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On the c-Si surface passivation mechanism by the negative-charge-dielectric Al₂O₃

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Al₂O₃ is a versatile high-κ dielectric that has excellent surface passivation properties on crystalline Si (c-Si), which are of vital importance for devices such as light emitting diodes and high-efficiency solar cells. We demonstrate both experimentally and by simulations that the surface passivation can be related to a satisfactory low interface defect density in combination with a strong field-effect passivation induced by a negative fixed charge density \(Q_f\) of up to \(10^{13}\) cm\(^{-2}\) present in the Al₂O₃ film at the interface with the underlying Si substrate. The negative polarity of \(Q_f\) in Al₂O₃ is especially beneficial for the passivation of p-type c-Si as the bulk minority carriers are shielded from the c-Si surface. As the level of field-effect passivation is shown to scale with \(Q_f^2\), the high \(Q_f\) in Al₂O₃ tolerates a higher interface defect density on c-Si compared to alternative surface passivation schemes. © 2008 American Institute of Physics. [DOI: 10.1063/1.3021091]

I. INTRODUCTION

An excellent electrical interface quality is essential for many devices relying on the bulk electronic properties of semiconductors.\(^4\) Electrical losses at a semiconductor interface or surface should be minimized in photonic devices based on group III-V or group IV semiconductors when radiative recombination should be the dominant process.\(^2,3\) In complementary metal-oxide-semiconductor (CMOS) devices, the channel is in direct contact with the interface between the gate dielectric and the semiconductor, and therefore interface defect trapping should be minimized.\(^4\) Moreover, electronic losses at the crystalline Si (c-Si) surface have become increasingly important in the field of c-Si solar cells due to the trend toward thinner c-Si wafers used as base material.\(^5\) Consequently, the reduction of recombination losses at semiconductor interfaces is a prime concern for numerous semiconductor applications.

Recombination losses at a semiconductor interface or surface can be reduced by two different passivation strategies. As the recombination rate is directly proportional to the interface defect density, the first strategy is based on the reduction in the number of defect states at the interface. The interface defect density can be reduced significantly by the passivation of undercoordinated atoms (dangling bonds) by, e.g., atomic H or by a thin dielectric or semiconductor film. This strategy is commonly referred to as chemical passivation. For example, the midgap interface defect density of c-Si can be as low as \(1 \times 10^{7}\) eV\(^{-1}\) cm\(^{-2}\) after the growth of a high quality thermal SiO₂ film and a subsequent anneal in a H₂ atmosphere, e.g., a forming gas anneal.\(^6\)

The second strategy to reach surface passivation is based on a significant reduction of the electron or hole concentration at the semiconductor interface by means of a built-in electric field. As recombination processes require both electrons and holes, the highest recombination rate is obtained when the electron and hole concentration at the interface are approximately equal in magnitude (assuming identical capture cross sections for electrons and holes). In other cases the recombination rate scales with the minority carrier concentration at the surface. In the so-called field-effect passivation, the electron or hole concentration at the semiconductor interface is altered by electrostatic shielding of the charge carriers through an internal electric field present at the interface. This internal electric field can either be obtained by a doping profile below the interface or by the presence of fixed electrical charges at the semiconductor interface. Obviously, the principle of field-effect passivation does not apply for CMOS devices such as field effect transistors. A high fixed charge density is even deleterious for the transistor performance as it influences the threshold voltage and the transport of electron and holes in the semiconductor channel.\(^4,7\) Consequently, the application areas of field-effect passivation are limited but the effect can be employed successfully in devices such as light emitting diodes and solar cells.

Recently it was demonstrated that amorphous Al₂O₃ films synthesized by atomic layer deposition (ALD) yield an excellent level of surface passivation on c-Si.\(^8-13\) In our previous work, a similar level of surface passivation as state-of-the-art thermal SiO₂ was demonstrated on low resistivity n- and p-type c-Si,\(^9\) whereas highly doped p-type Si surfaces were found to be even more effectively passivated by Al₂O₃ than by thermal SiO₂.\(^10\) Remarkably, the Al₂O₃ films, synthesized by plasma-assisted ALD at a substrate temperature of 200 °C, demonstrated no significant level of surface passivation in the as-deposited state.\(^9,10\) A 30 min postdeposition anneal at 425 °C in N₂ was required to obtain the level of surface passivation reported. A nonspecified thermal treatment was also required for an optimal level of surface passivation in the study of Agostinelli et al. for Al₂O₃ films

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The effective lifetime of a 1.9 Ω cm n-type c-Si wafer passivated on both sides by a 26 nm thick Al2O3 film is presented as a function of the positive charge density $Q_{f}$, deposited on the Al2O3 on one side of the wafer in a corona charging experiment. Field-effect passivation is ruled by the sum of the negative fixed charge density $Q_{f}$ in the Al2O3 film and the positive $Q_{surface}$. The effective lifetime was determined at an injection level of $10^{14}-10^{15}$ cm$^{-3}$.

