rutherford Backscattering Spectrometry (RBS) and Elastic Recoil Detection (ERD). These measurements were performed by Detect99. A setup using a 2 MeV He 2+ ion beam was used for both methods. ERD was performed with the detector at a recoil angle of 25°. RBS was performed in channeling mode with detectors at scattering angles of 100° and 170°. The experimental data were matched to simulations to extract the layer compositions in terms of thin film units (10^{15} atoms/cm^{3}), which can be combined with the film thickness to obtain the mass density.

The film composition as a function of depth of as-deposited and annealed PO/Al2O3 samples was analyzed using Time-of-Flight Secondary-Ion Mass Spectroscopy (ToF-SIMS). These measurements were performed by Eurofins Materials Science Netherlands BV with
an IONTOF ToF-SIMS IV instrument used in the negative mode. The instrument uses an ultrahigh vacuum and is pumped down for an extended amount of time after loading the samples to ensure the lowest amount of hydrogen background. Material was sputtered from the PO$_x$/Al$_2$O$_3$ samples using 1 keV Cs$^+$ ions, while 25 keV Bi$^+$ ions were used for analysis over an area of $50 \times 50 \mu$m$^2$. The depth scale was calibrated by assuming that the total thickness of the PO$_x$ and Al$_2$O$_3$ layers is 15 nm and that the sputtering rate is constant throughout the measurement. The former assumption was confirmed by cross-section transmission electron microscopy (TEM) measurements.

A Corona Charging System of Delft Spectral Technologies was used to conduct corona-lifetime experiments, from which $Q_1$ can be extracted. This setup applies a high voltage to a tungsten needle positioned above the sample to deposit corona charges uniformly on the PO$_x$/Al$_2$O$_3$ samples, which is done on both sides by flipping the sample over. A Kelvin probe measures the surface potential, which is used to calculate the corona charge density ($Q$) through: $Q = \frac{\varepsilon_0 \varepsilon S}{V'}$, where $Q$ is the corona charge density, $\varepsilon$ is the relative permittivity, $\varepsilon_0$ is the vacuum permittivity, $S$ is the elementary charge, $d$ is the layer thickness, and $V'$ is the surface potential. The relative permittivity of the PO$_x$/Al$_2$O$_3$ stack is determined from the effective oxide thickness obtained from CV characterization and was found to range between 6.4 and 7.4 for the different deposition temperatures. More details of the used methodology are described elsewhere.

CV characterization was used to extract $D_0$ and $Q_1$ of the PO$_x$/Al$_2$O$_3$ stacks on Si. This was done following the same methodology as described in ref 18. The Al contacts had a diameter of 890 nm, which was verified using optical microscopy. $D_0$ was derived from the quasi-static capacitance following the method of Berglund, while $Q_1$ was inferred from the flatband voltage shift.

The bonding configurations of as-deposited and annealed PO$_x$/Al$_2$O$_3$ stacks were studied using infrared spectroscopy. These measurements were conducted in transmittance mode on symmetric PO$_x$/Al$_2$O$_3$ stacks using a Bruker Vector 22 Fourier transform infrared (FTIR) spectrometer setup equipped with a mid-infrared light source (Globar: 10 000–50 cm$^{-1}$) in the spectral range of 4000–400 cm$^{-1}$. The spectra represent the absorbance difference between PO$_x$/Al$_2$O$_3$ on a c-Si substrate and an HF-dipped bare c-Si substrate.

TEM images were taken using a JEOL ARM 200F TEM operated at 200 kV. The TEM sample was prepared with a FEI Nova 200 Nanolab SDB using a focused ion-beam (FIB).

Hydrogen effusion measurements were carried out on samples with the PO$_x$/Al$_2$O$_3$ stack on both sides of c-Si substrates. The measurements followed the same procedure as described elsewhere. A heating rate of 20 °C min$^{-1}$ was used.

