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Al_2O_3/SiN_x-Stacks at Increased Temperatures: Avoiding Blistering During Contact Firing

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Abstract

We investigate the passivation stability and blister formation during firing at 800°C of an Al_2O_3/SiN_x stack deposited on p-type float zone silicon at different Al_2O_3 deposition set temperatures ranging from 170°C to 400°C. The actual wafer temperatures during Al_2O_3 deposition in the FlexAL reactor are determined using spectroscopic ellipsometry. After the firing step blistering can be observed for stacks featuring 15 nm thick Al_2O_3 layers grown at 170°C set temperature. We show that the deposition of the layer at higher set temperatures of 250°C, 300°C and 400°C reduces blister formation significantly. After firing, stacks with 15 nm thick Al_2O_3 layers deposited at set temperatures of 250°C and 300°C show the best passivation resulting in effective surface recombination velocities below 5 cm/s without significant blister formation.

Keywords: Al_2O_3; Passivation; Deposition Temperature; Firing; Blistering Stability

1. Introduction

Al_2O_3 thin films grown by atomic layer deposition are suited for the passivation of p-type crystalline silicon due to both chemical and field effect passivation whereas the latter is caused by negative fixed charges at the Al_2O_3/Si interface [1]. However, using Al_2O_3 for the passivation of screen printed silicon solar cells the layer must withstand a high temperature firing step, needed to alloy the metal paste into the silicon. Previous work has shown that a firing step can lead to both blister formation and loss in passivation quality of the layer [2]. However, it was demonstrated that blistering of Al_2O_3/SiN_x stacks

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caused by high temperature steps can be avoided by either using thin Al_2O_3 layers (≤ 10 nm) or outgasing hydrogen from the Al_2O_3 layer at 600 or 700°C before SiN_x-deposition [2].

We investigate the passivation quality and blistering stability after firing of an Al_2O_3/SiN_x stack featuring an Al_2O_3 thickness up to 15 nm and deposited on p-type float zone (FZ) silicon at different Al_2O_3 deposition set temperatures ranging from 170°C to 400°C *without* any additional outgasing step in between Al_2O_3 and SiN_x deposition. The actual temperature at the wafer surface during deposition is determined using *in situ* spectroscopic ellipsometry.

2. Experimental

Shiny etched FZ-Si wafers (p-type, 2 Ωcm, thickness: 250 µm, (100) crystal orientation) are cut into pieces of ~5 × 5 cm^2 by a laser beam. The wafers are then etched in a chemical polishing (CP) solution to remove the laser damage at the edges [3] followed by an RCA clean [4]. Subsequently, Al_2O_3 is deposited on both sides by plasma-assisted atomic layer deposition (ALD) using trimethylaluminum (TMA) and oxygen as precursors. Substrate set temperatures of 170°C, 250°C, 300°C and 400°C as well as different cycle numbers are applied to get equal layer thicknesses. Following the procedure described in [3] the temperature profiles of the wafers in the FlexAL chamber during heat up for the different set temperatures are determined by in situ spectroscopic ellipsometry using a Woollam M-2000 ellipsometer. Fig. 1(a) visualizes the temperature profiles and root mean square errors (MSE) resulting from the fit of the ellipsometric data. It is clearly shown, that the wafer temperatures reach saturation before the deposition of Al_2O_3, which starts after the heat up. The determined temperatures in the saturation regime are given in Table 1.

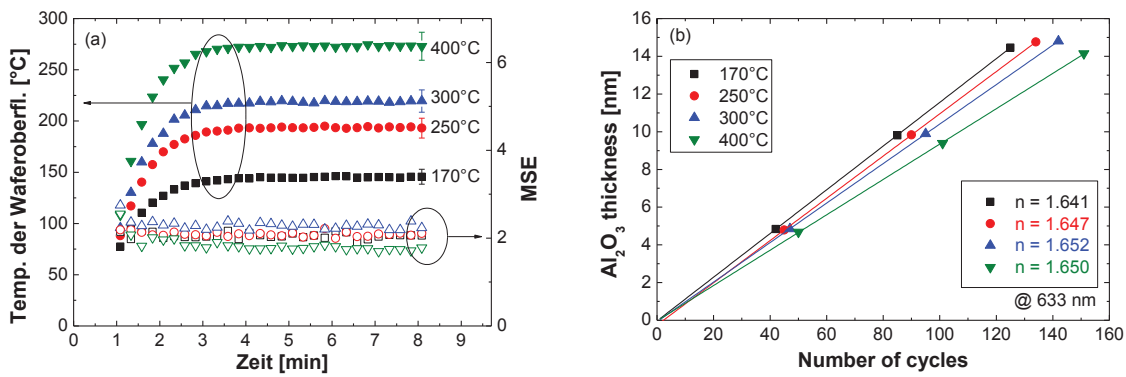

Fig. 1. Spectroscopic ellipsometry measurements to determine (a) the temperature profiles of the wafers during heat up; (b) the Al_2O_3 layer thicknesses vs. the number of ALD cycles.