The effective lifetime of a 1.9 Ω cm n-type c-Si wafer passivated on both sides by a 26 nm thick Al2O3 film synthesized by plasma-assisted ALD is presented. The effective lifetime is ruled by the sum of the negative fixed charge density $Q_{f}$ in the Al2O3 film and the positive $Q_{surface}$. The effective lifetime was determined at an injection level of $10^{14}-10^{15}$ cm$^{-3}$.

Synthesized by thermal ALD. The excellent level of surface passivation that can be achieved by ALD-synthesized Al2O3 films was recently also confirmed at the device level. Al2O3 applied at the rear of a diffused emitter p-type c-Si solar cells yielded a conversion efficiency of 20.6%, and Al2O3 applied at the front side p-type emitter of n-type solar cells yielded a conversion efficiency of 23.2%.

In this paper, we will address the underlying mechanism of c-Si surface passivation as obtained by amorphous Al2O3 films. From results obtained on Al2O3 films synthesized by plasma-assisted ALD, it will be demonstrated that in addition to a satisfactory low interface defect density, the surface passivation is ruled for a large part by a strong field-effect passivation induced by a relatively high negative fixed charge density $Q_{f}$ in the Al2O3 film. On the basis of simulations, it will be discussed that the field-effect passivation scales with $Q_{f}$ and, consequently, the high $Q_{f}$ in Al2O3 tolerates a higher interface defect density than other passivation films with lower $Q_{f}$ values. It will be shown that the postdeposition anneal increases the negative $Q_{f}$ and lowers the interface defect density of the Si/SiO2/Al2O3 system resulting in a significant improvement of the level of surface passivation. The presence of an interfacial SiO2 film between c-Si and the Al2O3 appears to play a key role in both the origin of the negative $Q_{f}$ and the interface defect density. As a negative $Q_{f}$ in combination with a sufficiently low interface defect density is routinely reported for Al2O3 films deposited on c-Si, irrespective of the deposition technique, it is argued that the findings presented in this paper are not limited to Al2O3 films synthesized by (plasma-assisted) ALD.

II. Al2O3 AS NEGATIVE CHARGE DIELECTRIC

The field-effect passivation of c-Si by Al2O3 is experimentally demonstrated in Fig. 1. A high quality 1.9 Ω cm n-type c-Si wafer with a thickness of 275 μm was passivated on both sides by a 26 nm thick Al2O3 film synthesized by plasma-assisted ALD. The resulting effective lifetime of the passivated c-Si wafer exceeds 6 ms indicating that the c-Si surfaces are adequately passivated by Al2O3. Subsequently a positive charge density $Q_{surface}$ is applied at the Al2O3 surface in a corona charging experiment. In this case, the field-effect passivation is ruled by the sum of $Q_{f}$ and $Q_{surface}$. From the figure, it is clear that a positive $Q_{surface}$ up to $10^{13}$ cm$^{-2}$ hardly affects the effective lifetime of the c-Si wafer. However, a positive $Q_{surface}$ in the range of $(1.2-1.4) \times 10^{-13}$ cm$^{-2}$ leads to a strong decrease in the effective lifetime. A minimum effective lifetime of ~100 μs is obtained for a positive $Q_{surface}$ of $1.3 \times 10^{13}$ cm$^{-2}$. At this stage, the positive $Q_{surface}$ balances the negative $Q_{f}$ in the Al2O3 film, which nullifies the level of field-effect passivation. For a positive $Q_{surface}$ exceeding the amount of negative $Q_{f}$ [ $Q_{surface}$ in the range of $(1.3-2.0) \times 10^{13}$ cm$^{-2}$ ] field-effect passivation is provided by the positive charge density at the c-Si surface. Summarizing, Fig. 1 clearly demonstrates the mechanism of field-effect passivation on c-Si, and it reveals that the negative $Q_{f}$ in this 26 nm thick Al2O3 film is $(1.3 \pm 0.1) \times 10^{13}$ cm$^{-2}$.

