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Silicon surface passivation by mixed aluminum precursors in Al₂O₃ atomic layer deposition

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Abstract

Dimethylaluminum chloride (DMACl) is a cost-effective aluminium precursor alternative to conventional trimethylaluminium (TMA) for Atomic Layer Deposited (ALD) Al₂O₃. The DMACl water process shows better passivation after high temperature firing when compared with conventional TMA water process. However, after low-temperature post-anneal its passivation quality is slightly worse than with TMA. Here we show that a mixed use of TMA and DMACl precursors in the ALD process results in better surface passivation both after 400°C post-anneal and after an 800°C firing step. The high-quality passivation results from the low interface defect density and high negative charge at the surface. Specifically, we investigate the role of chlorine in the ALD Al₂O₃ passivation by varying the TMA and DMACl pulse proportions.

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Keywords: Silicon surface passivation; Atomic layer deposition; Dimethylaluminum chloride

1. Introduction

ALD Al₂O₃ passivation has drawn a numerous attention around the photovoltaic society for its application in silicon surface passivation due to its high negative charge density (Q_f) and low interface defect density (D_{it}) at the passivated surface [1]. On the other hand, a poor stability of the passivation film can be a problem when the wafers experience post-anneal and firing processes during the solar cell fabrication process [2].

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PECVD SiN_x is a good thermal barrier that can protect the passivation film from the harmful high temperature firing atmosphere [3]. Replacing TMA with DMACl in the ALD is also a promising alternative for obtaining higher passivation quality after firing [4]. Here we present a different approach, by replacing a proportion of TMA with DMACl in the ALD process, to increase further the thermal tolerance of the film for the subsequent high-temperature treatment. The chlorine content from the DMACl most likely brings the main difference to the passivation as compared to the TMA process. Therefore, it needs further investigation to clarify if the chlorine content is beneficial for ALD Al₂O₃ passivation, similar to the high temperature thermal oxidation process [5].

2. Experimental

4 inch MCz p-type wafers were used as substrates with $\sim 2 \Omega\cdot\text{cm}$ resistivity, (100) orientation and 400 μm thickness. The wafers were HF (1%) dipped before ALD. Thermal ALD reactions at 250°C were carried out firstly, as it was considered as the optimal deposition temperature for the DMACl based process based on an earlier study [4]. 200 ALD cycles were performed using the following sequence: DMACl (TMA) (0.2 s) - nitrogen purge (1 s) – water (0.2 s) – nitrogen purge (1 s). The ALD laminates were realized by the recipes summarized in Table 1. Additionally, ALD processes with recipe C were deposited at different temperatures at 100, 200 and 300°C to study the influence of growth temperature on the passivation.

Table 1. ALD recipes used in this study.

Recipe #	ALD cycle details
A	200 (TMA & water)
B	50 × [3(TMA & Water)+1(DMACl & Water)]
C	50 × [2(TMA & Water)+2(DMACl & Water)]
D	50 × [1(TMA & Water)+3(DMACl & Water)]
E	200 (DMACl & Water)

After the ALD, post-anneal at 400°C for 30 min in a tube furnace in nitrogen ambient was performed, followed by a firing at 800°C for 3 s in a Rapid Thermal Annealing furnace (RTA) in nitrogen ambient. For the RTA firing, a contact thermocouple was used to monitor the wafer temperatures. The actual peak temperature of the wafers was below 810°C during the RTA firing. For the characterization of the deposited film, spectroscopic ellipsometer and X-ray reflectivity (XRR) method were used to determine the thickness, refractive index and the density of the films. The effective minority carrier lifetime (τ_{eff}) was measured by Quasi-Steady State Photoconductance Decay (QSSPC). The interface defect density (D_{it}) and the density of fixed charge (Q_f) of the films were analyzed by corona capacitance-voltage (CV) measurement.

