Mitigating Process Induced Degradation in *p*- and *n*-Czochralski Silicon Wafers with *Tabula Rasa*

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Mitigating Process Induced Degradation in *p*- and *n*-Czochralski Silicon Wafers with *Tabula Rasa*

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***Abstract* — We report on the bulk properties of of *n*- and *p*-type Czochralski silicon (Cz-Si) after a high-temperature annealing process known as *Tabula Rasa* (TR), which is primarily used to annihilate oxygen precipitates. We find significant differences in *n*- and *p*-type substrates as well as a strong dependence on the ambient in the resulting process induced degradation. We attribute this ambient dependence to either injection of interstitials or vacancies into the bulk during TR. Finally, we show that subsequent gettering is enhanced due to the annihilation of oxygen precipitates.**

***Index Terms* — process-induced degradation, *Tabula Rasa*, light-induced degradation, silicon**

I. INTRODUCTION

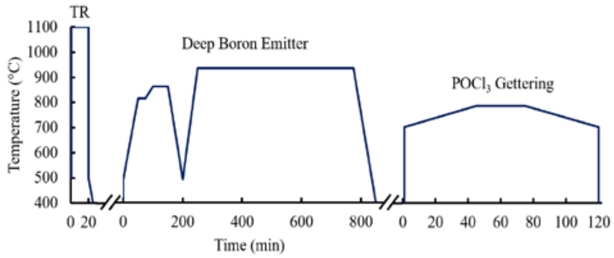
Boron-doped, *p*-type passivated emitter rear contact (*p*-PERC) Si solar cells are the fastest growing solar technology in the market today, with efficiencies reaching over 22% [1]. This transition from the aluminum back surface field (Al-BSF) architecture to *p*-PERC was a consequence of the discovery of a "regeneration" process by Herguth *et al.*, which allowed for reversal of light induced degradation (LID) of boron-doped Cz Si [2]. This methodology has since been implemented at an industrial level. However, in addition to LID, the bulk lifetime (τ_{bulk}) in *p*-Cz Si is also very sensitive to certain impurities present within the bulk [3]. On the other hand, phosphorous-doped, *n*-type Si does not exhibit a high sensitivity to impurities, and is the preferred material for ultra-high efficiency *c*-Si solar cells [4]. One advancement to improve bulk lifetime in *n*-type solar cells is a high-temperature annealing step known as *Tabula Rasa* (TR). It has been shown that TR treatment of *n*-type Cz-Si results in enhancement of τ_{bulk} and the implied open-circuit voltage (iV_{oc}). Due to TR, an improvement in the bulk properties of *n*-type Cz-Si is observed after thermal processing for the boron emitter. TR is also shown to enhance the gettering of impurities found within the *n*-type Cz-Si [5]. However, no work has been conducted to investigate the effect of TR on *p*-type Cz-Si, and how this thermal treatment step may improve τ_{bulk} and iV_{oc} after harsh thermal budgets within the solar cell manufacturing process. In addition, this TR process has not been explored to enhance gettering of detrimental impurities in *p*-type Cz-Si.

In this work, we explore the mechanism through which oxygen precipitates are dissolved in both *n*- and *p*-type Cz-Si. We also study how TR treatment mitigates process-induced degradation due to the thermal budget introduced during the boron emitter fabrication step. For *p*-Cz Si annealed in O_2 and N_2 environments, we do not observe a significant drop in τ_{bulk} and iV_{oc} after a boron emitter thermal process, but samples treated in O_2 ambient outperformed the those treated in N_2 ambient. We see different results in the *n*-Cz Si with samples treated in N_2 ambient showing an iV_{oc}, close to the samples treated in O_2 ambient along with improved performance with a longer O_2 ambient dwell time.

Finally, we explore how effectively samples exposed to TR treatments getter impurities within the bulk. With these results we see that after $POCl_3$ gettering, samples with prior exposure to TR exhibit an increase in τ_{bulk} and iV_{oc}, except the low resistivity samples, while witness samples that were not exposed to TR show a significant decrease in τ_{bulk} and iV_{oc}.

