HPM silicon: The next generation of multicrystalline silicon for PV

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ABSTRACT

High-performance multicrystalline (HPM) silicon, achieved by nucleation on special seed layers at the crucible bottom, is now increasingly replacing conventional multicrystalline (mc) silicon, which is solidified on the standard silicon nitride coating. The HPM material is characterized by a very fine initial grain structure consisting of small, regularly shaped grains surrounded by a large number of random-angle grain boundaries. These grain structure properties, which differ significantly from those of conventional multicrystalline silicon, lead to a much lower dislocation content in the material, and therefore result in higher efficiencies of the silicon solar cells produced. This paper gives a rough overview of the worldwide R&D activities on HPM silicon in recent years, supplemented by several research results obtained at Fraunhofer IISB/THM. The focus is on the different seeding methods, the grain structure properties and the development of the grain and defect structure over the ingot height, as well as on the main challenges for further improvements in material quality and production costs.

Introduction

Today, multicrystalline (mc) silicon is used for roughly 50% of all silicon solar cells produced worldwide. Even though the cell efficiency of mc silicon solar cells is a little lower than that of monocrystalline cells, mc silicon is expected to hold a significant market share over the next ten years, given its good material quality at reasonable production costs [1].

The most popular crystallization method for producing mc silicon is the *directional solidification technique*: silicon feedstock is melted in a square-shaped fused silica crucible that is coated with a silicon nitride powder on the inner surfaces. By extracting the heat in a downward direction, an mc silicon ingot (ingots with a weight of 600–800kg and an edge length of 840–1,000mm are typical nowadays [1]) is solidified from bottom to top. As a result, the initial nucleation of the silicon melt at the crucible bottom leads to the typical mc grain structure consisting of irregularly shaped grains, including many dendrites and twins. Until recently, the view of the majority of the mc silicon crystal growth community was that an mc grain structure with large grains and electrically inactive grain boundaries (especially twin boundaries) should lead to the best cell efficiencies [2]. Special growth methods – such as 'dendritic casting' in 2006 [3] or the 'mono-like approach' in 2008 [4] – were therefore developed in order to enhance the grain size and reduce the most harmful crystal defects in mc silicon, namely grain boundaries and dislocation clusters. However, both of the above-mentioned techniques presented some insurmountable problems concerning the propagation of dislocations in the ingot volume, especially on an industrial scale, and were therefore practically discontinued.

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In 2011 a kind of revolution took place with regard to considerations about the best-quality mc grain structure. A new silicon material, the so-called 'high performance mc silicon', or HPM silicon, was first announced by the Taiwanese company Sino-American Silicon Productions Inc. (SAS) [5,6]. This type of material, obtained by special nucleation techniques (see below), exhibits a very fine grain structure in contrast to conventional mc silicon. It has been found that HPM silicon results in ~0.5%$_{abs.}$ higher solar cell efficiencies [6,7], which means that the grain structure properties significantly influence the eventual cell properties.

Since 2011 much R&D activity has been conducted in order to: 1) investigate the grain structure of this HPM material in detail; 2) understand the development of the grain structure as well as the crystal defects over the ingot height; and 3) further improve the material quality and the yield of high-quality wafers per ingot.

Grain structure and defect development in HPM silicon

In 2011 SAS found that the degree of undercooling of the silicon melt, adjusted at the initial state of solidification, was a strong factor in influencing the grain structure [5,6].

