Will remain crystalline silicon the material of choice for micro- and -optoelectronic applications?

Sergio Pizzini

InovaLab, Padova (Italy): former full professor at the Materials Science Department, University of Milano -Bicocca

Semiconductor silicon

- Semiconductor silicon is the purest(*) syntetic material today available, with a success history of more than 50 years. It is produced in more than 250.000 tons/year amount, with a cumulative annual production growth rate of 38% in a multibillion (projection for 2012, 253 Billion $) market
- Its key application is still microelectronics but the main stream today is for photovoltaics, where it covers the 80% of the market (see slide)
- It is commercially available as single crystal ingots, single crystal wafers, multicrystalline ingots and wafers, (ribbon) and thin films →

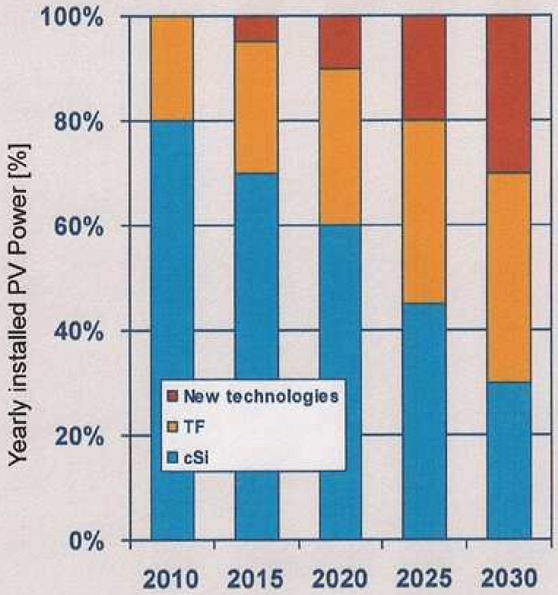
(*)Acceptors (B,Ga) concentration ≤1 ppba; Donors (P,As,Sb) concentration ≤1 ppba

Carbon concentration≤0,3 (ppma); Total transition metal concentration ≤10 (ppba)

Total concentration of alkali and alkali earths metals ≤10 (ppba)

Possible Shares of PV materials

WÜRTH SOLAR



	2010	2020	2030
c-Si	80	60	30%
Thin Films	20	30	40%
Others (CPV+organic+dye+new)	<2	10	30%

Reference: EPIA

Winfried Hoffmann, Bernhard Dimmler

4 © Würth Solar / Bernhard Dimmler / "3rd Thin Film Summit USA " San Francisco, 2010-11-30

Power, -micro-and -optoelectronic applications of silicon

- Rectification @ power control (SCR, Tyristors)
- Integrated circuits
- Terrestrial PV cells
- High energy particles detectors
- Substrate for GaN field effect transistors, LEDs and PV cells

All these applications require an high quality material in terms of surface and crystal defects (point-like and extended) & impurities. But we already know how to live toghether using defect engineering (see dr. Kissinger talk)

Silicon solar cells

- Single junction commercial cells 18 ≤η(%) ≤ 24.2 (Sunpower) already close to the Shockley-Queisser limit
- Well above (48,2 %) under concentrated light and optimized optics (Barnett, 2007)

