

CONTROL AND OPTIMIZATION OF THERMAL OXIDATION PROCESSES FOR INDUSTRIAL SOLAR CELL FABRICATION

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ABSTRACT

We present a systematic process control procedure that enables an integrated process optimization of wet chemical cleaning and subsequent thermal oxidation processes. Our approach uses distinct experiments to reveal the impact of individual parameters on the effective minority carrier lifetime. Special focus is put on an application in a production line. Therefore, both wet-chemical processing and thermal oxidation take place in industry-size equipment.

On 1 Ω cm p-type floatzone (FZ) wafers with saw-damage etched surfaces, surface recombination velocities as low as (26 ± 3) cm/s directly after oxidation and (13 ± 1) cm/s after annealing in forming gas are achieved for an optimized process sequence.

INTRODUCTION

Thermal oxides are an adequate mean for surface passivation of crystalline silicon solar cells, and have been used to fabricate highly efficient silicon solar cells [1]. However, to a great extent, thermal oxides are still waiting for their use in large scale solar cell production as the process is time and energy consuming and the high throughput demands of an industrial production are challenging. Nevertheless, solar cell concepts that utilize thermal oxidation are currently being transferred to industrial production [2], which requires concepts for process control and quality assurance.

In this paper, a systematic process control procedure is presented that enables an integrated process optimization of industrial-scale wet chemical cleaning and thermal oxidation.

EXPERIMENTAL

In our experiments 125x125 mm² (pseudo square) Czochralski (Cz) as-cut wafers as well as equivalent sized 250 μ m thick boron-doped FZ as-cut wafers (resistivity $\rho = 1 \Omega$ cm) are used. In a first step these samples are etched in KOH to remove the saw damage, a wet chemical cleaning sequence follows. Our cleaning procedure is a modified RCA clean [3] that starts with the growth of a chemical oxide on the Si surface in a heated $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ bath. The oxide is then removed in diluted HF. This sequence is denoted standard clean 1 (SC1). A second sequence of a heated $\text{HCl}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ bath with a subsequent HF dip (SC2) follows. Due to the instability of H_2O_2 , this species is freshly added before every use of one of the two baths. Other chemicals are

not redosed and might be consumed during consecutive processing. Moreover, the chemical concentrations change due to evaporation. For processing, up to 50 wafers are loaded into a wet chemistry carrier of industry-size. These carriers can hold up to 100 wafers, but only every second slot is used. Up to four subsequent batches of these cleaned wafers are then oxidized in a quartz tube furnace, also of industry-size, leading to a quartz boat loaded with 100 to 200 wafers for each experiment. Oxidation takes place at 900 to 950 $^\circ\text{C}$ in a steam-rich atmosphere, produced by burning of hydrogen. The oxide thickness ranges from 200 to 250 nm.

The quasi steady-state photoconductance decay (QSSPC) method [4] permits the determination of the effective minority carrier lifetime τ_{eff} of the FZ samples at an injection level of $\Delta n = 5 \cdot 10^{14} \text{ cm}^{-3}$. Measurements are performed directly after oxidation as well as after a forming gas anneal (FGA) at 425 $^\circ\text{C}$ for 25 minutes. Note that no aluminum is deposited on the wafers before annealing. The effective surface recombination velocity S is calculated according to [5]

$$S = \frac{W}{2} \left[\left(\frac{1}{\tau_{\text{eff}}} - \frac{1}{\tau_{\text{bulk}}} \right)^{-1} - \frac{1}{D} \left(\frac{W}{\pi} \right)^2 \right]^{-1} \quad (1)$$

from the sample thickness W , the bulk lifetime $\tau_{\text{bulk}} = 3$ ms (Auger limit) [6], and the diffusion constant $D = 27.1 \text{ cm}^2/\text{s}$ for the used 1 Ω cm material.

Systematic process control scheme

Several process parameters affect the passivation quality and industrial fabrication requires homogeneous processing of a large number of wafers. For an integrated process optimization of both wet chemical cleaning and the subsequent thermal oxidation process, we suggest a systematic process control scheme. Our approach uses distinct experiments to investigate how different sets of processing conditions affect the passivation quality. For this purpose we place FZ-Si reference wafers at distinct positions of the above described batch. Figure 1 illustrates the four experiments performed in this work, the green lines mark the position of the FZ references.

