Project no. COOP-CT-2002-508202

SISI
Silicon for solar cells at low costs on an intermediate scale

a Co-operative Research Project

Publishable final activity report

Period covered: *from month 13 to month 26*	Date of preparation: *December 2006*
Start date of project: *15 September 2004*	Duration: 26 *months*

Project coordinator name: *Ms. Boukje E. Ehlen, MSc*
Project coordinator organisation name: *Energy research Centre of the Netherlands (ECN)*

Revision: *[vs0.1 December 2006]*

This document provides an overview of the public project summary, articles published based on SISI results and conference contributions related to the work executed in SISI.

1.1 Publishable summary of the project

Crystalline Silicon photovoltaic (PV) cells will be the dominant technology for the next 20 years with a 30% average annual growth rate. Currently 17% of module costs relate to feedstock. Even though cells will be thinner and more efficient, demand for solar grade silicon (SoG-Si) will grow from the current 18,000 metric tons (costs more then 30 €/kg) to over 50,000 metric tons per year in 2010. A dedicated SoG-Si source is needed or growth will stagnate, jeopardising compliance with the EC White Paper objectives.

SISI aimed at alleviating the PV industry dependence on the limited and expensive supply of silicon from the electronics industry. The consortium is convinced that the most promising option to provide the very large quantities of high-purity silicon required is the direct carbothermic reduction of quartz. In SISI, major European industry and institutes were included with expertise in ultra-high-purity quartz, silicon production & purification, and solar cell-processing. The project's goal was to demonstrate on an intermediate scale (approx. 200 kg per batch) an integral direct carbothermic route for SoG-Si production that can be industrialised.

In the preceding SOLSILC project, the direct carbothermic process was developed based on a selected combination of raw materials and a two-step silicon production process with silicon carbide as an intermediate product. In the SPURT project the most economical large-scale purification techniques were selected. In the SISI project this combination of technologies is integrally scaled up with the following innovations:

- optimised raw material preparation and furnace operation for a stable and high-yield Si-production, suitable quartz purification and pelletising techniques.
- transfer of the purification techniques to intermediate scale, including new steps such as filtering.

The SISI project was organised in 6 work packages following the value chain and production steps: Raw materials, Si-production, Purification, Wafer & cell process, Technology implementation and Consortium management. Several integral production runs have been executed from raw materials to cells. These runs have proven the quality and reproducibility of the results.

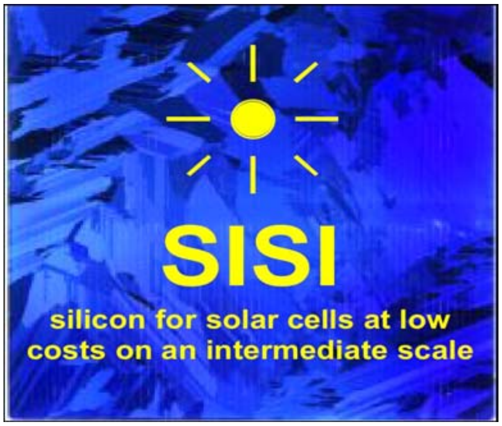
The SISI project was very successful in achieving the goals and objectives as planned. Most prominent results achieved in the project are listed below:

- With a ‘quartz for solar cells’ programme, we adapted separation and refining methods and assessed the form of the quartz in order to reduce or improve the pelletising step. Based on the results of this programme, we have selected the best price / benefit alternative.
- A study was made on possible optimisation of carbon black supply. Both Scanarc and SINTEF have contributed in developing new industrial processes for production of high purity and “SiO reactive” carbon black. The production of SiC and silicon were done with selected high purity qualities from commercial producers, and proved to be satisfactory. Alternative processes will be considered in the future.
- To obtain a high quality SiC material as feed to the smelting furnace, a special designed pilot production unit has been developed. The up-scaling and optimizing of the unit with regard to a large scale pilot unit will be continued outside SISI during 2007.
- During the smelting tests in year I, we developed a well operating furnace design for high purity silicon smelting. Also the new reaction concept was proved and a stable and predictable Si production was established. In spite of this we encountered problems with the physical behaviour of the charge during long term operation . Our main work during year II has been devoted to the development of the pellets. The smelting tests have been used in particular for testing new types of pellets. Further development of the solar grade silicon smelting process will continue without any interruption outside SISI in close cooperation with the commercial silicon producer.
- Models and calculations of settling and filtration have been carried out, and the results are verified by small scale testing. Design and construction of a filter unit for removal

of SiC in intermediate and pilot scale are finished, and implemented, according to the objective of the project.

- In the Kerf-program a suitable method for reclaiming silicon from spent sawing sludge has been tested. Promising results have been obtained and the consortium participants in SISI will continue the development of this work outside SISI during 2007..
- From three different ingots, wafers were produced and cells were processed using industry standard cell processing techniques. The efficiency levels have been compared with other SoG-Si feedstock sources. The measured efficiency of the SISI cells was 1% below reference for n-type material (13.7% on a 33% SOLSILC wafer) and 4% below reference for p-type material (7.0% on a 100% SOLSILC wafer). Based on these result it was estimated that p-type wafers need to be 98% cleaner for the 2% limit that was set as a goal for the SISI project. N-type wafer are significantly more tolerant to impurities.
- To enable the exploitation of the knowledge developed in SISI, the SISI consortium partners established an IPR company called SOLSILC Development Company (SDC). Together with the establishment of this company an IPR agreement between the SISI partners has been signed to organise exploitation of IPR from the SISI project.
- Several possible partners have been evaluated. SDC has granted a licence with a investment company and signed a long lasting R&D contract to scale up the SOLSILC concept through a large scale pilot phase into industrial scale production
- A plan has been made for the development and realisation of a pilot facility, aiming at a start of pilot production in 2007/2008.

The SiSi results have been evaluated and assessed with several market parties. Raw material suppliers, Silicon producers, refining companies as well as wafer and cell manufacturers have shown interest in the results and the SOLSILC/SISI technology. As predicted some years ago by the SOLSILC partnership, the actual demand for silicon is much higher than the supply and prices are still rising. The present shortage of feedstock increases prices for SoG-Si dramatically (current prices end of 2006 on spot market are higher than 300 €/kg as a result of the growing shortage). Several companies have shown interest in the SoG-Si to be produced and have requested quotations to supply SoG-Si even though the development of the technology is not yet completed.
Market parties have even shown interest for intermediate products and even asked for participation in the SOLSILC concept. The time schedule for this R&D cooperation between the SDC partners and the selected investment company is end 2010.



1.2 Published articles and conference contributions

During the SISI project we could only share public information, of general nature. It is very difficult to protect the knowledge, so we worked very carefully with non disclosure agreements and confidentiality agreements. However for scientific purposes and for marketing purposes the RTD partners ECN and Sintef published several times in different bodies.

All foreground information that was judged by the project partners to belong to the public domain has been presented at international conferences and published in journals dedicated to Photovoltaics issues. This has been done after a careful selection of the information to be published and on the basis of a mutual consent prior to making it available to the public. Some examples are stated below.

- A.N. Waernes, O.S. Raaness, E.J. Øvrelid, B. Paul, L.J. Geerligs, G.P. Wyers, S. Santen and B. Wiersma, The Solsilc route to low-cost solar grade Silicon. PHOTON International, 2nd Solar Silicon Conference on April 11, 2005, in Munich, Germany. Invited presentation (see Annex I).

- L.J. Geerligs, P. Manshanden, G.P. Wyers, E.J. Øvrelid, O.S. Raaness, A.N. Waernes, and B. Wiersma, SPECIFICATION OF SOLAR GRADE SILICON: HOW COMMON IMPURITIES AFFECT THE CELL EFFICIENCY OF MC-SI SOLAR CELLS. Proceedings of the 20th European Photovoltaic Solar Energy Conference, 6-10 June 2005, Barcelona, Spain, p. 619-622.
  Oral presentation and article (see Annex II).

- L.J. Geerligs, DIRECT CARBOTHERMAL REDUCTION TO LOW-COST SOLAR GRADE SILICON. Photon International 3rd Solar Silicon Conference, Munich, 3 April, 2006. Invited presentation (see Annex III).

- Progress of the SISI project. European Commission Photo Voltaic Technical Days, 17 and 18 May 2006, Brussels.
  Poster (see Annex IV) and presentation.

- L.J. Geerligs, P. Manshanden, I. Solheim, E.J. Ovrelid, A.N. Waernes, IMPACT OF COMMON METALLURGICAL IMPURITIES ON MC-SI SOLAR CELL EFFICIENCY: P-TYPE VERSUS N-TYPE DOPED INGOTS. Proceedings of the 21st European Photovoltaic Solar Energy Conference, 4-8 September 2006, Dresden, Germany, p. 1285-1288.
  Poster presentation and article (see Annex V).

- L.J. Geerligs, IMPACT OF SPECIFIC METALLURGICAL IMPURITIES IN SILICON FEEDSTOCK ON SOLAR CELL EFFICIENCY, AND POTENTIAL BENEFITS OF N-TYPE DOPING. International workshop on Science an d Technology of Crystalline Si Solar Cells. 2-3 October 2006, Institute for Materials Research, Tohoku University, Sendai, Japan. Presentation and extended abstract.

Annex I

A.N. Waernes, O.S. Raaness, E.J. Øvrelid, B. Paul, L.J. Geerligs,
G.P. Wyers, S. Santen and B. Wiersma

THE SOLSILC ROUTE TO LOW-COST SOLAR GRADE SILICON.

Invited presentation at the PHOTON International, 2nd Solar Silicon Conference

April 11, 2005, Munich, Germany.

The SOLSILC Route to Low-Cost Solar Grade Silicon

A.N.Waernes, E.J.Ovrelid, O. S. Raaness, Bart Paul,
L.J. Geerligs, G.P.Wyers, Sven Santen and B. Wiersma

Presented by Research Director Aud Nina Waenes
SINTEF Materials and Chemistry
Department of Metallurgy

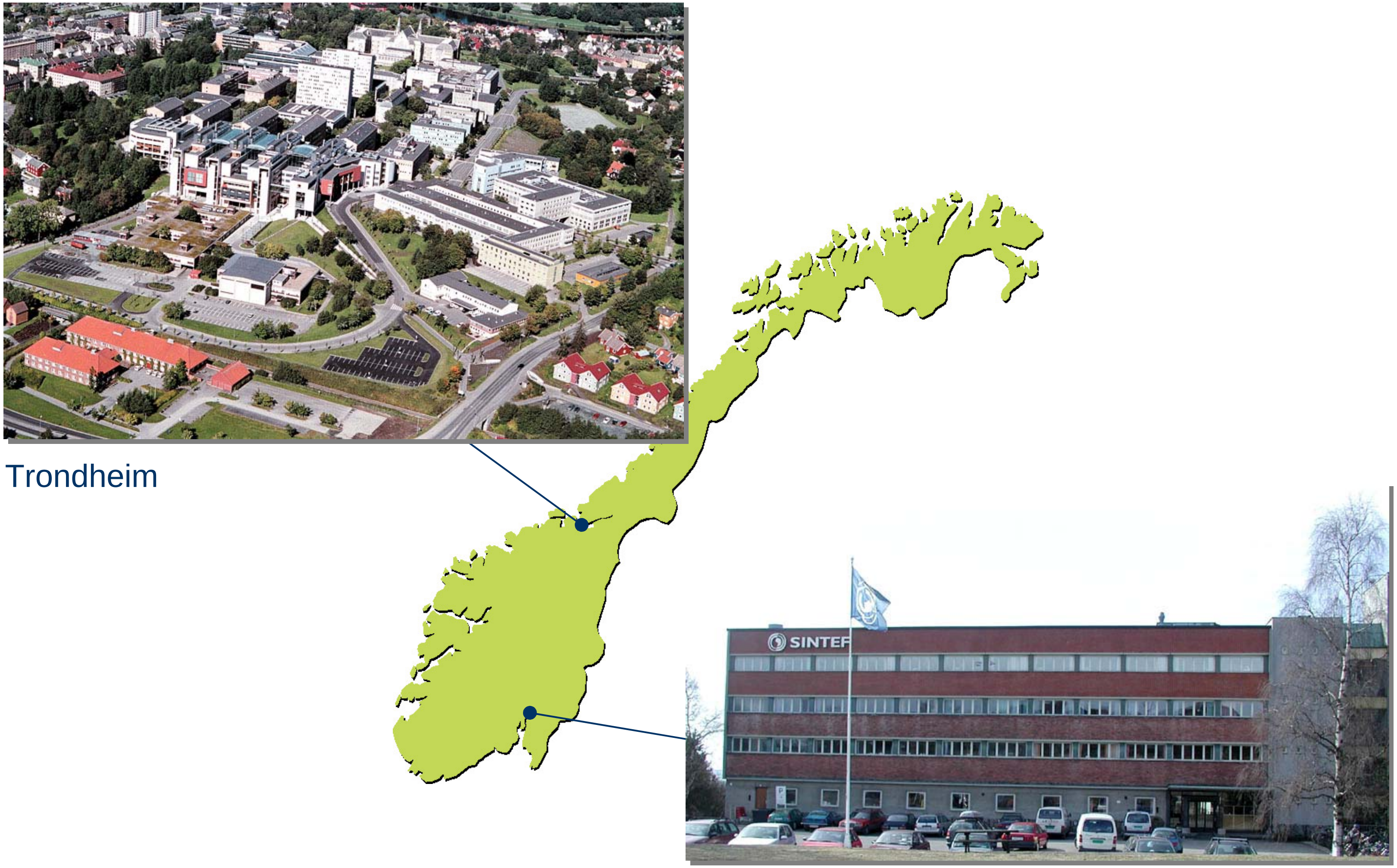
2nd Solar Silicon Conference April 11 2005, Munich

Acknowledgements: EC, EESD programme
Projects ERKG-1999-0005, ENK6 – CT- 2001- 30006
and COOP-CT-2004-508202

Outline

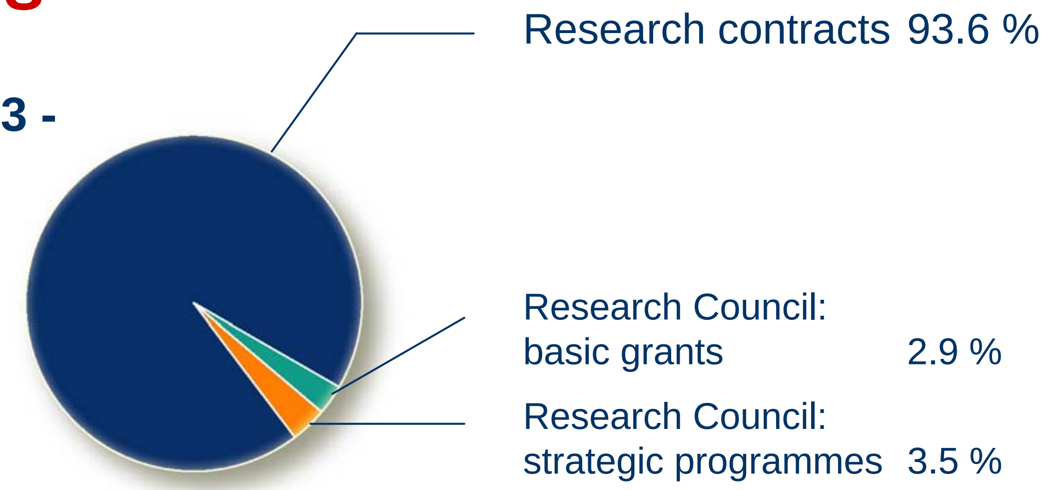
- Introduction
- Feedstock Solar Grade Silicon
- SOLSILC process
- Outlook

SINTEF in Trondheim and Oslo



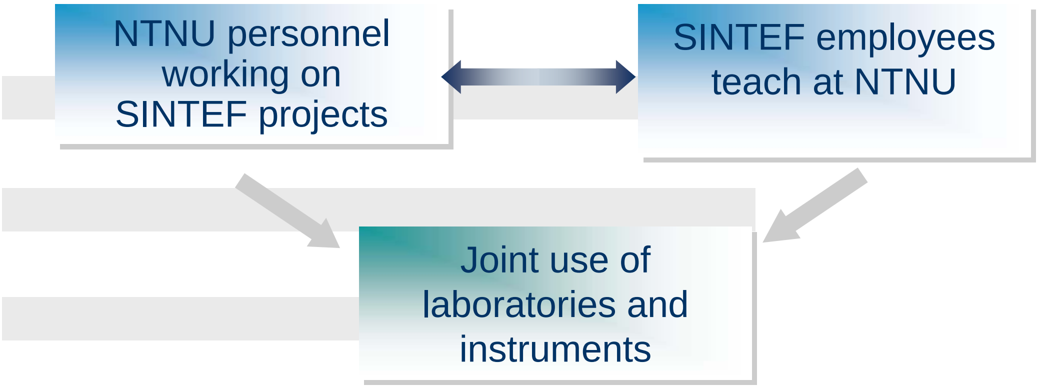
SINTEF Group – Technology for a better society - Key figures

SINTEF Group turnover in 2003 - NOK 1,618 billion



SINTEF has 1750 employees, about 1400 in Trondheim and about 350 in Oslo with offices in Bergen and Stavanger

Our Partners:



- NTNU - The Norwegian University of Science and Technology 20 000 full-time students and ca 1 600 scientific employees
- University of Oslo, UiO, Faculty of mathematics and natural sciences:4 330 full-time students ca 664 scientific man-years

Solar energy

- The amount of solar energy supplied to the earth is in the order of 10000 times the world energy consumption.
- Using current technology, solar cells may produce all the consumed electric energy in the USA by covering a land area of ca 0.4%. A similar number applies for Norway where the average annual radiated effect received from the sun is in the order of 1000 kWh/m^2.
- The increasing demand for renewable forms of energy is making solar energy an important part of the energy supply system for the future.
- The costs of producing solar cell modules have been significantly reduced during the last decade as manufacturing costs per watt have decreased from more than US$ 6/Wp to less than US$ 3/Wp today.
- Since the mid 1980s, the average annual growth in produced installed solar electrical power capacity have been approx 25%.
- With 100 000 installations, Norway has more solar cells per capita than any other country in the world. Solar cells supply remote areas and technical installations.