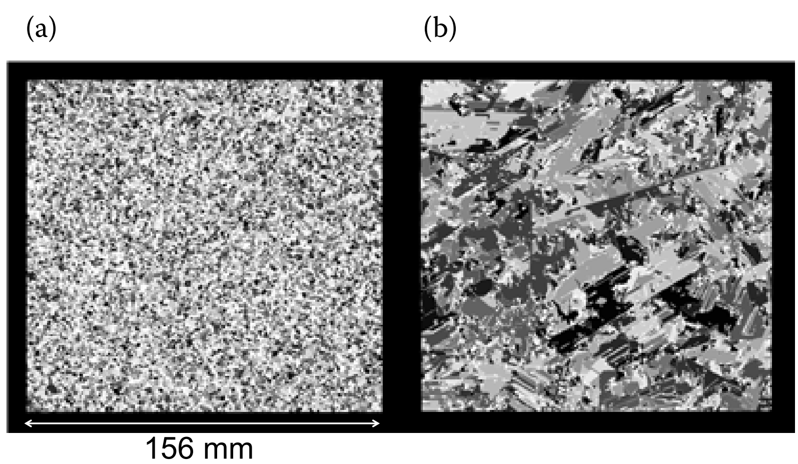


Figure 1. Images of typical grain structures, at a height of 20mm, of G1 silicon bricks grown at Fraunhofer IISB/THM: (a) HPM; (b) conventional mc.

However, the company also stated that the 'undercooling window' to generate a HPM structure with small uniform grains was quite narrow. Thus, if the undercooling is too low, a grain structure with large and non-uniformly shaped grains is generated, whereas if the undercooling is too high, very large dendritic grains are the result. In consequence, the implementation of a reproducible industrial-scale crystallization process to influence the grain structure by controlling just the undercooling is quite challenging.

Today, the most frequently used method for producing HPM silicon on an industrial scale is through solidification on a non-melted silicon feedstock layer [6,8], which is achieved by melting the feedstock charge downwards inside the crucible, from top to bottom. The melting-down has to be carried out very carefully in order to avoid a complete melting of the feedstock, especially in the border regions of the crucible. As a result, a layer of non-melted silicon feedstock particles, several millimetres thick, remains; these particles act as nucleation sites for the silicon melt. When the silicon melt solidifies on these silicon particles, the typical HPM grain structure containing very small grains (Fig. 1(a)) is uniformly generated; this is significantly different from the structure obtained using the conventional method without a seeding layer, just by nucleation on the standard silicon nitride coating (Fig. 1(b)).

At the beginning of HPM material development, there was a lack of suitable characterization tools that would allow an overall grain structure analysis on a full 156 × 156mm^2 wafer area in a reasonable timescale. A new tool was therefore developed at Fraunhofer IISB/THM in 2011 [9], which was a combination of optical grain detection and Laue measurements, enabling the determination of grain size, grain orientation and grain boundary type, including several statistic evaluations [10]. Typical images obtained from these measurements are shown in Fig. 2.

With the use of this tool, a comparison of several industrially grown silicon ingots created by the group at Fraunhofer [7] revealed typical grain structure parameters: for HPM silicon at 20mm growth length, the typical findings were: 1) a mean grain size of < 4mm^2; 2) a homogeneous distribution of grain orientations (coefficient of variation $CV_{GO} < 1.5$; the smaller this value, the more homogeneously distributed the grain orientations); and 3) a length fraction of random grain boundaries of greater than 60%. In contrast to those findings, conventional mc silicon ingots exhibit a much coarser grain structure with a mean grain size of 4–9mm^2, a $CV_{GO} > 3$, and a length fraction of random grain boundaries of less than 35% [7].

In the last few years, different researchers have found that this large difference in the initial grain structure is the main reason for the better performance of the HPM material in comparison to conventional mc silicon (e.g. [5,6,11–13]). Dislocations are inevitably formed during the growth of any mc silicon material; these can easily spread and multiply into the volume of conventional mc silicon ingots because of the large grains and the large number of Σ3 twin grain boundaries which the dislocations can go past [14]. In contrast, the dislocation movement within HPM silicon is prevented by a large number of random grain boundaries which the dislocations cannot pass [14]; further, the amount of spreading within the grains is limited because of their small size. In summary, there is a need for the smallest possible grain sizes, in combination with

