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Lifetime degradation on n-type wafers with boron-diffused and SiO₂/SiN-passivated surface

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Abstract

We observe minority carrier lifetime degradation in *n*-type wafers with boron-diffused surface and SiO₂/SiN passivation when exposed to illumination or thermal aging. This degradation is not observed on control wafers with phosphorus-diffused surfaces and identical passivation under the same treatment. Boron-diffused wafers with Si-rich SiN or Al₂O₃ passivation do not degrade either. Both boron-diffused layer and SiO₂/SiN are thus necessary to observe this degradation. Experiments on different aging conditions indicate that the degradation is due to a thermal effect accelerated by injection of excess carriers.

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Keywords: n-type silicon; boron diffusion; lifetime degradation

1. Introduction

During the past few years, bifacial solar cells made on *n*-type silicon (Si) substrates – with boron (B) diffusion on the front side, phosphorus (P) diffusion on the rear side, and silicon dioxide/silicon nitride (SiO₂/SiN) stack pas-

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sivation on both sides – have gained much interest from research institutes [1 – 3] and solar cell manufacturers [4 – 6]. The main advantages of this solar cell concept are: the bifacial characteristic; relatively low manufacturing costs (compared to heterojunction or IBC solar cells); and potential for very high efficiency made possible by the high bulk lifetime of *n*-type Si – due to its stronger immunity to most metallic impurities, as well as to the absence of the boron-oxygen complex related lifetime degradation [7].

A significant degradation of B-diffused surfaces passivated with thermally-grown SiO₂ was however reported to occur during long-term storage in the dark [8] or after a few hours at elevated temperature [9]. Despite the severity of this degradation, it is scarcely documented and its physical origins and consequences for the performance stability of *n*-type industrial bifacial solar cells remain unclear.

The aim of this study is to check whether this degradation also takes place when the SiO₂ layer is capped with PECVD SiN and to determine the physical mechanisms underlying it, in order to develop efficient strategies to avoid it.

2. Experimental procedure

We prepared four different groups of test structures on Czochralski (Cz)-grown *n*-type Si wafers with a resistivity comprised between 1 and 5 Ω.cm. They were submitted to different diffusion processes, using a low-pressure Lydop® furnace developed by Semco Engineering (POCl₃ for phosphorus and BCl₃ for boron). The denomination of the different batches (PP, BB, BP and PB) is related to the order of diffusions (Table 1). The BP structure is the standard solar cell configuration. Both surfaces are passivated by a combination of 10 nm of thermally grown oxide in a Lytox® furnace, capped by a plasma enhanced chemical vapour deposited (PECVD-TWYN) hydrogenated silicon nitride (SiN_x:H, abbreviated SiN) layer.

Table 1. Process steps to which each group of wafers is subjected to and order of the B and P diffusions

Batch	PP	BB	PB	BP
P diffusion	Double sided		First	Second
B diffusion		Double sided	Second	First
Passivation	SiO ₂ /SiN	SiO ₂ /SiN	SiO ₂ /SiN	SiO ₂ /SiN

The purpose of our test protocol (Fig. 1) is to isolate the zone responsible for lifetime degradation: interface below passivation layer, diffused layer, or bulk; and to identify a possible interaction between two processes (for instance surface oxidation with boron diffusion). Testing different diffusion orders allows identifying a possible role of gettering effect. Indeed, it has been shown in a recent study [10] that high-temperature anneals following phosphorus diffusion reduce its gettering effectiveness. Non-diffused wafers were added to test the stability of the bulk and the surface passivation. In order to investigate the influence of the boron rich layer (BRL) on the degradation, the latter was also removed by oxidation and etching of the oxide on a group of wafers before SiN passivation. The diffused layers were etched off for some samples using chemical polishing (HF+HNO₃). Finally a comparison was made between these different structures using three different surface passivations: thermally grown SiO₂ (10 nm) with PECVD SiN_x:H (abbreviated SiN) followed by rapid thermal annealing (firing), PECVD Si-rich SiN_x:H as deposited (abbreviated SiNr in the following) for surface passivation [11], and Al₂O₃ (20 nm) combined with PECVD SiN_x:H (60 nm). All samples are subjected to the same firing treatment as that used after screen printing of bifacial solar cells, in a belt furnace. There is however no firing step after SiNr deposition. Float zone silicon wafers have been used as control to verify the stability of the Si-rich SiN_x:H passivation layers throughout aging conditions.

