Excellent Passivation of n-Type Silicon Surfaces Enabled by Pulsed-Flow Plasma-Enhanced Chemical Vapor Deposition of Phosphorus Oxide Capped by Aluminum Oxide

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Phosphorus oxide (POx) capped by aluminum oxide (Al2O3), prepared by atomic layer deposition (ALD), has recently been introduced as a surface passivation scheme for planar n-type FZ silicon. In this work, a fast pulsed-flow plasma-enhanced chemical vapor deposition (PECVD) process for the POx layer is introduced, making it possible to increase the POx deposition rate significantly while maintaining the POx/Al2O3 passivation quality. An excellent surface passivation is realized on n-type planar FZ and Cz substrates (J0 = 3.0 fA cm−2). Furthermore, it is demonstrated that the POx/Al2O3 stack can passivate textured surfaces and that the application of an additional PECVD SiNx capping layer renders the stack stable to a firing treatment that is typically used in fire-through contact formation (J0 = 12 fA cm−2). The excellent surface passivation is enabled by a high positive fixed charge density (Qfi ≈ 4 × 1012 cm−2) and an ultralow interface defect density (Dn ≈ 5 × 1010 eV−1 cm−2). Finally, outstanding passivation is demonstrated on textured silicon with a heavy n+ surface doping, as is used in solar cells, on par with annealed SiO2. These findings indicate that POx/Al2O3 is a highly suited passivation scheme for n-type silicon surfaces in typical industrial solar cells.

To realize high-efficiency crystalline silicon (c-Si) solar cells it is essential to have excellent surface passivation, which is ideally achieved by combining a high degree of chemical passivation to reduce the interface defect density with field-effect passivation to strongly reduce the minority carrier concentration near the silicon surface.[1–3] While new passivating materials continue to be identified,[4] only few are known to provide good chemical passivation in combination with a high fixed charge density. A prominent example is the negative fixed charge that aluminum oxide (Al2O3) induces near the Si surface, which makes Al2O3 ideal for the passivation of p-type Si surfaces.[5–7] Similarly, the surface passivation and positive charge that is associated with silicon nitride (SiNx) has made SiNx the standard material for passivating n-type Si surfaces,[8] although the SiNx films that provide the highest degree of chemical passivation typically only exhibit a mildly positive fixed charge density.[9–12]

In this context, it is interesting to consider phosphorus oxide (POx) capped by Al2O3, which was first reported as a high-quality passivation stack on indium phosphide (InP) nanowires.[13] This layer stack can also provide excellent surface passivation on c-Si, which is attributed to a low interface defect density (inferred from lifetime and high-frequency parallel conductance data) in combination with a high positive fixed charge near the c-Si surface.[14,15] In addition, there are also opportunities to achieve local contact formation by doping from the POx/Al2O3 layer stack.[16] The excellent surface passivation provided by POx/Al2O3 has so far been
The precursors are predominantly gases, such as C14 (Al2O3) and SiH4 (SiN), which are typically injected into the process chamber at a constant flow rate. The precursors are dosed in a pulsed-plasma Enhanced Chemical Vapor Deposition (PCVD) reactor, where the plasma is turned on at a specific time to facilitate precursor dissociation. The plasma is then turned off, allowing the precursors to react on the substrate surface. This process is repeated until the desired layer thickness is achieved.

In this study, we focus on the integration of POx/Al2O3 stack structures in industrial solar cell processing. The POx passivation layer is known to be hygroscopic, requiring a capping layer for stability. Potential changes to this POx passivation process are not strictly self-limiting, indicating the need for further investigation.

First, the passivation quality of the POx/Al2O3 layers fabricated using a pulsed-flow PCVD process has been assessed using quasi-steady-state capacitance-voltage (C–V) analysis and corona charging experiments. In Figure 2a, both these processes yield an excellent passivation quality, with an extremely low recombination parameter of J0 = 3.0 fA cm⁻² per side for the PCVD process after postdeposition annealing in N2 (400 °C for 10 min). This confirms that the strongly reduced deposition time for the PCVD POx layer does not come at the expense of a deterioration in passivation quality for the POx/Al2O3 stack with respect to the previously used ALD-like process.