Solar cells:
The market grows faster than anticipated

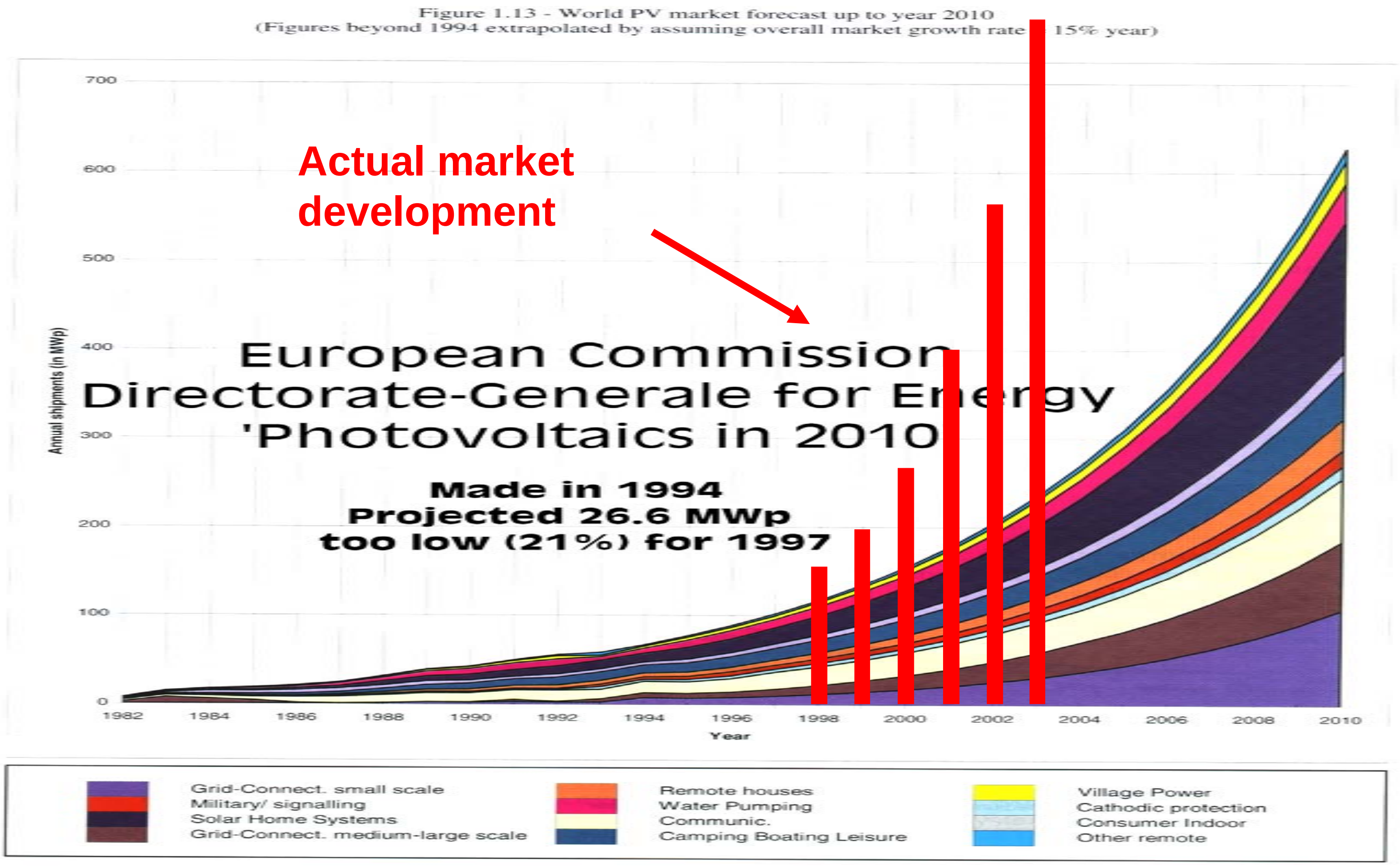


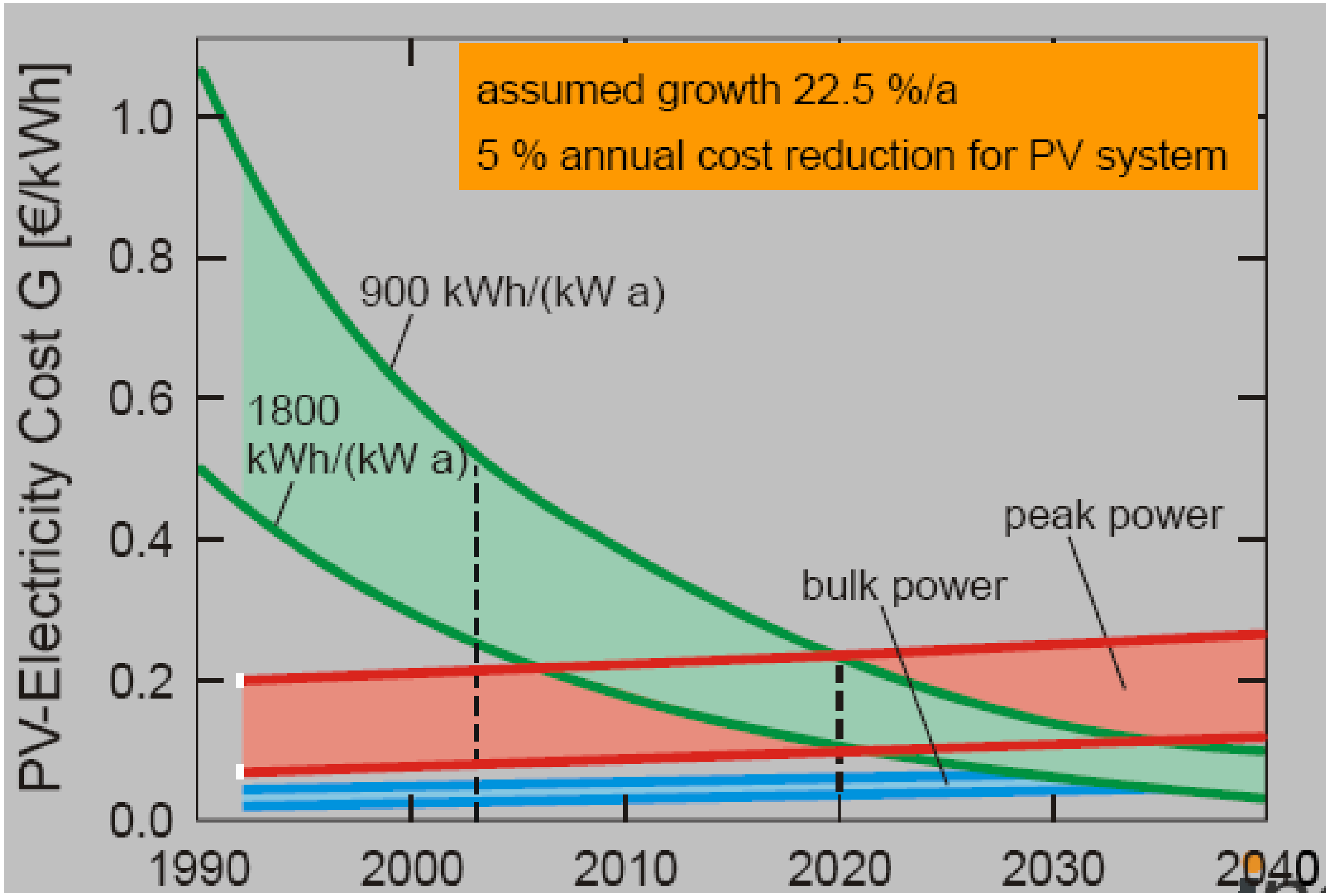
Figure 1.13 - World PV market forecast up to year 2010
(Figures beyond 1994 extrapolated by assuming overall market growth rate 15% year)

Actual market development

European Commission Directorate-Generale for Energy 'Photovoltaics in 2010'

Made in 1994
Projected 26.6 MWp
too low (21%) for 1997

Solar electricity is becoming competitive in certain areas during peak periods (daytime)



Source: prof. J. Werner, univ. Stuttgart

Long term outlook

Indicative figures what could be the demand for Si by 2020

- growth to 45 GWp
- c-Si 70% of production
- Si consumption 6g/Wp
- Si demand 2x10^5 ton/a

Why Norway?

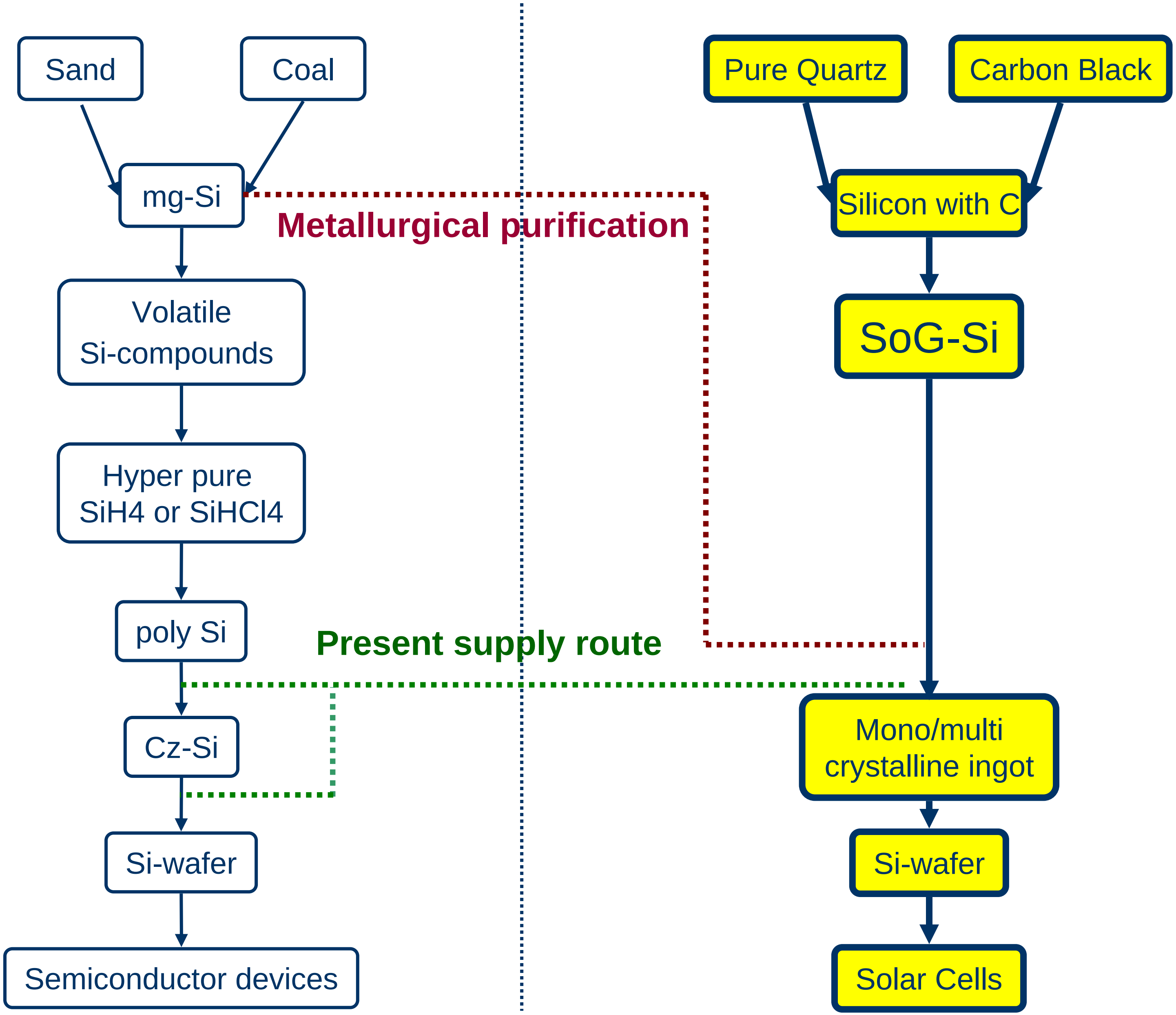
- Norway has for decades been the world's main producer of raw material silicon for solar cells.

- **High purity quartz**
  Norwegian Crystallites produces high purity crystalline quartz for high tech end uses. This raw material in cleaned up to high standard crystal quartz products.

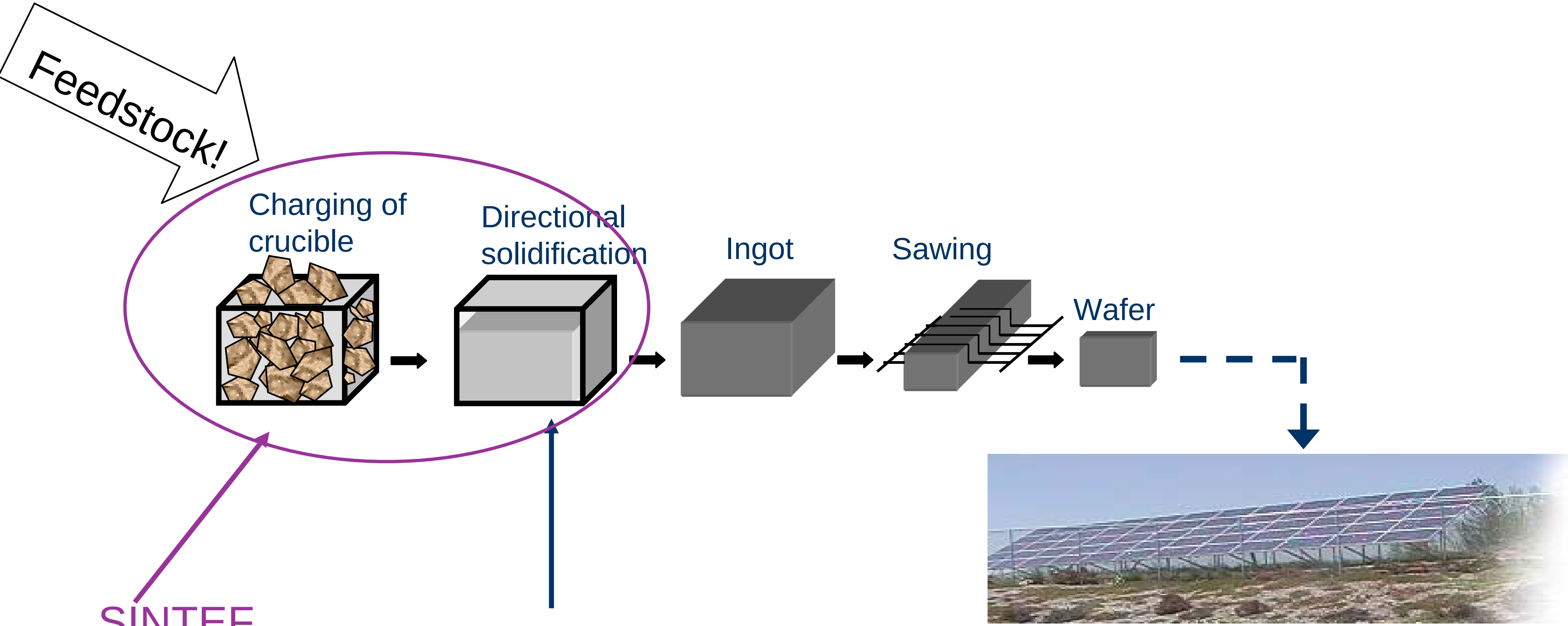
- **Carbon Black**
  SINTEF has developed a process for production of Carbon Black and hydrogen. High purity Carbon Black is very suitable as a raw material for SoG-Si.

Solar cell wall at NTNU

Silicon value chain – Cost effective alternatives



Value chain from feedstock to Solar cells



SINTEF spinoff:

CruSiN as

Crucible technology

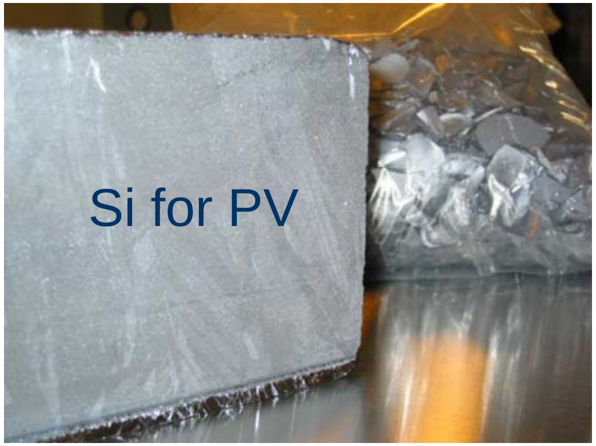
HELIOSI:
A unique test laboratory
at SINTEF & NTNU
for directional solidification

Feedstock for solar cells

Electronic grade
Spec. < 5 ppb

High End
approach

Lowering specs
to reduce costs


Si for PV

Improving purity to match
PV requirements

Low End
approach

Upgraded metallurgical
or Direct route
Spec: < 10.000 ppb

SOLSILC - SPURT - SISI

EC funded projects to support the development of Solsilc technology.

Duration period 01/03/2000 - 15/09/2006

Objective

- development of a new 2-step process for the production of solar grade silicon
- Develop and demonstrate Solsilc technology on medium scale
- To enable the cost effective production of solar grade silicon (SoG-Si) as a dedicated feedstock source for the PV industry

Partners

ECN and Sunergy,Netherlands, ScanArc, Sweden, SINTEF, ScanWafer (SPURT), Metallkraft (SISI) and Norwegian Crystallites(SISI) Norway

The direct route to Solar Grade Silicon

- Metallurgical process: reaction of SiO_2 with C
- Ultra-Pure raw materials to reduce requirements on purification
- Related to work by Dow Corning, Siemens, ENEA and Nippon Steel Glass Co. in 70’s and 80’s
- Important part of purification: carbon removal
- Potential for low cost

SOLSILC process: Silicon production

Raw materials

SiO_2 powder

Carbon Black powder

Pelletising

SiC production in plasma-furnace

Pellet.