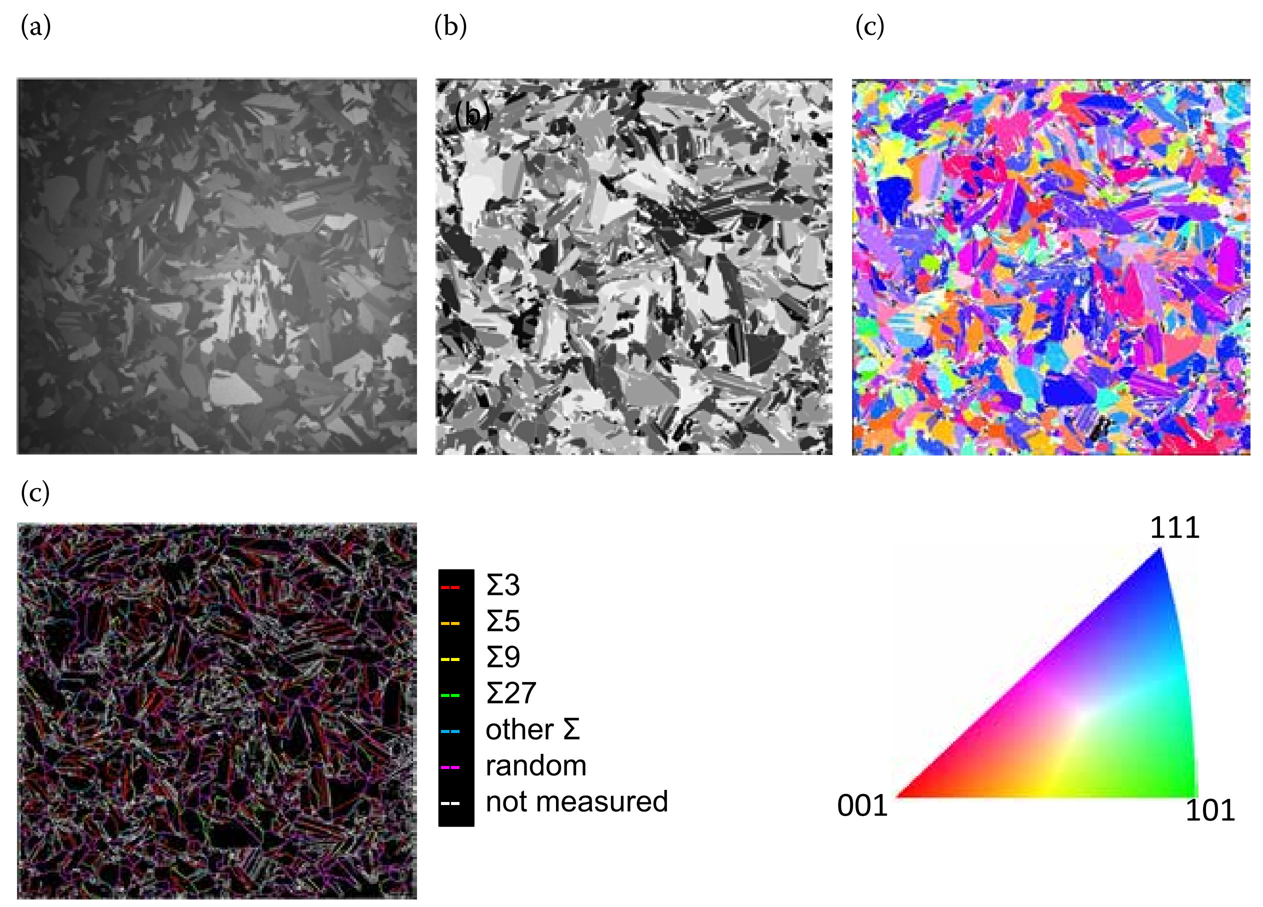


Figure 2. Resulting images from the characterization of a 156mm × 156 mm mc Si wafer: (a) photograph of the investigated wafer; (b) detected grain structure; (c) exact grain orientation; (d) calculated grain boundary types.

the largest possible number of random grain boundaries, in order to achieve a high-quality mc silicon material with a low dislocation content and thus a small recombination-active area.

