On the nature of striations in n-type silicon solar cells

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In n-type Czochralski silicon (Cz-Si) wafer, swirl shaped regions with low lifetime (known as striations) can cause degradation up to 1% absolute or even more in homojunction industrial solar cells. Nevertheless, the nature of the defects responsible for the occurrence of these striations is still unclear. In this work, n-type Cz-Si solar cell precursors cut from industrial size ingots with different feedstock quality and oxygen content were analyzed by microwave photo-conductance decay and photoluminescence in order to investigate the nature of such defects. The results demonstrate that the defects responsible for the occurrence of striations are oxide nanoprecipitates formed during the high temperature steps for the solar cell realization, due to the presence of grown-in oxygen nuclei. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4959558]

Currently, n-type Czochralski silicon (Cz-Si) accounts for 6% of total photovoltaic (PV) module production and a PV market share over 30% is foreseen in 2023.[1,2] This trend is driven by the major advantage of n-type silicon with respect to the p-type counterpart. In particular, n-type silicon shows a higher carrier lifetime due to the absence of boron-oxygen complexes, responsible for the light-induced degradation that negatively affects p-type solar cell efficiency,[3] and a smaller sensitivity to metal impurities recombination like in the case of Fe.[4] Nevertheless, during Cz-Si growth, other detrimental defects consisting of self-interstitials, dislocations, or oxygen agglomerates can be generated in the ingot. These defects are present also in p-type silicon; however, due to the presence of the above mentioned defects, their effect is not visible as it is secondary to the overall recombination. Among them, ring shaped regions consisting of grown-in oxide precipitates (the so called P-band rings)[5] and swirl shaped regions (also known as striations) show low carrier lifetime.[6] While proper modifications of the growth process allowed removing the P-band rings,[7] the impact on the solar cell performance and the formation mechanism of striations is still under investigation. Coletti *et al.*[8] showed the effect of such striations on the performance of n-type solar cells and showed that an annealing at 200 °C resulted in mitigation of their effect on N-PASHA[9] Cz-Si solar cells. However, a deeper understanding of the nature of defects responsible for the occurrence of striations is mandatory in view of an elimination of their presence either during the ingot formation or during the cell processing.

In this work, n-type Cz-Si solar cell precursors[10] manufactured with wafers cut from the top, middle, and bottom regions of ingots grown with different feedstock quality and oxygen content were studied in order to investigate the nature of the defects that give rise to striations (see Ref. 8 for details on the processing).

The n-type Cz-Si solar cell precursors analyzed in this work were obtained from three different ingots 20 cm in diameter, labelled as Reference (REF: $\rho_{top} = 5\,\Omega\,$cm, $[O_i]_{top} < 18$ ppma), Low Grade Poly (LGP: $\rho_{top} = 5\,\Omega\,$cm, $[O_i]_{top} < 18$ ppma), and Low Oxygen (LOO: $\rho_{top} = 5\,\Omega\,$cm, $[O_i]_{top} < 16$ ppma), respectively. Further details about the ingots are reported in Ref. 8.

Wafers cut from the top, middle, and bottom regions of each ingot were submitted to standard random pyramid texturing, junction formation by boron diffusion, and surface passivation by silicon nitride, and then analyzed by the following techniques.

Striations were identified by Microwave Photo-Conductance Decay (μW-PCD) (see Fig. 1) and photoluminescence (PL) imaging,[8] and then proper cutting grids were designed by AutoCAD® to precisely define areas with and without striations. Finally, each wafer was laser cut into small pieces ($5 \times 10\,mm^2$) corresponding exactly to regions with or without striations. These small pieces were analyzed by local PL in the 850–1700 nm spectral range both at room temperature (RT) and at 15 K. All PL measurements were performed with a spectral resolution of 6.6 nm using a standard lock-in technique in conjunction with a single grating monochromator and a short wavelength enhanced InGaAs detector with maximum responsivity at 1540 nm. A quantum well laser ($\lambda_{exc} = 805$ nm) with a spot size of $0.3 \times 0.3\,mm^2$ and a power density of 15.5 W cm^{-2} was used as excitation source. A cooling system consisting of rotary pump, turbomolecular pump, and He closed circuit cryostat was used to perform PL spectra at low temperature. A resistance heater coupled with the cooling system allowed PL measurements in the temperature range between 15 and 300 K. Some reference samples from the LOO ingot were repeatedly measured in the above mentioned experimental conditions to determine the error on the PL intensity from the mean standard deviations, which resulted around 3%.