Al2O3 has extensively been investigated for the application as gate and charge trapping dielectric on c-Si where also high negative $Q_{f}$ values have been reported. For gate dielectric applications in CMOS, a low interface defect density and a low $Q_{f}$ are essential, whereas a low interface defect density in combination with a high density of electronically active bulk defects is desired for charge trapping dielectrics such as applied in nonvolatile memory. Table I summarizes the bulk and interface electronic properties reported in the literature for Al2O3 films deposited on c-Si by various techniques. The sign of $Q_{f}$ is always negative for the Al2O3 films after annealing, irrespective of the deposition technique. The magnitude of $Q_{f}$ is typically in the range of $10^{12}-10^{13}$ cm$^{-2}$ for annealed Al2O3 films, in good agreement with our results in Fig. 1. From thickness dependent capacitance-voltage measurements, it was deduced that the negative $Q_{f}$ is independent of the Al2O3 thickness and is located at the interface with the substrate.

It is interesting to note that negative fixed charges are detected in Al2O3 films deposited on H-terminated c-Si as well as Al2O3 films deposited on c-Si covered by a 1–100 nm thick SiO2 film. Despite the fact that Al2O3 is thermodynamically stable on c-Si, Al2O3 deposition processes occur under nonequilibrium conditions, and as a result an interfacial SiO2 layer is commonly formed between the Al2O3 film and the c-Si substrate. This SiO2 layer can be formed during the Al2O3 deposition process but also during the postdeposition annealing treatment. The unintentional formation of an interfacial SiO2 is undesired for the application of Al2O3 as gate dielectric in CMOS devices as it lowers the effective dielectric constant of the layer stack. Nevertheless, only a very limited number of studies (e.g., in the work of Gusev et al.) report on the absence of an interfacial SiO2 layer between the Al2O3 film and c-Si substrate. An interfacial SiO2 film was also detected by high resolution transmission electron microscopy (HR-TEM) in the Al2O3 films synthesized by plasma-assisted ALD, both in the as-deposited and annealed state, that demonstrated an excellent level of surface passivation on c-Si.
TABLE I. Bulk and interface electronic properties for Al2O3 films deposited on c-Si as reported in the literature. All films were deposited on H-terminated c-Si unless indicated otherwise. In all cases, $Q_f$ was extracted from the flatband voltage shift determined from capacitance-voltage (CV) measurements of MOS structures. The interface defect density was extracted from CV and/or conductance measurements of MOS structures. Most samples were analyzed after a postdeposition anneal, however, some samples were also measured as-deposited (indicated with “a–d”).