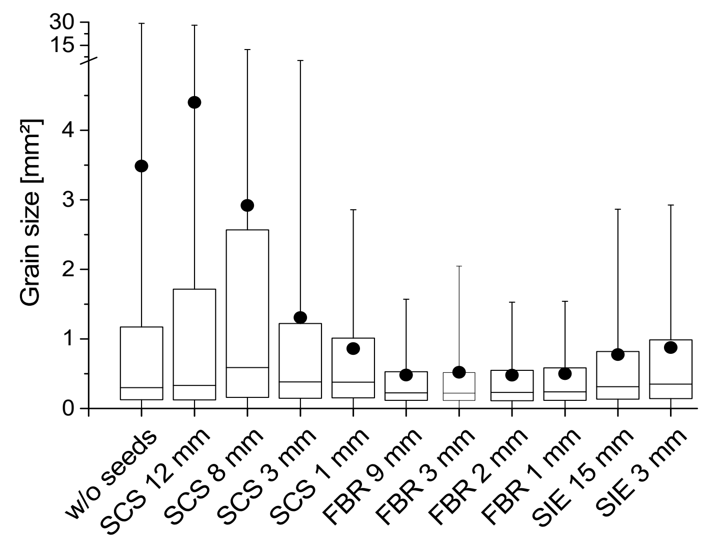
During the research activities at Fraunhofer IISB/THM concerning HPM material, the initial seeding process was investigated in lab-scale HPM silicon experiments [15]. It was found that the initial grain size of the mc structure depends on the size of the microstructure of the feedstock used within the seeding layer (Fig. 3).

When single-crystalline silicon (SCS) feedstock particles from 12mm to less than 1mm in diameter are used, the resulting mean grain size decreases with decreasing feedstock particle size; this is because each particle represents one seed, and for small diameters more seeds can be located on the crucible bottom area (Fig. 3, left). On the other hand, when polycrystalline feedstock (e.g. from Siemens process (SIE) or fluidized bed reactor (FBR)) is used, one feedstock particle provides more than one seed because of its microstructure, which is characterized by an inner grain size of less than 1mm. As a result, the achievable mean grain size is slightly smaller than that for the smallest single-crystalline feedstock, whereas the differences between the tested polycrystalline feedstocks are not as large (Fig. 3, right). This conclusion has also been reached by other researchers [16], who measured a smaller inner grain size for the SIE chips (70–270μm) than for the FBR granules (700μm); however, the larger gaps between the irregularly shaped SIE chips also lead to bigger grains, and therefore offset this difference. The investigations have also shown that the initial length fraction of random grain boundaries slightly increases if the initial grain size becomes smaller [15].

A study of the dislocation content reveals a clear correlation between the random grain boundaries and the dislocation content (Fig. 4): specifically, the higher the length fraction of random grain boundaries, the lower the dislocation content or recombination-active wafer area. This means that a smaller initial grain size results in a higher random grain boundary fraction, and ultimately in a lower dislocation content in the HPM material.

Investigations of the grain structure development over the ingot, for both lab-scale [12,13,17] and industrial-scale ingots [6,7], reveal that the initially high random grain boundary fraction of 60–70% decreases during the growth of the ingot, while the number of Σ3 twin boundaries increases. This phenomenon has been studied in detail by different groups (e.g. [17,18]); they found that different grain boundary annihilation and formation mechanisms take place during growth, leading to a permanent diminishing of grain boundaries (especially high-fraction types), and simultaneously to the formation of new grain boundaries with low energy (especially Σ3 twin boundaries). In consequence, the dislocation content, and therefore the recombination active area, of HPM wafers increases with increasing ingot height.

> "The advantage of HPM silicon is most evident in the lower parts of the ingot, where the difference in grain structure between HPM and conventional mc silicon is largest."



SCS = single-crystalline silicon, FBR = fluidized bed reactor, SIE = Siemens

Figure 3. Grain size data at 5mm above the seeding position for HPM lab-scale ingots using several silicon feedstocks of different particle sizes, compared with a conventional mc silicon ingot without silicon seeds. (Data collected from Reimann et al. [15] with permission from Elsevier.)

