

DEGRADATION OF SI-SiO₂ INTERFACES DURING RAPID THERMAL ANNEALING

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ABSTRACT: This work investigates the degradation of oxide-passivated silicon during a rapid thermal anneal (RTA). We find that at 500 and 600 °C, but not 400 °C, the oxide passivation is degraded when exposed to the illumination of the heating lamps, and that the degradation increases as the sample temperature increases. We also find that the oxide passivation does not degrade when shielded from the illumination for temperatures of 400, 500 and 600 °C. The results suggest that the illumination-induced degradation is due to the injection of electrons from the silicon into the oxide by one or both of the following mechanisms: (i) photoinjection from the silicon's valence band during the RTA's ramp-up, when the filaments of the heating lamps are > 2100 K and emit a large number of photons with an energy > 4.2 eV; and (ii) thermal-assisted photoinjection from the silicon's conduction band during the RTA's steady-state period, which requires the sample to be sufficiently hot that the conduction band is highly populated with electrons, and the filaments to be sufficiently hot that they emit a large number of energetic photons.
Keywords: Rapid Thermal Processing, Annealing, Passivation

1 INTRODUCTION

Silicon dioxide (SiO₂) passivates the surfaces of several types of high-efficiency silicon solar cells [1–5]. A low defect density is attained at the Si–SiO₂ interface after annealing in N₂ or Ar at high temperature (900–1100 °C) [6], and by hydrogenating the Si–SiO₂ interface with a forming-gas anneal (FGA: 5% H₂, 95% N₂ or Ar) at 400 °C [7], particularly in the presence of Al [8]. But the SiO₂ passivation is degraded when exposed to water vapour or oxygen at elevated temperature [9, 10], and the effect of the H₂ can be mitigated by subsequent anneals in N₂ [11]. SiO₂ passivation also degrades under UV illumination [12, 13] and even under visible illumination when the SiO₂ is positively charged [13]. Interestingly, atomic hydrogen—whether emanating from PECVD SiN_x during firing or from hydrogen plasma—can both create and passivate defects at the Si–SiO₂ interface [14]. (In fact, H₂ can also create defects at higher temperature [7]). Contributing to the complicated nature of SiO₂ passivation is its dependence on the orientation, dopant species and surface doping of the silicon [15].

The study of SiO₂ passivation is assisted by rapid-thermal anneals (RTAs) [14, 16–18]. The simplicity and rapidity of applying an RTA permits detailed study of the dependence of interface recombination on temperature and ambient gas (N₂, O₂, FGA, Ar). It also permits simulation of the metal firing step used in solar cell fabrication [19]. In such studies, it is useful to distinguish the mechanisms that alter the recombination rate so that one mechanism is not confused with another. For example, Figure 1 presents the effective lifetime τ_{eff} of hydrogenated SiO₂-passivated silicon when exposed to moderate temperatures [18]. The figure contains three distinct regions, each attributable to a different mechanism: the initial decline in τ_{eff} is due to a loss of hydrogen from the Si–SiO₂ interface, where the hydrogen originated from an FGA; the subsequent rise in τ_{eff} is due to the deposition of surface charge during the RTA, though it is not known how the charge evolves; and the final decline in τ_{eff} relates to a degradation of the Si–SiO₂ interface for which the underlying mechanism is not understood [18]. This work investigates the cause of the final decline in τ_{eff} .

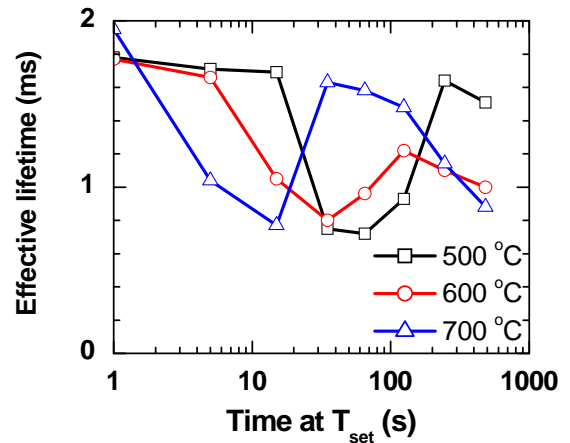


Figure 1: Dependence of τ_{eff} on time at T_{set} , from [18].

