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Purifying UMG silicon at the French PHOTOSIL project

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ABSTRACT
This paper gives an overview of the French PHOTOSIL project that deals with the purification of metallurgical-grade (MG) silicon via different stages of upgraded metallurgical-grade (UMG) silicon to finally arrive at a purity level that is compatible with the requirements of the silicon-based PV industry. However, purified UMG silicon in general and by definition does not reach the ultra-high purity levels of electronic-grade (EG) silicon. Based on the PHOTOSIL project, this paper presents the typical technical challenges and problems encountered with less pure purified UMG silicon and how they were resolved, both during silicon purification and crystallization and the processing of solar cells.

EG silicon is obtained by gas phase purification, applying Siemens-type or related simplified processes and most widely used by the silicon-based PV industry at the moment. The ultra-high purity levels of EG silicon and its reproducibility almost automatically guarantee high PV performances in a controlled and reliable way. The challenge for purified UMG silicon therefore is to close the gap with EG silicon as much as possible by arriving at quality levels that allow for sufficiently high solar cell performances, while at the same time putting forward its potential economic advantages in terms of reduced costs and higher material availability. Ultimately, the goal for purified UMG silicon is to bring the cost per watt of converted energy further down towards €1/W, towards grid parity and to give crystalline silicon-based photovoltaics a long-term perspective alongside other emerging second- and third-generation techniques.

The results and data contained in this paper were obtained from members of the PHOTOSIL consortium: FerroPEM, CEA-INES, CNRS-SiMAP and APOLLONSOLAR. At present, the PHOTOSIL project is in an advanced industrial pilot line stage, working on batch sizes of 90kg for the different purification operations and 120kg for the crystallization of multicrystalline silicon ingots.

> “The distinctive major advantage of PV is the quasi unlimited supply of solar radiation arriving on the earth’s surface.”

PV energy conversion will play a major role for the world’s future long-term energy supply. The distinctive major advantage of PV is the quasi unlimited supply of solar radiation arriving on the earth’s surface. In a simplified but striking comparison, the energy ‘consumption’ of the human civilization per annum corresponds roughly to one hour of incoming solar radiation on the entire surface of the earth [1]. PV energy conversion can therefore be regarded as a truly sustainable form of energy supply. In addition and contrary to other currently used forms of energy conversion based on fossil fuels for example, PV energy conversion is pollution- and noise-free, and no moving particles are involved.

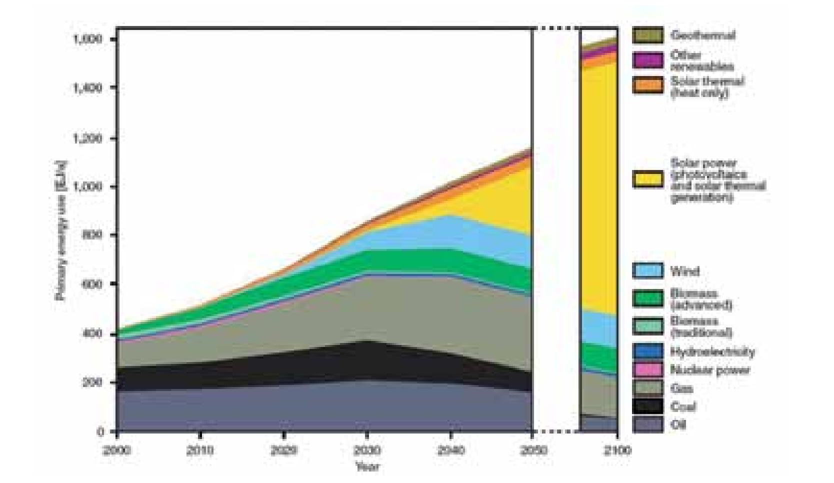

Figure 1. “Exemplary Transition Scenario” – Study by the German Advisory Council on Global Change on the future global primary energy supply (WBGU).

