FoXy-DEVELOPMENT OF SOLAR-GRADE SILICON FEEDSTOCK FOR CRYSTALLINE WAFERS AND CELLS BY PURIFICATION AND CRYSTALLISATION

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ABSTRACT

This work reports on the results obtained in the EU project FoXy (contract nr SES6-019811). FoXy has been carried out in the 6th Framework Program in the Sustainable Energy Systems. It consists of a Europe-wide consortium of small and medium size enterprises, research institutes and universities. The project has aimed at developing cleaning and crystallisation processes for metallurgical SoG-Si feedstock, optimize associated cell and module processes, and set parameters for these types of feedstock. The major goals of the project have been: (i) achieve a significant cost reduction through more efficient cleaning processes for raw materials, (ii) secure high volume production of SoG-Si, (iii) develop recycling techniques for end-of-life products, (iv) shorten the energy payback time significantly, (v) manufacture wafers on a large-scale industrial production line 150x150mm^2 aiming at 16-17% cell efficiency with increased yield. This work summarizes the highlight results of this three-year project.

Keywords: Silicon, Feedstock, Solar cell, Efficiency

INTRODUCTION

FoXy is a R&D project which aims at developing refining and crystallisation processes for metallurgical SoG-Si feedstock, optimise associated cell and module processes, and set parameters for these types of feedstock.

Under the realistic assumption that Si-wafer based PV modules will dominate the market in the coming decade, the FoXy partnership has focused on the need of the PV market for low price and high quality solar grade silicon (SoG-Si) feedstock by:

1. Further developing and optimising refining, purification, and crystallisation processes for metallurgical SoG-Si feedstock, as well as for recycled n-type electronic grade Si.
2. Optimising associated cell and module processes.
3. Setting input criteria for metallurgical and electronic n-type silicon to be used as raw materials for SoG-Si feedstock.
4. Transferring the technology from laboratory to industrial pilot tests.

The overall objectives of the FoXy project have been:

1. Achieve a significant cost reduction (down to 15€ per kg) through more efficient cleaning processes for raw materials.
2. Secure high volume production of SoG-Si.
3. Develop recycling techniques for end-of-life products.
4. Shorten energy payback time to six months.
5. Manufacture wafers on a large-scale industrial production line 150x150mm^2 aiming at 16-17% cell-efficiency with increased yield.

The achievement of these aims allows the PV industry to strengthen its position on the world market and fulfil the EU policy targets. The project has had a total budget of 4.7 M€, of which 2.7 M€ has been the requested EC contribution.

A schematic structure of the project is shown in Figure 1. The project has been subdivided into the following tasks:
WP1 - Feedstock via direct route
WP2 -Refining of highly doped feedstock and production of n-type ingots
WP3 -Electrochemical refining of metallurgical feedstock
WP4 -Material characterisation
WP5 -Cell process optimisation
WP6 -Modules and Recycling 'end of life'
WP7 -Integration &Exploitation

SINTEF has been coordinator for the project. The FoXy consortium has consisted of 11 partners, divided in:

- **Industry partners**
  Deutsche Solar (DE), Isofoton (ES), FESIL (NO), PILLAR (UA), SUNERGY (NL), ScanArc (SE)
- **Universities**
  NTNU (NO), UNIMIB (IT)
- **Research Institutes**
  ECN (NL), ISC (DE), SINTEF (NO)

The FoXy project started on January 1st, 2006 and has been running for 36 months. During this period, the project has achieved important results. Among these, new feedstock processing routes have been investigated, refining techniques have been developed and a new passivation process has been patented, etc. In this work, we present and summarize some of the major results from the subprojects WP4 and WP5.