Si production in arc furnace

Main purpose of 2-step process:

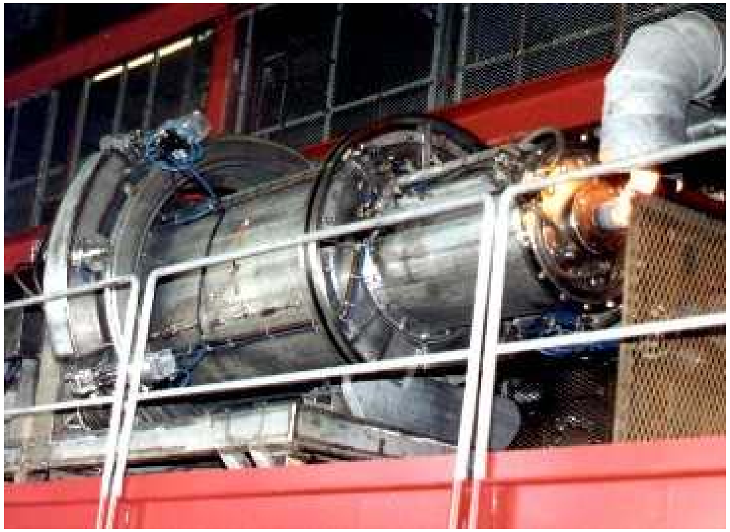
- **Control over furnace reactions**
- **Stability of furnace operation**
- **Yield**

Solsilc –
Pilot Si metal production

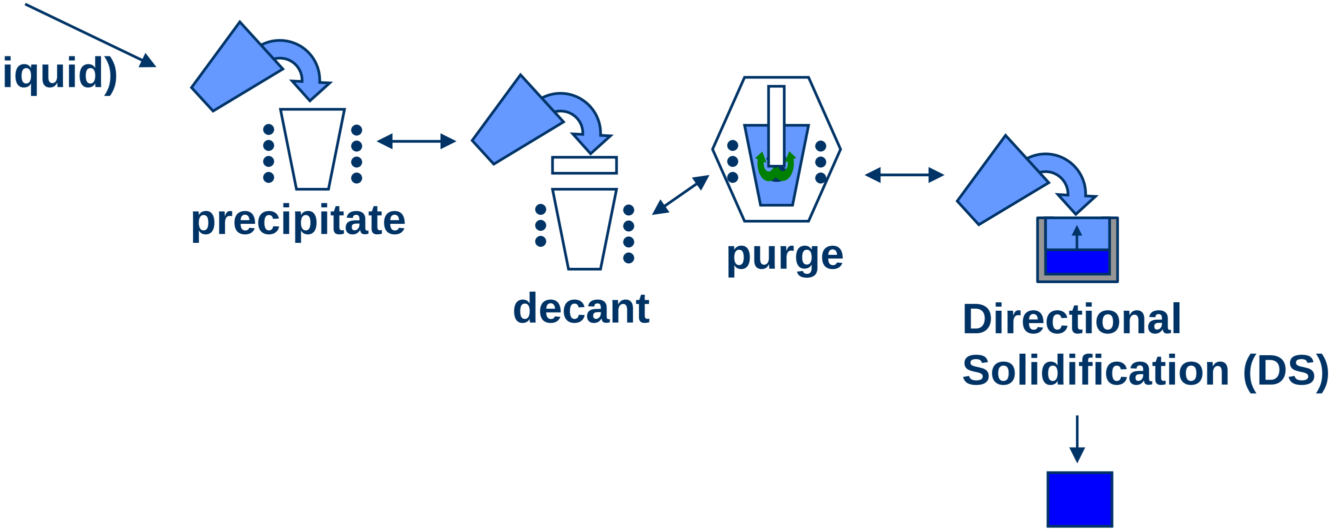
Goal: Production costs lower than 20 Euro/kg

- SiC from SiO_2 and C in rotary plasma furnace
- Existing technology at SINTEF (20 kg/h)

- Si from SiC and SiO_2 in electric arc furnace
- Novel design at ScanArc (20 kg/h)



SOLSILC process: Carbon removal/solidification



Si (liquid)

precipitate

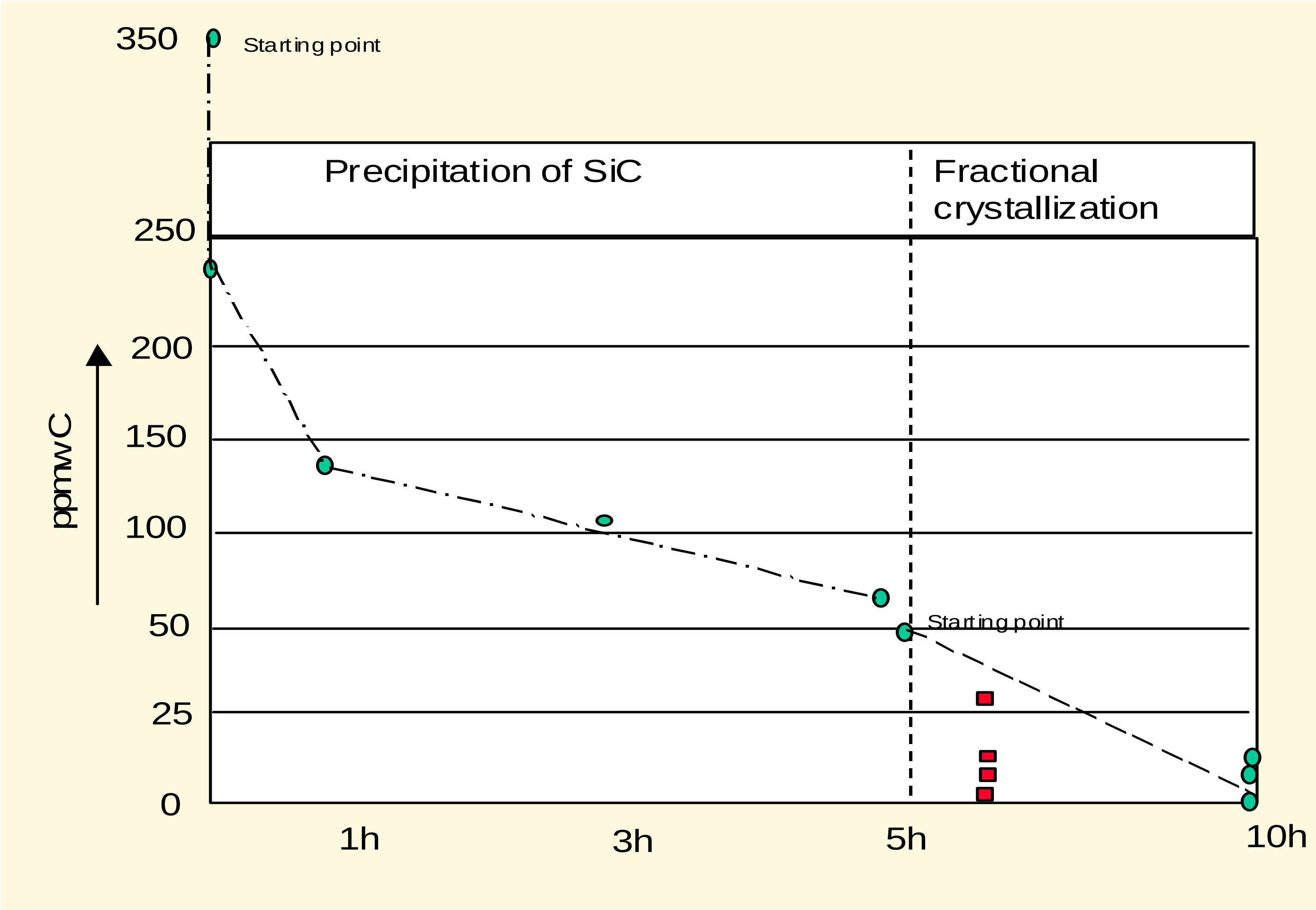
decant

purge

Directional Solidification (DS)

Purge-step typically not used

Si metal purification-
C removal results



Required purity of SoG-Si: tests on mc-Si and modelling

- A Carbothermic reduction route will end up with silicon saturated with carbon.
- Major contaminants in available quartz sources are Fe, Ti and Al.
- The most important source of contamination from Carbon Black is the process equipment

Results from tests and modelling has shown that cell efficiency is acceptable with a contamination level of

C	Fe	Al	Ti
1 - 10	1 - 10	0.1 - 1	0.1 - 1

This means that SoG-Si is within reach of a clean metallurgical process

Outlook

- Direct route to SoG-Si is feasible with available raw materials, and careful (clean) processes
- Direct route avoids purification steps compared to upgraded metallurgical route
- Favorable environmental assessment
- Good cell results from mixed pilot/lab-scale process

Annex II

L.J. Geerligs, P. Manshanden, G.P. Wyers, E.J. Øvrelid,
O.S. Raaness, A.N. Waernes, and B. Wiersma,

SPECIFICATION OF SOLAR GRADE SILICON: HOW COMMON IMPURITIES AFFECT THE CELL EFFICIENCY OF MC-SI SOLAR CELLS.

Proceedings of the 20th European Photovoltaic Solar Energy Conference

6-10 June 2005, Barcelona, Spain, p. 619-622.

Presented at the 20th European Photovoltaic Solar Energy Conference and Exhibition,
Barcelona, Spain, 6-10 June 2005

SPECIFICATION OF SOLAR GRADE SILICON: HOW COMMON IMPURITIES AFFECT THE CELL EFFICIENCY OF MC-SI SOLAR CELLS

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ABSTRACT: This paper presents and analyses cell efficiencies obtained from mc-Si ingots intentionally doped with C, Al, Ti, and a mix of C, Ti and Fe. The dependence of cell efficiency on concentration of these contaminants is modeled. The aim of this work is to determine which levels of impurities can be tolerated in silicon feedstock leading to acceptable reduction of the solar cell efficiency. The estimated impurity levels for $3\%_{rel}$ reduction of cell efficiency are: for aluminum and titanium around 0.1 ppmw, and for iron and carbon higher than 1, possibly higher than 10 ppmw. (ppmw=parts-per-million-by-weight). In addition, the relation between feedstock cost and allowable efficiency reduction are modelled for an industrial solar cell.
Keywords: Silicon Feedstock, Impurities, Recombination

1 INTRODUCTION

Soon, solar grade silicon will be available for PV. One potential source of solar grade silicon is from the direct carbothermic reduction of quartz and carbon. New solar grade silicon might contain significant higher fractions of impurities. In this study, we will report on the impact of such impurities on cell efficiency. The investigated impurities, Fe, Ti, Al, and C, were chosen because of their foreseen relevance in silicon produced by a metallurgical process [1,2,3]. They are also important for today's multicrystalline silicon (mc-Si) wafers because they are present in crucible materials and ingot growth equipment.

There have been several efforts in the past on specifying acceptable impurity levels in silicon feedstock [4,5,6]. Ref. 4 involved Cz-growth rather than mc-Si ingot growth. Ref. 5 involved mc-Si ingots, but did not include Ti. Both did not use a modern cell process with SiN_x:H antireflection coating. Therefore we found it appropriate to revisit the question of feedstock specification.

2 EXPERIMENT

2.1 Ingot growth

All ingots were grown in a small Crystalox furnace with standard crystallisation conditions, not optimised for impure feedstock. The ingots were approx. 12 kg weight and 100 mm height. All ingots were doped with boron to a base resistivity of 1.5 to 2 Ωcm.

Ingot code and impurity concentrations in feedstock are given in Table 1.

Ingot	Impurities
S4	C: 50 ppmw (no Boron base doping)
S5	C: 50 ppmw +Fe: 16 ppmw + Ti: 10 ppmw
S6	Al: 5 ppmw
S8	C: 50 ppmw
S9	C: 15 ppmw
S10	Ti: 10 ppmw
S11	C: 50 ppmw +Fe: 16 ppmw + Ti: 10 ppmw

Table I: List of ingots with concentration of impurities in the feedstock.

The estimated fraction of wafers missing due to loss, breakage, or accident varied considerably, from 15% in S10 to 70% in S6. This made the determination of the position in the ingot of a wafer (an important parameter in the analysis of the results) in S6 quite uncertain. In lack of any better information, it was assumed that lost wafers were distributed homogeneously throughout the ingots. The wafer position as given in figures in this paper refer to the *full height* of the ingot (including edges which are normally cut off).

2.3 Cell process

The cell process was a standard industrial process: alkaline saw-damage etch, phosphorous diffusion in an IR belt furnace, remote plasma-enhanced CVD of a SiNx front surface coating, screen printed metallisation, and co-firing. For the experiments in this abstract, the typical cell efficiency with this process on good quality wafers was 14.5-15.0%.

3 RESULTS

We display results in this paper using the product $J_{sc}V_{oc}$ to avoid uncertainty due to variations in fill factor caused by other reasons than impurity variations. Commercial wafers are used as reference in this paper. The cell results from an experimental reference ingot (from the Crystalox furnace) were indistinguishable from normal commercial wafers in $J_{sc}V_{oc}$ product.

3.1 Carbon in feedstock

Feedstock was doped with carbon by addition of SiC particles (C-content 15 and 50 ppmw). This is much higher than what is usually assumed to be acceptable for feedstock, and also higher than the solubility limit in solid silicon.

In Fig. 1, Fourier Transform Infrared (FTIR) analysis of the substitutional carbon concentration shows an increase to the top, which indicates that the ingots are not saturated with carbon. This is generally confirmed by measurements of the total carbon concentration (Fig. 1, open symbols). The solubility of substitutional carbon in silicon depends on other defects and crystallisation conditions; it is approximately 10 ppmw.

Only in the top 20% of some of the ingots doped with 50 ppmw carbon in the feedstock, the FTIR profile shows a ceiling, and the total carbon measurements exceed the solid solubility limit.

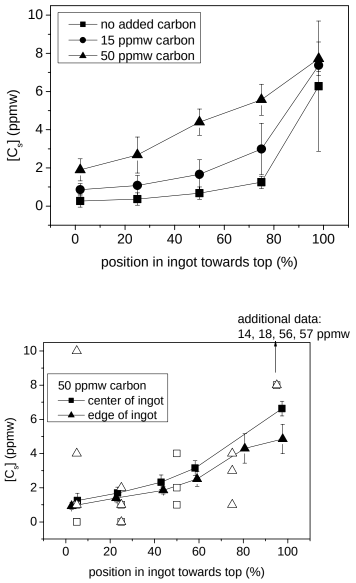

Figure 1: Carbon concentration profiles. Top: substitutional carbon concentration measured with FTIR in ingots doped with no carbon, 15 ppmw, and 50 ppmw in feedstock. Averages over several ingots. Bottom: FTIR and total carbon in ingot S4; feedstock doped with 50 ppmw.

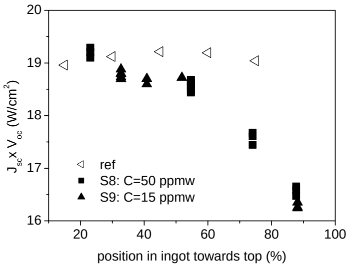

Figure 2: Top: $J_{sc}V_{oc}$ product of ingot S9 doped with 15 ppmw and S8 doped with 50 ppmw of carbon. Open triangles: Results on reference wafers.

Fig. 2 shows cell results from these ingots. The carbon-doped ingots S8 and S9 show a slight degradation of the $J_{sc}V_{oc}$ product in the bottom half of the ingot, and significant degradation in the top 25%. The internal quantum efficiency (IQE) in Fig. 3 shows that the degradation in the top is due to reduced red-response of the cells. There is no difference between S8 and S9, despite the different amounts of carbon added. Therefore we are not certain that this degradation can be attributed to the added carbon. Possibly it is the result of a combination of:

- Edge effect: the usual contamination of the edges of an ingot by solid state indiffusion.
- Impurities in the added SiC particles.
- Less optimal crystal quality (growth conditions) than the reference wafers.

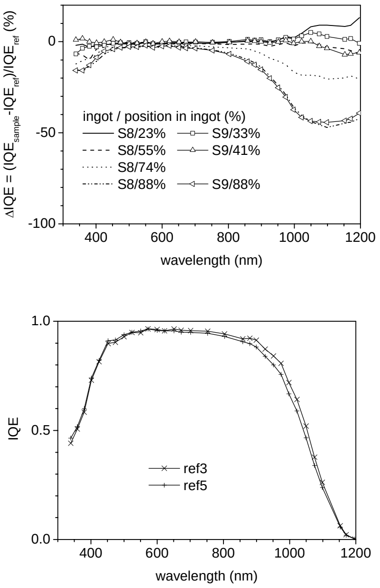

Figure 3: Top: Change of IQE of ingot S9 doped with 15 ppmw and S8 doped with 50 ppmw of carbon, along ingot height, relative to average of reference cells. Bottom: IQE of the reference cells.

3.2 Titanium and aluminum in feedstock

Fig. 4 shows the effect of feedstock contamination with Ti (10 ppmw, ingot S10) and Al (5 ppmw, ingot S6), respectively. These impurities have a strong effect on cell efficiency. The cell efficiency decreases towards the top of the ingot. DLTS measurements indicate a very small segregation coefficient (very good segregation) for Ti.

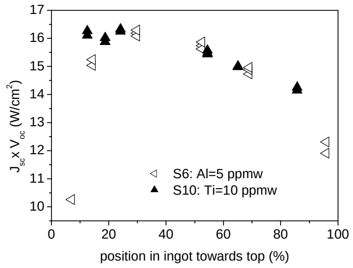

Figure 4: Top: $J_{sc}V_{oc}$ products of ingots from feedstock doped with 10 ppmw Ti and 5 ppmw Al. Note the different scale from Fig. 2.

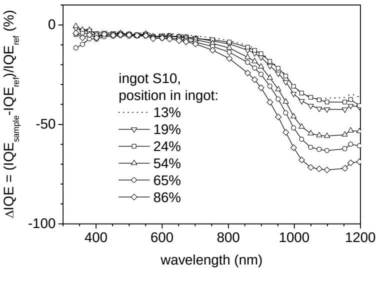

Figure 5: ΔIQE of the S10 (Ti-doped) ingot relative to reference cells.

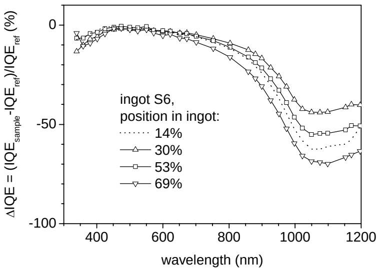

Figure 6: ΔIQE of the S6 (Al-doped) ingot relative to reference cells.

Fig. 5 and 6 show that in both ingots the reduction of $J_{sc}V_{oc}$ product is due to very strong suppression of the red-response of the cells. This effect increases towards the top of the ingot.

3.3 A representative mix of impurities

Fig. 7 shows the cell efficiency for feedstock with a mix of Fe, Ti, and C impurities (S11). These would typically be encountered in low-cost metallurgical silicon. Al was not included in this experiment because Al changes the base resistivity as well as the base recombination.

The amount of Ti in this mix is the same as in S10. The reduction of cell efficiency is similar, too. This leads to the conclusion that the main effect of this impurity mix is due to Ti, and the impact of even 16 ppmw of Fe is limited to a reduction of cell efficiency of at most a few percent.