### RESULTS AND DISCUSSION

#### Passivation Quality

The effect of annealing temperature ($T_{\text{ann}}$) and deposition temperature ($T_{\text{dep}}$) on the passivation quality of PO$_x$/Al$_2$O$_3$ stacks was investigated by determining the maximum surface recombination velocity ($S_{\text{eff,max}}$). $S_{\text{eff,max}}$ was determined as a function of $T_{\text{dep}}$ = 100–300 °C and $T_{\text{ann}}$ = 300–500 °C, both with 50 °C increments. The results are shown in Figure 2. A clear decrease in $S_{\text{eff,max}}$ corresponding to an increase in passivation quality, is visible up to $T_{\text{ann}}$ = 400 °C for all deposition temperatures. Annealing at higher temperatures results in a decrease in passivation quality. Since $T_{\text{ann}}$ = 400 °C results in the best passivation quality for all deposition temperatures, this annealing temperature is used in all subsequent investigations, unless indicated otherwise.

The passivation quality was found to increase with lower deposition temperatures, where the highest passivation quality is reached for $T_{\text{dep}}$ = 100 °C at $T_{\text{ann}}$ = 400 °C. The surface recombination velocity varies from around 2 cm s$^{-1}$ to 6 cm s$^{-1}$ ($T_{\text{dep}}$ ≈ 8 ms to 2 ms), for $T_{\text{dep}}$ = 100 °C to $T_{\text{dep}}$ = 300 °C, respectively. The passivation quality obtained at $T_{\text{dep}}$ = 100 °C is similar to the results obtained on PO$_x$/Al$_2$O$_3$ stacks in earlier work, which were deposited at the same temperature. This passivation quality has been found to be stable in ambient conditions for at least 2 years. The decrease in passivation quality at higher deposition temperatures can mainly be attributed to an increase in the interface defect density, as will be discussed later.

#### Bulk Material Properties

In Figure 3, the refractive index, mass density, and atomic composition of PO$_x$/Al$_2$O$_3$ stacks are shown, together with reference values for Al$_2$O$_3$ passivation layers, which can be used to compare the influence of the POx in the PO$_x$/Al$_2$O$_3$ stack. It should be noted that these measurements were performed on annealed PO$_x$/Al$_2$O$_3$ stacks ($T_{\text{ann}}$ = 400 °C), for which it is found that the Al$_2$O$_3$ and PO$_x$ layers can partially mix and form AlPO$_4$, as will also be addressed later. Therefore, these stacks are treated (for simplicity) as a single (mixed) layer for the determination of the optical properties by ellipsometry and mass density determination by RBS/ERD, resulting in overall values for refractive index and mass density, respectively.

The refractive index ($\lambda = 589$ nm) of the stack (Figure 3a) varies slightly between 1.56 and 1.58. The mass density follows the same general trend as the refractive index and varies between 2.3 and 3.0 g cm$^{-3}$, but there appears to be no clear trend with deposition temperature. The refractive index and mass density of the PO$_x$/Al$_2$O$_3$ stacks are lower than that of Al$_2$O$_3$ (see Figure 3), which is likely due to the lower density of the PO$_x$ layer, lowering the overall density of the PO$_x$/Al$_2$O$_3$ stacks. The refractive index and mass density of the PO$_x$/Al$_2$O$_3$ stacks are still higher than that of AlPO$_4$, which has a refractive index of around 1.52 and a density of 2.1 g cm$^{-3}$. This is likely caused by the relatively larger part of Al$_2$O$_3$ in the PO$_x$/Al$_2$O$_3$ stacks.

