COST EFFECTIVE GROWTH OF SILICON MONO INGOTS BY THE APPLICATION OF A MOBILE RECHARGE SYSTEM IN CZ-PULLER

F. Mosel[1], A.V. Denisov[1], B. Klipp[1], B. Spill[1], R. Sharma[2], R. Kunert[2], P. Dold[2]
[1] PVA Crystal Growing Systems GmbH, Im Westpark 10-12, 35435 Wettenberg, Germany
[2] Fraunhofer CSP, Otto-Eissfeldt-Str. 12, 06120 Halle/Saale, Germany
frank.mosel@pvatepla.com, phone: +49 64168690-125, fax: +49 64168690-822

ABSTRACT: The permanent demand on the improvement of solar cell efficiency and reduction of production costs has placed much focus on the multiple Cz-crystal pulling technique from one crucible. The use of lower quality silicon as feedstock for monocrystalline material is not an alternative track because it is in contradiction to the quest for high cell efficiencies.
PVA Crystal Growing Systems Gmbh has developed a novel mobile recharge system for Czochralski pullers, the SiCharger MRS. This systems is capable of handling silicon feedstock material up to a chip size of 15 mm and was extensively tested under industrial conditions. The assignment for a chip size of 40 mm is currently under series of tests, the results are promising. One MRS-system can serve several pullers, presuming a suitable production organization. Investment cost and thus amortization period are minimized.
In this paper the MRS-system is presented in detail as well as its operation during the recharging of the hot crucible. The influence of the different types of feedstock on the recharge process is presented. The segregation effect of impurities on the quality of multiple ingots grown in one crucible is shown.

Keywords: Czochralski, Melt Recharge, Economic Analysis

1 INTRODUCTION

About 90% of the solar cells produced in the world are based on crystalline silicon (c-Si). Currently, the wafer market is dominated by casted materials. It is expected that in the next 10 years the market share of mono-Si will increase up to 50%, coupled with a strong trend towards high efficient cells on n-type wafers. Fig.1 shows the expected proportions of the different crystal growing technologies and wafer types for the next ten years.

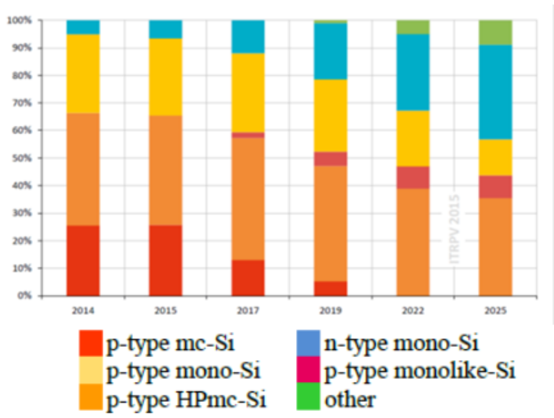

Figure 1: World market shares for wafer / ingot types. (International Technology Roadmap for Photovoltaic ITRPV 2014 Results, www.itrpv.net).

The casting process of mc-silicon might be scaled rather easily, today, G6 is already standard and G7 or G8 are in use, too. Up-scaling in the case of Czochralski mono-ingot growth is more difficult, the diameter and the length of the ingots are more or less fixed. Multipulling, i.e. the growth of several ingots out of the same crucible is a powerful method to reduce production costs: in a standard Czochralski process, costs for the crucible amount to approximately one quarter of the total consumable expenses. Furthermore, multipulling reduces the process time (no lengthy cool-down period between single runs) and extends the life-time of the graphite hot-zone. The challenge is the design and operation of a sophisticated but still economic feeding system, which allows the refill of the crucibles in a well-controlled way.