in comparison with

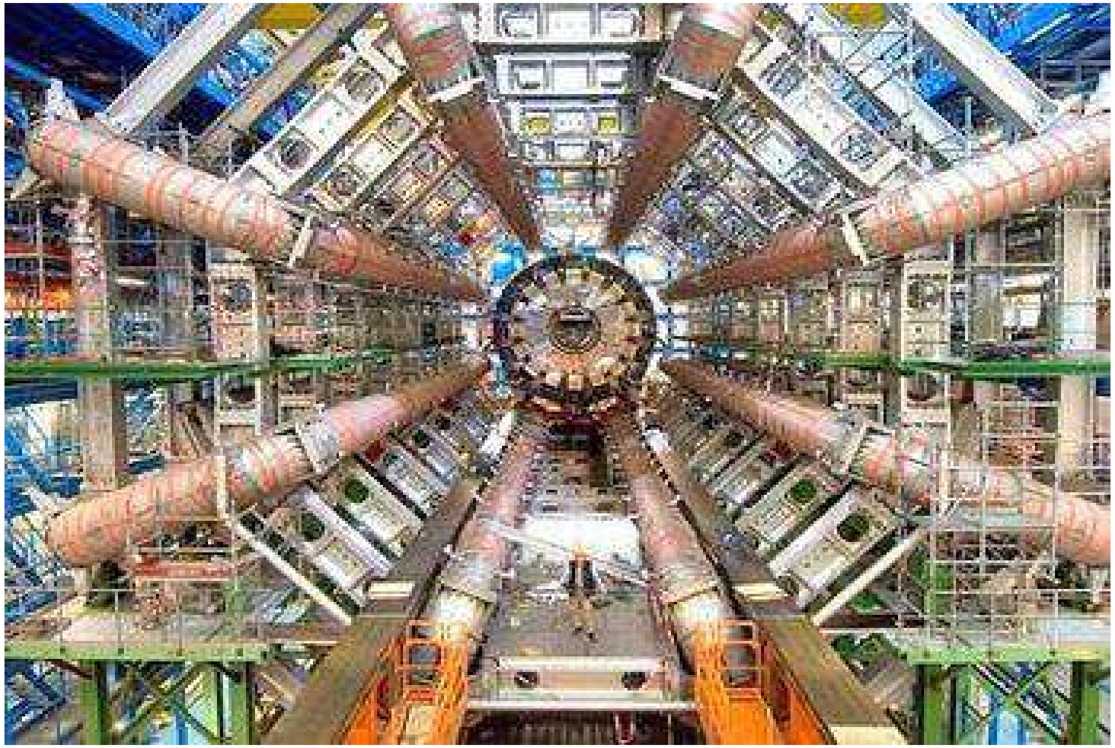
- Compound semiconductor triple junction 40% (Sharp)
- Single junction compond semiconductor thin film cells (CdTe, CIGS) 14 ≤η ≤8%
- Triple junction (a-Si , nc-Si) (Sharp 13%) *Only Sharp in the market after Solyndra bankrupt*
- Dye sensitized organic cells max 6%

High energy particles detectors at LHC (large hadronic collider)

- Hadrons energy =3,5 TeV and fluencies= 3 x 10^{14} particles/cm^2 at LHC and up to 10^{16} cm^2 in future
- A detector should work for 6 months/y over 10 years
- Knock out energy ($Si \rightarrow Si_i + V_{Si}$) = 25 eV
- Damage unavoidable but segmented 2D silicon detectors are shown to provide long life, excellent submicrometric spatial resolution, cost-effectivness due VLSI technologies used in their fabrication.
- Materials used oxygenated n-type FZ (O improves radiation hardness) or high resistivity Cz silicon

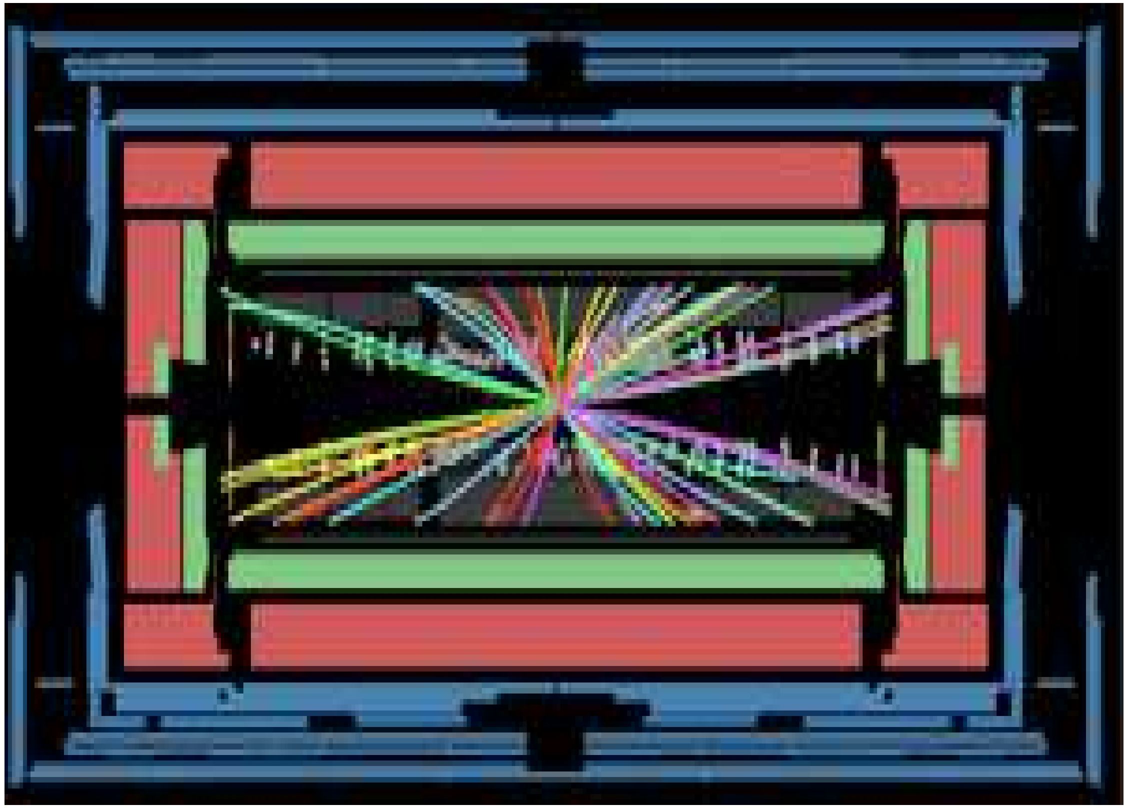
(C. Leroy, P.G Rancoita *Particle interaction and displacement damage in silicon devices operated in radiation environments* Rep. Prog. Phys. **70** 493–625 (2007) with 416 references)