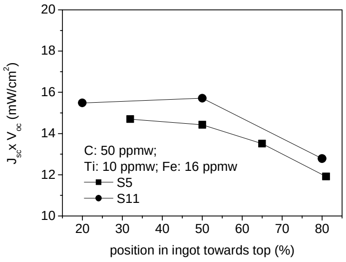

Figure 7: The $J_{sc}V_{oc}$ product of two ingots from feedstock doped with 10 ppmw Ti, 16 ppmw Fe, and 50 ppmw C.

4 MODELLING SEGREGATION AND THE EFFECT OF OTHER CONCENTRATIONS OF IMPURITIES

4.1 Comparison of IQE with segregation model

An important question is how these cell results would change if the impurity concentration changes. At the impurity levels shown here, the cell efficiency is reduced by around 20%. This is much too high to be economically attractive. Therefore, the question arises how high the acceptable impurity level can be and if it is possible to determine this level based on the available data.

In the Shockley-Read-Hall recombination model, the recombination lifetime scales inversely with the concentration of a defect. In a simple assumption therefore, changing the impurity concentration C in the feedstock would change the carrier lifetime τ_{eff} in the cell as

$$1/L_{eff}^2 \propto 1/\tau_{eff} \propto C \qquad (1)$$

Using this assumption, the dependence of cell efficiency on feedstock contamination can be modelled with PC1D.

However, in reality, a change of the impurity concentration could change all sorts of interactions (with the crystallisation process, crystal defects, other impurities, etc.) so that this scaling might be lost. Our experiments allow us to verify whether this scaling holds, because:

- In each ingot there is a range of impurity concentration, increasing from bottom to top due to segregation.
- The bulk recombination lifetime in the cell can be derived from a Basore-fit (i.e., from the red-response) of the IQE.

The basis of our analysis is the Scheil equation for segregation [7]:

$$C_S = k_{eff} C_0 (1-f_s)^{k_{eff}-1}$$

where C_0 is the initial concentration in the liquid silicon and f_s the solidified fraction. k_{eff} is the segregation coefficient, normally k_{eff}<<1. The concentration of impurities incorporated into the solid phase C_S during crystallization is given by $C_S=k_{eff}C_L$.

Fig. 8 shows the Al-concentration in ingot S6, derived from the difference of resistivity between S6 and the other ingots. It follows the Scheil equation with k_{eff}=0.007. Fig. 9 shows that also $1/\tau_{eff}$ (or equivalently, $1/L_{eff}^2$) follows the Scheil equation. This is a strong indication that scaling as discussed above is valid, both for S6 (Al) and S10 (Ti). It may be assumed that extrapolation of such scaling to *lower* impurity concentrations is then also allowed.

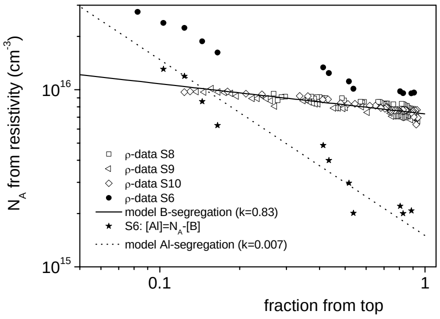

Figure 8: Comparison of excess acceptor concentration in S6 with Scheil equation (dotted line).

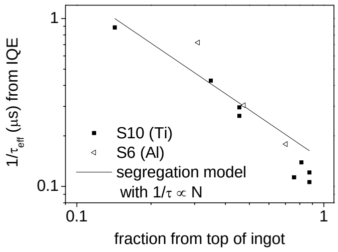

Figure 9: Comparison, for S6 and S10, of $1/\tau_{eff}$ from IQE

with the Scheil equation.

4.2 Cell efficiency versus impurity concentration

Under the assumption of scaling as described by eq. (1), one can model in PC1D the effect of a range of impurity concentrations in feedstock. The results are given in Fig. 10, for a standard industrial cell process, and for an improved 17% efficiency cell process as developed by ECN [8].

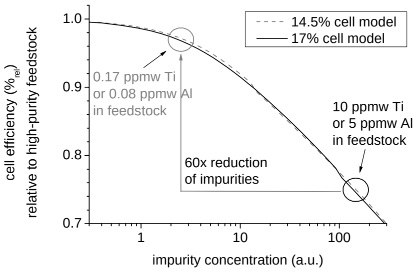

Figure 10: Cell efficiency modelled under assumption of scaling of lifetime degradation in the cell with impurity concentration in feedstock (based on eq. 1, as observed in the experiments). Translation of experimental data to example cell spec of $97\%_{rel}$ is indicated with grey arrow.

For example, our data for Al and Ti both show approx. $25\%_{rel}$ reduction of $J_{sc}V_{oc}$ at a position of 15mm below the top of the ingot. According to Fig. 10, the impurity concentration will have to be reduced by a factor 60 to arrive at $3\%_{rel}$ reduction. This implies a feedstock specification of 0.08 ppmw for Al, or 0.17 ppmw for Ti.

4.3 Tolerable impurity levels

The tolerable impurity level is, in principle, an economic consideration. The trade-off is between cost of feedstock and cell efficiency. The production cost for a PV system, per Wp, can be described very generally as

$$p.c._{ref} = m_{ref}\, p_{ref} + c_{1,A} + c_2$$

where m_{ref} is the mass of silicon used, p_{ref} the price of the silicon feedstock per kg, $c_{1,A}$ the area-related production costs excluding feedstock, and c_2 area-unrelated (only Wp-related) production costs. If by using another feedstock the cell efficiency η changes, the production cost will change to

$$p.c._{new} = m_{ref}\left(\frac{\eta_{ref}}{\eta_{new}}\right) p_{new} + \left(\frac{\eta_{ref}}{\eta_{new}}\right) c_{1,A} + c_2 \qquad (2)$$

Eq. (2) allows to visualise the economic trade-off as in Fig. 11. In Fig. 11, which is somewhat representative of today's production situation, feedstock would still have to result in cells of $90\%_{rel}$ efficiency, even if it were available for free. However, as total production cost will go down, and material costs thus become more relevant, the requirements on feedstock purity versus cost will be relaxed.

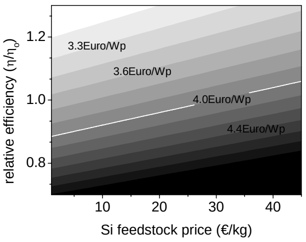

Figure 11: Diagram of constant-production-cost as a function of feedstock price and relative cell efficiency. (according to eq. (2), with p_{ref}=30 €/kg; m_{ref}=13 g/Wp; p.c.$_{ref}$= 4 €/Wp, $c_{1,A}=5c_2$).

5 CONCLUSIONS

In conclusion, we have presented and modeled the effect on mc-Si cell efficiency of certain impurities in silicon feedstock:

- concrete data on reduction of cell efficiency due to Al and Ti,
- limited effect of additional 16 ppmw Fe,
- evidence on how to model the effect of other impurity concentrations,
- high tolerance for high carbon-concentrations, more careful analysis of the carbon effects is however necessary.

Of course, our *results* are to some extent specific for this Crystalox furnace. However, we expect that our *approach* and the *order of magnitude of results* should be useful for other crystallisation furnaces too.

Finally, we have provided simple scaling equations to evaluate the economic tradeoff of feedstock cost and cell efficiency.

6 ACKNOWLEDGMENTS

This work was supported by the European Commission in the research projects SOLSILC (ERKG-1999-00005) and SPURT (ENK6-CT-2001-30006) and SISI (COOP-CT-2004-508202). We thank project partners ScanArc SA and Scanwafer SA for technical assistance and useful discussions, and Oyvind Mjøs of NTNU for assistance with growing the ingots. We thank HCT Shaping Systems SA for wafering several ingots.

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[4] J.R. Davis et al., IEEE Trans. El. Dev. ED-27 (1980) 677.

[5] J. Fally et al., Revue Phys. Appl. 22 (1987) 529.

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[7] E. Scheil, Z. Metallk. **34**, 70 (1942).

[8] Weeber et al., this conference.

ECN

Energy research Centre of the Netherlands

Specification of solar grade silicon: How impurities affect efficiency

Bart Geerligs

Outline

- Objective and introduction
- Ingots and cells from artificially contaminated silicon feedstock:
  - Titanium
  - Aluminum
- Analysis of results
- Implications for feedstock specification

Objective

Determine allowable concentrations of impurities in silicon feedstock for mc-Si solar cells.

Reasons:

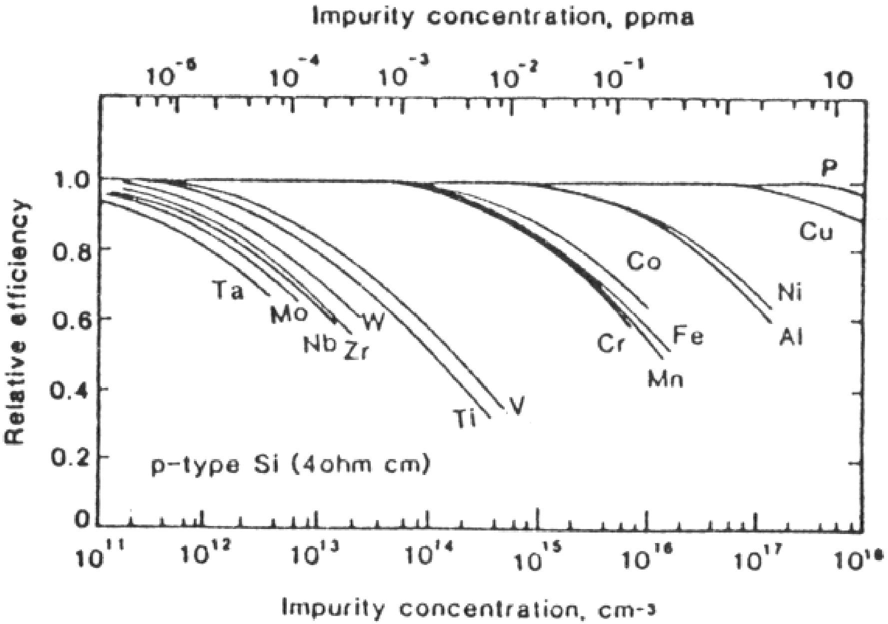
- specific Silicon produced for Photovoltaics
- possibility of **Low-cost and abundant Silicon feedstock from carbothermic reduction of quartz.**

$$\mathbf{SiO_2 + 2C \rightarrow Si + 2CO}$$

Fe, **Ti**, **Al**, and **C** are major impurities in silicon from carbothermic reduction. What are the target levels for these impurities?

Which specs are available?

- Si wafer manufacturers: “we like to be on the safe side, the SEMI poly-Si spec [<0.1 ppmw total metals] works for us…”
- For PV, there exist more specific earlier studies:

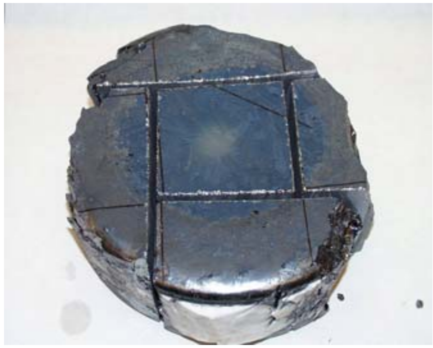


J.R. Davis, et al.,
IEEE Trans El. Dev. ED-27, 677 (1980)

Cz-growth

also, Fally et al.,
Revue Phys. Appl. 22, 529 (1987)
mc-Si, but no info on Ti

Experimental procedure



poly-Si feedstock
with added impurity

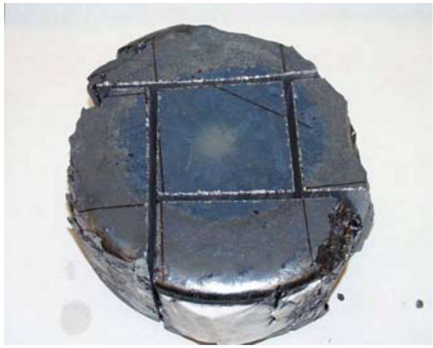
→

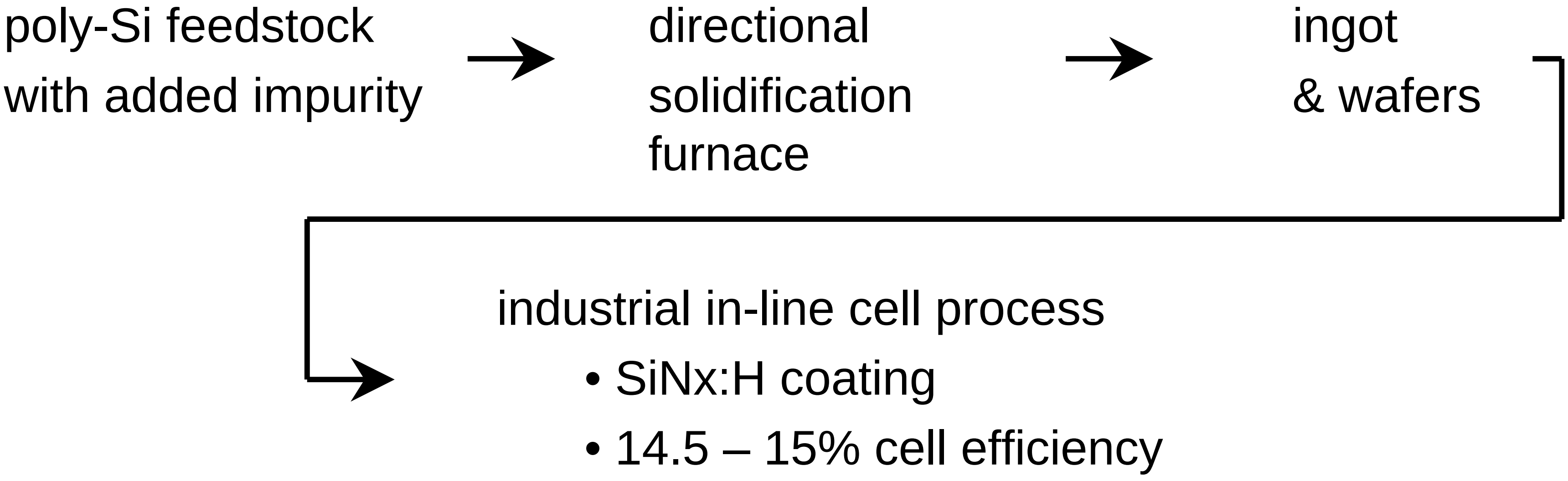
directional
solidification
furnace

→

ingot
& wafers

Experimental procedure





poly-Si feedstock
with added impurity

→

directional
solidification
furnace

→

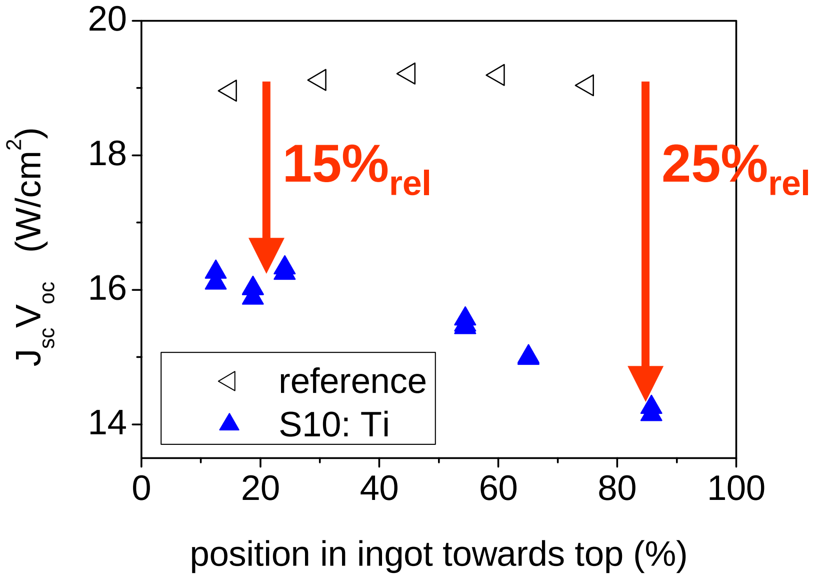
ingot
& wafers

industrial in-line cell process

- SiNx:H coating
- 14.5 – 15% cell efficiency

Titanium

10 ppmw (parts-per-million by weight) of Ti were added to the feedstock



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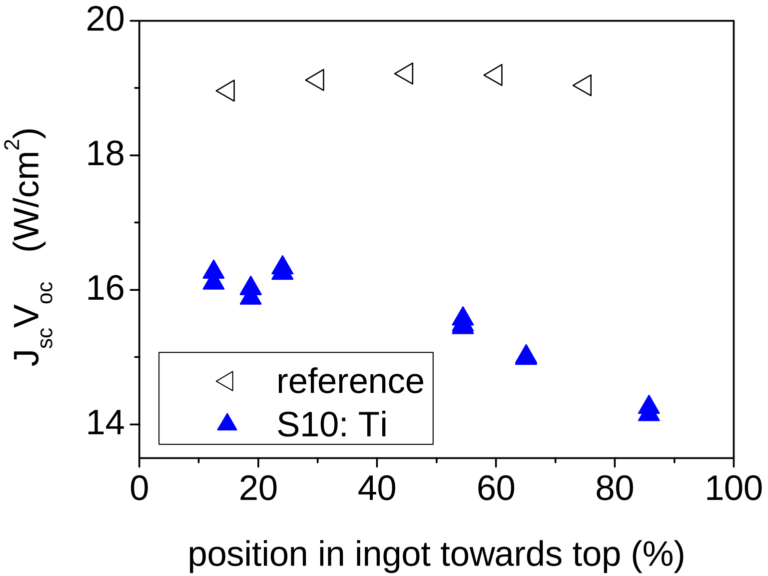
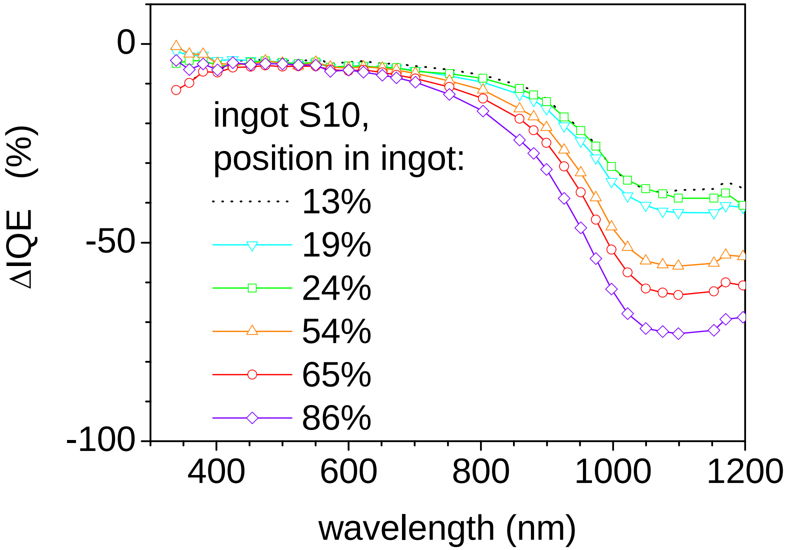
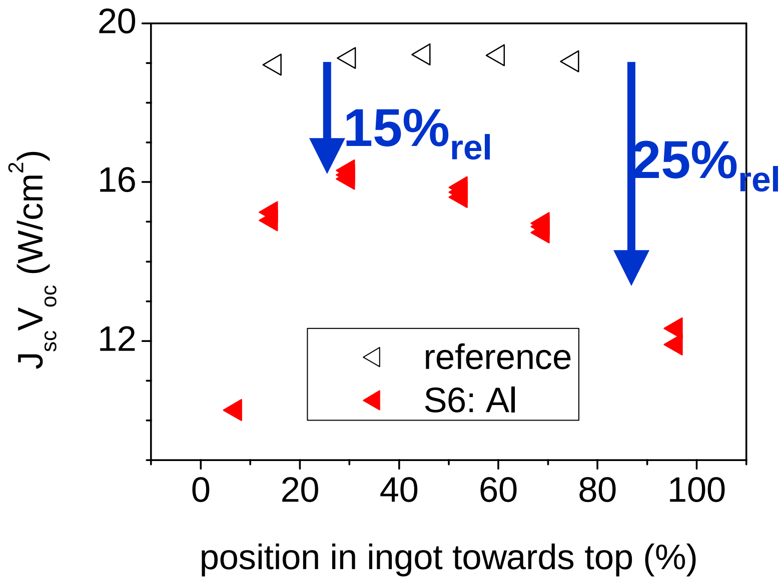