All samples were then exposed to 0.4 suns at 65°C for 120 h. Equivalent samples were also annealed in the dark at 65°C for the same time to determine whether the degradation is due to a thermal effect only. Lifetime measurements were done at regular time intervals using a Sinton WCT-120 lifetime tester [12].

Bifacial solar cells – fabricated using the BP diffusion sequence – were also submitted to light-soaking in the same conditions.

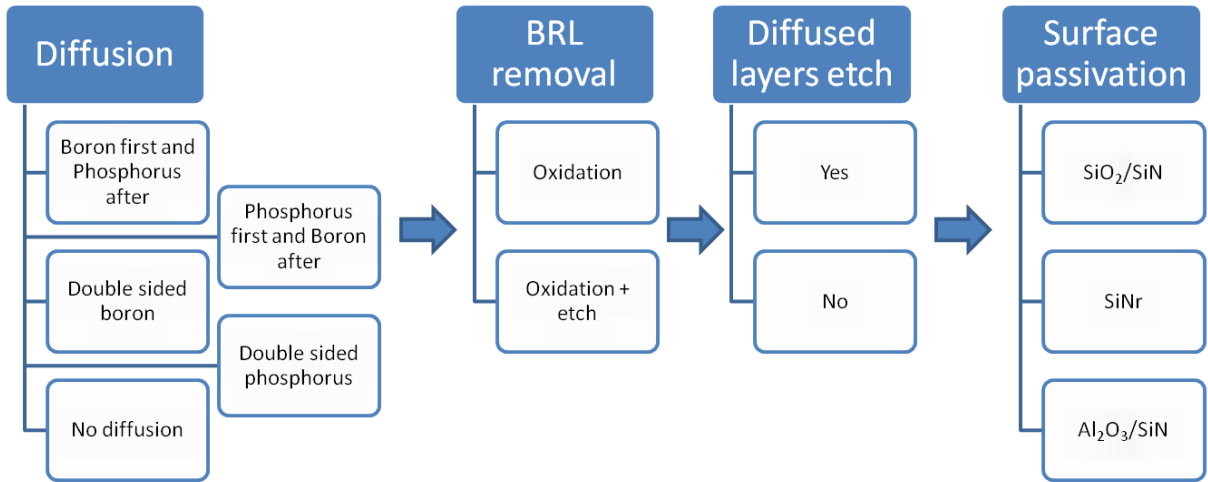


Fig. 1. Different combinations of processes to study the origins of the degradation

3. Results

3.1. Degradation on boron-diffused wafers with SiO_2/SiN passivation

Degradation of minority carrier lifetime for double sided boron-diffused wafers is clearly observed during aging at 0.4 suns and 65°C (Fig. 2). Degradation is also observed for PB wafers (with boron diffusion after phosphorus diffusion), whereas double sided phosphorus-diffused wafers and BP (with phosphorus diffusion after boron diffusion) wafers show no lifetime degradation under illumination at 65°C over 120 hours (Fig. 3).