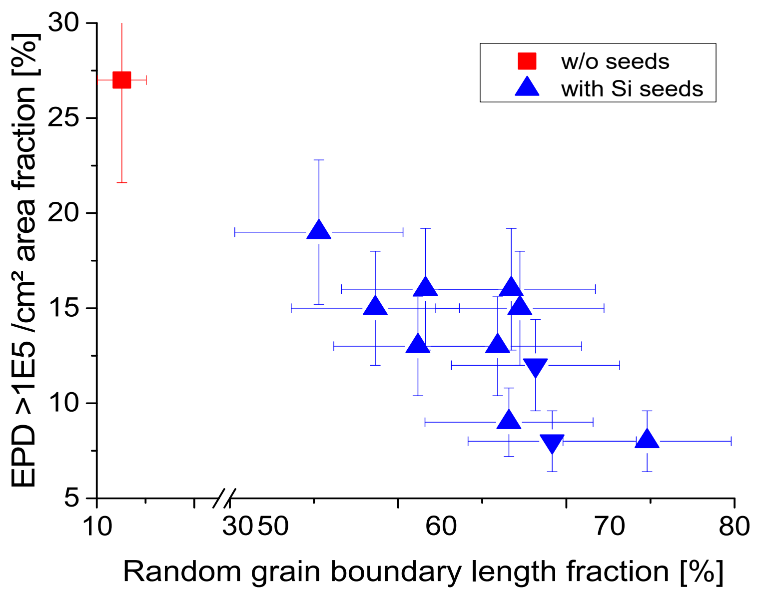


Figure 4. Fraction of areas with an etch pit density (EPD) >1E5/cm² vs. the random grain boundary length fraction at an ingot height of 25mm, for lab-scale HPM material experiments performed without and with silicon seeds. (Data adapted from Reimann et al. [15] with permission from Elsevier.)

If one compares the grain structure and recombination active area of industrial-grown HPM and conventional mc silicon ingots near the ingot top (~250–300mm ingot height), it is observed that the difference in grain structure properties, and also in the recombination active area between the two material types, is not as significant in the top region, since it initially occurs in the bottom region of the ingots [7]. From this observation, it seems that the advantage of HPM silicon is most evident in the lower parts of the ingot, where the difference in grain structure between HPM and conventional mc silicon is largest.

This theory has been confirmed by further investigations carried out by the group at Fraunhofer, for which exceptionally tall HPM and conventional ingots, up to 710mm in height, were grown [11]. The exceptional ingot height was obtained by the successive growth of eight G1 ingots (each with a height of 130mm), while a 20mm horizontal cut from the top region of the preceding ingot was used as the seed-plate for the subsequent ingot. The results show that the grain structure properties of both material types, although quite different at the ingot bottom, align with each other with increasing ingot height. This is already observable in the grain structure itself, but also in the grain-boundary-type distribution, which was identified as one key parameter in influencing the dislocation movement in the silicon ingots (see Fig. 5). While at the ingot bottom the grain-boundary-type distributions are significantly different between the conventional ingot (high Σ3 twin fraction, low random fraction) and the HPM ingot (high random fraction, low Σ3 twin fraction), the distributions align with each other with increasing ingot height, finally becoming very similar at a height of 250–300mm. Further, it was shown that, during the growth above 350mm, no significant changes occur through this region to the top of the ingots at 710mm.

For the recombination-active area it was found that, after an initial discrepancy up to an ingot height of 200mm due to the above-described mechanisms, an alignment takes place up to a height of 350–400mm. Finally, from this height to the top (710mm), constant values occur, which are equal for both material types (see Fig. 6). From this observation it is concluded that the growth of even higher HPM silicon ingots is of no benefit to industrial producers in terms of the advantage of HPM silicon over conventional mc silicon.

In general, it is clear that there is a strong correlation between the grain structure properties and the dislocation development over the ingot height. Thus, the control of the grain structure throughout the complete ingot is one of the main tasks for further improving the HPM material quality.