Table 1. Set temperatures and corresponding wafer temperatures in saturation.

Table Set Temperature [°C]	Wafer Temperature [°C]
170	145±8
250	194±10
300	218±11
400	274±14

The temperatures on the wafers are lower than the set temperatures which can be explained by the cooler chamber walls. Note, that the measured interval of actual wafer temperatures is much smaller than the interval of set temperatures. Al_2O_3 thin films of 5 nm, 10 nm and 15 nm are grown by ALD at these set temperatures. The thickness and optical properties of the films are confirmed by *ex situ* spectroscopic ellipsometry using a Cauchy model for the Al_2O_3 film. Taking the refractive indices extracted before on thicker layers of ~100 nm, the thickness of the thin Al_2O_3 layers is determined. Fig. 1(b) shows the Al_2O_3 film thickness and a refractive index of ~1.65 which is a typical value for Al_2O_3 [5]. The decreasing growth per cycle with increased deposition temperatures has also been reported in [6].

After ALD the wafers are coated with ~85 nm silicon nitride by plasma-enhanced chemical vapor deposition (PECVD). All FZ-Si wafers are then fired in an industrial belt furnace from Centrotherm reaching a peak temperature of ~800°C for ~1 s determined at the wafer surface. Before firing, some wafers are additionally annealed in a tube furnace at a set temperature of 420°C for 30 min in nitrogen atmosphere to activate the Al_2O_3 passivation already before firing. The passivation quality of the layers and stacks is determined by photoconductance measurements at an injection level of 1×10^{15} cm^{-3} using a Sinton lifetime tester WCT-120. The Si wafer surfaces are studied by optical and scanning electron microscopy.

3. Results and Discussion

To determine the influence of the firing temperature on the passivation of the stacks and single layers grown at different Al_2O_3 deposition temperatures, the effective carrier lifetimes, shown in Fig. 2, are measured before and after the firing step. Each point represents the calculated mean value resulting from two identically treated samples whereas the error bars indicate actual values of both wafers.

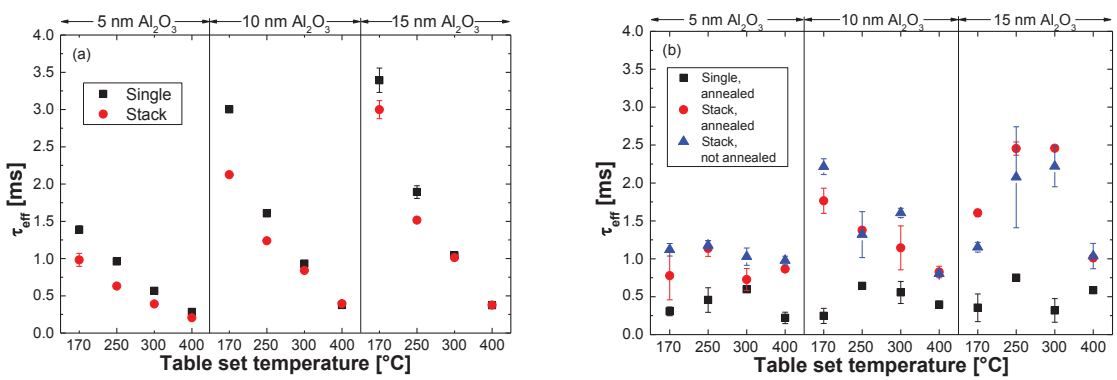

Fig. 2. Effective minority carrier lifetimes of Al_2O_3 single layers and Al_2O_3/SiN_x stacks at different deposition temperatures and layer thicknesses (a) after annealing; (b) after firing (with different pre-treatments (annealed or not annealed). Each point represents the calculated mean value resulting from two identically treated samples whereas the error bars indicate actual values of both wafers.

