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Al_2O_3/SiN_x Stacks with Ozone-based ALD Al_2O_3 for Surface Passivation: Superior Layer Stability after Firing

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Abstract We present a systematic study on effective passivation of p-type crystalline silicon (c-Si) by Al_2O_3 and Al_2O_3/SiN_x stacks. Ozone-based atomic layer deposition (ALD) Al_2O_3 was deposited with varied thickness, ozone concentration and deposition temperature. Thermal stability of fabricated samples was investigated systematically varying post-deposition thermal treatments, such as forming gas annealing (FGA) and fast firing. Blister free Al_2O_3/SiN_x stacks were obtained for Al_2O_3 thicknesses between 3.5-10 nm yielding effective charge carrier lifetimes (τ_{eff}) above 1.5 ms, which correspond to an implied open-circuit voltage (iV_{oc}) above 730 mV. The best performing Al_2O_3 layers in terms of their passivation quality, deposition uniformity and firing stability after being capped by SiN_x were obtained when a low ozone concentration was utilized in the ALD process. As no additional out-gassing process is necessary between ALD Al_2O_3 and PECVD SiN_x deposition, these ozone-based ALD Al_2O_3 layers have the potential to simplify the rear-side passivation of PERC solar cells in mass production.

INTRODUCTION

The key to fabricate high-efficiency crystalline silicon (c-Si) solar cells is the efficient passivation of c-Si surfaces. Thermal and plasma-enhanced atomic layer deposition (ALD) aluminum oxide (Al_2O_3) has been used extensively due to its excellent passivation performance on c-Si. Al_2O_3 films are generally capped with silicon nitride (SiN_x) layers, which is the mainstream for passivated emitter and rear cell (PERC) applications. However, Al_2O_3/SiN_x stacks are prone to blister formation, which deteriorates the surface passivation quality, when subjected to thermal treatments at high temperatures (e.g. firing), which is essential for contact formation of screen-printed metals in industrial silicon solar cell production [1-3]. Therefore, the application of ALD Al_2O_3 on c-Si solar cells becomes challenging. An additional out-gassing step, which was found to be beneficial to avoid blister formation, is generally applied after H_2O-based thermal ALD Al_2O_3, prior to any capping layer deposition [4]. In this study, we show that blister-free films with efficient passivation quality can be obtained by careful control of ozone-based Al_2O_3 deposition, without the necessity of an additional out-gassing step.

Thermal ALD Al_2O_3 based on trimethylaluminum (TMA, $Al(CH_3)_3$) and water (H_2O) has been a benchmark for a while for effective surface passivation of c-Si in solar cell production. However, ozone-based ALD Al_2O_3 is stated to have lower interface defect density (D_{it}) and higher fixed negative charge density (Q_f), resulting in better surface passivation compared to H_2O-based ALD Al_2O_3 [5-6]. Ozone-based ALD processes are also reported to result in lower carbon contamination compared with those deposited with H_2O-based ALD [7].

In this study, we investigate the effect of ozone concentration and deposition temperature on passivation quality and stability (blistering) of Al_2O_3 films and Al_2O_3/SiN_x stacks with a broad range of post-deposition thermal

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treatments. In particular, the effect of ozone concentration on passivation properties of Al_2O_3 films and industrial more relevant Al_2O_3/SiN_x stacks are shown [8]. Our study on ozone-based ALD Al_2O_3 can be an industrial roadmap for simplified fabrication of blister-free rear-side passivation of PERC solar cells without requiring an extra out-gassing step.

EXPERIMENTAL

Symmetrical lifetime test structures were fabricated on shiny-etched p-type float-zone (FZ) c-Si wafers with a resistivity of 1 Ωcm and a thickness of 250 µm. The c-Si wafers were subjected to standard RCA cleaning followed by thermal oxidation at 1050 °C to remove FZ defects [9]. The oxide was removed prior to Al_2O_3 depositions. 3.5 nm, 6.5 nm and 10nm thick Al_2O_3 layers were deposited on c-Si via thermal-ALD (Oxford Instruments, FlexAL) using TMA and ozone (O_3) precursors at deposition temperatures (T_{Dep}) of 200 °C and 300 °C. Ozone concentration in ALD cycles was tuned via MKS Instruments O3CS AX8561 ozone system from 5% wt. (73 g/Nm^3) to 20% wt. (306 g/Nm^3). Total number of cycles in ALD processes were adapted according to the ozone concentration to be able to obtain the same Al_2O_3 thickness.