3. Passivation in as-deposited films

Fig 1(a) presents the minority carrier lifetime results for as-deposited samples using different ALD recipes, where the chlorine concentration increases from sample A to E. By comparing the sample A with other samples, we see that an addition of DMACl dramatically reduces the D_{it} , so the film provides better chemical passivation for the silicon surface. On the other hand, the values of Q_f are quite low in all samples as compared to normal post-annealed Al₂O₃, but it constantly grows when DMACl pulse time increases. This can be explained by two aspects. Firstly, the field effect passivation of ALD Al₂O₃ has not been fully activated during the ALD growth. Also, a relatively high ALD temperature at 250°C leads to a thicker interfacial SiO_x that has a positive charge, which compensates the negative charge from Al₂O₃. The measurement by spectroscopic ellipsometry and X-ray reflectometry confirm the presence of about 1 nm low density oxide at the interface. Secondly, the chlorine content from DMACl itself may reduce the compensation effect of the interface silicon oxide. Furthermore, the chlorine might provide additional silicon surface dangling bonds passivation via Si-Cl bonds [6].

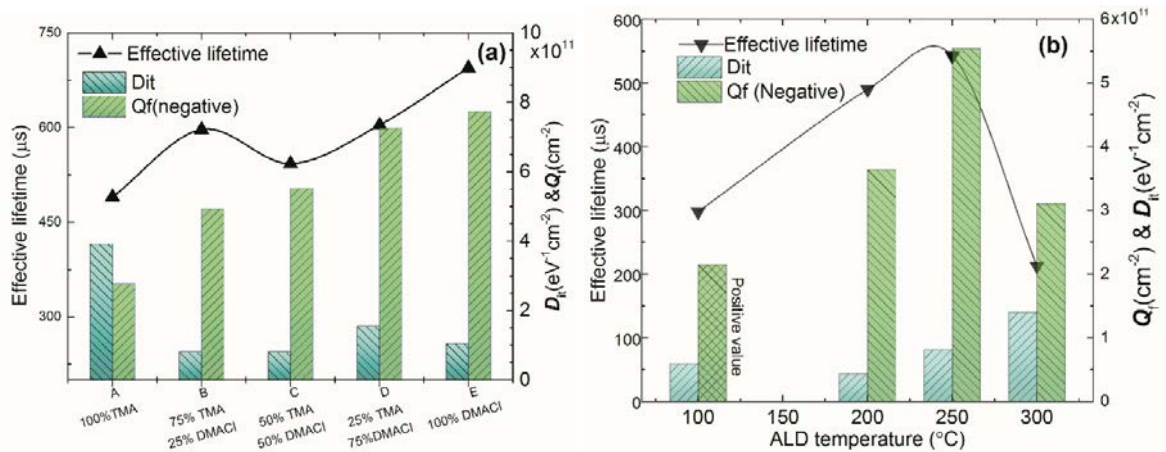


Fig. 1. (a) Silicon surface passivation (τ_{eff} , D_{it} and Q_f) in as-deposited films as a function of different Al precursor proportions in ALD Al_2O_3 deposited at 250°C. (b) The effect of growth temperature on the passivation with recipe C in as-deposited films. Note: Q_f for 100°C sample in (b) was positive. The τ_{eff} was obtained at the injection level of $3 \times 10^{15} \text{cm}^{-3}$.

Fig 1(b) shows the passivation quality of Al_2O_3 film from the mixture of TMA and DMACI with 50% to 50% ratio under different ALD growth temperatures. As is shown in the figure, the best passivation is achieved at 250°C, which mainly results from the higher negative charge density. While in general a higher growth temperature results in higher negative charge, a sample prepared at 300°C shows opposite behavior having lower Q_f and higher D_{it} . This may be due to a thicker interlayer silicon oxide, which provides positive charge [7]. Secondly, higher ALD temperature reduces hydrogen concentration due to hydrogen release, resulting in poorer passivation of the dangling bonds.

4. Passivation after post-anneal and firing

Although the D_{it} value for as-deposited samples was really low, below $10^{11} \text{eV}^{-1}\text{cm}^{-2}$ for most samples with mixed aluminium precursor, the passivation quality remained below 1 millisecond due to low Q_f . It is known that the field-effect passivation can be improved by annealing the wafers at 400°C [8]. Fig 2(a) shows the results after such post-anneal, and as assumed, the best passivation was reached by pure TMA water process. On the other hand, similar to previous results [9], during firing the pure TMA based ALD suffered a lifetime drop, while the DMACI addition in the process improved the passivation quality, which can be seen more clearly in Fig. 2(a). However, the best passivation after firing was achieved with ALD recipe C with 50% TMA and 50% DMACI. As τ_{eff} differences for all fired samples were quite small, we can conclude that all the mixed processes deposited at 250°C result in relatively high passivation quality after firing.

