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FZ and CZ crystal growth: Cost driving factors and new perspectives

Expert Opinion

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In the field of monosilicon crystal growth, the Czochralski (CZ) as well as the floating zone (FZ) method have grown to a mature technology over the last 60 years and, until today, the costs have been continuously reduced. The cost driving factors for CZ and FZ are reviewed with respect to further potential improvements. Generally, the cost for the feedstock material is still dominanting the cost of ownership for both methods despite the dramtic decrease of the poly silicon price over the last years. This is particularly true for FZ where notably more than 50% of the production costs are related to the polysilicon feed rods which are much more expensive as compared to the chunk polysilicon as used for CZ. As a consequence, the FZ method is only used for applications where silicon crystals with very low oxygen concentration are required. Due to the strong influence of the feedstock material on cost, the main focus of the

development work has been on the increase of crystal yield and the identification of factors impacting the yield. However, for most electronic and, in particular, for solar application, the crystal yield has reached a level where significant improvements cannot be expected anymore. With the potential change from p- to n-type silicon in the solar industry, previously developed techniques, like continuously recharged CZ, which were finally stopped for electronic applications, are reconsidered and will be discussed with respect to their future potential. Special attention will be given to the advantages and disadvantages of the FZ method. It will be shown that most of the current drawbacks of FZ can be remedied by a new technique which avoids the use of expensive polysilicon feed rods and enables the FZ method to grow dislocation free crystals with inexpensive silicon granules.

1 Introduction Silicon crystal growth technology has rapidly advanced during the past decades. The main driving forces have been the need to increase the wafer diameter step by step to follow the technological roadmap of the semiconductor industry, on one hand, and, at the same time, to reduce the cost of ownership (CoO) of the growth processes, on the other hand. While, in the past, the consumption of silicon was dominated by electronic applications, the photovoltaic industry has meanwhile surpassed the electronic device manufacturers as the main consumer of silicon and substantial further growth is expected in this field for the next decade. This shift of silicon usage has forced the silicon crystal suppliers to even expedite their cost reduction programs. Due to the strong trend to higher cell efficiencies in the solar industry, high quality base materials, i.e. dislocation free single crystalline silicon, has become more attractive again as they offer an increase of cell efficiency by ca. 2% (absolute) as compared to multicrystalline silicon. However, the high quality silicon

must come at a lower price in the near future to meet the cost reduction roadmap of the PV industry.

Today, two different techniques, i.e. the Czochralski (CZ) and the floating zone (FZ) growth method, are well established for the growth of dislocation free silicon crystals. While the CZ method accounts for more than 95% of the total monocrystalline silicon production, the FZ technique is commercially used for niche products, only, e.g. high power devices. This huge difference in market acceptance is attributed to at least three major drawbacks of the FZ growth technique. Firstly, the low oxygen content of FZ material prevents any internal gettering capability of the wafer and, in addition, makes the wafer more susceptible to slippage during high temperature process steps. Secondly, the cost of ownership is higher for FZ as will be shown in Section 4. Thirdly, it has been much easier to follow the trend to larger crystal diameters with the CZ method than with the FZ technology. However, the W_p-price of a solar panel does not depend as much on the wafer size as compared to the chip

price in the semiconductor industry. Secondly, the relatively high oxygen content of CZ wafers degrades the efficiencies of p-type based cells over time due to light induced B-O complex formation [1–3]. Thus, for example, high efficiency solar cells manufactured on FZ wafers usually exhibit 1–2% (absolute) higher efficiencies as those made on CZ wafers [4]. This latter advantage in conjunction with the fact that the PV industry will stay at 200 mm as the largest wafer diameter for the time being has recently drawn more attention to the FZ technology again [5]. However, the high production costs of FZ crystals have been prohibitive for solar applications, so far.

In this paper, we first will briefly review the CZ and FZ processes and compare them with their respective advantages and drawbacks. Finally, a new method is described as a possible perspective which has been proposed earlier [6] and which combines the qualitative advantages of FZ with the potential of competitive production costs for solar applications.

2 Standard CZ technology On the way to a progressively higher economy, the biggest challenge has been the improvement of the good-for-order yield. This includes not only losses due to structure loss, but also considers useless crystal portions that do not meet the material requirements of the customer. Yield has the by far dominant impact on the cost of ownership of crystal growth processes as the by far largest fraction of the cost of ownership is related to the cost of the feedstock material. All measures, even if they are costly at first sight, usually pay off, if they result in a higher yield. This is demonstrated in Fig. 1 which compares the costs per kg of good-for-order material for several 300 mm CZ processes with different hot zones, charge sizes and puller types as a function of yield. It can clearly be seen that the various cost–yield curves of the respective configurations are relatively close to each other.
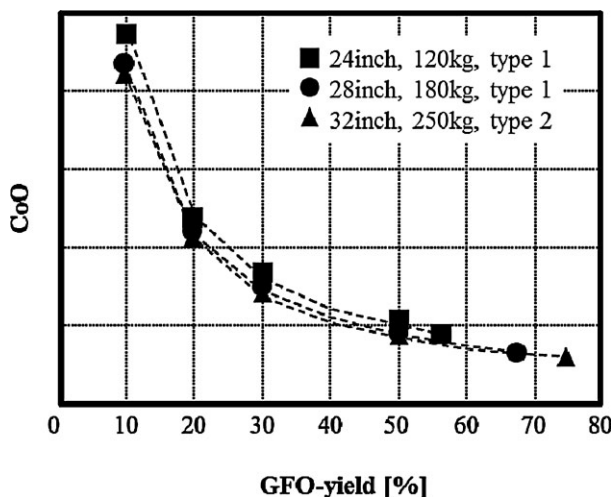

Figure 1 Comparison of cost of ownership (CoO) for 300 mm CZ processes as a function of good for order (GFO) yield for various crucible and charge sizes as well as puller types (after [7]).