Al_2O_3 deposited samples were subjected to consecutive FGA with varied temperatures from 350 °C to 500 °C with 50 °C increments for 15 minutes in a tube furnace. Another set of Al_2O_3 samples were capped with 70 nm of anti-reflection coating SiN_x deposited at 350 °C using inline PECVD (MAiA, Meyer Burger). Al_2O_3/SiN_x stacks were either subjected to consecutive FGA as described above or fast firing (at 750 °C or 800 °C) in rapid thermal annealing furnace.

Passivation quality and blistering behavior of both Al_2O_3 films and Al_2O_3/SiN_x stacks were investigated with injection dependent effective minority carrier lifetime measurements (Sinton WCT-120 lifetime tester) and microscope imaging (Olympus MX61). Thickness and uniformity of the deposited films were analyzed via spectroscopic ellipsometry measurements (J.A. Woollam Co.).

RESULTS & DISCUSSION

Ozone-based ALD processes were optimized to ensure the complete saturation on the c-Si surface for different ozone concentrations and deposition temperatures. Growth per ALD cycle (GPC) varied in the range of 0.46-0.83 Å/cycle (Fig. 1) for different O_3 concentrations and O_3 dose times. Linear increase in GPC is observed with increasing O_3 concentration. Dashed line is a guide for the eye to indicate the linear increase with respect to O_3 concentration.

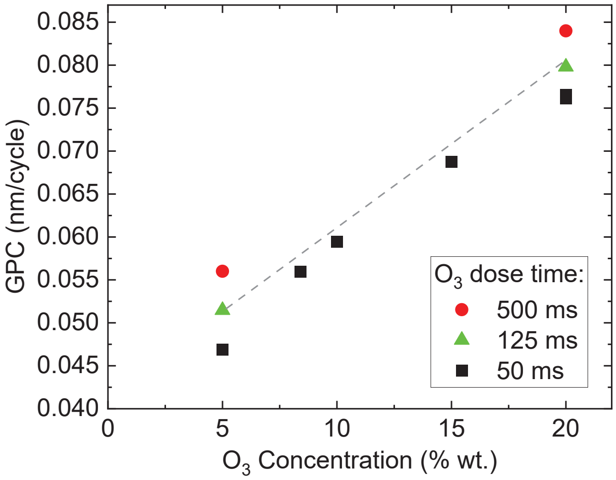


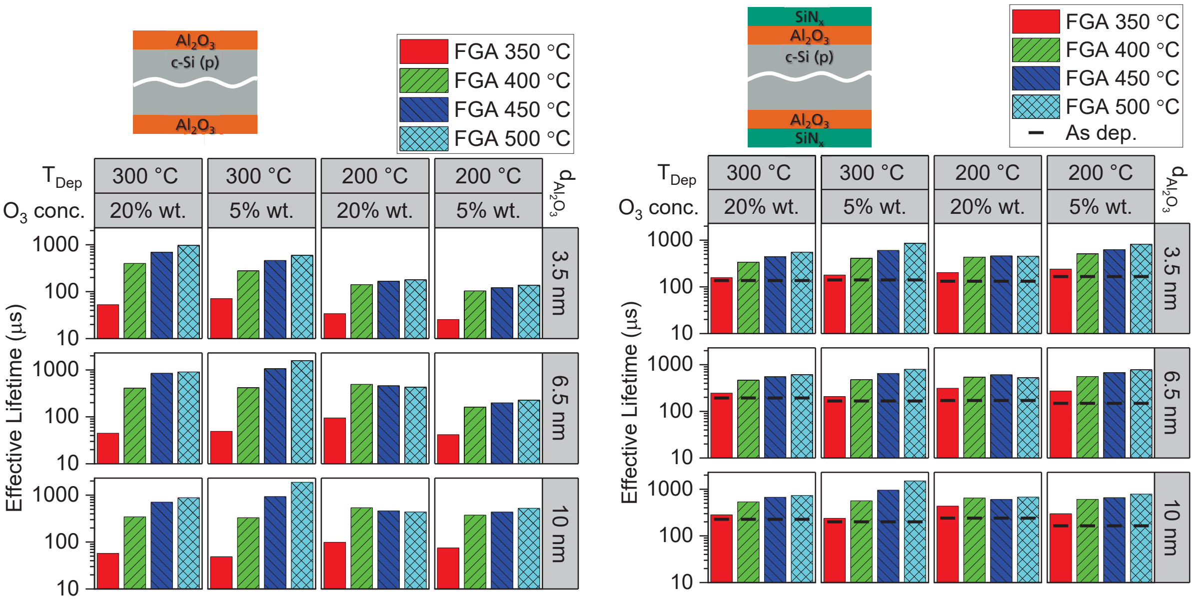
FIGURE 1. Growth per ALD cycle (GPC) of Al_2O_3 films depending on ozone concentration and O_3 dose time

