ABSTRACT: For the purpose of reducing recombination activity in crystalline silicon solar cells, atomic layer deposited aluminum oxide (Al₂O₃) has proven a promising candidate. Its excellent surface passivation is effected by an exceptionally high density of fixed negative charges \( Q_f \) generating a strong field-effect along with a chemical passivation reducing the density of interface traps \( D_i \). The dependence of these two measures on the temperature and the duration of the post-deposition anneal activating the passivation of Al₂O₃ is investigated by measuring the capacitance-voltage (C-V) characteristics. To directly correlate \( Q_f \) and \( D_i \) with the effective minority carrier lifetime \( \tau_{\text{eff}} \), a new kind of sample structure is developed, whereby both measurement types can be conducted on the same test sample. The interface properties of samples with thermal and electron beam evaporated metal contacts are compared and a correlation with the obtained passivation quality quantified by \( \tau_{\text{eff}} \) is identified in order to investigate the influence of the radiation damage. It is found that \( Q_f \) and \( \tau_{\text{eff}} \) of Al₂O₃ passivated float-zone Si wafers exhibit a correlation when annealing parameters are varied and that an electron beam evaporation of Al damages the Al₂O₃/Si interface and significantly reduces \( \tau_{\text{eff}} \). Finally, a method to restore the effective lifetime is developed and investigated which yields a recovery rate of 65% corresponding to a reduction of \( Q_f \). 

Keywords: Al₂O₃, Lifetime, C-V, Radiation Damage

1 INTRODUCTION

In recent years, atomic layer deposited Al₂O₃ has been proven to feature excellent surface passivation properties on \( p \)-type silicon wafers being the most common solar cell base material [1, 2]. Accordingly, Al₂O₃ is used as rear side dielectric passivation layer in high efficiency \( p \)-type silicon solar cells with local rear contacts established, for example, by laser-firing, thus known as Laser-Fired Contacts (LFC) [3].

The passivating character of Al₂O₃ on silicon surfaces is based on two pivotal mechanisms. On the one hand, the Al₂O₃ layer provides chemical passivation as it is able to saturate the dangling bonds on the silicon surface which previously exhibits a high density of interface states \( D_i \) in the silicon band gap [4, 5]. On the other hand, a high density of negative fixed charges up to the range of \( Q_f = 10^{13} \text{ cm}^2 \) has been evidenced in dielectric Al₂O₃ [5]. This high density of fixed negative charges induces field-effect passivation.

Potential techniques for the rear side metalization of dielectrically passivated silicon solar cells are thermal evaporation and electron beam evaporation. During electron beam evaporation, radiation damage raises the surface recombination velocity of surfaces coated with a thermal SiO₂ layer [6]. Instead of the latter, we therefore examine Al₂O₃ passivated Si wafers surfaces in respect of the metallization techniques’ impact upon \( D_i \) and \( Q_f \), being characteristic measures of passivated Si wafer surfaces.

2 EXPERIMENTAL

2.1 Characterization techniques

Electrical properties of the Al₂O₃/Si (100) interface like the density of interface traps and the density of fixed charges are investigated by capacitance-voltage (C-V) measurements on metal-oxide-semiconductor (MOS) structures [7]. From the C-V characteristic, the density of fixed charges \( Q_f \) can be calculated by

\[
Q_f = \frac{C_{\text{OX}}}{q} \cdot (V_{\text{FB}} + \phi_{\text{MS}}),
\]

wherein \( C_{\text{OX}} \) is the oxide capacitance determined in accumulation, \( q \) the elementary electric charge, \( V_{\text{FB}} \) the voltage under flatband conditions and \( \phi_{\text{MS}} \) the difference between the work functions of metal and semiconductor.

