SAND2018-1390PE

Exceptional service in the national interest

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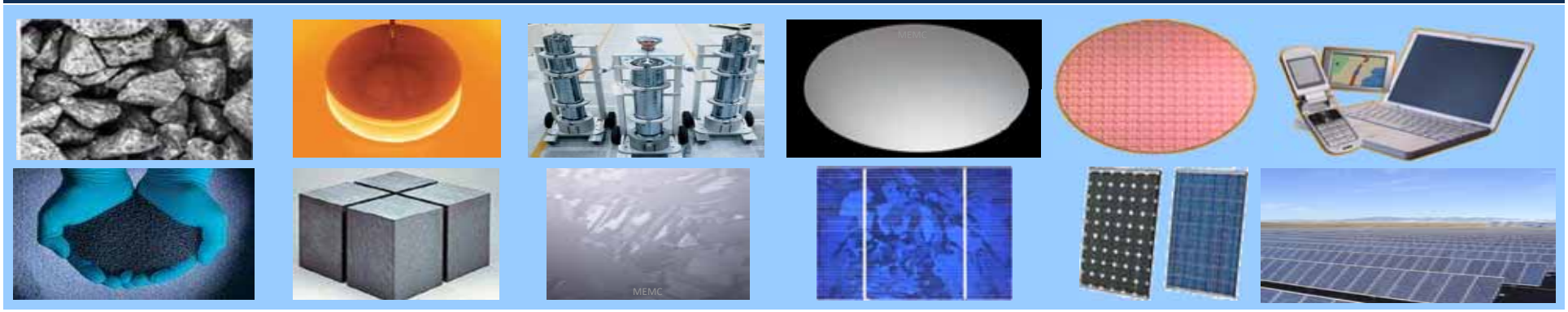

Manufacturing of Silicon Materials for Microelectronics and Solar PV

Babu Chalamala, Ph.D.

U.S. DEPARTMENT OF ENERGY | NNSA

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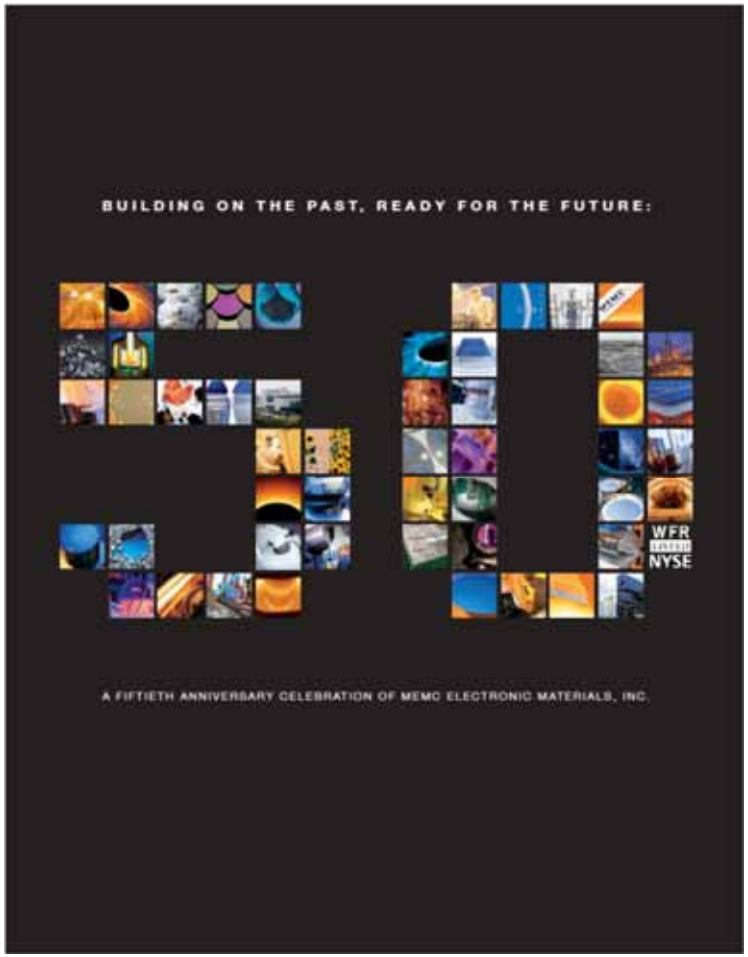
Background Material