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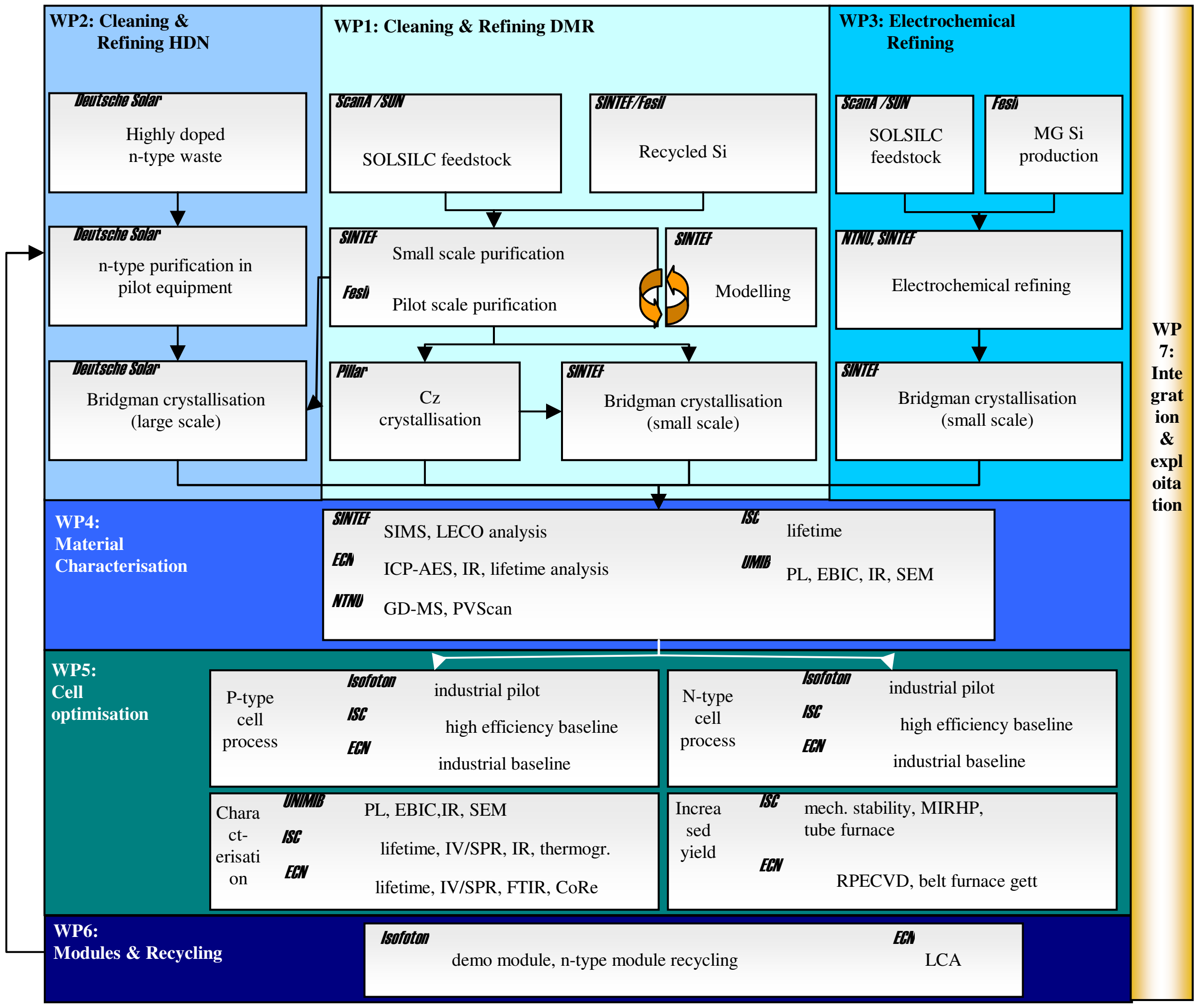

Figure 1: Schematic structure of the FoXy project.

RESULTS

Different types of silicon ingots for solar cells have been produced and studied within the FoXy project. Table 1 summarizes some of these ingots.

Table 1. List of the ingots made in the FoXy project, characterized and reported in this work.

Ingot	Crys.	Type	Feedstock
FS1	mc	p-n	SoG-Si without filtration
FP1	Cz	p	Cz-Si +10%SoG
FP2		p (ref)	100%EG+B
FP6		n	Cz-Si+10%SoG
FP7		n (ref)	100%EG+P
FS9	mc	p	10%SOLSIC*-Si +B
FS10		p	25%SOLSIC*-Si
FS11		p (ref)	Reference (100% EG)+B+P
F1	mc	p	Off-cuts (Uncompensated)
F2		p-n	Off-cuts (Compensated)
F3		p-n	Off-cuts (Highly compensated)

* Solsic process- ref [1]

The feedstock to produce the ingot FS1 was made by carbothermal reduction of very pure quartz and carbon (direct route). This process results in an upgraded metallurgical grade silicon (UMG-Si) which features lower energy consumption and higher purity compared to conventional metallurgical Si, but has to be further purified to satisfy the requirements for the production of efficient solar cells. Ingot FS1 was grown on a directional solidification (DS) pilot-scale furnace. Ingots FS9, FS10 and FS11 were made with a mixture of feedstock from the Solsic process [1] and commercially available polysilicon. They were also grown in a DS pilot-scale furnace.

