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Plasma-Assisted ALD for the Conformal Deposition of SiO2: Process, Material and Electronic Properties

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Plasma-assisted atomic layer deposition (ALD) was used to deposit SiO2 films in the temperature range of Tdep = 50–400 °C on Si(100). H2Si[N(C2H5)2]2 and an O2 plasma were used as Si precursor and oxidant, respectively. The ALD growth process and material properties were characterized in detail. Ultrathin precursor doses (~50 ms) were found to be sufficient to reach self-limiting ALD growth with a growth-per-cycle of ~1.2 Å (Tdep = ~200 °C) leading to SiO2 films with O/Si ratio of ~2.1. Moreover, the plasma ALD process led to a high conformity (95–100%) for trenches with aspect ratios of ~30. In addition, the electronic (interface) properties of ultrathin ALD SiO2 films and ALD SiO2/Al2O3 stacks were studied by capacitance-voltage and photoconductance decay measurements. The interface quality associated with SiO2 was improved significantly by using a ultrathin ALD Al2O3 capping layer and annealing. The interface defect densities decreased from ~1 × 1012 eV−1 cm−2 (at mid gap) for single layer SiO2 to < 1011 eV−1 cm−2 for the stacks. Correspondingly, ultralow surface recombination velocities < 3 cm/s were obtained for n-type Si. The density and polarity of the fixed charges associated with the stacks were found to be critically dependent on the SiO2 thickness (~1–3 nm).

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The key importance of thermally grown silicon dioxide (SiO2) for applications in silicon-based microelectronics needs no introduction.1,2 Also in silicon photovoltaics, SiO2 is a very important material. The low interface defect densities associated with the Si/SiO2 interface reduce surface recombination significantly and have enabled high solar cell efficiencies.3–6 Temperatures > 800 °C are typically required to form SiO2 by thermal oxidation of Si. Alternative methods for the synthesis of SiO2 have been developed to avoid such high temperatures and long processing times. They may also enable single side deposition and a high level of control of the material properties and film thickness. These alternative methods include (wet) chemical oxidation, (plasma-enhanced) chemical vapor deposition, sputtering and electron beam evaporation.

Atomic layer deposition (ALD) is an alternative CVD-like method that recently gained considerable attention. In ALD, the substrate is sequentially exposed to two precursors (e.g., a Si precursor and an oxidant) which each react with the surface until saturation. ALD allows for precise thickness control, optimal large-area uniformity, and the conformal coating of demanding substrate topologies.7–9 Therefore, the advantages of ALD may expand the range of applications for SiO2. ALD SiO2 films may find application as protective or insulator coating, or can be used in nanolaminate structures with tailored optical and electronic properties.10,11 The films can also be used in spacer coating, or can be used in nanolaminate structures with tailored optical and electronic properties.10,11 The films can also be used in spacer coating, or can be used in nanolaminate structures with tailored optical and electronic properties.10,11

In the first reports, ALD SiO2 was synthesized employing SiCl4 and H2O which required relatively high substrate temperatures (>300 °C) and long precursor exposures.12–14 In recent years, various alternative Si precursors have been tested in combination with O2 or H2O as the oxidants. These processes include the use of pyridine (C5H5N) and Al as catalysts on the surface.17,11,19 The approach employing Al was referred to as rapid ALD as it resulted in deposition rates above the “theoretical” maximum of one monolayer per ALD cycle. In addition, more recently a thermal ALD process for low-temperature SiO2 was reported which was free of catalysts or corrosive by-products.20 In this respect, the use of precursors with amino ligands has also shown promising results, in particular when combined with H2O2, O3, or O2 plasma as the oxidant.21–24 Very recently, also SiH4 has been used as Si precursor during plasma-assisted ALD with CO2 plasma as oxidant.25 SiO2 films grown with ALD have been reported to exhibit low carbon content, and a high electrical breakdown field.10,22 Nevertheless, to improve properties such as the chemical etch rate or the interface defect density, annealing at a temperature of 1000 °C was shown to be beneficial.20 Here, we report on a plasma-assisted ALD process for synthesis of SiO2 at low substrate temperatures of 50–400 °C. The ALD process employed H2Si[N(C2H5)2]2 as the Si precursor (Figure 1). The plasma-assisted ALD process was characterized in detail and the results are compared to the well-understood ALD process of Al2O3 using Al(CH3)3. We show that the ALD SiO2 process was compatible with short cycle times and led to an excellent conformity even on structures with an aspect ratio of ~30. The electronic properties of the Si(100)/SiO2 interface were investigated using photodischarge conductance decay and capacitance-voltage measurements. We demonstrate that interface defect densities < 1011 eV−1 cm−2 (at mid gap) can be reached when using ultrathin Al2O3 capping layers and annealing at moderate temperatures (~400 °C).

The paper is organized as follows. After the experimental details, the characterization of the ALD SiO2 process will be presented. In addition, the material properties and the influence of the substrate temperature will be addressed and data with respect to the conformity will be presented. Subsequently, a brief discussion on the surface chemistry is included on the basis of in situ measurements. The final sections discuss the surface passivation properties and the electronic (interface) properties of the SiO2 films and SiO2/Al2O3 stacks.

Experimental

The SiO2 films were deposited in the Oxford Instruments OpAL reactor. This is an open-load system, suited for both plasma and thermal ALD and operating at typical pressures of 150 mTorr. A remote O2 plasma was used during the oxidation step in the ALD cycle. H2Si[N(C2H5)2]2 (SAM.24, Air Liquide) was used as the Si precursor (Fig. 1). This is a liquid (melting point < ~10 °C) which exhibits a high vapor pressure, i.e. ~100 Torr at 100 °C (Fig. 1). The SAM.24 was held in a stainless steel bubbler heated to 50 °C.