Interestingly, the atomic composition of the PO$_x$/Al$_2$O$_3$ stacks (Figure 3c,d) does not seem to change significantly with deposition temperature. Even the hydrogen content is constant at around 7–8 at % for all deposition temperatures. This is in stark contrast with the hydrogen content of Al$_2$O$_3$.
films, which in the as-deposited state already show a significant decrease with increasing deposition temperature (see Figure 3c). It therefore seems likely that the PO layers in the PO/Al2O3 stack contain a significant amount of hydrogen, which could compensate the decrease of hydrogen content in the Al2O3 layers with increasing deposition temperature. Phosphorus oxides are well-known to be highly hygroscopic, which could partly explain such a high hydrogen content. In Figure 3d, it can be seen that the phosphorus content stays constant at around ∼5 at. %, with a slight decrease at 300 °C, which relates to a slight decrease in thickness of the POx layer. Aluminum and oxygen make up most of the stack and stay constant with deposition temperature at ∼28 at. % and ∼60 at. %, respectively.

The bulk material properties of PO/Al2O3 stacks show no obvious trend over the investigated deposition temperature range. It seems that the addition of a POx layer between the c-Si substrate and the Al2O3 layer results in a stack with fairly constant bulk material properties over a wide range of deposition temperatures. This indicates that the PO/Al2O3 stacks have a relatively broad processing window with respect to their material properties, however, it will be shown later that the deposition temperature is important for the bonding configurations of the PO/Al2O3 stack.

**Interface Properties.** The interface properties have been quantified in terms of $D_S$ and $Q_S$. For this purpose, CV characterization and corona-lifetime experiments were carried out. From the corona charging-lifetime experiments, $Q_S$ can be determined, while from the CV characterization, both $Q_S$ and $D_S$ can be determined.

In Figure 4, the results of the corona-lifetime experiments for PO/Al2O3 stacks with deposition temperatures from 100

![Figure 4](image-url)
In Figure 5, the values for $D_a$ and $Q_f$ obtained by CV characterization are shown, where the findings from the corona-lifetime experiments are also plotted. $S_{\text{eff,max peak}}$ is plotted next to $D_a$ since both give a measure of the chemical passivation quality. The capacitance—voltage and conductance—voltage curves can be found in the Supporting Information (SI) Figure S1. Besides the annealed stacks at varying $T_{\text{dep}}$, also data for an as-deposited stack prepared at $T_{\text{dep}} = 100 \, ^\circ\text{C}$ is given.

From Figure 5a, it can be seen that for the various deposition temperatures, the $Q_f$ derived from the CV characterization follows a similar trend to $Q_f$ inferred from the corona-lifetime experiments. In all cases, $Q_f$ is positive and relatively high with values around $+(4−9) \times 10^{12}$ cm$^{-2}$. From Figure 5b, it can be seen that $D_a$ increases significantly up to a deposition temperature of $200 \, ^\circ\text{C}$. More specifically, $D_a$ increases from $5 \times 10^{10}$ to $1 \times 10^{12}$ EV$^{-1}$ cm$^{-2}$, indicating that there is a decrease in chemical passivation quality, which is in line with the trend in $S_{\text{eff,max peak}}$ from corona-lifetime experiments. Note that the stacks deposited at 200 and 250 °C exhibited too high leakage currents to enable a determination of $D_a$ from the quasi-static capacitance. $D_a$ for these stacks was therefore estimated from the peak magnitude of the series-resistance-corrected parallel conductance $G_p^{SS}$ measured as a function of voltage, which occurs near flatband conditions at 1 MHz. This value was calibrated against the midgap $D_a$ obtained from the quasi-static capacitance at temperatures where this was possible. It was found that this quantity was closely proportional to the midgap $D_a$ obtained by quasi-static capacitance at temperatures where both could be determined.

This method therefore seems to be a reliable indicator of the midgap $D_a$ at 200 and 250 °C. The findings from both the corona-lifetime experiments and the CV characterization show that the trend of the passivation quality with deposition temperature observed in Figure 2 can be explained by changes in interface properties, mainly due to an increase in $D_a$ with increasing $T_{\text{dep}}$.