II. EXPERIMENTAL DETAILS

Samples used in this study were comprised of both *p*- and *n*-type Cz-Si scribed into four 60 mm x 60 mm sizes from single 156 mm wafers. High and low resistivity (ρ) boron-doped samples were studied while the *n*-type samples had a single resistivity value. Characteristics of all samples can be found in Fig. 1. Samples received SDR in 22.5% KOH for 15 min followed by a HF/HCl dip for 10 min. Samples then underwent a Piranha/RCA clean before TR treatment.



Sample Group	ρ Before TR	ρ After TR	O_i Content
Low ρ *p*-Cz	2.16 Ω·cm	1.73 Ω·cm	6.7×10^{17} cm^{-3}
High ρ *p*-Cz	23.0 Ω·cm	8.47 Ω·cm	8.8×10^{17} cm^{-3}
***n*-Cz**	3.74 Ω·cm	5.34 Ω·cm	5.6×10^{17} cm^{-3}

Fig. 1. Schematic showing the thermal annealing steps used for all samples in this study, including TR treatment, deep boron emitter formation, and $POCl_3$ gettering. The table shows bulk resistivities and oxygen concentration for *c*-Si wafers used in this study.

Three quarters of each of the full wafers underwent a different TR process of O_2 ambient for 10 min, O_2 ambient for 30 min, or N_2 ambient for 10 min. Each TR anneal was conducted in a conventional tube furnace at a temperature of

1100 °C. The remaining quarter of each full wafer did not receive a TR treatment to act as a witness. Subsequently, all sample's thermal oxide formed on the surface was stripped in HF and τ_{bulk} were measured via HF/HCl liquid passivation with a Sinton lifetime tester.

All quarters were then exposed to a thermal budget of a deep diffused boron emitter. This boron budget lasting ~800 min and reaching temperatures of ~900 °C allows for extended oxygen precipitate formation. Subsequently, samples were recleaned followed by passivation of the surfaces via 15 nm of Al_2O_3 deposited with atomic layer deposition. Passivation was activated via a forming gas anneal for 20 min at 400 °C.

Samples were analyzed via a Sinton lifetime tester to determine the τ_{bulk} and iV_{oc}. Samples were analyzed with PL measurements. Finally, all samples have Al_2O_3 passivation removed via HF and are recleaned prior to $POCl_3$ gettering. Gettering was conducted at 785 °C with a 30 min dwell. The phosphosilicate glass (PSG) and resulting emitter were removed with 10% HF and 22.5% KOH, respectively. τ_{bulk} was determined via HF/HCl liquid passivation.

III. Results and discussion

A. Effect of Tabula Rasa annealing ambient on bulk lifetime and implied voltage

Lifetime curves of both high and low ρ *p*-type samples are shown in Fig. 2. It can be seen that there is a similar trend between both the high and low ρ samples. We observe a decrease in τ_{bulk} for samples that underwent a N_2 ambient TR while samples that saw an O_2 ambient TR increased in τ_{bulk}. This phenomenon can be explained through mechanisms in which either interstitials or vacancies are injected into the bulk during an O_2 or N_2 ambient, respectively. A schematic of these mechanisms can be seen in Fig. 3.

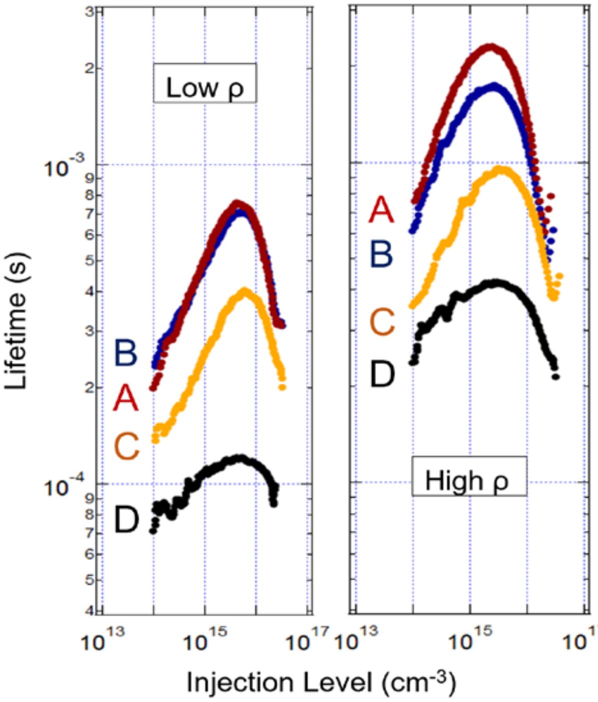


Fig. 2. Lifetime curves of *p*-Cz Si samples immediately after TR processing. Four different TR processes are, (A) red circles: O_2 ambient for 30 min, (B) blue circles: O_2 ambient for 10 min, (C) yellow circles: no TR, and (D) black circles: N_2 ambient for 10 min. Samples are low and high resistivity on the left and right, respectively.