<table>
<thead>
<tr>
<th>Negative $Q_f$</th>
<th>$D_s$ at midgap</th>
<th>Deposition method</th>
<th>Deposition temperature</th>
<th>Postdeposition thermal treatment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^{13} cm^{-2})</td>
<td>(10^{11} eV^{-1} cm^{-2})</td>
<td></td>
<td>(°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2–0.5</td>
<td>...</td>
<td>Pyrolysis of Al(C,H,O) on c-Si</td>
<td>425</td>
<td>30 min FGA at 425 °C</td>
<td>17</td>
</tr>
<tr>
<td>0.2–0.5</td>
<td>...</td>
<td>CVD from AlBr3 + NO on c-Si</td>
<td>910</td>
<td>30 min FGA at 425 °C</td>
<td>17</td>
</tr>
<tr>
<td>3.2</td>
<td>0.8</td>
<td>Pyrolysis of AlCl3 in CO2/H2 environment</td>
<td>360</td>
<td>15 min FGA at 510 °C</td>
<td>39</td>
</tr>
<tr>
<td>10–11</td>
<td>(a–d)</td>
<td>Oxidation of evaporated Al</td>
<td>&lt;400</td>
<td>Various at 585 °C and 800 °C</td>
<td>49</td>
</tr>
<tr>
<td>0.6</td>
<td>(a–d)</td>
<td>ALD from Al(CH3)3 + H2O</td>
<td>450</td>
<td>None</td>
<td>48</td>
</tr>
<tr>
<td>0–2</td>
<td>0.8</td>
<td>ALD from Al(CH3)3 and H2O</td>
<td>350</td>
<td>Various at 585 °C and 800 °C</td>
<td>49</td>
</tr>
<tr>
<td>...</td>
<td>0.3</td>
<td>Oxidation of evaporated Al</td>
<td>800 °C in N2</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>1–3</td>
<td>ALD from AlCl3 and H2O</td>
<td>370</td>
<td>None</td>
<td>19</td>
</tr>
<tr>
<td>7 (a–d)</td>
<td>13 (a–d)</td>
<td>ALD from Al(CH3)3 and O3</td>
<td>350</td>
<td>FGA at 300–450 °C and anneal in N2 at 450 °C</td>
<td>46</td>
</tr>
<tr>
<td>6–7</td>
<td>1</td>
<td>ALD from Al(CH3)3 and H2O</td>
<td>380</td>
<td>FGA</td>
<td>51</td>
</tr>
<tr>
<td>5–10 (a–d)</td>
<td>2–5</td>
<td>Reactive target sputtering in Ar/O2</td>
<td>300–800</td>
<td>None</td>
<td>52</td>
</tr>
<tr>
<td>...</td>
<td>2–10 (a–d)</td>
<td>ALD from AlCl3 and H2O</td>
<td>300–800</td>
<td>None</td>
<td>52</td>
</tr>
<tr>
<td>...</td>
<td>20</td>
<td>ALD from Al(CH3)3 and H2O</td>
<td>300</td>
<td>30 min FGA at 400 °C</td>
<td>53</td>
</tr>
<tr>
<td>13 (a–d)</td>
<td>6</td>
<td>ALD from Al(CH3)3 and O3</td>
<td>400</td>
<td>None or 10 min at 800 °C in N2</td>
<td>54</td>
</tr>
<tr>
<td>3–9</td>
<td>...</td>
<td>Molecular beam epitaxy from Al and N2O on c-Si with an interfacial layer</td>
<td>750</td>
<td>None or anneal at 600 °C</td>
<td>55</td>
</tr>
<tr>
<td>3–8 (a–d)</td>
<td>7</td>
<td>ALD from Al(CH3)3 and H2O</td>
<td>160–350</td>
<td>None</td>
<td>56</td>
</tr>
<tr>
<td>Up to 10</td>
<td>...</td>
<td>ALD from Al(CH3)3 and H2O</td>
<td>&lt;300</td>
<td>Yes, not specified</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>...</td>
<td>Remote plasma enhanced CVD from metal organic and O on c-Si</td>
<td>300</td>
<td>30 min FGA at 425 °C</td>
<td>18</td>
</tr>
<tr>
<td>0.2–2 (a–d)</td>
<td>5–8</td>
<td>ALD from Al(CH3)3 and O2 plasma</td>
<td>200</td>
<td>30 min anneal at 425 °C</td>
<td>44</td>
</tr>
</tbody>
</table>

*a*Forming gas anneal, typically 5%–10% H2 in N2.

*b*The pretreatment of the c-Si wafer was not specified.

*c*The defect density could be lowered by the addition of Zr or Si in the Al2O3 to values in the mid 10^{10} eV^{-1} cm^{-2} range.

*d*The Al2O3 films were grown under UV radiation.

*e*The Al2O3 film was covered with a HfO2 film.

*f*Polycrystalline Al2O3 was grown in this study due to epitaxy process.

*g*Four-coordinate Al was found in a ratio of 3:1 to assure charge neutrality.

