Casting Technologies for Solar Silicon Wafers: Block Casting and Ribbon-Growth-on Substrate

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Abstract. Multi-crystalline silicon solar wafer are the working horses of the rapidly developing photovoltaic market. The availability and cost efficiency but, even more important, the improved wafer quality and the understanding how to process multi-crystalline silicon wafers into highly efficient solar cells are important factors in this development. In this paper multi-crystalline silicon wafer manufacturing technologies both in industrial production as well as under development are outlined. Important wafer characteristics such as oxygen-, carbon and metallic impurities are described and experimental links to solar cell efficiency are exemplary demonstrated.

Introduction

In the last decade the photovoltaic solar energy market saw an explosive growth. Growth rates well above the long-term average of 15% could be realized and both politicians and PV module producers foresee growth scenarios in excess of 25% in the next years (up to 2010). These extraordinary growth rates are partially the result of governmental incentives such as the German 100.000 roof program, the Japanese 75.000 roof program and the one million-roof program in the US. Similar programs will most probably emerge in other countries of the European Union, to meet the ambitious target of the European Commission of 3 GWp PV installed in 2010.

![Figure 1: World photovoltaic module shipments per technology. [1]](image)

The potential of Silicon wafer based solar cells is demonstrated by its still increasing market share of more than 90% (figure 1). Cost efficiency, stability and reliability of the silicon wafer based solar modules resulted in a superior market leadership of this technology. Nevertheless this also means that, in order for photovoltaics to become more cost efficient, the complete production chain from solar grade silicon to wafers, solar cells and modules has to be improved.

In the following we will focus on the possibilities and challenges of multi-crystalline silicon wafer manufacturing as one of the key technologies to lower PV module costs. Crystalline silicon wafers not only contribute to 35% - 45% of the total module manufacturing costs, but are also an
important factor that determines solar cell respectively solar module efficiency. Thus both wafer manufacturing costs as also wafer quality are the drivers for further development of existing technologies and the benchmark for the introduction of new manufacturing methods.

**Challenges in multi-crystalline silicon wafer manufacturing**

The strong need in photovoltaics to minimize the manufacturing costs per solar electricity generation capacity (W_p), drives multi-crystalline silicon wafer manufacturers to improve the economical optimum between production efficiency and product quality. Although directionally solidified ingots [2] allowing for large area solar cell efficiency up to 18.3% [3] in a high-efficiency process are demonstrated, the commercially available wafers typically result in solar cell efficiencies around 15% in industrial solar cell processes.

The necessity to improve on wafer quality and manufacturing costs results in an ongoing effort to further develop production technology and machines as well as crystallization- and solar cell processes. With respect to crystallization- and solar cell process, the relation between silicon wafer material characteristics and solar cell efficiency is an area of ongoing research. Although the knowledge on silicon wafers developed by the semiconductor industry is inherited, the complex interaction between impurities, crystal structure and their behavior during the solar cell process as well as the large variation between solar cell processes makes it impossible to predict solar cell efficiencies from wafer parameters. This resulted in the situation that there is no generally accepted set of wafer parameters available that defines the quality of a silicon wafer completely [4]. The suitability of a wafer for a solar cell process cannot be described but must empirically be tested in the cell process. With changes in either the material or the solar cell process these links have to be re-established.

Although the detailed mechanisms that control the relation between multi-crystalline silicon wafer characteristics and solar cell efficiency are very complex, there are guidelines for wafer quality with respect to oxygen, carbon, metallic impurities and crystal structures that can be used in the improvement of existing and the development of new silicon wafer materials.

In the following the development of multi-crystalline silicon wafer manufacturing technology will be outlined for two examples: the generic silicon block crystallization methods and the ribbon-growth-on-substrate (RGS) wafer casting as a promising representative of silicon ribbon manufacturing. Thereafter an overview on the relation between wafer characteristics and solar cell efficiency will be presented.

