Stability of Al2O3 and Al2O3/a-SiNx:H stacks for surface passivation of crystalline silicon

Citation for published version (APA):

DOI:
10.1063/1.3264572

Document status and date:
Published: 01/01/2009

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

Please check the document version of this publication:

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

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

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

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 29. Sep. 2019
Stability of Al₂O₃ and Al₂O₃/a-SiNₓ:H stacks for surface passivation of crystalline silicon

G. Dingemans,¹,a) P. Engelhart,² R. Seguin,² F. Einsele,³ B. Hoex,¹,b) M. C. M. van de Sanden,¹ and W. M. M. Kessels¹,c)
¹Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
²Q-CELLS SE, Sonnenallee 17-21, 06766 Bitterfeld-Wolfen, Germany
³IFE-5, Photovoltaik, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

(Received 26 March 2009; accepted 22 October 2009; published online 4 December 2009)

The thermal and ultraviolet (UV) stability of crystalline silicon (c-Si) surface passivation provided by atomic layer deposited Al₂O₃ was compared with results for thermal SiO₂. For Al₂O₃ and Al₂O₃/a-SiNₓ:H stacks on 2 Ω cm n-type c-Si, ultralow surface recombination velocities of S_eff < 3 cm/s were obtained and the passivation proved sufficiently stable (S_eff < 14 cm/s) against a high temperature “firing” process (>800 °C) used for screen printed c-Si solar cells. Effusion measurements revealed the loss of hydrogen and oxygen during firing through the detection of H₂ and H₂O. Al₂O₃ also demonstrated UV stability with the surface passivation improving during UV irradiation. © 2009 American Institute of Physics. [doi:10.1063/1.3264572]

Al₂O₃ synthesized by atomic layer deposition (ALD) provides a high level of surface passivation for p- and n-type crystalline silicon (c-Si).¹,² The field effect passivation associated with the negative fixed charges near the Al₂O₃/c-Si interface,² proved to be especially beneficial for the passivation of highly doped p-type c-Si, with Al₂O₃ even outperforming thermally grown SiO₂.³ The application of a thin Al₂O₃ film as a front passivation layer on a B-doped emitter has recently led to efficiencies as high as 23.2% for n-type c-Si solar cells.⁴ For the implementation of Al₂O₃-based passivation schemes in high-volume manufacturing of c-Si solar cells, the compatibility of Al₂O₃ with high temperature processing steps becomes a key issue. For example, a good thermal stability against high temperature “firing” processes of metal contacts is required for screen-printed solar cells. Research efforts on various passivation schemes have already shown that optimized a-SiNₓ:H,⁵ a-SiCₓ:H,⁶ SiO₂/a-SiNₓ:H,⁷-⁹ SiO₂/a-SiNₓ:H/SiO₂,¹⁰ and a-Si:H/a-SiNₓ:H,¹¹ generally outperform SiO₂/SiO₂, a-Si:H,¹² and a-Si:H/SiO₂ layers in terms of thermal stability. Also, the stability of the passivation scheme against ultraviolet (UV) irradiation is essential when the material is applied on an illuminated surface. In this communication, the thermal and UV stability of Al₂O₃ and Al₂O₃/a-SiNₓ:H stacks will therefore be addressed on the basis of lifetime spectroscopy experiments. The results will be compared with those obtained for thermal SiO₂, as Al₂O₃ is a potential alternative for solar cell applications where SiO₂ would usually be considered.