The origin of the negative $Q_f$ in Al2O3 deposited on c-Si has been attributed to intrinsic and extrinsic defects in Al2O3. Matsunaga et al. calculated the energetics of intrinsic vacancies and interstitials in Al2O3 from first principles. These calculations showed that each intrinsic point defect is most stable in their fully ionized form. Hence, Al vacancies and O interstitials exhibit a negative charge and Al interstitials and O vacancies exhibit a positive charge in good agreement with the ionic nature of the Al2O3. Extrinsic H has also been proposed as origin for the negative fixed charges in Al2O3. Peacock and Robertson calculated that interstitial H acts as a deep trap site for electrons in Al2O3. H is, for example, a common constituent in Al2O3 synthesized by ALD because H-containing precursors such as Al(CH3)3 and H2O are used in the deposition process. Hence, Al vacancies, O interstitials, and interstitial H are proposed as the origin of the negative $Q_f$ in Al2O3. Based on the ionic nature of Al2O3, Lucovský postulated that Al2O3 consists of tetrahedrally coordinated Al in AlO4 units and octahedrally coordinated Al3+ in a ratio of 3:1 to assure charge neutrality. Kimoto et al. demonstrated that both tetrahedrally and octahedrally coordinated Al are present in Al2O3 grown by thermal ALD on H-terminated c-Si. However, tetrahedrally coordinated Al was found to be dominant at the interface. This dominance was attributed to the fact that Si in the interfacial SiO2 film also has a tetrahedral coordination. Consequently, the interfacial SiO2 film could fulfill an important role in the origin of the negative $Q_f$ that is found in Al2O3 films grown on c-Si by inducing a high density of negatively charged Al vacancies close to the interface. This hypothesis is in good agreement with the location of the negative $Q_f$ extracted from thickness dependent CV measurements by various authors.
highly doped n-type c-Si surfaces. A positive $Q_f$ has, however, been shown to be detrimental for the passivation of highly p-type surfaces such as in p-type emitters on n-type solar cells because the minority electrons are attracted to the c-Si surface and thereby enhance the recombination rate. Positive-charge dielectrics also demonstrate a strong injection level dependence for the surface passivation properties on lightly doped p-type c-Si. The level of surface passivation decreases when going to lower excess carrier concentrations (i.e., lower injection levels), which is, for example, detrimental for the c-Si solar cell efficiency under low illumination conditions. This injection level dependence is attributed to additional bulk recombination losses in the inversion layer close to the c-Si surface. Hence, a similar bulk passivation decreases when going to lower injection level, whereas positive-charge dielectrics demonstrate a constant level of surface passivation in this case. Hence, a similar bulk recombination in the inversion layer could explain this injection level behavior of lightly doped n-type c-Si passivated by the negative-charge dielectric Al$_2$O$_3$. Furthermore, the high positive $Q_f$ in a-SiN$_x$:H causes the so-called parasitic shunting effect when applied at the rear of p-type c-Si solar cells and thereby significantly decreases the short-circuit current of c-Si solar cells. This effect is absent when the negative-charge dielectric Al$_2$O$_3$ is used at the rear of diffused front side emitter p-type c-Si solar cells, which has resulted in solar cell efficiencies of 20.6%. The negative charge in Al$_2$O$_3$ is even more important in the passivation of highly doped p-type c-Si surfaces as the shielding of the minority carriers, the electrons, from the surface by the negative charges leads to a much higher level of passivation than positive-charge dielectrics such as thermal SiO$_2$ and as-deposited a-SiN$_x$:H. The latter was recently also demonstrated at the device level by an exceptionally high conversion efficiency of 23.2% obtained for an n-type solar cell with a front side B-doped p-type emitter passivated by a 30 nm thick Al$_2$O$_3$ film.

### III. FIELD EFFECT PASSIVATION VERSUS CHEMICAL PASSIVATION

It is evident that besides the polarity of the fixed charge, the amount of fixed charge is also important for field-effect passivation. Figure 2 shows the effective surface recombination velocity $S_{\text{eff}}$ at an injection level of $5 \times 10^{14}$ cm$^{-3}$ (corresponding to approximately 1 sun illumination) as a function of the negative $Q_f$ located at the surface for moderately doped n-type ([P]=7×10$^{15}$ cm$^{-3}$) and p-type ([B]=7×10$^{15}$ cm$^{-3}$) c-Si. The simulations were performed using the extended Shockley–Read–Hall model as proposed by Girisch et al. The fundamental recombination velocities of the electrons and holes were taken to be energy independent and equal to 100 cm/s. Figure 2 clearly shows that a negative $Q_f$ decreases the $S_{\text{eff}}$ at a p-type c-Si surface. On the other hand, Fig. 2 demonstrates that a relatively small negative $Q_f$ up to $5 \times 10^{10}$ cm$^{-2}$ increases the $S_{\text{eff}}$ for moderately doped n-type c-Si. For higher negative $Q_f$ values, the $S_{\text{eff}}$ decreases for n-type c-Si, and for a negative $Q_f$ of $3 \times 10^{11}$ cm$^{-2}$ the $S_{\text{eff}}$ is practically equal for n- and p-type c-Si. As already mentioned, the surface recombination rate is proportional to the minority carrier concentration at the surface. For a negative $Q_f$, in the range of $5 \times 10^{10} \text{–} 1 \times 10^{13}$ cm$^{-2}$, electrons are still the minority carrier at the c-Si surface and the hole concentration, hence the recombination, is increased by electrostatic interaction by the presence of the negative charge at the surface. A similar effect can be observed for p-type c-Si passivated by positive charge dielectrics as was shown by Aberle et al. For negative $Q_f$ of $5 \times 10^{11}$ cm$^{-2}$, $S_{\text{eff}}$ scales with $1/Q_f^2$ for both n- and p-type c-Si. This is in good agreement with the results reported by Kuhlmann et al. for inverted p-type c-Si surfaces.