Effect of FGA on Al_2O_3 Samples

Effective charge carrier lifetimes measured at an injection level of $\Delta n = 1 \times 10^{15}$ cm^{-3} after each FGA step are shown in Fig. 2. Lifetimes of Al_2O_3 samples (Fig. 2a) are improved clearly when T_{Dep} increased from 200 °C to 300 °C. Al_2O_3 samples deposited at 200 °C reach almost their highest lifetimes after annealing at 400 °C. Lifetime of Al_2O_3 samples deposited at 300 °C even increases for annealing temperatures up to 500 °C for both low and high ozone concentrations. Al_2O_3 samples are generally annealed at temperature range between 400 °C - 425 °C in standard FGA processes in literature [10-11]. Our study shows that lifetime of ozone-based ALD Al_2O_3 samples are further improved with higher FGA temperatures especially for higher T_{Dep}. There is a slight increase in lifetime with increased Al_2O_3 thickness. The highest lifetime is achieved with 10 nm thick Al_2O_3 deposited at 300 °C T_{Dep} with 5% wt. O_3 concentration after FGA at 500 °C, resulting in effective lifetime of 1.9 ms. None of Al_2O_3 samples show blistering after any FGA step.

Effect of FGA on Al_2O_3/SiN_x Stacks

Effective lifetime results of Al_2O_3/SiN_x stacks after each consecutive FGA step are shown in Fig. 2b. They exhibit similar lifetime trend as Al_2O_3 samples when FGA temperature increases. Lifetime of Al_2O_3/SiN_x stacks after SiN_x deposition indicated by black straight lines (denoted by "as dep.") exhibit better results than Al_2O_3 samples annealed at 350 °C because of SiN_x deposition. In addition, lifetimes of samples with single Al_2O_3 films, which have poorer passivation quality, improve with SiN_x capping layer. For instance, an increase in the passivation quality of Al_2O_3 samples for T_{Dep} of 200 °C is observed after capping with SiN_x. However, Al_2O_3 samples already exhibiting high lifetimes are not improved with SiN_x capping. Even if the deposition parameters (i.e. T_{Dep}, O_3 concentration, $d_{Al_2O_3}$) are varied, relatively similar lifetime results are obtained with Al_2O_3/SiN_x stacks compared to samples with single Al_2O_3 layers. The highest lifetime is achieved with 10 nm thick Al_2O_3 deposited at 300 °C T_{Dep} with 5% wt. of O_3 concentration after FGA at 500 °C (like Al_2O_3 single layers) resulting in effective lifetime of 1.5 ms. Blistering is not observed for any of Al_2O_3/SiN_x stacks after FGA process.



(a) (b)

FIGURE 2. Effective charge carrier lifetime results of Al_2O_3 samples (a) and Al_2O_3/SiN_x stacks (b) after consecutive FGA

Effect of Fast Firing on Al_2O_3/SiN_x Stacks

Effective lifetime results of Al_2O_3/SiN_x stacks after firing are shown in Fig. 3. Lower O_3 concentration outperforms significantly for all ALD Al_2O_3 T_{Dep} and film thicknesses. Surprisingly, passivation quality decreases for thicker Al_2O_3 films deposited with 20% wt. O_3 concentration while it is improved for thicker Al_2O_3 films deposited with 5% wt. O_3 concentration. Similar lifetime results are obtained after fast firing either at 750 °C or 800 °C. However, blistering is more pronounced for higher firing temperature (denoted by the letter 'B' in the lifetime graphs). In addition to high firing temperature, Al_2O_3/SiN_x stacks are prone to have more blistering for higher Al_2O_3 T_{Dep}. However, blister-free Al_2O_3/SiN_x stacks with excellent surface passivation can be fabricated by choosing suitable deposition parameters.