The Al₂O₃ films were synthesized by remote plasma ALD by a process that consisted of alternating steps of Al(CH₃)₃ dosing and O₂ plasma oxidation. Two Oxford instruments reactors, the FlexAL™ and the Opal™, were used for deposition at operating pressures of 16 and 150 mTorr and ALD cycle times of 4 and 7 s, respectively. The fact that the optimized Al₂O₃ deposition process for the FlexAL™ was readily adapted and transferred to the newly installed Opal™ reactor without any differences in material and surface passivation properties clearly demonstrates the robustness of the ALD process. Al₂O₃ with a thickness of 30 nm, unless stated otherwise, was deposited on both sides of low resistivity (~2 Ω cm) n- and p-type double-side polished floatzone (100) c-Si wafers, which received a short dip in diluted HF (1%) prior to deposition at a temperature of ~200 °C. The Al₂O₃ passivation was activated by a post-deposition anneal at 425 °C for a 30 min time interval in N₂ environment. The thermal stability of the Al₂O₃ and Al₂O₃/a-SiNₓ:H stacks was tested by carrying out a so-called “firing” process in an industrial beltline furnace, reaching peak temperatures >800 °C for a number of seconds. The same recipe as that for contact firing during solar cell processing was used but without the metal paste applied. The a-SiNₓ:H, in brief SiN, was grown by remote plasma-enhanced chemical vapor deposition at temperatures of ~400 °C. The SiN films, with a thickness of ~70 nm, were optimized for antireflection coating performance. For reference, c-Si wafers were passivated by ~200 nm SiO₂ films grown by a wet thermal process in a tube furnace. When applied, forming gas anneals (FGAs, 10% H₂ in N₂) took place at 400 °C for 30 min. The effective lifetime of the minority carriers (τ_eff) was determined using a Sinton lifetime tester. The upper limit for the surface recombination velocity (S_eff,max) was calculated from τ_eff by assuming an infinite bulk lifetime and is quoted at an injection level of 1 × 10¹⁵ cm⁻³.

The impact of SiN deposition, postdeposition anneal, and firing on the surface passivation by Al₂O₃ is shown for a representative selection of n-type c-Si samples in Table I. Sample D coated with Al₂O₃/SiN exhibits a high lifetime

---

¹Electronic mail: g.dingemans@tue.nl.
²Present address: Solar Energy Research Institute Singapore, National University of Singapore
³Electronic mail: w.m.m.kessels@tue.nl.
>4 ms without any postdeposition anneal. As remote plasma ALD Al2O3 does not provide surface passivation in the as-deposited state, reflected by lifetimes of the order of 1–10 μs, it can be concluded that the thermal budget during subsequent SiN deposition was sufficient to activate the surface passivation by Al2O3. Sample E was annealed after the SiN deposition, and comparable low values of $S_{\text{eff}}$ < 3 cm/s were obtained as for sample D. Samples A and B, which were passivated by Al2O3, exhibit the same level of surface passivation as the Al2O3/SiN coated wafers. These results lead to the conclusion that the deposition of a SiN capping layer does not compromise the quality of the Al2O3 surface passivation, which is in agreement with the excellent performance of solar cells incorporating Al2O3/SiN stacks.13

Subsequently, the samples were exposed to the high temperature firing step. The effective lifetime of sample B (Al2O3) and samples D and E (Al2O3/SiN) decreased during firing, but remained in the millisecond range. The lifetime of sample A remained constant during firing, which could indicate that, for this sample, bulk recombination instead of surface recombination largely determines the effective lifetime. From these observations, we infer that a SiN capping layer does not increase the already good thermal stability of the Al2O3 passivation scheme, which contrasts with observations for $a$-Si:H and SiO2 passivation schemes.5–7,11 Values of $S_{\text{eff,max}} < 14$ cm/s after firing Al2O3 suggest that surface recombination will not be the efficiency limiting step for solar cells that combine Al2O3 passivation and screen printed metalization as recombination in the metalized area will dominate.14 The firing stability of Al2O3 with a metal layer atop however still needs to be investigated.

Sample C, without postdeposition anneal and with a lifetime in the μs-range, demonstrates that the firing process does not activate the Al2O3 surface passivation. Also, a subsequent anneal did not improve the measured lifetime. Annealing after the firing process resulted in a slight decrease of lifetime for samples A and D, whereas some improvement of the surface passivation was observed for samples B and E. Also, a FGA could not significantly improve the level of surface passivation after firing. The observations, as listed in Table I, clearly indicate that the relatively minor decrease in surface passivation by Al2O3 during firing cannot be restored by an additional anneal.