The effect of annealing on the interface properties of the $\text{PO}_x/\text{Al}_2\text{O}_3$ stacks can be understood by comparing the data of as-deposited and annealed stacks at $T_{\text{dep}} = 100 \, ^\circ\text{C}$. In the as-deposited state, the $\text{PO}_x/\text{Al}_2\text{O}_3$ stack already has a very high positive $Q_f$ around $+4 \times 10^{12}$ cm$^{-2}$, which does not change significantly upon annealing, as can be seen from Figure 5a. The value of $D_a$, however, decreases by almost 3 orders of magnitude ($\sim 10^{13}$ to $\sim 10^{10}$ EV$^{-1}$ cm$^{-2}$) upon annealing, as can be seen from Figure 5b. This significant decrease in defect density is in line with observed changes in passivation quality between as-deposited and annealed $\text{PO}_x/\text{Al}_2\text{O}_3$ stacks, for which the $S_{\text{eff,max}}$ values are $\sim 1400$ cm s$^{-1}$ and $\sim 2$ cm s$^{-1}$, respectively. Note that because of the poor initial passivation quality, the as-deposited stacks cannot be characterized using the corona-lifetime method. Clearly, annealing results in a decrease in $D_a$ while the positively charged entities responsible for the $Q_f$ are generated during the deposition process and are not significantly affected by annealing.

Figure 6 shows a cross-sectional bright-field TEM image of a $\text{PO}_x/\text{Al}_2\text{O}_3$ stack deposited at 100 °C and annealed at 400 °C.

Only an annealed stack is shown, since the as-deposited stack did not remain stable under illumination of the electron beam of the TEM. In the image, the individual layers show a distinctly different contrast. The c-Si substrate is followed by a 9.6 nm brighter layer and a 9.6 nm darker layer on top, corresponding to the $\text{PO}_x$ and $\text{Al}_2\text{O}_3$ layers, respectively. Note that the layers are labeled as “$\text{PO}_x$” and “$\text{Al}_2\text{O}_3$” even though the individual layers are not perfectly flat.
though these may be partially mixed layers, as will be shown later. The presence of a SiOₓ layer is not distinguishable from the POₓ layer, however, it is expected to be present. The thicknesses determined via the TEM analysis correspond well to those found from in situ ellipsometry, which were about 1.2 nm SiOₓ, 4.4 nm POₓ, and 10 nm Al₂O₃ for this sample in the as-deposited state.

Composition and Bonding Configurations. To investigate in more detail how annealing leads to a significant improvement in chemical passivation as compared to the as-deposited stacks, infrared spectroscopy and ToF-SIMS were employed on as-deposited and annealed POₓ/Al₂O₃ stacks, to investigate changes in bonding configurations and structural composition.

In Figure 7, infrared spectra of POₓ/Al₂O₃ stacks deposited at 100 °C, 200 °C, and 300 °C on 280 Ωm-thick double-side polished 1−5 Ω cm n-type float zone (FZ) Si (100) wafers. The stacks were measured in the as-deposited state and after subsequent annealing (10 min in N₂) starting at 200 °C with 50 °C increments up to 500 °C, as indicated by the color bar.

Figure 7. Infrared spectra revealing oxygen-related bonding configurations of POₓ/Al₂O₃ stacks deposited at (a) 100 °C, (b) 200 °C, and (c) 300 °C on 280 Ωm-thick double-side polished 1−5 Ω cm n-type float zone (FZ) Si (100) wafers. The stacks were measured in the as-deposited state and after subsequent annealing (10 min in N₂) starting at 200 °C with 50 °C increments up to 500 °C, as indicated by the color bar.