**Block Casting Multi-Crystalline Silicon Wafer Manufacturing**

**Outline Technology.** Historically, most of the multi-crystalline silicon wafers were and still are produced by crystallization of liquid silicon in the form of a block, which is then cut into wafers (see figure 2). Important milestones in the development of these technologies were the improved control of the planarity of the liquid-solid interface, which resulted in reduced stress of the silicon block. Also improvement of refractory material for the crucibles and the application of crucible coatings clearly enhanced wafer quality and reduced contamination from crucible walls.

As the crucible normally breaks during block cool down, increasing wafer production per crucible is of major importance. Separating melting from solidification units, as was applied in block-casting, improves the effective use of both melting crucible as well as solidification crucible (complete filling by liquid). The separation of these steps also allows enhanced control of melted silicon and solidification environment. Replenishment of the continuous melting unit could in principle enhance the cost effectiveness of block-casting even further.

**Characteristics of block-cast multi-crystalline silicon wafers.** Inherent to all forms of silicon block crystallization is the inhomogeneous distribution of the wafer characteristics due to the batch-wise process with changing process conditions. One of the major effects is the segregation of
impurities due to the higher solubility of most materials in the liquid silicon phase. The positive effect is a cleaning of the silicon material by segregation of impurities into the top of the block. The disadvantage is the changing oxygen, carbon and doping concentration in the wafers, which depend on the height of the wafers in the block. Additional contamination from the crucible also results in different wafer characteristics in the areas of the wafer being in close contact to the crucible walls (bottom, sides). This results in a location dependent behavior of the silicon wafers, which leads to a broadening of the solar cell efficiency distribution, e.g. a variation in short circuit current of 5-10% in dependence on the position of the wafer in a block [5].

Figure 2: The principles of Bridgman, Heat Exchange Method (HEM) and Block-Casting as technologies to solidify a multi-crystalline silicon block.

Ribbon-Growth-on-Substrate (RGS) Multi-Crystalline Silicon Wafer Manufacturing

Figure 3: Principle of the RGS ribbon growth process. The relatively cold substrate extracts the crystallization heat from the liquid silicon in the casting frame. This causes the growth of a silicon ribbon in contact with the substrate. By transporting the substrate from the casting zone into the cooling down section, crystal growth is stopped and the silicon ribbon can be removed.

Outline Technology. The ribbon-growth on substrate (RGS) wafer casting technology is a silicon wafer manufacturing method, where liquid silicon is poured in a casting frame under which a colder substrate is moving, which causes the growth of a thin silicon layer (see principle of the RGS technology in figure 3). This technology was developed by Bayer AG [6] throughout the 80’s and 90’s and is now further developed by a Dutch consortium of ECN and S’Energy.

The challenges in the development of the RGS technology are the improvement of the material quality in order to become a cost competitive material and the realization of a reliable production machine.

Characteristics of RGS multi-crystalline silicon wafers. From a principle point of view one of the major advantages of the RGS technology is that it is a continuously operating process opposite to the batch-wise block-casting. This should result in homogeneous wafer properties. The challenges for the RGS material are the speed of the process (1 wafer/second) resulting in rapid
thermal profiles and fast crystal growth (typically 300 µm/s) [7] and the close contact of the liquid and solid silicon to refractory materials (melting crucible, casting frame and substrates). Therefore improvements in process control and materials are very important for RGS wafer manufacturing and the main reason for the progress in material quality and related to it solar cell efficiency.

Record solar cell efficiencies achieved with RGS wafer-based solar cells show a remarkable trend over the last 10 years, which was the result of a good co-operation between wafer manufacturer (Bayer AG), solar cell process developers as well as basic silicon material research and development (HEXSi, KoSi, RGSells projects). This led to an increased understanding of the material characteristic and the behavior of the RGS wafer in a solar cell process. The consequences of this development can be seen by the steady efficiency increase as shown in figure 4. Latest record solar cell efficiency reached at the University of Konstanz are 12.8% [11].