Measuring the high frequency capacitance \( C_V \) as well as the quasi-static capacitance \( C_{\text{it}} \) as a function of the applied voltage to the MOS structure, the density of interface traps \( D_i \) is determined employing the following equation

\[
D_i = \frac{C_{\text{it}}}{q} - \frac{1}{q} \left[ \left( \frac{1}{C_{\text{it}}} - \frac{1}{C_{\text{OX}}} \right)^{-1} - \left( \frac{1}{C_{\text{it}}} - \frac{1}{C_{\text{OX}}} \right)^{-1} \right].
\]

The resulting passivation quality is quantified by the effective minority carrier lifetime \( \tau_{\text{eff}} \) in the surface-passivated wafer determined by means of photoconductance decay (PCD) measurement [8], where

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{2S_{\text{eff}}}{W}
\]

with \( \tau_{\text{bulk}} \) being carrier lifetime in the silicon bulk, \( S_{\text{eff}} \) representing effective surface recombination velocity and \( W \) denoting wafer thickness. For the calculation of \( S_{\text{eff}} \), Auger recombination is neglected and thus infinite bulk lifetime \( \tau_{\text{bulk}} \) is assumed for the float-zone wafers used yielding an upper limit of \( S_{\text{eff}} \).

In order to be able to reliably correlate \( D_i \), \( Q_f \) and \( \tau_{\text{eff}} \), a new sample design, which we name combined lifetime/C-V sample, is developed. After the Si wafer is passivated by an Al₂O₃ layer on both faces, lifetime measurements can be conducted on the symmetrical test sample. Subsequently, this lifetime sample is remanufactured to a MOS structure by applying spot-shaped Al gate contacts. In order to obtain a complete C-V sample, an ohmic contact is established on the rear by full area metallization and subsequent laser-firing the Al through the Al₂O₃ layer. The described test sample is depicted in Fig. 1, including this second step metalization.
2.2 Fabrication of combined lifetime/C-V samples

In order to manufacture such test samples, first of all symmetrical lifetime samples are prepared from boron-doped, 5×5 cm² float-zone wafers with a specific resistivity of 2 Ω cm and a thickness of 250 or 525 µm. Manufacturing steps are illustrated in Fig. 2.

These wafers, damaged by laser cutting, are etched in a chemical polishing solution [9], and afterwards the surface is subjected to a standard RCA cleaning step [10]. Then, Al₂O₃ layers with a thickness of 30 nm are deposited on both sides of the wafers by plasma assisted atomic layer deposition (PA-ALD) at ≈200 °C using a FlexAL device from Oxford Instruments. The thickness is verified by spectral ellipsometry. To "activate" the passivation property of the Al₂O₃ layers, an annealing step has been proven necessary [2].

In the first part of our analysis, the effect of this annealing step is investigated regarding various annealing temperatures between 340 and 470 °C as well as different annealing periods of 10 to 400 min in order to determine the settings for optimal passivation quality and to identify the respective electronic states at the Al₂O₃/Si interface. Processing Al₂O₃ passivated wafers, the thickness of the passivation layer represents another parameter. In this context, investigations concerning passivation quality, Qᵢ, and Dᵢ were carried out by Werner [11].

With our lifetime samples, photoconductance decay measurements are conducted and the effective minority carrier lifetime τₑff is determined (eq. 3) at an injection density of Δn = 10¹⁵ cm⁻³ utilizing a Sinton Lifetime Tester. In order to get a spatially resolved image of the carrier recombination activity, photoluminescence (PL) measurements are carried out. Thereby, it has to be taken into account that, due to metrological properties of the setup employed, a higher signal is measured at the center of samples with high lifetimes and that identical colors in different images cannot be assigned to the same lifetime value. However, for the investigations in this work, the knowledge of the qualitative PL signal distribution is sufficient.

After lifetime measurement, the passivated wafers are processed to C-V samples. For this purpose, using a shadow mask, Al gate contacts (area ≈ 1 mm²) are evaporated on top of the Al₂O₃ layer on the front of each sample to create a MOS structure needed for C-V measurements. On the rear, Al is evaporated over the entire surface.

In the initial part of the experiment, all metal contacts of the samples are thermally evaporated. In the second part, the Al contacts are deposited using an electron beam evaporator in order to investigate the influence of different physical vapor deposition methods upon the Al₂O₃/Si interface properties. The ohmic contact on the rear side through the Al₂O₃ layer is established by means of the Laser-Fired Contacts (LFC) technique. Finally, the sample is used for capacitance-voltage profiling. The C-V measurements are performed in high-frequency [12] and quasi-static [13] mode which allows the calculation of Qᵢ in the Al₂O₃ layer at the interface to the silicon (eq. 1) and the calculation of Dᵢ (eq. 2).