Upon annealing, significant structural changes can be observed, which occur gradually and seem to reach completion at Tann = 300 °C. With increasing annealing temperature, there is a reduction in the 950 and 1250 cm⁻¹ contributions and a prominent peak at 1100 cm⁻¹ appears. The peak at 1100 cm⁻¹ can be attributed to the stretching of P−O bonds present in [PO₄]³⁻ tetrahedra. These PO₄ tetrahedra can cross-link with AlO₄ tetrahedra to form AlPO₄ structural clusters. The infrared spectra of the annealed (Tann ≥ 300 °C) POₓ/Al₂O₃ stack are similar to that of AlPO₄ films, which also show a prominent absorption peak at 1100 cm⁻¹ and a rising absorption at 700−900 cm⁻¹. It therefore seems likely that annealing the POₓ/Al₂O₃ stack leads to the formation of AlPO₄, where likely AlPO₄ is formed upon annealing.

Figure 8. ToF-SIMS measurements of POₓ/Al₂O₃ stacks deposited at 100 °C, in the as-deposited state and annealed at 400 °C. The intensity of the negative ions originating from the sample is plotted as a function of depth. The depth is calculated by assuming a constant sputter rate throughout all layers and a total stack thickness of 15 nm. The vertical dashed lines indicate the different layers in the stack, which consist of around 10 nm Al₂O₃, 5 nm POₓ, 1 nm SiOₓ, and finally the Si substrate. A set of ions is shown in each panel: (a) hydrogen- and oxygen-related, (b) aluminum-related, (c) phosphorus-related, and (d) silicon-related ions. The intensities are normalized to the Si bulk signal (set to 1000).
In the infrared spectra of POₓ/Al₂O₃ stacks prepared at higher temperatures (Figure 7b and 7c), there appear to be some differences as compared to the T₀= 100 °C POₓ/Al₂O₃ stacks. In the as-deposited state, there is a slightly lower contribution at 1250 cm⁻¹ for T₀= 200 °C, while for T₀= 300 °C no more clearly distinct peaks at 1250 and 950 cm⁻¹ are visible. These differences indicate that there are already structural differences in POₓ layer in the as-deposited state due to the higher deposition temperature, although part of the difference at T₀= 300 °C may also be explained by the thinner POₓ layer. Upon annealing, the formation of a peak at 1100 cm⁻¹, indicating the likely formation of AlPOₓ, is still observed in both cases, however the intensity of this peak decreases with increasing deposition temperature. The structural changes with subsequently higher annealing temperature also appear to be more gradual and require higher annealing temperatures to be completed. For T₀= 200 °C, the formation of POₓ tetrahedra is paired with a reduction in contributions at 950 and 1250 cm⁻¹ similarly as for T₀= 100 °C. But for both T₀= 200 °C and T₀= 300 °C, there also appears to be a gradual shift in the peak from 1050 to 1100 cm⁻¹ with annealing, while for T₀= 100 °C no gradual shift is observed. At 1050 cm⁻¹ there is a contribution of Si=O−Si bonds present, however the SiOₓ interlayer is not expected to change significantly upon annealing. Therefore, the shift of 1050 cm⁻¹ to 1100 cm⁻¹ upon annealing is likely related to changes in the POₓ layer due to formation of the POₓ tetrahedra, possibly due to changes in P=O(H) bonds and P−O stretch modes of P₂O₁₀⁻.

For all deposition temperatures, there appears to be the formation of an AlPOₓ layer upon annealing, evidenced by the peak at 1100 cm⁻¹, which is paired with a reduction in contributions at 950 and 1250 cm⁻¹, indicating the likely formation of AlPOₓ, as determined from the CV measurements. It is possible that the formation of an AlPOₓ layer, which has analogous properties to SiOₓ, can aid in the chemical passivation quality provided by the POₓ/Al₂O₃ stacks. The formation of less AlPOₓ at higher deposition temperatures is correlated to a higher Dₓ as determined from the CV measurements. However, at Tₓ≥ 300 °C there are no additional structural changes observed in the infrared spectra for POₓ/Al₂O₃ stacks deposited at T₀= 100 °C (Figure 7a), while quite significant changes in passivation quality could be observed in the annealing range Tₓ= 300−500 °C (see Figure 2). It is therefore unlikely that the excellent chemical passivation quality of the POₓ/Al₂O₃ stack is solely related to the formation of AlPOₓ. It will be shown below that hydrogen likely also plays an important role in the chemical passivation provided by the POₓ/Al₂O₃ stack.