LHC'Atlas Experiment at CERN in Geneve



ATLAS is about 45 meters long, more than 25 meters high, and weighs about 7,000 tons. It is about half as big as the Notre Dame Cathedral in Paris and weighs the same as the Eiffel Tower or a hundred 747 jets (empty).

Tracks of a collision event at LHC



GaN devices on silicon:a new application of silicon substrates

LEDs and FET's on silicon (today)

- Translucent, Inc. (Palo Alto, CA), a manufacturer of rare-earth-oxide (REO) engineered silicon substrates, announced the commercial availability of its GaN family of virtual GaN silicon- wafer substrates in 100 mm diameter.

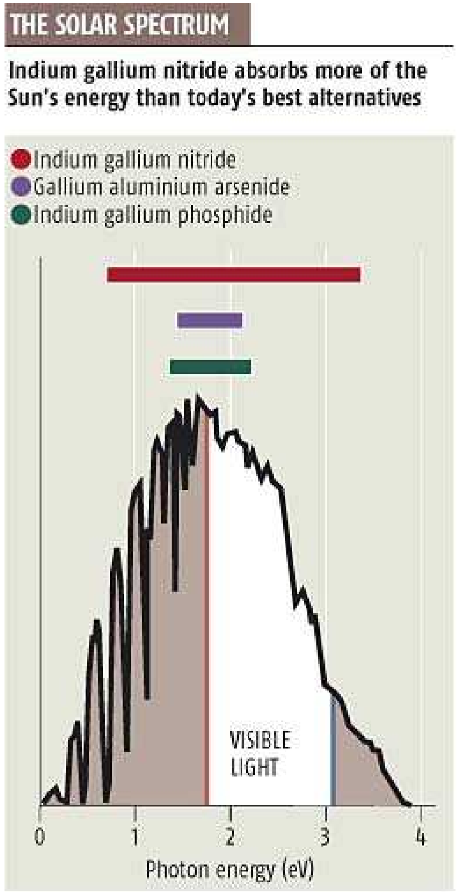
  These "virtual gallium nitride" wafer substrates are designed to provide a lower-cost alternative to sapphire wafers, while delivering a high-quality epitaxial surface upon which gallium nitride (GaN)-based devices such as LEDs or semiconductor field-effect transistors (FETs) can be fabricated.
- For solid-state lighting, the wafer stack involves two layers of rare-earth oxide (such as gadolinium oxide, Gd_2O_3), a silicon substrate with <111> orientation, a (111) silicon interlayer, and a GaN cap.

and more

- Imec's proprietary Gallium nitride (GaN) on silicon epi technology is the foundation to the development of low cost and high performing GaN-on-silicon power devices and LEDs on 100-200 and 300 mm silicon wafers in a CMoS compatible processing environment

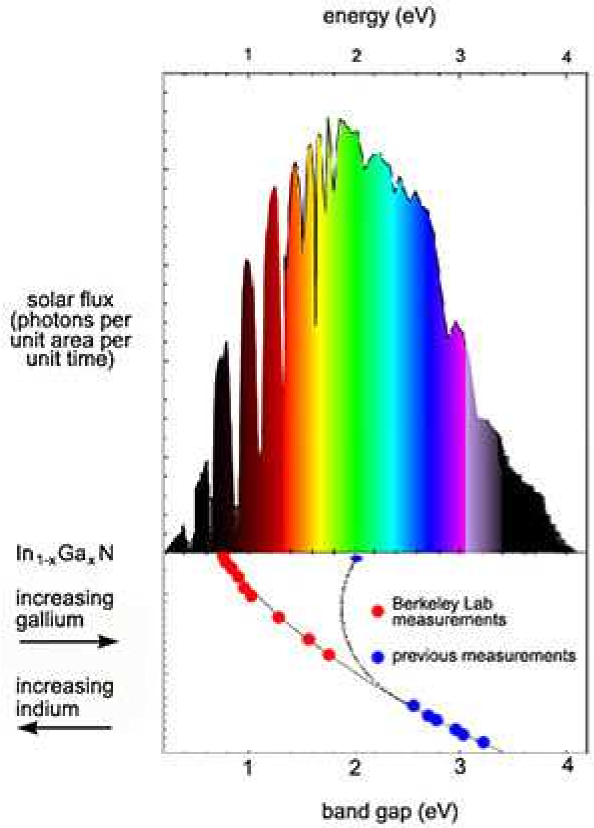
It is now possible to foresee the design of high efficiency nitride based solar cells on GaN-silicon substrates. →

Indium nitride for PV applications



Indium Gallium Nitride and the AM1.5 solar spectrum.