Only at rather high yields, when the curves flatten out, costly measures which increase yield may not result in a cost advantage. Although, hot zone type and charge size in Fig. 1 are not representative for today's 300 mm processes, the dependency of CoO on the GFO yield is not notably changed by further increased hot zones and charge sizes. Many development activities during the past decades were focused on the identification of the various root causes for structure loss and the respective remedies. A huge challenge has also been the increase of the good-for-order yield of very sophisticated processes like the growth of so called "defect free" silicon, which suffered from significant out-of-spec losses when this material was originally introduced in the market.

Factors which impact the yield of dislocation free ingots:
1. Quality of silica crucibles
The continuous improvement of the crucible quality has been of great importance to achieve further progress in the economy of CZ processes. The chemically very aggressive silicon melt does not only slowly dissolve the inner surface of the silica crucible, but the chemical attack also results in the formation of crystobalite islands on the inner surface, which grow in size over time and finally form a more or less porous cristobalite layer [8]. Due to pitting corrosion, this cristobalite layer becomes a source of particles which are released into the melt and, thus, can drift to the growth interface and stop dislocation free growth. Another corrosion effect which eventually results in the release of particles into the melt, is the existence of tiny bubbles below and near the inner crucible surface [9]. Today, most high quality crucibles are equipped with an additional lining of the inner crucible surface by a synthetic silica layer [10]. This layer is very clean and dense and contains nearly no bubbles. However, it substantially increases the manufacturing cost of such crucibles and, consequently, the yield improvement must be notable in order to justify the higher crucible costs. In particular, large diameter growth processes like 300 mm which have a rather high thermal budget achieve higher yields with these crucibles.
2. Quality of poly silicon
The quality of poly silicon can have a severe impact on the generation of dislocations during growth. However, the actual quality parameters and mechanisms are less known as compared to the crucible effects. The general belief is that polysilicon may contain particles like silicon nitride or silicon carbide which dissolve very slowly in the silicon melt and, hence, they live long enough to drift to the growth interface. It also seems that a rough, popcorn like surface of the polysilicon chunks has a negative effect. This is probably related to the difficulty to properly clean the surface of such chunks by chemical treatments. The handling and treatment of these chunks may even result in the deposition of particles in deep grooves of the rough surface. The cleanliness of the chunk surface and, thus, a low level of impurities on the chunk surface is important for the avoidance of oxidation induced stacking faults and excessive oxygen precipitation in the growing crystal.

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3. Particles in the gas ambient

There are several sources in a hot zone which can generate particles in the gas ambient. One source is related to corroded graphite parts on which a SiC layer has formed. Due to the difference in thermal expansion, the SiC tends to flake off. Another source are SiO condensates which are detached from surfaces inside the growth chamber by turbulences or sudden changes in the gas flow. If the particles adhere to the melt surface in close proximity to the growth interface, they may be incorporated before they dissolve. In general, the particle issue is well handled by an appropriate design and management of the gas flow and a careful maintenance of the hot zone and vessel.

4. Temperature fluctuations

Abrupt temperature changes significantly increase the risk of structure loss. The origin are often instabilities in the melt flow pattern. Owing to the steadily decreasing melt volume, the melt flow pattern can suddenly switch to another flow structure which, in turn, can drastically modify the temperature field in the melt. A typical example for the generation of sudden melt flow instabilities is the application of vertical magnetic fields to the growth process. Consequently, other magnetic fields like the horizontal or cusp field are used.

It is also suspected that hot plumes can form in the melt at the crucible bottom [11, 12]. When they get large enough they drift upwards to the growth interface and stop dislocation free growth. The formation of such plumes is probably strongly dependent on the hot zone design.

5. Process parameters

The proper control of the crystal diameter requires a relatively complicated concept with at least two levels. The short term loop controls the diameter by variations of the pull rate, while the long term loop uses the heater power as a control parameter. In particular, the set point curve and control of the heater power has to match with the desired pull rate scheme as a function of crystal length. A particular critical process phase in this regard is the shoulder growth and rollover to the body growth phase. During this period, large changes in the deflection of the growth interface as well as in the pull rate and power occur, which must be well balanced in order to avoid oscillations which, otherwise, can grow out of control. A real challenge is the growth of so called defect free silicon which requires the control of V/G (V = pull rate, G = axial temperature gradient at the growth interface) within very small tolerances. This can only be achieved by advanced control systems and growth processes where the setpoint curves for the pull rate and the heater power precisely match. In addition, special measures have to be taken to homogenize G in radial direction as, in standard growth processes, $G(r)$ is strongly increasing towards the crystal periphery.