In Figure 8, SIMS depth profiles for POₓ/Al₂O₃ stacks deposited at 100 °C are shown for an as-deposited and annealed (Tₓ= 400 °C) stack. Various ions detected by the ToF-SIMS are plotted. It should be noted that in SIMS measurements, the ions are generated during the measuring process and do not provide information on the bonding configurations within the stack.

In Figure 8a, the signals of H⁻, ₁⁸O⁺, and OH⁻ ions are shown. In the as-deposited state, hydrogen is seen to be present throughout both the Al₂O₃ and the POₓ layers, with a peak in intensity at the SiOₓ/Si interface. Upon annealing, the overall intensity slightly decreases, which could be associated with effusion of hydrogen. However, the overall distribution remains the same, which indicates that hydrogen does not significantly redistribute throughout the layer stack upon annealing. For oxygen, there seems to be no significant change to distribution or intensity upon annealing. In Figure 8b,c, the signals of aluminum-related (AlO₂⁻) and phosphorus-related (POₓ⁻) ions are shown, respectively. In the as-deposited state, phosphorus is present only in the POₓ layer, while aluminum is present in both the Al₂O₃ layer and the POₓ layer. Aluminum therefore appears to be mixed into the POₓ layer already in the as-deposited state. Upon annealing, slight changes to AlO₂⁻ and POₓ⁻ ions are visible. The AlO₂⁻ intensities decrease within the Al₂O₃ layer and there is some change in distribution of POₓ⁻ in the POₓ layer. The POₓ⁻ intensity in the POₓ layer increases and the POₓ⁻ peaks broaden slightly. These observed changes upon annealing are likely related to structural changes in the POₓ/Al₂O₃ stack upon annealing, evidenced by the infrared spectra. Note that these structural changes upon annealing might give rise to a change in SIMS matrix effects, which may also partly affect the observed intensities. In Figure 8d, the signals of silicon-related ions are shown. An interlayer of silicon oxide is present between the Si bulk and POₓ layer. Note that the apparent penetration of the signals into the Si bulk is attributed to the limited depth resolution of the SIMS caused mainly by local variations in film thickness or sputter rate over the measured area.

Strikingly, aluminum appears to be mixed into the POₓ layer already in the as-deposited state. This mixing seems to be aluminum mixing into the POₓ layer, but not vice versa, which can explain why still two distinct layers are visible in the TEM image. The presence of Al in the POₓ layer was also found for as-deposited POₓ/Al₂O₃ stacks deposited at 200 and 300 °C (see SI Figure S2). The presence of Al in the POₓ layer is quite surprising at such low deposition temperatures, as it must involve a rather fast diffusion of Al through the POₓ layer. To explain this fast diffusion of Al, four possible mechanisms are considered. We note that more investigation is needed to find out which mechanisms play the most important role in this mixing. The first mechanism is based on the assumption that the POₓ layer is highly porous. During the initial cycles of the Al₂O₃ deposition, TMA may infiltrate the porous POₓ layer and react with it to form Al₂O₃ inside the pores of the POₓ. The second and third mechanisms take into account that phosphorus oxides and phosphoric acids (phosphorus oxides containing hydrogen) have a wide range of glass transition temperatures and melting points, many of which can be even lower than 100 °C, i.e., the deposition temperature. The glass transition temperature relates to the energy required for breaking and formation of covalent bonds in the amorphous POₓ network. Therefore, if the deposition temperature is above the glass transition temperature of the POₓ, this implies that sufficient thermal energy is available to allow substantial bond breakage within the POₓ layer, which might allow for diffusion of Al through it. Similarly, if the deposition temperature is above the melting temperature of the POₓ layer, then it would enter a liquid state which would permit fast diffusion of Al into it. Mixing of Al into the POₓ layer is expected to increase its melting point, which would result in resolidification. The fourth mechanism is based on an interface reaction between POₓ and Al₂O₃, which may lead to AlPOₓ with a highly porous zeolite structure that could allow fast surface diffusion of Al into the POₓ layer. We note however that according to the infrared spectra, AlPOₓ is not yet formed in the as-deposited...
state, rather, an annealing step appears to be required for the formation of AlPO₄, since annealing gives rise to the characteristic peak at 1100 cm⁻¹.