Our first experiment focuses on the influence of the position of wafers in the carrier during wet chemical cleaning. Four wet chemistry carriers are damage-etched and cleaned. Among a large number of Cz-Si wafers, two

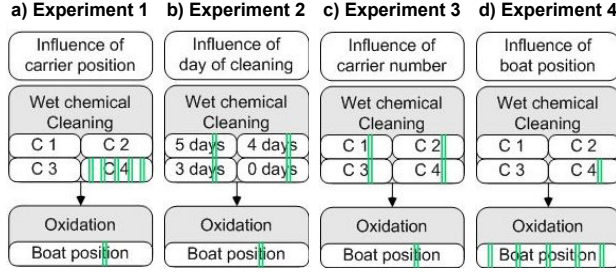


Fig. 1. Illustration of the four experiments performed in this work. The green lines mark the position of the FZ reference wafers.

- a) Experiment 1: Two FZ wafers each are placed at five positions in the fourth wet chemistry carrier C4. During oxidation the ten FZ wafers are grouped together.
- b) Experiment 2: Two FZ wafers each are placed at the same positions in the last wet chemistry carriers and cleaned on different days. During oxidation the eight FZ wafers are grouped together.
- c) Experiment 3: Two FZ wafers each are placed at the same positions in each of the four wet chemistry carriers. During oxidation the eight FZ wafers are grouped together.
- d) Experiment 4: Ten FZ wafers are grouped together in the last wet chemistry carrier and then distributed along the oxidation boat.

FZ wafers are placed at different positions in the fourth carrier. Fig. 1 a) illustrates the experimental sequence, the green lines mark the position of the FZ references. The 200 wafers are oxidized afterwards, whereas the FZ wafers are grouped together in the oxidation boat.

The second experiment investigates the effect of the waiting time of wafers between cleaning and oxidation. Therefore, FZ wafers are cleaned on different days, withdrawn after cleaning and put in a closed box. Oxidation takes place five days after the first wafers are cleaned. Other wafers wait for four and three days, respectively, two wafers are cleaned at the day of oxidation. The course of action is illustrated in Fig. 1 b).

The third experiment covers the influence of the change in reservoir composition during wet chemical cleaning. For this purpose, two FZ wafers are placed at the same position in each of the four subsequently processed wet chemistry carriers. The rest of the open slots is filled with Cz wafers, leading to a fully loaded carrier. Fig. 1 c) gives an idea about the experimental sequence. As in the experiments described above, after cleaning, the FZ wafers are grouped together in the oxidation boat to allow the separation of the impact of different boat positions (see experiment 4 below).

In a fourth experiment, a set of ten FZ wafers is grouped together in the fourth wet chemical carrier C4 and then distributed along the oxidation boat, as illustrated in Fig. 1 d).

RESULTS AND DISCUSSION

Influence of carrier position

As can be seen from Fig. 2, the effective lifetime of all FZ wafers is on the same high level, with $(180 \pm 20) \mu\text{s}$ after oxidation and $(400 \pm 40) \mu\text{s}$ after a FGA, corresponding to $(60 \pm 6) \text{ cm/s}$ and $(24 \pm 2) \text{ cm/s}$. Thus, the effective lifetime does not depend on the position of the wafers in the carrier itself.

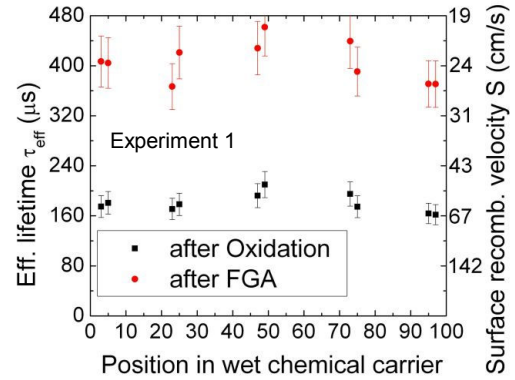


Fig. 2. Effective lifetime τ_{eff} measured for the FZ references after oxidation (black squares) and after FGA (red circles) plotted vs. position in the wet chemistry carrier. Figure 1 a) illustrates the corresponding experimental sequence.

Influence of waiting time

Figure 3 shows the impact of the waiting time between cleaning and oxidation on the effective carrier lifetime. A slight dependence of the waiting time is visible, samples that have waited longer after cleaning show lower lifetimes. Nevertheless, surface conditioning after cleaning is remarkably stable. Even after five days of waiting, a level of around $(300 \pm 30) \mu\text{s}$ after FGA, equivalent to $(34 \pm 4) \text{ cm/s}$, is measured. This could be explained by an efficient hydrogen termination of surfaces states, following the final HF-dip before rinsing [7]. Still, further experiments in this direction have to be performed in order to get a deeper understanding of the processes involved.