For these reasons, PV plays a major role in studies and projected scenarios on how to meet the constantly increasing primary energy requirements of the earth, as shown in a study by the German Advisory Council on Global Change (WBGU) [2]. The scenario in this example concludes that by 2050, 25% of the global primary energy supply will be provided by solar energy, which rises to 64% in 2100 (see Fig. 1).

Although the PV industry continues to show impressive annual growth rates of 60% in average for grid-connected PV systems and 102% on average for large utility-scale installations between 2004 and 2009 [3], its share of the total energy production is still marginal. In 2008, PV energy conversion systems contributed only 0.2% to the total global electricity production [3]. However, to be able to contribute to the future global energy supply as implied by the aforementioned WBGU study, the PV industry needs to further accelerate its growth and innovation rates, while also bringing down the costs per produced watt further to achieve grid parity.

Regarding the PV industry, crystalline silicon as a base material for PV cells and modules plays by far the dominant role and is expected to keep this important role for some time. Although second-generation thin-film technologies are expected to gain more important market shares in the future, last year (2009) saw 78% of the worldwide PV production capacity based on crystalline silicon technology, with the remaining 22% comprising thin-film technologies [4].

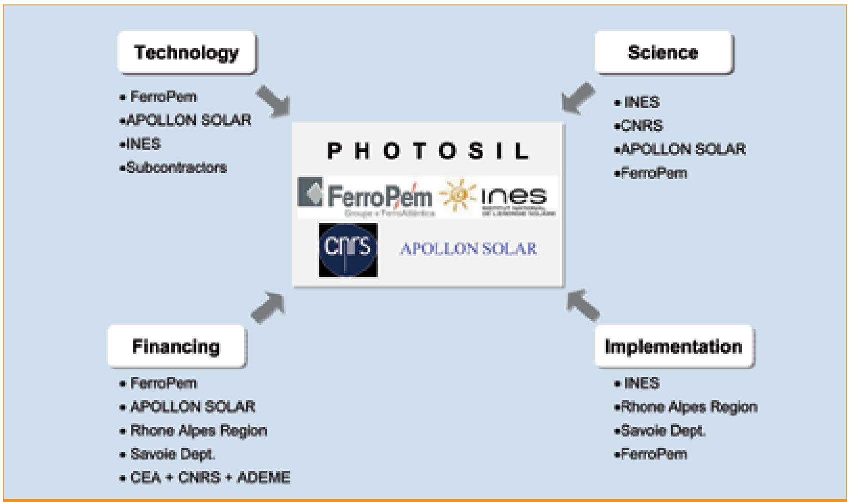

Figure 2. The PHOTOSIL Consortium and project organization.

Silicon feedstock, the raw material for crystalline silicon-based PV solar cells and modules, plays a key role for the future expansion of this branch of the PV industry – specifically its availability and cost. Although silicon is the most abundant element on the earth, it still needs to be reduced from SiO_2 and further purified. Depending on the applied technology and the market situation, the costs of silicon feedstock can comprise between 20 and 30% of the total PV module's costs. Traditionally, the crystalline silicon-based PV industry has used high purity EG silicon as feedstock for mono- and multicrystalline ingot and wafer production. Due to the accelerating growth of the PV industry, which began in the late 1990s, the classical silicon feedstock sources for PV became more and more limited, resulting in drastic price increases for EG silicon feedstock.

This situation has triggered a dual reaction (see [5] for more details): (i), an increase of production capacities for EG silicon using the chemical purification route based on gas phase purification (for example, the Siemens process); and (ii), direct purification of widely available MG silicon.