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as no evidence was found for reactions between the Si precursor and O₂ under the experimental conditions used. The substrate temperature during deposition, T_{dep}, was varied between 50 and 400 °C. The reactor wall temperature was 180 °C unless the substrate temperature was lower. Under these conditions the wall and substrate temperature were equal. To allow for direct comparison, Al₂O₃ was synthesized in the same reactor using Al(CH₃)₃ as the metal precursor and O₂ plasma as the oxidant. 26–28 All films were deposited on Si (100) wafers to fit the ellipsometry data. Rutherford backscattering spectroscopy (RBS) and elastic recoil detection (ERD) employing to determine the refractive index were determined by using a Cauchy optical model for optimizing the ALD process. The growth-per-cycle, GPC, and absorption (FTIR) measurements were used to analyze the film composition. The surface morphology was investigated by atomic force microscopy (AFM) measurements in semi-contact mode and by optical emission spectroscopy (OES) through a view port located on top of the ALD reactor.

In situ spectroscopic ellipsometry (SE) measurements were used for optimizing the ALD process. The growth-per-cycle, GPC, and refractive index were determined by using a Cauchy optical model to fit the ellipsometry data. Rutherford backscattering spectroscopy (RBS) and elastic recoil detection (ERD) employing ~2 MeV He²⁺-ions from the singletron at the Eindhoven University of Technology (Acctec B.V.) and transmission Fourier transform infrared absorption (FTIR) measurements were used to analyze the film composition. The surface morphology was investigated by atomic force microscopy (AFM) measurements in semi-contact mode and by high-resolution transmission electron microscopy (TEM). Scanning electron microscopy (SEM) was employed to visualize the conformal deposition of SiO₂ in high aspect ratio trenches. The deposition process itself was studied in real time by quadrupole mass spectrometry (QMS) probing the gas in the exhaust line and by optical emission spectroscopy (OES) through a view port located on top of the ALD reactor.

The interface quality and surface passivation properties of the ALD SiO₂ films was evaluated from the effective lifetime τ_{eff} of the minority carriers in double-side coated floatzone (FZ) n-type Si wafers (~3.5 Ω cm). τ_{eff} was determined with photoconductance decay in the transient mode and quasi-steady-state-mode (for τ_{eff} < 100 μs) using a Sinton lifetime tester (WCT 100). The upper level for the surface recombination velocity S_{eff,max} was extracted at an injection level of 5×10^{14} cm⁻³ by the expression:

\[ S_{eff,max} = \frac{W}{2 \cdot \tau_{eff}} \]  

with W the thickness of the silicon wafer (~280 μm). In the derivation of this expression it is assumed that all recombination takes place at the surface. Capacitance-voltage measurements were performed on metal-oxide-semiconductor structures to extract the interface defect density (D_{it}) and the fixed charge density Q_f. 26 Evaporated Al was used for the metal contacts which were applied after post-deposition annealing of the samples. The latter was performed in a rapid thermal annealing furnace (ramp up > 30 °C/s) in N₂/H₂ or N₂ environment.

Figure 1. Vapor pressure of the H₃Si[N(CH₃)₂]₂ (SAM.24) precursor used for ALD of SiO₂ as a function of the temperature. The vapor pressure is compared to the one of Al(CH₃)₃ (TMA). This precursor is commonly used for ALD of Al₂O₃. The precursors are schematically represented in the figure.

Figure 2. SiO₂ film thickness as a function of the number of ALD cycles. (a) Substrate temperatures of 50° C, 200° C and 250° C. The film thickness was measured by in situ spectroscopic ellipsometry (SE). (b) SiO₂ film thickness extracted from the transmission electron microscopy (TEM) image of Fig. 3, compared with values determined by in situ SE on the same sample. The substrate temperature T_{dep} was 200° C.

Figure 3. High-resolution cross-sectional TEM image of a stack with alternating layers of ALD Al₂O₃ and ALD SiO₂ deposited using 10–40 cycles each. The substrate temperature was 200° C. The extracted layer thicknesses are shown in Fig. 2b.

**ALD Process and Material Characterization**

The ALD process was monitored by in situ spectroscopic ellipsometry (SE) by taking data points after a certain number of cycles. The SiO₂ film thickness is plotted as a function of the number of ALD cycles in Fig. 2a for substrate temperatures of 50° C, 200° C and 250° C. For the latter two temperatures, the SiO₂ thickness increased linearly with the number of cycles. A slight non-linearity was observed for T_{dep} = 50° C, which we attribute to parasitic CVD reactions as will be discussed below. In addition to SE, thickness information was extracted from a cross-sectional TEM micrograph of a sample which consisted of alternating layers of Al₂O₃ and SiO₂ with each a varying thickness as set by the number of cycles per layer (Fig. 3). The TEM and SE data proved to be in excellent agreement (Fig. 2b). The growth-per-cycle (GPC) was determined from the slope of the curves in Fig. 2, with values of 1.2 Å/cycle and 1.1 Å/cycle obtained for substrate temperatures of 200° C and 250° C, respectively. These GPC values are similar to those obtained for plasma ALD of Al₂O₃. 26, 27 Moreover, no indications for a significant growth delay on H-terminated Si(100) substrates were found for the SiO₂ ALD process, which is also similar to what has been observed for Al₂O₃. 26