6. Out of spec losses

The semiconductor industry usually specifies rather tight tolerances for material parameters. Tolerances for dopant concentrations of 10–30% are common. The most important parameters are resistivity, oxygen concentration and grown-in oxygen precipitates, size/density distribution of intrinsic point defect aggregates and oxidation induced stacking faults. The real challenge is to find a suitable compromise for the growth parameters as, with the exception of resistivity, all other material parameters depend on the same process parameters, but their dependencies are quite different and often contrary to eachother. Owing to the problematic shoulder and rollover phase, the first few centimeters of body growth are needed for stabilization. They usually have to be scrapped as, at least, one material parameter, e.g. oxygen concentration, is out of spec. A real challenge can be the above mentioned growth of defect free silicon, where the out of spec losses can be substantial, if a matured process capability is not yet available. For solar applications, the situation is much more relaxed, as nearly all material parameter specifications are comparatively wide.

7. Other losses

At the end of the body growth phase, a sufficient melt volume is needed to allow for a stable growth of the final tail end cone. This cone avoids the generation of dislocations which, otherwise, would propagate back into the dislocation free grown body part rendering this section partially useless. Hence, a residual melt volume always has to be left in the crucible and must be scrapped. Unavoidable losses are also the seed and tail end cones. These losses obviously depend on the diameter/length ratio of the grown crystal. Typical values are in the range of 20–40% with 450 mm crystals representing the higher value. Additional losses occur by grinding the as-grown crystals to a precise diameter and cylindrical shape for further processing like sawing, edge rounding, etc. As the losses are dependent on the exact diameter control during the growth process, they can be substantial for sophisticated processes like the growth of "defect free" silicon. Further losses are generated by test slugs which are cut out of the crystal to characterize the as-grown ingot with respect to oxygen and carbon content, oxygen precipitation behavior, OSF's, minority carrier lifetime and intrinsic point defect aggregates (COP's, Lpits). Depending on the specification, the number of test slugs can have a notable effect on the final yield. It has become common to recycle most of the scrapped silicon for reuse as feedstock material.

Factors which impact cycle time (productivity):

1. Pull rate

The first step to higher pull rates was the introduction of heat shields in the 70ies of the last century. Since then, the design of the heat shield has been subject to numerous modifications with the goal to optimize pull rate and the axial temperature field of the growing crystal. The latter has a strong effect on the defect behavior and, thus, material quality of the grown ingot. A further substantial increase of the pull rate was obtained by water cooled heat shields in the 90ies. The challenge of this technology has been the safty issue as a contact of the melt with a water bearing duct can result in an explosive reaction of hydrogen and oxygen. Today, water cooled heat shields are used in mass production and severe malfunctions have not been reported up to now.

They allow for pull rates which are close to those of FZ grown crystals. For water cooled heat shields, the limit is determined by the built up of thermal stress in the growing crystal which must not exceed the critical shear stress of silicon [13]. The higher the pull rate and the larger the crystal diameter, the higher the thermal stress. Thus, the pull rate must be decreased for larger crystal diameter. For certain growth processes, the pull rate may also be limited by a destabilization of the growth process which manifests itself by a loss of the cylindrical shape of the growing crystal. As more latent heat is released at higher pull rate, the lateral temperature gradient on the melt surface near the triple point can decrease below a critical value with the consequence of a deformation of the cylindrical shape [14]. The pull rate only impacts the body growth of the crystal and, thus, particularly influences the cycle time of long crystals.

2. Thermal budget

The thermal budget of CZ growth process is not only determined by the crucible and silicon charge size, but also by the graphite hot zone which accommodates the silicon charge and the silica crucible. The hot zone is relatively large and its size obviously depends on crystal diameter. A larger diameter entails a larger charge size and crucible and, hence, the size of the hot zone must be increased accordingly. Besides the pull rate, the thermal budget of the hotzone has the biggest impact on cycle time, as it has a strong influence on the duration of the warm-up, melt down, stabilization and, in particular, the cool down phase of the process. For large diameter processes like 300 mm, these process phases can add up to more than one day and, in case of 450 mm, they reach up to several days. If relatively short crystals are grown, these process phases even dominate the cycle time. The thermal budget can be reduced by using thinner CFC material instead of graphite. However, CFC is much more expensive than graphite. It is therefore not always clear, if there is a real trade-off in using expensive CFC. Usually, a compromise is made by choosing only certain hot zone parts to be manufactured by CFC.

3. Other process times

A substantial part of the cycle time is related to operative activities like the insertion of the charged crucible into the hot zone, the evacuation of the vessel after process start, the removal of the grown crystal and the silica crucible with the residual melt as well as the cleaning of the hot zone and vessel at the end of process. The latter is necessary in order to remove SiO deposits which stick to the surface of various hot zone parts and the upper vessel section. The by far major fraction of evaporated SiO is collected in certain areas or containers where it must be removed for disposal after every run. These process times also increase with crystal diameter and hot zone size, but the changes are not as pronounced as with pull rate and thermal budget related times.