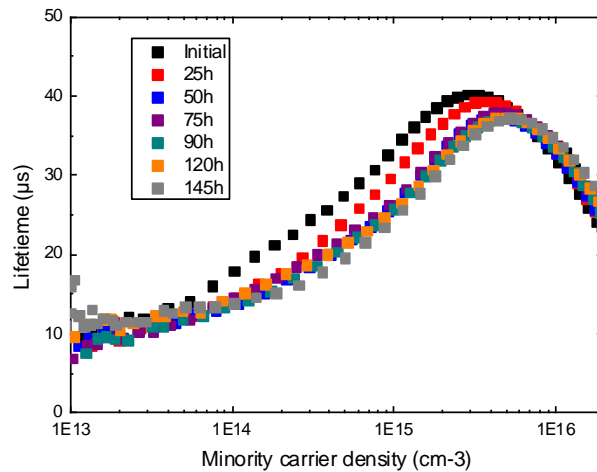


Fig. 2 : Example of lifetime measurements of a BB wafer passivated by SiO_2/SiN during the degradation under illumination.

First of all, our results confirm that the degradation reported in [8, 9] can also occur when B-diffused surfaces are passivated with a stack of thermal oxide capped with PECVD SiN (Fig. 3). We will discuss in the following about the low minority carrier lifetimes obtained here. Our measurements also show that this degradation only occurs when at least one side of the wafer has a B-diffused surface, suggesting that it originates from the interaction of the SiO_2 layers with highly B-doped Si surface. The fact that PB samples degrade while BP samples remain unaffected proves the order of B and P diffusions to be critical. This infers that P-diffusion gettering might play a role in preventing the degradation, suggesting the participation of metallic impurities in the degradation process. Note that

the absence of degradation in BP samples shows that with the appropriate process sequence, *n*-type bifacial solar cells with stable efficiency should be possible to fabricate despite the presence of a B-diffused surface passivated with SiO₂ (see section 3.4). Another noteworthy point is that the degradation is stronger at low injection (below 10¹⁵ cm⁻³) than at high injection levels, as shown on Figure 2. Such injection level dependence usually results from bulk SRH recombination.

The lifetime values are low for Cz *n*-type silicon, suggesting that a contamination of the bulk may have occurred during one of the processes step. The surface passivation was also not optimized, but it is important to note that the same processes have been applied to all the wafers, depending on the chosen run. And despite the low lifetimes observed in certain cases, the degradation throughout time only occurs for BB samples. However we cannot directly compare the degradation at this level with the degradation reported in [8, 9].

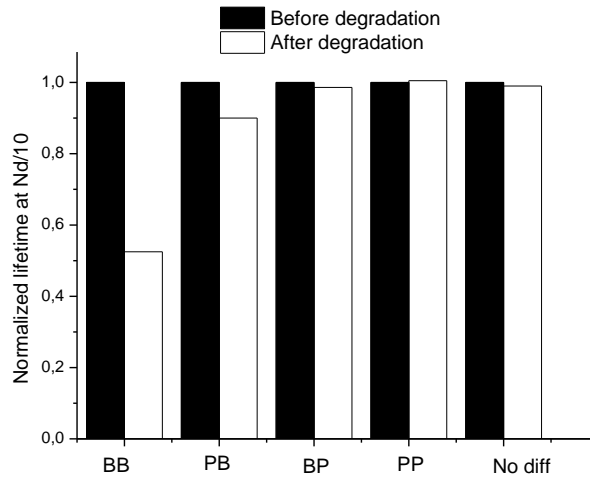


Fig. 3. Lifetime measured at a constant injection level ($N/10 \text{ cm}^{-3}$ where N is the net doping level) before and after applying the degradation treatment (0.4 suns and 65°C for 120 h) for different test structures.

3.2. Degradation under illumination and in the dark

On Figure 4 we can see that for BB wafers the degradation in the dark has the same behavior as the degradation under illumination shown on Figure 2, suggesting that the degradation mechanism is similar.