Figure 4 shows the effect of the duration of the successive steps in the ALD recipe, i.e., the precursor dosing, precursor purge step, plasma exposure, and plasma exposure purge step. In the corresponding experiments one process parameter in the ALD recipe was varied whereas the duration of the other steps was taken sufficiently long to avoid any influence from these steps on the properties of the ALD films.
guarantee saturated ALD conditions for the non-varied process parameters. The substrate temperature was set to 250 °C. The growth process of SiO₂ is compared to plasma-assisted ALD of Al₂O₃ at 250 °C (Figures 4e–4h). From the figure it is evident that ultrashort precursor dosing times (≈50 ms) were already sufficient to reach self-limiting growth with a GPC of ∼1.1 Å. These short dosing times were only slightly higher compared to those used for the Al(CH₃)₃ precursor for ALD of Al₂O₃. The fact that short dosing times are sufficient is in agreement with the expectations based on the relatively high vapor pressure of the SAM.²⁴ precursor. Many processes for other oxides using different precursors require much longer dosing times. For instance, ALD of TiO₂ and Ta₂O₅ require dosing times >1 s using alkylamide precursors in a similar remote plasma and thermal ALD reactor.³⁰,³¹ The duration of the purge step after precursor dosing was required to be ≈2 s. For shorter purge times, residual precursor remaining in the reactor volume can react in the plasma, causing parasitic (PE) CVD-like growth and a higher GPC value. Regarding the O₂ plasma step, a plasma exposure time >1 s was found to be sufficient to reach a saturated GPC, indicating the rapid removal of the precursor ligands. For very short plasma exposure times, a drop in the refractive index below ∼1.46 was observed. This decrease can be attributed to the incorporation of impurities in the SiO₂ film that originate from the Si precursor. The plasma exposure time required for ALD SiO₂ is slightly shorter than for plasma ALD of Al₂O₃ which requires plasma times of ∼2 s to reach saturated growth. However, with in situ spectroscopic ellipsometry only the center of the Si wafer is probed and to ensure saturation over the full wafer surface, a plasma exposure time of 4 s was employed in all subsequent experiments. Interestingly, the purge after the plasma step had a significant impact on the GPC. This is in contrast to the ALD process for Al₂O₃, where the purge step after O₂ plasma exposure was found to have little influence on the GPC and could be reduced well below 0.5 s. We attribute the higher GPC for shorter purges (<1 s) to reactions between residual H₂O₂ formed during the plasma process,³⁵ with the Si precursor injected in the subsequent step. Although it is known that the H₂Si[NC₂H₅]₂ precursor reacts with H₂O, it is relevant to mention here that we were unable to develop a thermal ALD process for SiO₂ using SAM.²⁴ as precursor and H₂O as the oxidant. No film growth was observed. Instead, even with the shortest possible H₂O doses applied, powder formation occurred in the reactor as was noticeable by the naked eye.

The thickness uniformity of the SiO₂ films deposited by plasma-assisted ALD at 250 °C was evaluated by mapping the thickness by spectroscopic ellipsometry. A precursor dose time of 50 ms was used, while all other steps in the ALD cycle (Fig. 4) were set to 3 s. For a 8 inch (∼200 mm) wafer the nonuniformity, defined by the difference between the maximum and minimum thicknesses divided by twice the average thickness of all data points measured,²⁶ was <3.5%. The thickness nonuniformity achieved on 4 inch (100 mm) wafers was ∼1%.

**Material properties and role of substrate temperature.** Figure 5 shows the effect of the substrate temperature between 50 and 400 °C on the growth rate and refractive index of SiO₂. The length of the purge steps in the lower temperature regime was extended (up to 10 s

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**Figure 5.** Influence of the substrate temperature during deposition on (a) the refractive index, n, and (b) the growth-per-cycle, GPC, of SiO₂ as determined with in situ spectroscopic ellipsometry.
at 50°C, as it is more difficult to remove H₂O at lower temperatures which could impact the saturation behavior of the process. The GPC was observed to decrease with increasing deposition temperature from ~1.7 Å/cycle at 50°C to 0.8 Å/cycle at 400°C. The refractive index was fairly constant with a value of n = 1.46 ± 0.02 (photon energy of 2 eV) between 100 and 300°C. Below 100°C and above 300°C the refractive index was somewhat lower. It can therefore not be excluded that some non-ideal ALD behavior takes place at the lowest and highest temperatures investigated. At the low substrate temperature of 50°C, additional CVD reactions may contribute to the higher GPC and lower n. This might also explain the slightly non-linear trend between the film thickness and number of cycles observed at this deposition temperature as shown in Figure 1. Despite the long purging times (10 s) after the plasma step, the accumulation of some residual H₂O in the reactor, with which the precursor can react, may play a role in these observations. For temperatures reaching 400°C, thermal stability issues of the precursor and its ligands can start to play a role.

Table I. Data on ALD SiO₂ as determined from the RBS and ERD measurements. In the calculation of the mass density the film thickness as obtained by SE was used. The thickness of the films was in the range of 35–45 nm.

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>Si atoms per cycle (10¹⁴ cm⁻²)</th>
<th>[Si] (atom%)</th>
<th>[O] (atom%)</th>
<th>[H] (atom%)</th>
<th>O/Si ratio</th>
<th>ρmass (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2.8 ± 0.1</td>
<td>29.1 ± 0.8</td>
<td>61.3 ± 1.5</td>
<td>9.6 ± 0.9</td>
<td>2.1 ± 0.1</td>
<td>2.0 ± 0.1</td>
</tr>
<tr>
<td>200</td>
<td>2.3 ± 0.1</td>
<td>29.9 ± 0.8</td>
<td>62.9 ± 1.5</td>
<td>7.1 ± 0.7</td>
<td>2.1 ± 0.1</td>
<td>2.0 ± 0.1</td>
</tr>
<tr>
<td>300</td>
<td>1.9 ± 0.1</td>
<td>29.6 ± 0.8</td>
<td>62.3 ± 1.5</td>
<td>8.1 ± 0.8</td>
<td>2.1 ± 0.1</td>
<td>2.1 ± 0.1</td>
</tr>
</tbody>
</table>

For comparison, the surface roughness of 1.9 and 1.6 Å was obtained for films deposited at 100°C (film thickness 51 nm) and 200°C (48 nm), respectively. The fact that these values were not higher than those obtained for uncoated polished Si wafers demonstrates that the SiO₂ films were deposited with negligible roughening on the Si(100) substrate. The latter can also be appreciated from the interface morphology as visualized in the TEM image of a SiO₂/Al₂O₃ stack displayed in Fig. 7. Perfectly smooth Si/SiO₂ and SiO₂/Al₂O₃ interfaces can be observed. From the AFM data, it also follows that the aforementioned small (PE)/CVD growth component at low substrate temperatures is not pronounced yet at 100°C as this would likely have resulted in enhanced surface roughness.