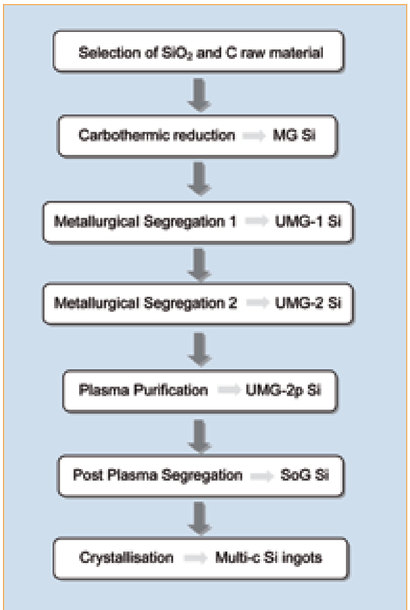

Figure 3. PHOTOSIL process flow.

"The production of solar-grade silicon via the metallurgical route is attractive due to its low cost potential."

The production of solar-grade silicon via the metallurgical route is attractive due to its low cost potential, a result of the fact that capex for production facilities and energy costs are much lower than those incurred by the chemical purification route. However, solar-grade silicon from this route needs to have quality levels that are compatible with the requirements of the PV industry in terms of solar cell performance, material yield and reproducibility.

The PHOTOSIL project

The PHOTOSIL project is part of the metallurgical route taken to directly produce solar-grade silicon from MG silicon. The diagram in Fig. 2 shows PHOTOSIL's partners and their main roles within the consortium. The project started in 2004, inspired by early encouraging results from the European ARTIST project [5], which also dealt with the purification of MG silicon. Development work on pilot-plant level started in 2006, and in 2009 operations ran on a continuous level using the first-generation pilot equipment, which led to the development of second-generation equipment – currently in the design phase – that will be used for industrial production.

In order to industrially exploit the PHOTOSIL technology, the company PHOTOSIL INDUSTRIES was created in 2009 by FerroPEM and APOLLONSOLAR.

The technico/economical objectives of the PHOTOSIL project can be summarized as follows:

- Solar-grade silicon feedstock costs of €15/kg and multicrystalline ingots at €35/kg
- Crystallization yield of >85% (usable p-type ingot part)
- Sufficient high purity and crystal quality for solar cell efficiencies >15.0% on average
- Use of 100% PHOTOSIL silicon – no blending with EG silicon
- Ready-to-use silicon feedstock – no additional doping required.

PHOTOSIL technology: standard purification process and results

Looking at the generic flow of the PHOTOSIL process as depicted in Fig. 3, one important point of note is the process's complete vertical integration, starting with the selection of raw material (quartz and carbon reductant) for the reduction of MG silicon and ending with the crystallization of multicrystalline silicon ingots from purified silicon. Effectively, the process combines metallurgical segregation processes with an inductive plasma treatment.

The vertical process integration brings two major advantages: (i), the transfer of silicon in its liquid state between certain purification steps, thus conserving the melting enthalpy; and (ii), the possibility of recycling silicon rejects after different purification steps. Both points allow for improved material yields and process times, and consequently lower processing costs. In the following section, the different purification process steps will be described in chronological order, followed by a review of obtained results.

The first three steps – selection of raw material, carbothermic reduction of silica to produce MG silicon and a first segregation of this MG silicon – take place under the operation of FerroPem outside of the proper PHOTOSIL facilities. This relocation is basically to simplify logistics and to benefit from existing production facilities and know-how. The great advantage of this approach is that the process is started with a lower impurity content – which can be a problem, especially regarding difficult-to-remove impurities like the major dopants, boron and phosphorous. The special selection of the two raw materials, quartz and carbon reductant, reduces MG silicon using dedicated electrical arc furnaces of FerroPEM. The silicon is directly transferred in its liquid state to the first segregation process that allows the reduction of impurities with a low segregation coefficient, which includes all metals but also phosphorous to a certain extent. The impurity characteristics of

Element	B	P	Fe	Al
	ppm_w	ppm_w	ppm_w	ppm_w
PHOTOSIL UMG-1 Silicon	7-8	10-12	150	30

Table 1. UMG-1 silicon characteristics.