The two samples that were used to compare degradations under illumination and in the dark are two parts of the same wafer but their initial lifetimes are different because of initial inhomogeneities. Both degradations can be fitted

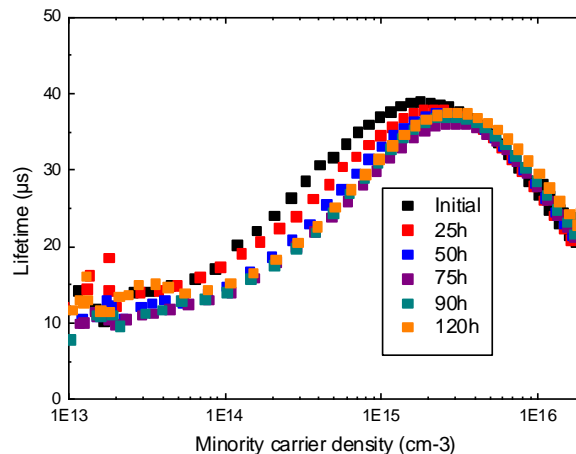


Fig. 4. Example of lifetime measurements of a BB wafer passivated with SiO₂/SiN during the degradation under dark.

using a first order exponential law:

$$y(t) = y_0 + e^{-\frac{t}{T}} \tag{1}$$

The time constants of the reactions (T) presented on Figure 5 are 36 hours for the thermal aging and 17 hours for the illumination treatment showing that the degradation mechanism is faster under illumination. However the lifetimes after complete degradation are the same in both cases suggesting the same thermal mechanism, which could be accelerated by light.

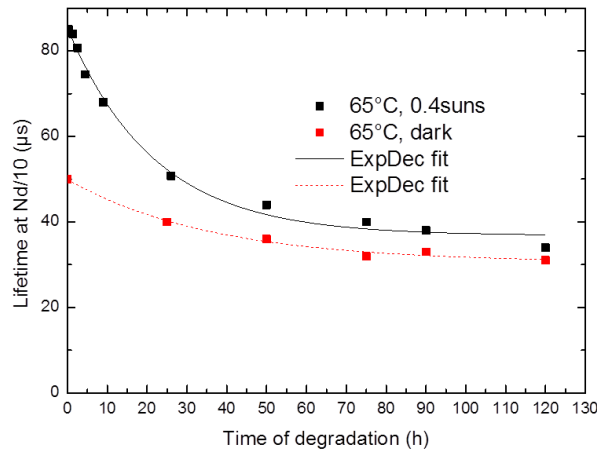


Fig. 5. Lifetime versus degradation time for a BB wafer under light and thermal treatment fitted using a first order law

3.3. Comparison with SiNr- and Al₂O₃-passivated wafers

No lifetime degradation was observed after 120 h of aging under illumination for SiNr and Al₂O₃-passivated wafers, as shown on Figure 6. The stability of the double sided boron-diffused wafers and PB wafers with etched emitters shows also that the degradation mechanism does not take place in the bulk. There is no degradation of SiNr-passivated BB wafers regardless of whether the BRL was etched or not, showing that the degradation cannot be attributed to the boron-rich layer solely.

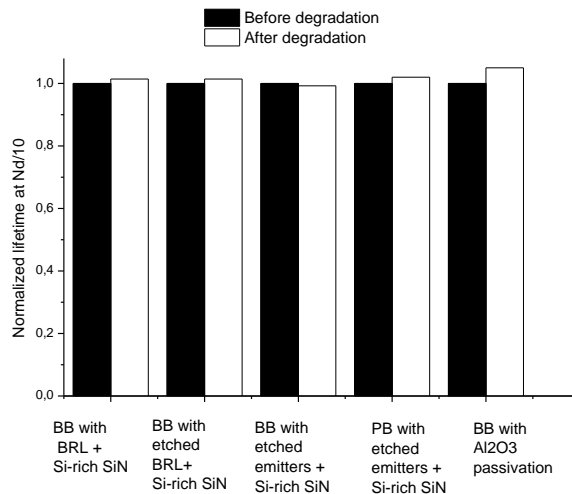


Fig. 6. Lifetime measured at a constant injection level ($N/10 \text{ cm}^{-3}$ where N is the net doping level) before and after applying the degradation treatment (0.4 suns and 65°C for 120 h) for Si-rich SiNr-passivated wafers.