Conformality.— The conformality of the ALD process was examined on a structure with high-aspect ratio trenches using high-resolution SEM. The various trenches exhibited aspect ratios (AR, i.e., depth of trench divided by average width) between ~10 and ~30 and were fabricated by deep reactive ion etching (DRIE). The trenches exhibited a thermal SiO₂ layer of ~100 nm on the surfaces. To obtain sufficient optical contrast between the layers, an Al₂O₃ film was deposited prior to ALD SiO₂ deposition. The length of the various steps in the ALD SiO₂ recipe was increased slightly compared to the requirements for ALD growth on a planar surface (see Fig. 4). The recipe included a dose time of 90 ms, a purge time of 5 s, a plasma time of 4.5 s and a subsequent purge time of 6 s. Figure 8 shows the SEM image of a trench with an aspect ratio of AR = ~30. The SiO₂ film was deposited using 830 cycles. The film thickness at the surface was determined with SEM to be 100 ± 5 nm, which was in good agreement with the 102 ± 1 nm obtained by spectroscopic ellipsometry for a planar reference sample. At the bottom of the trench a thickness of 95 ± 5 nm was extracted from the SEM graph. This demonstrates a very high conformality (95–100%) for the plasma-assisted ALD process. These results are important as there is only a limited amount of literature available on the conformality of plasma-assisted ALD processes (see Ref. 35 and references therein). For example, good results have previously been reported for AR up to ~15. 36

Surface Morphology.— The surface morphology of the SiO₂ films was studied by AFM in semi-contact mode. A root-mean-square surface roughness of 1.9 and 1.6 Å was obtained for films deposited at 100°C (film thickness 51 nm) and 200°C (48 nm), respectively. The fact that these values were not higher than those obtained for uncoated polished Si wafers demonstrates that the SiO₂ films were deposited with negligible roughening on the Si(100) substrate. The latter can also be appreciated from the interface morphology as visualized in the TEM image of a SiO₂/Al₂O₃ stack displayed in Fig. 7. Perfectly smooth Si/SiO₂ and SiO₂/Al₂O₃ interfaces can be observed. From the AFM data, it also follows that the aforementioned small (PE)/CVD growth component at low substrate temperatures is not pronounced yet at 100°C as this would likely have resulted in enhanced surface roughness.
Surf ace Chemistry

From the data presented and on the basis of literature reports, some aspects of the surface chemistry during ALD SiO\textsubscript{2} can be briefly addressed. As mentioned previously, from the decrease of the GPC for increasing substrate temperatures (Fig. 5b), we can conclude that the ALD process is governed by surface chemical reactions involving –OH groups. Note here that the presence of residual –OH groups was demonstrated by the FTIR spectrum showing a clear signature of SiO-H bonds in the films (Fig. 6). During the precursor step, it is therefore most likely that the –N(C\textsubscript{2}H\textsubscript{5})\textsubscript{2} ligands of the precursor react with the surface –OH groups producing volatile HN(C\textsubscript{2}H\textsubscript{5})\textsubscript{2}. A reaction involving the breaking of the Si-H bond in the precursor is very unlikely.\textsuperscript{28} We propose therefore similar surface chemical reactions during the first ALD half cycle as reported by Burton et al.\textsuperscript{19} for the SiH(N(CH\textsubscript{3})\textsubscript{2})\textsubscript{3} precursor which is comparable to the present precursor:

\[
\text{Si-OH}^+ + H_2SiN(C\textsubscript{2}H\textsubscript{5})\textsubscript{2} \rightarrow \text{SiO} - \text{SiH}_2N(C\textsubscript{2}H\textsubscript{5})_2 + x\text{HN(C}\textsubscript{2}H\textsubscript{5})\textsubscript{2},
\]

where surface species are indicated by \(^+\). In this precursor adsorption reaction, only one \((x = 1)\) or both \((x = 2)\) of the –N(C\textsubscript{2}H\textsubscript{5})\textsubscript{2} ligands may react. In the second half cycle, the surface reactions will be dominated by O radical species delivered by the plasma.\textsuperscript{32} From similar cases studied previously (e.g., Al\textsubscript{2}O\textsubscript{3} from Al(CH\textsubscript{3})\textsubscript{3} and O\textsubscript{2} plasma\textsuperscript{34} and Ta\textsubscript{2}O\textsubscript{5} from Ta[N(CH\textsubscript{3})\textsubscript{2}]\textsubscript{3} and O\textsubscript{2} plasma\textsuperscript{30} it can be hypothesized that combustion-like reactions dominate:

\[
\text{SiH}_2N(C\textsubscript{2}H\textsubscript{5})\textsubscript{2} + O \rightarrow \text{Si-OH}^+ + H_2O + CO_x + \text{other (N-containing) species},
\]

In the latter expression the species are not balanced as it is unclear what reaction products are actually created. In the second half cycle also N-containing species need to be produced for the case that not all precursor molecules react with the –OH covered surface through the release of both –N(C\textsubscript{2}H\textsubscript{5})\textsubscript{2} ligands, i.e. when \(x \neq 2\) for all precursor molecules adsorbing.