Reduction of J_{sc} due to strongly reduced red-response in IQE

Aluminum

5 ppmw of Al were added to the feedstock



Aluminum

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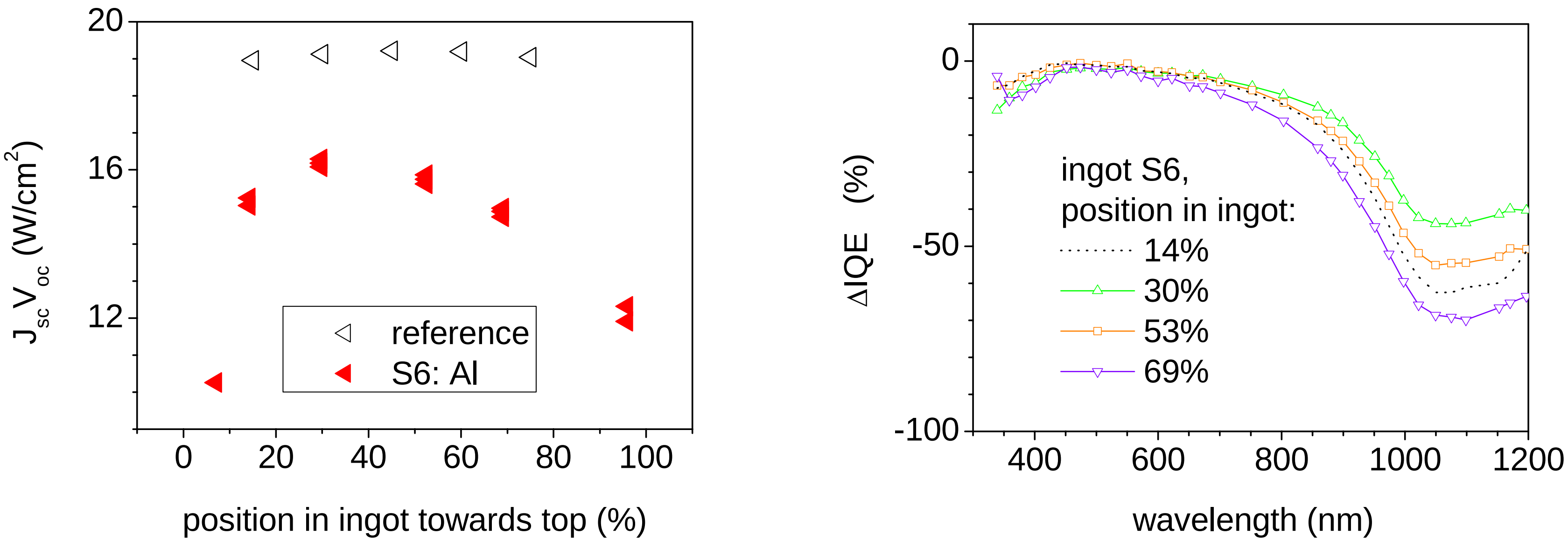


Reduction of J_{sc} again due to reduced red-response in IQE

Analysis of results

15-25% reduction of $J_{sc}V_{oc}$ due to 5 ppmw Al or 10 ppmw of Ti is too much to be acceptable.

How can we determine the maximum allowable concentration?

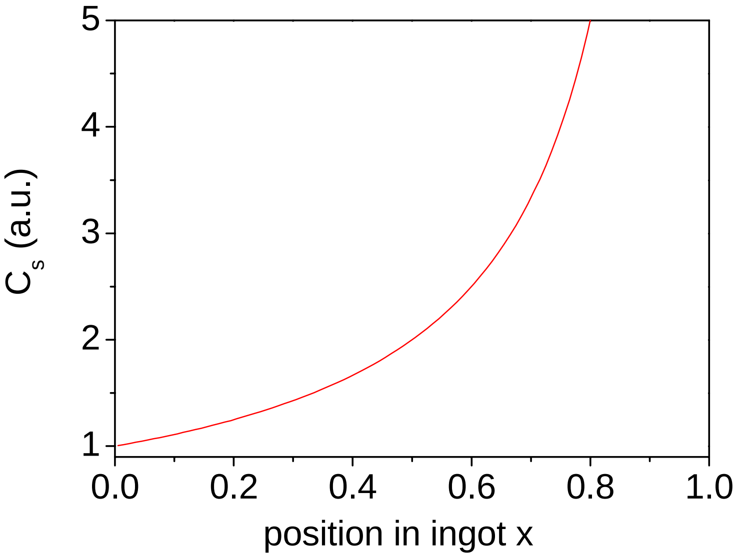
- Can the cell efficiency for other concentrations be modeled and predicted?
- Is there experimental data to verify such a model?

Model for analysis

segregation during ingot growth

↓

impurity concentration $C_s \propto \dfrac{1}{1-x}$



Model for analysis

segregation during ingot growth

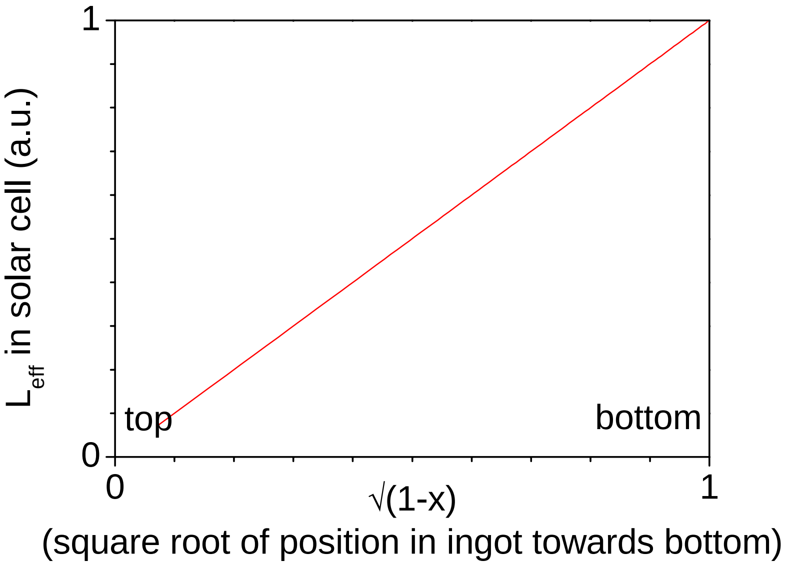
↓

impurity concentration $C_s \propto \frac{1}{1-x}$

If impurity dominates recombination

$$\frac{1}{L_{eff}^2} \propto \frac{1}{\tau_{eff}} \propto C_s$$

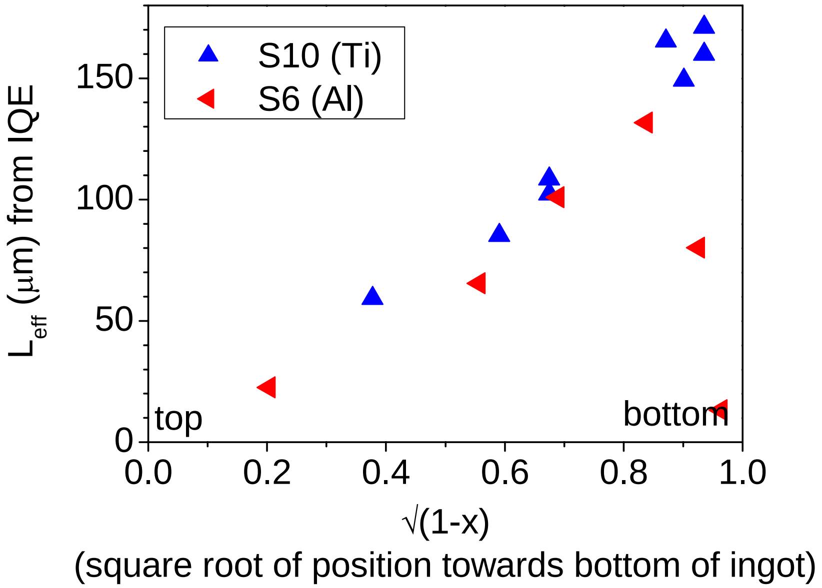
$$\Rightarrow L_{eff} \propto \sqrt{1-x}$$



L_{eff} can be determined from the red-response of the IQE

Comparing L_{eff} from IQE with model

- L_{eff} follows expected decrease to top of ingot. (exception: bottom of S6)



Comparing L_{eff} from IQE with model

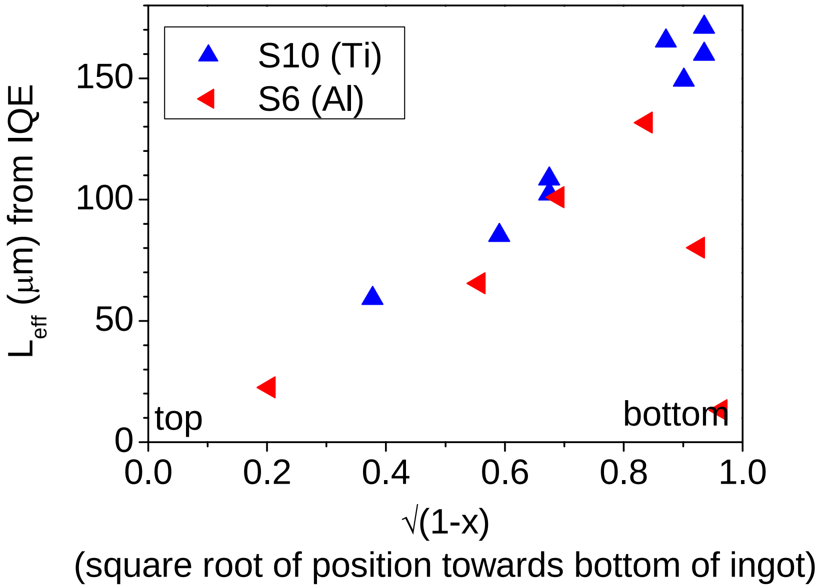
- L_{eff} follows expected decrease to top of ingot. (exception: bottom of S6)

- Conclusion:

  Relation between feedstock contamination and recombination is

  linear

  (no non-linear effects from precipitation, etc.).



Comparing L_{eff} from IQE with model

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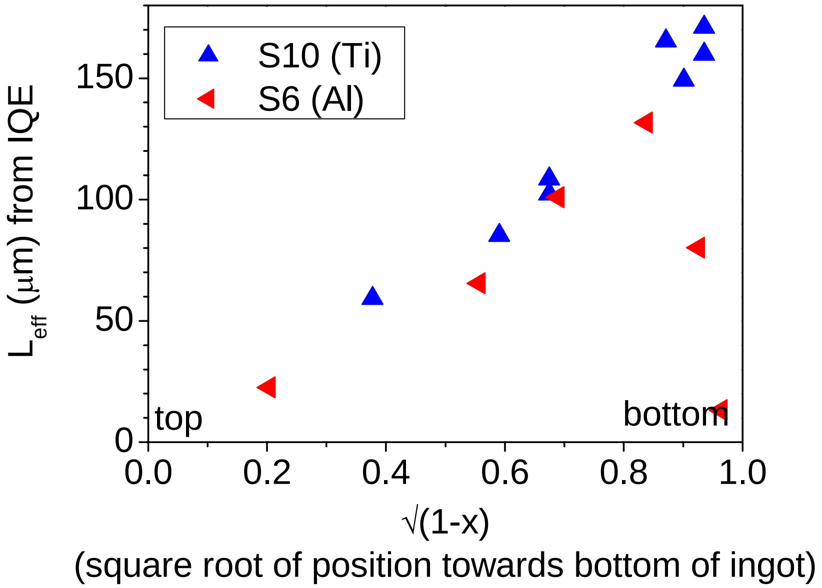


(at least for Al, Ti, for the used concentrations and probably lower)

Do-It-Yourself specification of solar grade silicon

1. Construct PC1D model for your cell process, and
   calculate cell efficiency versus L_{eff}

2. Use $1/L_{eff}^2 \propto C_L$
   (C_L is impurity concentration in the feedstock)

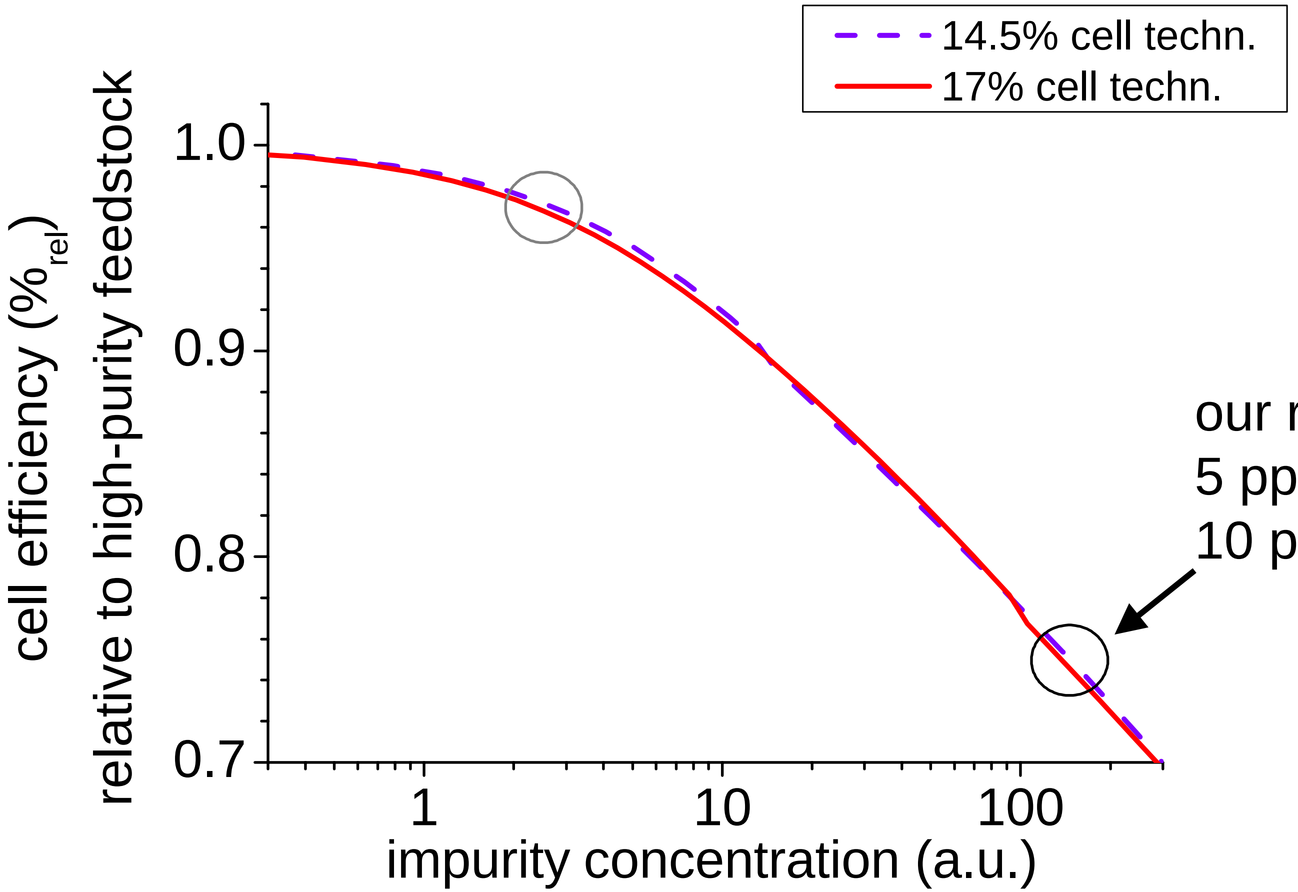
⇒ “generic” plot of cell efficiency versus C_L (C_L in a.u.).

3. One data point (impurity concentration and cell efficiency) to
   calibrate C_L-scale.

4. Choose acceptance level of cell efficiency
   (cost analysis! e.g. $97\%_{rel}$ efficiency if feedstock 25% lower cost).