3 RESULTS

3.1 Process parameter variation

The first part of our analysis shows that the setting temperature of the 30 minute annealing step after Al₂O₃ deposition has significant influence on the passivation quality. This is evidenced by the measured effective lifetime of the different samples.
Fig. 3 represents that without any annealing, this lifetime is below 10 µs. With increasing temperature, effective lifetime continuously increases and reaches its maximum at an annealing temperature set at 420 °C. Above this temperature, passivation quality decreases.

The PL images of the samples annealed at different temperatures are exhibited exemplarily in Fig. 4. The sample annealed at 420 °C features a very homogeneous distribution of PL signal neglecting measurement artifacts which corresponds very well to the maximum $\tau_{\text{eff}}$ value in Fig. 3. With decreasing temperatures an augmented number of small areas with a lower PL signal occurs. With increasing temperatures above 420 °C, the PL signal decreases extensively, originating from the edges.

In order to examine whether metalization by thermal evaporation of Al changes passivation quality, the Al layers are etched away from metalized wafers (without LFC) by means of a hydrochloric acid (HCl) solution; subsequently, carrier lifetime is measured. It has been found that thermal evaporation is a damage-free deposition technique since the $\tau_{\text{eff}}$ values obtained by PCD measurement as well as the PL images of the recombination activity distribution before and after the metalization step do not diverge [14]. Hence, results derived from lifetime measurements before the metalization step can be correlated to results calculated from C-V measurements after the metalization step.

In Fig. 5 the density of negative fixed charges in the Al2O3 layer and the interface trap density in the middle of the Si energy gap both extracted from the $C-V$ curves of a combined lifetime/C-V sample are represented versus the annealing temperature. The course of the curves reveals the reason for the temperature dependence of the Al2O3 passivation quality.

Without any annealing step, only a very low density of fixed charges is detectable. Annealing at 340 °C raises the value of $Q_f$ only marginally. The greatest increase is observable at an annealing temperature between 400 and 420 °C. The sample annealed at 420 °C features a density of fixed charges of $Q_f = 1.2 \times 10^{13} \text{ cm}^{-2}$.

The density of interface traps without an annealing step is very high at almost $1 \times 10^{13} \text{ cm}^{-2} \text{eV}^{-1}$. Even an annealing step at only 340 °C reduces the $D_{\text{it}}$ value by one order of magnitude. The minimum is observable at the same temperature at which $Q_f$ reaches its maximum, namely at 420 °C, where effective lifetime is maximal, too.

From experiments dealing with the dependence of the minority carrier lifetime of samples coated with Al2O3 layers and accumulatively subjected to different annealing periods, it can be deduced that the passivation quality of Al2O3 depends on the duration of the annealing step as well.

Fig. 6 displays that only ten minutes at 420 °C are needed to increase $\tau_{\text{eff}}$ from below 10 µs to 3.4 ms which, with a wafer thickness of 250 µm, corresponds to an effective surface recombination velocity of 3.7 cm/s. After a total annealing period of 30 min, effective lifetime reaches its maximum, subsequently decreasing with additional annealing steps.
In Fig. 7 the significant change in the density of fixed charges and the density of interface traps at midgap during the first ten minutes of annealing is illustrated. For longer annealing periods $Q_f$ is nearly stable. $D_{it}$ increases after approximately 150 min to $2 \times 10^{12} \text{ cm}^{-2} \text{eV}^{-1}$.

$0 \quad 100 \quad 200 \quad 300 \quad 400$

$-2 \times 10^{12}$

$-4 \times 10^{12}$

$-6 \times 10^{12}$

Annealing period (min)

$0 \quad 10 \quad 100 \quad 2 \times 10 \quad 3 \times 10 \quad 4 \times 10$

$Q_f$ (cm$^{-2}$)

$D_{it}$ (cm$^{-2}$ eV$^{-1}$)

**Figure 7:** Density of fixed charges (left ordinate) and density of interface traps at midgap (right ordinate) after annealing at 420 °C versus accumulated annealing period.

