Al-neal Degrades Al$_2$O$_3$ Passivation of Silicon Surface

Olli E. Setälä,* Toni P. Pasanen, Jennifer Ott, Ville Vähänissi, and Hele Savin

Atomic layer deposited (ALD) aluminum oxide (Al$_2$O$_3$) has emerged as a useful material for silicon devices due to its capability for effective surface passivation and ability to generate p$^+$ region underneath the oxide as active or passive component in semiconductor devices. However, it is uncertain how Al$_2$O$_3$ films tolerate the so-called Al-neal treatment that is a necessary process step in devices that also contain silicon dioxide (SiO$_2$) passivation layers. Herein, it is reported that the Al-neal process is harmful for the passivation performance of Al$_2$O$_3$, causing over eightfold increase in surface recombination velocity (SRV) (from 0.9 to 7.3 cm s$^{-1}$). Interestingly, it is also observed that the stage at which the so-called activation of Al$_2$O$_3$ passivation is performed impacts the final degradation strength. The best result is obtained when the activation step is done at the end of the process together with the Al-neal thermal treatment, which results in SRV of 1.7 cm s$^{-1}$. The results correlate well with the measured interface defect density, indicating that the Al-neal affects defects at the Si/SiO$_2$/Al$_2$O$_3$ interface. The root causes for the defect reactions are discussed and possible reasons for the observed phenomena are suggested.

1. Introduction

Surface defects are well known to limit the performance of silicon devices. These defects cause increased recombination and leakage current, and therefore, their avoidance is an important factor in device processing. The detrimental effect of surface defects has traditionally been reduced by passivating them with thermally grown silicon dioxide (SiO$_2$). The passivating effect of SiO$_2$ relies mostly on elimination of interface defects, which is typically achieved optimally by annealing the film with a thin aluminum layer on top in a process called the Al-neal. The improved passivation performance obtained by Al-neal is based on a chemical reaction between the Al and hydroxyl ions (OH$^-$) in the oxide, which generates atomic hydrogen that neutralizes dangling bonds at the Si/SiO$_2$ interface.

In addition to thermal SiO$_2$, the recent development of materials and processes has led to increasing utilization of other surface passivation thin films, including aluminum oxide (Al$_2$O$_3$) grown with atomic layer deposition (ALD). Unlike with thermal SiO$_2$, no Al layer is needed to activate the surface passivation of Al$_2$O$_3$; instead, a pure anneal in nitrogen or forming gas (FG) ambient at around 400 °C is typically conducted to improve the passivation. It is well known that during the ALD a thin 1–2 nm SiO$_2$ layer is formed between Si and Al$_2$O$_3$ and in the subsequent activation anneal hydrogen that is present in the Al$_2$O$_3$ film (≈1–3 at%) diffuses to Si/SiO$_2$ interface and passivates the dangling bonds, thus improving the chemical passivation. The Al$_2$O$_3$ activation anneal often improves also the field-effect passivation by increasing the magnitude of the negative charge (≈10$^{13}$ cm$^{-2}$) formed at the SiO$_2$/Al$_2$O$_3$ interface, the effect being most prominent for water-based thermal ALD.

While Al$_2$O$_3$ thin films are today commonly used in silicon devices, thermal SiO$_2$ films are still often needed alongside them to provide, e.g., high-quality neutral (or small positive) charge insulator in the same device, a typical example being an induced junction photodiode. Consequently, when both Al$_2$O$_3$ and SiO$_2$ are present on the same wafer, it can be difficult to perform optimized passivation anneal for both films. One good example is the Al-neal of SiO$_2$ that is usually performed as one of the last steps in device fabrication to allow performing it alongside contact metallization. While it can be difficult to perform deposition and patterning of the Al$_2$O$_3$ film after metallization and Al-neal due to, e.g., etch selectivity between Al and Al$_2$O$_3$, it needs to be studied how such Al-neal would affect the passivation performance of Al$_2$O$_3$.