Ternary nitride alloys



With a multijunction nitride based solar cells the entire solar spectrum could be fitted, but the substrate on which these alloys should be deposited was high cost single crystal sapphire since yesterday

What more with silicon?

- Reduce the cost/energy content of the today available feedstock while mantaining its high purity (*but* PV is less sensible to impurities and defects than EG silicon) and improve the environmental friendship of the entire silicon production chain
- Introduce new feedstock fabrication /ingot growth processes or new routes for solar grade silicon
- Use micrometric silicon powders from ingot abrasive operation as feedstock
- Introduce n-type silicon in PV manufacturing (lifetime in n-type silicon is higher(*), mostly because metallic impurities with donor-type character have an increased capture rate for minorities (electrons) in p-type silicon not for holes in n-type materials)
- Introduce/ improve epitaxial processes for epi devices also on low cost substrates (e.g.MG silicon)

Feedstock

- Better management of the Siemens or the fluidized bed processes
- Solar silicon from upgraded MG silicon
- Carbonless solar silicon from direct or indirect electrochemical SiO_2 reduction

Siemens process

TCS purification (high rejection rate for B)

TCS reduction to Si on Si bars at 1150 °C in H_2 atmosphere (30% yield on a single stage)

$$SiHCl_3 + H_2 \leftrightarrow Si + SiCl_4 + 2\ HCl$$

recycling and $SiCl_4$ conversion to TCS necessary

⇓

Ultrapure polycrystalline silicon bars

Energy costs (year 2005 ca 200 KWhr/Kg, year 2011 min 60 KWhr/Kg

Production costs (estimates 30 EU/Kg)

Investment costs ca 100 MEU/ 1000 tons plant

Polycrystalline silicon reactor working with 27 pairs of electrodes, final rod diameter 150-170 mm, rod height max 2600 mm, operating pressure 6 bar, operating temperature 1000-1100℃, production capacity up to 402 -516 tons/year, Cycle time 96 h, Energy consumption ~45 kWh/kg Polysilicon. Reactor diameter ~2,3 m, Reactor height ~ 5,5m

Ethil process (now MEMC Electronic Materials)

MG-Si +4HF (FB reactor)-> SiF_4+ H_2

SiF_4 purification

MG-Ca + H_2 (FB reactor)-> CaH_2

2CaH_2+ SiF_4 (ms reactor)-> 2 CaF_2+ SiH_4

SiH_4 (FB reactor)-> Si powder + 2 H_2

$\Downarrow$

Ultrapure granular silicon

Electrical energy costs ca 19 kWhr/Kg

Production costs (estimates) 23 USD/Kg

Investment costs (estimates for 1000 tons plant) 56M USD

A mixture of poly & powder is used in CZ growth

Environmental problems with Siemens type of processes

Every 1000 tons of Si, 3750 tons of TCS are processed. TCS spills are rare but possible (one spill in the MEMC factory close to Merano(Italy) is noticed, with only local damage with an HCl-rich cloud). With the recent huge increase of Si production, there has been widespread concern within the PV industry about environmental accidents. The recent leakage at Jinko and claims of previous noncompliance could have far-reaching consequences for the worldwide industry in general.

It is for me hard to imagine that this process technology could survive in a far future when hundreds of GW of solar cells will be produced

MG- and UMG-Si

- MG-Si is produced in millions of tons/yr worldwide with a relatively low energy consumption (15 KWhr/Kg). It purity is around 98-99% (1000-2000 ppmw) and should be purified to be converted to solar uses
- UMG-Si is an upgraded type of MG-Si dedicated to the PV market, prepared (Crystal Systems, Elkem, Timminco) and many others by a complex purification process involving hydro-and pyro metallurgical processes addressed at the removal of B,P and metals. The final step is allways a directional solidification yielding (only Elkem) a 16% solar cell efficiency
- Very known problems are the limited quality stability of the process

Potential alternatives

- MG-Si of solar quality from pure raw materials (mine quartz with B<0,1 ppmw and pure carbon reductants) plus a directional solidification.
- Direct reduction of syntetic SiC with quartz (Solsilc Project)