Finally, BB wafers were passivated with Al_2O_3 and did not degrade. The high temperature oxidation step of the boron layer entails redistribution and a modification of the boron concentration profile, which may be of importance in the degradation process, as already noted by Zhao *et al.* [8]. The degradation mechanism seems thus to happen at the interface between SiO_2 and boron-diffused silicon.

3.4. Bifacial cell stability

As shown in section 3.1., wafers that underwent the same process as bifacial solar cells (BP) did not degrade neither under illumination treatment nor under thermal treatment. To verify this stability, bifacial solar cells were exposed to 0.1 sun and 60°C and the V_{oc} was monitored during 100 h.

On Figure 7, the evolution of the V_{oc} of two bifacial solar cells with different resistivities ($0.77 \Omega\cdot\text{cm}$ for Fig. 7 left and $2.26 \Omega\cdot\text{cm}$ for Fig. 7 right) are shown not to decrease during 100 h under illumination, which proves the stability of these cells.

Despite the degradation observed on B-diffused n-type silicon wafers passivated by SiO_2/SiN , it is thus possible to fabricate boron-diffused bifacial solar cells with n-type silicon which are stable, when the phosphorus diffusion is made after the boron diffusion in the fabrication sequence.

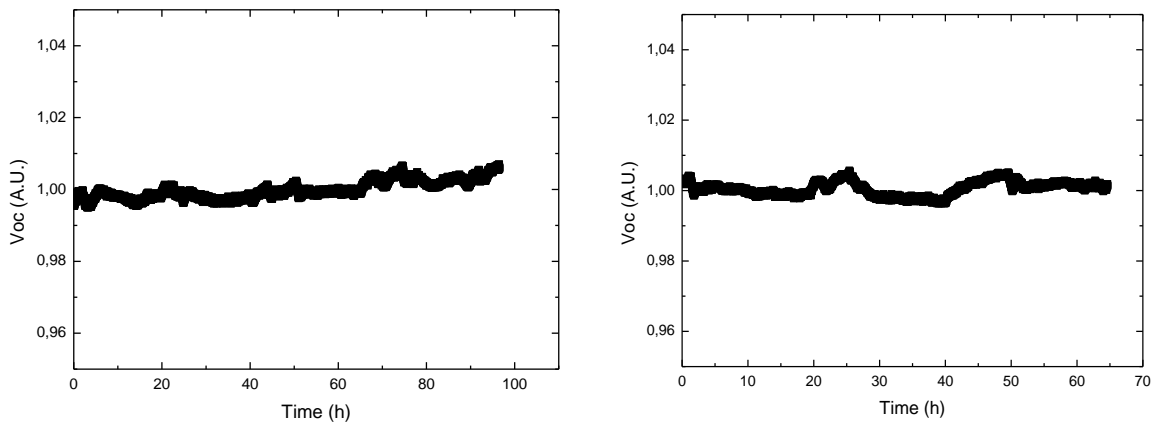


Fig. 7. Evolution under illumination of the V_{oc} of 2 bifacial solar cells with 2 different resistivities (0.77 and $2.26 \Omega\cdot\text{cm}$), normalized by their average values

4. Conclusion

The results presented in this work show a degradation of minority carrier lifetime for *n*-type wafers with B-doped surfaces passivated with SiO_2/SiN under thermal or light aging. This degradation is shown to be a thermal effect accelerated by carrier injection. The comparison of samples with B and P diffusions being processed in a different order suggests that gettering influences the degradation, thereby suggesting the participation of metallic impurities. The stability of SiN_r - and Al_2O_3 -passivated wafers shows that the bulk, the diffused layers and the passivation are independently stable and that the degradation mechanism takes place only in the case of combined boron-diffused and SiO_2 passivated surface.

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