As it can be seen in Fig. 2(a), the Al_2O_3 single layers (black squares) show a decreasing passivation with increasing deposition temperature which can be explained by a lower hydrogen content in the as deposited Al_2O_3 layer [6] diffusing to the Al_2O_3/Si interface during annealing [7].

The passivation of the *fired* single layers is mostly degraded and does *not* show this temperature dependency. Therefore, we conclude that the decreased passivation is attributed to the diffusion of hydrogen from the Si/SiO_2-like Al_2O_3/Si interface during firing, depassivating interface defects. This is

supported by hydrogen and deuterium effusion experiments with deuterated SiO_2 layers [7] proving the effusion of both elements at temperatures > 400°C. Regarding the stacks, it can be seen that the passivation after firing is much higher compared to the single layers, as also reported in [8]. Moreover, the passivation of some stacks is even better after firing compared to the annealed state. We conclude that hydrogen from the SiN_x diffuses through the Al_2O_3 layer to the Al_2O_3/Si interface during firing, passivating interface defects and increasing the lifetime. However, the passivation of the stacks after firing still shows the decreasing trend with increasing deposition temperature as the stacks in the annealed state where the Al_2O_3 layer dominates the passivation. Therefore, it might also be possible that the SiN_x capping layer acts as a diffusion barrier restraining effusion of hydrogen from the Al_2O_3 layer into the air during firing. Such an effusion into vacuum is reported in [7]. Note that similar effective carrier lifetimes are obtained without any prior annealing step. Therefore, the passivation of the stacks can be activated by a short firing step at 800°C similar to the results with single Al_2O_3 layers fired at 600°C [9].

At an Al_2O_3 thickness of ~15 nm the stacks deposited at set temperatures of 250°C and 300°C, not 170°C as for the thinner Al_2O_3 layers, show the best passivation quality after firing leading to effective minority carrier lifetimes up to ~2.5 ms which corresponds to effective surface recombination velocities lower than 5 cm/s, assuming an infinite lifetime for the carriers in the bulk. The lack in passivation after firing of the stacks deposited at 170°C correlates with optical microscope images of the surfaces shown in Fig. 3.

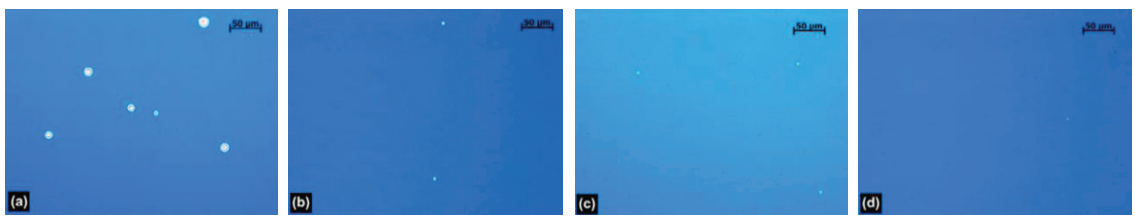

Fig. 3. Optical microscope images of fired stacks (not annealed) with 15 nm Al_2O_3: (a) 170°C; (b) 250°C; (c) 300°C; (d) 400°C

The stacks with an Al_2O_3 layer deposited at 170°C show large blister formation after the firing step. It has already been stated that this detrimental effect is caused by the release of hydrogen inside the Al_2O_3 due to high temperature steps [2] and that it can be avoided either by using thin Al_2O_3 layers (< 10 nm) or by an outgasing step at higher temperatures prior to SiN_x deposition. *In contrast we show that blistering can be reduced without an extra process step just by increasing the deposition temperature of the Al_2O_3 layer. Using set temperatures of 250°C and higher (see Table. 1) reduces blistering significantly. With this technique thicker layers of Al_2O_3 can be used.* Taking into account that hydrogen, forming inside the Al_2O_3 layer, is the reason for blistering, we conclude that the decreasing hydrogen content within the Al_2O_3 layers is responsible for the lower blister formation. The increased blister formation of stacks featuring 15 nm Al_2O_3 deposited at 170°C is attributed to be the reason for the lower passivation quality of these stacks. Note that at these blisters the stack de-laminates locally, but the stack layer is still intact as confirmed by SEM measurements. The observed blister behavior after firing is the same for annealed and not annealed samples. Before firing, no blisters can be observed.