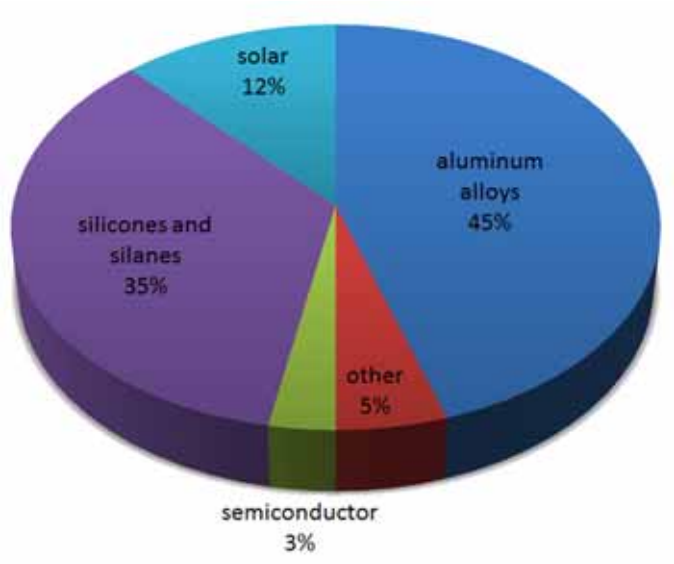


http://www.memc.com/assets/file/company/MEMC_book-optimized.pdf

http://ieeexplore.ieee.org/xpl/tocresult.jsp?isnumber=6259910&punumber=5

Silicon as an Industrial Material

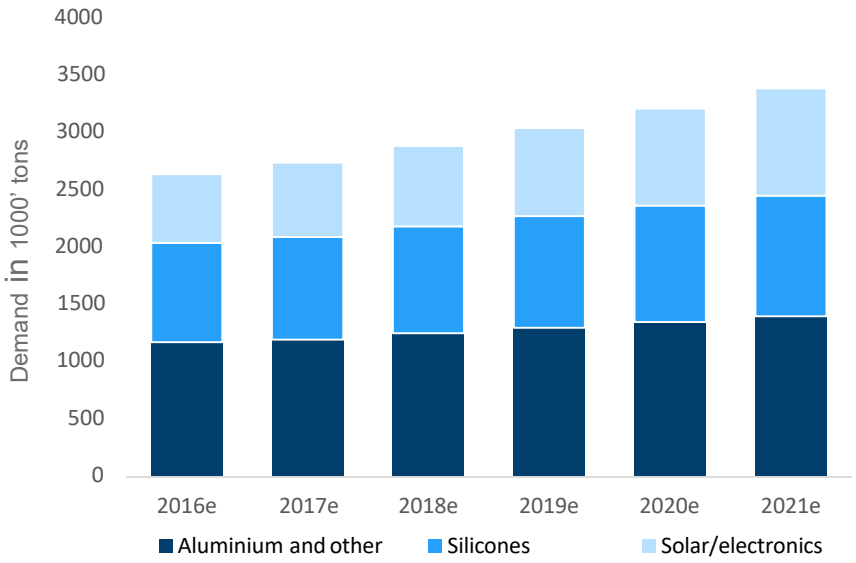
Silicon Metal			
			
Composition	99% Silicon		
Main Market	Aluminum	Silicones	Semiconductors
Usage	Silicon source	Feedstock	Bulk Material



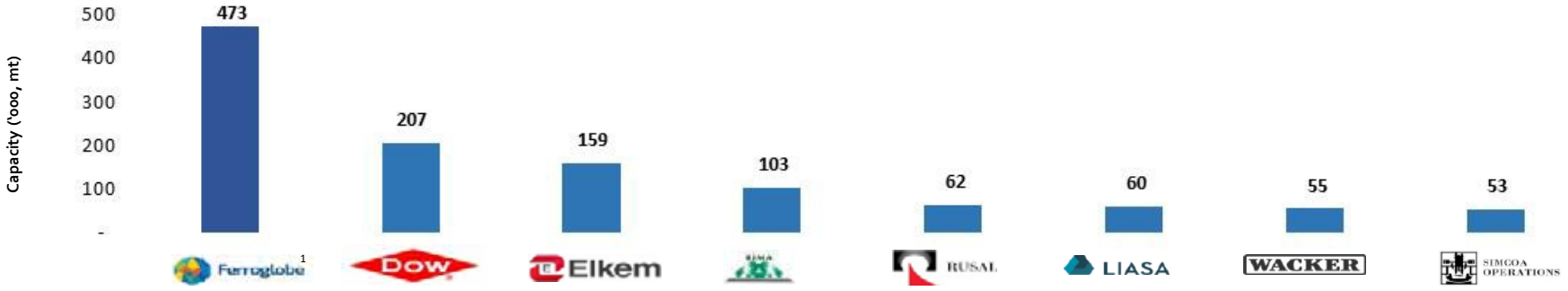
CRU Market Data, 2017

- Out of the 2.5 million of tons of silicon metal produced, about 300k tons goes into producing wafers for solar and microelectronics
- Metallurgical and chemical applications consume over 80% of Si produced

Silicon Materials Market



- With raising demand for Si in PV, both demand and production continues to grow.