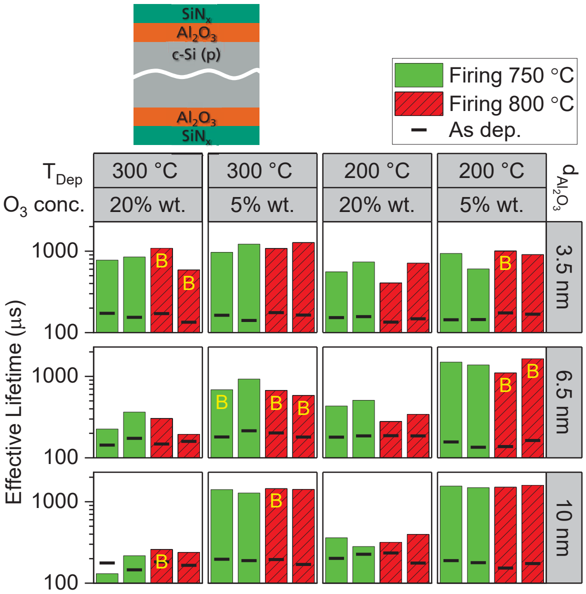
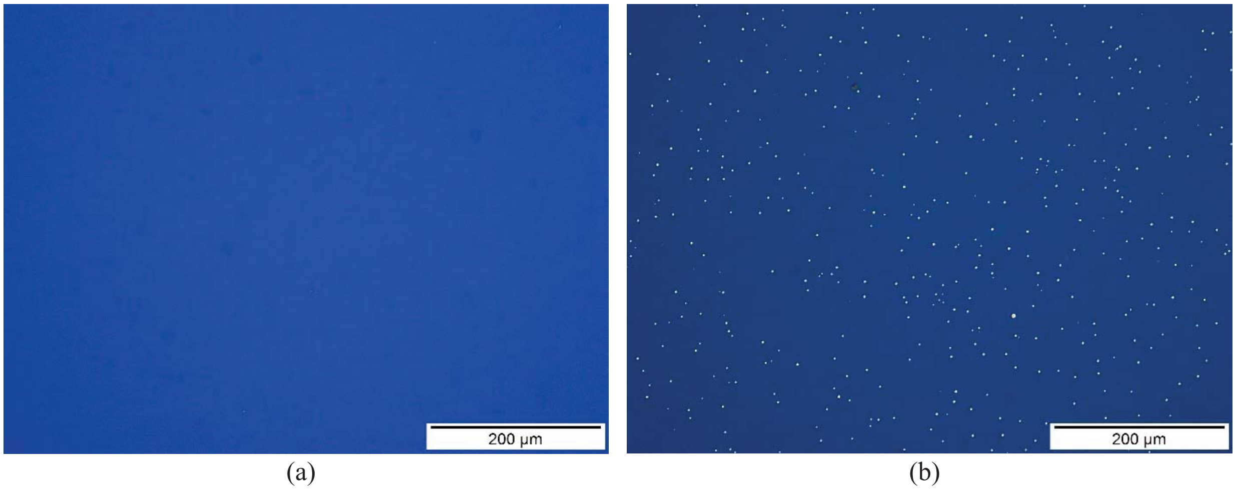


FIGURE 3. Effective charge carrier lifetime results of Al_2O_3/SiN_x stacks after fast firing. Samples showing blistering are indicated by the letter 'B'.

Microscope images of Al_2O_3/SiN_x stacks with 6.5 thick Al_2O_3 layers deposited at 200 °C with low O_3 concentration are shown in Fig. 4 with and without blistering formation after firing at 800 °C and 750 °C, respectively. Al_2O_3/SiN_x stacks having lifetimes of 1.5 ms are fabricated with both 10 nm and 6.5 nm thick Al_2O_3 films deposited at 200 °C with low O_3 concentration. Similar lifetime results are also obtained with 10 nm thick Al_2O_3 films deposited at 300 °C. Low O_3 concentration, therefore, gives more flexibility while choosing the Al_2O_3 deposition temperature.



(a) (b)

FIGURE 4. Microscope images of Al_2O_3/SiN_x stacks after fast firing at 750 °C (a) and 800 °C (b)

CONCLUSION

We present a systematic study on thermal stability of ozone-based thermal-ALD Al_2O_3 deposited samples and Al_2O_3/PECVD SiN_x stacks with varied post-deposition thermal treatments. Tuning the ALD parameters are more crucial for single Al_2O_3 layer when FGA is utilized for the activation of surface passivation. Al_2O_3 films showing poor passivation quality are improved to some extend by SiN_x capping layer. Although the blistering is more likely to be present on Al_2O_3/SiN_x stacks after fired at high temperatures, blister-free Al_2O_3/SiN_x stacks are obtained with suitable deposition parameters. Hence, blister-free Al_2O_3/SiN_x stacks fired at high temperature allow for effective lifetime of 1.5 ms and iV_{oc} of 730 mV when optimized ozone-based ALD Al_2O_3 deposition parameters are applied. Therefore, it can provide an industrial roadmap for simplified fabrication of blister-free rear-side passivation of PERC solar cells.

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