If one breaks down the CZ cost of ownership into the various contributions (Fig. 2), it is clearly seen that the largest impact stems from the cost for the feedstock material followed by the cost for the silica crucibles. In particular, 300 mm and 450 mm growth processes require rather
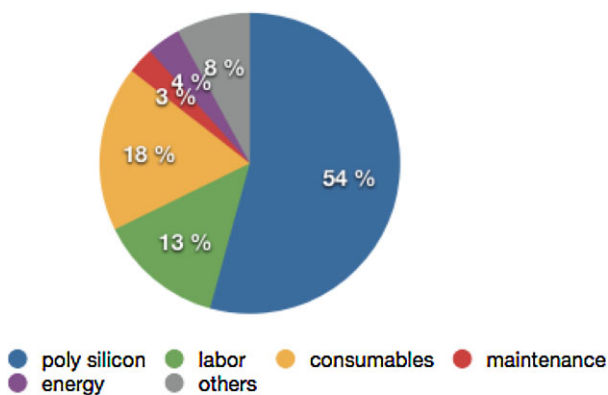

Figure 2 Typical cost breakdown of a CZ process.

expensive crucibles with long lifetimes owing to their long cycle times. The graphite parts for a complete hot zone is a substantial investment and reaches up to more than 100 000 Euros for large diameter processes. However, only those parts which are exposed to excessive SiO vapor during the process time have to be replaced after a certain number of runs and, thus, add to operating costs. The major part of the hot zone has a lifetime of many years and can therefore often be considered as part of the initial investment. The initial investment which is mainly the puller is often the third largest contribution to the cost of ownership. The actual reason for this can be attributed to the high level of process automization. Today, an operator can service many pullers which reduces the cost for personal, accordingly. Timewise, operators are mainly needed for handling the crystals and crucibles and the maintance and cleaning of the hot zones. Energy and argon consumption often have a minor impact in comparison to the above mentioned cost factors. However, the prices for energy and argon can vary considerably depending on the location of a fab which may change the ranking of the contributions.

The CZ method has matured to a standard technology which is highly developed. Meanwhile, the crystal yield is rather close to its theoretical limit, in particular, for growth processes with solar specifications. In the latter case, the specification is not only rather wide, but it is also produced in large quantities. Consequently, statistical process control can effectively be used to optimize yields. Moreover, since the introduction of water cooled heat shields, the potential for a further substantial reduction of the cycle time is limited. The same applies for the costs of consumables and the CZ pullers. Thus, it is not expected that the cost of ownership of CZ grown crystals can be significantly lowered in the near future.

Finally, it should be mentioned that the costs per kg of grown ingot strongly increase for larger diameters like 300 mm and, in particular, 450 mm. The main reason is the significantly higher cycle time as these processes already severely suffer from the limitations of the growth rate and the large thermal budget of the process and hot zone,

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respectively [15]. In addition, the occurence of structure loss has dramatic consequences. As nearly a length of one diameter of already dislocation free grown material has to be scrapped upon structure loss – which means almost half a meter in case of 450 mm – the yield is strongly lowered with increasing diameter unless the process is so perfect that the likelyhood of a dislocation is nearly zero. However, in reality, the generation of dislocations during growth cannot be completely avoided. In addition, the ratio of diameter to crystal lenght which also impacts the yield becomes more and more unfavorable as it is technologically very challenging to enlarge the charge size to the extent that the diameter/length ratio is comparable to smaller diameter processes. Consequently, the crystal yield has the general tendency to decrease with increasing crystal diameter as shown in Fig. 3. It is therefore expected that 450 mm as the next standard crystal diameter which is currently introduced into mass production will be the largest diameter for the time being.

3 CCZ technology With the trend to n-type solar cells, continuously recharged CZ (CCZ) [17, 18] is reconsidered. Principally, there are two different methods for melt replenishment (Fig. 4). The first variant works with a double crucible. Silicon granules are continuously charged into the outer ring volume of the double crucible where they are melted by the higher temperature at the periphery of the crucible. A second variant replenishes the melt by a continuous supply of liquid silicon. The silicon granules are first conveyed into a small melting unit where they are molten and from where the generated melt flows down to the melt bath of the main crucible. The latter variant is not known to be used in production.

The CCZ technique provides a homogeneous axial dopant profile, has a lower thermal budget and allows for growth of longer crystals. As growth and melting are carried out simultaneously – except for the start of the growth process – the melt down phase is considerably shortened.
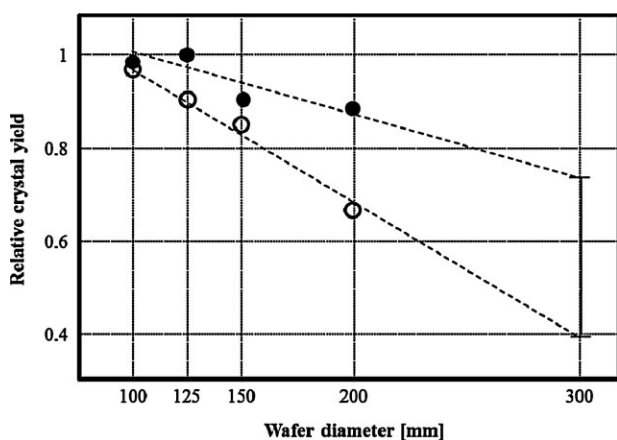