Open problems: the mangement of the carbothermic process is complex. Massive CO_2 evolution should be considered in the frame of the Kyoto Protocol

Plasmochemical purification of MG-Si

- A plasma process for the purification of silicon has been proposed, tested and used by the company Kawasaki more than 10 years ago. The rationale behind the process is the formation of volatile metallic oxides (and oxyhydrates) in a plasma of argon and water, at a temperature higher than the boiling point of silicon (2027°C). At this temperature the process is much more efficient than at the temperatures 1410-1700°C, which are the process temperatures applied at Crystal Systems and in the Timminco-Becancour process
- The combination of an inductive plasma torch and electromagnetic stirring of molten silicon has been used to refine MG-Si in the french Photosil Process under the addition of reactive gases (O_2 and H_2). By this process, where the electromagnetic stirring facilitates the continuous renewal of the melt surface, on which the plasmochemical reaction takes place, a significant reduction of the contaminants (B, 0,3 ppm; C, P (1ppm), Al, Ca and Fe, ppm amounts) concentration is obtained, before further reduction by a directional solidification step.

Electrochemical processes

- Fluoride and Ca Cl_2 melts might work as electrolytes, with K_2SiF_4 or SiO_2 as the silicon bearing species. Temperatures from 800 to >1000°C
- Feasibility of fluoride melts demonstrated at the beginning of the last century
- Growing interest in Japan, China and India,CaCl2 melts preferred for their minor reactivity with container materials

Conclusions

- Siemens process and variant of its will remain unrivalled for every microelectronic application thanks to its purity. Cost, even under continous increase of yield, energy consumption and environmental pollution, will possibly limit its mass application in photovoltaics
- The full feasibility of metallurgical processes towards solar grade silicon has not yet being demonstrated
- Direct or indirect (via $CaCl_2$ melts) electrochemical reduction of silica very attractive, but still at the lab stage
- High temperature operation both in MG and electrochemical processes brings however to a thermodynamic and kinetic limit to the silicon purity

Comprehensive technical/physical analysis in S.Pizzini *Advanced silicon materials* , Wiley (in press)

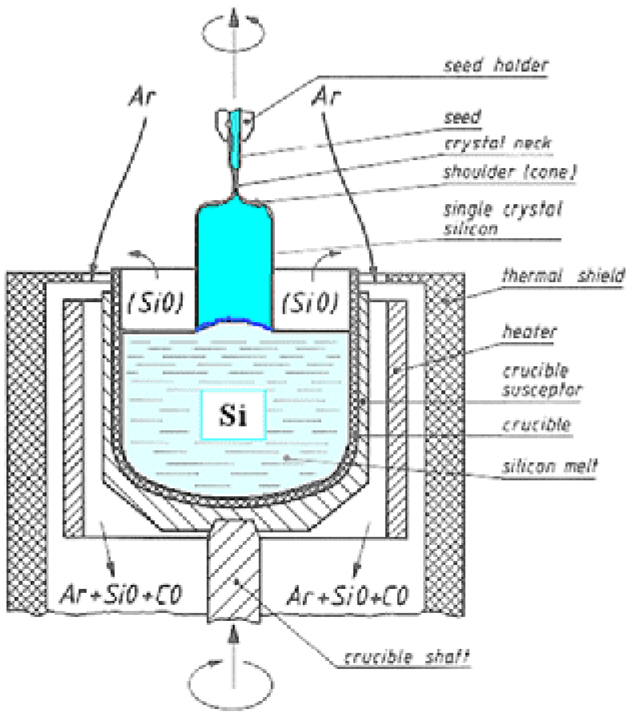
Silicon ingots growth processes

Growth of silicon ingots

- Czochralski single crystal
- Float zone single crystal
- Directional solidification of multicrystalline ingots
- Mono-cast growth