In this work, we study the aforementioned issue, i.e., the impact of the Al-neal process on Al$_2$O$_3$ passivation in high-resistivity silicon wafers that are typical for detector fabrication. First, we investigate how the Al-neal affects the performance of ALD Al$_2$O$_3$ passivation film using standard minority carrier lifetime measurements. Interface defect density and total charge of the film are then measured to gain understanding about the interface and oxide properties that are affected by the Al-neal. Next, we study how the stage at which the activation anneal of Al$_2$O$_3$ is performed affects the passivation and oxide interface properties. Finally, the results and underlying causes for the observed phenomena are discussed.
2. Experimental Section

To investigate the impact of the Al-neal on the passivation performance of Al₂O₃, the quality of surface passivation in various processing scenarios, which are shown in Figure 1, is assessed. The wafers used in these experiments were 300 µm-thick high resistivity (>5 kΩ·cm) n-type single-side polished Float Zone (FZ) silicon wafers with (111) crystal orientation and 100 mm diameter. Before the actual processing, the lifetime-limiting bulk defects in the FZ wafers were deactivated by a typical anneal at 1050 °C in an oxygen atmosphere for 30 min,[18,19] followed by a subsequent oxide removal. Two wafers (dashed and solid blue arrows in Figure 1) were RCA-cleaned followed by the double-sided deposition of a 50 nm-thick Al₂O₃ film with ALD in 200 °C with trimethylaluminum (TMA) and water as the precursors. Surface passivation was activated by annealing the wafers in FG at 425 °C for 30 min (“Al₂O₃ activation” in Figure 1). On one of the wafers, the Al-neal was performed. As shown in Figure 1, it consisted of the following three steps: 1) sputtering of a 300 nm-thick Al-layer on both sides of the wafer, 2) annealing in FG at 425 °C for 30 min, and 3) removal of the Al layer with a commercial phosphoric acid-based Al etchant.

To investigate how the stage of the process at which Al₂O₃ passivation is activated affects the passivation performance, another Al₂O₃ sample was prepared, where a separate Al₂O₃ activation anneal prior to Al deposition was omitted (dotted blue line in Figure 1). Otherwise the fabrication process followed the steps of the earlier Al-nealed Al₂O₃ wafer.

The level of surface passivation that can be obtained by SiO₂ with and without the Al-neal process (solid and dashed red arrows, respectively, in Figure 1) was evaluated for reference. After standard cleanings, two SiO₂ samples were oxidized in O₂ atmosphere at 1000 °C for 90 min, which resulted in an 85 nm-thick oxide. The Al-neal was then performed for the other SiO₂ sample the way described before.

The passivation performance in all samples was evaluated by the measurement of minority charge carrier recombination lifetime as a function of injection level using quasi-steady-state photoconductance (QSSPC) method with Sinton Instruments WCT-120TS tool. The maximum surface recombination velocity (SRVₘₐₓ hereinafter referred to simply as SRV) was calculated from the carrier lifetimes assuming finite bulk lifetime with[20]

\[
SRVₘₐₓ = \frac{W}{2 \cdot \tau_{eff}}
\]

where \( W \) is the thickness of the wafer and \( \tau_{eff} \) is the measured effective carrier lifetime. Finally, thin film properties, such as the total charge (\( Q_{total} \)) and interface defect density (\( D_{it} \)), were assessed with a method called corona oxide characterization of semiconductor (COCOS),[21] using Semilab SDI PV-2000 Lifetime Scanner. Linear dependence between deposited corona charge and the measured contact potential difference indicates that no charge leakage occurred during any of the measurements, ensuring reliable determination of \( Q_{total} \) and \( D_{it} \).

3. Results

Figure 2 shows the impact of the Al-neal process on the carrier lifetimes of Al₂O₃, and as a reference, SiO₂ passivated silicon samples. It is evident that the Al-neal process has a large effect on the lifetimes achieved with both films and due to identical substrates, the differences in lifetimes reflect changes in surface passivation. As expected, passivation performance of SiO₂ increases vastly from microsecond range to milliseconds. Interestingly, a totally opposite phenomenon is observed in the case of Al₂O₃ passivation. The Al-neal causes the lifetime of the Al₂O₃-passivated wafer to decrease from 16.45 to 2.05 ms.

![Figure 1](https://example.com/figure1.png)  
**Figure 1.** Process flows for each fabricated test sample containing the most important processing steps.

