STABLE AND EFFICIENT P-TYPE MULTICRYSTALLINE SILICON CELLS CONTAINING 20 PPMA INTERSTITIAL OXYGEN

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ABSTRACT: Interstitial oxygen is the most prevalent impurity in crystalline silicon. An upper limit of around 12 ppma [O_i] has long been accepted for multicrystalline solar cells. This paper demonstrates that it is possible to manufacture solar cells with an efficiency of over 15.4% at 20 ppma interstitial oxygen from commercial multicrystalline p-type silicon (mc-Si) wafers using ECN standard screen-print process. We also show that 20 ppma [O_i] wafers can be processed with industrial processing temperatures at least up to 900 ^oC.
Keywords: Multicrystalline Silicon, Interstitial Oxygen

1 INTRODUCTION

Multicrystalline silicon is the source material for a large portion of the world production of solar cells. The permissible levels of all common impurities are necessary knowledge to decrease the cost of silicon feedstock and wafers. One of the most common impurities is interstitial oxygen. Oxygen has a reverse segregation coefficient, meaning that the highest concentration of oxygen is found in the bottom of the ingot, contrary to most other impurities. The commonly accepted upper limit of [O_i] in multicrystalline wafers is between 12 and 15 ppma. The proposed causes of this limit have been a failure to effectively respond to gettering [1], the non-linear dependence of precipitation and intrinsic gettering on oxygen concentration [2] and boron-oxygen related light-induced degradation [3].

We show that for cells processed with commercial multicrystalline material with oxygen concentrations up to 20 ppma the conversion efficiency is approximately identical to that of wafers with lower oxygen content and the light induced degradation is less than 3 mV.

2 EXPERIMENT

Five columns from three commercial ingots were selected. We processed wafers into cells, using the ECN baseline cell process of 2006. The process flow of the baseline is depicted in figure 1. The wafers were also processed with an emitter diffused at 900 ^oC.

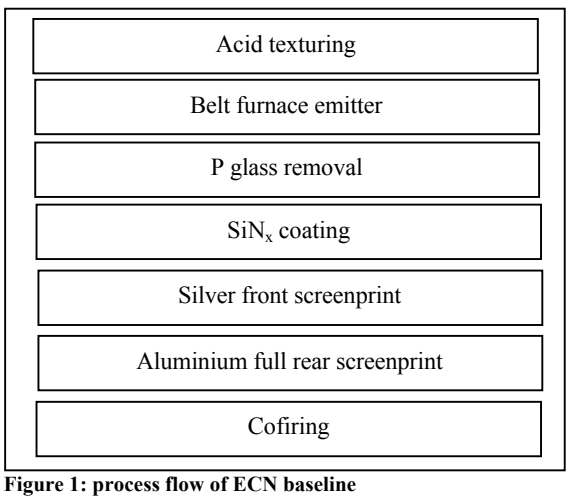

Figure 1: process flow of ECN baseline

Neighbour wafers were processed at each temperature. The minority carrier lifetime was determined by QSSPC. The conversion efficiency of the solar cells was measured before and after light soaking with a WACOM Class A Solar Simulator according to IEC 60904-3 ed.1. A Perkin-Elmer FT-IR instrument was used to measure O_i according to ASTM F1188.

2.2 FTIR for [O_i] determination on wafers

ASTM F1188 excludes measurement on wafers, since the minimum thickness described is 400 µm and minimum resistivity is 3 Ohm cm. Commercial wafers can fullfill neither requirements, as those are 200 µm thick and has a resistivity between 0.5 and 2 Ohm cm.

ASTM F1188 describes a method to handle lower resistivities by using a reference with equal resisitivity, but no validation for thin wafers has been described. To check the validity of our method, we compared sets of neighbour wafers of thickness between 1.5 mm and 200 µm, in order to demonstrate that O_i can be measured with sufficient accuracy in our wafers.

3 RESULTS

3.1 [O_i] for a range of thicknesses

In figure 2, the values for [O_i] are depicted for wafers which are known to have identical oxygen concentrations, either because the wafers are neighbours or because the values are measured on the same physical wafer before and after etching.

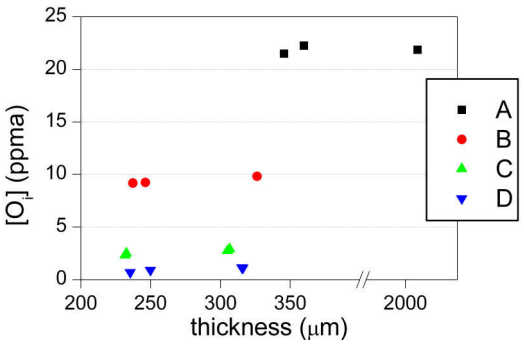

Figure 2: [O_i] for different thicknesses of the same wafer A-D

Together with a previous round robin [4] and the noise of the measurements themselves, we can estimate an absolute error for the measurements, which is approximately 1.3 ppma for all measurements.

3.2 Wafer efficiencies for high O_i wafers

The efficiency values of the wafers as a function of oxygen concentration is depicted in figure 3.