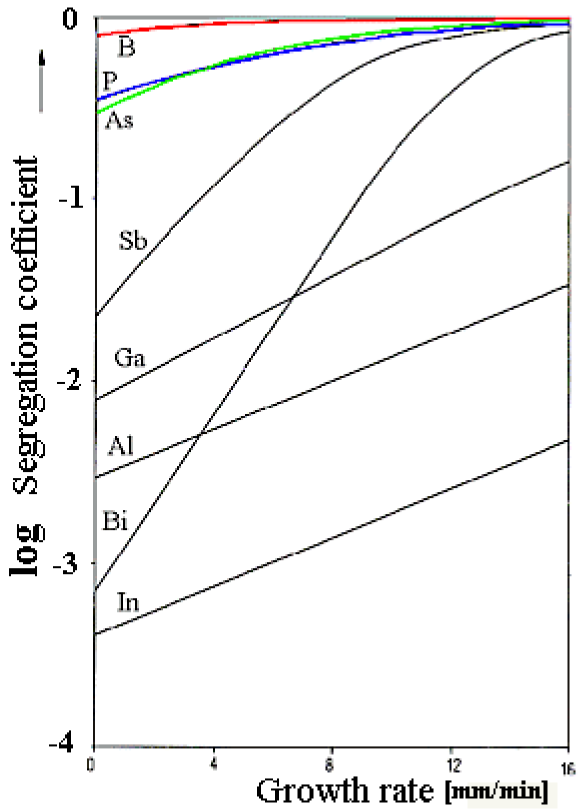
Czochralski growth

Beginning of crystal growth



Today modern pullers use charge replenishment with silicon granules and magnetic stirring for better oxygen distribution and limit the irradiation losses by graphite or Mo [cones]

Continous Cz



Drawbaks: limited potentiality of melt replenishment due to impurity accumulation in the liquid charge

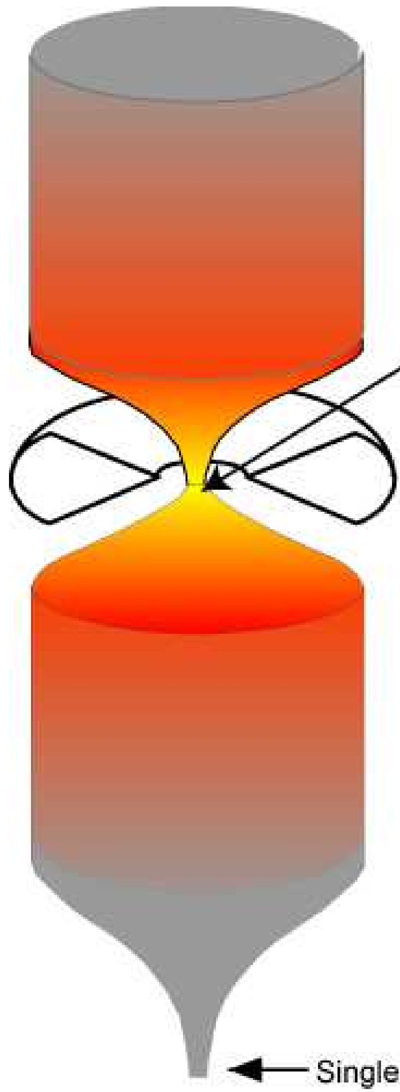
Czochralsky growth

max diameter 400 mm, max height 2 m , weight 500 -650 Kg

Challenges for improved Cz furnaces

- Increase the production yield (today 2 Kg h^{-1})
- Reduce the energy input (today >30 KWh/Kg) by reducing the irradiation losses by the introduction of Mo ar graphite cones (already in progress)
- Reduce the carbon transport by CO using an Ar cover

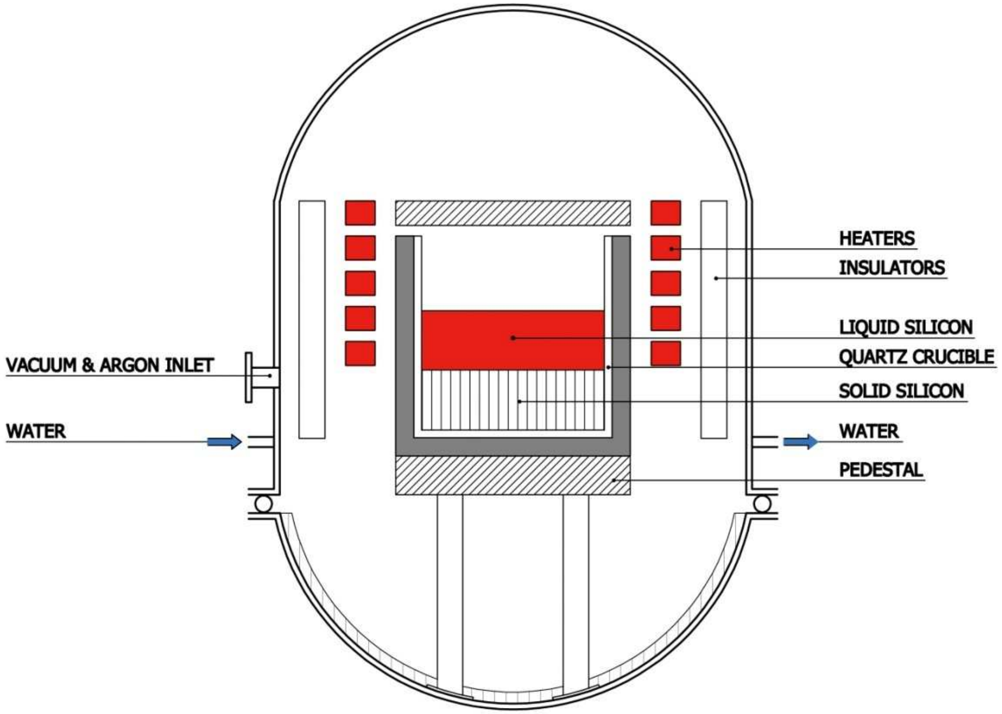
Float zone growth



Advantages and challenges of FZ

- Very high purity, very high resistivity (> $10^4 \Omega$ cm→ tyristors, radiation detectors, also solar cells
- Limited by the today diameter of polycrystalline ingots from Siemens < 200mm)
- and by the higher cost