2 SAMPLE FABRICATION

Samples were fabricated from 170 μm , 2.25 ± 0.75 $\Omega\text{-cm}$, n-type FZ <100> silicon wafers with a diameter of 100 mm. The wafers were oxidized in dry O₂ at 1100 °C for 10 mins, and annealed in N₂ at 1100 °C for 30 mins. This procedure led to an SiO₂ thickness of 40 ± 5 nm. The wafers were then divided into quarters to increase the number of near-identical samples.

The samples were submitted to repeated RTAs in a Unitemp 1100 oven [20]. To assess whether the final decline in τ_{eff} was dependent on the illumination associated with the heating lamps, some samples were left exposed to the illumination while others were sandwiched between two ‘filter wafers’, as shown in Figure 2. These filters were, in fact, identical to the samples. Being silicon, they therefore prevented light of wavelengths less than 1000 nm from reaching the sample wafers. In all cases, a thermocouple was attached to the lower exposed surface to monitor temperature, and the edges of the lower wafer rested on quartz feet.

After loading the sample, the chamber was purged in N₂ for 1 minute before the lamps in the lower portion of the chamber were switched on to heat the sample. The sample temperature was then ramped at 50 °C/s to a set temperature T_{set} of 400, 500 or 600 °C. The samples were

maintained at T_{set} for a given period and then cooled rapidly by turning off the lamps and flushing the chamber with N_2 and cool water. The temperature overshoot T_{set} by $(35 \pm 15^\circ\text{C})$ for several seconds. Figure 3 plots the sample temperature and lamp power for the case of holding T_{set} at 500°C for 30 s.

The samples' recombination rate was monitored by measuring their effective lifetime τ_{eff} , where τ_{eff} is equal to the excess carrier density Δn divided by the total recombination rate U_{tot} . It therefore decreases as the recombination rate increases, whether the recombination occurs at the surfaces or in the bulk of the wafer. In this work, τ_{eff} was measured with the WCT-100 photoconductance tool [21] in transient mode [22]. Prior to every measurement the samples were washed in isopropyl alcohol (IPA) to remove charge deposited during the deposition [18]. All τ_{eff} were determined for an excess carrier density of $\Delta n = 10^{15} \text{ cm}^{-3}$, and are plotted against time at T_{set} where the time axis has a log scale; for simplicity, we plot the pre-RTA data at 1 s.

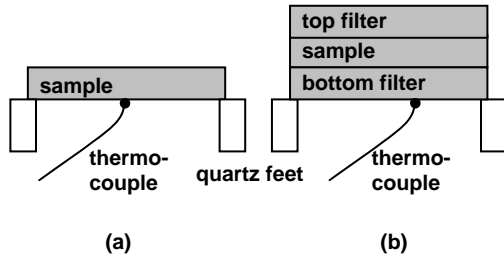


Figure 2: Placement of samples in the RTA. Some were exposed to the illumination of the heating lamps (a), while others were protected by filter wafers (b). Figure not to scale: samples were $150 \mu\text{m}$ thick and $\sim 5 \text{ cm}$ wide.

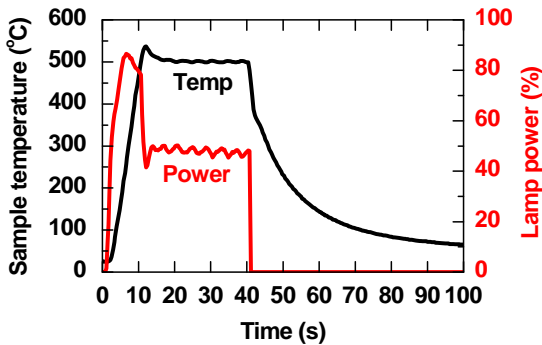


Figure 3: Sample temperature and lamp power for the case of holding T_{set} at 500°C for 30 s with no filters.

3 RESULTS

Figure 4 plots τ_{eff} for samples exposed to 400, 500 and 600°C . Before describing the results and comparing them to those found previously [18], we first describe differences between the studies.

Firstly, these samples were ~ 4 times thinner, which would reduce τ_{eff} by the same ratio if bulk recombination were negligible. We believe this to be the case, since the samples were fabricated on FZ wafers by high-lifetime procedures, and because surface recombination is relatively high due to the lack of hydrogenation.

Secondly, the wafers did not receive an FGA and, therefore, their starting lifetime is low. This omission was deliberate. It prevented the occurrence of a rapid initial decay in τ_{eff} due to hydrogen loss, as seen in Figure 1.

And thirdly, the wafers were washed in IPA prior to every measurement to remove surface charge that results from the RTA [18]. As will be shown, it is possible that some of this charge was not removed, contributing to a higher τ_{eff} than would otherwise have occurred.