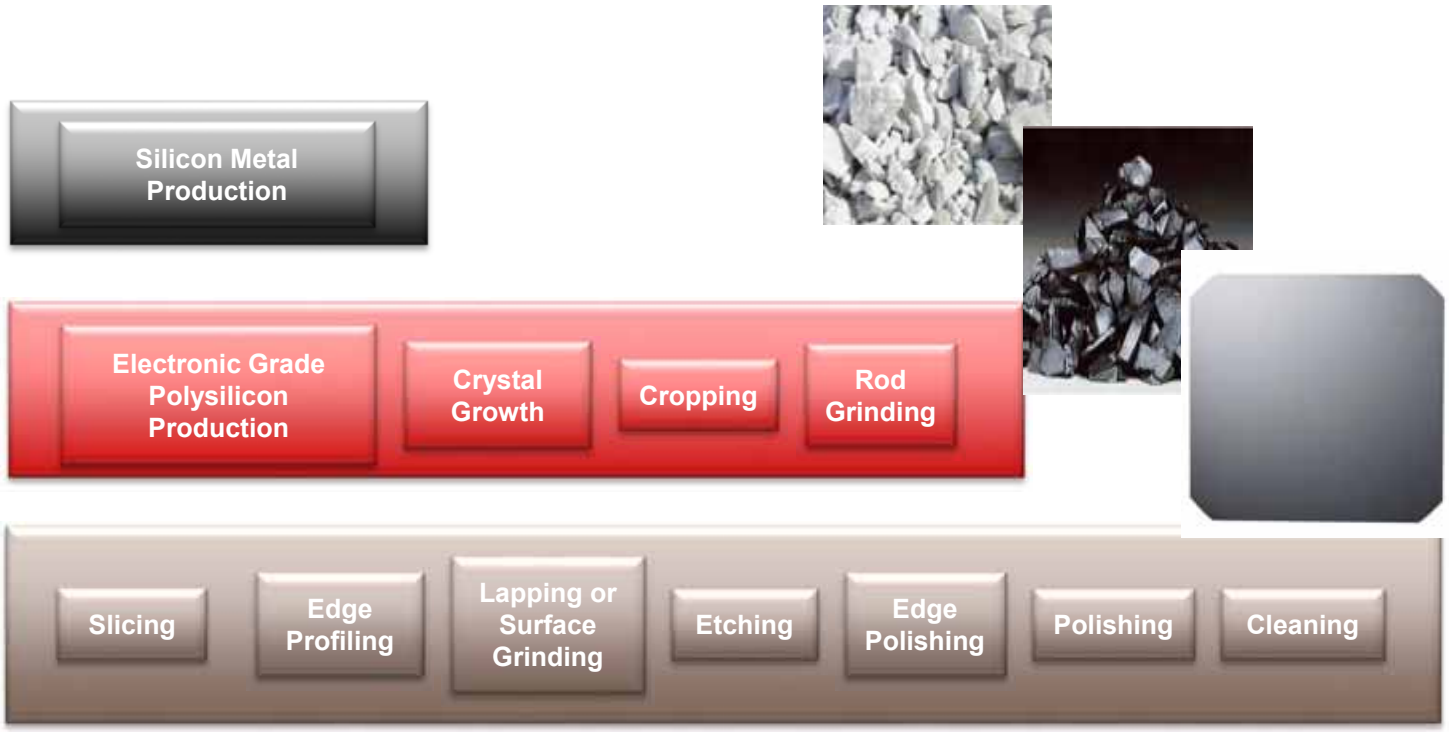
From Quartz to Silicon Wafers

Sandia National Laboratories

Silicon Metal Production

Silicon Ingot Manufacturing

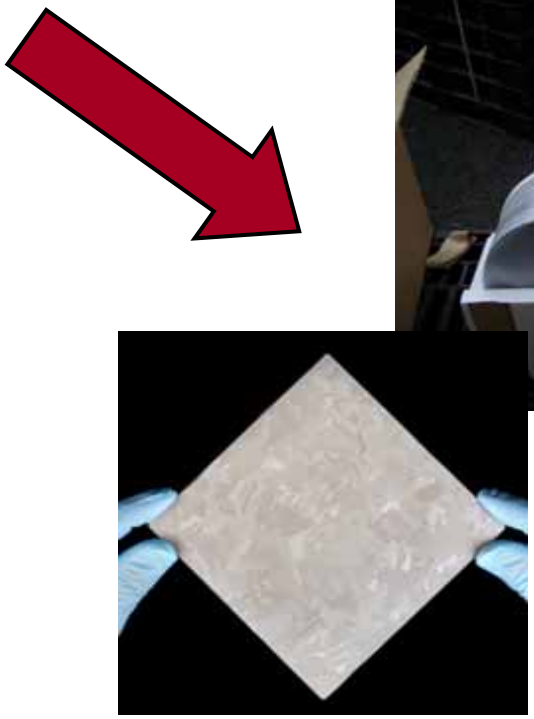
Silicon Wafer Processing

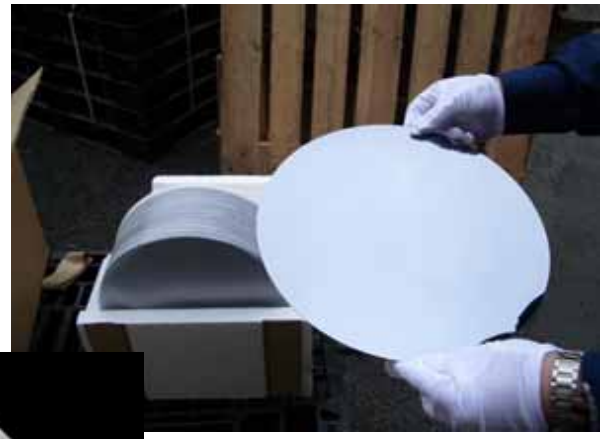


How Do We Make Silicon?

How do we go from quartz …

…to make silicon?





Silicon Metal Production

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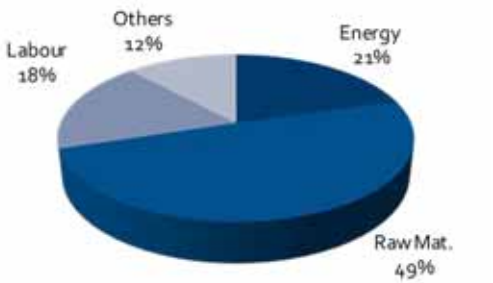
PRODUCT:	Metallurgical	Chemical	Polysilicon
MAIN MARKET:	Aluminum	Silicones	Solar
TYPICAL COMPOSITION:	99% Silicon		
MAIN CHEMICAL REACTION:	$SiO_2 \rightarrow Si$		
ORE:	High purity quartz		
CARBON SOURCE:	Low ash coal, charcoal, wood		
ENERGY REQUIRED (kWh/t)	12,000		