Figure 3 Relative crystal yield (good for order) versus crystal diameter. The black dots refer to wide specifications, the white dots refer to tight specifications (after [16]).
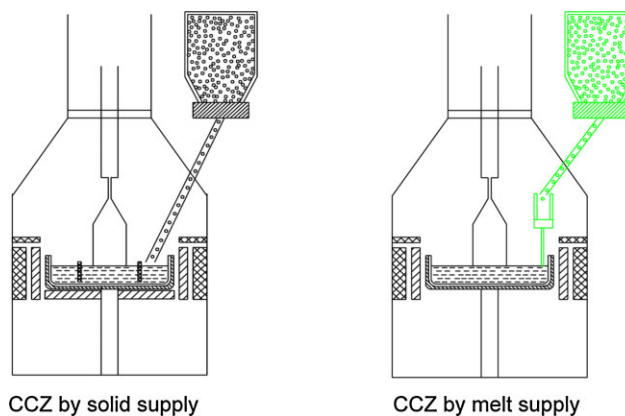

Figure 4 Variants of continuously recharched CZ (CCZ).

Consequently, process productivity is expected to be significantly higher and out of spec losses are substantially reduced, in particular for n-type crystals. This translates into lower cost of ownership and, thus, CCZ should be a done deal. It is therefore surprising that the CCZ method has not found acceptance in the past and was finally phased out for electronic grade crystals by the silicon suppliers despite of almost two decades of development.

The reasons are manifold. First of all, process complexity is significantly increased by the recharging process which makes the process more susceptible to failures. E.g., the introduction of dust particles into the environment of the growing crystal generated by the recharging process as well as the drift of unmolten silicon particles to the growth interface can result in structure loss and, thus, must be avoided. Moreover, in the event of a structure loss, the crystal cannot be dumped back and the growth process restarted, as the small CCZ crucible cannot accommodate additional melt volume. As a consequence, the dislocated crystal has to be removed before the growth process can be started again. This can considerably lower crystal yield and, hence, increase cost of ownership. As crystal yield is much more important with respect to cost than cycle time, a shorter cycle time can usually not compensate losses in crystal yield. Moreover, the double crucible is more expensive as a standard CZ crucible. However, the final show stopper for electronic applications was the finding that CCZ grown crystals exhibited special defects, i.e. large voids of several micrometers [19], which were unacceptable for most electronic devices. It is believed that these defects are related to the relatively high hydrogen content of the recharged Si granules. With respect to solar application, it is unlikely that these defects have an adverse effect on solar cell performance, as their density is relatively low and recombination of charge carriers at the void surface is strongly suppressed by the as-grown passivating oxide layer, which is well known for voids in as-grown CZ crystals [20, 21]. In addition, the capability to produce n-type crystals with a very thight resistivity distribution may be important for solar cell applications, as, depending on

the cell design, the cell efficiency is often a function of the resistivity of the base material. Thus, optimization of cell efficiency is easier and cell sorting for module manufacturing is greatly simplified. A revival of CCZ to supply n-type crystals for high efficiency solar cells is therefore a realistic new perspective and, indeed, respective activities have already been launched by several companies.

In contrast to CCZ, multipulling, also called discontinuous recharging, has become a standard method in the past [22, 23]. The process is started with the growth of one ingot which is removed from the melt and cooled down in the upper chamber of the puller. Meanwhile, the crucible is replenished with silicon chunks and the new charge is melted. When the crystal has cooled down, it is removed from the upper chamber and a new seeding and growth process is started. This procedure can be repeated several times until the crucible lifetime is exhausted. Hence, the method allows for the growth of several ingots out of one crucible. It is particularily useful for the growth of n-type material, as many short crystals with a small axial resistivity variation can be economically grown. However, in case of boron doped material (p-type), where the axial resistivity variation is relatively small, as the segregation coefficient of boron is nearly one, the advantage of growing many short crystals is offset by the loss of a relatively large portion of unusable crystal sections, i.e. seed and tail end cones, which entails a decrease of crystal yield. The growth of several long crystals out of one crucible is not only limited by the crucible lifetime, but also by the length of the upper chamber. Consequently, the improvement of CoO by multipulling is only mariginal for p-type.

4 Standard FZ technology There are principally two different concepts for the floating zone (FZ) technique [24, 25]. One is the pedestal method where a poly silicon is inductively melted at its upper end by a high frequency (HF) coil (Fig. 5a). This method is limited to a maximum crystal diameter of 10–20 mm, as the liquid bridge between the poly silicon rod and the growing crystal cannot be maintained for larger diameters. The so called needle-eye method (Fig. 5b) overcomes this diameter limitation and, consequently, has become the standard FZ technology. The fact that the FZ method avoids any contact of the silicon with other materials during the growth process allows for the
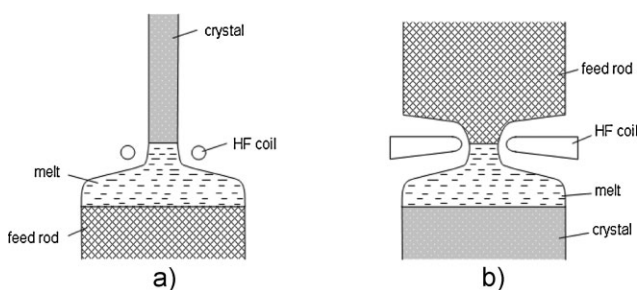

Figure 5 Two different floating zone (FZ) techniques: pedestal (a) and needle-eye (b) method [27].

production of extremely pure crystals. FZ grown crystals offer a significantly higher minority carrier lifetime as compared to CZ as the very low oxygen content not only suppresses the formation of light induced B–O complexes, but also the nucleation of oxygen precipitates. Similar to CCZ, the axial variation of dopants is flat. Consequently, FZ grown crystals would be the ideal base material for high efficiency solar cells from a qualitative point of view. With respect to electronic applications, it is very advantageous that FZ crystals can be produced free of harmful crystal defects if they are slightly doped with nitrogen [26].