Second, the passivation quality of POx/Al2O3 capped by SiNx (75 nm) has been evaluated on planar and textured Cz substrates after a postdeposition firing treatment. The firing process is critical to achieve the surface passivation because there is no significant surface passivation in the as-deposited state. In a pulsed-flow PCVD process, the precursor dosage time is significantly reduced in comparison to the ALD-like process for the POx layer (note that the percentage of precursor consumed in both cases is not known).

Regarding thickness uniformity we note that this is superior for the ALD-like process in comparison to the PECVD process (8% vs 23% thickness variation over an 8 in. round area). The relatively low uniformity is believed to be mainly due to the use of a reactor which is not optimized for uniform precursor flow. This can, however, be circumvented when transferring this process to PECVD reactors which are designed with uniform precursor injection in mind. Furthermore, PECVD processes are attractive because they are common in industrial solar cell processing, for instance, for the fabrication of SiN layers. For Al2O3, a high passivation quality has already been reported for layers fabricated using a pulsed-flow PCVD process developed in an ALD reactor, while PECVD Al2O3 (combined with an integrated capping layer) is widely used as a rear side passivation technology in industrial solar cell processing.

To assess the POx/Al2O3 passivation quality when using pulsed-flow PCVD as a fabrication method for the POx layer, we consider planar n-FZ as well as planar and textured n-Cz substrates. Furthermore, we assess the firing stability and compatibility with a SiN capping layer, which are critical aspects for integration of POx/Al2O3 in industrial solar cells. Finally, we consider textured n-Cz substrates with n-type surfaces. We thereby significantly extend the range of substrates and surfaces on which POx/Al2O3 passivation has been demonstrated compared with previous studies which only examined the passivation quality on planar FZ substrates.

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passivation can be reached on both planar ($J_0 = 7.2 \text{ fA cm}^{-2}$) and textured ($J_0 = 12 \text{ fA cm}^{-2}$) Cz substrates. We also report the corresponding implied open-circuit voltage ($iV_{oc}$) values here, as this parameter includes the wafer bulk quality and any light in-coupling effects that play a role in solar cells in addition to the surface passivation quality. The high passivation quality after SiN$_x$ capping and subsequent firing is thought to be due to the SiN$_x$ layer that can act both as a hydrogenation source and a hydrogen effusion barrier. This hypothesis is supported by the fact that the passivation quality of PO$_x$/Al$_2$O$_3$ stacks without SiN$_x$ capping layer does not improve but rather degrades after firing ($J_0$ can increase by $\approx 20 \text{ fA cm}^{-2}$). Such loss of passivation upon annealing or firing is often attributed to effusion of hydrogen from the film and interface and comparable cases have been reported for Al$_2$O$_3$[3] as well as poly-Si[21] and ZnO[22] with and without capping layer. In addition, when depositing the SiN$_x$ layer, an increase in $J_0$ of $\approx 20\text{--}40 \text{ fA cm}^{-2}$ can be observed, which can be largely repaired by the firing treatment, thus explaining the difference in $J_0$ for the planar samples without and with SiN$_x$ capping layer and firing treatment, as shown in Figure 2a,b, respectively. Interestingly, in case of the textured substrates, we observe a 22 mV improvement in $iV_{oc}$ for the fired, symmetric PO$_x$/Al$_2$O$_3$/SiN$_x$ stack compared with a fired, symmetric and optimized, industry-ready SiN$_x$ reference that was processed in the same batch.