Alternative nucleation methods for achieving HPM silicon

The main advantage of the above-described method which incorporates the seeding on a non-melted silicon particle layer is its high reproducibility in industrial production. However, some drawbacks also exist, which reduce the economic profitability: first, the more complex melting process entails longer process times in comparison to the conventional growth of mc silicon; second, there are some yield losses in the bottom region of the ingot caused by the non-usability of the seeding layer for the wafer production and by an increased bottom red zone.

In the last few years some new approaches for the production of HPM silicon have been proposed with the aim of overcoming these problems. The key aspect of these methods is to provide foreign nucleating agents on the crucible bottom and to solidify the silicon melt directly on them in order to achieve the fine-grained HPM structure. These nucleation agents should be stable at high temperatures, should be wettable by the silicon melt in order to reduce the nucleation energy in comparison to the standard silicon nitride coating, and should not, of course, contain a large content of electrically harmful impurities (e.g. metals).

Initial investigations on small lab-scale ingots were performed in 2014 by Wong et al. [19] by applying silicon and silica particles in different mixing ratios (1:3 and 3:1) as a coating on the crucible bottom. It was observed that the higher the silica content in the coating, the larger the number of resulting small and uniform grains. However, those authors found no clear correlation with the random grain boundary fraction, which was less than 30% and still quite low. In all likelihood, the silica seed density on the bottom surface was too low to significantly influence the grain structure properties.

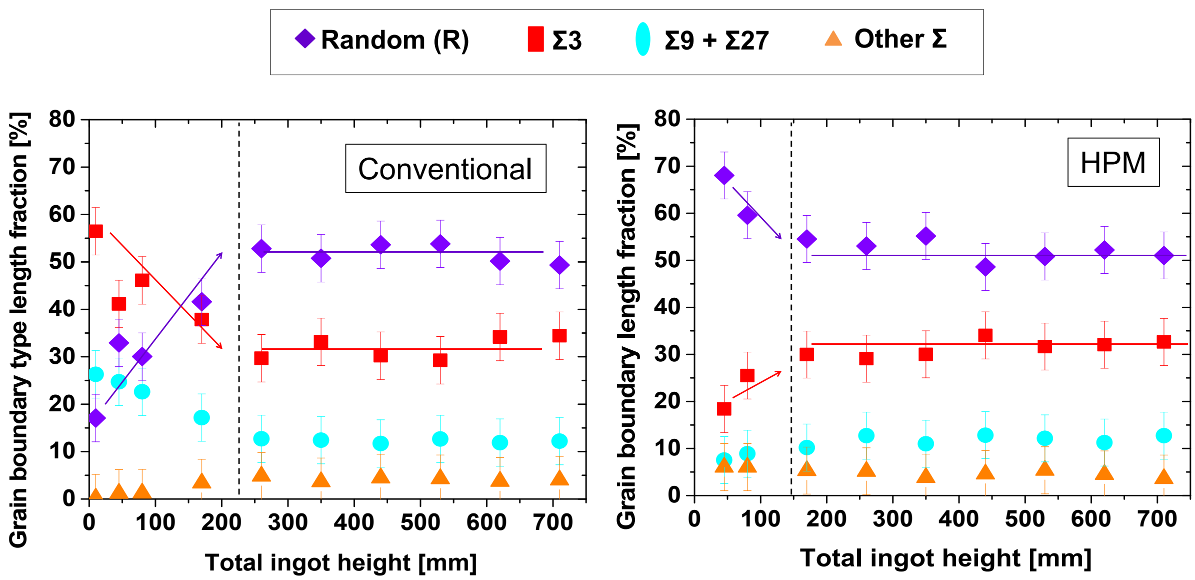


Figure 5. Grain boundary length fraction vs. total ingot height for the 710mm G1 conventional ingot (left) and the 710mm G1 HPM ingot (right). (Reprinted from Trempa et al. [11] with permission from Elsevier.)