The μW-PCD maps reported in Figure 1 show that striations are present only in solar cell precursors coming from top wafers of REF and LGP ingots. The presence of striations both in REF and LGP wafers suggests that no direct correlation exists between the feedstock quality and the

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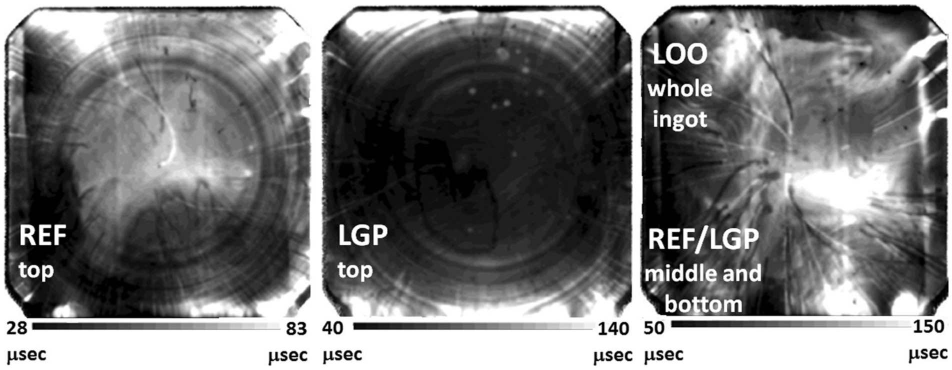

FIG. 1. μW-PCD maps of the analyzed samples. On the left and in the centre are μW-PCD maps of REF and LGP top solar cell precursors, respectively, which clearly show the presence of striations. On the right is a typical μW-PCD map that shows the absence of striations, obtained for the whole LOO ingot and for both REF and LGP middle and bottom solar cell precursors.

occurrence of striations. Conversely, the absence of striations in the middle and bottom wafers of the REF/LGP ingots (where [O_i] decreases with respect to the top) and in the whole LOO ingot suggests the involvement of oxygen in the formation of such defects.

Figure 2 shows the intensity decrease of the free exciton (FE) emission from 0.015 ± 0.00045 (in regions without striations) to 0.010 ± 0.0003 (in regions with striations) observed at low temperature for both REF and LGP top solar cell precursors. The same behavior was observed for the band-to-band emission at RT, in good agreement with μW-PCD maps and PL imaging (not shown here). Furthermore, similar intensity values of the band-edge emission were observed at 15 K and at RT in regions with striations coming from both REF and LGP top samples. This is an unusual behavior, not observed for LOO samples. Therefore, it was studied in detail by temperature dependent PL analyses. The results, reported in Fig. 3, showed that in regions with striations the band-edge emission intensity decreases, as expected, in the range between 15 and 110 K. Unexpectedly, for temperature above 110 K it progressively increases up to similar value observed at 15 K (see Fig. 3(a)). Moreover, in the spectral region where the PL fingerprints of oxide precipitates are usually observed,[11–18] a deep-level band around 0.87 eV grows up in the range between 15 and 110 K (see Figs. 3(b) and 3(c)), and then progressively decreases (see Fig. 3(c)). As demonstrated in Ref. 17 by some of the present authors, the strain associated to the presence of oxide nano-precipitates in the Si matrix induces the formation of levels in the bandgap and is responsible for the shape, position, and intensity of the broad band between 0.8 and 0.9 eV.

