SIN PRECIPITATE FORMATION RELATED TO METAL CONTAMINATION OF MULTICRYSTALLINE SILICON FOR SOLAR CELLS

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ABSTRACT: Elongated filaments and periodically waved sheets were observed along the grain boundaries of etched multi-crystalline wafers from intentionally contaminated ingots. The filaments and sheets consist of silicon nitride, as was confirmed by Energy Dispersive X-ray analysis (EDX). The abundance of the SiN sheets and filaments increases with a higher concentration of metal impurities and, except for the absolute top and bottom, was not observed in the uncontaminated reference ingots. Solar cells made from filament regions of the ingot display strong FF losses due to the presence of shunts, depending on the level of metal contamination. The shunt patterns, observed using lock-in thermography, are correlated to the regions where the filaments are present.

Keywords: multi-crystalline silicon, impurities, silicon nitride precipitates, shunts

1 INTRODUCTION

Most commonly, multi-crystalline ingots are cast in a crucible made of quartz that is covered with a silicon nitride coating to avoid sticking of the ingot to the crucible wall. This coating can also act as a source of nitrogen in the liquid silicon, which can enhance the formation of SiN precipitates under certain operating conditions of the crystallization furnace [1-3]. Large precipitates (e.g. SiC) can have a detrimental influence on the wafer sawing process and/or lead to shunts in solar cells. It is therefore desirable to understand their origin and effect, and find a way to prevent their formation.

In this paper, we demonstrate that there is a correlation between the contamination of the liquid silicon with metal impurities and the formation of silicon nitride precipitates that reside on the grain boundaries. We show that the abundance and formation of these precipitates depends on the level of metal contamination of the silicon feedstock.

2 EXPERIMENTAL

Several pilot scale 12 kg multi-crystalline silicon ingots were grown in a Crystalox DS 250 furnace [4] that was designed to solidify mc-Si ingots using a Bridgman type directional solidification method. For these experiments, the polysilicon feedstock was intentionally contaminated by a predetermined amount of the metal under investigation [6-7]. In this paper, we focus on the impact of Fe, an overview also including other metal contaminants will be given in another paper, which is to be submitted [4]. Prime quality polysilicon, high purity crucibles (with a spherical bottom) and purified Si_3N_4 lining were used, to keep unintentional contamination as low as possible. The resistivity and the amount of impurities that was introduced in the feedstock charge are given in table 1.

A reference ingot was grown using the same materials and crystallization parameters but without intentional contamination. This ingot was used as a baseline reference for the entire manufacturing chain, from crystallization to solar cell manufacturing. A full description of the crystallization and solar cell process and characterization can be found in refs. [5-7].

From each ingot a centre block of 125×125 mm^2 was cut and sliced into 200-240 μm thick wafers, of which 20 representative wafers were processed into solar cells using a state of the art industrial P diffusion, full aluminum Back Surface Field and SiN_x:H firing through, to determine the effect of impurity level on cell characteristics [6,7].

To reveal the SiN particles, the ‘as-cut’ wafers were etched in a HNO_3:HF based solution. The precipitates are chemically resistant to this mixture, so removing 10-20 microns of the silicon surface makes them protrude from the surface (see Figs. 1 and 2).

After etching, some wafers were coated with a SiN_x coating, to enhance the contrast under the optical microscope and enable a fast scanning on the presence of the precipitates. It was checked on samples before and after applying this additional coating, that the coating colored the filaments yellow and the background wafer blue, but did not affect either the shape or abundance of the filaments. The Scanning Electron Microscope (SEM) and EDX analyses were made on an etched as-cut sample, without any coating applied.

In the following, the Fe-contaminated ingots will be referred to as [impurity] [impurity concentration in ppmw], for example Fe 50 will be the name of the ingot contaminated with 50 ppmw of Fe.