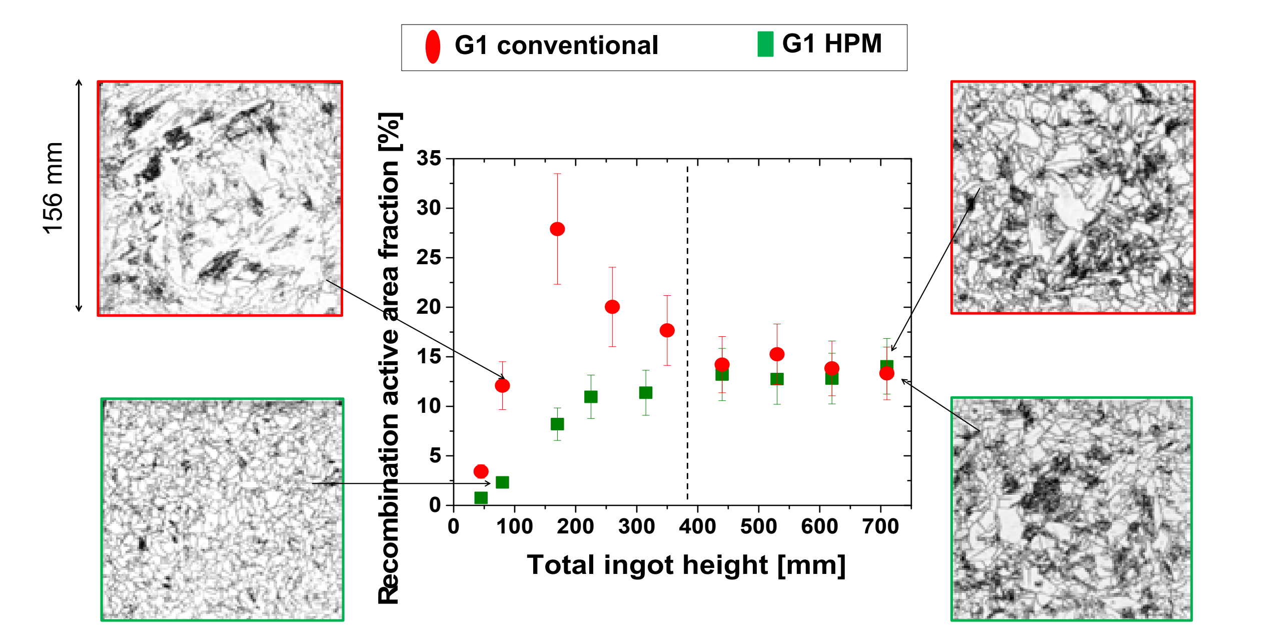


Figure 6. Recombination-active area fraction vs. total ingot height for the 710mm G1 conventional ingot (red circles) and the 710mm G1 HPM ingot (green squares). Photoluminescence (PL) images of both 710mm G1 ingots are shown for total ingot heights of 80mm (left side) and 710mm (right side). (Reprinted from Trempa et al. [11] with permission from Elsevier.)

The potential of a functional coating based on silicon dioxide (SiO_2) and silicon carbide (SiC) particles was investigated by Fraunhofer IISB/THM (the results will be reported in a forthcoming publication). This coating was applied to the bottom of G1 crucibles (220mm × 220mm) on top of the standard silicon nitride coating, either by spraying a particle–water suspension or by embedding particles in an additional wet silicon nitride layer. It was shown that, by the use of small SiO_2 particles (3µm in diameter), independently from the coating procedure, an initial grain structure with mean grain sizes of 1–4mm^2 and a random grain boundary fraction of about 60% could be obtained (see Fig. 7(a)); this is almost the same as for HPM silicon seeded on a silicon feedstock layer, shown in Fig. 1(a). The SiC-based coatings also reduce the mean grain size, but many dendrites and twins were also generated, leading to relatively low random fractions of less than 40% (Fig. 7(b)).