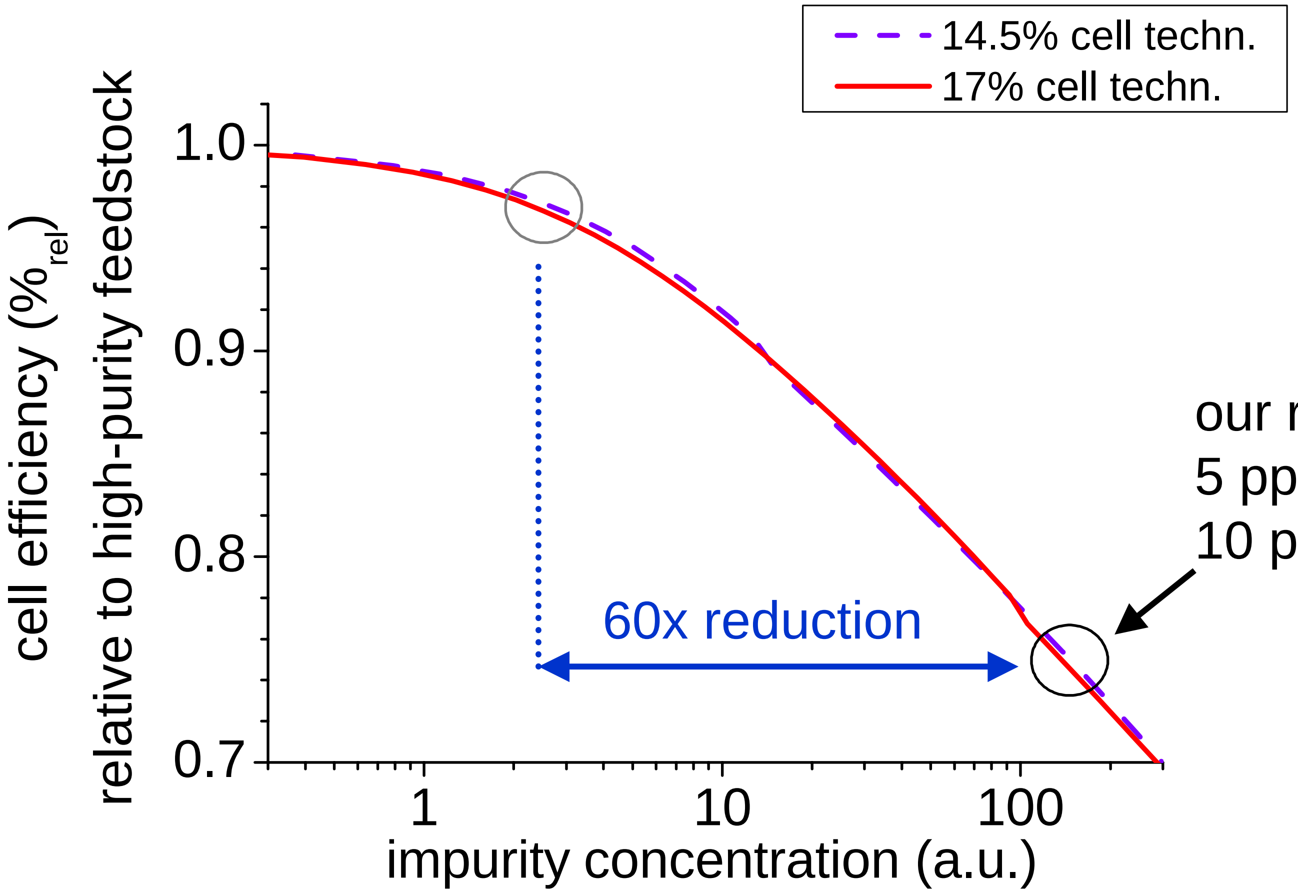
5. Read required impurity concentration from plot.

Graphical presentation of D-I-Y feedstock specification



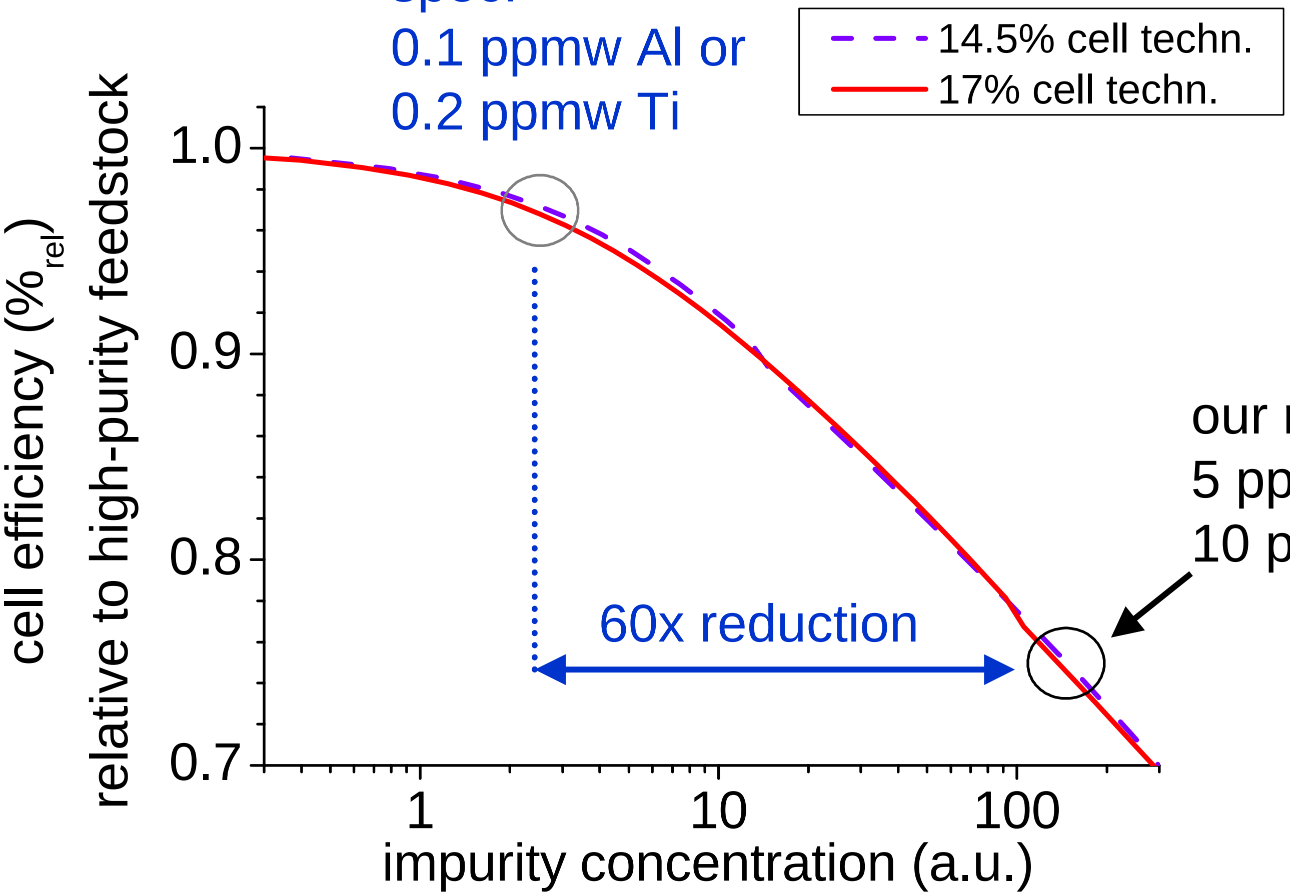
our results:
5 ppmw Al or
10 ppmw Ti

Graphical presentation of D-I-Y feedstock specification



our results:
5 ppmw Al or
10 ppmw Ti

Graphical presentation of D-I-Y feedstock specification



spec:
0.1 ppmw Al or
0.2 ppmw Ti

our results:
5 ppmw Al or
10 ppmw Ti

Conclusions

- Clear impact of Ti and Al at ppm level.

- Dependence of impact on position in ingot
  modeled according to segregation
  and linear relation between L_{eff}^{-2} and $C_{feedstock}$.

- Extrapolated feedstock specification based on $3\%_{rel}$ cell efficiency reduction:
  Al: 0.1 ppmw
  Ti: 0.2 ppmw

See the paper for more details, also on carbon, mix of impurities, Fe, and modelling of economics!

Thank you for your attention

Acknowledgements

- Oyvind Mjøs, NTNU Trondheim
- ScanArc, Scanwafer, HCT
- EC for contracts SOLSILC, SPURT, and SISI
- Coauthors: Petra Manshanden, Paul Wyers (ECN Solar Energy), Eivind Øvrelid, Ola Raaness, Aud Waernes (Sintef), Benno Wiersma (Sunergy)

Annex III

L.J. Geerligs

DIRECT CARBOTHERMAL REDUCTION TO LOW-COST SOLAR GRADE SILICON

Invited presentation at the PHOTON International, 3rd Solar Silicon Conference

April 3, 2006, Munich, Germany.

ECN

Energy research Centre of the Netherlands

Direct carbothermal reduction to low-cost solar grade silicon

Bart Geerligs

www.ecn.nl

Consortium partners

Sunergy (NLD)

Sintef (NOR)

Scanarc (SWE)

Energy research Centre
of the Netherlands (NLD)

Outline

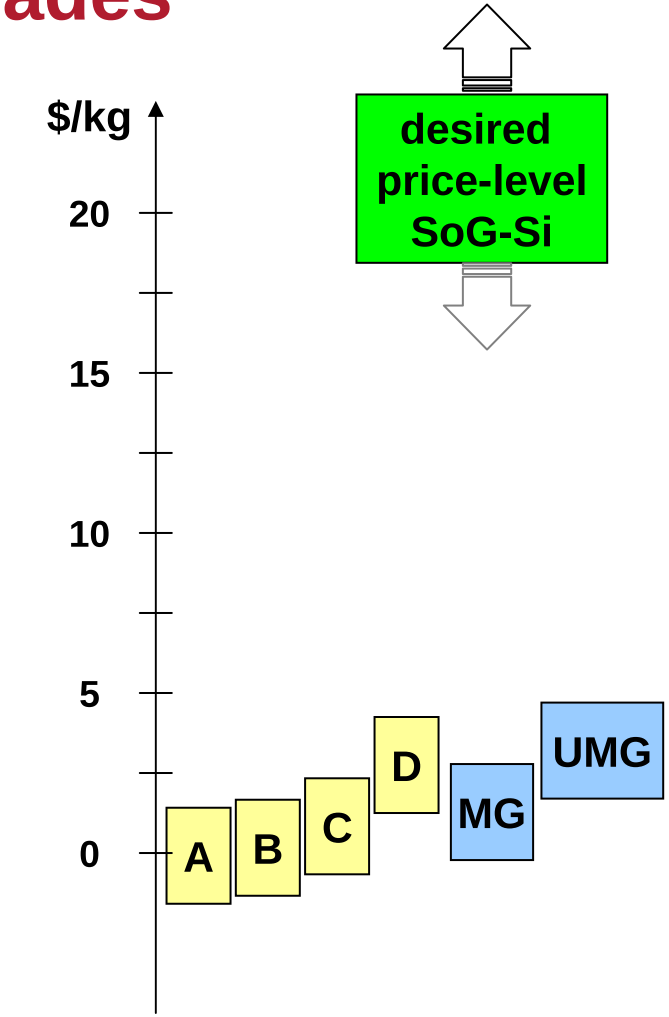
- Advantages of direct carbothermic reduction
- Status of technology
- Planning of exploitation

Quartz and silicon grades

	Quartz				Silicon metal	
	A	B	C	D	MG	UMG
B		<1		<0.04	15-50	<30
P	<5	0.2	<5	0.05	10-50	<15
Fe	600	15	0.1	<0.03	2000	<150
Al	400	30	7	7	100-200	<50
Ca	150	15	0.1	0.5	100-600	<500
Ti	30	1.2	4	1.2	200	<5
Cr	15	2-5	<0.01	<0.003	50	<15

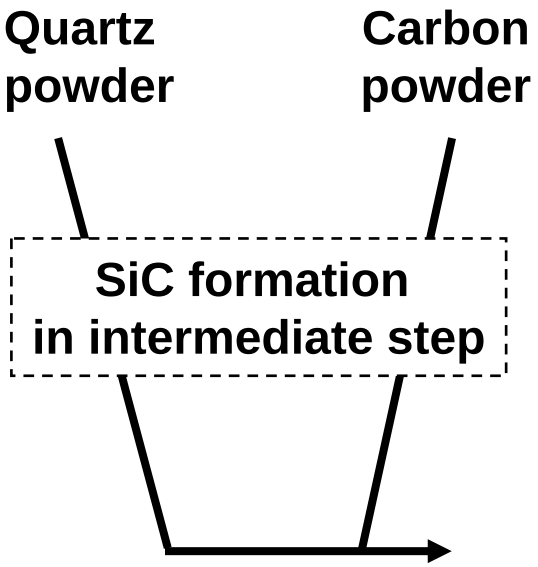
A - Good quality lump quartz
B - Processed hydrothermal quartz
C - Processed pegmatite core quartz
D - Hydrochemically treated quartz

MG - Metallurgical grade
UMG - Upgraded metallurgical grade



Source: Larsen and Sandvik, NTNU, Trondheim

Direct carbothermic reduction in SOLSILC



Quartz powder

Carbon powder

SiC formation in intermediate step

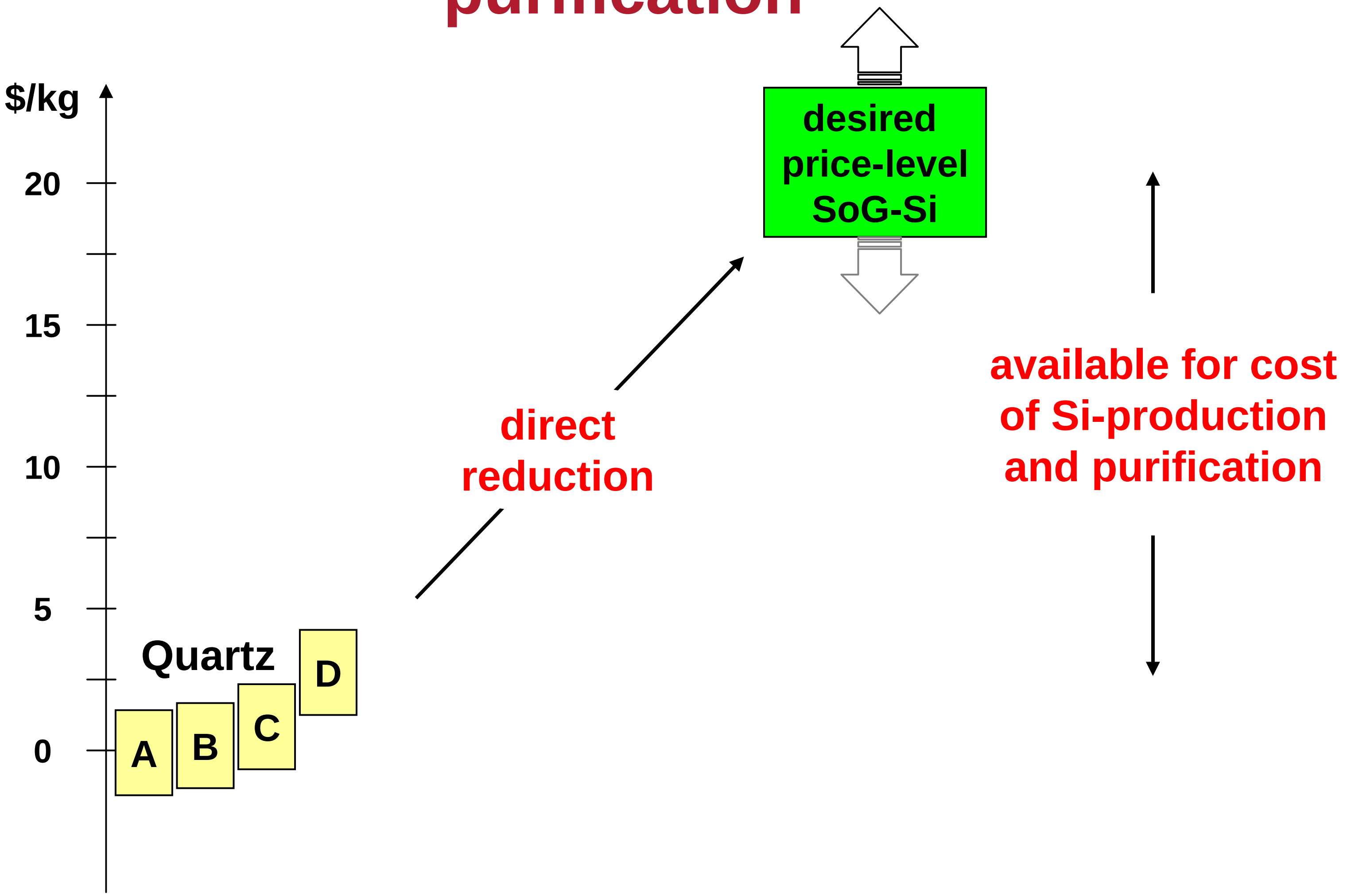
Si production in arc furnace

Liquid Silicon

Advantages of direct carbothermic reduction

- readily available raw materials
- no elaborate costly refining steps
- purity levels close to requirements SoG-Si
  - no “overkill”
  - no excessive impurities