During this 1100 °C anneal, Frenkel pairs are created spontaneously in bulk in large concentrations [3]. The excess silicon interstitials are able to diffuse much faster than the vacancies created and can reach the surface of the wafer and annihilate. Thus, when exposed to a N_2 ambient a steady state concentration of vacancies accumulates in the bulk. When the samples are cooled rapidly, these vacancies are frozen in and act as harmful recombination centers, which correlates in a decrease in τ_{bulk}.

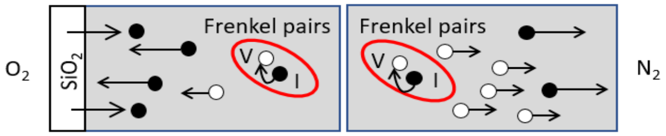


Fig. 3. Schematic of the atomistic-level mechanisms hypothesized to occur during TR treatment in a O_2 and N_2 ambient.

When TR is conducted in an O_2 ambient, a thick SiO_2 film forms on the surface of the wafer. This causes immense strain at the surface as a result of the longer silicon-oxygen bonds forming in the silicon lattice. A consequence of this strain is silicon interstitials are injected into the bulk at large quantities. These interstitials are then able to suppress the large vacancy concentration formed by Frenkel pairs. When this large concentration of interstitials is frozen in during cooling, they are benign compared to the recombination active vacancies.

B. Effect of Tabula Rasa and subsequent thermal budget identical to a deep boron emitter

Fig. 4(b) displays the PL images of the low resistivity *p*-Cz quarters after the thermal boron emitter budget has been applied. It can be seen the witness quarter that did not receive TR degrades significantly during the boron emitter thermal budget while the other three quarters survive the process-induced degradation. We also observe oxygen ambient samples have a higher resulting iV_{oc} than nitrogen ambient samples which suggests a lower concentration of vacancies within the bulk that result in recombination. Comparing the three samples that received a TR treatment and the witness sample, 'ring like" features appear on the witness sample. These rings signify oxygen precipitates [6] and we can conclude that TR prior to the boron budget dissolves oxygen precipitate nuclei and allows for a minimal loss in τ_{bulk} and iV_{oc} compared to the witness sample.

We observe similar results in Fig. 4(a) which displays the high resistivity *p*-Cz PL images. One exception to this is the long oxygen ambient TR sample experiences significant τ_{bulk} and iV_{oc} degradation accompanied by the witness sample. We attribute this decline in the longer oxygen sample to contamination within the bulk experienced during processing or other phenomena different than that of the low resistivity samples. We can rule out recombination due to oxygen precipitates due to the eradication of the characteristic ring like structures which implies that TR was successful.