The D_{it} obtained from CV measurements show the changes of the chemical passivation during the heat treatments. Generally, for all DMACI recipes, there was a clear increase in D_{it} after annealing and firing, while the differences among the samples under the same heat treatment were relatively small. Specifically, D_{it} increased to $1.5\sim 2.5 \times 10^{11} \text{eV}^{-1}\text{cm}^{-2}$ from $0.7\sim 1.4 \times 10^{11} \text{eV}^{-1}\text{cm}^{-2}$ in as-deposited samples during post anneal, then it degraded to $2.6\sim 3.8 \times 10^{11} \text{eV}^{-1}\text{cm}^{-2}$ after firing. On the contrary, in pure TMA process A, D_{it} showed a slight decrease during annealing and a similar deterioration as other samples after firing. The constant deterioration in the chemical passivation mainly comes from the reduced interface Si-H bonds. Despite the clear D_{it} increase during different thermal treatments, the observed D_{it} differences cannot fully explain the lifetime variation in Fig 2(a).

The field effect passivation shown in Fig 2(b) has a more clear evolution than the chemical passivation. Clearly, the improvement in Q_f leads to the lifetime improvement after annealing in all samples. Additionally, a further improvement in Q_f in all DMACI processes further improves the total passivation quality. However, the charge density drop in pure TMA based process during firing correlates with the passivation quality decrease observed in Fig 2(a).

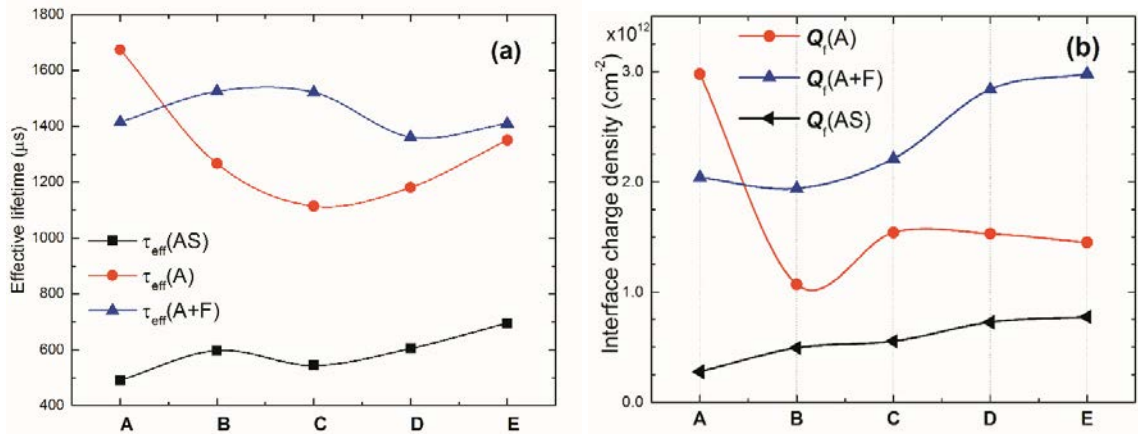


Fig. 2. (a) The impact of heat treatment on the minority carrier lifetime with ALD recipes A to E. The ALD growth temperature was 250°C. τ_{eff} was obtained at the injection level of $3 \times 10^{15} \text{ cm}^{-3}$ for as-deposited samples (AS), annealed samples (A) and fired samples (A+F). (b) The evolution of the interface negative charge density as a function of ALD recipe under different heat treatments.