Cost of high-purity raw materials vs. purification



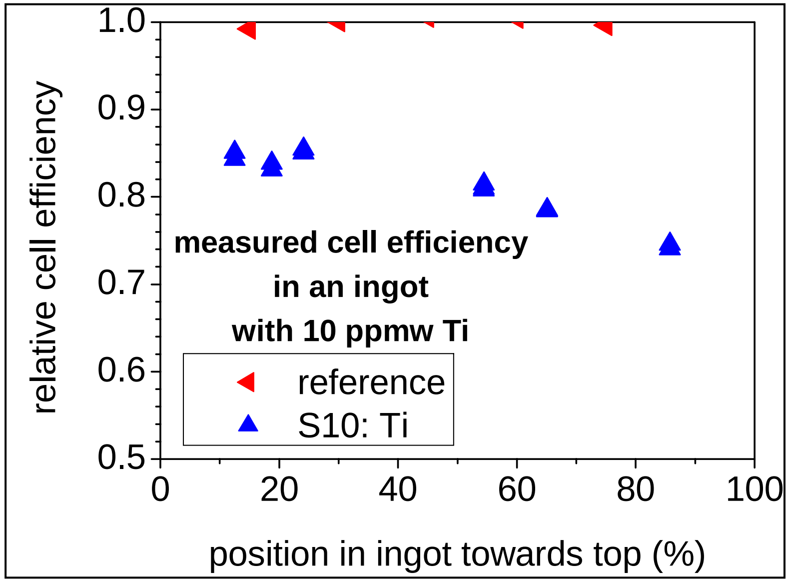
desired price-level SoG-Si

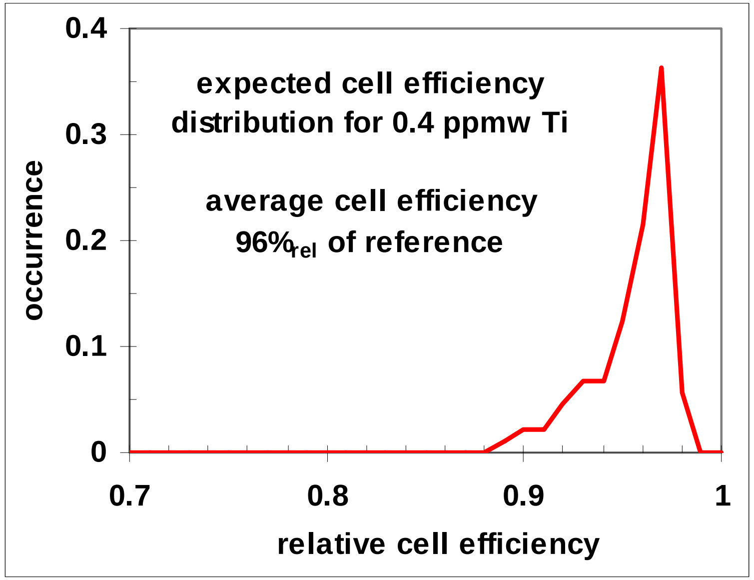
direct reduction

available for cost of Si-production and purification

Limits on impurities

Tests with intentionally contaminated high-purity silicon





Test ingot with 10 ppmw Ti added →

Prognosis for other Ti-concentrations

For example 0.4 ppmw Ti:

Average cell efficiency reduced by 4%$_{rel}$

Impurity limits vs. raw materials

Supposing 4%$_{rel}$ reduction of cell efficiency defines limit:

	B	P	Al	Fe	Ti
Estimated limits	~1	~0.8	0.2	~5	0.4
Materials for carbothermic reduction:					
Carbon example	<0.05	<0.3	0.5	3	<0.5
Quartz D example	<0.04	0.05	7	<0.03	1.2
Best available	<0.2	<0.1			

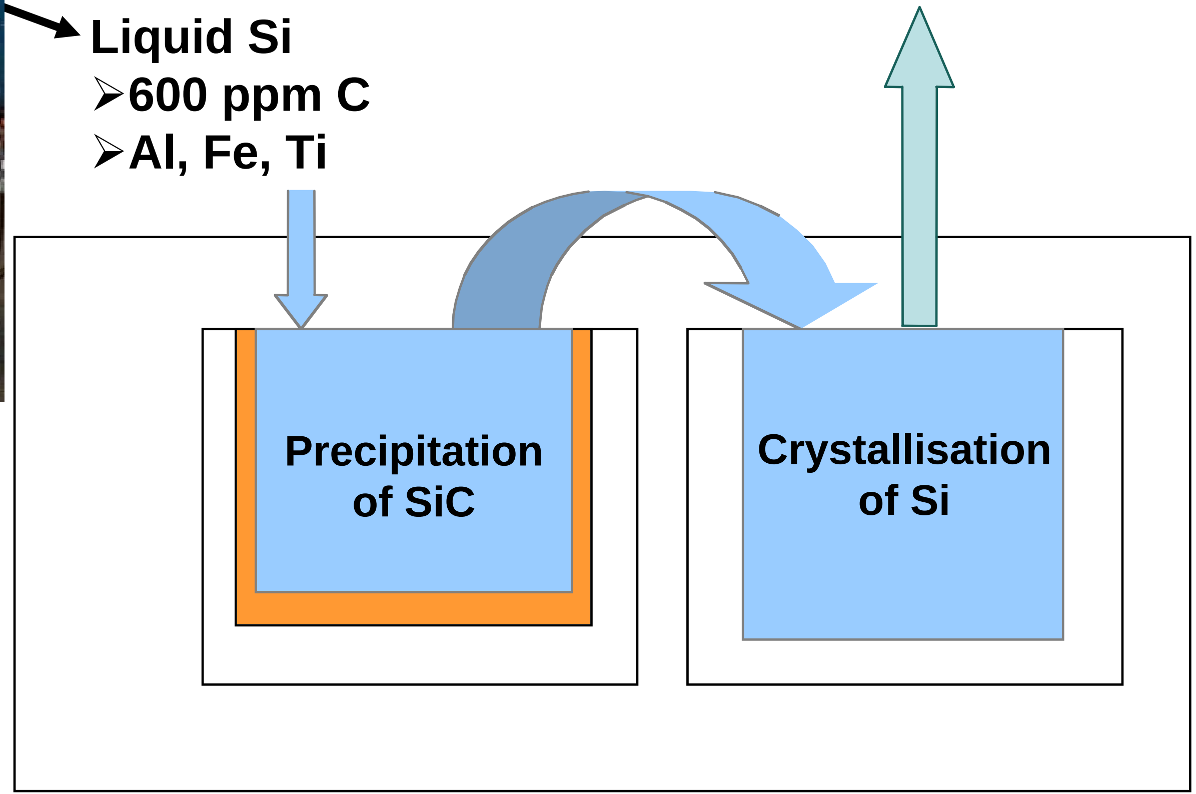
Concentrations in ppmw

Current tests:

- **Phosphorous higher than Boron content → n-type doped**
- **Fe, Al and Ti too high → some purification needed**

Carbon removal and ingot growth

Arc furnace



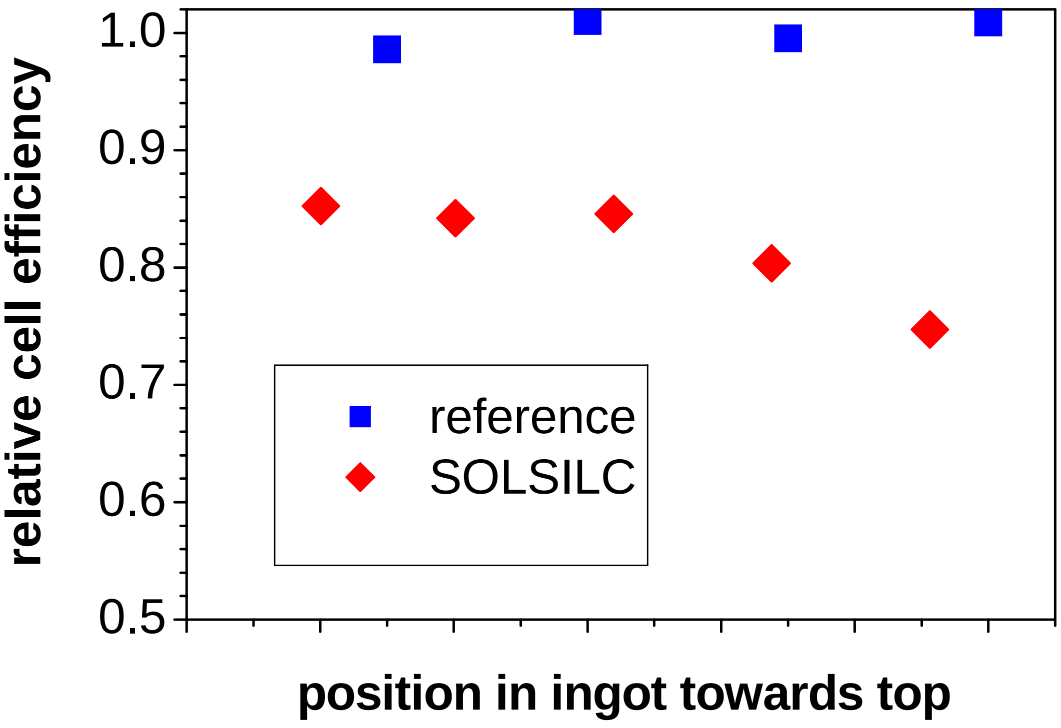
Liquid Si

- ➢600 ppm C
- ➢Al, Fe, Ti

Multi-Crystalline Si:
< 10 ppm C
Low Al, Fe, Ti

Cell results

n-type base doping → experimental cell process



SOLSILC @ 80% of reference efficiencies

Low cost Si production without purification

To improve:

1. **Avoid contamination**
2. **Purer raw materials**
3. **Add'l purification step**

Solsilc Development

- Consortium partners have formed SOLSILC Development Co.
- Transfer of technology in progress

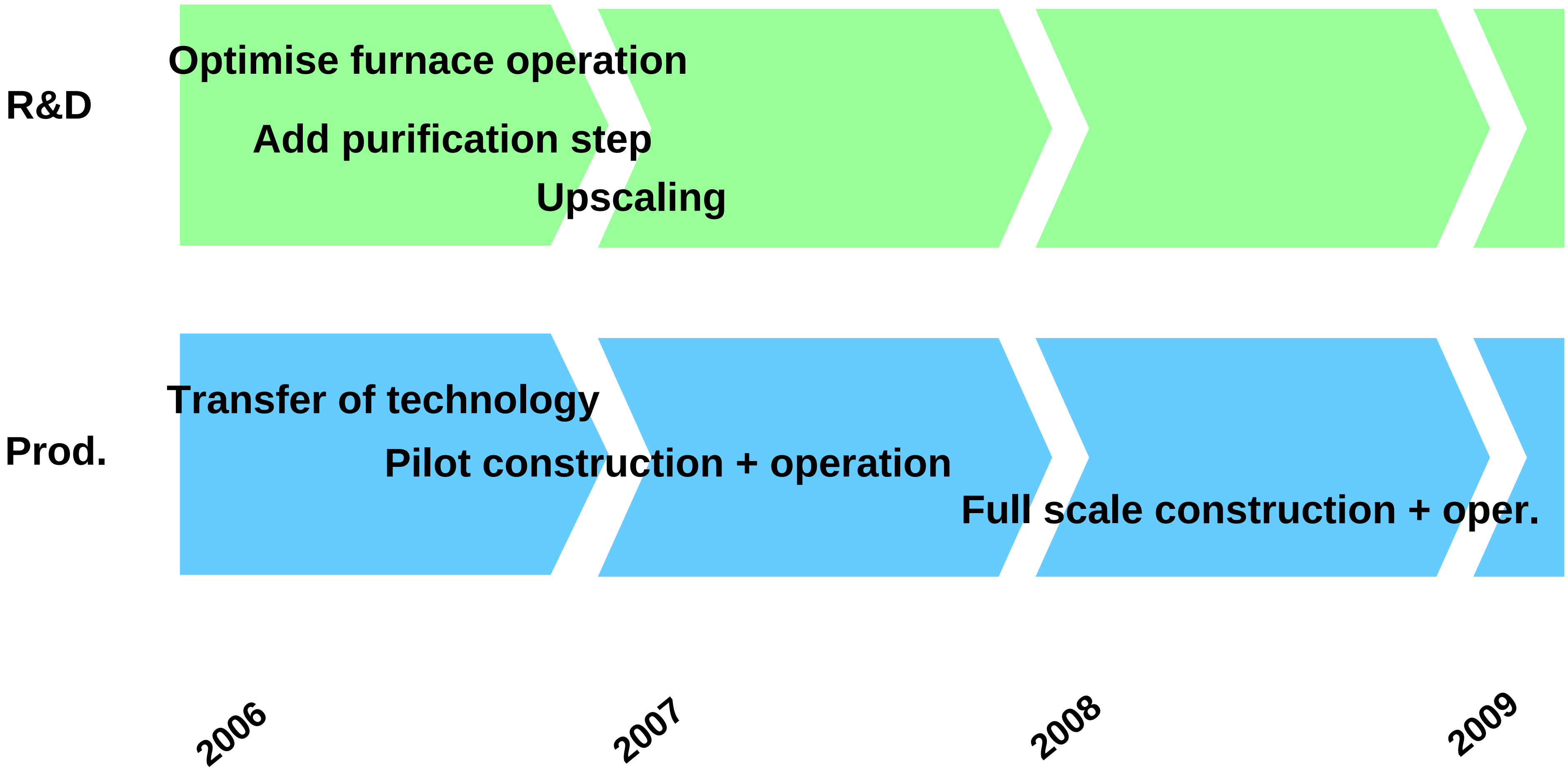
SUNERGY

SINTEF
Materials Technology

ScanArc
PLASMA TECHNOLOGIES AB

ECN

Solsilc Development



R&D

Optimise furnace operation

Add purification step

Upscaling

Prod.

Transfer of technology

Pilot construction + operation

Full scale construction + oper.

Annex IV

poster for the

European Commission Photo Voltaic Technical Days

17 and 18 May 2006, Brussels

ECN Solar Energy
P.O. Box 1
1755 ZG Petten
The Netherlands

ScanArc PLASMA TECHNOLOGIES AB

NC | NORWEGIAN CRYSTALLITES

SISI

silicon for solar cells at low costs on an intermediate scale

Metallkraft

SINTEF Materials Technology

SUNERGY

Objective:

Demonstrate on intermediate scale (approx. 200 kg per batch) an integral direct carbothermic route for sog-Si production that can be industrialised.

The project is organised in 6 work packages, which follow the value chain and production steps:

WP 1 Raw materials → **WP 2 Si-production** → **WP 3 Purification** → **WP 4 Wafer & Cell process** → **WP 5 Techn. Implementation**

WP 6 Project management

Progress to date:

- Solar cells, resulting from SISI have led to 80% relative cell efficiency compared to reference.
- Good progress with tests on kerf loss purification.
- Latest silicon production run resulted in good quality material with promising lifetime.

Next actions:

- Focus will on optimising:
  - silicon production process,
  - purification process
  - cell process for the SISI-material,
- Leading to cell efficiencies close to the reference.

- Continue adapting purified silicon kerf for recycling as solar grade silicon.

Exploitation plans

- Develop large-scale plant (5000 ton/yr)
- EC-funding requested for demonstration project to validate this route on 5000 ton/yr scale.

- Kerf loss recycling on medium long term:
  - process still under development
  - optimising parameters will be challenging.

General Information

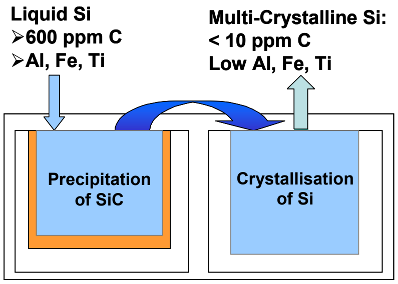
CO-OPERATIVE RESEARCH project
Coordinator: ECN, Ms Boukje Ehlen, MSc.
ehlen@ecn.nl
+31 6 225 25 469
Duration of the project: 15/09/2004 – 14/09/2006
Budget: € 1,918,500
EU contribution: € 994,000

Quartz and carbon are conversed to SiC, after which Si-metal production takes place

Arc furnace to produce Si-metal

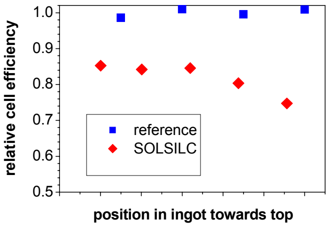
Liquid Silicon

Purification of the silicon melt



Purification

SoG-Si is processed into solar cells with promising results



n-type base doping → experimental cell process

Annex V

L.J. Geerligs, P. Manshanden, I. Solheim, E.J. Ovrelid, A.N. Waernes

IMPACT OF COMMON METALLURGICAL IMPURITIES ON MC-SI SOLAR CELL EFFICIENCY: P-TYPE VERSUS N-TYPE DOPED INGOTS.

Proceedings of the 21st European PV Solar Energy Conference

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ECN Solar Energy
P.O. Box 1
1755 ZG Petten
The Netherlands

Effect of metallurgical impurities: p-type versus n-type mc-Si ingots

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Goal and approach

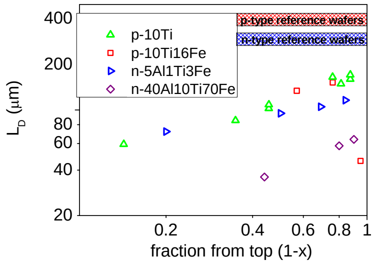
Compare the tolerance for metallurgical impurities (Al, Fe, and Ti) in n-type versus p-type doped mc-Si, by:

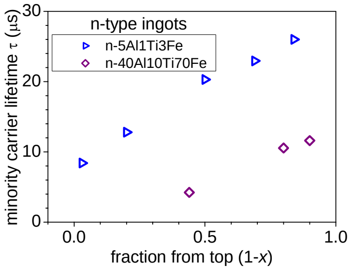
- Contaminating feedstock with known concentrations of the contaminants.
- Growing standard mc-Si ingots and process to solar cells.
- Measuring internal quantum efficiency; derive the diffusion length and carrier lifetime.

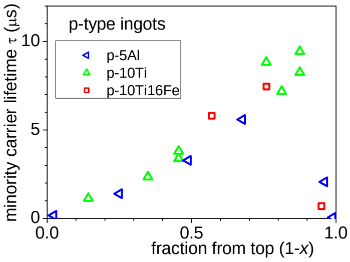
Ingots

Ingot	type	resistivity	Impurities (ppmw)		
		Ωcm	Al	Ti	Fe
p-5Al	p	1	5		
p-10Ti	p	2		10	
p-10Ti16Fe	p	2		10	16
n-5Al1Ti3Fe	n	0.1	5	1	3
n-40Al10Ti70Fe	n	0.2	40±20	10±5	70±30

Diffusion length and lifetime







Results in agreement with:

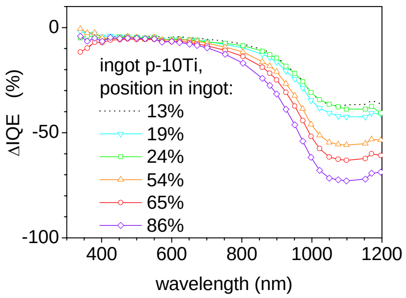
$$C_S = k_{eff} C_0 (1 - f_s)^{k_{eff} - 1}$$

$$\frac{1}{\tau} \propto N_t \propto \frac{1}{1-x}$$

- p-5Al and n-5Al1Ti3Fe: higher lifetime for n-5Al1Ti3Fe, although it has same amount of Al and *additionally* low resistivity.
- p-10Ti and n-40Al10Ti70Fe: same lifetime, although n-40Al10Ti70Fe has same amount of Ti, and *additionally* 20-60 ppmw of Al, 40-100 ppmw of Fe and low resistivity.
- Quantitative comparison of recombination strength in n-type vs p-type not performed because of different resistivities.