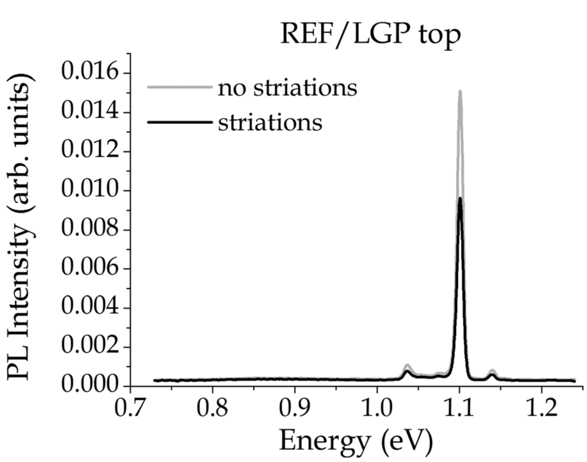

FIG. 2. PL spectra of typical REF and LGP top solar cell precursors at 15 K, collected in regions with (black line) and without (grey line) striations.

The behavior shown in Figs. 3(a) and 3(c) can be explained as follows. At low temperature, excitonic emissions rule the recombination process, so the band-edge emission intensity decreases with increasing temperature due to thermal dissociation of excitons. Meanwhile, the intensity of the emission at 0.87 eV increases, possibly as a result of the competition for exciton capture between optical centers and other shallow traps. With increasing temperature, the excitons freed from the shallow traps become available for capture by other deeper exciton traps, including the one responsible for the emission at 0.87 eV. At higher temperature, free-to-bound recombinations rule, so the competition of recombination channels between band-edge and deep-level recombinations determines the band-edge emission intensity. After 110 K, the intensity decrease of the emission at 0.87 eV pushes up the band-edge emission.

Temperature dependent PL analyses performed both on REF/LGP samples in regions without striations and on samples with low O_i content (LOO samples) (not shown here) demonstrated the absence of the band at 0.87 eV and showed, as expected, band-edge emission intensities which decrease with increasing temperature.

Not only do these evidences seem to confirm the involvement of oxygen, but also some previous literature works[8,14,17,19,20] strongly support such hypothesis. Temperature dependence of the band-edge emission similar to that reported in Fig. 3 was observed by Tajima and coworkers in annealed Cz-Si for microelectronics and as-grown p-type mc-Si,[19,20] where the deep-level emission around 0.8 eV appeared quite stronger than that in the present work. The presence of oxygen precipitates in p-type mc-Si regions showing a strong emission at 0.87 eV was demonstrated by highly spatially resolved and highly sensitive secondary ion mass spectroscopy and by mapping of oxygen by luminescence activation using electron irradiation.[19,20] Furthermore, the presence of phosphorus-vacancy defects or other intrinsic defects that can participate in the formation of oxide precipitates was suggested in Ref. 8. The experimental evidences shown in this work confirm, therefore, the involvement of oxygen also in the occurrence of striations in n-type Cz-Si for PV applications. As far as the density and size of these oxygen related defects are concerned, the results reported by some of the present authors in Refs. 14 and 17 allow a deeper insight. First, Leoni *et al.*[17] demonstrated that the broad band between 0.8 and 0.9 eV observed in Si samples

