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

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(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 $S_{\text{eff}} < 3$ cm/s were obtained and the passivation proved sufficiently stable ($S_{\text{eff}} < 14$ 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 SiO₂/a-SiNₓ:H/SiO₂,⁸ and a-Si:H/a-SiNₓ:H times of 4 and 7 s, respectively. The fact that the optimized Al₂O₃ deposition process for the FlexAL™ 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 ($\tau_{\text{eff}}$) was determined using a Sinton lifetime tester. The upper limit for the surface recombination velocity ($S_{\text{eff}}$) was calculated from $\tau_{\text{eff}}$ by assuming an infinite bulk lifetime and is quoted at an injection level of $1 \times 10^{15}$ 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.
>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.4

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.5–11 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 metallization as recombination in the metallized 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.10 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 the wafer during the heating process.
the sample at elevated temperatures. In Fig. 2, we show the effusion of \( \text{H}_2, \text{H}_2\text{O}, \text{CO}, \) and \( \text{CO}_2 \) at high temperature as these were the majority species released from the \( \text{Al}_2\text{O}_3 \) sample. Distinct effusion peaks are observed at 625 °C for \( \text{CO}_2 \) and at 910 °C for \( \text{CO}_2 \) and \( \text{CO} \). The formation of these volatile species indicates the incorporation of \( \text{CO}_2 \) impurities into the \( \text{Al}_2\text{O}_3 \) bulk by remote plasma ALD.\(^{17}\) Effusion peaks also appear in the transients at 660 °C for \( \text{H}_2\text{O} \) and \( \text{H}_2 \) (with the \( \text{H}_2 \) signal probably mainly originating from \( \text{H}_2\text{O} \)), at 850 °C for \( \text{H}_2\text{O} \), and at 890 °C for \( \text{H}_2 \). In addition, a small \( \text{H}_2 \) feature is observed in the spectrum at 510 °C, which could possibly originate from cracking \( \text{C}_x\text{H}_y \) species that were detected through mass 15 and 29. The detection of \( \text{H}_2\text{O} \) and \( \text{H}_2 \) is consistent with the presence of a significant density of \( \text{-OH} \) groups in the \( \text{Al}_2\text{O}_3 \) 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 \( \text{Al}_2\text{O}_3 \). From Fig. 2, we conclude that the effusion from the \( \text{Al}_2\text{O}_3 \) films at temperatures up to 800 °C is dominated by the formation and release of \( \text{H}_2\text{O} \). Apparently, hydrogen in the form of \( \text{H}_2 \) is primarily released from the film at temperature >800 °C. Consequently, during a firing process, the \( \text{Al}_2\text{O}_3 \) loses both hydrogen and oxygen which indicates significant structural changes of the \( \text{Al}_2\text{O}_3 \) film that adversely affect the passivation. Furthermore, hydrogen is depleted from the film predominantly in the form of \( \text{H}_2\text{O} \) which is different from the dehydrogenation of \( \text{SiO}_2/\text{-Si} \) interface after firing. The depletion of hydrogen from the \( \text{Al}_2\text{O}_3/\text{-Si} \) interface likely contributes to the decrease of the surface passivation by \( \text{Al}_2\text{O}_3 \) after firing.\(^{2,18,19}\) Furthermore, the structural changes of the \( \text{Al}_2\text{O}_3 \) will render the influence of the firing step irreversible.

Apart from thermal stability, long term and UV stability are also important criteria for \( \text{-Si} \) surface passivation. The long term stability of the passivation by \( \text{Al}_2\text{O}_3 \) was verified by monitoring a large number of passivated \( \text{-Si} \) 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 \( \text{Al}_2\text{O}_3 \) 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 \( \text{SiO}_2 \) passivated sample (from a different wafer ingot than the sample in Fig. 1), which received a so-called anneal\(^{20}\) at 425 °C for 15 min to activate the passivation. Figure 3 shows as a function of cumulative exposure time for representative samples. The effective lifetime of the \( \text{Al}_2\text{O}_3 \) coated sample increased up to 40% after exposing both wafer surfaces. Additional UV irradiation did not result in a significant further increase of \( \tau_{\text{eff}} \). The lifetime of the \( \text{SiO}_2 \) 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.\(^{20,21}\) Both the improved surface passivation by \( \text{Al}_2\text{O}_3 \) and the degraded passivation by \( \text{SiO}_2 \) remained stable over time. We explain the improvement of the \( \text{Al}_2\text{O}_3 \) 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 \( \text{Al}_2\text{O}_3 \).\(^{22}\) This photon induced charge injection process was recently also observed for \( \text{Al}_2\text{O}_3 \) films synthesized by ALD during a laser spectroscopic study.\(^{23}\) A similar beneficial effect from charge injection was also reported for \( \text{AlF}_3 \) films.\(^{24}\) Furthermore, the reported UV stability of the interface defect density suggests that the impact of UV irradiation on the chemical passivation by \( \text{Al}_2\text{O}_3 \) is less significant.

In summary, the surface passivation provided by atomic layer synthesized \( \text{Al}_2\text{O}_3 \) 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.