To understand why the passivation quality of annealed stacks consisting of PECVD PO$_x$ and Al$_2$O$_3$ can reach such high levels, quasi-static C–V characterization and a combination of corona charging and lifetime measurements, i.e., corona-lifetime experiments, are used to assess both the chemical passivation in terms of the interface defect density ($D_{it}$) and the field-effect passivation in terms of the fixed charge density ($Q_f$). Note that the quasi-static measurement mode in the C–V analysis enables a more accurate determination of the $D_{it}$ value in comparison to the previously used high-frequency mode.[14] The results of the combined C–V and corona charging analysis are shown in Figure 3. Multiple C–V measurements on the same PO$_x$/Al$_2$O$_3$ sample have been conducted for statistical accuracy, which provides extra support for the conclusion that the excellent passivation quality enabled by the stack is due to an exceptionally low $D_{it}$ ($4.5 \pm 0.2 \times 10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$) combined with a high positive $Q_f$ ($3.7 \pm 0.3 \times 10^{12} \text{ cm}^{-2}$). When comparing these results with $D_{it}$ and $Q_f$ values from the literature for a broad selection of different types of passivating Al$_2$O$_3$ [23,24] ($D_{it} \approx (4\text{--}70) \times 10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$; $Q_f \approx -(1\text{--}10) \times 10^{12} \text{ cm}^{-2}$) and SiN$_x$[19–12] ($D_{it} \approx (6\text{--}500) \times 10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$; $Q_f \approx +(0.2\text{--}10) \times 10^{12} \text{ cm}^{-2}$), it is clear that PO$_x$/Al$_2$O$_3$ indeed enables a state-of-the-art passivation quality that appears highly suitable for n-type Si surfaces. Further confirmation of the existence of a high positive fixed charge that is induced by the annealed PO$_x$/Al$_2$O$_3$ stack is provided by the corona charging experiments which indicate that $Q_f = 4.5 \pm 0.2 \times 10^{12} \text{ cm}^{-2}$, which approximately corresponds to the $Q_f$ value determined via C–V measurements. Here, it is noted that single-sided
samples were used for the C–V characterization, while symmetrical samples were used for the corona charging experiments, which can introduce small sample-to-sample variations in the $Q_f$ comparison. The combination of a very low $D_{it}$ and a high positive $Q_f$ is particularly striking. SiNx, which is typically used to passivate n-type Si surfaces, can also yield a low $D_{it}$, although this is accompanied by a rather low positive $Q_f$ ($\approx 1 \times 10^{12}$ cm$^{-2}$). On the contrary, higher positive $Q_f$ values are only attainable for SiNx at the expense of a strongly increased $D_{it}$.[9–12,25,26] Electrostatic charges can yield an improved passivation quality up to charge densities of $\approx 5 \times 10^{12}$ cm$^{-2}$ beyond which the passivation quality saturates,[27] indicating that PO$_x$/Al$_2$O$_3$ exhibits a nearly ideal $Q_f$. The undesirable trade-off between low $D_{it}$ and high $Q_f$ that exists for SiNx appears to be more lenient for PO$_x$/Al$_2$O$_3$, which adds to the promise of the latter as a passivation scheme for n-type Si surfaces. The reason why a combination of low $D_{it}$ and high $Q_f$ can be achieved with PO$_x$/Al$_2$O$_3$ is not fully understood yet. It is, however, likely that a hydrogenation of the Si surface by the stack is responsible for the low $D_{it}$.

More specifically, for the PO$_x$/Al$_2$O$_3$ stack it is plausible that there is a significant presence of $\text{–OH}$ groups and that the hydrogen that is bonded in this way can contribute to the surface passivation. This would be similar to Al$_2$O$_3$ for which it is well established that some of the hydrogen in $\text{–CH}_3$ groups in the trimethylaluminium (TMA) precursor ends up as $\text{–OH}$ groups in the film and this H can provide interface passivation.[23]

This hydrogenation can be especially effective when the PO$_x$/Al$_2$O$_3$ stack is capped by a hydrogen-rich layer like SiNx. The latter can act not only as a hydrogenation source, but also as a hydrogen effusion barrier for the underlying PO$_x$/Al$_2$O$_3$ stack. On a microscopic level, the high $Q_f$ could be related to the presence of the diamagnetic $[O\text{–H}_2\text{P}]^+$ defect center in PO$_x$ as a possible origin for the positive fixed charge density, as suggested previously.[14]

To investigate the potential of PO$_x$/Al$_2$O$_3$ as a passivation scheme further, we finally explore its passivation quality on n-type Si substrates with an n$^+$ diffused surface. These kinds of surfaces benefit from a high positive $Q_f$ (together with a low $D_{it}$) and they occur in practical solar cells, e.g., the n$^+$ layer on the front side of a passivated emitter rear contact (PERC) solar cell. Given this context, we investigate the passivation quality on textured n-type Cz substrates with two different n-type surface diffusions: a relatively light surface diffusion ($R_{sheet} = 260 \pm 7 \text{ }\Omega \text{ cm}^{-1}$) and a heavier surface diffusion ($R_{sheet} = 137 \pm 7 \text{ }\Omega \text{ cm}^{-1}$). The symmetric PO$_x$/Al$_2$O$_3$ samples on n$^+$ Si are annealed in N$_2$ at 400 °C to assess the passivation quality. The results for both the 137 and 260 $\Omega \text{ cm}^{-1}$ substrates are shown in Figure 4a and clearly indicate excellent $J_0$ values for passivated diffused n$^+$ surfaces, with values of 30 and 12 fA cm$^{-2}$ per side, respectively, after annealing.