![Figure 2](https://example.com/figure2.png)  
**Figure 2.** The effect of the Al-neal process on the minority charge carrier lifetimes on Al₂O₃ and SiO₂ passivated Si. Contrary to SiO₂, passivation performance of Al₂O₃ is impaired by the Al-neal.
(or SRV to increase from 0.9 to 7.3 cm s⁻¹) at 10¹⁵ cm⁻³ carrier density, deteriorating the passivation performance below that of SiO₂.

To understand the mechanism of passivation degradation during the Al-neal process, we need to study the behavior of \( D_i \) and \( Q_{\text{tot}} \), which are the two major components constituting the passivation performance of a film.²² Table 1 shows these values measured from Al₂O₃ and SiO₂-passivated samples with and without the Al-neal. Similar to the lifetime results, the behavior of Al₂O₃ film properties during the Al-neal is completely opposite to SiO₂. A substantial increase in \( D_i \) (from \( \approx 10^{11} \) to \( \approx 10^{12} \) eV⁻¹ cm⁻²) is observed in the Al₂O₃ samples after the Al-neal process, which indicates that the Si/SiO₂/Al₂O₃ interface seems to degrade due to the deterioration of chemical passivation. COCOS results reveal also that there is a slight increase in the film charge due to the Al-neal; however, the higher field-effect passivation cannot compensate the decline of chemical passivation. The observed lifetime degradation with Al-nealed Al₂O₃ can be thus explained by increased recombination at the Si/SiO₂/Al₂O₃ interface. In SiO₂ passivated reference samples, on the contrary, \( D_i \) behavior is opposite and the Al-neal reduces it considerably. Consequently, the observations imply that the Al-neal process affects the chemistry of the Si/film interfaces differently in SiO₂ than in Al₂O₃ films.

In the aforementioned samples, surface passivation was activated by annealing the Al₂O₃ film directly after the deposition of the thin film. As the sample experiences similar heat treatment also during the Al-neal process, it raises a question if the negative effect of the Al-neal could be reduced by changing the stage of the process when the Al₂O₃ passivation is activated. To study this, another Al₂O₃-passivated sample was fabricated without a separate Al₂O₃ activation step (blue dotted line in Figure 1). Figure 3 compares the carrier lifetimes of such sample (dotted line) with the ones presented earlier (solid and dashed lines). At 10¹⁵ cm⁻³ carrier density, lifetime of 8.66 ms (SRV 1.7 cm s⁻¹) is achieved after the Al-neal process, which is a significant improvement from 2.05 ms (SRV 7.3 cm s⁻¹) that was measured from the sample that experienced a separate Al₂O₃ activation before the Al-neal process. A slight reduction in \( D_i \) (1.8 × 10¹⁴ vs \( 2.3 \times 10¹² \) eV⁻¹ cm⁻²) and increase in charge density (\(-3.9 \times 10¹²\) vs \(-3.2 \times 10¹⁴\) cm⁻³) is achieved by removing the separate activation step. Although both values change to favorable direction for improved surface passivation, the magnitude of change is surprisingly small to completely explain the clear improvement seen in passivation performance. Interestingly, the lifetimes do not reach the initial values measured without the Al-neal process. This indicates that indeed something harmful happens during the Al-neal process that cannot be recovered during the Al₂O₃ activation anneal integrated in the Al-neal step.

4. Discussion

The Al-neal process was observed earlier to be harmful for the passivation performance of an ALD Al₂O₃ film. The result raises questions about the physical and chemical mechanisms taking place during the Al-neal of Al₂O₃. In case of thermal SiO₂, a chemical reaction takes place between the oxide and aluminum, in which atomic hydrogen is released.⁵ As hydrogen is known to be effective at passivating defects both at silicon surface and in the bulk,⁶ this reaction explains the increase in the passivation performance of SiO₂. Indeed, Table 1 shows that Al-nealing of SiO₂ sample decreased \( D_i \) by a factor of four.