At first sight, one would expect that FZ crystals could be produced at lower costs as compared to CZ crystals, as neither a crucible nor a hot zone is needed. However, these advantages are more than offset by the much higher costs for the feedstock material, i.e. solid feed rods instead of poly silicon chunks. The origin of the latter cost difference is the rather low deposition rate during the production of poly feed rods, the so called Siemens process, as the rods must come with a smooth surface and with no cracks. Furthermore, the poly rods often must be ground to a precise cylindrical shape to ensure a constant inductive coupling of the high frequency (HF) field of the coil to the rotating poly rod which additionally increases the cost for the feedstock material. As a consequence, the contribution of the feedstock material to the CoO is far more than 50%. Therefore, as compared to CZ, crystal yield is even more important for FZ.

Factors which impact the yield of dislocation free FZ ingots:

1. Quality of poly silicon feed rods

Originally, at least two float zone passes were necessary to obtain a dislocation free crystal. The reason was the unsuitable quality of the poly rods which resulted in frequent structure loss during the first pass. However, the poly silicon suppliers have learned to tune their deposition processes so that a one-pass quality of their poly rods is now standard. Nevertheless, crystal yield can still notably depend on the poly rod supplier and is generally much more susceptible to the feedstock quality as compared to CZ. A crack free bulk is needed as cracks may not only cause breakage of the poly rod during growth, but also entail an inhomogeneous heat dissipation in axial direction of the poly rod which disturbs the melting process at its lower end (formation of protrusions or meltdrops at the outer periphery of the poly rod/melt interface). A smooth surface is required, as, otherwise, too much poly material has to be ground off to obtain a smooth surface. In addition, rough surfaces are often accompanied by cracks.

Since the poly rods are rather expensive as compared to poly silicon chunks, it has been considered to grow a polycrystalline crystal by the CZ method, first, and, then, use this crystal as a feed rod for the final FZ pass. Most of the oxygen in this feed rod evaporates during the final FZ pass which results in a rather low oxygen content of the final single crystal. Although, the procedure makes use of the much cheaper silicon chunks, this advantage is more than offset by the additional costs for the CZ poly crystal in

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comparison to a one pass FZ process. Therefore, this concept is only economically meaningful, if suitable poly rods are not available, which may be the case for 200 mm FZ growth processes.

2. *Process interruptions*

A severe drawback of the FZ technology is the risk of arcing between the two electrodes of the HF power supply at the coil or between the poly rod and the coil. Arcing stops the growth process due to the break down of the HF-field and, in addition, often damages the HF coil. The risk of arcing increases with larger diameters due the higher voltage at the coil.

The process is also interrupted when, owing to variations of the melting process, local protrusions at the interface melt/poly rod occur. Such protrusions are preferably cooled by the gas flow and tend to grow rather thin. If they get thin enough, the HF-field does not couple to these thin tips anymore and, thus, cannot melt them away. As a result, they will finally touch the coil and cause arcing.

As the HF-field also exerts a mechanical force on the melt surface, any HF power oscillation/variation may excite surface waves on the melt cap on top of the growing crystal. The consequence is usually a melt spill which destroys the already grown crystal section.

On the other hand, process control is rather simple as the meniscus angle at the triple point of the growing crystal which determines the diameter growth/shrinkage of the growing crystal is clearly visible and, thus, can be measured with high accuracy. In addition, the melt flow is precisely controllable, as the HF field couples directly to the thin melt layer at the lower end of the feed rod, so that the melt flow reacts almost instantaneously to changes of the HF power. Furthermore, the growth process is not disturbed by sudden variations of melt flow patterns, as melt convection is driven by the electromagnetic forces of the HF field and Marangoni forces, which are both very stable during growth. Hence, process interruptions due to instabilities in the process control are rather rare for FZ.

It should also be mentioned that the tuning of a HF generator and the HF transmission requires much more expertise as the comparatively simple DC power supply of a CZ furnace.

Nevertheless, despite of the mentioned risks of process interruptions, modern FZ processes are quite stable if the necessary expertise for the maintanance of these processes is available.

3. *Residual poly rod pieces*

Unlike CZ, the FZ growth process has to be stopped, if the growing crystal dislocates. The residual poly rod, if long enough, might be reused for the next run or, has to be downgraded for CZ growth. This not only lowers the crystal yield, but also requires a sophisticated poly rod management to minimize poly silicon losses.

4. *Out of spec losses*

The possibility of continuous gas doping of the melt during the growth process along with the constant melt volume results in an axially flat resistivity profile nearly independent of the segregation coefficient of the dopant. Thus, FZ crystals can be produced within very tight resisivity ranges for p- and n-type in contrast with CZ and, consequently, out of spec losses are usually significantly lower as compared to CZ. The later is particularly true for n-type material as all n-type dopants have relatively small segregation coefficients.

