HYDROGENATION OF STRIATION RINGS IN N-TYPE SILICON WAFERS

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ABSTRACT: N-type silicon has become more popular as base material for solar cells and receives an increasing amount of attention as a result. One of the defects occurring in n-type silicon are ring shaped patterns in lifetime maps (aka striation rings), which cause a steep decrease in conversion efficiency. Striation rings are linked to oxygen and can decrease recombination activity by anneals, illuminations and hydrogen in-diffusions, all which are usable on cell level. A decrease in recombination activity can be affected at temperatures up to 375 °C, whereas this decrease can be reversed by anneals above 500 °C. A side effect of these treatments is a change in resistivity even at temperatures below thermal donor formation. Investigations to the field stability of these treatments show no increase in recombination activity so far.
Keywords: n-type, c-Si, Czochralski, defects, hydrogenation

1 INTRODUCTION

N-type solar cells are increasing their market share, which a predicted share of 35% in 2025 [1]. This shift is inspired by higher conversion efficiencies of n-type and lack of boron-oxygen complexes which lead to light induced degradation. N-type solar cells exits in various types, from H-pattern cells [2] to IBC [3] and HIT [4]. All share the use of n-type monocrystalline material, and for commercial uses this will be Czochraski grown n-type material.

Material research in silicon material will focus on different aspects for p and n-type silicon in general, as the lifetime of p-type silicon is dominated by the B-O complex and impurities like Fe whereas for n-type silicon structural defects exert the main influence. One of these structural defects is characterised by a ring or disk shape in lifetime maps. It can be a remnant of the P-band at the top of the ingot [5], or be caused by fluctuations in the growing parameters causing swirls or striations [6,7]. Although in principle these are different phenomena, in this study we investigate both types of ring structures.

Our previous results have shown that for n-type cells an anneal at 200 °C can diminish or remove striation rings in solar cells and half-fabricates [8]. Similar cell improvements under illumination have also been presented [9]. They have been shown to be linked to oxygen precipitates [10] and to be passivated with hydrogen [11]. These results are consistent with an hypothesis of an oxygen recombination complex which can be passivated with hydrogen. This article further explores this hypothesis, and conducts some investigations into the feasibility of a hydrogen passivation of n-type solar cells in the field.

2 EXPERIMENT

2.1 Samples

The samples for this experiment were made following the n-pasha process up until the diffusions [12]. Samples were selected from wafers known to contain striation rings after processing. As metallization line causes visual interference in our measurements, the samples were not metallized. A portion of the samples were processed up until the normal silicon nitride front and rear anti-reflection coatings. Another portion was stripped of diffusions and had the surface passivated with amorphous silicon (a-Si), silicon nitride (SiNx) or ALD aluminium oxide (AlOx) by Levitech [13]. Half of the wafers received a forming gas anneal (FGA) at 375 °C during 20 minutes before coating. The schematic of the processing is shown in Figure 1.

<table>
<tr><td>Group 1</td><td>Group 2</td><td>Group 3</td><td>Group 4</td></tr>
<tr><td colspan="4">Texture</td></tr>
<tr><td colspan="4">Co-diffusion</td></tr>
<tr><td colspan="4">Glass removal</td></tr>
<tr><td></td><td colspan="3">Polishing</td></tr>
<tr><td></td><td colspan="2">FGA</td><td></td></tr>
<tr><td>SiNx</td><td>a-Si</td><td>AlOx</td><td>SiNx</td></tr>
</table>

Figure 1: schematic process flow. FGA is applied to half of the samples, which are then evenly redistributed across the coatings.

2.2 Post-processing

After the samples were finished, samples received some additional processing steps after measurement. Not all types post-processing steps were applied to all samples, as some steps are unsuitable to a number of samples. The post-processing steps were: firing, anneals, light-soaking, forming gas anneals and UV weathering tests. Firings were performed in a belt furnace. Anneals were performed in a box furnace. Light-soaking was done with a class AAA solar simulator. Forming gas anneals were performed in a PECVD system. UV weathering tests were performed with a system designed for module degradation tests with a wavelength centred around 351 nm wavelength, which is typically the range which is missing from solar simulators yet transmitted through the module glass and EVA.

2.3 Measurements

The samples were measured using uPCD, QSSPCD/transient PCD and photoluminescence measurements. Several unprocessed cells were also subjected to post-processing steps to study the effect on the resistance.