Influence of reservoir composition

Apparent from Fig. 4, the effective lifetime slightly increases from one wet chemical carrier to the next. This trend persists also after a FGA, which increases the lifetime by around $60 \mu\text{s}$, decreasing S from $(56 \pm 5) \text{ cm/s}$ after oxidation to $(40 \pm 4) \text{ cm/s}$. One cause for the trend could be the different durations between cleaning and oxidation, since the wafers from carrier C1 have to wait

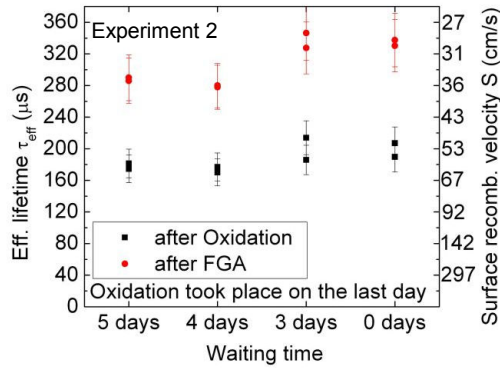


Fig. 3. Effective lifetime τ_{eff} measured for the FZ references after oxidation (black squares) and after FGA (red circles). The wafers have been cleaned on different days and oxidized together. Figure 1 c) illustrates the corresponding experimental sequence.

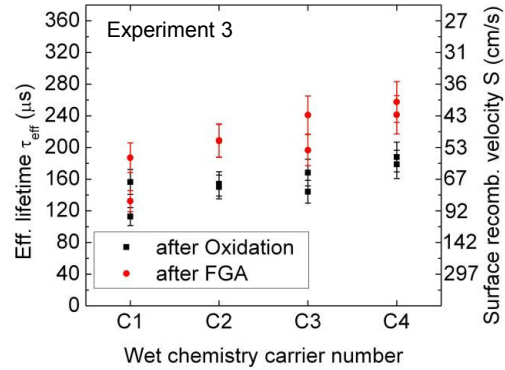


Fig. 4. Effective lifetime τ_{eff} measured for the FZ references after oxidation (black squares) and after FGA (red circles), plotted vs. wet chemistry carrier number. Figure 1 b) illustrates the corresponding experimental sequence.

until carrier C4 is processed. However, as shown in experiment 2 above, the time between cleaning and oxidation does not significantly affect τ_{eff} . Thus, the effective lifetime depends on how many wafers were cleaned before or for how long the cleaning solution was used.

For finding the cause of the observed trend, we repeat experiment 3 and track the concentration of the chemicals in the cleaning reservoirs by means of titration. To measure a change of reservoir composition, eight carriers with 50 wafers each are processed through a KOH damage etch and the above described cleaning procedure. The first carrier C1 contains three and the last four carriers C5 to C8 each contain two FZ silicon reference wafers, which are subsequently oxidized in a fully loaded boat, similar to the experiment illustrated in Fig. 1 c). Titration enables the determination of the concentration of the relevant chemicals. Samples are drawn just before each carrier enters the reservoir.

Figure 5 presents the measured concentration of H_2O_2 , NH_4OH , and HCl (left axis). The H_2O_2 -concentration of both reservoirs scatters between 20% and 109% of the target value, whereas the values for NH_4OH , and HCl both decrease monotonically from around 100% to 29% and 84%, respectively. In recent experiments, the scattering of the H_2O_2 concentrations could be considerably reduced by means of faster titration.

Apparent from Fig. 5 (red dots, right axis), the lifetime measured for the FZ references after FGA increases from carrier C1 to C8, as already observed above (see Fig. 4). The wafers cleaned in carriers C5 to C8 exhibit a carrier lifetime at a constant level of $(270 \pm 30) \mu\text{s}$, which corresponds to $(39 \pm 4) \text{ cm/s}$. The effective lifetime is higher than the initial one of wafers cleaned in carrier C1. The lifetime seems to anticorrelate with the NH_4OH or HCl concentration. So far an impact of other factors that are not tracked can not be excluded. Further experiments are planned to isolate the impact of combination of chemicals on the effective lifetime. Although the exact composition of

SC1 (i.e. NH_4OH and H_2O_2) and SC2 (i.e. HCl and H_2O_2) is supposed to be not critical for a proper performance [3,7], the results indicate the need to control and supervise the concentration of chemicals during processing [8].