Thus, these samples were specifically fabricated and tested to monitor the steady and slow decline in τ_{eff} observed in past experiments.

Figure 4 shows that of the wafers that were not protected from the illumination, the sample held at 400°C did not degrade, the sample held at 500°C degraded slowly, and the sample held at 600°C degraded more rapidly. These observations are consistent with those made previously [18].

Figure 4 also shows that of the wafers that were protected from the illumination, none degraded over the course of the experiment. If anything, they improve slightly, probably due to an alteration in surface charge not completely removed by the IPA wash (possibly related to thermal stress [23, 24]).

To further investigate the effect of illumination on the degradation, Figure 5 plots τ_{eff} of the two filters as well as the filtered sample for $T_{set} = 500^\circ\text{C}$. All wafers were washed in IPA prior to each measurement to remove (or minimise) the effect of surface charge. The figure shows that the bottom filter, which faces the illumination lamps, degrades the most. It is inconclusive but the upper filter, which is illuminated by light reflected from the internal walls of the chamber, might also degrade a little.

The importance of washing the samples in IPA is illustrated by Figure 6, which plots pre-IPA data in addition to post-IPA data for the same experiment. Thus, at each time interval there are two measurements, where the first is pre-IPA and the second is post-IPA. The resulting plots have a saw-tooth progression, where τ_{eff} of pre-IPA measurements tends to be higher than post-IPA measurements due to surface charge that results from the RTA [18]. It is relevant to note that in Figures 4–6, τ_{eff} increases slightly for samples that are filtered from the lamps, even with an IPA wash prior to each measurement; this suggests that some of the charge that results from the RTA is embedded in the SiO_2 and cannot be removed by an IPA wash.

The role of surface charge was also investigated in an identical experiment where the samples were not washed in IPA at all. Figure 7 plots the results. It indicates that for $T_{set} = 500^\circ\text{C}$, τ_{eff} of all samples increases over the first 1000 s, and significantly more so than for equivalent samples that were washed in IPA (Figure 5). Importantly, the sample that was protected from illumination exhibited the greatest improvement, while the sample that faced the lamps exhibited the least improvement.

We conclude from these experiments that exposure to the lamps induces surface degradation in SiO_2 passivated silicon for $T_{set} = 500^\circ\text{C}$ and 600°C . As in previous work [18], the RTA introduces surface charge, which is not entirely removed by a subsequent IPA wash.

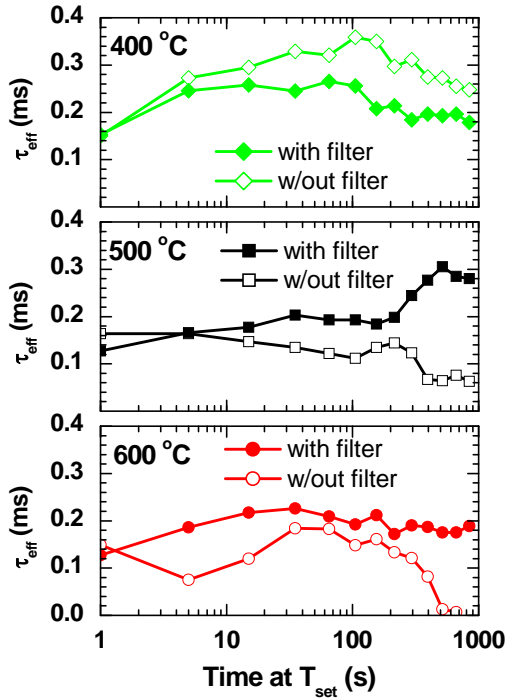


Figure 4: τ_{eff} against time, comparing sample exposed to illumination to those that were protected from the illumination at 400, 500 and 600 °C.

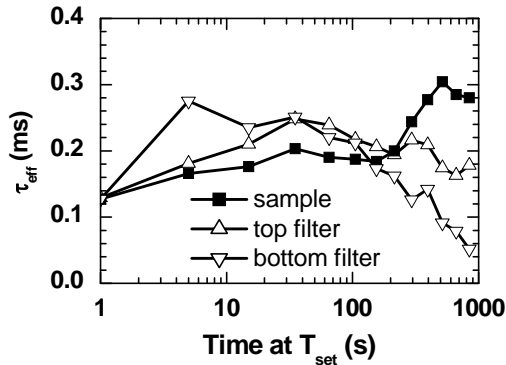


Figure 5: τ_{eff} against time of the sample and filters for $T_{set} = 500$ °C, where data is only shown for post-IPA measurements.