3 RESULTS

3.1 Anneal and light soaking

The anneals have been done previously on completed cells and it was shown the effect on efficiency was in the order of 0.8%$_{abs}$ maximum for the samples used, which is a significant change [8]. We compared on type 1 samples the effect of a 200 degree anneal for 10 minutes and the effect of a 64 h light-soaking. The change in lifetime as measured by uPCD is shown in Figure 2.

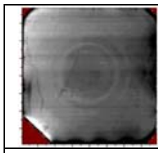
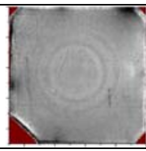
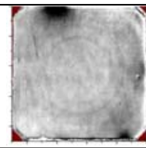
		
Lifetime map of the wafer	Change in lifetime map due to anneal	Change in lifetime map due to light soaking

Figure 2: effect of anneal and light soaking. Black corresponds to low values, white to high values.

For the annealed samples the darker inner ring is not so clear. In both cases the two dark rings correspond to the high lifetime rings in the initial sample, indicating that the lifetime is less changed outside the rings than inside the rings.

3.2 Effect of firing

As neither a-Si nor AlOx are sufficiently firing stable, the effect of firing can only be studied on SiNx samples (type 1 and 4) (see Figure 3). The firing used identical settings to n-pasha, which will in the case of type 4 on sample level be a lower effective temperature on the sample [14]; the estimated temperature is 600 °C. As it is a firing setting, this temperature will not be applied for more than a few seconds.

Rings appear very strongly in wafers without doped layers (4), and less strongly for the samples with doped layers (1) due to the firing. The low lifetimes of the doped layers due to Auger recombination dominate the doped samples to such an extent that differences in the bulk of the sample need to be strong to be visible in the effective lifetime of the sample.

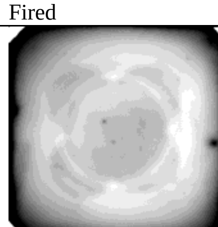
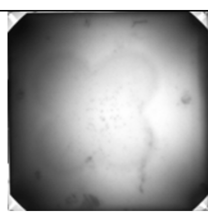
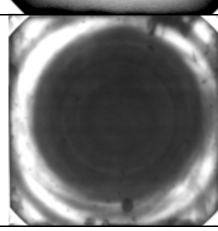
Type	Unfired	Fired
1		
4		

Figure 3: effect of firing on group 1 (SiN with emitter + BSF) or group 4 (SiN doped layers removed) for neighbouring wafers. The doped layers decrease the ring effect due to relatively low lifetimes in the doped layers.

Forming gas anneals (FGA) can be performed before capping with SiNx, AlOx and a-Si, or after. In the case of a-Si, a FGA after passivation can only be done with a temperature of 200 °C instead of 375 °C as high temperatures will destroy the surface passivation of the amorphous silicon. [15]

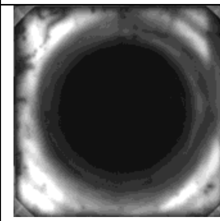
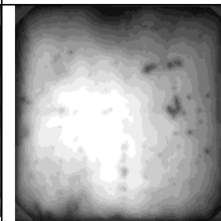
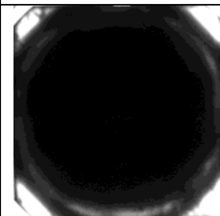
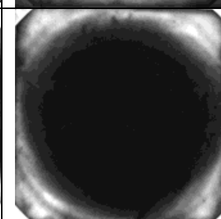
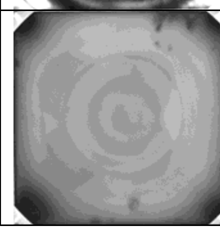
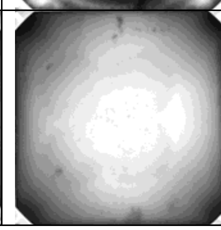
Type	No FGA	FGA
2		
3		
4		

Figure 4: Effect of FGA performed before capping the samples for a-Si (2) AlOx(3) and SiN (4) capped samples. The SiN samples are unfired as firing negates the differences between the samples.

When a FGA is performed before capping (Figure 4), the capping procedure is expected to have an influence on the final product. For an a-Si capping (2) the difference caused by a FGA is very clear. As the a-Si is deposited at low temperatures, this deposition likely had the least influence on the sample.