To put these results into perspective, it is worthwhile to compare the PO$_x$/Al$_2$O$_3$ passivation on n$^+$ Si with a variety of state-of-the-art passivation schemes based on SiNx or SiO$_2$ reported in the literature[28–32] which were also fabricated on textured n-Cz substrates with different levels of n$^+$ surface doping resulting in different $R_{sheet}$ values. This comparison is shown in Figure 4b and illustrates that the passivation quality of PO$_x$/Al$_2$O$_3$ surpasses the passivation quality of SiNx on textured n$^+$ Si surfaces and is on par with state-of-the-art alaneated SiO$_2$ as well as ONO (SiO$_2$/SiNx/SiO$_2$) stacks. This latter result is especially excellent and illustrates the promise of PO$_x$/Al$_2$O$_3$ as a candidate passivation scheme for n$^+$ Si surfaces. These combined findings underline that PO$_x$/Al$_2$O$_3$ is not only promising in the context of planar, lowly doped n-type regions, but also for the passivation of textured n$^+$ diffused Si surfaces. Hereby we remark that the passivation quality of a PO$_x$/Al$_2$O$_3$/SiNx stack on textured n$^+$ diffused Si surfaces as well as the compatibility with metallization schemes still need to be evaluated before the promise of PO$_x$/Al$_2$O$_3$ as demonstrated in this work can prove to bring a benefit as a passivation scheme to, for instance, p-type PERC solar cells.

In conclusion, a fast, pulsed-flow PECVD process has been introduced to deposit PO$_x$, and it is shown that a high passivation quality on various n-type Si substrates can be achieved when capping this PO$_x$ layer by Al$_2$O$_3$. More specifically, excellent surface passivation is demonstrated on planar FZ substrates.
(\(J_0 = 3.0 \text{ fA cm}^{-2}\)). High-quality surface passivation on planar and textured Cz substrates is also demonstrated for PO\(_x\)/Al\(_2\)O\(_3\) stacks capped with PECVD SiN\(_x\) after a firing treatment that is typical for screen-printed metallization of silicon solar cells. The excellent level of surface passivation is enabled by a combination of chemical and field-effect passivation, as illustrated by C–V analysis and corona charging experiments (\(D_d \approx 5 \times 10^{10} \text{ eV}^{-1} \text{ cm}^{-2}\) and \(Q_f \approx 4 \times 10^{12} \text{ cm}^{-2}\)). Finally, an excellent surface passivation quality is demonstrated on n\(^+\) textured Si surfaces, on par with state-of-the-art alaneled SiO\(_2\) and ONO stacks. Together these findings underline the promise of PO\(_x\)/Al\(_2\)O\(_3\) as a passivation scheme for n\(^+\) type Si surfaces, with a particular appeal for the passivation of n\(^+\) diffused regions in industrial solar cells.