Influence of boat position

Figure 6 displays the dependence of the effective lifetime on the position in the oxidation boat. From the gas inlet at the front towards the exhaust at the rear the lifetime first increases and then saturates. Again, this trend persists after a FGA and S goes down to $(29 \pm 3) \text{ cm/s}$. The result might imply an influence of gas flow on the lifetime. Therefore, further experiments that focus on the gas flow in the oxidation tube are carried out.

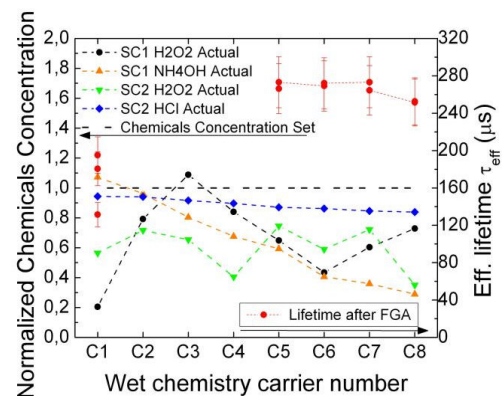


Fig. 5. Normalized concentration of chemicals before a wet chemistry carrier enters the reservoir (left axis) and effective lifetime measured for FZ wafers that are placed in the specific carrier (red dots, right axis). All FZ wafers are grouped together during oxidation (See Fig. 1 a). The lifetime is measured after a FGA.

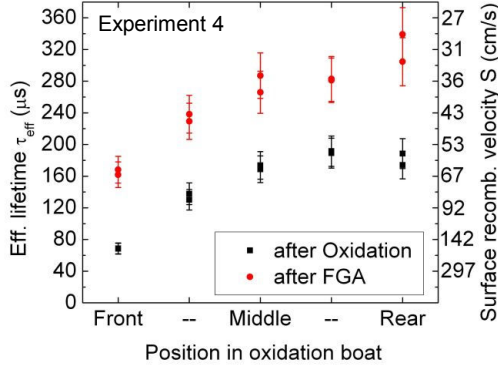


Fig. 6. Effective lifetime τ_{eff} measured for the FZ references after oxidation (black squares) and after FGA (red circles) and plotted vs. the position in the oxidation boat. Figure 1 d) illustrates the corresponding experimental sequence.

Industrial applications require high throughput as well as high uniformity and reproducibility. After the actual oxidation process, the oxidation atmosphere is changed to an inert gas ambient. Regularly used gases are argon or nitrogen. The gas flow must be high enough to ensure a homogeneous oxide quality along the boat, but selecting this value too high, results in increased costs for the gases involved. This post oxidation anneal (POA), which is normally performed at the same temperature, serves as a mean to reduce oxide charges and to diminish the amount of water in the oxide [9].

In a further experiment, the N_2 flow during the POA is varied. For this experiment, FZ and Cz Si wafers are cleaned in two subsequently processed carriers and the boat is only loaded with 100 wafers. Five pairs of two FZ Si wafers each are distributed along the oxidation boat. Placing the remaining 90 Cz Si wafers around the FZ Si wafer pairs simulates a fully loaded boat.

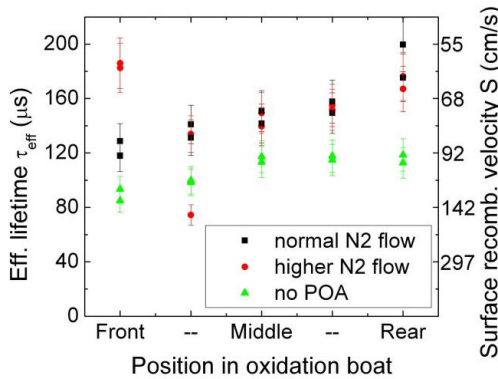


Fig. 7. Effective lifetime τ_{eff} measured for the FZ references after a FGA plotted vs. position in the oxidation boat for different post oxidation anneal parameters.

Figure 7 displays the influence of the different processes on the lifetimes measured for the FZ wafers after a FGA. Again, a raise in the effective lifetime towards the end of the boat is visible for the standard recipe (black squares), confirming the results from experiment 4 (see Fig. 6). Changing the gas flow for different experiments strongly affects the lifetime. If the POA is skipped (green triangles), lower effective lifetimes only between 80 μs and 120 μs are measured, corresponding to $S \approx 100 \text{ cm/s}$, which indicates the necessity of the POA. Except for the first two wafers positioned close to the gas inlet (front), increasing the gas flow during the POA (red circles) does not change the effective lifetime compared to the standard recipe. The effect of a position-dependent lifetime in the boat persists, regardless of the height of the nitrogen flow. At the rear of the boat the highest lifetimes are reached, with $(200 \pm 20) \mu\text{s}$, which corresponds to $S = 55 \text{ cm/s}$.

