ANNEALING BEHAVIOR OF Al_2O_3 THIN FILMS GROWN ON CRYSTALLINE SILICON BY ATOMIC LAYER DEPOSITION

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ABSTRACT: Al_2O_3 thin films deposited by Atomic Layer Deposition provide an excellent passivation on both n-type and p-type silicon surfaces due to a field effect caused by negative fixed charges. To activate the passivation an annealing step at moderate temperatures (~ 425°C) for 30 min after deposition was reported to be essential. A drop in minority carrier lifetime was reported if an additional firing step was carried out.

This work demonstrates that the order of the annealing and firing step determines the quality of the surface recombination velocity (SRV). Applying the firing step before the annealing step results in a lower SRV compared to the SRV of samples subjected to the reference process. The short firing step is carried out at a peak temperature of ~ 600°C as determined at the wafer surface.

The maximum surface recombination velocity assuming an infinite bulk lifetime of the best samples after firing and subsequent anneal is determined to be 5.1 cm/s and 5.8 cm/s, whereas the lowest values for the reference process are 8.3 cm/s and 9.7 cm/s for n- and p-type Si wafers, respectively. Moreover, the minority carrier lifetime of the n-type samples after firing and subsequent annealing is comparable to the one of only annealed samples without any firing step.

Keywords: Al_2O_3, Atomic Layer Deposition, Firing, Passivation

1 INTRODUCTION

Aiming at cost reduction, the industrial fabrication processes of silicon solar cells point to the application of thinner silicon wafers. With the reduction of wafer thickness the influence of the recombination at the surfaces becomes more and more relevant for the cell efficiency. In order to reduce the recombination losses at the surfaces several passivation techniques were developed. Recently Hoex et al. reported that Al_2O_3 thin films grown by Atomic Layer Deposition (ALD) provide excellent surface passivation on both n- and p-type crystalline silicon surfaces by the field effect due to negative fixed charges in the dielectric layer [1]. To activate the passivation an annealing step at moderate temperatures (~ 425°C) for 30 min after deposition was reported to be essential [2]. However, the minority carrier lifetime decreased during a short firing step at temperatures higher than 700°C as reported by Benick et al. [3].

We investigate the dependence of the activation of passivation on the design of the temperature step. We apply a short firing step at a peak temperature of ~ 600°C measured on the wafer surface in combination with the standard annealing process. The order of the two temperature steps is studied.

2 EXPERIMENTAL

For this study shiny etched float zone wafers of n- and p-type crystalline silicon (area: ~ 5 × 5 cm², thickness: 525 µm) are used. The resistivity is 1 Ωcm and 2 Ωcm for n- and p-type silicon, respectively. Prior to the deposition of Al_2O_3 the wafers receive a RCA clean. The Al_2O_3 thin films are deposited by ALD (FLEX AL from Oxford) using a cyclic dosing of trimethylaluminum (TMA) and oxygen plasma with several purging steps in between. Figure 1 shows a schematic process sequence for one cycle. Each sample is coated on both sides with 250 cycles corresponding to an Al_2O_3 layer thickness of about 29 nm. After deposition the wafers are subjected to the combination of two different heat treatments: annealing and firing. The two heat treatments are arranged in two sequences distinguished by applying either the firing step first or the annealing step. Samples which are fired in the belt furnace after annealing are used as reference.

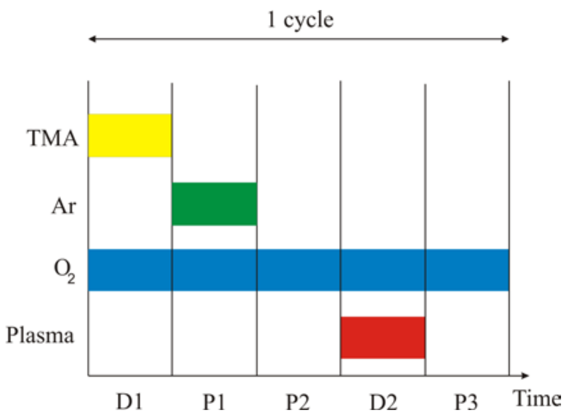

Figure 1 Schematic process sequence for one ALD cycle. D1 and D2 are dosing steps for TMA and oxygen plasma, respectively. P1, P2 and P3 are purging steps.

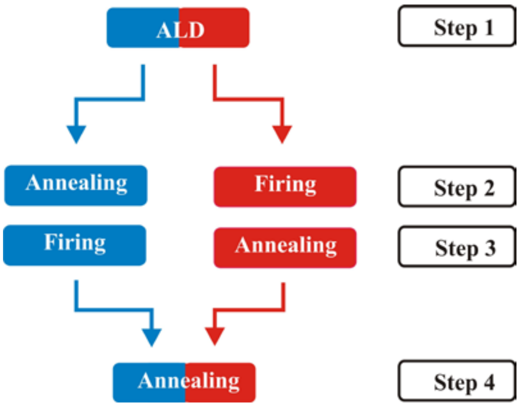

Figure 2 Schematic flowchart of the sample processing.

Figure 2 shows the schematic flowchart. The *annealing* step takes place at a set temperature of 420°C for 30 min in nitrogen atmosphere. The *firing* step is carried out at a temperature of 600°C in the hottest zone as measured on the wafer surface. A commercial industrial belt furnace from Centrotherm is used. The temperature profile of the wafer surface is measured by two thermocouples attached at different locations on the wafer. The lifetime of minority carriers is determined by photoconductance decay (PCD) measurements with a Sinton lifetime tester WTC 120 after each process step.