2 EXPERIMENTAL

2.1 Multipulling of Silicon Monocrystals

At present, silicon monocrystals are still produced mostly according to the standard Cz-process. In this batch process the quartz crucible is filled to top with silicon feedstock and a crystal is pulled by the well-known Cz-procedure. After the process the entire Cz-puller is cooled down, which inevitably leads to the destruction of the quartz crucible. Besides the loss of the expensive crucible, hotzone components may deteriorate by the temperature changes of the heat-up and cool-down cycles. In order to reduce the production costs, in particular the crucible costs, and to economize the Cz-process by saving unproductive down times during the heat-up and cool-down cycles, multiple batch recharging is a favorable track. This multiple batch recharging is also called “multipulling Czochralski” and is defined here as the growing of several ingots in one crucible with melt replenishment after each growth process. During the cool down of the crystal in the gate chamber, which is separated from growth chamber by means of a gate valve, the hotzone is maintained under melting conditions. Thus, the crucible can be recharged during the cool down cycle of the ingot. Several concepts of replenishing the hot crucible are well known since the early days of silicon mass production [1].
Simple, but effective recharge systems are the “slab-feeder”, where the side slabs of squared ingots are attached to the central pulling drive and are slowly lowered into the hot crucible, or the “central feeder”, where a quartz tube filled with silicon chunks also attached to the central pulling device is lowered into the crucible and emptied into the restmelt [2]. The

disadvantage of both systems is that the previous ingot had to be cooled down and taken out of the gate. This procedure is quite time consuming. Fig. 2 shows another concept of a “stationary feeding unit” from PVA Crystal Growing Systems GmbH. The feeder is permanently

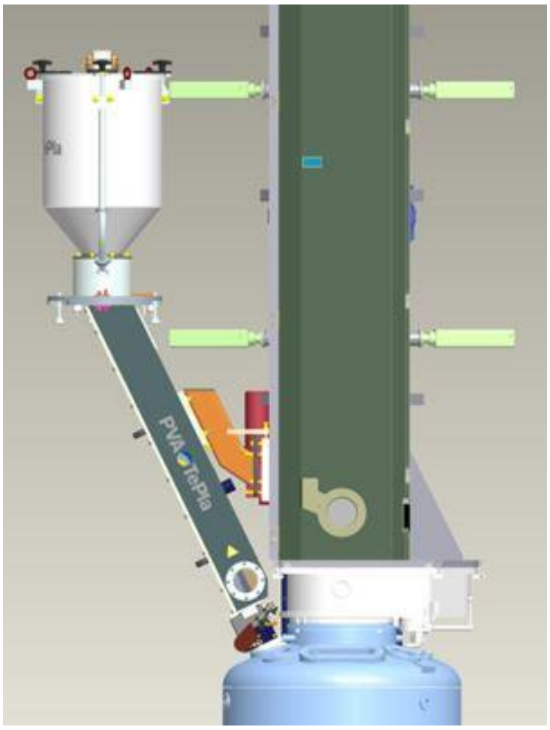

Figure 2: Stationary feeding unit mounted on Cz-puller

mounted to the puller. The storage vessel (hopper) is removable for charging with silicon feedstock material up to a chip size of 10mm. Inside the connection piece between the hopper and the furnace vessel a system of movable quartz tubes is installed, which can be moved back and forth, depending whether the feeder is in operation for feeding or separated from the growth chamber by means of a gate valve for refilling the hopper. This kind of feeding system is commonly used when multiple Czochralski growth is performed. However for each Cz-puller a separate feeding unit is required which implies high installation costs.

2.2 Mobile Recharge System

The PVA Crystal Growing Systems GmbH has developed a mobile recharge system, which offers the unique possibility to serve several Cz-pullers time-delayed. To make the mobile feeding unit compact and easy to move, the hopper is separated from the passive conveyor, the quartz tube system. The connection of the hopper with the quartz tube is realized by an active vibratory conveyor. The advantage of the vibratory conveyor is that no moving parts of the conveyor have contact to the silicon charge and thus contamination is avoided. Therefore the conveyor drain is lined with silicon plates. The silicon chips are drawn off from the hopper by the active vibratory conveyor and are transported to the quartz tube and thus feeded into the crucible.