The $Q_f$ dependence of the field-effect passivation allows us to compare the relative strength of field-effect passivation by Al$_2$O$_3$ and other charge containing dielectrics used for c-Si surface passivation. For thermal SiO$_2$ and a-SiC$_x$:H, a relatively low positive $Q_f$ around $10^{11}$ cm$^{-2}$ on p-type c-Si is commonly reported, whereas for a-SiN$_x$:H, a positive $Q_f$ in the range of $10^{12}$ cm$^{-2}$ is typically found. Consequently, the field-effect passivation provided by Al$_2$O$_3$ is up to four orders of magnitude stronger compared to thermal SiO$_2$ and a-SiC$_x$:H and up to two orders of magnitude stronger compared to a-SiN$_x$:H.

Besides field-effect passivation, chemical passivation also reduces the recombination losses at c-Si surfaces. For example, the state-of-the-art surface passivation by thermal SiO$_2$ can mainly be attributed to chemical passivation due to its extremely low interface defect density. A strong field-effect passivation as in the case of Al$_2$O$_3$, however, relaxes...
the requirements on the interface defect density. Using the $Q_f^2$ scaling of the field-effect passivation, we can estimate the relative importance of the chemical passivation for $\text{Al}_2\text{O}_3$ compared to thermal SiO$_2$ for lightly doped c-Si. Assuming similar electron and hole capture cross sections for the dominant defects, the midgap defect density at the c-Si surface is allowed to be as high as $10^{13}$ eV$^{-1}$ cm$^{-2}$ to yield a similar level of surface passivation compared to thermal SiO$_2$ with a midgap interface defect density of $10^9$ eV$^{-1}$ cm$^{-2}$. However, from Fig. 1, it can be concluded that the $\text{Al}_2\text{O}_3$ film with the interfacial SiO$_2$ film also provides a good level of chemical passivation because the effective lifetime is still relative high at $\sim$100 $\mu$s when the negative $Q_f$ in the $\text{Al}_2\text{O}_3$ film is balanced (for a poorly passivated surface the effective lifetime would only be $\sim$5 $\mu$s). Hence, the interface defect density between the $\text{Al}_2\text{O}_3$/SiO$_2$ film and the c-Si substrate is expected to be reasonably low. As can be seen in Table I, typically interface defect densities in the range of $10^{11}$ eV$^{-1}$ cm$^{-2}$ have been reported for annealed $\text{Al}_2\text{O}_3$ films on c-Si, which is up to two orders of magnitude higher compared to thermal SiO$_2$. Similar to thermal SiO$_2$, the lowest interface defect density is obtained by postdeposition annealing treatments, either an anneal in a H$_2$ containing atmosphere in the 300–500 °C temperature range or a short high temperature anneal in N$_2$ below the crystallization temperature of $\text{Al}_2\text{O}_3$. Moreover, the interface defect density of dielectrics on c-Si has empirically been related to the average bonding concentration at the interface by Lucovsky et al. Dielectrics with an average bonding concentration above 3 would exhibit a high interface defect density and vice versa.

As the average bonding concentration of $\text{Al}_2\text{O}_3$ is 3.6, the interface defect density at the c-Si surface could be significantly lowered by the presence of a thin SiO$_2$-like film between the c-Si and the $\text{Al}_2\text{O}_3$ because SiO$_2$ has an average bonding density of 2.8. The interface defect density is also of relevance due to the fact that interface defect states can trap charges and thereby could potentially cancel part of the field-effect passivation provided by the $Q_f$ in the passivation film. The influence of the charging of interface defects on the surface passivation of a-Si:H on c-Si has been reported by Garin et al. and Obilet et al. Nevertheless, the effect of trapped charges becomes only of significance when the interface defect density is of the same order as $Q_f$. Hence, for $\text{Al}_2\text{O}_3$ on c-Si, it is not expected that this effect can be significant because the defect densities are typically at least one order of magnitude lower than the magnitude of the negative $Q_f$ in the film (see Table I).