A peak in the hydrogen signal is seen to be present at the SiO₂/Si interface in the as-deposited state (Figure 8a). Importantly, after annealing, the hydrogen signal at the c-Si/ SiO₂ interface remains high. At this interface, reactions with hydrogen can lead to the passivation of silicon dangling bonds. However, since the passivation quality of as-deposited PO/Al₂O₃ is very low, this hydrogen is likely not effectively used for passivation of Si dangling bonds in the as-deposited state. Upon annealing, the hydrogen may become activated and aid in the passivation of this interface. Passivation provided by hydrogen can also explain why there is a significant difference in passivation quality in the annealing range from 300–500 °C, while the infrared spectra showed no additional structural changes (for Tₐₐₙ = 100 °C) in this annealing range. It is therefore likely that hydrogen passivation also plays an important role in the excellent (chemical) passivation quality provided by the PO/Al₂O₃ stacks.

**Hydrogen Effusion.** Hydrogen effusion measurements were performed to gain additional insight into the behavior of hydrogen upon annealing. The results are shown in Figure 9, where the hydrogen effusion rate dN/dt is plotted as a function of temperature for PO/Al₂O₃ stacks deposited at different temperatures. In Figure 9, it can be seen that hydrogen starts to effuse from the stacks at around 200 °C. An effusion maximum occurs near 360 °C for the stack deposited at 100 °C. This maximum shifts to around 450 °C for the stacks deposited at 200 °C and 300 °C. The total amount of effused hydrogen (when annealed up to about 1000 °C) for each deposition temperature is roughly constant at about 20 at. %.

In previous work on hydrogen content and hydrogen effusion from Al₂O₃ layers, it was shown that for Tₐₐₙ ≥ 100 °C, the hydrogen effusion maxima occurred at Tₐₐₙ > 500 °C. The PO/Al₂O₃ stacks show hydrogen effusion maxima at lower annealing temperatures, which indicates that hydrogen effuses more easily from the PO/Al₂O₃ stack than it does from an Al₂O₃ film. Interestingly, the temperatures at which the effusion maxima occur, seem to be correlated with the temperature where the structural transition of PO₄ and Al₂O₃ is complete as concluded from the infrared spectra. For Tₐₐₙ = 100 °C, the structural transition is completed at around Tₐₐₙ ≈ 300 °C and the hydrogen effusion maximum is located at around Tₐₐₙ = 360 °C. For both Tₐₐₙ = 200 and 300 °C, the structural transition is completed at Tₐₐₙ ≈ 450 °C and the effusion maxima are present at around Tₐₐₙ = 450 °C. For Tₐₐₙ = 200 and 300 °C, both the temperature where the structural transition is complete and the temperature at which the hydrogen effusion maxima occur are shifted to higher temperatures as compared to Tₐₐₙ = 100 °C. Therefore, it is likely that the occurrence of the hydrogen effusion maxima is related to the formation of AlPO₄, which may lead to the release and effusion of hydrogen.