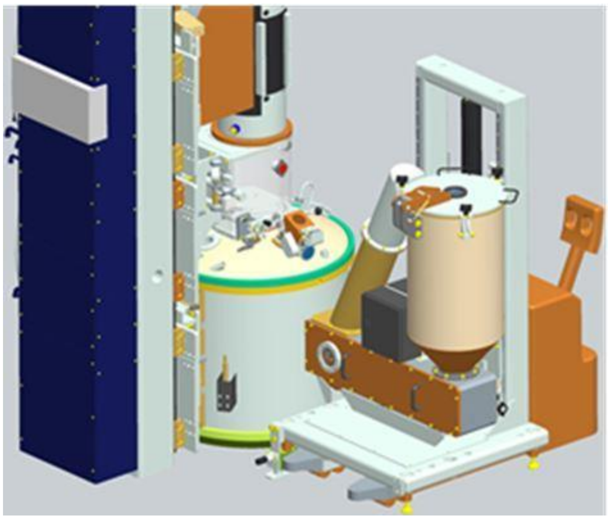

Figure 3: Mobile recharge system MRS undocked on transportation cart

The active conveyor is a small-parts conveyor drive, which is a linear vibration conveyor excited by means of an oscillating electromagnet at a fixed frequency of 100Hz. The working unit is a V-shaped drain which transmits the oscillation of the vibration unit to the transported silicon chunks. The mass flow is controlled by the magnitude of the oscillating amplitude and can be adjusted in a wide range up to several kg/min. It is also possible to control the oscillation of the vibratory unit by a closed control loop. This ensures the compatibility of different mobile SiChargers.

Figure 4: Mobile Recharge System docked on Cz-puller

The MRS-system can be docked in any phase of the growth process, for instance in the melting or in the endcone phase. The docking valve is closed and after

docking, the MRS-system is evacuated and leak tested. When the melting phase or the ingot growth is completed and the ingot is separated from the growth chamber, the feeding of the hot crucible can be initiated. Therefore the whole feeding system is pressurized to the growth chamber condition. The docking valve is opened and the quartz tube is lowered to its feeding position in the hot crucible. Feeding can be executed under argon gas flow. The feeder system is attached to the Czochralski puller only for the time of topping up the crucible or refilling after crystal growth. Once the crucible is filled up, the quartz-tube is retracted in its chamber and the docking valve is closed. The tightness of the docking valve is proven by means of pressure drop test. The MRS-system is disconnected and can be recharged for the next refill process.
The MRS-system is controlled by the PLC of the puller, which is the case for Cz-pullers from PVA CGS Gmbh. For other manufactures it is also possible to control the mobile feeder by its own PLC, assuming a flange for the docking valve is available.

2.3 Influence of particle size and distribution

Well controlled feeding rates are crucial for a successful operation of the system. If the amount of recharged silicon is too high, the residual melt might freeze and the crucible would be damaged. If the recharge rate is less than the amount, which the system could handle, economics are affected negatively. We performed measurements of feed rate for different types of feedstock using a stationary feeder. Not surprising, applying similar parameters, the granular material from Fluidized Bed Reactors (FBR) showed the highest feeding rate[1]. Crushed silicon feedstock from Siemens rods, even if they had the same size than the granules, resulted in significantly lower feed rates (Fig. 3). Compared to the spherical granules, the crushed silicon pieces are strongly elongated, an aspect ratio of 1:4 or higher is found quite often. This results in strong interdigitating and increased friction. Even clogging might be seen, if the transport system is not several times larger in diameter than the maximum length of the silicon pieces. In any case, it makes clear that a sophisticated control system is essential, which is capable to measure reliably the amount of transported silicon and which can control the feeding process as part of the overall control loop. In our presentation, we will demonstrate the correlation between feed rate, feedstock type and feeder design.
Particle release during the feeding process is a rather critical issue. Although most of the particles are in the lower micrometer or in the sub-micrometer range, as our measurements have shown, they might accumulate in certain areas of the growth chamber and might be released at a later point, in particular, when the gas flow or the flow configuration changes. Typically, this is the case, when the crystal body enters the area of the gate valve: the cross-section for the argon flow is reduced and the overall flow pattern changes. We identified two sources for particle formation: (I) extrinsic reasons, the material is already delivered with a certain dust load and (II) intrinsic reasons, particles are formed during the feeding process due to abrasion and friction. The dust load of the virgin material might be removed by proper pre-conditioning (inert gas blowing, washing), but it will increase cost. Dust formation during the process itself might be minimized by short transport length, by a low-angel conveyer system, and by a sophisticated gas flow system. We will present corresponding measurements and design solutions.