Table I: Resistivity and concentration of intentionally added Fe for some of the test ingots.

	resistivity (Ω cm)	[Fe] (ppmw)
Reference	0.9-1.1	0
Fe 50	0.9-1.1	53
Fe 200	1.0-1.2	200

3 RESULTS AND DISCUSSION

3.1 Microscopic observations of filaments

After HNO_3:HF etching and SiN_x coating of Fe contaminated wafers, some grain boundaries appear as dark colored lines (figure 1). At a larger magnification, as shown in figure 2, it can be observed that these dark colored grain boundaries are covered with small filaments, sticking out from the grain boundaries and pointing in the direction of solidification. The filaments reside only on the grain boundaries and no filaments are found in the bulk Si.

The length of the long filaments (figures 2 and 3) corresponds roughly to the polishing thickness (~10-20 micron) and is shorter for observations on wafers that were etched for shorter times. Also, the filaments are always observed on both sides of the wafer for the same grain boundaries. Therefore, it is most likely that the silicon nitride filaments were formed during ingot growth and extend throughout the grain boundaries. They are exposed by etching due to their chemical resistance to the etching liquid and the removal of the surrounding silicon.

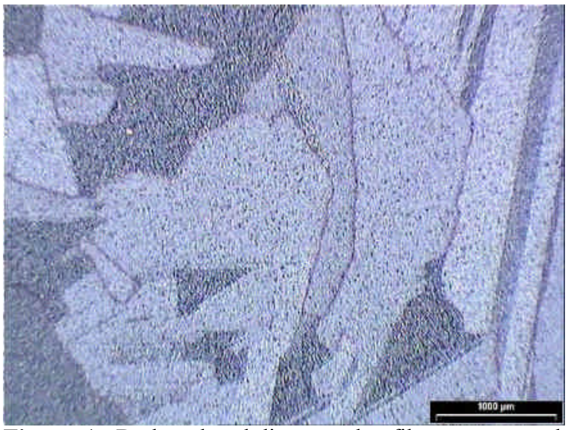

Figure 1: Dark colored lines at the filament covered boundaries. The contrast is better for eye-observation.

One sample of a contaminated wafer was inspected by SEM (figure 3). Here again filaments, but also periodically waved sheets, were found along the grain boundaries. The chemical composition of both filaments and sheets was tested by EDX (figure 4), which revealed that they contain nitrogen but no carbon. Also, if there are any metal impurities present at the location of these precipitates, then their concentration must lie below the detection limit of EDX, and they are, in any case, not the main compound of the precipitates.

Such irregularly shaped filaments in grain boundaries are commonly attributed to SiC precipitates [2] but not to SiN, which is usually found in the form of sharp (bunches of) needles or rods. Also the formation of broad sheets and their waviness was, to our knowledge, not reported before. The waviness of the sheets seems highly periodic, with a period in the order of half a micron, for which we do not have an explanation at this moment.

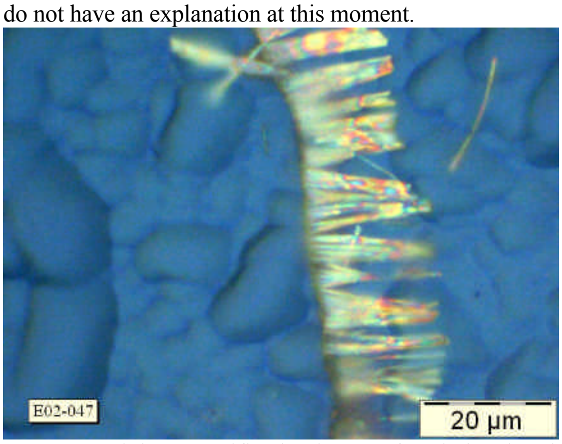

Figure 2: Higher magnification image of a "dark colored boundary". This image is taken on a chemically etched wafer from a Cr contaminated ingot.