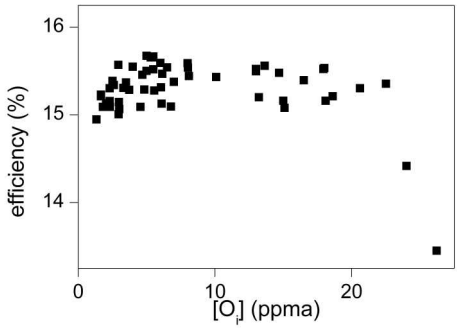

Figure 3: interstitial oxygen concentration vs efficiency

The cell efficiency is not influenced by interstitial oxygen up to 22 ppma, but above 22 ppma the cell efficiency deteriorates. It should be noted that these high-oxygen wafers originate from bottom of the ingot and thus typically contain many impurities in high concentrations. Other bottom wafers besides those are also present in the graph, but their efficiency values are not distinguisable.

The ECN baseline is using a low temperature belt furnace emitter, but high temperature processing has been frequently used in the past. Oxygen precipitation which occurs at high temperatures might explain the poor results in the past. We therefore included high-temperature emitter diffusion experiments. The results are included in figure 4, together with the low temperature route on neighbours.

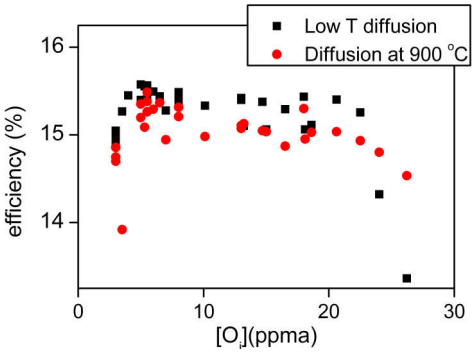

Figure 4: [O_i] vs η for high T emitters

In general, the high temperature emitters perform worse than the low temperature emitters, except for the high oxygen wafers. Probably, the high oxygen bottom wafers need extra gettering which it gets from a higher temperature.

To prove that the gettering of high oxygen wafers is not impaired, we compared the minority carrier lifetime of high oxygen wafers and cell efficiency. The wafers were taken from two columns, A and B.

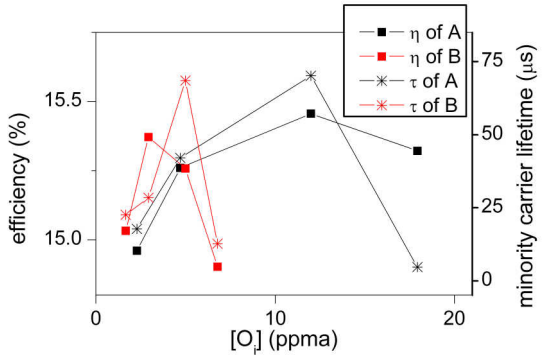

Figure 5: η and τ for columns A and B

The wafers with highest oxygen concentration of each column have a low minority carrier lifetime of below 5 µs prior to processing. Nevertheless, the high oxygen column gives efficiencies above 15.3% for the bottom wafer. This is only possible if the wafer has been gettered. Note that these lifetime vs oxygen findings are itself in perfect agreement with values from the literature [3, 5]. It is the resulting cell efficiency which deviates from the expected. An explanation for this deviation has been given by Geerligs [6].

High oxygen wafers doped with boron are affected by boron-oxygen light induced degradation. Selected cells were placed under a solar simulator for 24 hours, after which they were measured, annealed for 15 minutes at 250 ºC and remeasured. The open circuit voltage can be found in figure 6.

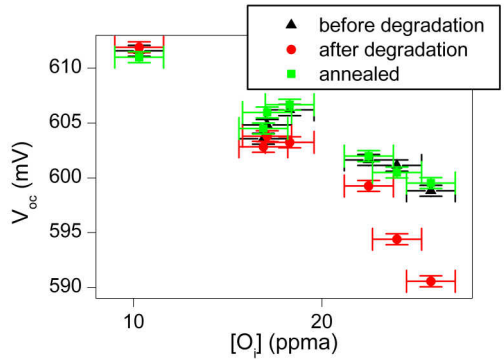

Figure 6: light induced degradation

The difference between the voltage values before illumination and after anneal at 250 °C are within 1 mV. At 17 ppma O_i the V_{oc} values before and after illumination overlap. For 24 ppma cell, the difference is over 9 mV, which corresponds to a loss in cell efficiency of 0.25% absolute. This is approximately half of degradation values commonly seen in Cz material.

4 CONCLUSIONS

Wafers with 22 ppma O_i yield reasonable efficiencies of above 15%. At the current standard of 2009 (16.5% average), this is a low efficiency; however these results have been obtained in 2006 at which time the values were reasonable. The changes in processing between 2006 and 2009 are not expected to lead to different conclusions.

We have examined the proposed causes of the supposed inability to process reasonable quality wafers with O_i above 12 ppma. The wafers seem to getter sufficiently, as wafers with an as-cut lifetime of below 5

μs yield cells of 15.3%, which can not be achieved if no gettering occurs.

The boron-oxygen complex is present and active in high oxygen multicrystalline wafers. However, up until 17 ppma the difference between degraded and non-degraded cells lies within error. Even after the cell efficiency has dropped below usable, the effect of the B-O degradation is only 1.5% relative. The difference with Czochralski grown material might be explained by the presence of other impurities (e.g. transition metals) in multicrystalline material with a different reaction to illumination.

A point of note: these results have been obtained with standard commercial multicrystalline material. While this material is known to contain a range of impurities, the concentrations are fairly low compared to that of O_i. In other types of material, e.g. solar grade material or even intentionally contaminated material, the role of O_i may differ markedly from the results presented here [e.g. 8].

In summary, we have shown for a range of wafers from different manufacturers that multicrystalline wafers with oxygen contents up to 20 ppma can be processed without any significant conversion efficiency penalties.

5 ACKNOWLEDGEMENTS

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