It is expected that the hydrogen effusion rate from the layers is proportional to the amount of hydrogen that is mobile in the layers (at a given temperature) and therefore likely also proportional to the amount of hydrogen that can reach the SiO₂/Si interface and lead to passivation of Si dangling bonds. From Figure 9, it can be seen that the hydrogen effusion rate at Tₐₐₙ = 400 °C decreases with increasing deposition temperature. This is correlated to the passivation quality observed for annealing at 400 °C for the various deposition temperatures (see Figure 2), which also decreases with increasing deposition temperature. This decrease in passivation quality can likely be related to a reduced amount of hydrogen reaching the SiO₂/Si interface, leading to reduced (chemical) passivation. It also seems likely that the decrease in passivation quality at Tₐₐₙ > 400 °C (see Figure 2) can be explained by hydrogen leaving the SiO₂/Si interface and effusing from the PO/Al₂O₃ stacks. These results underline that hydrogen likely plays an important role in the passivation quality provided by the PO/Al₂O₃ stacks.

## CONCLUSIONS

In conclusion, we have studied the effects of deposition temperature and annealing on the passivation provided by PO/Al₂O₃ stacks, to gain a better understanding of the passivation mechanism of PO/Al₂O₃ stacks on c-Si surfaces. It is shown that deposition temperature mainly impacts the structural properties and interface defect density after annealing, while other material properties remain fairly constant over the investigated temperature range. The lowest defect density is obtained at Tₐₐₙ = 100 °C and Tₐₐₙ = 400 °C. Annealing the PO/Al₂O₃ stacks is essential to obtain excellent passivation quality and leads to a significant improvement in chemical passivation, due to the defect density dropping by almost 3 orders of magnitude (∼10¹³ to ∼10¹⁰ eV⁻¹ cm⁻²). This decrease in defect density is found to be likely related to the passivation of Si dangling bonds provided by hydrogen from the PO₄/Al₂O₃ stack and mixing of aluminum into the PO₄ layer, which leads to the formation of AlPO₄ upon annealing. The entities responsible for the high positive fixed charge (∼10¹² cm⁻²) are generated during the deposition process and are not significantly affected by annealing. Taken together, these findings strongly suggest that the chemical passivation mechanism of the PO₄/Al₂O₃ stack consists of a combination of the structural transition toward AlPO₄ and hydrogen passivation, which can be tuned with deposition
temperature and annealing. The positively charged entities responsible for the field-effect passivation appear to be more inherent to the PO/Al2O3 stack on c-Si itself and were not affected significantly by deposition temperature and annealing. The improved understanding of the passivation mechanism by PO/Al2O3 stacks is expected to contribute to the adoption of this passivation scheme in silicon devices.

**ASSOCIATED CONTENT**

1. Supporting Information
   
   The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaelm.1c00516.
   
   Capacitance–voltage and conductance–voltage data of as-deposited and annealed PO/Al2O3 stacks and ToF-SIMS depth profiles of as-deposited PO/Al2O3 stacks (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

Roel J. Theeuwes — Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands; orcid.org/0000-0002-9843-9796; Email: r.j.theeuwes@tue.nl

Wilhelms M. M. Kessels — Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands; orcid.org/0000-0002-7630-8226; Email: w.m.m.kessels@tue.nl

**Authors**

Jimmy Melskens — Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands; Present Address: TNO Energy Transition, Solar Energy, Westerduinweg 3, 1755 ZG Petten, The Netherlands; orcid.org/0000-0001-6877-7340

Lachlan E. Black — School of Engineering, The Australian National University, Canberra, Australian Capital Territory 2600, Australia; orcid.org/0000-0002-9807-8433

Wolfgang Beyer — IEKS-Photovoltaik, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

Dibyashree Koushik — Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands; orcid.org/0000-0002-7609-3544

Wilhelmus J. H. Berghuis — Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands; orcid.org/0000-0002-8261-4318

Bart Macco — Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands; orcid.org/0000-0003-1197-441X

**Complete contact information is available at:**

https://pubs.acs.org/10.1021/acsaelm.1c00516

**Author Contributions**

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