Factors which impact cycle time (productivity):

1. *Pull rate*

The pull rate of standard FZ growth processes is already near the limit that is set by the critical shear stress which must not be exceeded by the growing crystal. Crystals with $\langle 111 \rangle$ orientation are specifically susceptible to thermal stress. At a diameter of 150 mm, a $\langle 111 \rangle$ crystal may even crack and fall into pieces during growth. The same is true for $\langle 100 \rangle$ crystals with 200 mm diameter.

2. *Thermal budget*

As no hot zone and crucible is required and no large silicon charge has to be melted down prior to the actual growth process, the thermal budget of the FZ process is very small in comparison to CZ which dramatically shortens the start up and cool down phase.

3. *No melt down phase*

As melting and crystallization occur simultaneously during the FZ process, no melt down phase is required and the cycle time is shortened accordingly.

With respect to cycle time, the FZ technology has a clear advantage over CZ and, consequently, FZ pullers achieve considerably higher outputs.

For a crystal diameter of ≥ 100 mm, rigid HF power transmissions have to be used which entail an essentially fixed position of the coil. As a consequence, the poly rod as well as the growing crystal must be axially moved over relatively long distances according to the grown crystal length. FZ pullers for large diameter crystals are therefore expensive due to their enormous height. The costs for the puller are further increased by the HF generator which is technically much more complex than the DC power supply for CZ pullers.

In contrast to CZ, the FZ process works with a stagnant argon gas ambient which reduces the argon consumption.

A severe drawback of the FZ technology are also the higher technical hurdles which have to be overcome when the crystal diameter is increased. The main challenges in this regard are the suppression of arcing and the reduction of thermal stress in the growing crystal. A major problem is also the availability of FZ suitable poly rods of a sufficiently large diameter. There seems to be a diameter limit of 160–180 mm for FZ suitable poly rods which will be difficult to be surmounted by the Siemens process. As a consequence, the FZ crystal diameter is limited to 200 mm up to now and it is not expected that this limit can be exceeded in the foreseeable future.

5 New method The new method, which was proposed in [6], is similar to FZ, but it replaces the expensive poly silicon rod by a device which is capable to

melt much cheaper Si granules and to supply the generated melt to the growing crystal. Thus, an FZ like process is recharged by silicon granules and will therefore be referred to as GFZ. An important feature of the new method is that two HF coils instead of one are used, one for melting the feedstock material and another one for heating the melt on top of the growing crystal. This considerably reduces the voltage at the HF coils which, in turn, lowers the risk of arcing. Furthermore, an individual optimization of the coil designs for melting and growing is now possible, respectively, while, in standard FZ, an often agonizing compromise between optimization of melting and growth has to be found. The switch to Si granules not only significantly lowers the costs for the feedstock material, but also minimizes the losses of poly silicon if the crystal dislocates. The granule supply and the growth process can be stopped without the consequence of down grading unusuable feedstock material. A further advantage is that the new method does not depend on the availability of suitable poly rods, anymore.

The principal setup of the new method is shown in Fig. 6. A first HF coil arranged above a rotating silicon plate heats up and melts the surface of the silicon plate. The plate sits on three rotating wheels which support the plate at the edge and also serve as a rotary drive for the plate. Silicon granules are supplied through a funnel onto the surface of the silicon plate and are continuously molten by the upper HF coil. The melt flows through a tubular opening in the center of the silicon plate which is created by a section of a pipe that is drawn downward. The tubular opening is heated from above by an additional heat source in order to prevent freezing of the melt flow and the melt neck. The melt neck forms a liquid bridge between the silicon plate with its tubular opening and the melt bath on top of the growing crystal. Hence, a continuous melt flow from the top of the silicon plate, where the silicon granules are molten, down onto the top of the growing crystal is established. A second HF coil for pulling the crystal is arranged between the melting device and the melt bath of the growing crystal to prevent uncontrolled freezing of the melt bath.

The silicon plate and the integrally molded section of the pipe are protected against the introduction of the HF field of the pulling coil from below and from the side by a water-cooled metal plate. Thus, melting of the silicon plate and the pipe from below and the side is prevented. Moreover, the metal plate also acts as a heat sink which dissipates the heat generated by the melting coil in the silicon plate. Consequently, a strong thermal gradient builds up in the silicon plate and the integrally formed section of the pipe and ensures that a stable pool of melt is formed on the top side of the silicon plate and that the inner side of the section of the pipe is covered by a liquid film, while the base of the plate and the outer side of the integrally formed section of the pipe remains in solid form.

The new method is particularly designed to assure that residual solid Si particles in the melt cannot drift to the growth interface of the crystal which would terminate dislocation free growth. The main barrier for the particles is the surface of silicon melt inside the tubular opening which closes the opening. As solid silicon is lighter than the silicon melt, the particles tend to stay at the melt surface. The design also facilitates a dust proof separation of the melting device where the granules are supplied and the space below the pulling coil where the crystal is grown. Thus, dust particles in the gas ambient generated during the recharge process of Si granules onto the silicon plate are kept away from the growing crystal.