Figure 4. UMG Si segregation unit.

the resulting UMG-1 silicon are shown in Table 1.

The UMG-1 silicon is subjected to a second metallurgical segregation treatment to further reduce metal and phosphorous concentrations, as depicted in the photos in Fig. 4. This is the first of several operations that take place within the PHOTOSIL facilities. The UMG-1 Silicon is first re-melted in an induction furnace and then transferred into a specially designed segregation vessel, in which a large volume of the silicon solidifies in a controlled way. The remaining liquid part in which metals and phosphorous have segregated is then poured into a waste container.

In a following purification step, the solidified UMG-2 is re-melted inside a graphite crucible by induction and submitted to an inductive plasma purification process, described in more detail elsewhere [7]. This crucial process, which mainly serves to reduce the boron concentration, consists of an argon plasma gas being projected towards the surface of the melted silicon. The argon plasma gas contains reactive species via injection of oxygen and hydrogen gases that are activated by high-frequency induction.

At the surface, which is constantly renewed by electromagnetic stirring of the melted silicon, the reactive species from the plasma gas react with the boron at the surface of the silicon bath and render it volatile (see Fig. 5). The progress of the boron volatilization is monitored by taking samples from the liquid silicon and performing resistivity- and conductivity-type measurements. This method turned out to be the simplest and most reliable one for monitoring this crucial process step.

“The progress of the boron volatilization is monitored by taking samples from the liquid silicon and performing resistivity- and conductivity-type measurements.”

Once the target resistivity is reached, the purified liquid silicon is either transferred into a cooling unit, where it randomly cools, or to another controlled segregation step. In fact, as the PHOTOSIL project progressed, it was found that this additional post-plasma segregation is necessary, since the plasma treatment introduced oxygen (from the plasma gas), carbon (from the graphite crucible) and aluminium (from the thermal insulating material) into the silicon. These three elements are present in stable compound form at the temperature in question, around 1500°C, and were found to segregate well.

Impurity concentrations for selected impurities following this entire PHOTOSIL purification process are listed in Table 2. The chemical analysis technique used for the determination of the concentrations of these impurities was GDMS and the metal concentrations were below the detection limit. These data reflect the status of the PHOTOSIL project in 2008/09 using the consolidated base purification process.

It can be seen that the boron and phosphorous concentrations are still relatively high; however, acceptable results were still achieved after crystallization of multicrystalline ingots from this silicon and processing of solar cells from this material. In total, 10 multicrystalline ingots of 60kg each have been crystallized with the intention of verifying the reproducibility of the entire process chain. The crystallization process and equipment used for the these ingots feature some innovative aspects in terms of heat management, high thermal gradients at the crystallization interface and time cycles for the crystallization operation [7].

Detailed characterization results from these 10 ingots are available [8]. Among other data, this publication gives a detailed analysis of the carbon and oxygen concentrations and their influence on the material quality after crystallization. In summary, the average

Element	B	P	Fe	Al	Ti	Cu
	ppm_w	ppm_w	ppm_w	ppm_w	ppm_w	ppm_w
PHOTOSIL SoG Silicon	1.5	4.0	<5.0	<2.0	<2.0	<2.0

Table 2. GDMS chemical analysis data of characteristic impurities in the silicon obtained through the standard PHOTOSIL process.