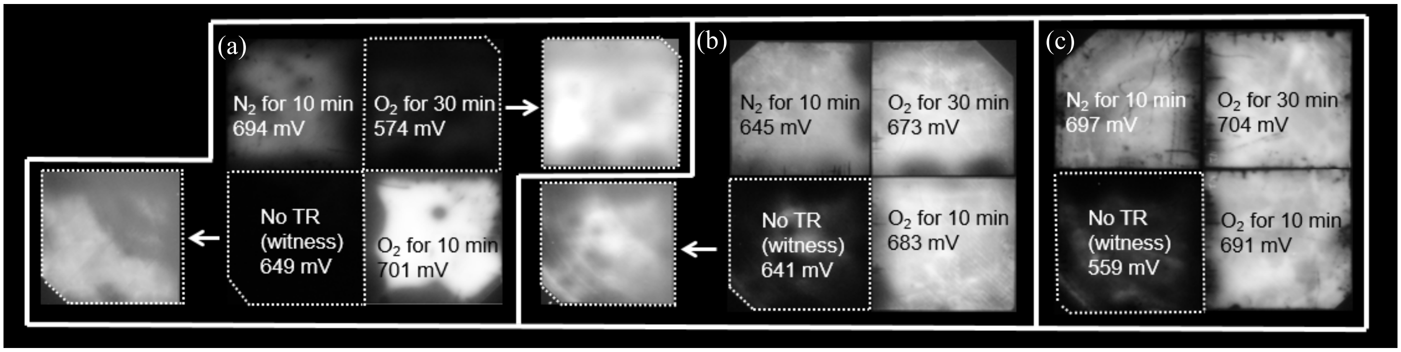


Fig. 4. PL images of (a) high resistivity *p*-type Cz-Si, (b) low resistivity *p*-type Cz-Si, and (c) *n*-type Cz-Si with various TR treatments noted on the appropriate quarters, subsequent to a thermal budget identical to a deep boron emitter diffusion. The quarters with an additional image have been photographed a second time with 12X the laser intensity to reveal oxygen precipitate rings.

Fig. 4(c) displays PL images on *n*-type Cz-Si in which we observe a different trend compared to the low resistivity *p*-type samples. We observe the extended oxygen anneal is beneficial compared to a short anneal in *n*-type samples while in *p*-type samples, the longer anneal does not result in an improvement to iV_{oc}. These results are similar to ones produced by LaSalvia *et al.* to which they observed mitigated process induced degradation after a harsh boron emitter budget [5].

C. Effect of POCl$_3$ gettering on implied voltage

Fig. 5 shows the iV_{oc} of both *n*- and *p*-Cz immediately after TR, boron budget (BB), and gettering (G). We observe a general decrease in iV_{oc} after the BB which is expected due to harsh annealing conditions. When gettering is conducted, we observe an increase in iV_{oc} in all samples with the exception of the low resistivity *p*-Cz wafer and all quarters that did not receive a TR treatment. We expect the POCl$_3$ gettering to increase iV_{oc} and τ_{bulk} due to the lack of oxygen precipitates binding to impurities within the bulk [3]. By eliminating precipitates, impurities can move more freely and experience enhanced gettering. We are currently investigating how *p*-Cz samples respond to LID processes such as degradation and regeneration. We expect samples with lower oxygen precipitate formation to have lower LID compared to samples with high oxygen precipitation. These results will be presented at the conference.

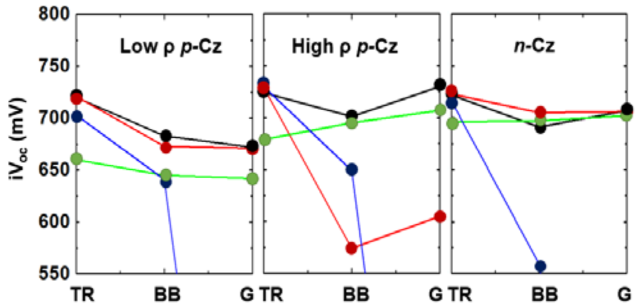


Fig. 5. Display of iV$_{oc}$ immediately after *Tabula Rasa* (TR), boron budget (BB), and POCl$_3$ gettering (G). Black lines denote O$_2$ ambient for 10 min, red lines denote O$_2$ ambient for 30 min, green lines denote N$_2$ ambient for 10 min, and blue lines denote no TR.

IV. CONCLUSIONS AND ACKNOWLEDGEMENTS

We have shown that performing TR treatment prior to harsh thermal processing can prevent oxygen bulk precipitation in both *n*- and *p*-Cz Si, and thus mitigate process-induced degradation. For both materials, samples treated in an O$_2$ ambient exceed their counterparts treated in an N$_2$ ambient. Samples with no TR treatment show significant degradation. Finally, we show that subsequent POCl$_3$ gettering increases τ_{bulk} and iV_{oc} of all samples except low-resistivity *p*-Cz Si. This research was supported by US DOE EERE under the Photovoltaic Research and Development 2 (PVRD2) program of the Solar Energy Technology Office under Award Number DE-EE0001871 and under contract number DE-AC36-08GO28308.

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