The effect of the Al-neal seems to, however, be completely opposite on Al₂O₃. The root cause for the difference between the behavior of Al₂O₃ and SiO₂ films during the Al-neal cannot be concluded from the aforementioned experiments, but we will discuss here some hypotheses along with further experimental results. The obvious starting point is the \( D_i \) and \( Q_{\text{tot}} \) values shown in Table 1. The immense increase in the \( D_i \) during the Al-neal of Al₂O₃ indicates that the deteriorated passivation performance is caused by weakened chemical passivation resulting from additional defect states that are formed to the Si/SiO₂/Al₂O₃ interface. It is known from the literature that chemical passivation can be destroyed by sputtering of the Al film, as it can cause damage to the silicon lattice and substrate/film interface.⁷ Indeed, this was confirmed to be the case here as well because the measured lifetime dropped to 30 μs directly after sputtering. Such large changes in interface quality may be
unrecoverable by anneal afterward. The $D_{\text{it}}$ of the Al$_2$O$_3$ samples could be thus related to the damage inflicted to the interface by sputtering, as the density of interface defects is five times larger in both cases where the Al-neal (and consequently sputtering) has been performed compared with the situation after only Al$_2$O$_3$ activation ($\approx 2 \times 10^{12}$ vs $4.1 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$). Conversely, the Al-neal seems to increase the negative charge in Al$_2$O$_3$ (and SiO$_2$ but in its case the change is far less prominent and seen as decreased positive charge), which should be advantageous regarding field-effect passivation. Indeed, the generated interface defect states have been reported to trap charges and therefore can affect the amount of field-effect passivation.$^{[26,27]}$

In our case, this effect was still rather modest and the increased $D_{\text{it}}$ dominated in the measured lifetime.

To assess the damage resulting from the mere sputtering step speculated earlier, additional experiments were conducted. The processing sequence for these extra samples was the following: ALD Al$_2$O$_3$ deposition, optional Al$_2$O$_3$ activation anneal, Al sputtering, Al etch, FG anneal, and characterization. In other words, in these wafers, both with and without a separate Al$_2$O$_3$ activation anneal preceding the sputtering, the Al layer was immediately etched away after sputtering and an FG anneal was then performed without Al on the wafers. The results, also shown in Table 2 (rows 1 and 2), were as follows. If the Al$_2$O$_3$ activation anneal was done preceding the sputtering, the lifetime and SRV were 7.1 ms and 2.5 cm s$^{-1}$, respectively. If there was no Al$_2$O$_3$ activation anneal done preceding the sputtering, the lifetime and SRV were 10.59 ms and 1.7 cm s$^{-1}$, respectively. As shown earlier in Table 1 (and also in Table 2 as row 3), the corresponding values for Al$_2$O$_3$ without Al-neal were 16.45 ms and 0.9 cm s$^{-1}$, respectively. Thus, as hypothesized earlier, the SRVs of the sputtered wafers without Al-neal (2.5 and 1.7 cm s$^{-1}$) differ from the wafer that experienced only Al$_2$O$_3$ deposition and postdeposition activation (0.9 cm s$^{-1}$), indicating that sputtering does indeed cause some unrecoverable damage.

To see the effect of the presence of Al layer during the FG anneal, one needs to compare the aforementioned extra results (Table 2, rows 1 and 2) to their counterparts (Table 2, rows 4 and 5). The $D_{\text{it}}$ and the lifetime are much worse if the Al layer is present during the FG anneal, indicating that the sputtering step cannot be solely responsible for degraded passivation. Furthermore, there is a clear disparity between the passivation performances of Al-nealed Al$_2$O$_3$ films with and without a separate Al$_2$O$_3$ activation step (Table 2, rows 4 and 5). In both of these samples, the Al$_2$O$_3$ films experience the same sputtering process, but the sample without separate Al$_2$O$_3$ activation recovers from the sputtering-induced damage considerably better. Interestingly, the same effect is seen in the results obtained from the additional experiments as there is similar disparity (Table 2, rows 1 and 2). Consequently, more efficient passivation is again achieved without a separate activation step.