For higher nitrogen gas flows during the POA, the atmosphere exchanges faster. Therefore, the time in which the wafers are exposed to the oxidizing ambient reduces. Therefore an approximately 15 nm thinner oxide compared to the standard recipe is measured. In almost the same manner reducing the nitrogen flow during the POA yields a slightly thicker oxide. The lower overall lifetimes compared to experiment 4 (see Fig. 6) might be caused by a lower quality of the wet chemical cleaning.

Different water vapor flows during the oxidation process are also investigated (not shown). Nevertheless, no reproducible effect on the effective lifetime could be derived. Nor could we diminish the trend along the oxidation boat.

Optimized process

The integrated process control scheme described above reveals the influence of parameters in wet chemical processing and thermal oxidation. Optimizing these parameters carefully in regard to high lifetimes after oxidation, on damage-etched p-type $1 \Omega\text{cm}$ FZ as-cut material of 250 μm starting thickness, very high lifetimes of $(340 \pm 40) \mu\text{s}$ after oxidation and $(660 \pm 70) \mu\text{s}$ after an FGA are achieved, which equals very low surface recombination velocities of $(26 \pm 3) \text{ cm/s}$ and $(13 \pm 1) \text{ cm/s}$, respectively (see Table 1). We presume, that after aluminum deposition and a post-metallization anneal, S should be considerably below 10 cm/s .

To determine the effective lifetime at lower injection densities, the quasi steady-state photoluminescence method is used [10]. At an injection density of $\sim 10^{14} \text{ cm}^{-3}$, which is relevant for back-surface passivated and point-contacted silicon solar cells under 1 sun illumination [11], the thermal oxide yields very low surface recombination velocities of $(21 \pm 2) \text{ cm/s}$. Additionally, in a solar cell the thermal oxide is usually covered by aluminum, which further decreases the surface recombination velocity due to differences in the work function of both materials [12],[13]. Nevertheless, as was shown by Aberle et al. [14], at maximum power point conditions for high-efficiency silicon solar cells, rear surface recombination

Table 1. Effective carrier lifetime τ_{eff} and surface recombination velocity S measured at different injection densities applying the QSSPC and the QSSPL technique for an oxidized 1 Ωcm boron-doped silicon FZ wafer with damage-etched surfaces for an optimized cleaning and oxidation process.

	τ_{eff} at $5 \cdot 10^{14} \text{cm}^{-3}$ (μs)	S at $5 \cdot 10^{14} \text{cm}^{-3}$ (cm/s)	S at $1 \cdot 10^{14} \text{cm}^{-3}$ (cm/s)
After oxidation	340 ± 40	26 ± 3	-
After FGA	660 ± 70	13 ± 1	21 ± 2

can be one of the dominating loss mechanisms. It is therefore important to reduce S as far as possible.

The authors would like to stress that the cleaning is done in a batch cleaning system and the oxidation in a quartz tube, both of industry-size and both with focus on implementation in a production line, regarding use of chemicals, temperatures involved and throughput.

SUMMARY AND OUTLOOK

A systematic procedure for process control and optimization is presented, which permits the control and improvement of parameters for wet chemical cleaning and subsequent thermal oxidation. Applying this approach reveals an influence of chemicals concentration during wet chemical cleaning on achievable lifetimes after thermal oxidation, underlining the necessity for inline-control during processing. A dependence of the effective lifetime of the position in the oxidation boat is observed, but can not be fully explained so far and will be due to more experiments. The waiting time of wafers between cleaning and oxidation is shown to not be a crucial factor. On the contrary, surface conditioning after cleaning is remarkably stable, allowing high carrier lifetimes for an oxidation even five days after cleaning. More detailed experiments in this direction are planned.

Although industrial processes require high throughput, a post-oxidation anneal should not be skipped, as it has a big influence on the surface passivation quality. Lower lifetimes are measured on wafers that did not receive a POA. This effect persists even after a subsequent FGA.

After optimizing parameters for wet chemical processing and thermal oxidation, on 1 Ωcm p-type FZ as-cut material of 250 μm starting thickness, very low surface recombination velocities of 13 cm/s are obtained after annealing in forming gas.

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