Evidence for the fact that \(x \neq 2\) for all precursor molecules was obtained from quadrupole mass spectrometry (QMS) measurements. Figure 8 shows time-dependent mass spectrometry data for a number of selected mass-over-charge \(m/z\) ratios. The enhanced signals at \(m/z = 72\ (N(C\textsubscript{2}H\textsubscript{5})\textsubscript{2}^+)\) and \(m/z = 73\ (HN(C\textsubscript{2}H\textsubscript{5})\textsubscript{2}^+)\) during the first half cycle are consistent with the removal of the precursor ligands during precursor adsorption. However, it should be noted that these signals can also originate from the cracking of the precursor molecule in the mass spectrometer. Very small signals at these \(m/z\) values were also observed during the second half cycle whereas the signals were absent during steps in which the plasma was ignited without preceding precursor dosing. This suggests that after the first half cycle indeed a fraction of the -N(C\textsubscript{2}H\textsubscript{5})\textsubscript{2} ligands remain intact on the surface.\textsuperscript{24}

The latter can also be concluded from the other species observed during the second half cycle. During this plasma step, the prominent \(m/z\) ratios that were detected included \(m/z = 2\ (H^+), m/z = 18\ (H_2O^+), m/z = 28\ (CO^+)\) and \(m/z = 44\ (CO_2^-).\) Figure 9 shows the signals at \(m/z = 18\) and \(m/z = 44\). The fact that combustion products such as CO\textsubscript{2} are observed during the plasma step clearly indicates that some -N(C\textsubscript{2}H\textsubscript{5})\textsubscript{2} ligands remain on the surface after precursor adsorption.

The interpretation of mass spectrometry for plasma-assisted ALD processes is more complicated than for thermal ALD as the reaction products released from the surface can react in the plasma leading to the creation of other species and fragments. The mass spectrometry data as shown in Figure 9 should therefore be interpreted with care.\textsuperscript{32} However, plasma-assisted ALD also allows investigation of the optical emission spectrum during the plasma step.\textsuperscript{18} Figure 10 shows two optical emission spectra, one for a plasma step during ALD (recorded immediately after plasma ignition) and one for a regular O\textsubscript{2} plasma without preceding precursor dosing step. The presence of OH and H emission (i.e., H\textsubscript{g}, H\textsubscript{p}, H\textsubscript{f} of the Balmer series) is clearly observed.

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**Figure 7.** High-resolution TEM image of an ALD SiO\textsubscript{2} film of 7.0 ± 0.3 nm thickness deposited on a H-terminated Si(100) wafer. The SiO\textsubscript{2} was covered by an Al\textsubscript{2}O\textsubscript{3} film deposited by plasma-assisted ALD.

**Figure 8.** High-resolution SEM images of a high-aspect ratio trench in Si coated by 830 cycles of ALD SiO\textsubscript{2}. The SiO\textsubscript{2} was deposited on top of thermal SiO\textsubscript{2}/ALD Al\textsubscript{2}O\textsubscript{3} layers for optical contrast. The depth and average width of the trench were 18.5 and 0.6 μm, respectively, resulting in an aspect ratio of ~30.
prominently present in the emission spectra during plasma ALD from CN emission is observed during the plasma step. This emission was mTorr). This indicates that the surface reactions take place almost the gas species in our reactor at the operating pressure used (3–4 s after plasma ignition which is similar to the residence time of ignition. This interpretation is consistent with the fast saturation be-

for the plasma step during ALD. These excited fragments are formed in the plasma by (electron-induced) dissociation of volatile species originating from the reactor surfaces and substrate. The inset shows the transient H\textsubscript{2} emission during the plasma step in the ALD cycle. The increase and subsequent decrease of the signal suggests that the reaction products are formed within the first second after plasma ignition. This interpretation is consistent with the fast saturation behavior as displayed in Figure 4c. The H\textsubscript{2} emission disappears within 3–4 s after plasma ignition which is similar to the residence time of the gas species in our reactor at the operating pressure used (≈150 mTorr). This indicates that the surface reactions take place almost instantly after plasma ignition. Interesting is also that no signal due to CN emission is observed during the plasma step. This emission was prominently present in the emission spectra during plasma ALD from Ta\textsubscript{2}O\textsubscript{5} from Ta[N(CH\textsubscript{3})\textsubscript{3}] and O\textsubscript{2} plasma.\textsuperscript{30}

Figure 9. Data from quadrupole mass spectrometry (QMS) for selected mass-over-charge ratios, i.e., m/z = 18 (H\textsubscript{2}O\textsuperscript{+}), 44 (CO\textsuperscript{+}), 72 (N[CH\textsubscript{3}]\textsubscript{2}\textsuperscript{+}), and 73 (HN[CH\textsubscript{3}]\textsubscript{2}\textsuperscript{+}). During the measurements the substrate temperature was 250°C and the wall temperature was 180°C. In the first part of the figure only the precursor is pulsed, in the second part only the plasma and in third part both the precursor and plasma are pulsed (regular ALD cycle, with extended purge times for clarity).

![Figure 9](image-url)

Figure 10. Optical emission spectra (OES) for the plasma step during plasma-assisted ALD and for a regular plasma step without preceding precursor dosing. The latter served as a reference. The most prominent emission lines have been assigned. The inset shows the transient signal due to H\textsubscript{2} emission after the ignition of the plasma at 0 s.

![Figure 10](image-url)