Ingots FP1, FP2, FP6 and FP7 were grown in a Czochralski furnace using a mix of 10% of SoG-Si feedstock from direct carbothermal reduction and 90% of pure electronic grade silicon. FP1 and FP2 were p-type (target resistivity 2Ωcm), while FP6 and FP7 were n-type. FP6 had resistivity in the range 0.5 - 10 Ωcm (larger range due to compensation), while FP7 had 2-3 Ωcm. After crystallization the ingots were cut into around 1200 wafers (125x125 mm^2) of 200µm thickness.

Ingots F1, F2 and F3 were grown from off-cut materials in a DS industrial furnace. In this case, three levels of compensation were investigated and compared.

For each ingot, chemical composition, resistivity and minority carrier lifetime were measured. The lifetime of the as-grown material was <2 for all ingot positions in FS1, between 20 and 40 µs for FS9 and FS10 (Figure 2), 10µs for all ingot positions in FP1. The lifetime in the uncompensated ingot F1 (max

36µs) was higher than in the compensated ingots F2 (max 25µs) and F3 (max 17µs).

Ingot FS1 has the highest amount of impurities among the ingots investigated. The distribution of B, P, Al and Fe along the ingot height is shown in Figure 3. Also the measured dissolved oxygen and oxygen precipitates density are very high. Therefore, this ingot has the lowest lifetime. Optical, chemical and electrical characterization of this ingot has been reported [2,3].

As expected and as shown in Figure 4, the resistivity distributions of ingot F1 (no compensation) and F2 (weak compensation) are quite flat, whereas there is a strong increase towards the top of the ingot in the case of F3, due to the strong compensation of this ingot.

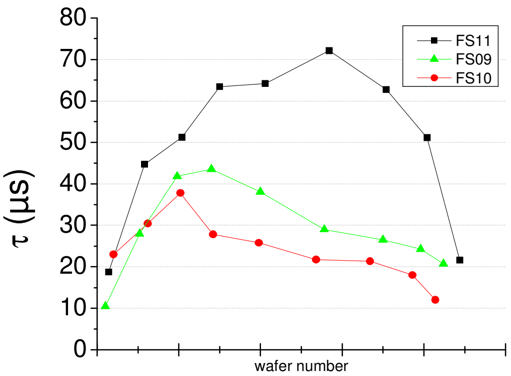

Figure 2: Lifetime of ingots FS9, FS10 and FS11.

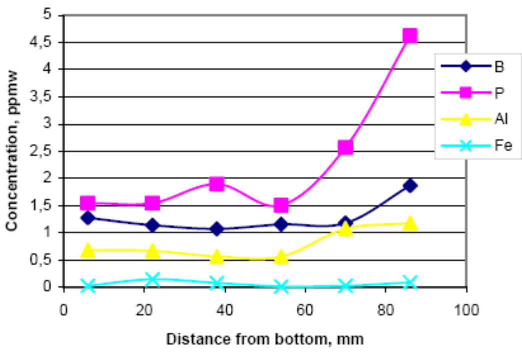

Figure 3: Chemical concentration of the B, P, Al and Fe for ingot FS1 as measured by GDMS.

For all ingots, except FS1, it was shown that solar cell processing can give conversion efficiencies which are relatively good. This is mostly due to removal of detrimental impurities during the P-gettering process. As an example, the lifetime of ingot FP1 increased from 10 µs to > 100 µs after solar cell processing, as shown in Figure 5.

The solar cells made from the ingot FP1, on an untextured front surface and an industrial cell process, had efficiencies of up to 16.7% (17.1% on textured surface). In addition, as no decrease towards ingot positions with higher resistivity and higher compensation (low mobility of the majority charge carriers) was visible, the high compensation of the samples from the bottom of the ingot seems to have no detrimental impact on the cell efficiency and consequently on the diffusion length of the minority charge carriers. More details on the characterization and solar cell properties of this ingot have been reported [4].

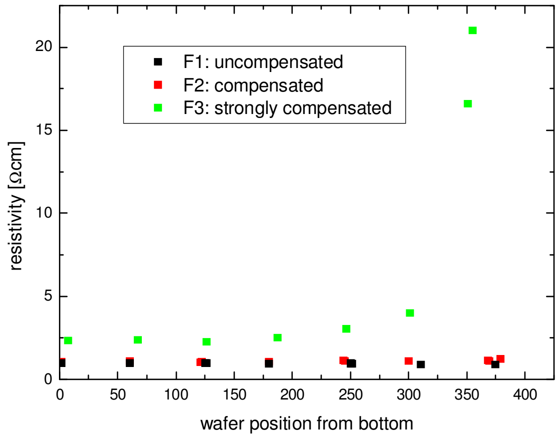

Figure 4: Lifetime of as-grown and after cell process for wafers from ingot FP1.