To benchmark the thermal stability of Al2O3, $c$-Si wafers were passivated by SiO2 with subsequent FGA. Figure 1 shows injection level dependent $\tau_{\text{eff}}$ for SiO2 and Al2O3 samples measured before and after firing, and for SiO2 also after a successive FGA after firing. The exceptionally high effective lifetime for the SiO2 passivated sample (with $\tau_{\text{eff}}$ = 3.7 ms and $S_{\text{eff}} < 3.5$ cm/s) decreases due to the firing process to values of ~5 μs, indicating that the surface passivation is completely lost, in agreement with observations by Schultz et al.9 A subsequent FGA can reactivate the surface passivation by SiO2 after firing to some extent ($S_{\text{eff}} < 115$ cm/s). The passivation by SiO2, which is predominantly chemical in nature (passivation of surface defects), can be improved by hydrogenation during annealing.15 The passivation by Al2O3, which is a combination of chemical passivation with a strong field-effect passivation,2 clearly shows a much higher stability against firing. However, the minor decrease in surface passivation could not be improved by hydrogenation during FGA (not shown here). Moreover, the hydrogen released from the SiN capping layer during firing10,15 did also not lead to such an improvement, as concluded from Table I.

Apparently, the Al2O3 surface passivation is affected differently by the firing process than thermal SiO2. Therefore, to gain more insight into the influence of the firing process on the Al2O3 properties, effusion experiments were carried out. In an ultrahigh vacuum quartz tube with a base pressure $< 10^{-7}$ mbar, a $c$-Si wafer double-side coated with 100 nm Al2O3 was heated up to 1000 °C with a constant heating rate of 20 °C/min.16 A quadrupole mass spectrometer detected the hydrogen and other volatile species that desorbed from

### Table I. $\tau_{\text{eff}}$ and corresponding $S_{\text{eff,max}}$ for various ~275 μm thick 2 Ω cm n-type $c$-Si samples passivated by Al2O3 or Al2O3/SiN stacks after the successive processing steps indicated 1–3. A dash means that the process step was not carried out.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_{\text{eff}}$ (ms)</th>
<th>$S_{\text{eff,max}}$ (cm/s)</th>
<th>$\tau_{\text{eff}}$ (ms)</th>
<th>$S_{\text{eff,max}}$ (cm/s)</th>
<th>$\tau_{\text{eff}}$ (ms)</th>
<th>$S_{\text{eff,max}}$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A) Al2O3</td>
<td>1.6</td>
<td>8.6</td>
<td>1.5</td>
<td>9.2</td>
<td>1.0</td>
<td>13.8</td>
</tr>
<tr>
<td>B) Al2O3</td>
<td>5.2</td>
<td>2.6</td>
<td>1.0</td>
<td>13.8</td>
<td>1.5</td>
<td>9.2</td>
</tr>
<tr>
<td>C) Al2O3</td>
<td>–</td>
<td>–</td>
<td>$1 \times 10^{-3}$</td>
<td>$1.4 \times 10^{4}$</td>
<td>$1 \times 10^{-3}$</td>
<td>$1.4 \times 10^{4}$</td>
</tr>
<tr>
<td>D) Al2O3/SiN</td>
<td>–</td>
<td>–</td>
<td>1.0</td>
<td>13.8</td>
<td>0.6</td>
<td>22.9</td>
</tr>
<tr>
<td>E) Al2O3/SiN</td>
<td>5.0</td>
<td>2.8</td>
<td>1.2</td>
<td>11.5</td>
<td>1.7</td>
<td>8.1</td>
</tr>
</tbody>
</table>