The production of a single crystal begins by first of all melting a closure at the lower end of the pipe section and forming a droplet of liquid silicon which adheres to the lower end of the pipe section. The closure used may be a piece of silicon which has been inserted into the pipe section or the melt neck which solidified after pulling of a previously grown crystal. After forming the droplet, seed neck growth and the formation of the first part of a seed cone is carried out in the same manner as in standard FZ growth. At the same time or subsequently, the upper side of the silicon plate and the closure of the tubular central opening are melted with the aid of the upper HF coil and the radiation heating means and further molten material is fed to the growing crystal. Then, as the demand of molten material increases, additional granules are supplied, so that a stable melt pool is formed on the upper side of the silicon plate, from which there is a continuous, controllable melt flow to the melt on top of the growing crystal.

The schematic drawings in Fig. 7 compare the total heights of a standard FZ and a GFZ puller. It is clearly seen that the height of the GFZ puller is substantially smaller. The upper chamber with the shaft for the poly rod is replaced by a hopper, which contains the silicon granules, and a unit, which meters the granules and conveys them to the silicon plate where they are molten.

Due to their much larger surface, the purity of the Si granules is somewhat lower as compared to poly rods. In particular, the carbon content may be higher. The higher carbon concentration has no impact on the performance of solar cells, but may have adverse effects on electronic devices.
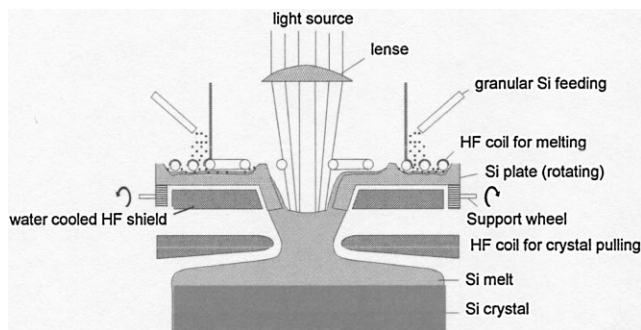
6 Cost comparison In Table 1, the most important cost driving parameters are listed and qualitatively compared

light source
lense
granular Si feeding
HF coil for melting
Si plate (rotating)
water cooled HF shield
Support wheel
HF coil for crystal pulling
Si melt
Si crystal

Figure 6 Principal setup of a new FZ like method with continuous recharging of silicon granules (after [6]).

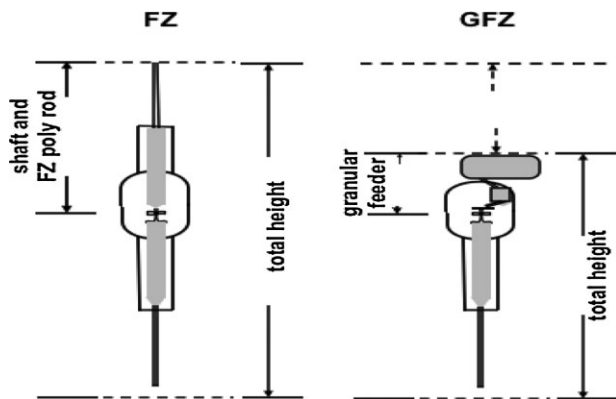Phys. Status Solidi A 211, No. 11 (2014)

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Figure 7 Schematic comparison of heights of a standard FZ puller and a crystal puller applying the new GFZ method.

Table 1 Qualitative cost comparison between CZ, FZ and the new method (GFZ) ("+": advantage; "−": disadvantage).

	CZ	FZ	GFZ
poly silicon	+	− −	+
consumables	− −	+	+
energy	−	+	+
cycle time	− −	+	+
losses	+	−	++
investment	+	−	−

for the different growth technologies. With regard to feedstock material, CZ and GFZ are on the same cost level, while FZ, as mentioned above, faces a severe drawback here. On the other hand, FZ and GFZ do not need consumables like crucibles and certain graphite parts of a hot zone and consume less energy and argon gas. A significant advantage of FZ and GFZ, respectively, is the substantially shorter cycle time as compared to CZ owing to the simultaneous melting and growing and the much shorter warm up and cool down times. The GFZ technique is also superior with respect to losses, as, upon the occurrence of a structure loss, the process can be stopped at any time without the need to scrap residual feedstock material. Thus, GFZ is expected to have the highest crystal yield of all three technologies. The only tangible drawback of GFZ may be the higher investment costs for the puller as two HF generators are necessary. However, in comparison to standard FZ, a large part of this drawback is compensated by the significantly smaller height of the vessel.

7 Conclusions The standard CZ and FZ method are not expected to have a realistic potential for further substantial cost reductions. Marginal improvements of crystal yield and cycle time as well as consumables are still possible, but they will not dramatically alter cost of ownership. A revival of CCZ may be a new perspective, if

the solar cell technology continues to switch to n-type silicon as a base material. Compared to CZ, there would be more cost reduction potential for FZ, if the poly silicon suppliers manage to supply FZ suitable poly rods at significantly lower costs. Up to now, respective efforts were not known to be successful. A new method circumvents the poly rod cost issue by using much cheaper silicon granules as a feedstock material. If this method can be successfully implemented for high volume production, a significant reduction of CoO for monocrystalline silicon is feasible.

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