**Surface Passivation Properties**

Surface passivation by single layer SiO\textsubscript{2}.— The surface passivation properties were evaluated for n-type Si wafers that were coated on both sides with SiO\textsubscript{2} (20–45 nm) using a deposition temperature of ≈200°C. The films afforded no significant surface passivation in the as-deposited state indicated by a very low effective lifetime of \( \tau_{\text{eff}} = \sim 4 \mu s \). Similar results were reported for plasma ALD Al\textsubscript{2}O\textsubscript{3} films.\textsuperscript{39, 40} The as-deposited Al\textsubscript{2}O\textsubscript{3} films exhibited a very high defect density at mid gap (\( D_{\text{it}} \approx 10^{13} \text{ cm}^{-2} \text{ eV}^{-1} \)), at least partially related to the vacuum UV (VUV) radiation present in the plasma.\textsuperscript{40} It is expected that VUV also plays a role in the poor passivation quality obtained for as-deposited ALD SiO\textsubscript{2}. Figure 11 shows the injection-level dependent effective lifetime after annealing the ALD SiO\textsubscript{2} films in forming gas (mixture of \( \sim 10\% \) H\textsubscript{2} in N\textsubscript{2}) at a temperature of 400°C. The passivation properties improved significantly during annealing, resulting in \( \tau_{\text{eff}} \) values up to 560 µs (\( \Delta\tau = 1 \times 10^{14} \text{ cm}^{-2} \)), which correspond to \( S_{\text{eff}} < 25 \text{ cm/s} \). Nonetheless, the level of surface passivation after annealing was not stable in time and gradually deteriorated (inset Fig. 11). This transient behavior is indicative of progressively higher \( D_{\text{it}} \) values. Issues with the long term stability of the passivation by silicon oxides have been reported before for chemical oxides.\textsuperscript{41} In an attempt to improve the passivation properties of ALD SiO\textsubscript{2}, the effect of a high temperature annealing step at 900°C (1 min) was studied. A reduction of the film thickness by \( \sim 10\% \) was observed during this annealing step and also the refractive index decreased, indicating densification of the film. However, subsequent annealing in forming gas at 400°C did not lead to a significantly improved level of passivation or stability compared to a reference sample which did not receive the 900°C annealing step. The results show that the level of passivation associated with ALD SiO\textsubscript{2} was significantly lower than obtained by thermally-grown SiO\textsubscript{2} for which typically \( S_{\text{eff}} < 5 \text{ cm/s} \) are obtained.

Surface passivation by SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} stacks.— We have recently demonstrated that the interface properties of SiO\textsubscript{2} films synthesized by high-rate plasma enhanced chemical vapor deposition (PECVD) could be improved dramatically by the application of an Al\textsubscript{2}O\textsubscript{3} capping film and subsequent annealing.\textsuperscript{14} For these stacks, comprising Al\textsubscript{2}O\textsubscript{3} films with a thickness down to \( \sim 5 \text{ nm} \), very low surface recombination velocities with values of \( S_{\text{eff}} < 5 \text{ cm/s} \) were achieved.\textsuperscript{14} Figure 11 shows the effective lifetime for a 12 nm ALD SiO\textsubscript{2}/30 nm Al\textsubscript{2}O\textsubscript{3} stack after annealing in N\textsubscript{2} (400°C, 10 min). Note that in contrast to single layer ALD SiO\textsubscript{2}, annealing in N\textsubscript{2}/H\textsubscript{2} was not necessary. The high effective lifetimes up to \( \sim 7 \text{ ms} \) correspond to exceptionally low \( S_{\text{eff}} < 3 \text{ cm/s} \) for n-type Si.\textsuperscript{15} It is furthermore important to mention that the effective lifetime induced by the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} stacks remained

![Figure 11](image-url)
Dielectric constant.— The dielectric constant $k$ was determined from the capacitance density $C_{ox}$ of the dielectric (by the Hauser model) and the thickness information from SE, by:

$$k = \frac{d \times C_{ox}}{\varepsilon_0}$$

(2)

with $d$ the film thickness, and $\varepsilon_0$ the vacuum permittivity. Table II gives the dielectric constants obtained for the SiO$_2$ films and the stacks after annealing at 400°C. For the thinnest film (~5 nm), for example, a dielectric constant of $k = 4.7 \pm 0.4$ was extracted from the C-V data. The higher $k$-values obtained for ALD SiO$_2$ relative to thermally-grown SiO$_2$ ($k \sim 3.9$) can likely be attributed to the presence of residual OH groups in the material (Table I).\textsuperscript{20, 42} In comparison, Hiller et al. reported a value of $k = 6.1$ (as-deposited) and $k = 3.6$ for ALD SiO$_2$ films after annealing at 1000°C.\textsuperscript{26} For a stack comprising an ALD SiO$_2$ film of 1 nm and an Al$_2$O$_3$ layer of 30 nm, a value of $k = 8 \pm 0.4$ was determined. This value was similar (within measurement accuracy) to the value obtained for an Al$_2$O$_3$ reference film deposited directly on H-terminated Si (Table II). These values are in good agreement with those reported in the literature for single layer Al$_2$O$_3$ ($k \sim 7–9$).\textsuperscript{26, 43–45} As expected, the dielectric constants of the stacks are observed to decrease for increasing SiO$_2$ interlayer thickness due to the lower $k$-value associated with SiO$_2$.

Capacitance-Voltage Measurements

Capacitance-voltage measurements were carried out to study the electronic interface properties corresponding to the ALD SiO$_2$ films and SiO$_2$/Al$_2$O$_3$ stacks. The C-V data are shown in Fig. 12, for SiO$_2$ thicknesses in the range of 1–30 nm. The measurements were performed using frequencies of 1, 10, 100 kHz. The voltage was swept from $-4$ to $4\text{V}$ to go from accumulation to inversion conditions.

Table II. SiO$_2$ thickness dependent electronic properties of ALD SiO$_2$ films and ALD SiO$_2$/Al$_2$O$_3$ stacks. As a reference, the data for Al$_2$O$_3$ on Si is shown.\textsuperscript{20} The relative dielectric constant $k$, effective fixed charge density $Q_{ef}$ (Eq. 3), negative charge at SiO$_2$/Al$_2$O$_3$ interface $Q_{neg}$ (Eq. 4) and interface defect density at mid gap $D_n$ were extracted from the C-V measurements (Fig. 12). The estimated error in the dielectric constant is $\sim 0.4$; the error in $Q_{ef}$ for single layer SiO$_2$ and Al$_2$O$_3$ is estimated to be $\pm 2 \times 10^{11} \text{cm}^{-2}$; the error in $D_n$ for single layer SiO$_2$ is $\sim 8.5 \times 10^{12} \text{cm}^{-2}$. The error in the $D_n$ values for the stacks leads to maximum $D_n$ values of $10^{11} \text{cm}^{-2} \text{eV}^{-1}$. The SiO$_2$ films were annealed in H$_2$/N$_2$, while the Al$_2$O$_3$ and SiO$_2$/Al$_2$O$_3$ stacks were annealed in N$_2$.