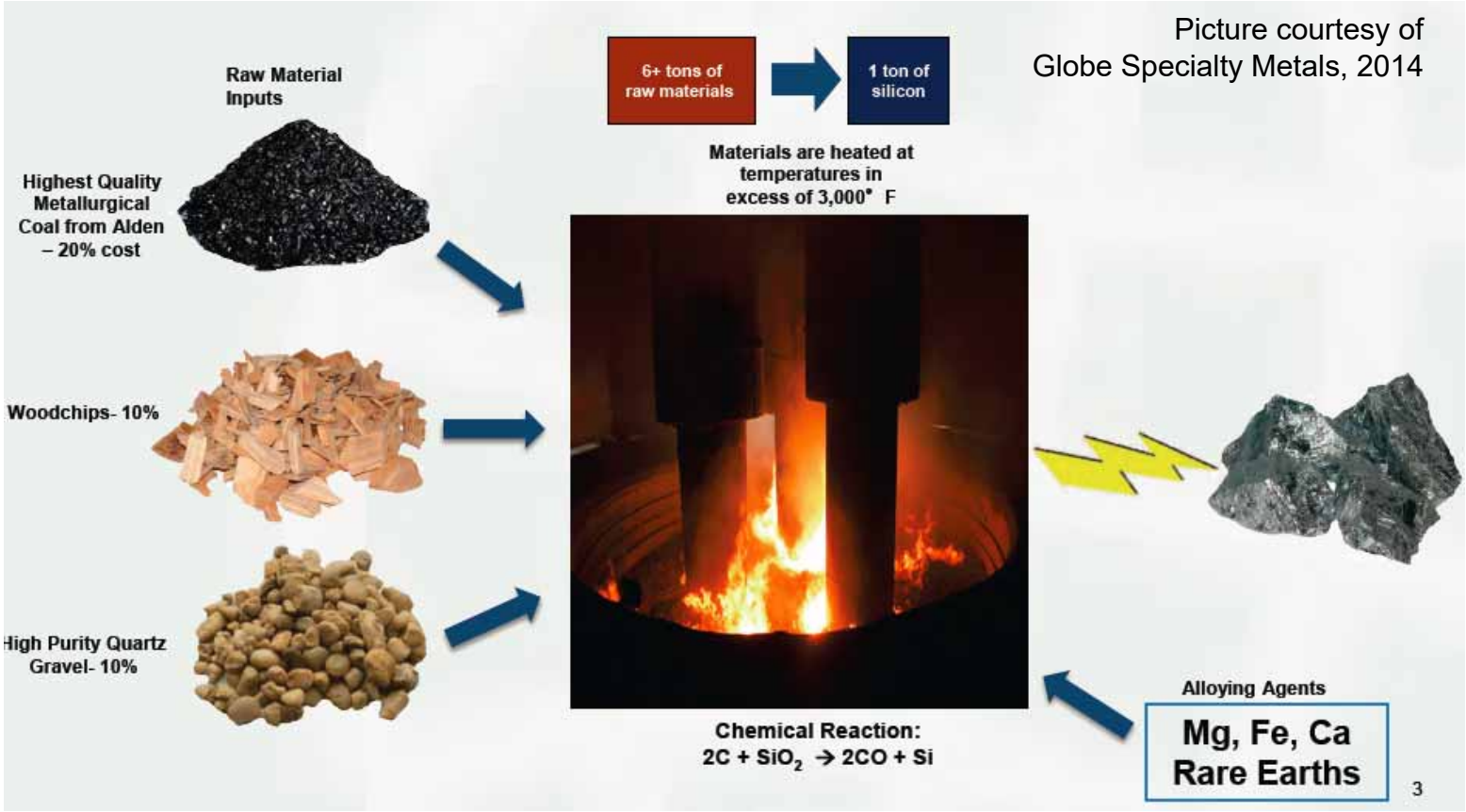


6 tons of Raw Material = 1 ton of SiMe

PRODUCTION COST BREAKDOWN

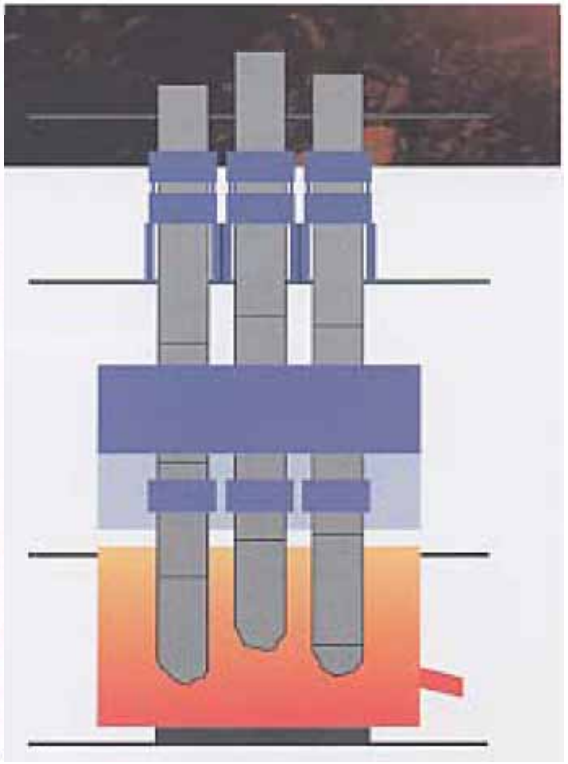
Source: Ferroglobe, CRU

How is Metallurgical Si Made?