In the future, it is expected that this development can be continued at the same or even increased speed. In order to do so, the next step was to reduce the high oxygen content of the wafers. This limits at the moment the hydrogen diffusion from a SiN coating and thus the efficiency of an RGS solar cell in an industrial-type cell process. Further efficiency influencing factors are the formation of oxygen related recombination centers (thermal and new donors) [8, 9, 10]. In the past RGS wafers with high oxygen content were annealed in order to form larger oxygen precipitates and to avoid the formation of oxygen related donor complexes in the solar cell process. Recent machine improvements resulted in a low oxygen concentration RGS wafer ($5 \times 10^{17}$ cm$^{-3}$), which made it possible to reach high open-circuit voltages in a solar cell process without pre-annealing [11].

**Figure 4:** Record RGS solar cell efficiencies. Earliest results were from Telefunken and its successor ASE. In later projects the Fraunhofer Institute for Solar Energy Systems (FhG-ISE) and the University of Konstanz (UKN) held the efficiency records. [12].

**RGS prototype machine development.** One of the major challenges of the RGS technology is the development of a new RGS wafer-manufacturing machine. The design is based upon the following ideas:

- The machine should translate the batch-wise process into a continuous operation.
- The machine should maintain operation even in the case of processing problems of limited duration. For this purpose, silicon melt control, replacement of substrates on the fly and many other safety mechanisms will be included.
- In contrast to silicon ingot growth or CZ crystal pulling, RGS wafer production involves mechanical movement with high precision at high temperatures. The design was made in a way that the mechanical movement is not in contradiction with the demand of minimum contamination of the hot silicon by particles from metallic parts of the machine.
Although silicon crystal pulling machines are state-of-the-art technology in the semiconductor and solar industry, the intended RGS machine will push the limits. The continuous silicon melt rate will be a factor 2 higher than the melting rate achieved during CZ-growth melt replenishment. Substrate materials have to be developed and optimized that can withstand the repetitive contact with liquid silicon and the temperature cycles in the machine for a long time. Mechanical and thermal stress of the wafers and machine parts has to be minimized during operation at high speed under large temperature variations.

All these conditions combined with the experience of the consortium led to a machine design (cross section see figure 5), which will be realized in the near future.

Figure 5: Cross section from the design of the continuously operating RGS machine. In the lower part of the vacuum vessel the mechanical drive is enclosed, while in the upper section the furnace and casting sections are situated. Wafer stacker and wafer load lock is shown on the right. The diameter of the machine will be about 3.5 m.

Multi-Crystalline Silicon Wafer Characteristics and Solar Cell Efficiency

In the following, wafer characteristics for multi-crystalline silicon wafers are shown and their relation with minority carrier lifetime respectively solar cell efficiency is outlined. The most important wafer characteristics are oxygen and carbon content, metallic impurities (e.g. iron) and crystal imperfections, dislocations and grain boundaries.

**Oxygen and Carbon.** The solubility limits from literature for oxygen and carbon in crystalline silicon at the melting point are $2.6 \cdot 10^{18} \text{ cm}^{-3}$ (52 ppma) and $3.5 \cdot 10^{17} \text{ cm}^{-3}$ (7 ppma), respectively [13]. While the concentration of oxygen can usually be kept far below its limit in cast material, the concentration of substitutional carbon is often found to be much higher. This is attributed to strain release in the presence of interaction with oxygen [14], but also lattice defects and non-equilibrium effects during crystallisation may be expected to have an effect.

Shown in figure 6 are typical concentration profiles of oxygen and carbon found in a variety of multi-crystalline ingots, produced by casting, Bridgman, and HEM techniques.
The source of carbon in ingots is both carbon present as contaminant in the feedstock as well as carbon monoxide from the furnace environment, which dissolves into the liquid silicon. Probably the latter is by far the most important. The source of oxygen contamination is mostly dissolution of the quartz crucible into the silicon melt, which mainly influences silicon material at the bottom of the ingot.

In general cast ingots can have lower oxygen concentrations than Bridgman or HEM ingots, due to different gas ambient and better silicon volume to crucible surface ratio. However, it was also found that block casting material shows higher oxygen concentrations than HEM and Bridgman at the bottom of the ingot and reaches lower values in the middle and top part (figure 6). It is likely that the coating of the quartz crucible plays an important role in preventing quartz dissolution into the silicon. Damage of the coating (e.g., by sharp edges of the feedstock chunks) can therefore strongly affect the oxygen concentration.