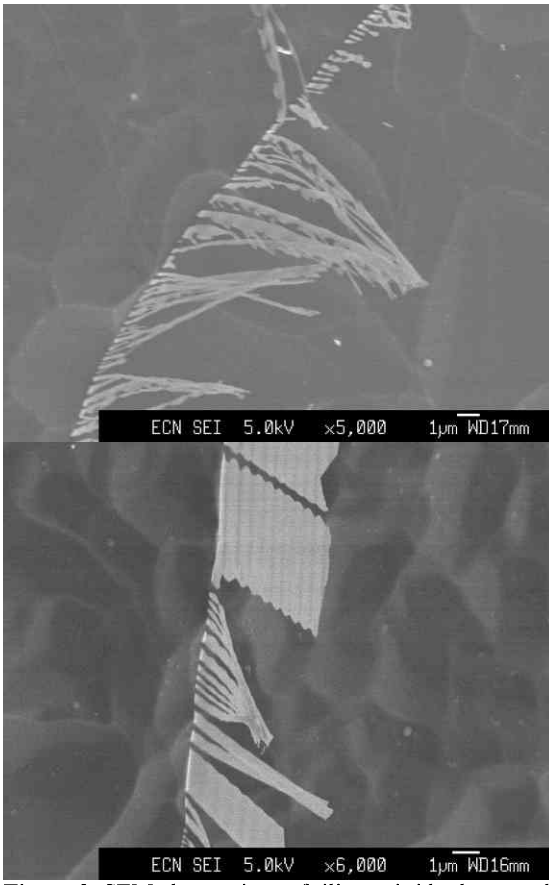

Figure 3: SEM observations of silicon nitride sheets and filaments sticking out of the grain boundaries. Very peculiar is the "waviness" of these sheets, which seems to be periodic.

A selection of wafers, distributed over the height of the ingot, was inspected closely, by optical microscope, on the presence of filaments and categorized in four qualitative groups: containing dark coloured grain boundaries in over 30% of the whole wafer area, containing more than 10 grains with one or more coloured boundaries but less than 30% of the wafer area, containing less than 10 grains with coloured boundaries and containing no dark coloured grain boundaries. The results are presented in figure 5. In the contaminated ingots, filaments were observed <35% and >85% of the ingot height, but in the reference ingot only a few filaments were found more close to the top and bottom of the ingot. The abundance of filaments in the bottom seems related to the amount of added impurities (see also [4]).

3.2 Solar cell results

In Figure 6, the trend in FF as a function of ingot position is given for two different levels of Fe contamination and for the reference. The cells from the reference ingot display a constant fill factor as a function of ingot position except for the top of the ingot. For the solar cells that were made from the contaminated ingots, a distinct decrease in FF was observed below about 35% and above about 85% of the ingot height. These solar cells are mainly affected by shunts (low shunt resistance) [7].

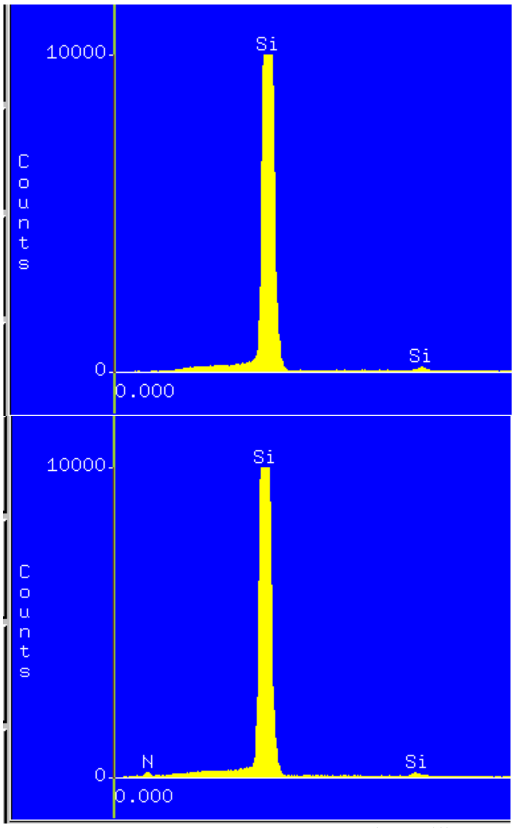

Figure 4: Top: EDX measurement on bare silicon surface. Bottom: EDX measurement on silicon nitride sheet (with silicon surface background). Evidently, the sheet contains nitrogen.