Reduction of quartz in a submerged electric arc furnace. Highly energy intensive process. Large plants. A medium sized EAF has a crucible diameter of 7 m, graphite electrodes each 15 m tall, weighing 20 tons each.

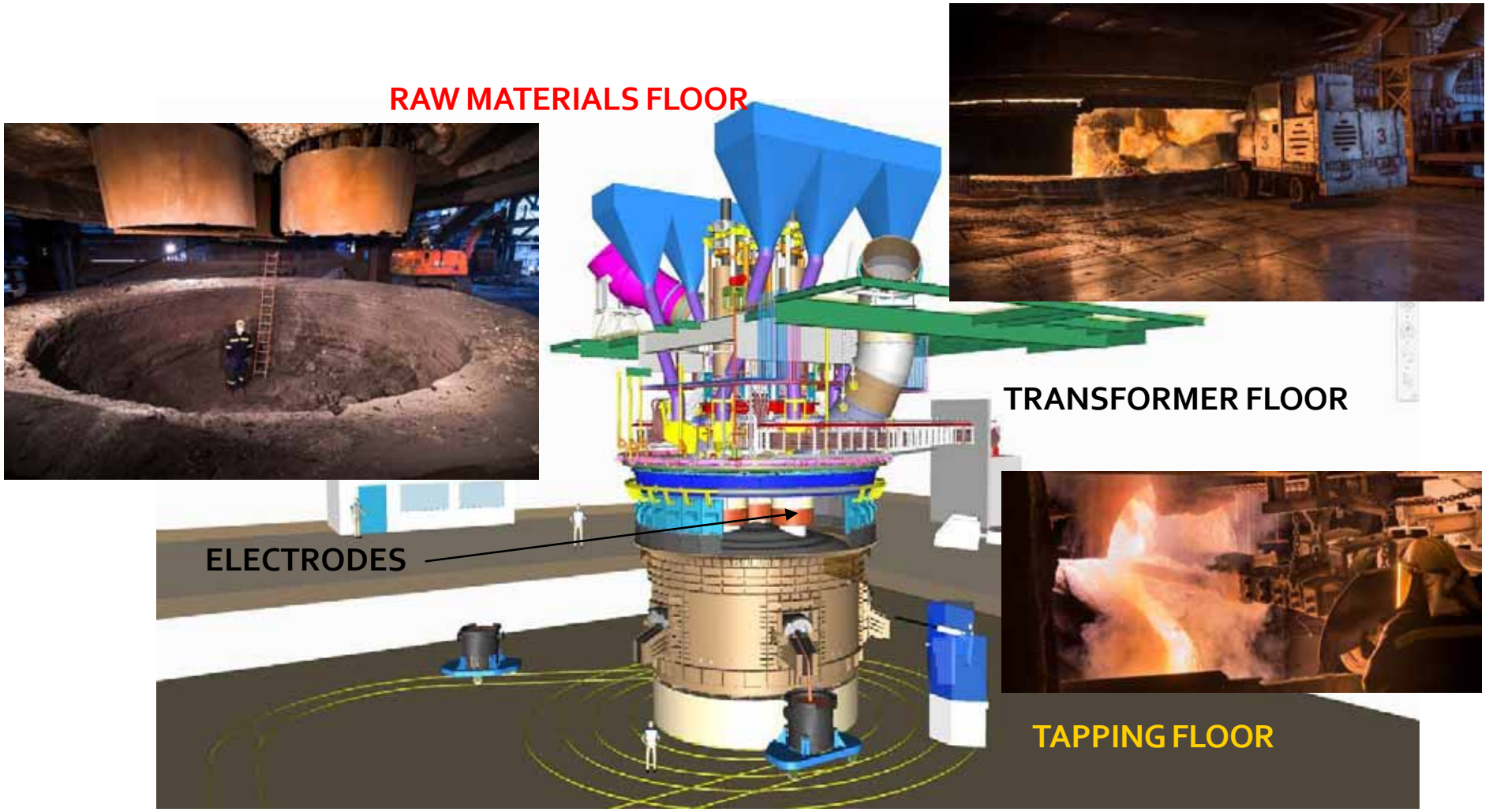
How is Metallurgical Grade Silicon Made #2



A medium sized submerged arc furnace has a crucible diameter of about 7 metres. It is fed by three carbon electrode columns about 15 metres high and weighing about 20 tons each.

Source: http://www.carbonandgraphite.org/pdf/silicon_production.pdf

Si Smelting in a Submerged EAF



Graphics: Ferroglobe, 2017

Facility layout – Ferroglobe, Polokwane, South Africa

Graphics: Ferroglobe, 2017

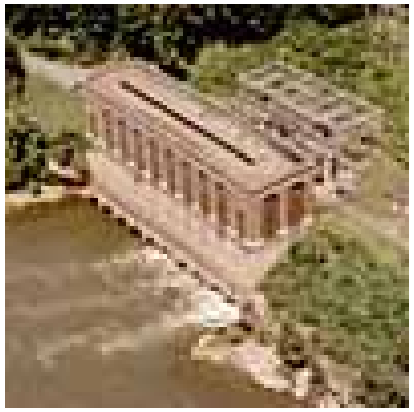
For Si Metal Plants – Low Cost Electricity is Critical