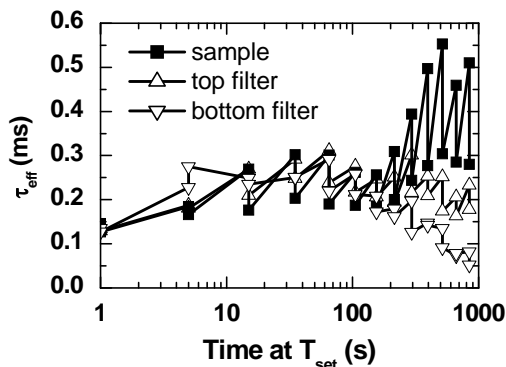


Figure 6: τ_{eff} against time, measuring the sample and filters exposed $T_{set} = 500$ °C, where measurements are plotted before and after an IPA wash at each time interval.

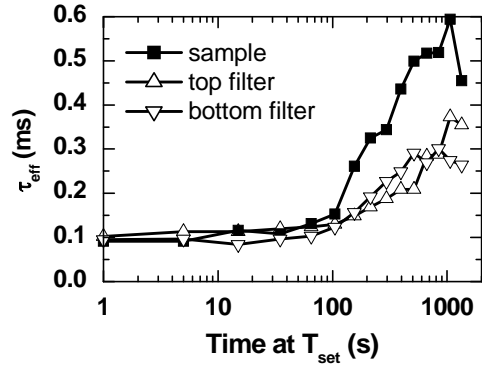


Figure 7: τ_{eff} against time of the sample and filters for $T_{set} = 500$ °C for samples that were not washed in IPA at all during the experiment.

4 DISCUSSION

The results of Figures 4–6 indicate that samples at 500 °C and 600 °C degrade when exposed to illumination from the RTA lamps, but do not degrade when they are protected from the illumination. A mechanism that is consistent with this finding relates to the injection of electrons from the silicon to the conduction band (CB) of the SiO₂ [12, 13, 25], where reasons for the injection are discussed below. The injection of electrons into the SiO₂ is known to degrade the Si–SiO₂ interface, possibly through the release of atomic hydrogen that resides in the SiO₂ and its subsequent reaction with the Si–SiO₂ interface [14, 26].

Figure 8 illustrates how electrons can be injected from the silicon into the CB of the SiO₂. Injection occurs either by (a) emission from the silicon's valence band (VB), which requires 4.2 eV, or (b) from the silicon's CB, which requires 3.1 eV.

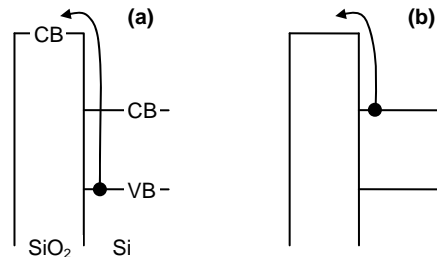


Figure 8: Mechanisms for the injection of an electron from either the valence band (VB) or conduction band (CB) of the silicon (Si) to the conduction band (CB) of the SiO₂: (a) photoemission, (b) thermionic emission

One way to inject electrons into the SiO₂ is via thermionic emission from the silicon's CB [27]. Without illumination, however, thermionic emission is not significant until temperatures exceed 600 °C, increasing rapidly with temperature. While the threshold temperature decreases for positively charged SiO₂ (due to barrier lowering and tunnelling [28]), our results indicate that thermionic emission is insignificant. This can be construed from the stability of the filtered samples at all temperatures.

A second way to inject electrons into the SiO₂ is via photoemission. This requires photons of $\lambda < 400$ nm to

inject from the silicon's CB, and $\lambda < 295$ nm to inject from the silicon's VB

To assess the contribution from photoemission, we consider the spectrum of the lamps during the RTA. The manufacturers of the RTA estimate the filament temperature of the lamps to scale linearly with the supplied power, where $T = 2500$ K for 100% power [20]. Thus, in the case of Figure 4, the filament temperature would peak at ~ 2200 K during the ramp-up, but remain at ~ 1200 K to maintain a sample temperature of 500 °C. Table I lists the peak and steady-state power supplied to the lamps for each T_{set} . A higher power is required during the ramp-up when the samples are filtered because a three-wafer stack has a higher thermal mass than a single wafer.