Directional solidification furnace



Higher productivity than CZ (ca 7 Kg h^{-1})The same advantages and limits as with CZ coming from impurity segregation

Industrial GT furnaces

Advantages and challenges of DS processes

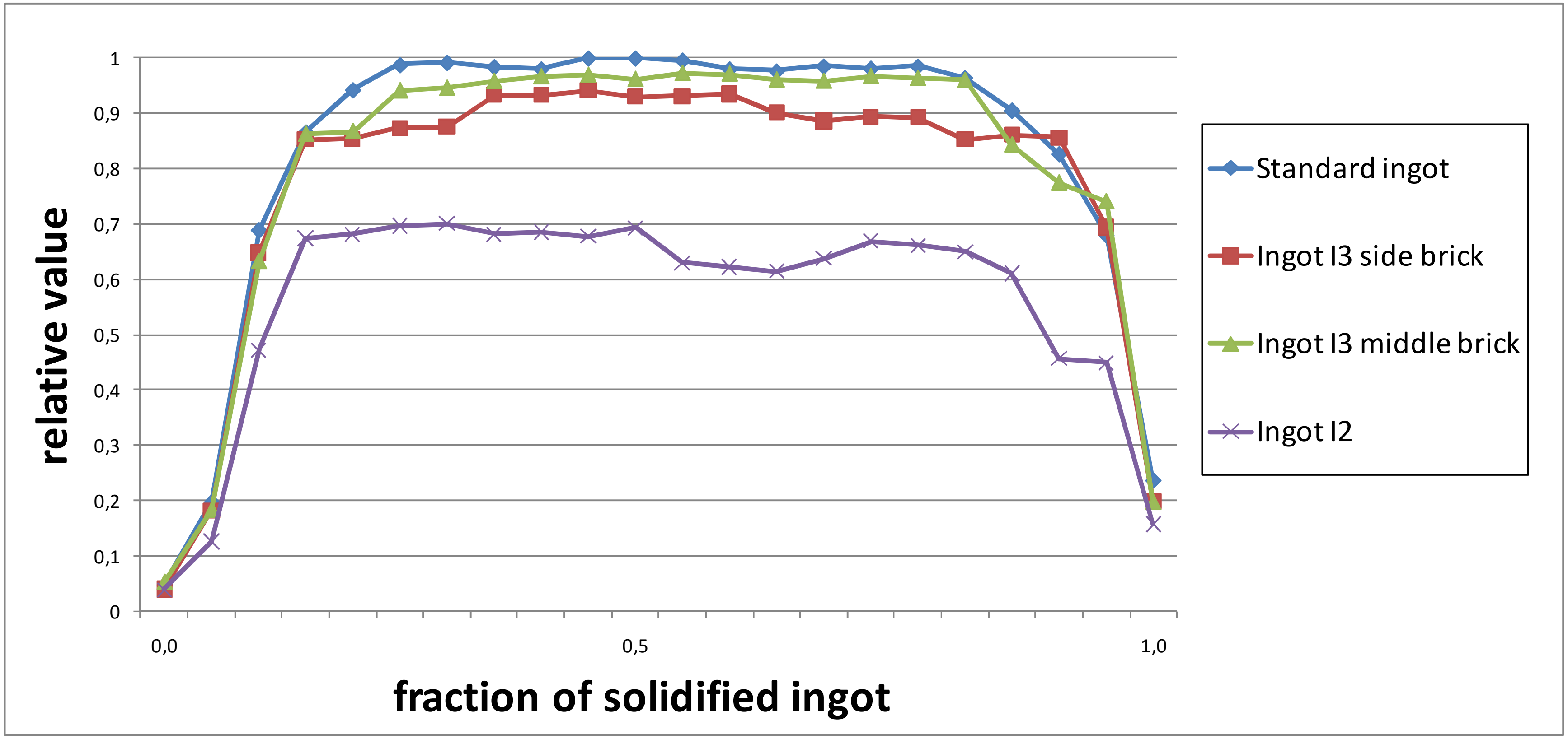
- Large columnar grains→low density of grain boundaries
- Lower energy costs than Cz (10 KWhr/Kg vs 30 KWhr/Kg and higher productivity (7Kg/h vs 2 Kg/h)
- Ingots weight up to 800 Kg
- 1% less than CZ in PV efficiency
- Yield and quality could be improved