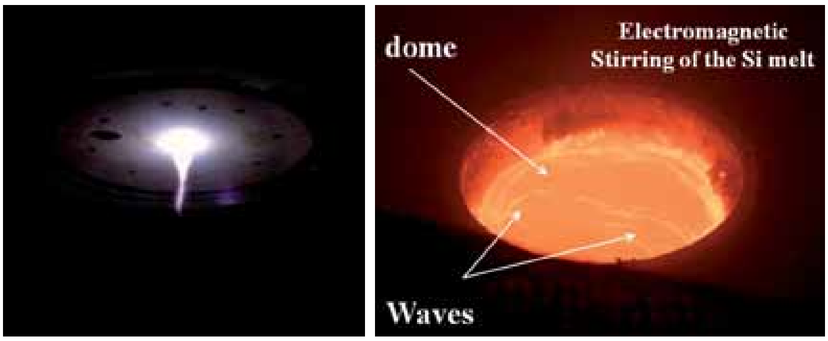

Figure 5. Photos of the inductive plasma gas (left) and the surface of the molten silicon inside the graphite crucible used during plasma purification. The visible waves at the surface of the silicon are an indication of the electromagnetic stirring.

Element	B	P	Fe	Al	Ti	Cu
	ppm_w	ppm_w	ppm_w	ppm_w	ppm_w	ppm_w
PHOTOSIL SoG Silicon	~ 0.3	~ 1.0	<2.0	<2.0	<2.0	<2.0

Table 3. GDMS chemical analysis data of characteristic impurities in the silicon obtained by the optimized PHOTOSIL process in 2010.

	h (%)	V_{oc} (mV)	I_{sc} (mA/cm²)	FF(%)
Average	17.4	617.5	35.5	79.5
Best cell	17.6	619.3	35.5	79.9

Table 4. IV characterization results of the solar cells processed from the monocrystalline ingot, made from ultimately purified PHOTOSIL silicon.

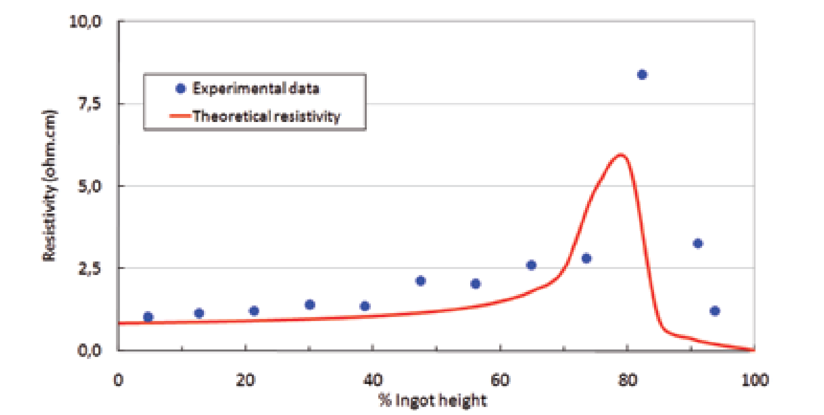

Figure 6. Resistivity distribution of the multicrystalline silicon ingot crystallized from ultimately purified PHOTOSIL silicon.

usable p-type part of the ingots with a resistivity range between XΩcm and YΩcm was 82% – very close to the objectives of the PHOTOSIL project. The change in conductivity type at a certain ingot height is due to the difference in segregation coefficient of phosphorous (0.35) and boron (0.8) and the fact that both are present in important concentrations in the starting material prior to crystallization. The more efficient segregation of phosphorous leads to its accumulation towards the upper part of the ingot and at a certain point to compensate for the boron concentration.

Using a standard industrial-type screen-printing process at the INES Restaure platform, cell efficiencies obtained reached 14.5%, with top efficiencies exceeding 15.5% – also satisfying the PHOTOSIL objectives. However, due to the presence of boron and oxygen in this material, some of the cells showed light-induced degradation in the range of 1% absolute.