**Experimental Section**

Sample Preparation: PO\(_x\) films with a 5 nm target thickness were deposited at a substrate temperature of 100 °C in an Oxford Instruments FlexAL ALD reactor equipped with a remote inductively coupled plasma source using trimethyl phosphate (TMPO: PO(CH\(_3\))\(_3\)) as the phosphorus precursor and an O\(_2\) plasma as the oxygen source. PO\(_x\) was deposited in a cyclical fashion using a pulsed-flow PECVD process in which a TMPO pulse was injected during the O\(_2\) plasma step (six cycles). Details of the PECVD process are shown in Figure 1. ALD Al\(_2\)O\(_3\) was deposited as a capping layer with a 10 nm target thickness (83 cycles) immediately following the PO\(_x\) deposition in the same reactor at the same substrate temperature using TMA (Al(CH\(_3\))\(_3\)) as the Al precursor and an O\(_2\) plasma as the oxygen source. Symmetric lifetime test structures with PO\(_x\)/Al\(_2\)O\(_3\) stacks were prepared on 280 \(\mu\)m-thick double-side polished 1–3 12 cm\(^2\) n-type FZ Si (100) wafers as well as 140–185 \(\mu\)m-thick textured and planar (double-side polished with or without random pyramid texturization through alkaline etching) 2.6–4.2 12 cm\(^2\) n-type Cz Si (100) wafers. Furthermore, 145 \(\mu\)m-thick textured symmetric n\(^+\) Si substrates were fabricated on 1.3 12 cm\(^2\) n-type Cz Si (100) wafers using a phosphorus diffusion in a tube furnace, yielding sheet resistance values of 137 ± 7 and 260 ± 7 \(\Omega\) cm\(^{-1}\) as measured by a four-point probe setup. These substrates underwent a treatment in hydrofluoric acid (HF; 5%, 5 min) prior to the PO\(_x\)/Al\(_2\)O\(_3\) deposition to remove the phosphosilicate glass that is formed as a consequence of the phosphorous diffusion. All substrates received a standard Radio Corporation of America (RCA) clean\(^{(33)}\) and were etched in diluted HF (1%, 1 min) just before being loaded in the ALD reactor. Immediately prior to the PO\(_x\) deposition, an O\(_2\) plasma (1 min, 15 mTorr, 200 W) was used in the ALD reactor to form a well-defined thin (≈1 nm) interfacial SiO\(_2\) layer between the PO\(_x\) layer and the substrate for all samples investigated in this work. This means that all PO\(_x\)/Al\(_2\)O\(_3\) stacks are in fact SiO\(_2)/PO\(_x\)/Al\(_2\)O\(_3\) stacks, although they are labeled as PO\(_x\)/Al\(_2\)O\(_3\) for brevity. Postdeposition annealing was performed for 10 min in N\(_2\) at 400 °C using a jipelec rapid thermal processing system. Some PO\(_x\)/Al\(_2\)O\(_3\) samples on Cz substrates were symmetrically capped by 75 nm PECVD SiN\(_x\) with a refractive index of 2.03 ± 0.03 at 633 nm deposited at 375 °C using a Meyer Burger MAIA PECVD system. To assess the firing stability of these PO\(_x\)/Al\(_2\)O\(_3)/SiN\(_x\) stacks, a subsequent firing treatment was conducted using a belt furnace that is typically used for contact formation using fire-through metallization paste (1 min firing profile, 720 °C peak temperature).

Characterization: The layer thicknesses were monitored in situ by spectrometric ellipsometry using a J. A. Woollam M-2000F UV–Vis ellipsometer (1.25–5 eV) with Sellmeier and Cauchy models for the PO\(_x\) and Al\(_2\)O\(_3\) layers, respectively. A Sinton WCT-120TS QSSPC setup was used to assess the passivation quality and \(J_0\) values were derived using the Kane–Swanson approach.\(^{(34)}\) A Corona Charging System of Delft Spectral Technologies was used to conduct corona-lifetime experiments using a voltage of –10 kV applied to a tungsten needle in the setup to deposit negative charges on both sides of the PO\(_x\)/Al\(_2\)O\(_3\) samples during subsequent 10 s charging treatments that were alternated with QSSPC measurements. The amount of deposited charge was measured after each charging step by a Kelvin probe that is part of the Corona Charging System. \(Q_f\) was derived from the deposited charge corresponding to the maximum in effective surface recombinination velocity, which is typically reached when the fixed charge introduced by the passivation layer(s) is matched by the amount of deposited corona charges with the opposite sign. This method has also been applied to determine \(Q_f\) for Al\(_2\)O\(_3\)\(^{(7,35)}\) and SiN\(_x\)\(^{(7,38)}\) while assuming a linear charge rate that is obtained from the Kelvin probe voltage as a function of charging time before the surface goes into inversion.\(^{(37)}\) For the C–V characterization, the PO\(_x)/Al\(_2\)O\(_3\) layer stack was fabricated on one side of the substrate and Al contacts with a 700 \(\mu\)m diameter were thermally evaporated through a shadow mask on the annealed PO\(_x)/Al\(_2\)O\(_3\) stacks. Galvanetatic paste was applied to form an ohmic rear contact to the side of the wafer without PO\(_x)/Al\(_2\)O\(_3\). High-frequency (1 MHz) and quasi-static C–V measurements were performed using an HP 4284A precision LCR meter and HP 4140B picoammeter/DC voltage source. \(D_d\) was derived from the quasi-static capacitance following Berglund\(^{(38)}\) and \(Q_f\) was inferred from the flatband voltage shift, as has been described elsewhere in more detail.\(^{(39)}\)

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

aluminum oxide, chemical vapor deposition, phosphorus oxide, silicon, surface passivation

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