Sandia National Laboratories

For every 1 ton of Si production
12 MWh of Electricity consumed

GSM Alloy Plant

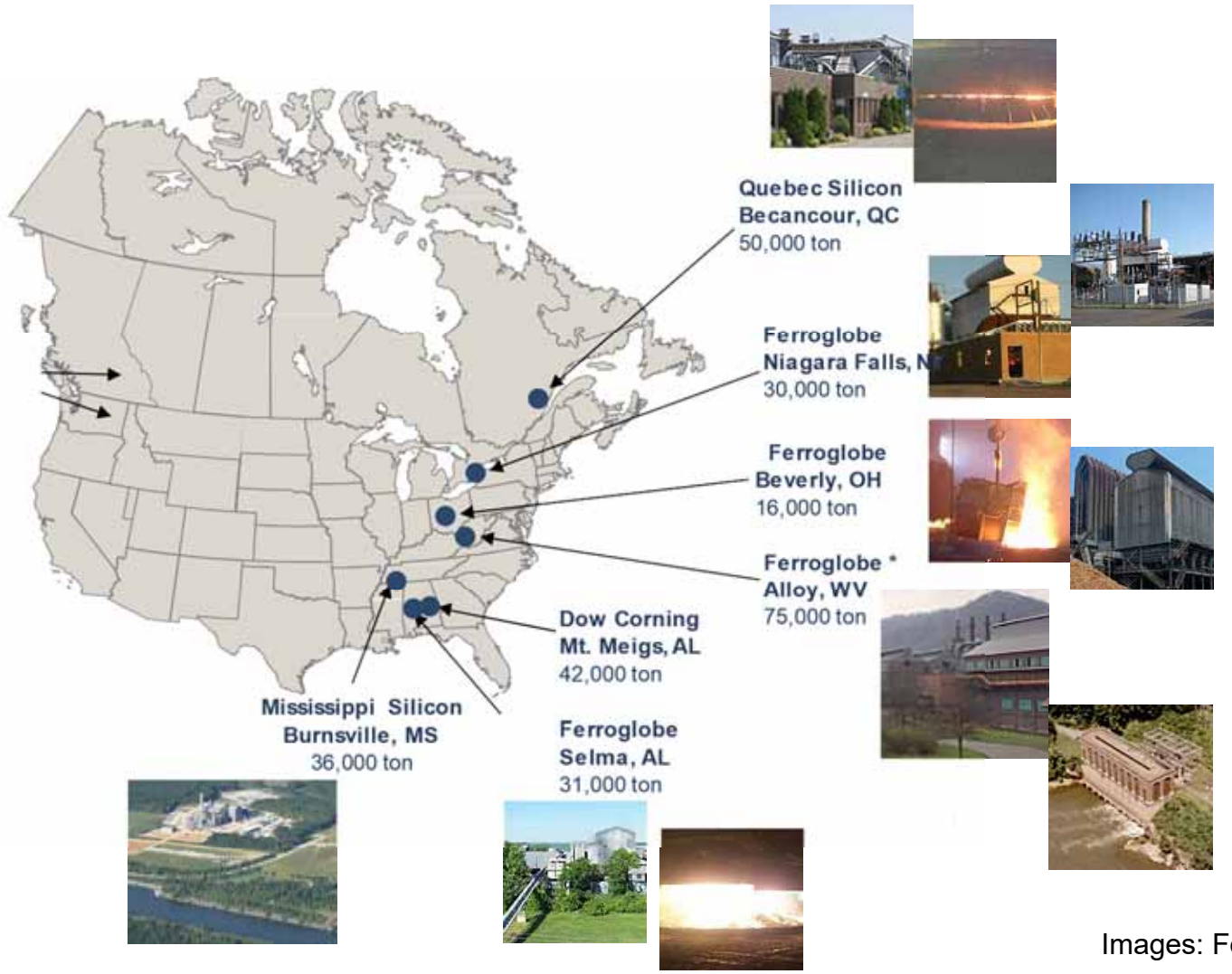
Electric Arc Furnace
in Operation



Hawk's Nest
Hydroelectric Plant

Source: Globe Specialty Metals

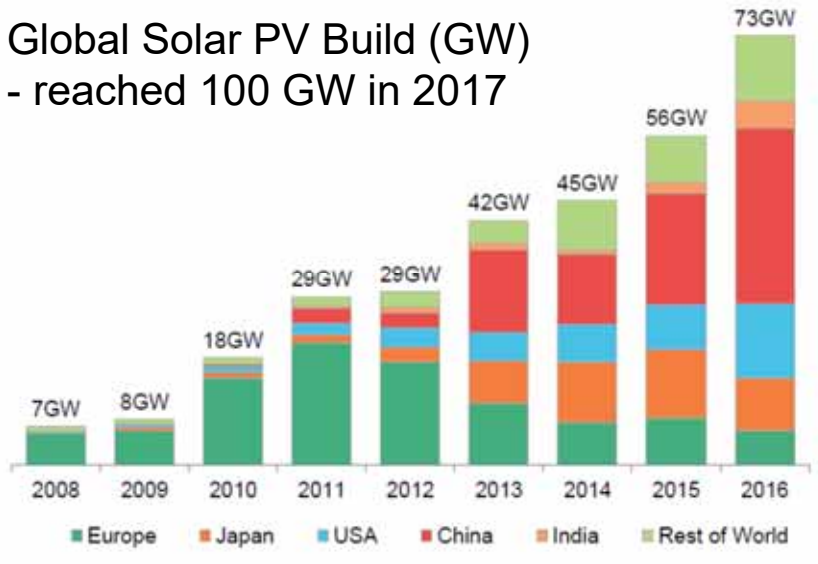
North American Si Metal Plants



Images: Ferroglobe, DowCorning

GROWING MG Si METAL MARKET

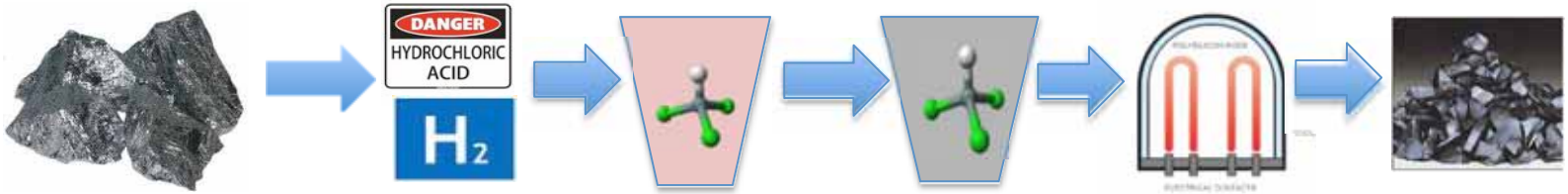
- MG Si consumption was 2.2 Million Tons
- Demand growing at 6.0% from 2016 – 2020
- Growth largely driven by the growing demand for polysilicon for PV panels



Source: Bloomberg New Energy Finance (2017)

Source: CRU 2015, Ferroglobe

Si metal to Semiconductor grade Polysilicon



MG Silicon Metal 98.0% to 99.5% Si

MG Silicon Metal Is Dissolved In Hydrochloric Acid To Form Trichlorosilane (HSiCl3)