For the AlOx sample (3) the differences between the samples is slight. We used a post deposition anneal for the AlOx of 500 °C which almost entirely negates the effect of the forming gas anneal. However, only our standard post deposition anneal has been used. It is possible to use lower temperatures for this anneal. [16]

For the SiN sample (4) the difference caused by FGA is slight. Without FGA ring shaped patterns are just visible. In this case the high deposition temperature of ~400 °C in a hydrogen containing plasma may mimic the FGA to sufficient extent to diminish the striation rings considerably in recombination activity.

For FGA with the coating on, the permeability of the coating for the gas influences the resulting effect as shown in Figure 5. The positive effect of the FGA has not changed, but the magnitude is less. The effect of the FGA is more clear if the change is shown. Amorphous silicon is the most permeable coating used here. AlOx is the least permeable coating.

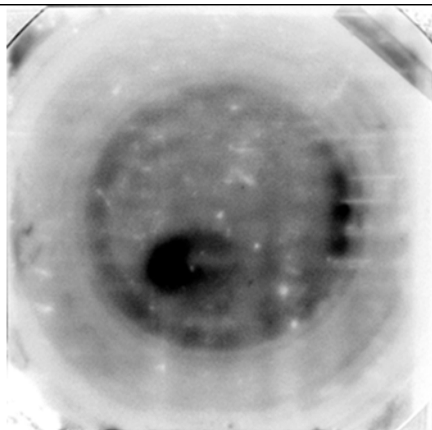
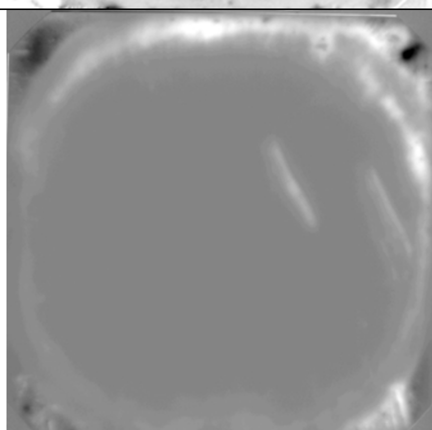
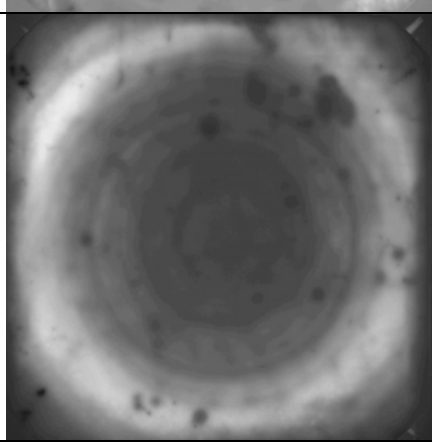
Type	Difference due to FGA
2	
3	
4	

Figure 5: Change in PL signal due to an FGA for aSi (2), AlOx (3) and SiN(4) coating. White is a positive change. The samples are all neighbours.

FGA also have an effect on the resistivity which changes with the ring locations as shown in Figure 6. These anneals are most efficiently performed on uncoated wafers, which are also easier to measure with a four point probe.

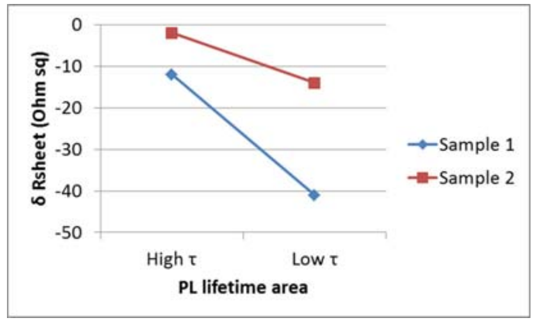


Figure 6: change in resistivity due to a forming gas anneal for high and low lifetime wafers. Samples originate from different ingots.

The entire sample has a slight decrease in resistivity; a slight increase in donors due to the forming gas anneal performed at 375 °C. The change is stronger for the low lifetime rings, which have been shown to coincide with high oxygen rings [17,18].

3.4 UV weathering tests

In order to use the proposed treatment safely on cells for modules, the effect of weathering on the cells should be investigated. The effect of visible and IR light has been sufficiently investigated in paragraph 3.1.

UV weathering will deplete the hydrogen from the K-centres of the silicon nitride coating [19], which is replaced in the relaxation stage, which occurs in the dark. Should the hydrogen get replaced from the bulk of the wafer, permanent hydrogenation of striation rings will not be feasible in the field.