Table I: The peak power P_{peak} during ramp-up and the steady-state power P_{ss} while holding the samples at T_{set} . Table includes the corresponding temperature estimated for the lamp filaments.

T_{set} (°C)	P_{peak} (T_{peak})	P_{ss} (T_{ss})
<i>Without filters, i.e. single wafer:</i>		
400	82% (2050 K)	32% (800 K)
500	88% (2200 K)	48% (1200 K)
600	96% (2400 K)	64% (1600 K)
<i>With filters, i.e. three-wafer stack:</i>		
400	100% (2500 K)	32% (800 K)
500	100% (2500 K)	44% (1100 K)
600	100% (2500 K)	54% (1350 K)

The manufacturers also estimate that the spectral irradiance of the filaments follows Planck's law,

$$I(\lambda, T) = (2hc^2 / \lambda^5) \cdot [\exp(hc / kT\lambda) - 1]^{-1}$$

plotted in Figure 9 at a few relevant temperatures. The figure shows that an increase in filament temperature causes a rapid increase in the fraction of photons with $\lambda < 295$ nm, i.e., with sufficient energy to inject carriers from the silicon's VB into the SiO₂. By considering the filament temperatures listed in Table I and the curves of Figure 9, it is clear that a significant amount of photoinjection from the silicon's VB can only occur during the short ramp-up period. And since we observed no degradation for the single wafers held at 400 °C, we can conclude that a power of at least 84% ($T_{peak} > 2100$ K) is required to invoke damage by photoinjection during the ramp-up period.

An alternative cause for injection that might occur during the longer steady-state period of the RTA is thermal-assisted photoinjection from the silicon's CB. At room temperature, it is implausible that significant injection would occur from the silicon's CB under any of the possible spectra. This is because there are very few electrons in the silicon's CB compared to its VB, and therefore few photons are absorbed by electrons in the silicon's CB, i.e. by free-carrier absorption of short-wavelength photons. As temperature increases, however, a greater fraction of electrons exist in the CB (n_i increases), and a greater fraction of electrons exist in excited states within the CB. The likelihood that CB electrons would absorb short-wavelength photons therefore increases with temperature, and as construed from Table I and Figure 9, the higher lamp power

required to maintain a higher temperature means that there is a larger fraction of short-wavelength photons. Our results are consistent with these trends, as they exhibit an increase in degradation as sample temperature and lamp power increases.

We conclude, therefore, that there are two possible causes of photoinjection: (i) Photoinjection from the silicon's VB during the ramp-up period when the filament temperature is at least 2100 K. This cause would be more dependent on the lamp power than the sample temperature. And (ii) thermal-assisted photoinjection from the silicon's CB during the steady-state period, which depends on both the sample temperature and the lamp power. Either hypothesis is consistent with the results of Figures 4–7, which show considerable degradation of the interface when the samples are exposed to illumination but not otherwise, and which show an increase in degradation as temperature and/or lamp power increase.

An experiment to test whether degradation occurs predominantly during the ramp-up period of the illumination (i.e., high power) or during the steady-state period would help discern the mechanism of injection. It is the subject of future work.

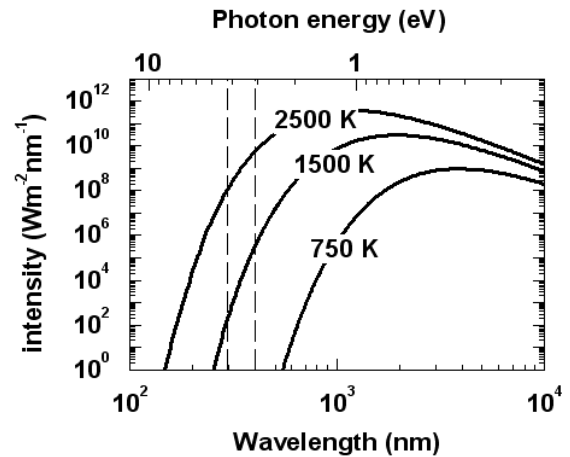


Figure 9: Blackbody emission as a function of wavelength at three temperatures; the dashed lines depict 295 nm (4.2 eV) and 400 nm (3.1 eV).

6 CONCLUSION

Degradation of oxide-passivated silicon wafers occurs during rapid-thermal annealing when the wafers are left exposed to the heating lamps. The degradation increases as the sample temperature increases, possibly due to the injection of electrons into the SiO₂. Two causes of injection were discussed.

7 ACKNOWLEDGEMENT

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