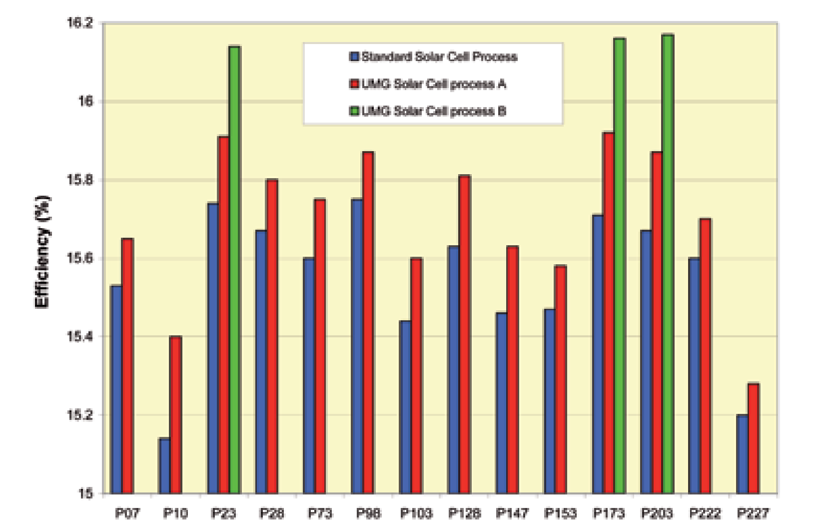

Figure 7. Efficiency distribution as a function of ingot height of solar cells obtained from the multicrystalline silicon ingot from ultimately purified PHOTOSIL silicon.

PHOTOSIL: optimized purification process and results

In order to demonstrate the potential of the purified metallurgical silicon obtained using the PHOTOSIL process, all of the various processing steps of the generic process flow presented in Fig. 3 underwent optimization in 2010 with first-generation pilot line equipment. This work also gave valuable input for design of second-generation purification equipment, which is currently underway. One important goal of this purification campaign was to demonstrate the competitiveness of PHOTOSIL-purified metallurgical silicon. Table 3 summarises the chemical analysis data, again obtained by GDMS of the ultimately purified PHOTOSIL silicon. Comparison of the values in Tables 2 and 3 shows that clear progress has been made on these standard values from 2008/09.

This ultimately purified silicon was again used to crystallize a 60kg multicrystalline ingot as well as a 15kg, 6-inch CZ ingot, neither of which had additional dopants applied. Both ingots were cut into 125 x 125mm² wafers (pseudo-square in the case of the CZ ingot), which were electrically characterized and processed into solar cells, again at the INES Restaure platform, detailed results of which have been published recently [10]. The most important results are summarized here, starting with the multicrystalline ingot, whose resistivity distribution as a function of ingot height is shown in Fig. 6.

As shown in the graph, the obtained resistivity in the p-type part is around 1.0Ωcm and above; the conductivity type change from p-type to n-type occurs at around 80% of the ingot height.

Three different processes were applied to the solar cells at the INES Restaure platform, all using screen-printed metallization – a standard one and two specially adapted to UMG-type silicon. Efficiency results from all three processes are summarized in Fig. 7, showing top efficiencies of 16.2%. Furthermore, these cells proved to be almost free of light-induced degradation, which came in at less than 1% relative.

From the same ultimately purified PHOTSIL silicon, an entirely monocrystalline CZ ingot was obtained, which is in itself already a material quality indicator of very low impurity content. The impurities effectively act as nucleation centres during crystallization and can lead