While in experiments on the materials of figure 6, carbon concentrations as high as 18 ppma were not found to be noticeably detrimental to minority carrier lifetime or solar cell efficiency, the high oxygen concentrations are clearly disadvantageous. This could be due to precipitation of oxygen, possibly together with other (metallic) contaminants or, the formation of new or thermal donors during heat treatments, which can all lead to recombination-active defects. It was found that hydrogen-passivation has a stronger beneficial effect on these oxygen-related defects than elsewhere in the ingots [5, 15].

Recently, a class of shunts in multi-crystalline silicon solar cells has been related to transmission electron microscopy images of carbon precipitates [16]. It is not published, however, under which conditions and at which carbon concentrations in the silicon, these precipitates developed.

For silicon wafers of lower initial quality, such as silicon films or ribbons, hydrogen passivation of defects during solar cell processing plays an important role in reaching competitive efficiencies. Both theoretical models [9] as well as experimental evidence [8] showed a relation between oxygen content and hydrogen diffusion speed and passivation potential. It was found that hydrogen in low oxygen EFG was diffusing much faster than in high oxygen RGS material.

At extremely high oxygen contents, such as in earlier RGS material, the formation of new donors during normal solar cell process steps and the low hydrogen diffusivity limited the solar cell efficiency. In order reduce the concentration of recombination active oxygen related defects, RGS material was therefore often annealed at high temperatures in order to form extended oxygen precipitates, which do not dissolve in a solar cell process. Recent changes in the RGS process reduced the oxygen content to values between $5 \times 10^{17}$ cm$^{-3}$ and $1 \times 10^{18}$ cm$^{-3}$. This allowed the use of RGS wafers in a standard solar cell process without oxygen precipitation annealing.

**Metallic impurities.** Metallic impurities are always present in cast silicon material. They originate from contaminants in the feedstock and in the quartz crucible and its coating. Present-day ingots are
partly produced from very clean ("semi-prime") silicon, produced specifically in reactors which are also used for electronic grade silicon production. This presently accounts for more than 50% of the feedstock for cast silicon. If handled properly, this material is very clean and hardly adds impurities to the silicon melt. The other part of feedstock used today consists of rejected and recycled silicon from the microelectronics industry, such as tops and tails from Czochralsky ingots and pot-scrap. These will contain higher levels of impurities. The most important source of contaminated feedstock is however, likely, the edges of ingots which are cut-off before wafering and recycled as feedstock for subsequent ingots. These have been contaminated by impurities diffusing from the quartz crucible and its coating into the silicon ingot during cool-down.

One of the most important recombination centers in cast material is the FeB pair, which develops from pairing of interstitial Fe impurities with a B dopant atom. FeB concentrations can be conveniently derived from carrier lifetime measurements before and after optically induced FeB pair dissociation. This is described in detail in ref [17].

Figure 7 shows FeB concentrations measured for a number of ingots. Figure 8 shows a detail for the bottom 100 mm of one particular ingot. An increased FeB concentration is found in the bottom and side edges of ingots. This Fe clearly has diffused in after solidification of the ingot [18]. Its source must be the crucible or crucible coating. This FeB is responsible for a very significant lifetime degradation: For example, a concentration of $2 \times 10^{12}$ cm$^{-3}$ FeB pairs will reduce the lifetime to 10 μs (at an non-equilibrium carrier density of $10^{15}$ cm$^{-3}$).

![Figure 7: FeB concentration in dependence of the wafer position in multi-crystalline silicon ingots.](image1)

![Figure 8: FeB and oxygen concentrations together with Short circuit current value variation of solar cells processed with and without hydrogen passivation from a SiN coating are presented in relation to FeB and oxygen concentration. The wafers are from the bottom of an ingot with high oxygen concentration.](image2)
Figure 9 shows the minority carrier lifetime and FeB profiles of one particular column. It is remarkable how well the lifetime follows the (inverse) trend of the FeB. There are potentially other impurities present in the crucible or coating material. However, these will generally have diffusivities very different from Fe, and will therefore diffuse to a different depth than the Fe during the cool-down of the ingot. The fact that the lifetime profile corresponds well with the FeB profile is an indication that Fe is the major detrimental impurity in ingots, when they are grown from high-purity feedstock. Indeed, below it will also be shown that when theoretically subtracting the effect of FeB, generally a high to very high lifetime results.