The effect of UV weathering on our samples is shown in Figure 7.

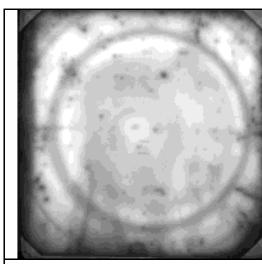
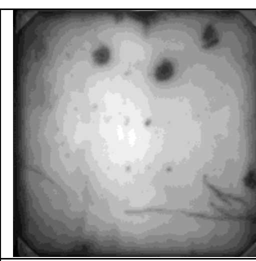
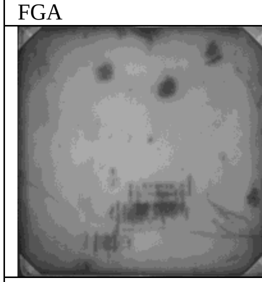
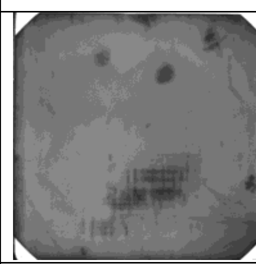
	
Neighbour sample without FGA	Sample with FGA, 0 h UV
	
Sample with FGA, 20 h UV	Sample with FGA, 110 h UV

Figure 7: PL images for a sample without FGA compared to a sample with FGA which is subjected to UV weathering.

After 110 h of UV exposure, the ring pattern which the wafer intrinsically has, is not yet returned to the wafer. The holders of the weathering chamber have caused scratches on the coating.

Roughly speaking, 110 h UV exposure corresponds to 1 year in the field, depending on the latitude, so this experiment does not yet constitute proof that the striation rings do never return in the solar cells. This does form a first indication of the stability however.

3 DISCUSSIONS

The strong response of the striation rings to hydrogen in-diffusion by a forming gas anneal shows that the disappearance of the rings is linked to hydrogen. The tendency of the striation rings to turn up only after firing of the silicon nitride coating does not contradict a hypothesis involving hydrogen, nor does activation of the passivation at either 200 °C or by light. Our data does show that the defect is deactivated below 375 °C and activated above 500 °C. The defect can be moved between activated and deactivated at will in the laboratory, provided the used coating is permeable.

Regarding the efficacy of the process, we note that the best treatment to reduce recombination activity of striation rings is the forming gas anneal as it is complete even for the worst cases we could find. The anneal in air is faster and easier to implement in a factory, and will be complete for less strong striation rings. Neither process has a detrimental effect on good cells [20]. For manufacturing purposes, using a close to impermeable coating like aluminium oxide has advantages when dealing with a complex passivated by hydrogen. The impermeability of the AlOx coating has been proven. The correct temperature to anneal the AlOx and keep the hydrogen in the cell has not yet been established.

Near UV light has a negative impact on the quality of the AR coating, although the silicon nitride will recover during the night by redistribution of hydrogen. This redistribution of hydrogen does not affect the visibility of the striation rings within the cells for the time used. As the used timeframe is approximately equal to only 1 year outdoor exposure, proof of the stability over 25 years has not been given, yet the lack of any effect on the striation rings so far is encouraging.

An increase in the doping has been measured for the passivated striation rings. As the striation rings are typically higher in oxygen than the surrounding material, this could be the difference in response of thermal donor formation. The temperature used is too low for normal thermal donor formation, however in the presence of hydrogen donor formation is facilitated [17]. This proves the simultaneous presence of hydrogen and oxygen within the rings. The proposed mechanism for this enhanced thermal donor formation [18] is reversible and activated below 500 °C.

4 CONCLUSIONS

Our data supports a passivation mechanism of striation rings involving hydrogen and oxygen which can be changed into a low recombination state below 375 °C and activated to a high recombination state above 500 °C. These temperatures have not been used in the same atmospheres, which will be a factor. Illumination with visible and infrared light can enhance the conversion to low recombination state. The change in doping at least supports the hypothesis that both hydrogen and oxygen are involved in the passivation of the defect causing the high recombination activity of the striation rings. The defects causing the striation recombination and the resistivity changes may have more in common than that.

The stability of the low recombination state in the field is encouraging, given that UV light does not appear to convert the low recombination state and visual light has been shown to increase the low recombination state at a much faster rate than the UV light has been tested at maximum.

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