The aforementioned results confirm that in addition to sputtering damage there are other harmful mechanisms taking place during the Al-neal process. One possibility could be the depletion of hydrogen in the film. During standard activation of Al$_2$O$_3$ passivation, hydrogen is created in atomic form in Al$_2$O$_3$ bulk in a mechanism, where OH-groups and Al atoms in the film form Al—O bonds and release hydrogen.$^{[28]}$ This hydrogen together with hydrogen already present in the as-deposited film diffuses toward the Si surface and is responsible for the significantly reduced $D_{\text{it}}$. Such process should occur in the film regardless of the presence of the Al capping layer, as the thermal treatment during the Al-neal can be considered only as an additional Al$_2$O$_3$ activation. Due to the existence of OH-groups, the presence of Al layer could actually even increase the amount of atomic hydrogen in a reaction that is similar to SiO$_2$ Al-neal passivation. However, when combining the activation steps with the damage caused by sputtering, the situation may become different. In such circumstances, the amount of hydrogen in the film may not be enough for effective passivation. Indeed, notable release of hydrogen has been reported in ALD Al$_2$O$_3$ films deposited in 200 °C: 15% of the total hydrogen content was released during 10 min thermal treatment in 400 °C.$^{[29]}$ Considering the similar Al$_2$O$_3$ activation temperature (425 °C) and longer duration (30 min) in our experiments, even larger depletion of hydrogen can be expected. Therefore, the hydrogen content in the once activated Al$_2$O$_3$ film might be too low to allow complete repassivation of the Si/SiO$_2$/Al$_2$O$_3$ interface after it has been damaged by sputtering. This could explain why separate Al$_2$O$_3$ activation has such detrimental impact on the passivation performance of Al-nealed Al$_2$O$_3$.

Table 2. Collection of the experimental results obtained for Al$_2$O$_3$ deposited samples. Thickness of the wafers annealed without Al on top is higher (350 vs 300 μm) explaining the same SRV with different lifetimes.

| Al$_2$O$_3$ activation prior sputtering | Anneal after sputtering | Midgap $D_{\text{it}}$ [eV$^{-1}$ cm$^{-2}$] | $Q_{\text{tot}}$ [cm$^{-2}$] | Lifetime at 10$^{-11}$ cm$^{-3}$ [ms] | SRV [cm s$^{-1}$] |
|--------------------------------------|------------------------|---------------------------------|------------------|-------------------------------|----------------|
| Yes                                  | FG anneal without Al    | $7.8 \times 10^{11}$           | $-2.1 \times 10^{2}$ | 7.10                          | 2.5            |
| No                                   | FG anneal without Al    | $3.2 \times 10^{11}$           | $-1.7 \times 10^{2}$ | 10.59                         | 1.7            |
| Yes                                  | No sputtering          | $4.1 \times 10^{11}$           | $-1.3 \times 10^{2}$ | 16.45                         | 0.9            |
| Yes                                  | Al-neal                | $2.3 \times 10^{12}$           | $-3.2 \times 10^{2}$ | 2.05                          | 7.3            |
| No                                   | Al-neal                | $1.8 \times 10^{12}$           | $-3.9 \times 10^{2}$ | 8.66                          | 1.7            |
without the Al-neal, due to its positive impact on the $Q_{\text{max}}$. In cases where sputtering of Al on Al$_2$O$_3$ cannot be avoided the best result is achieved by etching the metal off from Al$_2$O$_3$ before annealing or alternatively by performing the Al-neal without separate Al$_2$O$_3$ activation step.

5. Conclusions

We have investigated the effect of the Al-neal process on the ALD Al$_2$O$_3$ passivation. We observed that the Al-neal can be harmful for the passivation performance of Al$_2$O$_3$ causing over eightfold increase in SRV (from 0.9 to 7.3 cm$^{-1}$). Omitting a separate Al$_2$O$_3$ activation anneal between deposition of Al$_2$O$_3$ and the Al-neal was presented as a partial solution to the problem. Such fabrication scheme resulted in SRV of 1.7 cm$^{-1}$, which is already an adequate value for most applications. Possible reactivation performance with Al$_2$O$_3$, additional modifications to the device fabrication process are likely needed. The simplest way is to avoid the Al-neal step altogether, but another possible solution could be to use alternative metal deposition methods, such as evaporation, to prevent excessive damage at the Si/SiO$_2$/Al$_2$O$_3$ interface.

Acknowledgements

The authors thank Academy of Finland (projects: #328482 and #333131) and Tandem Industry Academy funding from the Finnish Research Impact Foundation for financial support. The authors acknowledge the provision of facilities by Aalto University at OtaNano – Micronova Nanofabrication Centre. The work is related to the Flagship on Photonics Research and Innovation “PREIN” funded by Academy of Finland.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

Al-neal, aluminum oxide, silicon devices, surface passivation

Received: April 15, 2021
Revised: June 24, 2021
Published online: July 18, 2021