Because the impurities are concentrated in the liquid silicon as solidification progresses, the concentration of FeB increases towards the top of the ingot. The concentrated impurities precipitate in the final stage of solidification, in the very top of the ingot. During the cool-down, the impurities can diffuse back from this precipitated layer into the ingot. This is responsible for the peak in FeB contamination in the top of the ingots in Figure 7.

Dislocations in multi-crystalline silicon wafers. As a rule of thumb it is generally thought that dislocation densities below $10^5$ cm$^{-2}$ are acceptable for solar cells. This is supported by results from experiments done on float-zone silicon wafers with varying dislocation densities. Below a dislocation density of $10^5$ cm$^{-2}$, minority carrier lifetime was high and dislocation density independent. Between $10^5$ cm$^{-2}$ and $10^6$ cm$^{-2}$ there is a transition region, while above a dislocation density of $10^6$ cm$^{-2}$ minority carrier lifetime drops rapidly [19, 20].

In block-cast multi-crystalline material dislocation density is typically in the range of or below $10^5$ cm$^{-2}$. However areas with low minority carrier lifetimes and very high dislocation densities are also found. These areas normally occur in neighboring wafers at identical locations, which results in the picture that they grow with the solid liquid interface vertically through the silicon block. As these areas are thought to be the quality-limiting factor for good multi-crystalline material, generation of highly dislocation rich areas and the further growth throughout the ingot are of major interest [21].

Dislocations also play an important role for RGS wafers. At the moment the general model is that dislocations in RGS wafers are generated by thermal or mechanical stress during the crystallization phase and the initial wafer cool-down. Dislocation densities between $10^5$ cm$^{-2}$ and $10^8$ cm$^{-2}$ are found in RGS wafers. Recent experiments indicates that it might be possible to control dislocation densities at an acceptable level, however more statistical evidence and analysis is needed.
Grain size and grain boundary recombination. During the development of the multi-crystalline silicon wafer technology, modelling work was done with respect to solar cell efficiency and grain size. In [22] grain boundaries were described by a barrier height and a space charge region around the grains. Depending on the parameters, grain boundaries are more or less recombination active, and also change their behaviour with injection level (typically recombination velocity decreases with increasing injection). The problem however is that there is insufficient knowledge about the grain boundaries in existing materials to describe real material completely with theoretical models. In directionally solidified and block-cast multi-crystalline silicon wafers typical grain sizes are large enough that grain boundary recombination is of no significant influence on solar cell efficiency. However, with the development of high-speed wafer production such as the ribbon-growth-on-substrate method or Astropower's Silicon Film, grain sizes become smaller and grain boundary recombination might become the ultimate efficiency limit to these technologies.

Summary

As was demonstrated, there is a strong ongoing drive to improve crystalline silicon wafer manufacturing technologies with respect to manufacturing costs and quality. With respect to manufacturing costs, reducing the silicon loss, wear part costs and machine throughput are the main challenges. With respect to material quality, an improved understanding of the relation between wafer parameters and solar cell efficiency allows to optimize the combination of wafer and solar cell process with respect to cost per Wp.

With respect to the development of sawing based multi-crystalline silicon wafer manufacturing technology, the development from Bridgman technology, via the planarization of the solidification front to the separation of melting and crystallization process in the block casting machine demonstrates the development from a relatively low throughput, static process environment to a flexible, high throughput wafer manufacturing technology. By enlarging melting- and solidification volumes there is a large potential for material improvements and cost reduction.

From this point a logical step in the direction of the optimum silicon wafer manufacturing technology would be to avoid any silicon material losses by the direct production of silicon wafers, without compromising high machine throughput, flexible process control and wafer quality. Ribbon-growth-on-substrate silicon wafer casting has the potential for all these characteristics, however machine and material development have to prove that the promises can be realized in relation to the moving target of directionally solidified and cut wafer technology.

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