IQE

- Diffusion length L_D is derived from IQE.
- The IQE, relative to reference mc-Si (of the same dopant type), shows reduced red-response due to the impurities.



Example of reduced red-response in IQE measurements

Conclusions

- n-type ingots clearly more tolerant to Al and Ti
- Difference for Fe not directly demonstrated in this work, but similar result expected.
- For low resistivity and high impurity concentrations diffusivity is also reduced, resulting in important reduction of diffusion length (additional to effect of recombination).

Acknowledgments:

- *EC Support in projects SISI (COOP-CT-2002-508202), SPURT (NNE5-CRAF-1999-70783), FOXY (SES6-019811)*
- *BBr3-diffusion for the n-type cells by T. Buck and R. Kopecek, University of Konstanz*
- *n-type mc-Si ingots for reference cells by I. Röver and K. Wambach, Deutsche Solar*

IMPACT OF COMMON METALLURGICAL IMPURITIES ON MC-SI SOLAR CELL EFFICIENCY: P-TYPE VERSUS N-TYPE DOPED INGOTS.

L.J. Geerligs,[1] P. Manshanden,[1] I. Solheim,[2] E.J. Ovrelid,[2] A.N. Waernes.[2]
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ABSTRACT: Silicon solar cells based on n-type silicon wafers are less sensitive to carrier lifetime degradation due to several common metal impurities than p-base cells. The theoretical and experimental indications for this have recently received considerable attention. This paper compares p-type and n-type cells purposely contaminated with relatively high levels of impurities, processed by industrial techniques. The impurities considered are Al, Ti, and Fe, which are the dominant impurities in metallurgical silicon and natural quartz. The work also preliminary addresses the question whether the optimal wafer resistivity is the same for n-type as for p-type base mc-Si cells.

Keywords: silicon, feedstock, impurities

1 INTRODUCTION

This paper compares p-type and n-type silicon solar cells purposely contaminated with relatively high levels of impurities, processed by industrial techniques. The impurities investigated, Al, Ti and Fe, are important in feedstock production involving quartz and carbon, such as by metallurgical routes, because they are the major impurities in natural quartz. A metallurgical process, i.e., reaction of quartz and carbon, offers a perspective for large scale and low cost production of solar grade silicon.

The work is also relevant for other feedstock production techniques and for ingot casting, because quartz and steel are dominant materials in equipment for feedstock production and ingot growth.

It is known that the interstitial point defects Ti, V, Cr, Mo, Fe in silicon capture electrons much more effectively than holes [1]. Therefore these defects are expected to be less detrimental for carrier recombination lifetime in n-type silicon, where holes are the less abundant (minority) carriers, than in p-type silicon, where electrons are the minority carriers. The same effect applies to the aluminium-related defect observed in Cz wafers [2]. This asymmetry in capture cross sections also causes a different sensitivity to wafer resistivity. Recombination lifetime in n-type wafers due to these defects is practically insensitive to resistivity, while in p-type wafers it can show a strong decrease with decreasing resistivity.

The aim of this work is to determine the optimum doping (type and resistivity) of mc-Si solar cells that contain a non-negligible amount of Ti, Al and/or Fe impurities. The first aim is to determine whether higher concentrations of these impurities can be tolerated better in n-type silicon than in p-type silicon. The second aim is to determine whether for n-base cells a lower resistivity is allowed than is commonly allowed for p-base wafers, thus enhancing the cell V_{oc} and efficiency. This paper presents first results mainly for silicon contaminated with a mix of the impurities.

2 EXPERIMENTAL

2.1 Experimental ingots

Two p-type and two n-type ingots were grown with a mix of impurities. Additional p-type ingots were grown with the individual impurity Al or Ti.

The silicon was crystallised by directional solidification into a 12 kg ingot, wafered, and processed to cells by industrial cell processing (experimental cell processing based on industrial techniques, for the case of n-type base).

The p-type ingots were doped with boron to result in a base resistivity of approx. 1.5 Ωcm. The n-type ingots so far were doped with phosphorous to a much lower base resistivity of around 0.1 Ωcm. N-type ingots without impurities but with low resistivity, as well as with individual impurities and normal resistivity have been made but have not yet been analysed.

Most ingots contained a significant amount of carbon. However, earlier studies [3] showed that this carbon has only a small effect on the cell properties. For the levels of impurities studied here, we neglect the effect of carbon.

Ingot code and impurity concentrations in feedstock are given in Table 1. Note the distinct difference between impurity level in feedstock versus in ingot or wafer. The ppm-levels in feedstock are reduced to ppb or less in the ingot due to segregation.

Table I: List of ingots and concentration of impurities in the feedstock. Impurity levels in ppmw (parts-per-million by weight).

ingot	type	ρ	impurities		
		Ωcm	Al	Ti	Fe
p-5Al	p	1	5		
p-10Ti	p	2		10	
p-10Ti16Fe-A	p	2		10	16
p-10Ti16Fe-B	p	2		10	16
n-5Al1Ti3Fe	n	0.1	5	1	3
n-40Al10Ti70Fe	n	0.2	40±20	10±5	70±30

2.1 Experimental ingots

The p-type cell process was a standard industrial process: alkaline saw-damage etch, phosphorous diffusion in an IR belt furnace, remote plasma-enhanced CVD of a SiNx front surface coating, screen printed metallisation, and co-firing. For the experiments in this abstract, the typical cell efficiency with this process on good quality wafers was 14.5-15.0%.

The n-type cell process was an early version of the cell process developed in the NESSI project [4]. It is mostly based on industrial process steps: alkaline saw-damage etch, boron diffusion in a quartz tube furnace, remote plasma-enhanced CVD of a SiNx front surface coating, screen printed metallisation, and co-firing. For the experiments in this paper, the typical cell efficiency with this process on good quality wafers was 12.5%. One of the aspects limiting the cell efficiency is the absence of surface passivation of the boron emitter by the SiNx coating.

The cell size was typically $(100\text{mm})^2$, in some cases $(125\text{mm})^2$.

As reference for the experimental ingots, conventional mc-Si ingots were used. For the p-type cells, several regular mc-Si ingots were used. For the n-type ingots, reference mc-Si wafers from several experimental n-type ingots were supplied by Deutsche Solar [4].

3 RESULTS

3.1 Experimental ingots

The results on the p-type doped ingots were analysed and published previously [3].

The resistivity profiles of the p-type ingots are relatively flat because boron hardly segregates (k_{eff}~0.8). Only the Al-contaminated p-type ingot shows some more resistivity variation due to doping by Al with segregation coefficient k_{eff}~0.007. The resistivity in the n-type ingots also follows a profile in approximate agreement with Al-segregation. This is consistent with the fact that while phosphorous dominates the type of doping, Al segregation dominates the change of resistivity through the ingot.

In ingots n-5Al1Ti3Fe and n-40Al10Ti70Fe the Al and P-concentrations were measured by chemical analysis. The resistivity is higher by a factor 2 (n-5Al1Ti3Fe) to 3 (n-40Al10Ti70Fe) than expected from the chemical dopant concentration. Most likely this indicates a reduced carrier mobility in these ingots (due to the other impurities).

3.2 Cell results: p-type ingots

Fig. 1 shows typical examples of the I-V parameters and the internal quantum efficiency for some of the p-type ingots. The IQE of one of the ingots (p-10Ti16Fe-B) is suppressed at short wavelengths because of insufficient removal of saw damage (the ingot was sawn with a different sawing technique - ID saw). The suppression of IQE at long wavelengths is due to the metallic contaminants in the experimental ingots. It was analysed more precisely for the individual impurities Ti and Al in a previous paper [3]. The suppression of IQE in p-10Ti and p-10Ti16Fe is similar, and therefore is concluded to be largely due to the Ti present in these ingots, rather than the Fe present additionally in p-10Ti16Fe.

3.3 Cell results: n-type ingots

Fig. 2 shows the I-V parameters and the internal quantum efficiency of n-type ingot n-40Al10Ti70Fe. For the ingot n-5Al1Ti3Fe, the I-V parameters are not directly comparable because of different cell process conditions.

The striking effect that V_{oc} for cells from ingot n-40Al10Ti70Fe is higher than for the reference wafers, was not observed for all cell batches from this ingot, nor for ingot n-5Al1Ti3Fe. The effect appears to depend on process conditions.

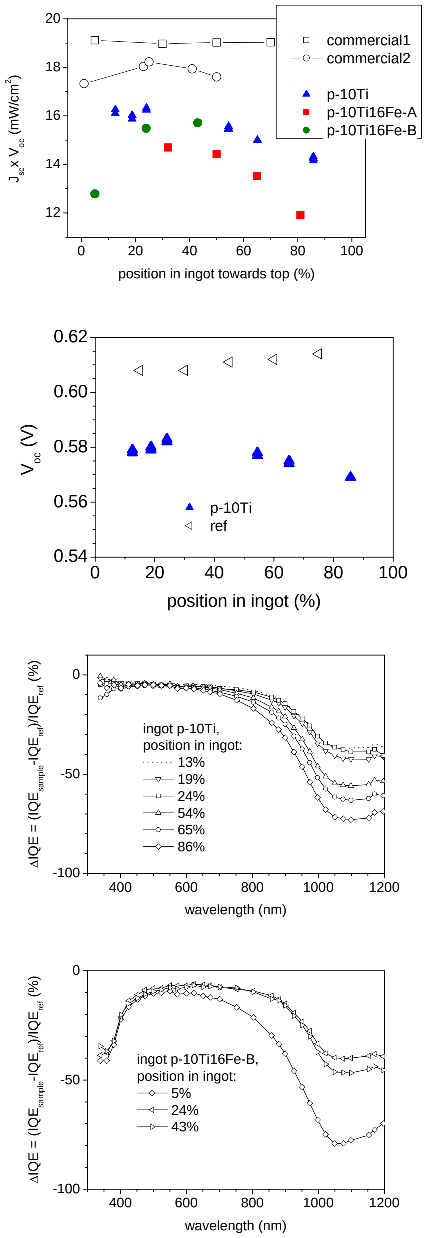

Figure 1: $J_{sc}V_{oc}$ product, V_{oc}, and internal quantum efficiency (the IQE is presented as deviation in % from average of reference ingot "commercial1") for the p-type ingots.

3.4 Cell results: L_D and recombination lifetime

The parameters of major importance in this paper, to characterise the impact of the impurities, are the carrier diffusion length and lifetime, derived from the internal quantum efficiency. These are shown for all investigated ingots in Fig. 3.

4 DISCUSSION

4.1 Internal quantum efficiency and carrier lifetime

The minority carrier diffusion length can be derived from a Basore-fit (1/IQE versus $1/\alpha(\lambda)$)of the infrared part of the internal quantum efficiencies. The impact of impurities on solar cell response is determined by this diffusion length. Since the lifetime is the parameter directly coupled to impurity concentrations, this discussion focuses on the lifetime. A disadvantage of n-type base material which should be kept in mind is that the minority carrier diffusivity in n-type Si is roughly a factor 3 lower than in p-type, for the same resistivities. In Fig. 3 both diffusion length and carrier lifetime are given (the estimated diffusivity was used to calculate the carrier lifetime).

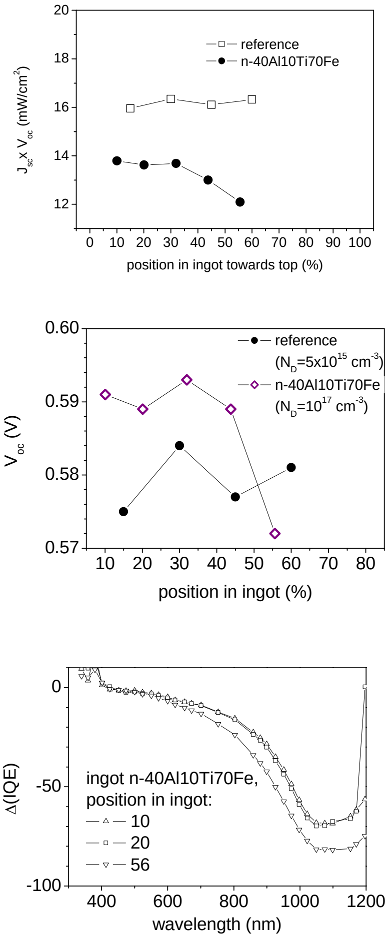

Figure 2: $J_{sc}V_{oc}$ product, V_{oc}, and internal quantum efficiency (the IQE is presented as deviation in % from average of the reference ingot) from n-type ingot n-40Al10Ti70Fe.

According to the Scheil equation,

$$C_S = k_{eff} C_0 (1 - f_s)^{k_{eff} - 1},$$

the concentration of an impurity as a function of position x in the ingot (x=0..1, from bottom to top) should be given by:

$$N_t \propto \frac{1}{1-x}, \text{ and therefore } \frac{1}{\tau} \propto N_t \propto \frac{1}{1-x}.$$

This behaviour is visible in Fig. 3.

Ingots n-5Al1Ti3Fe and p-5Al are both doped with approx. 5 ppmw of Al but ingot n-5Al1Ti3Fe has approx. 10-30x lower resistivity than ingot p-5Al. Nevertheless, ingot n-5Al1Ti3Fe has significantly higher lifetime than ingot p-5Al. Thus, Al is much less harmful for the recombination lifetime in the n-type ingot. However, due to the lower diffusivity of minority carriers in the n-type silicon, the difference in *diffusion length* in these two ingots is rather small.

Ingot n-40Al10Ti70Fe is doped with an amount of Ti comparable to the p-type ingot p-10Ti, and additionally has a large amount of Al and Fe, and a resistivity approx. 10x lower than the p-type ingots. Nevertheless, the carrier lifetime is similar to the p-type ingots with 10 ppmw of Ti, and only a factor 3 lower than ingot n-5Al1Ti3Fe. Due to the different minority carrier diffusivities, the *diffusion length* in ingot n-40Al10Ti70Fe is smaller than in the p-type ingots doped with 10 ppmw of Ti.

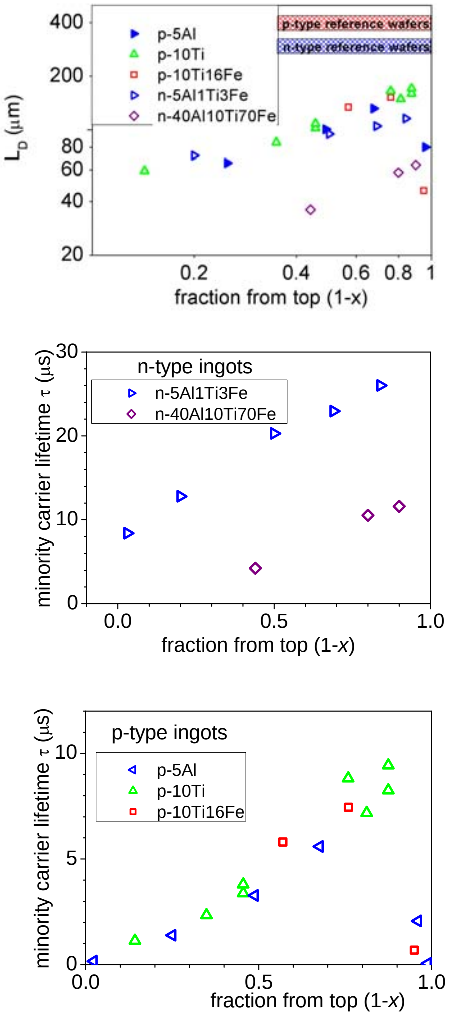

Figure 3: Minority carrier diffusion length (determined from the internal quantum efficiency) and corresponding minority carrier lifetime. For the conversion from diffusion length to lifetime, the additional suppression of carrier diffusion in the n-type ingots by a factor 2-3 was taken into account.

4.2 Ingot resistivity and V_{oc}

An advantage of low resistivity n-type wafers can be that it increases the open circuit voltage of the cell. Normally (in p-type cells with common impurities such as Fe) a low resistivity causes a decrease of carrier lifetime. Therefore the potential gain in V_{oc} is offset by lifetime-related losses, especially of J_{sc}. A typical optimal resistivity is 1 Ωcm.

In n-type silicon, according to our (preliminary) results, the low resistivity is less harmful for minority carrier lifetime, and the low resistivity may be used to some advantage. As shown in Fig. 2 the V_{oc} of the contaminated but highly doped wafers from ingot n-40Al10Ti70Fe is even better than the V_{oc} of the uncontaminated but normally doped reference wafers. This is probably why the $J_{sc}V_{oc}$ product of cells from ingot n-40Al10Ti70Fe, relative to the reference cells, is high, similar to that of the p-type ingots doped with 10 ppmw Ti, despite the lower diffusion length.

However, as mentioned in section 3.3, this remarkable effect in V_{oc} was not always observed and appears to depend on cell process conditions.

4 SUMMARY

The effects of contaminants in p-type and n-type doped multicrystalline silicon wafers were compared experimentally. The reduction of cell efficiency due to contamination of silicon feedstock with titanium, iron and aluminum was analysed. We observed favorable effects due to the n-type doping. The studied metal impurities have lower impact on carrier lifetime in the n-type doped wafers than in the p-type doped wafers. The situation with respect to carrier diffusion length is less clear.

The low n-type base resistivity (~0.1 Ωcm) leads, despite high metal impurity content, in some cases to higher open circuit voltages than the reference n-type cells with ~1 Ωcm base resistivity. Thus, the combination of low n-type resistivity and high impurity content performs better than expected.

So far, n-type ingots were investigated in which are present, simultaneously, high impurity concentrations as well as high doping levels. The effect of resistivity and the effects of individual impurities will be studied separately. This will allow to model and quantify the impact of the impurities in an n-base solar cell, so that it can be compared directly with our previous results for a p-type base. Such a more accurate analysis should also show whether the advantages for carrier lifetime observed in this paper are larger than the disadvantage of the lower diffusivity in n-type silicon.

5 ACKNOWLEDGMENTS

We gratefully acknowledge EC Support in projects SISI (COOP-CT-2002-508202), SPURT (NNE5-CRAF-1999-70783), and FOXY (SES6-019811). The BBr3-diffusion for the n-type cells was performed by T. Buck and R. Kopecek, at University of Konstanz. Reference n-type mc-Si ingots were provided by I. Röver and K. Wambach, at Deutsche Solar.

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Annex V

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