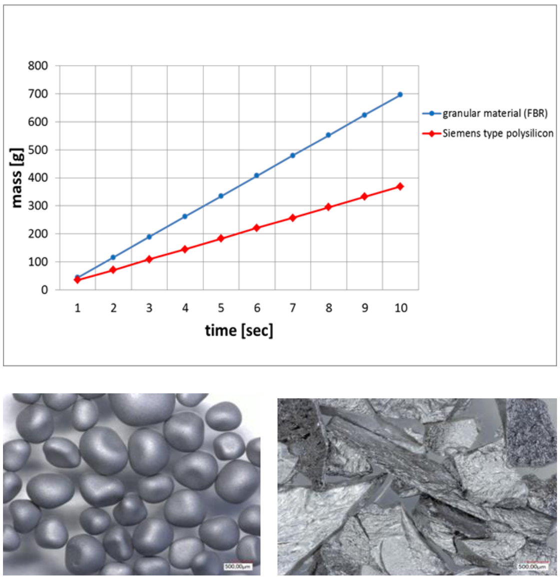

Figure 5: Feed rate for granular material (blue) and crushed Siemens rods. Size and feeding parameters had been identical, but the flow and transport properties vary significantly. Below: Magnified image of granules from FBR process (left) and crushed Siemens silicon (right).

particle size	below the crucible	above the crucible
1 µm	388656	361637
5 µm	10513	9655
10 µm	169	334

Table I: Measurement of particle load inside the growth chamber: The measurements have been performed at room temperature and under normal pressure. Within 4 minutes, about 6.7 kg of silicon had been filled into the crucible. A steady argon flow of 20 slm was used.

2.4 Impurity redistribution in Cz-ingots grown from a replenished melt

An estimation of impurity accumulation in the melt due to the sequential melt replenishment has been published by Hopkins et al. [3]. Using the well-known “normalfreeze” relation (1) given by Pfann [4]

$$(1) \quad C_S = k_{eff} C_0 (1-g)^{k_{eff}-1}$$

and the concept of the effective segregation coefficient k_{eff} [5], which is the ratio of the solute concentration in the growing crystal C_S to the solute concentration in the bulk liquid, the axial concentration profiles in Cz-ingots grown from replenished melts can be calculated as a function of the solidified fraction g, with C_0 is the initial

[1] Although FBR silicon shows the best flow behavior, other aspects like interaction with the crucible or splashing during melting have to be considered, too, when discussing the use of FBR granules.

concentration of the impurity in the liquid. The initial impurity concentration C_L^i (n) in the melt at the start of the n-th pull (2) can be calculated according to Hopkins with $p = (1-g)^{keff-1}$ [3].

$$(2)\ C_L^i(n) = C_0\left[p^{n-1} + g\left(\frac{p^{n-1}-1}{p-1}\right)\right]$$

Assuming a working life of a standard quartz crucible of ~150 h and a mean process duration of 40 hours for an 1.5 m long 8 inch ingot without heat up and cool down times it should be possible to grow three ingots out of one crucible.