As mentioned, $\text{Al}_2\text{O}_3$ synthesized by plasma-assisted ALD provides no significant level of surface passivation of c-Si in the as-deposited state, whereas the level of surface passivation is excellent after a 30 min anneal at 425 °C in N$_2$. This difference in surface passivation performance of the $\text{Al}_2\text{O}_3$ can partly be related to changes in the negative fixed charge density $Q_f$ after annealing. In Fig. 3, the effective lifetime for c-Si wafers is shown for $\text{Al}_2\text{O}_3$ films with a thickness between 6 and 32 nm in the as-deposited and annealed state. The films were deposited on both sides of 275 $\mu$m 1.9 $\Omega$ cm n-type c-Si wafers by plasma-assisted ALD at a substrate temperature of 200 °C. The $Q_f$ in the $\text{Al}_2\text{O}_3$ films was determined by the contactless optical second-harmonic generation technique (as described in detail in a separate publication), and the effective lifetime was determined by the contactless photoconductance technique. The as-deposited $\text{Al}_2\text{O}_3$ films already contain a negative $Q_f$ in the range of $(3–20)\times10^{11}$ cm$^{-2}$ without demonstrating any level of surface passivation as indicated by the low effective lifetime in the range of 3–5 $\mu$s. After annealing, the negative $Q_f$ has increased for all films and is within the range of $(5–8)\times10^{12}$ cm$^{-2}$. The effective lifetime also increases over more than two orders of magnitude and reaches a value of 1.2 ms for c-Si wafer passivated by the 32 nm thick $\text{Al}_2\text{O}_3$ film. Capacitance-voltage (CV) analysis also confirmed the increase in negative $Q_f$ after the postdeposition anneal. It should also be noted that the negative $Q_f$ in the as-deposited 32 nm $\text{Al}_2\text{O}_3$ film of $2\times10^{12}$ cm$^{-2}$ is significantly higher compared to the negative $Q_f$ of $\sim3\times10^{11}$ cm$^{-2}$ that is found in the as-deposited 6 and 11 nm thick $\text{Al}_2\text{O}_3$ films. This is possibly related to the significant longer deposition time of the 32 nm $\text{Al}_2\text{O}_3$ film, which leads to an annealing effect during the deposition process itself. The difference in effective lifetime between the annealed 11 and 32 nm $\text{Al}_2\text{O}_3$ film scales with $Q_f^2$ and can consequently be attributed to a difference in field-effect passivation. On the other hand, the relative low effective lifetime of the c-Si wafer passivated by the annealed 6 nm thick film indicates a lower chemical passivation and consequently a higher interface defect density compared to the annealed 11 and 32 nm thick $\text{Al}_2\text{O}_3$ films.

Using the $Q_f^2$ scaling of the field-effect passivation, it can be argued that the increase in $Q_f$ of the 32 nm $\text{Al}_2\text{O}_3$ film only leads in an increase in the level of field-effect passivation by a factor 16 compared to the $\text{Al}_2\text{O}_3$ film in the as-deposited state, while the effective lifetime actually increases by more than two orders of magnitude. Consequently the important conclusion can be drawn that the postdeposition anneal also improves the chemical passivation of the 32 nm thick $\text{Al}_2\text{O}_3$ film by a reduction of the interface defect density. As a matter of fact, the low effective lifetime in combi-
nation with a relative high fixed charge density of \(2 \times 10^{12} \text{cm}^{-2}\) for the c-Si wafer passivated by the as-deposited 32 nm Al\(_2\)O\(_3\) film clearly demonstrates that chemical passivation plays a very important role in the surface passivation mechanism of the annealed Al\(_2\)O\(_3\) films. The reduction of the interface defect density between the Al\(_2\)O\(_3\) film and the c-Si substrate after the postdeposition annealing treatment was also confirmed by CV measurements, which showed a significant decrease in the parallel conductance. It should be noted that a postdeposition anneal is routinely employed to improve the electrical quality of the interface between c-Si and dielectric films. This was also demonstrated for the c-Si/Al\(_2\)O\(_3\) system in the studies of Hezel and Jaeger and Jeon et al. In both studies, the c-Si/Al\(_2\)O\(_3\) interface defect density was lowered over more than one order of magnitude (down to \(\sim 1 \times 10^{11} \text{eV}^{-1} \text{cm}^{-2}\)) by a postdeposition annealing step similar to the anneal applied to the Al\(_2\)O\(_3\) films in Fig. 3.