A clear correlation is found between the FF results in figure 6 and the filament inspection results in figure 5. In regions of the ingot where the FF drops, filaments are found in neighbouring wafers and where no filaments are found the FF is comparable to the reference, so the presence of filaments in the wafer corresponds to an occurrence of shunts on cell level. The fact that in the bottom (see Fig. 5) the abundance of filaments increases with an increasing amount of added impurities, might explain the dramatic FF loss for the Fe 200 ingot, in the bottom, where the relative FF loss is more than 35%. It must be noted that also in the top of the reference ingot, where the concentration of unintended impurities is maximal due to segregation, some filaments were observed and a small decrease in FF was measured.

Evidence of spatial correlation between shunts and locations of filaments is obtained by Lock-In Thermography (LIT) images (figure 7). Heterogeneous shunt-patterns are observed at a reverse bias of 2V. The filament patterns, which can be observed on the etched wafers by low magnification microscope, correspond globally to the shunt patterns observed on neighbouring cells with LIT. In regions without shunts, no filaments are observed on the neighbouring wafer and, on the contrary, filaments are found in all shunt locations. Unfortunately the resolution of the LIT technique is too low, due to lateral heat transport, to recognize single grain boundaries on the locations of the shunts. The extent to which the locations of these shunts correlate directly with those of the filaments is currently under investigation.

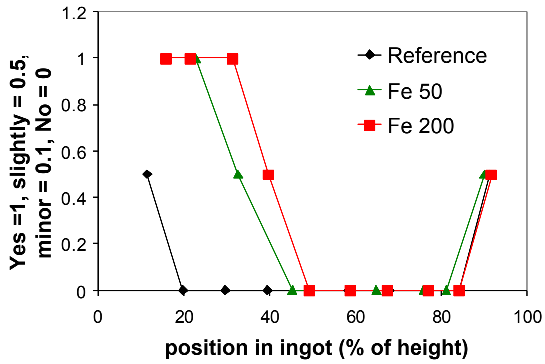

Figure 5: qualitative analysis of filament distribution over the ingot by dark lines in optical microscope (1 = filaments on more than 30% of the wafer area, 0.5 = more than 10 grains with filaments but less than 30% of the wafer area, 0.1 = less than 10 grains with filaments, 0 = no dark lines).

4 CONCLUSIONS

In this study the impact of metal impurities on the quality of silicon material was exaggerated, by adding large amounts of Fe to the feedstock, to relate specific limitations of the cell efficiency to the presence of metal impurities. It was found that, in particular, the interaction of Fe with nitrogen has a large impact on the cell performance, by inducing the formation of silicon nitride precipitates on the grain boundaries that cause shunts.

Filaments and sheets were observed along the grain boundaries on solar cells and etched wafers from the bottom and top, up to about 35% and above 85% height, of intentionally contaminated ingots. Shunt patterns of cells from these regions, shown by LIT, can be correlated by optical microscopy to the regions where the filaments were observed. The reference, without addition of contaminants, displayed some filaments in the very top and nearly none in the bottom.

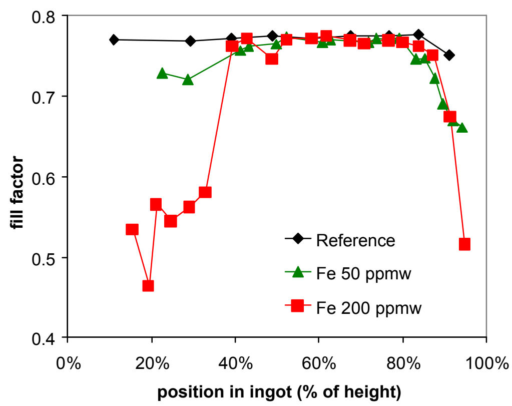

Figure 6: Fill factor distribution of solar cells as a function of ingot position. The two Fe contaminated ingots display a distinct drop in FF in the bottom region up to about 35% ingot height. The FF reduction in the bottom is considerably larger for the ingot with 200 ppmw of Fe than for the ingot with 50 ppmw of Fe.

Using a scanning electron microscope (SEM) with

EDX facility, it was confirmed that the filaments and sheets contain nitrogen, and not carbon, and display a periodically waved surface that, to our knowledge, has not been reported before. Fe, despite its high concentration, was not found as a compound of these filaments. This is interesting, since it shows that the presence of metals in the melt enhances the formation of SiN precipitates.