Trichlorosilane (HSiCl3) is Further Refined

Siemens or FBR Poly Silicon Process

Semiconductor Si 99.999+% Si

Polysilicon

70 MWh - 120 MWh
to produce 1 ton of polysilicon

Impurities in Silicon

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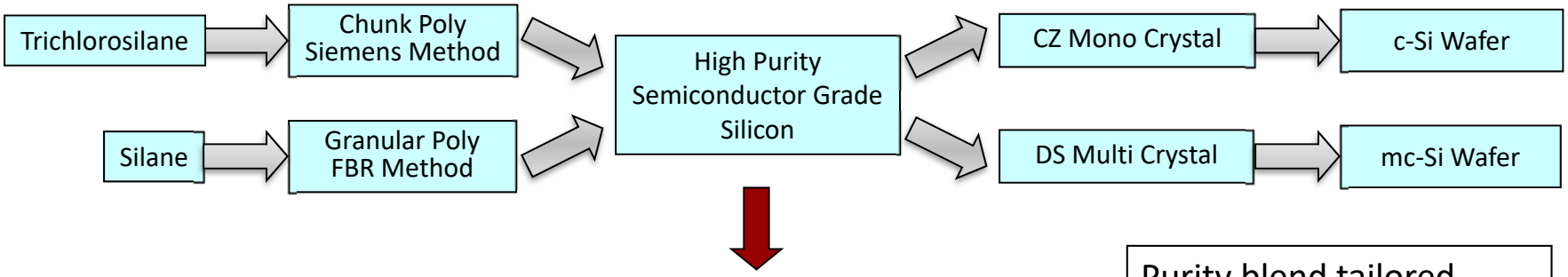
Metallurgical grade	Chemical grade	PolySilicon grade	Solar grade	High Purity
%Fe<0.5 %Ca<0.03 %Al<0.1 ppmP<limit	%Fe<0.4 %Ca<0.03 Min<%Al<Max ppmP<limit Trace elements <limit	%Fe<0.3 %Ca<0.03 Min<%Al<Max ppmP<limit ppmB<limit Trace elements <limit	%Fe<0.001 %Ca<0.0001 %Al<0.0001 ppmP<1 ppmB<1 ppm others <10	%Fe<0.001 %Ca<0.0001 %Al<0.0001 ppmP : tailormade ppmB : tailormade ppm others : tailormade

Semiconductor Grade Si

Typical Impurity Level	
Boron	< 0.1 ppba
Phosphorous	< 0.1 ppba
Other Donors	< 0.03 ppba
Carbon	< 0.15 ppma
Transition Metals (Total Cu, Ni, Fe)	< 1 ppba