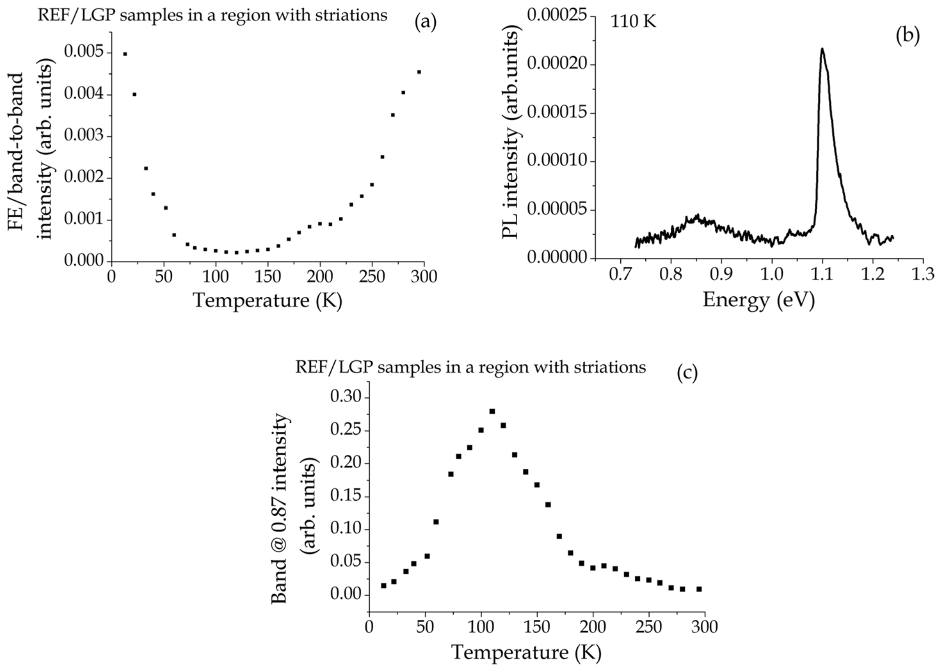

FIG. 3. Temperature dependent PL analysis of REF/LGP top samples performed in a region with striations: (a) trend for the FE/band-to-band emission; (b) PL spectrum at 110 K clearly showing the band at 0.87 eV; (c) trend for the defect related band at 0.87 eV (the intensity of the defect band was normalized with respect to the intensity of the FE/band-to-band emission).

with $[O_i] = 16$ ppma originated from oxide nanoprecipitates, whose density was $10^{11}\,cm^{-3}$. Due to the strong similarities between the experimental evidences reported in Ref. 17 and in this work, both in terms of initial oxygen concentrations and PL spectra, it can be argued that we are dealing with a similar density of oxide nanoprecipitates. Second, Binetti *et al.*[14] demonstrated that oxide precipitates larger than 50 nm are usually associated with dislocation loops, which give rise to the well-known D1 and D2 bands, not observed in our work. Therefore, it can be argued that in the present n-type Cz-Si for PV applications oxide nanoprecipitates smaller than 50 nm are present. Furthermore, the involvement of dislocations in the formation of such nanoprecipitates can be excluded since no dislocation related bands (especially the D1 emission which can be considered the PL fingerprint of the presence of dislocations) were observed.

Considering that—unlike Si for microelectronics[11,21]—no thermal treatment aimed to the dissolution of grown-in oxide nuclei is performed before the standard steps for the realization of Si solar cells, it can be reasonably deduced that striations are related to oxide nanoprecipitates formed during the high temperature step for the solar cell realization, as already observed in p-type Ribbon and mc-Si PV devices.[22] Their formation and density should therefore depend on the thermal history of the ingot, in particular, on the amount of grown-in oxide nuclei formed during the ingot solidification and on the overall oxygen content available in the wafer (i.e., on the wafer position along the ingot length).

On the basis of these considerations, a possible solution to overcome the problem of striations, besides the low temperature annealing on cell level already suggested in Ref. 8, is to use n-type Cz-Si solar cell precursors submitted to the classical high temperature dissolution step usually performed on silicon wafers for microelectronics (known as tabula rasa).[23] A thermal treatment at temperatures around 1000 °C in a clean environment[11,21,23] to be performed before any solar cell processing step can be therefore suggested in order to mitigate the presence of striations through to the dissolution of grown-in oxygen nuclei. Another solution is to mitigate the formation of oxide nuclei during the ingot growth and cooling down. This is difficult to control in a production environment, but could significantly contribute to the solar cell manufacturing cost reduction.

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[2]See http://www.itrpv.net/ for International Technology Roadmap for Photovoltaics (ITRPV)./
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