*After deposition of the SiN capping layer, this sample revealed $\tau_{\text{eff}}$=4.6 ms ($S_{\text{eff,max}}$=3.0 cm/s).
conclude that the effusion from the Al2O3 films at tempera-
to the Al2O3 bulk by remote plasma ALD. Effusion peaks
were detected through mass 15 and 29. The detection of H2O
of H2 is primarily
due changes of the Al2O3 film that adversely affect the passiva-
tion. Furthermore, hydrogen is depleted from the film pre-
sumably originates from cracking CxHy species that
were detected through mass 15 and 29. The detection of H2O and H2 is consistent with the presence of a significant density of –OH groups in the Al2O3 bulk as confirmed by infrared spectroscopy, Rutherford backscattering spectroscopy, and elastic recoil detection analysis revealing slightly O-rich films (O/Al ratio≈ 1.5–1.6) with a hydrogen concentration of ~3 at. % in the as-deposited Al2O3. From Fig. 2, we conclude that the effusion from the Al2O3 films at temperatures up to 800 °C is dominated by the formation and release of H2O. Apparently, hydrogen in the form of H2 is primarily released from the film at temperature >800 °C. Consequently, during a firing process, the Al2O3 loses both hydrogen and oxygen which indicates significant structural changes of the Al2O3 film that adversely affect the passivation. Furthermore, hydrogen is depleted from the film predominantly in the form of H2O which is different from the dehydrogenation of SiO2/c-Si interface after firing. The depletion of hydrogen from the Al2O3/c-Si interface likely contributes to the decrease of the surface passivation by Al2O3 after firing. Furthermore, the structural changes of the Al2O3 will render the influence of the firing step irreversible.

Apart from thermal stability, long term and UV stability are also important criteria for c-Si surface passivation. The long term stability of the passivation by Al2O3 was verified by monitoring a large number of passivated c-Si wafers over time up to six months. No degradation of the measured effective lifetime was observed. In fact, a significant number of samples exhibited even a positive aging effect after anneal, an effect of which the physical origin is still subject of research. The stability of the Al2O3 passivation against UV photons was tested by exposing various lifetime samples to UV irradiation during time intervals of 10 min alternating between the sample surfaces exposed. A ~100 W Hg lamp was used as UV source, which emits predominantly at 254 nm (4.9 eV). The distance between lamp and sample was kept at ~10 cm to avoid significant sample heating. It was verified that the surface passivation of an as-deposited sample could not be activated by UV irradiation for the conditions employed. For comparison, the experiment was also carried out for SiO2 passivated sample (from a different wafer ingot than the sample in Fig. 1), which received a so-called anneal at 425 °C for 15 min to activate the passivation. Figure 3 shows t eff as a function of cumulative exposure time for representative samples. The effective lifetime of the Al2O3 coated sample increased up to 40% after exposing both wafer surfaces. Additional UV irradiation did not result in a significant further increase of t eff. The lifetime of the SiO2 passivated sample, on the other hand, was observed to decrease under UV irradiation, which can be attributed to a higher interfacial defect density created by the incoming photons. Both the improved surface passivation by Al2O3 and the degraded passivation by SiO2 remained stable over time. We explain the improvement of the Al2O3 surface passivation under UV exposure by a significant increase of the fixed negative charge density, which was already reported in the pioneering work of Hezel et al. for pyrolysis-grown Al2O3. This photon induced charge injection process was recently also observed for Al2O3 films synthesized by ALD during a laser spectroscopic study. A similar beneficial effect from charge injection was also reported for AlF3 films. Furthermore, the reported UV stability of the interface defect density suggests that the impact of UV irradiation on the chemical passivation by Al2O3 is less significant.

In summary, the surface passivation provided by atomic layer synthesized Al2O3 was found sufficiently stable under a
high temperature firing step, with the surface recombination velocities remaining as low as <14 cm/s after reaching temperatures >800 °C. Effusion measurements revealed the loss of hydrogen and oxygen from the Al2O3 during firing through the detection of H2 and H2O indicating structural changes within the material. The application of a SiN capping layer affected neither the level of surface passivation nor the thermal stability of the Al2O3 significantly. The thermal stability that was demonstrated, in conjunction with the long term and UV stability, are prerequisites for the application of Al2O3 passivation schemes in high-volume manufactured solar cells.

W. Keuning (TU/e), Dr. W. Beyer (IEF-5 Jülich), K. Regenbrecht, and Dr. S. Wanka (Q-CELLS) are acknowledged for technical support and/or discussions.