<table>
<thead>
<tr>
<th>Layer(s)</th>
<th>$k$</th>
<th>$V_{FB}$</th>
<th>$Q_{ef}$ (cm$^{-2}$)</th>
<th>$Q_{neg}$ (cm$^{-2}$)</th>
<th>$D_n$ (eV$^{-1}$ cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 nm SiO$_2$</td>
<td>4.7</td>
<td>−1.26</td>
<td>$+6 \times 10^{11}$</td>
<td>−</td>
<td>$2 \times 10^{12}$</td>
</tr>
<tr>
<td>12.5 nm SiO$_2$</td>
<td>5.7</td>
<td>−1.45</td>
<td>$+8 \times 10^{11}$</td>
<td>−</td>
<td>$1 \times 10^{12}$</td>
</tr>
<tr>
<td>30 nm SiO$_2$</td>
<td>6.1</td>
<td>−1.86</td>
<td>$+8 \times 10^{11}$</td>
<td>−</td>
<td>$1 \times 10^{12}$</td>
</tr>
<tr>
<td>30 nm Al$_2$O$_3$ on Si (ref.)</td>
<td>8.0</td>
<td>2.5</td>
<td>$-5.8 \times 10^{12}$</td>
<td>$-3.6 \times 10^{12}$</td>
<td>$9 \times 10^{10}$</td>
</tr>
<tr>
<td>1 nm SiO$_2$/30 nm Al$_2$O$_3$</td>
<td>8.0</td>
<td>0.83</td>
<td>$-2.6 \times 10^{12}$</td>
<td>$3 \times 10^{11}$</td>
<td>$5 \times 10^{10}$</td>
</tr>
<tr>
<td>2.5 nm SiO$_2$/50 nm Al$_2$O$_3$</td>
<td>7.2</td>
<td>0.63</td>
<td>$-2.0 \times 10^{12}$</td>
<td>$-3.3 \times 10^{12}$</td>
<td>$4 \times 10^{10}$</td>
</tr>
<tr>
<td>12.5 nm SiO$_2$/50 nm Al$_2$O$_3$</td>
<td>6.8</td>
<td>0.69</td>
<td>$-4 \times 10^{11}$</td>
<td>$-1.9 \times 10^{11}$</td>
<td>$4 \times 10^{10}$</td>
</tr>
<tr>
<td>30 nm SiO$_2$/30 nm Al$_2$O$_3$</td>
<td>5.8</td>
<td>−2.2</td>
<td>$+6 \times 10^{11}$</td>
<td>$-4 \times 10^{11}$</td>
<td>$1 \times 10^{11}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Using Eq. 4, using $Q_{pos} = 8 \times 10^{11} \text{cm}^{-2}$

− not applicable.
a film would lead to a nonlinear thickness dependence. For ALD SiO$_2$, relatively small $V_{FB}$ values were observed with corresponding positive $Q_f$ values in the range of 6–8 x 10$^{11}$ cm$^{-2}$ (Table II). The fact that no hysteresis was observed in the C-V characteristics indicates that the $V_{FB}$ shifts were not caused by mobile charges. The presence of positive fixed charges is well-known for SiO$_2$ deposited at low temperatures, and has for instance been reported for PECVD and ALD SiO$_2$ films.14,20,46 This is in contrast to thermally-grown oxides for which the charge density is typically much lower, unless the films have been exposed to significant UV irradiation or electrical stressing.1,46 The microscopic origin of the positive charges is not unambiguous as it depends on the nature of the oxide and the post-treatments. One defect that can be responsible for positive charges is the so-called E’-center (Si atom backbonded by 3 O atoms).14 However, for PECVD SiO$_2$, Buchanan et al. have provided evidence that another (unknown) type of defect, also within tunneling distance (i.e. < 5 nm) of the Si substrate, is more likely to be responsible for the fixed charges.46 It has also been hypothesized that H may be involved in the generation of the positive charges.20,47

Fixed charges in SiO$_2$/Al$_2$O$_3$ stacks.— In contrast to the single layers, large positive $V_{FB}$ values were observed for the SiO$_2$/Al$_2$O$_3$ stacks comprising thin SiO$_2$ interlayers (thickness of 1 and 2.5 nm) and for a single layer ALD Al$_2$O$_3$ reference sample deposited directly on H-terminated Si (Table II). These $V_{FB}$ values indicate the presence of a significant amount of net negative charge. When we apply the model of Eq. 3, we find a decreasing negative $Q_f$ for increasing SiO$_2$ thickness (Table II). For the thickest SiO$_2$ interlayer of 30 nm, a negative $V_{FB}$ is found corresponding to a net positive $Q_f$ of $+6 \times 10^{11}$ cm$^{-2}$ when assuming that all charges are located at the Si/SiO$_2$ interface. However, the latter assumption is not realistic for the stacks. To further interpret the $V_{FB}$ values in terms of fixed charges, we can also consider the influence of multiple charge contributions. It is well known that the negative charges associated with Al$_2$O$_3$ are mainly located near the Si/SiO$_2$ interface.48 The negative charges will shift away from the Si interface when using SiO$_2$ interlayers between Si and Al$_2$O$_3$. In addition, positive charges associated with SiO$_2$ need to be taken into account. The latter can also be directly appreciated from the stack with a 30 nm interlayer. Therefore, in addition to the relation given in (3), an alternative, more complex model can be introduced which accounts for a positive charge contribution $Q_{pos}$ at the Si/SiO$_2$ interface and a negative charge contribution $Q_{neg}$ at the SiO$_2$/Al$_2$O$_3$ interface,49,51

\[
Q_f = \left( \frac{d_{SiO_2}}{\varepsilon_{SiO_2}} \right) (Q_{pos} + Q_{neg}) + \left( \frac{d_{Al_2O_3}}{\varepsilon_{Al_2O_3}} \right)
\]

\[
= -\frac{(V_{FB} - \phi_{ms})}{q}
\]