Other than changes in the bulk and interface electronic properties, structural changes in the c-Si/Al\(_2\)O\(_3\) system are also commonly reported after a postdeposition anneal. These structural changes are possibly related to the changes in the Al\(_2\)O\(_3\) bulk and interface electronic properties. HR-TEM revealed the presence of an interfacial oxide layer between the amorphous Al\(_2\)O\(_3\) film synthesized by plasma-assisted ALD and the c-Si substrate and this layer slightly increased in thickness from 1.2 nm in the as-deposited state to 1.5 nm after a postdeposition anneal. This interfacial oxide layer consists of SiO\(_x\) and the presence of Si–O bonds is confirmed by infrared absorbance spectra of as-deposited and annealed Al\(_2\)O\(_3\) films, as shown in Fig. 4. Particularly after the postdeposition anneal, the Si–O absorption peak in the infrared absorbance spectrum is very similar to the absorption peak observed for good quality thermal SiO\(_2\). Chowdhuri et al. and Kuse et al. also showed a strong increase in Si–O related absorption by infrared spectroscopy and x-ray photoelectron spectroscopy after annealing ALD-synthesized Al\(_2\)O\(_3\) films on c-Si. As the absorption intensity of both Si–O and Al–O bonds increase after the postdeposition anneal, it can be argued that the increase in interfacial oxide thickness by TEM can mainly be attributed to a restructuring in the interfacial oxide instead of an additional oxidation of the underlying c-Si substrate. As mentioned, the interfacial SiO\(_x\) film could play an important role in the origin of the negative \(Q_f\) in the Al\(_2\)O\(_3\) film, and hence the changes in the Si–O related absorption could correlate with the change in the magnitude of the negative \(Q_f\) in the Al\(_2\)O\(_3\) film. The infrared absorbance spectrum in Fig. 4 also confirms the presence of H in the form of O–H groups in the Al\(_2\)O\(_3\) film. The O–H density decreases after the postdeposition anneal and this decrease coincides with the formation of both Al–O and Si–O bonds. The H atoms released during the anneal can passivate Si dangling bond defects states at the interface as corroborated by an increase in Si–H related absorbance.

IV. CONCLUSIONS

To summarize, it has been demonstrated that the excellent surface passivation of c-Si by Al\(_2\)O\(_3\) films synthesized by plasma-assisted ALD can be explained by a satisfactory low interface defect density in combination with a very high negative \(Q_f\) in the Al\(_2\)O\(_3\) film. As schematically illustrated in Fig. 5, a high negative \(Q_f\) strongly reduces the electron concentration at the c-Si interface by means of electrostatic shielding. The negative charges are localized in the Al\(_2\)O\(_3\) close to the interface with the c-Si substrate that is separated from the Al\(_2\)O\(_3\) through an interfacial SiO\(_x\) layer. The charges most likely originate from Al vacancies resulting from a preferential tetrahedral coordination of Al in the region close to the interfacial SiO\(_x\). The unique negative polarity of \(Q_f\) is especially beneficial for the passivation of p-type c-Si, including p-type emitters on n-type solar cells, as the bulk minority carriers are shielded from the c-Si surface.
When the negative $Q_f$ in the Al$_2$O$_3$ film is balanced by a positive $Q_{\text{surface}}$, still some level of chemical passivation is provided indicating that the interface defect density is also relatively low. The significant improvement in the level of c-Si surface passivation by Al$_2$O$_3$ after a postdeposition anneal can be related to changes in both surface passivating mechanisms, i.e., the negative $Q_f$ can be related to changes in both surface passivating $Q_f$ and Dr. J. Schmidt measurements. Dr. I. Martin noted that relatively low. The significant improvement in the level of surface passivation is supported by OTB Solar.

In the studies of Chin et al., the positive flatband voltage shifts were reported indicating a negative fixed charge density.


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In the studies of Chin et al., (Ref. 50) and Duenas et al. (Ref. 52) also positive flatband voltage shifts were reported indicating a negative fixed charge density.