The result is not only relevant for these highly contaminated test-ingots, but also in the top of the reference ingot filaments are observed together with a FF decrease that corresponds to an absolute efficiency loss of about 0.5%. The nitrogen content and its distribution through the ingot is a commonly ignored parameter during casting and characterization of silicon blocks and wafers. Here it is demonstrated that this is not legitimate. If it would be possible to avoid the formation of nitrogen filaments, by controlling either the source of nitrogen or its interaction mechanism with metal impurities, larger yields, especially in the top, can be expected from multi-crystalline ingots.

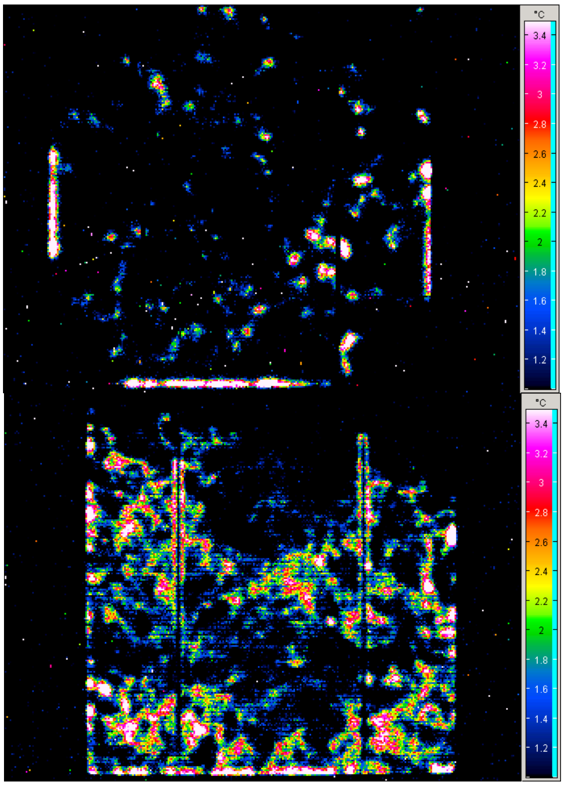

Figure 7: Lock-in Thermographs at 2V reverse bias for the Fe50 (top) and Fe200 (bottom) ingots at 23% and 32% ingot height, respectively. The pattern corresponds to microscope observations of the filament distribution on neighbouring wafers.

ACKNOWLEDGEMENTS
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REFERENCES

[1] J.P. Rakotonaina, O. Breitenstein, M. Werner, M. Hejjo Al-Rifai, T. Buonassisi, M.D. Pickett, M. Ghosh, A. Müller and N. Le Quang, “Distribution and formation of silicon carbide and silicon nitride precipitates in block-cast multicrystalline silicon”, Proceedings of the 20th EU PVSEC, Barcelona, Spain, 2005.

[2] H.J. Möller, C. Funke and S. Würzner, “Melt growth of SiC and Si_3N_4 precipitates during crystallization of multicrystalline silicon for solar cells” , Proceedings of the 3rd International Workshop of Crystalline Silicon Solar Cells, Trondheim, Norway, 2009

[3] C. Reimann, M.Trempa, J. Friedrich, S. Würzner, H.-J. Möller, Proceedings of the 3rd International Workshop on Crystalline Solar Cells, Trondheim, Norway, 2009

[4] P.C.P. Bronsveld, G. Coletti, E. Schuring, C.M. Roos, *to be submitted to Applied Physics Letters.*

[5] R. Kvande, L. J. Geerligs, G. Coletti, M. Di Sabatino, E. J. Øvrelid, C. C. Swanson, J. Appl. Phys., 104, 064905 (2008).

[6] G. Coletti, R. Kvande, V. D. Mihailetchi, L. J. Geerligs, L. Arnberg, and E. J. Øvrelid, J. Appl. Phys, 104, 104913 (2008).

[7] G. Coletti, P.C.P. Bronsveld, G. Hahn, W. Warta, D. Macdonald, B. Ceccaroli, K. Wambach, N. Le Quang and J.M. Fernandez, Accepted for publication in Advanced Functional Materials 2010. DOI: 10.1002/adfm.201000849