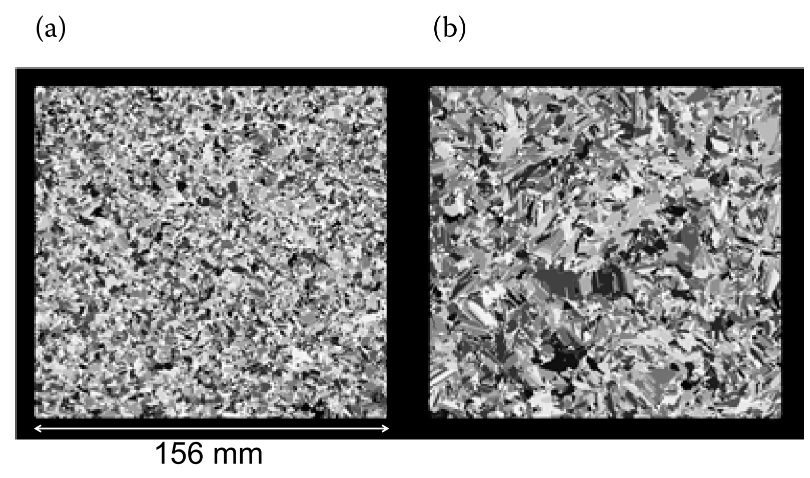


Figure 7. Grain structure images at 20mm height for two G1 mc silicon ingots grown at Fraunhofer THM by using (a) a SiO_2 coating, and (b) a SiC coating.

Another approach tested on lab-scale ingots was recently published by Babu et al. [20]; here, a mono-layer of small FBR granules (1mm in diameter) coated with a thin silicon nitride layer was used. Because of the thinness of the coating, the wavy surface morphology of the FBR layer, on which the nucleation process took place, was guaranteed. The results show that an initial random grain boundary fraction of 55% could be achieved by this method, leading to a reduced quantity of dislocation clusters in comparison to conventionally grown mc silicon.

Zhang et al. [21] have presented the first test results of the application of their method in an industrial G5 crucible with inner dimensions of 840mm × 840mm. They proposed a technique providing a SiO_2 incubation layer, thinly coated with silicon nitride, which was achieved by a mask process. The material analysis showed that the new seeding method yields a comparable grain structure, as well as very similar cell efficiencies in most parts of the ingot, to classical HPM material. The slightly higher oxygen content in the bottom region of the ingots could be the only problem with regard to solar cell properties.

Further investigations on an industrial scale were recently carried out by Buchovska et al. [22], who used silica knobs of 0.5–5mm in length as nucleation sites at the bottom of the crucible. The results show that both the dislocation content of the wafers and the cell efficiencies compare very well to those of HPM silicon seeded on silicon chips. In the side and edge regions in particular, the new HPM material has demonstrated even better properties than the classical HPM ingot because the seeding process in these regions is better optimized.

In summary, the alternative nucleation methods are on the right path to replace classical seeding on a silicon feedstock particle layer in order to reduce the production costs of high-quality HPM silicon wafers, as well as increasing the yield. However, much research still needs to be done to increase the initial random fraction to values above 60%, while ensuring the reproducibility of the results on an industrial scale, as well as their robustness, because of the use of different crystallization processes and furnaces. Additionally, the oxygen contamination problem when SiO_2-based layers are used has not yet been completely solved.

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Summary and outlook

It is concluded that HPM silicon material exhibits excellent structural and electrical properties and will thus increasingly replace conventional mc silicon over the next few years.

The main challenge for making further improvements to the material quality of HPM silicon will be to maintain a high value of the random grain boundary length fraction along the entire ingot height in order to minimize the dislocation content. It is possible that this can be achieved by optimizing the growth parameters, such as the growth rate, the temperature gradient or the phase boundary deflection. The first suggestions were offered by Wong et al. [12] and Lin et al. [17], who observed that the higher the growth rate, the faster the decrease in random grain boundary fraction with ingot height because of the increase in newly formed Σ3 twin boundaries. Lowering the growth rate could therefore be promising, even if this counteracts the economical aspect, where slow growth rates are unfavourable.

Another challenge for further increasing the material properties of HPM material relates to the absolute contamination level resulting from the feedstock, the crucible, the coating and the furnace components.

Acknowledgements

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