3 RESULTS

Figure 3 shows the measured temperature profile of the wafer surface during the firing process measured at two different spots. Both curves lie on top of each other. Therefore the temperature on the wafer surface is taken to be constant over the whole wafer for the whole temperature profile. It can be seen that the peak temperature at the wafer surface is ~ 600°C. The duration of the whole firing process including cooling is about 70 seconds.

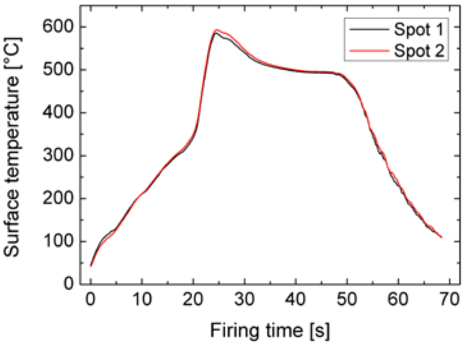

Figure 3 Temperature profile of the wafer surface during the firing step measured at two different positions.

Figure 4 shows the determined effective minority carrier lifetimes and maximum surface recombination velocities (assuming an infinite bulk lifetime) at an injection level of $\Delta n = 10^{15}$ cm^{-3} for all n-type wafers with a resistivity of 1 Ωcm. The different annealing processes are compared. After deposition (Step 1) the minority carrier lifetimes are less than 15 µs. That means the Al_2O_3 films in the as-deposited state do not show good surface passivation properties. This finding is supported by the results reported in [2].

The blue curve shows that an annealing step at 420°C (Step 2) activates the passivation of the Si wafer surface resulting in effective lifetimes higher than 3 ms. But the subsequent firing step (Step 3) causes a drop in the effective lifetimes of all samples. Further annealing cannot restore the passivation quality (Step 4) to the values determined after Step 2.

The samples subjected to the firing step directly after deposition (red curve) show a completely different behavior. First of all, the firing step after deposition activates the passivation ability of the Al_2O_3 layer resulting in a lifetime of up to 4.4 ms. Furthermore, two subsequent annealing steps decrease the surface recombination of the fired films in comparison to wafers from the standard process: Al_2O_3 deposition and just the annealing process. This behavior shown by *all* examined n-type samples clearly demonstrates an advantage when placing the firing step directly after deposition.

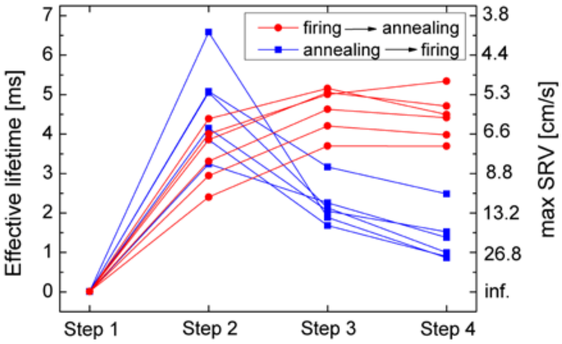

Figure 4 Characteristic recombination parameters of the n-type wafers (1 Ωcm) after different experimental steps (see Figure 2). The two different annealing sequences are indicated in blue and red.

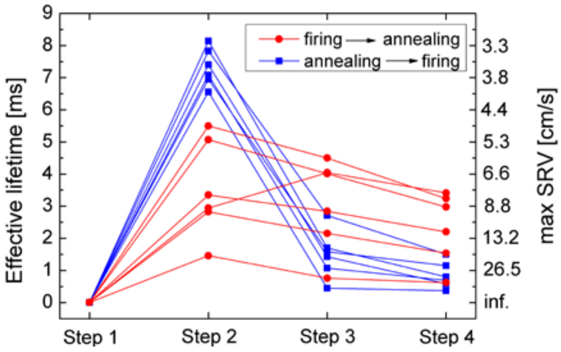

Figure 5 Characteristic recombination parameters of the p-type wafers (2 Ωcm).

Figure 5 shows the effective minority carrier lifetimes and maximum surface recombination velocities of the p-type wafers after each applied processing step. Again, in the as-deposited state the minority carrier lifetime of all samples is in the range of 1 - 15 µs, i. e. no significant surface passivation is achieved. The blue curve shows a decrease in SRV and thus the activation of the passivation mechanism after the annealing step only. Like for the n-type wafers a subsequent firing step causes a decrease of the effective lifetime resulting in a drop down to less than 50% of the initial value. Further annealing could not restore the low surface recombination velocity to the values determined after Step 2. The red curve indicates that the firing step alone activates the passivation. In contrast to the behavior of the n-type samples, annealing at 420°C does not further increase the carrier lifetimes. After the final annealing step all but one p-type sample for which the firing process is carried out directly after the deposition of the Al_2O_3 layers show higher minority carrier lifetimes compared to the lifetimes achieved within the reference process.

4 CONCLUSION

Al_2O_3 thin films do not passivate silicon surfaces in the as deposited state. The passivation mechanism has to be activated by a thermal process. As it is demonstrated, a temperature step of a few seconds at a wafer surface temperature of 500–600°C activates the passivation mechanism. Therefore, the duration of the activation process at these temperatures is in the order of seconds or less.

Furthermore, it is demonstrated that the wafers show different characteristics when placing the firing step at different positions within a heat treatment sequence although all of them are exposed to the same temperature load. The firing profile applied to n- or p-type Si allows for a lower surface recombination when placing the firing step in between the Al_2O_3 film deposition and the annealing process.

n-type and p-type wafers of 1 and 2 Ωcm respectively show a different behavior if the firing step is carried out before the annealing step. While the effective minority carrier lifetime of the n-type wafers further increases after the annealing step, the effective carrier lifetime of the p-type wafers starts to drop.

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