### 3.2 Electron beam evaporated contacts

In its second part, our analysis examines whether the deposition of Al contacts by means of an electron beam evaporator influences the Al$_2$O$_3$/Si interface of the combined lifetime/C-V samples. For this purpose, sister samples are manufactured, one for measuring lifetime, and one for C-V measurement. From the lifetime sample, the Al is etched off the surface again after electron beam evaporation so that lifetime can be measured afterwards.

In fact, a damage of the samples can be identified from $\tau_{\text{eff}}$ measurements represented in Fig. 8. The effective lifetime of the Al$_2$O$_3$ coated sample after a post-deposition annealing step at 420 °C is more than 9 ms, which, with a wafer thickness of 525 µm, corresponds to an effective surface recombination velocity of 2.7 cm/s.

![Figure 8: Effective minority carrier lifetime $\tau_{\text{eff}}$ versus subsequent process stages: post-deposition anneal (PDA; 420 °C, 30 min), Al electron beam evaporation and its subsequent etching off, 30 minute annealing at various temperatures.](image)

After treatment in the electron beam evaporator, $\tau_{\text{eff}}$ falls to less than 100 µs. Thus, in contrast to thermal evaporation, depositing Al contacts by means of an electron beam evaporator damages the Al$_2$O$_3$/Si interface of the combined lifetime/C-V samples. The damage could have been caused by high-energetic particles or X-rays. These are thought to have damaged SiO$_2$ passivated silicon wafers during electron beam evaporation [6].

Furthermore, it is demonstrated that an annealing step at different temperatures between 370 and 450 °C can raise $\tau_{\text{eff}}$ again up to approximately 6 ms, which corresponds to a recovery rate of 65%.

The respective PL images at the different process stages (Fig. 9) depict the spatial distribution of lifetime.

![Figure 9: PL images after (a) post-deposition anneal, (b) electron beam evaporation and etching of Al, (c) 420 °C anneal and (d) 450 °C anneal. Purple is tantamount to high, red to low recombination activity. The scaling of the wafers is not identical.](image)

Whereas directly after the post-deposition anneal (a) the sample shows a homogeneous high passivation quality, the measurement signal after evaporation and removal of Al (b) consists only of measurement artifacts. Annealing at 420 °C (c) partly recovers the passivation quality, whereupon at higher annealing temperatures (d) the recombination activity increases again in a large area.

![Figure 10: Density of fixed charges (left ordinate) and density of interface traps at midgap (right ordinate) versus subsequent process stages: Al electron beam evaporation, 30 minute annealing at various temperatures.](image)
In order to check the electrical interface properties, $Q_f$ and $D_{it}$ are determined on the C-V sister sample after each of the process stages. The course of the $Q_f$ curve features a shape similar to the one of the $\tau_{eff}$ values which once more evidences the correlation between these two quantities (Fig. 10). The $D_{it}$ values determined in the middle of the Si energy gap develop inversely explaining the $\tau_{eff}$ values.

4 CONCLUSION

Atomic layer deposited Al$_2$O$_3$ is extraordinarily effective at minimizing recombination activity in crystalline silicon solar cells. $Q_f$ and $D_{it}$, indicating passivation quality of Al$_2$O$_3$ layers on Si wafers, are determined by measuring the capacitance-voltage characteristics.

In order to directly correlate $Q_f$ and $D_{it}$ with the resulting effective carrier lifetime $\tau_{eff}$, a new kind of sample structure, the “combined lifetime/C-V sample”, has been developed. This structure allows measuring all three quantities on the same sample.

$Q_f$, $D_{it}$ and $\tau_{eff}$ of Al$_2$O$_3$ passivated $p$-doped Si wafers have been evidenced to exhibit an explicit correlation when applying various annealing temperatures and periods. Furthermore, electron beam evaporation of Al has been found to damage the Al$_2$O$_3$/Si interface and to significantly reduce $\tau_{eff}$. Eventually, a method to recover effective lifetime has been developed and investigated. This method yields a recovery rate of 65% corresponding to a reduction of $D_{it}$ and an increase of $Q_f$.

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6 REFERENCES