Fig 6 shows the accumulation of impurities with a small segregation coefficient in the melt calculated for the sequential replenishment of the crucible. The refill is calculated after solidified fraction of 90% (g=0.9). For the calculation an effective distribution coefficient $k_{eff} = 10^{-3}$ was applied, which is in the range for metal impurities, having a strong impact on the solar cell performance [6]. Tab. II shows measured segregation coefficients of main metal impurities in Cz-silicon [3].The main origins of the metal impurities have been identified by Harada et al [7] as the silicon feedstock and the quartz crucible.

metal	k_{eff}	metal	k_{eff}
Co	1.0×10^{-5}	Mo	4.5×10^{-8}
Cr	1.1×10^{-5}	Ni	3.2×10^{-5}
Cu	8.0×10^{-4}	Ti	2.0×10^{-6}
Fe	6.4×10^{-6}	V	4.0×10^{-6}
Mn	1.3×10^{-5}	Zn	1.0×10^{-5}

Table II: Effective distribution coefficient k_{eff} of metals derived by Hopkins et al. [3]

No remarkable difference is evident for segregation coefficients below this value. It can be estimated that the maximum accumulation of impurities in the melt with small segregation coefficients is less than a factor of 3. This holds also for the axial impurity distribution in the grown crystals, which can be estimated using equation (1) and (2).

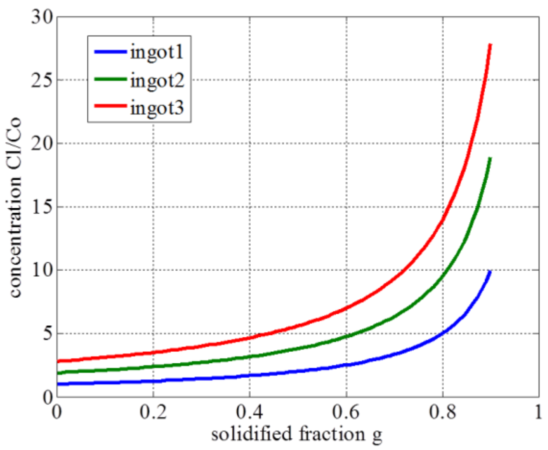

Figure 6: Impurity build-up curves for a replenished melt for the growth of 3 ingots in one crucible calculated according to Hopkins et al. [3].

Several ingots have been grown with the application of the SiCharger in the Crystal Growth department of the PVA CGS GmbH. The concentrations of the O_i and C_S have been measured by FTIR and compared to crystals grown under standard Cz-conditions. The results are shown in table: III. It can be seen that the process conditions of the MRS-system have no remarkable impact on the crystal quality.

Cz/MPCz	$O_i \times 10^{17}$ atoms/cm^3		$C_s \times 10^{16}$ atoms/cm^3	
	top	tail	top	tail
Cz 1	9.55	5.86	0.38	2.01
Cz 2	10.05	5.97	2.1	2.93
MPCz A1	9.97	6.43	0.01	1.62
MPCz A2	10.29	8.02	0.13	0.88
MPCz B1	10.42	5.19	0.24	2.05
MPCz B2	9.93	6.39	0.53	1.59
MPCz C1	10.97	5.4	0.18	2.41
MPCZ C2	9.81	6.08	0.36	1.73
MPCz D1	9.02	4.85	0.16	3.7
MPCz D2	8.42	5.71	2.26	3.92

Table III: O_i and C_S-concentration measured by FTIR at top and tail of crystals grown at PVA crystal growth department. Cz is standard grown ingot, MPCz X1 and MPCz X2 is 1st and 2nd crystal of growth run A,B,C,D grown by multipulling Cz-method.

3 ECONOMIC ANALYSIS OF THE MULTIPULLING Cz-PROCESS

An assessment of the economic potential cannot be presented quantitatively, because many factors depend on the technological condition of the process development as well as on the training level of the operational employees. Furthermore production costs may have different values depending on the location of the production plant and are subject to substantial fluctuations in the market.