For simplicity, we consider $d_{Al_2O_3}$ to be the nominal ALD SiO$_2$ thickness as determined by SE. In order to obtain an estimate of $Q_{neg}$ using Eq. 4, a value for $Q_{pos}$ of $+8 \times 10^{11}$ cm$^{-2}$ may be appropriate, i.e. the value obtained for thick SiO$_2$ films without capping layer. In addition, in contrast to Eq. 3, we cannot use the experimentally determined values for $\varepsilon_{SiO_2}$ in Eq. 4. Therefore, we consider $\varepsilon_{SiO_2}$ and $k_{Al_2O_3}$ to be constant, with values of 5.5 and 8, respectively. Using these values, it is found from the analysis that $Q_{neg}$ decreases with increasing SiO$_2$ interlayer thickness from $\sim$6 x 10$^{-12}$ cm$^{-2}$ (no ALD SiO$_2$) to $\sim$4 x 10$^{11}$ cm$^{-2}$ (30 nm SiO$_2$). Note that the latter value (and its polarity) should be interpreted with care as this value significantly depends on the accuracy of the substituted value for $Q_{pos}$. However, as expected, models (3) and (4) lead to the same main conclusion that the negative charge density associated with Al$_2$O$_3$ is strongly reduced for thicker SiO$_2$ interlayers. Moreover, for sufficiently thick SiO$_2$ films the fixed positive charges play a more dominant role.

In general, these considerations are in good agreement with a recent study by Wolf et al. using CV measurements.52 In addition, the results are in line with a recent study using optical second-harmonic generation (SHG) experiments.15 The SHG measurements are sensitive to electric fields induced in the space charge region below the Si surface caused by the fixed charges present in the passivation scheme.15,48 It was found that the induced electric field strongly decreased for increasing SiO$_2$ interlayers and vanished for a SiO$_2$ interlayer thickness of $\sim$5 nm. However, a small net positive charge density was determined by SHG for an interlayer thickness of 12.5 nm while the C-V results suggested a small, but negative $Q_f$ for this stack. These observations may be related to the fact that SHG is a fundamentally different measurement technique. For example, SHG is a non-contacting and non-intrusive technique, while the C-V measurements obviously require the application of metal contacts. The latter may influence directly or indirectly the fixed charges in the stack. For example, the exact value for $\phi_{ms}$ may slightly depend on the dielectric below (i.e. SiO$_2$ or Al$_2$O$_3$).47

The strong dependency of $Q_{pos}$ on the SiO$_2$ thickness may point to a role of charge injection from the Si substrate in defect states at the remote SiO$_2$/Al$_2$O$_3$ interface during annealing.13 The SiO$_2$ interlayer could serve as a barrier for charge injection and affect the formation of negative charges accordingly. As discussed in Ref. 15, the changes in net fixed charge density and associated field-effect passivation had a significant impact on the level of passivation but also on the injection level dependence of the effective lifetime.

Interface defect density.— The interface defect density was determined from the frequency dispersion in the C-V data.29 The difference in the high and low frequency C-V characteristics corresponding to the ALD SiO$_2$ films is indicative of the presence of a significant amount of electronically active interface defects (Fig. 12a). Relatively high $D_{it}$ values of $\sim$10$^{12}$ cm$^{-2}$ eV$^{-1}$ were obtained for single layer ALD SiO$_2$ films after forming gas annealing (Table II). This is consistent with the relatively high $S_{it}$ values that were measured for similar samples, especially after annealing (inset Fig. 11). In strong contrast, ultralow $D_{it}$ values were obtained for SiO$_2$/Al$_2$O$_3$ stacks, with $D_{it} < 10^{11}$ cm$^{-2}$ eV$^{-1}$. In addition, the data did not reveal a clear relation between $D_{it}$ and the SiO$_2$ film thickness (1–30 nm). Therefore, the stacks induced a high level of chemical passivation regardless of SiO$_2$ thickness. The low defect densities can be related to the effective hydrogenation of the interface under influence of hydrogen from the Al$_2$O$_3$ capping film.53 During annealing, the prominent $P_s$-type defects (Si dangling bond) at the Si/SiO$_2$ interface are effectively passivated by hydrogen. From the data in Table II, it can be concluded that the use of an Al$_2$O$_3$ capping layer leads to a significantly higher interface quality than obtained by annealing the ALD SiO$_2$ films in forming gas.

Conclusions

A plasma-assisted ALD process for SiO$_2$ has been developed employing $H_2$Si[N(C$_3$H$_5$)$_2$]$_3$ as Si precursor in combination with an O$_2$ plasma as the oxidant. It was demonstrated that the ALD process is suited for the low-temperature synthesis of high-quality SiO$_2$ films with the material properties being relatively insensitive to the substrate temperature in the range of 100 – 300 C. The ALD process combined comparatively high growth rates (0.8 – 1.7 Å/cycle) with relatively short dosing and purge times. Moreover, the plasma-assisted ALD process led to good conformality for trenches with an aspect ratio of $\sim$30, even for relatively short plasma exposure times of 4.5s.

Regarding the electronic properties, the interface defect density was relatively high ($\sim$10$^{12}$ cm$^{-2}$ eV$^{-1}$, after ageing) for single layer ALD SiO$_2$. The application of an Al$_2$O$_3$ capping layer in conjunction with a low-temperature anneal led to a dramatic improvement in the interface quality with $D_{it} < 10^{11}$ cm$^{-2}$ eV$^{-1}$. Corresponding ultralow surface recombination velocities $< 3$ cm/s were measured for these stacks. The thickness of the SiO$_2$ interlayer was found to control the fixed charge density associated with the SiO$_2$/Al$_2$O$_3$ stacks. A transition from a high negative net charge density to a relatively low positive net charge density was observed.

These results may have implications for a wide range of existing and future applications in which the thickness control and
conformality of the ALD SiO2 films are critical factors. Moreover, the ALD SiO2 nanolayers can be applied in effective surface passivation schemes for future high-efficiency silicon solar cells.

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