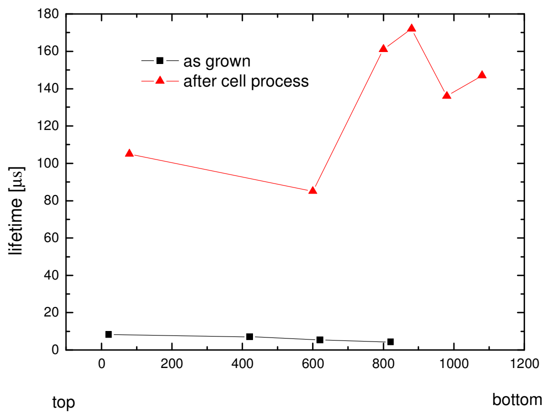

Figure 5: Resistivity measurements for ingots F1, F2 and F3.

In addition to these results, it is worth mentioning that during the project period, baseline solar cell processes for both p- and n-type were developed. A new interconnection of p-type solar cells was patented by one of the project partners (ISC Konstanz), as shown in Figure 6. Furthermore, a new passivation process was developed. It consists of an ultrathin SiO2 layer formed by nitric acid oxidation of Si (NAOS) combined with SiNx to passivated n-type solar cells. This process as shown to give higher internal quantum efficiency of the solar cells (Figure 7) [5].

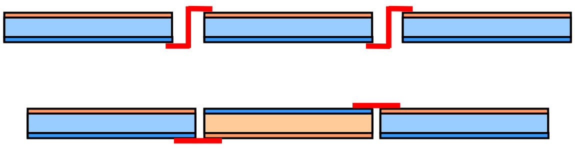

Figure 6: Interconnection of p-type solar cells in a standard module (top) and innovative alternate interconnection of p- and n-type solar cells in a pn-module (bottom) (pending patent by ISC Konstanz).

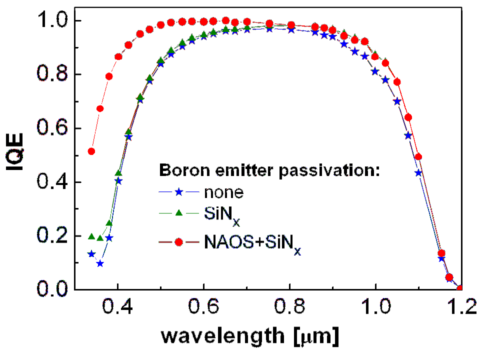

Figure 7: Internal quantum efficiency of the n-type solar cells measured for different passivation methods for boron emitter.

Table 2 summarizes the best efficiencies of selected solar cells produced within the FoXy project. Note that no solar cells were manufactured from ingots FS1 and F3 (Table 1).

Table 2. Best solar cell efficiencies achieved within the FoXy project.

Ingot	Crys.	Type	Size [mm^2]	Best Eff. [%]	Ref.
FP1	Cz	p	156x156	16.5	ISC
FP2		p (ref)	156x156	16.8	ISC
FP6		n	125x125	17.5	ECN
FP7		n (ref)	125x125	17.7	ECN
FS9	mc	p	125x125	15.8	ISC
FS10		p	125x125	15.6	ISC
FS11		p (ref)	125x125	15.7	ISC
F1	mc	p	156x156	15.0	ISC
F2		p	156x156	14.5	ISC

Note that the efficiency difference of about 1% absolute between p- and n-type Cz-Si cells is also due to an advanced cell structure for n-type cells which was developed within the project leading to record efficiencies for screen printed structures of 18.3% on n-type Cz-Si substrates [5].

CONCLUSIONS

This work summarizes some of the major results achieved in the European project FoXy.

1. The results presented show that solar cells with good efficiencies can be made with SoG silicon and blended feedstock. These achievements will secure high volume production of SoG-Si for the PV industry.
2. Good efficiency solar cells can also be made from recycled off-cut materials with significant cost reduction.
3. It has been shown that wafers on a large-scale industrial production line 150x150mm^2 with > 16% cell efficiency with increased yield can be manufactured.

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