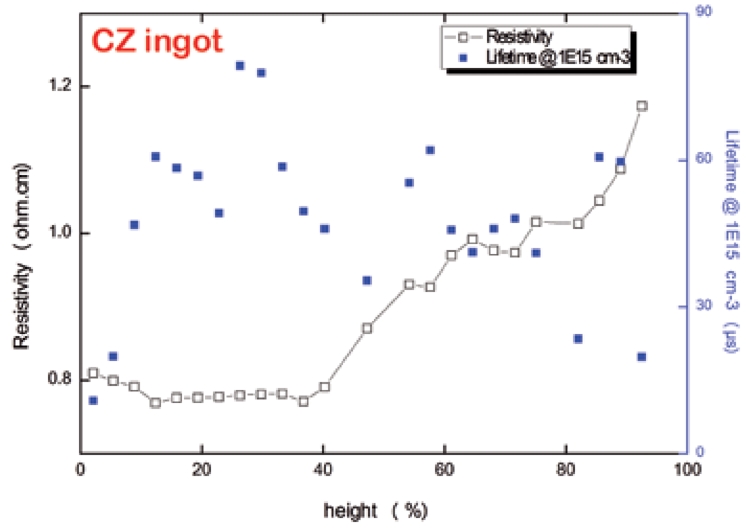

Figure 8. Resistivity and carrier lifetime data as a function of ingot height from the monocrystalline CZ ingot, crystallized from ultimately purified PHOTOSIL silicon.

to the appearance of dislocation and grain boundaries at certain stages.

Looking at the electrical characterization results in Fig. 8, one can see a resistivity between 0.8 and 1.2Ωcm throughout the ingot and considerably higher lifetimes in the order of 50 to 60µs. Solar cell data are summarized in Fig. 9 in terms of efficiency distribution as a function of ingot height, and more detailed IV data are presented in Table 4. The cells were again processed at the INES Restaure platform using screen-printed metallization and an industrial-type process.

As shown in Fig. 9, the efficiency distribution throughout the entire ingot is very uniform at high absolute values, far exceeding 17.0%. The IV data in Table 4 show that the average efficiency is 17.4%, with a best solar cell reaching 17.6%. To the authors' knowledge, these values are among the highest so far reported for solar cells processed on wafers of purified metallurgical silicon.

Conclusions

The quality and performance potential of PHOTOSIL silicon obtained by purification of metallurgical-grade silicon can be demonstrated by an optimized purification process. These encouraging results are in line with a recently published analysis of the economical viability of purified UMG silicon [11], provided the cost objectives of the PHOTOSIL projects are reached. The study defined economical breakeven points by relating solar cell efficiencies on purified UMG material to cost advantages of this material compared to solar-grade silicon obtained from the chemical purification route. To render it economically viable, purified UMG silicon that yields 15% solar cell efficiencies needs to be at least 12% lower in cost than chemically-purified solar-grade silicon.

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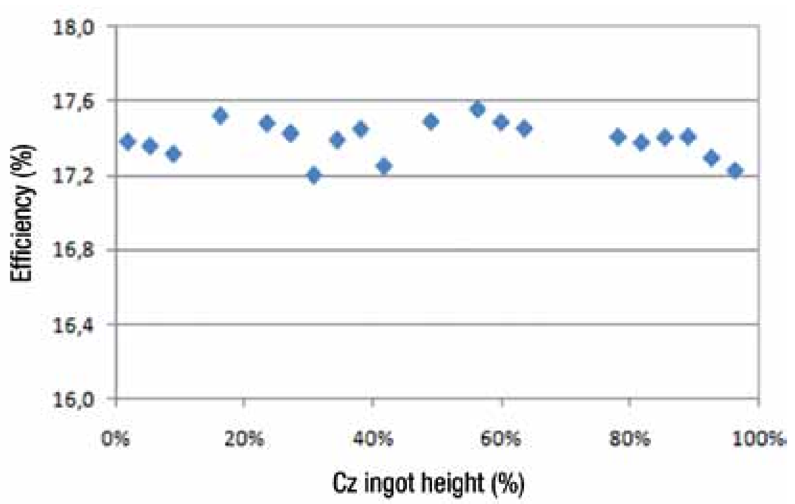

Figure 9. Solar cell efficiencies as a function of ingot height in case of the CZ ingot, made from ultimately purified PHOTOSIL silicon.

About the Authors

Roland Einhaus joined Apollonsolar in 2002, and currently holds the role of R&D Director. He has been working in PV research since 1994, focusing on the various steps of the silicon-based PV value chain from silicon purification and crystallization to silicon solar cell processes, characterization and PV modules. Before joining Apollonsolar, he worked at Photowatt, IMEC and the UNSW.

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