The main economic potentials are the cost-saving of crucible consumption and the reduction of the down-time between the standard batch processes. The crucible costs are indirectly proportional to the number of refill processes. Thus 50% of crucible costs can be reduced even with one refill process. The non-productive down-time between the growths of 2 crystals can be reduced effectively. This shown in fig. 7, where the heater power of a standard one batch process is sketched together with a refill process. The curves were derived from real crystal growth experiments performed at the crystal growth department of PVA CGS GmbH. The results are summarized in table IV. The standard charge weight is 140 kg for an 8 inch ingot with a body length of 1600 mm. The blue curve represents a complete standard process followed by the cool down and heat-up sequence for the second ingot ending at the dipping point. The red curve shows the course of the heater power for the crystal growth and the subsequent refill process of the hot crucible, also ending at the dipping point. The red curve has a time offset to the blue one due to an additional feeding procedure after the initial melting for a better fill level of the crucible. It is evident, that in the case of melt replenishment the down-time can be reduced in the range of 50-60%. The energy consumption for the refill process is in the same range as the standard Cz-process, as shown in figure 7.

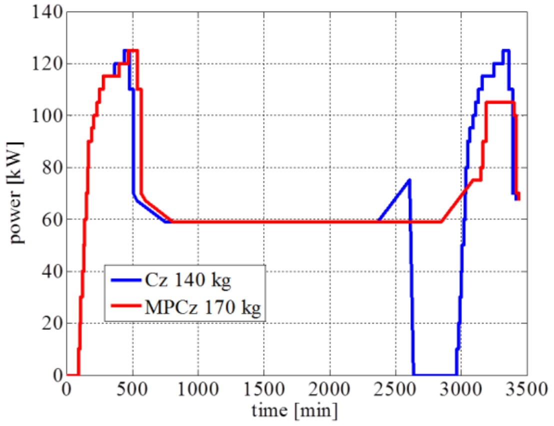

Figure 7: Power consumption of the heater versus process time for a standard Cz- (blue curve) and a recharge MPCz-process (red curve).

of the puller. This fact on the other hand takes care on the hotzone, especially the graphite felt, which degrades very rapidly, when the puller is opened in a hot state under atmosphere. A reduced temperature cycling may also be beneficial for the lifetime of the other rigid parts of the hotzone, due to reduced thermal stresses.
An uncomplex comparison of the throughput of a standard one batch Cz-process with a multiple recharge process and a simple cost analysis shows the economic potential of the MRS system.

process stage	time [h] Cz	time [h] MPCz
pump down (incl. leak test)	1.5	1.5
melting to diptemperature	7.5	8.5
stabilization, neck, crown	3.5	3.5
body	27	33
endcone	4	4
time to next diptemperature	13.5	6

Table IV: comparison of a standard Cz-process with a MPCz-process.

50 weeks of production per year with an output of 150 ingots per puller should result in an annual output of 100%. Assuming that 3 ingots can be grown out of one crucible, it is possible to optimize the fillevel of the crucible of about 20-30 % per ingot resulting in an equal increase of the throughput (20-30 ingots/year). The longer duration of the body growth due to the topping up of the crucible is compensated by reducing the downtime (see fig.7). An increase of productivity of 25 % (25 ingots/year) and an economization of 67 % of the crucible cost should be possible using the MRS system. One MRS-system should serve for 5-7 pullers.

4 CONCLUSIONS

High quality crystals can be grown by the application of the MPCz-technique. With this MRS-system capital costs can be minimized. It is shown that the additional investment for the recharge system is quickly amortized by the economization of crucibles and other operation costs.

5 ACKNOWLEDGEMENTS

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6 REFERENCES

[1] W.Zulehner, D. Huber, Crystals 8: Silicon Chemical Etching, J. Grabmeier ed., Springer Verlag, Berlin (1982)
[2] H.Kato et al.: U.S. Pat. Pub. No.: US 2012/0160156 A1, Pub. Date: Jun.28,2012
[3] R.H. Hopkins et al., Journal of Crystal Growth **42** (1977), 493-498
[4] W.G. Pfann, Zone melting, John Wiley, New York (1966)
[5] J.A. Burton, R.C. Prim, W.P. Slichter, J.Chem. Phys. **21** (1953) 1987-1991
[6] G. Coletti, Impurities in silicon and their impact on solar cell performance, thesis
[7] K. Harada et al., Journal of Crystal Growth **154** (1995), 47-53