Next developments

Recycling of fine powders

Fine powders from SiC abrasive operation on silicon ingots are a mixture of Si and SiC and useless. New fixed abrasive operation results in fine powders which could be used as feedstocks. We succeded in compactig, melting and casting these powders, with preliminarly satisfactory results

I.Lombardi, F.Tappa,G.Fragiacomo,S.Pizzini,F.Hugo *Progress in recycling of silicon fine powders from fixed abrasive operation on silicon ingots* Proc. 26th EUPVSEC (2011)1981-1985

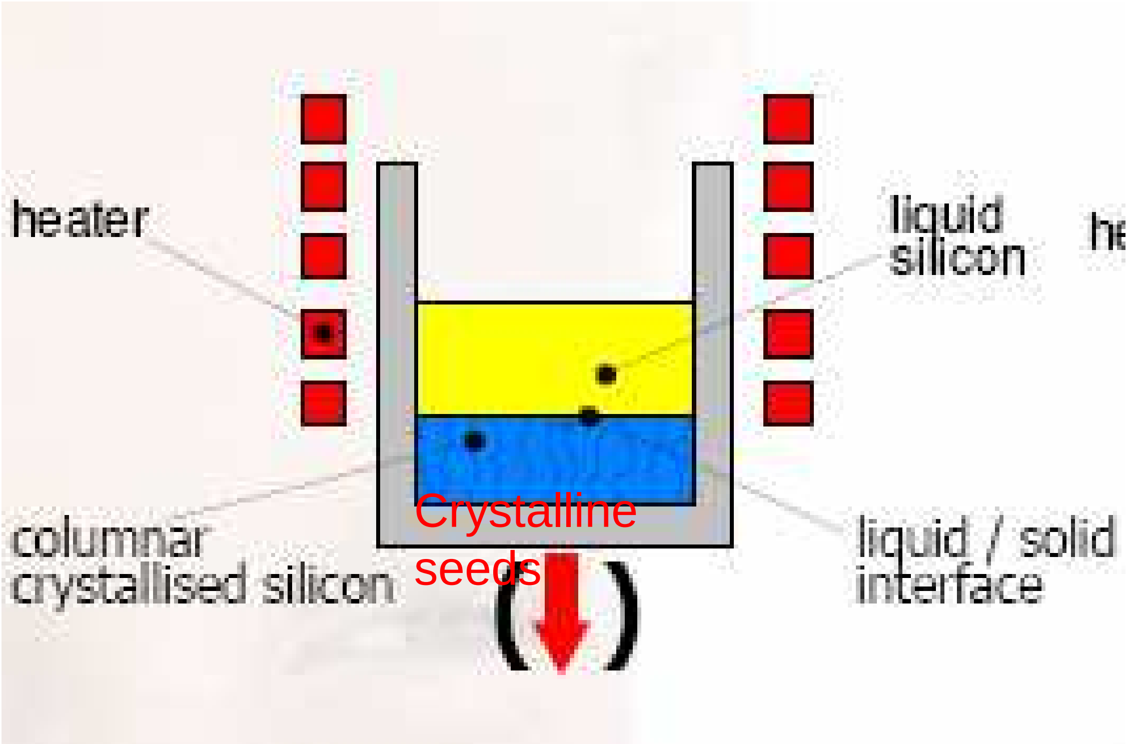


Relative PV efficiencies of cells fabricated with recycled fine powders

Induction heated DSS furnace

SAETSOLAR
INDUCTION FOR SOLAR WORLD

Monocast



The advantage is to limit the density of grain boundaries

Cold crucible furnaces (by Inductotherm)

Ribbon and direct wafer casting

- Ribbon growth from graphite crucibles and dies has reached the industrialization stage after more than 20 years, but has been recently abandoned (lack of planarity and high carbon content)
- Direct wafer casting by pooring liquid silicon on a wafer (SGR process, patented by Deutsche solar) still under development but limited by carbon content

Final conclusions

- Difficult to foresee the birth of an alternative winning technology to crystalline silicon itself for microelectronics, particle detectors and PV cell up to the Shockley-Queisser limit (η= 31% for a single junction Si cell).
- Process developments for solar silicon are possible, and research is still actively running to mitigate the role of defects and impurities (Chen and Yoshikawa)
- The potential role of nanocrystals is actively investigated (Li and Pavesi).
- Nitrides might be the most serious competitors as active components, but silicon will remain a kind of universal substrate

Long life to crystalline silicon!