5. Impact of the ALD growth temperature

With the optimal ALD recipe C, we investigated further the effect of ALD growth temperatures on the passivation. As shown in Fig 3(b), ALD at 250 °C is still the optimal temperature with the highest passivation quality after annealing and firing. The clear τ_{eff} improvement in passivation from 100 to 250 °C could be explained by a lower amount of impurities at the passivated surface combined with reduced hydrogen concentration at higher deposition temperature. Hydrogen usually plays a key role in the silicon surface passivation, while too high or too low hydrogen concentration can be harmful for the passivation [10]. The lower ALD temperature with highest hydrogen concentration could indeed introduce hydrogen related defects [11]. On the other hand, the hydrogen concentration at 300°C ALD may be too low for effective surface passivation. The XRR measurement revealed a film density of 2.6 g/cm^3 for 100°C ALD and 3.2 g/cm^3 for 300°C ALD, which also supports this finding, where highest hydrogen content in the film can dramatically lower the film density.

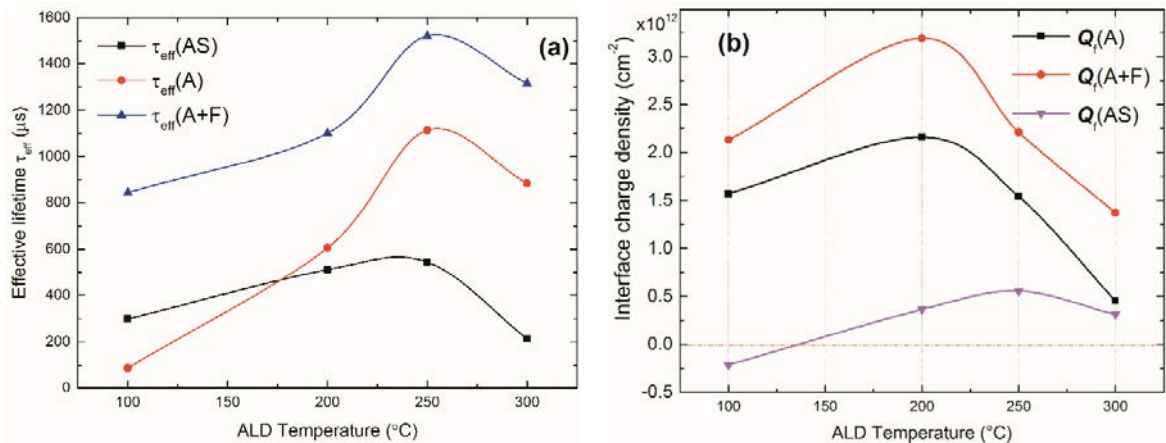


Fig. 3. (a) The impact of ALD temperature on the passivation quality of the mixed Al precursor recipe C. The evolution of passivation quality under annealing and firing are also shown. The interface charge density Q_f for all samples in (a) are shown in (b). The τ_{eff} is obtained at the injection level of $3 \times 10^{15} \text{ cm}^{-3}$ for as-deposited samples (AS), annealed samples (A) and fired samples (A+F).

Similar to the previous CV characterization, the increased D_{it} among the samples cannot explain the lifetime improvement with higher ALD temperature or the effect of the heat treatments. The change of the field effect passivation for samples presented in Fig 3(a) are shown in Fig 3(b). Due to the effect of thicker silicon oxide formed at higher ALD temperatures, the value of Q_f show a constant decrease from 200 °C. However, the peak Q_f at 200 °C does not coincidence with τ_{eff} peak in Fig 3(a). The ALD process temperature between 200 and 300 °C can provide satisfactory passivation for silicon solar cell.

6. Conclusions

We have shown that a combined use of TMA and DMAcI in the Al_2O_3 ALD process provides satisfactory silicon surface passivation with good thermal stability. Moreover, the ALD process with the mixed aluminium precursor seems to improve both post-anneal and post-firing passivation as compared to the process that uses either pure TMA or DMAcI.

The chlorine content introduced by DMAcI in the ALD process seems to lower the as-deposited interface defect density and improves the negative charge density both for as deposited samples and fired samples. The ALD at 250°C seems to be the best growth temperature for the mixed Al precursor process. Certain amount of chlorine content in the deposited film seems to be beneficial for the passivation during the firing process in solar cell fabrication.

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