In another experiment we examined blister phenomena of Al_2O_3/SiN_x stacks with much larger Al_2O_3 thicknesses of 58 and 116 nm. Similar to the previous experiment, annealed and not annealed sample are considered. The deposition temperature during the ALD process is set to be 170°C. Examining these samples with an optical microscope we found blistering features differently from those in Fig 3(a). Fig. 4(a) shows the surface of an Al_2O_3/SiN_x stack with 116 nm Al_2O_3 after firing, revealing a lot of gray and blue blisters. To get more insight into the nature of these features, a scanning electron microscope

(SEM) image is taken from this surface and shown in Fig. 4(b). Here, two height steps are revealed giving the impression that at this point the stack is completely missing. To confirm this result, energy-dispersive X-ray (EDX) spectroscopy maps are taken.

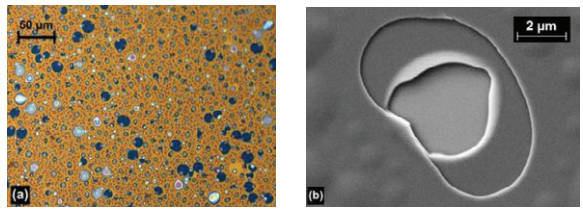

Fig. 4. Surface images of an Al_2O_3/SiN_x stack featuring an Al_2O_3 thickness of 116 nm after annealing and subsequent firing (a) opt. microscope; (b) SEM

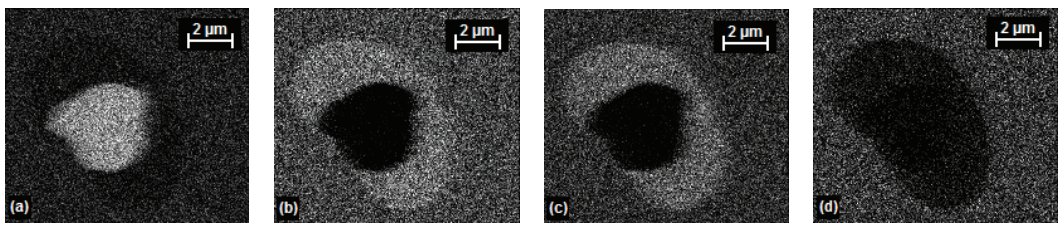

Fig. 5. EDX maps measuring different elements: (a) Si; (b) Al; (c) O; (d) N. The presence of the particular element is indicated by white dots

Fig. 5 shows the EDX maps for the elements Si, Al, O and N, revealing clearly that in the center the Al_2O_3 and SiN_x layers are missing as only Si is detected. The neighboring region is covered only by the Al_2O_3 layer without the SiN_x and in the outer region the whole stack is still present. At a deposition set temperature of 170°C chipping occurs also at Al_2O_3 thicknesses of 58 nm. Increasing the deposition set temperature to 300°C, no chipping occurs at a thickness of 58 nm, but there is still local de-lamination of the stack similar to the one shown in Fig. 3(a). Note that this observed blister behavior after firing is the same for annealed and not annealed samples.

Thus, the effect of chipping occurs on stacks featuring thick Al_2O_3 layers > 15 nm and can be reduced by higher Al_2O_3 deposition temperatures, similar to the effect in Fig. 3(a), where the stack de-laminates locally but stays complete. Therefore, we conclude that both effects have the same origin, which is the release of hydrogen from the Al_2O_3 during firing.

4. Conclusion

We demonstrated a processing sequence to avoid blistering of Al_2O_3 in stacks with SiN_x and Al_2O_3 single layers with a thickness of up to 15 nm. For this purpose we grew Al_2O_3/SiN_x stacks at different Al_2O_3 deposition temperatures and layer thicknesses. We show that the blister formation in stacks featuring 15 nm thick Al_2O_3 layers during firing can significantly be reduced by higher Al_2O_3 deposition temperatures. We conclude that the decreasing hydrogen content within the Al_2O_3 layers is responsible for the lower blister formation at increased deposition temperatures. The increased firing stability of the stacks compared to the Al_2O_3 single layers is attributed to the SiN_x capping layer acting as a hydrogen source or barrier during firing. Stacks with 15 nm Al_2O_3 layers deposited at set temperatures of 250°C and 300°C show the best passivation quality resulting in effective surface recombination velocities below

5 cm/s without significant blister formation and, consequently, are well suited for the passivation of screen printed silicon solar cells.

Acknowledgements

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