Silanes to Polysilicon to Wafers

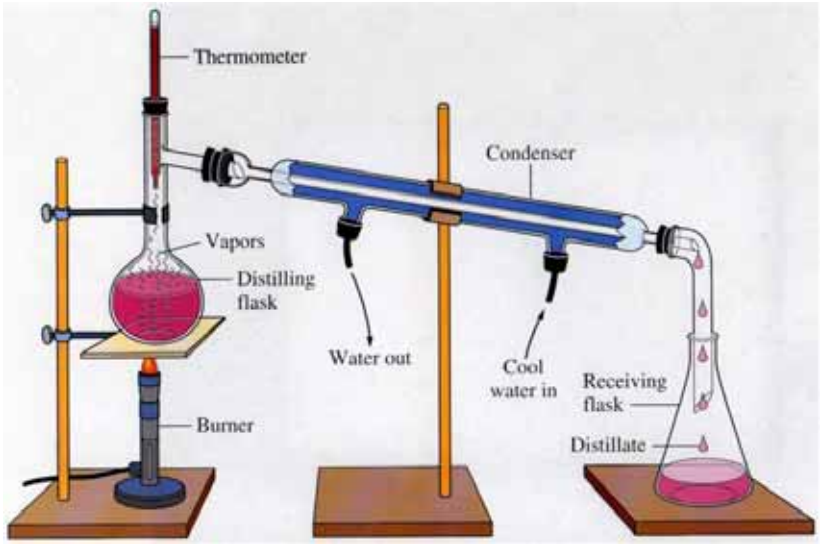


Purity blend tailored to application

Typical Impurity Level	
Boron	< 0.1 ppba
Phosphorous	< 0.1 ppba
Other Donors	< 0.03 ppba
Carbon	< 0.15 ppma
Transition Metals (Total Cu, Ni, Fe)	< 1 ppba

Purification of Metallurgical Grade Silicon

Laboratory scale distillation



Impure TCS in

Pure TCS out

Industrial scale distillation

Graphics: Courtesy of Graham Fisher
MEMC Electronic Materials

Purification of Metallurgical Grade Silicon

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Metallurgical silicon costs about $2 per kg

MG Si contains too many impurities for use in semiconductors or solar cells

In order to purify it we do this:

1) Convert it to a liquid compound containing silicon
2) Distillation of the liquid to purify it
3) Extract silicon from the high purity liquid

Step 1 is achieved through the following reaction

Silicon + Hydrochloric acid → Trichlorosilane + Hydrogen
Solid Liquid Liquid Gas

$$Si + 3HCl \rightarrow SiHCl_3 + H_2$$

TriChloroSilane is often referred to as TCS

Polysilicon Production

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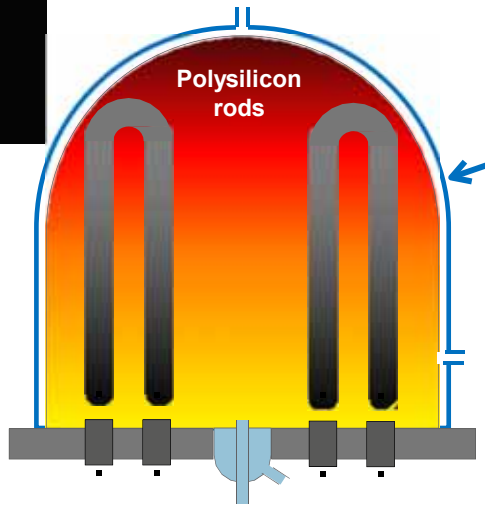
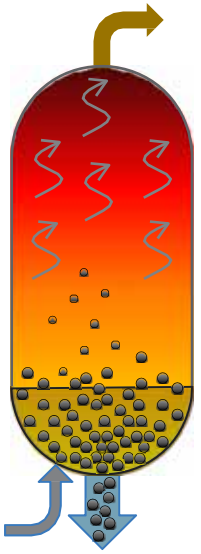
Siemens Reactor

TCS Based



CVD and Cooling account for 90% of Electricity Consumption

No Cooling required



FBR Reactor

Silane Based

Siemens Process

- Mature 40 year technology
- Batch process
- Requires post processing
- High cash cost

FBR Process

- Energy efficient
- Continuous production
- Lower cash cost

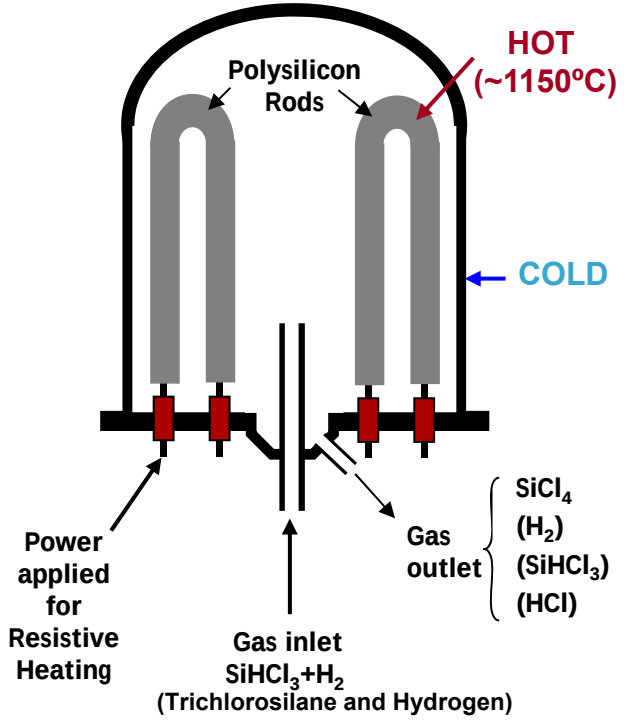
Siemens Process

- Convert metallurgical Silicon into Trichlorosilanes (TCS)

$$Si + 3HCl \rightarrow SiHCl_3 + H_2$$

- Purify TCS in distillation columns
- Recover pure Si using Chemical Vapor Deposition (CVD)

$$H_2 + SiHCl_3 \rightarrow 3HCl + Si$$



Cold wall reactor, high energy consumption. TCS conversion per pass is around 15%, recycling and lower productivity

Siemens Process

Sandia National Laboratories

The Siemens process is commonly used to produce semiconductor grade silicon

We used this reaction to make TCS:

$$Si + 3HCl \rightarrow SiHCl_3 + H_2$$

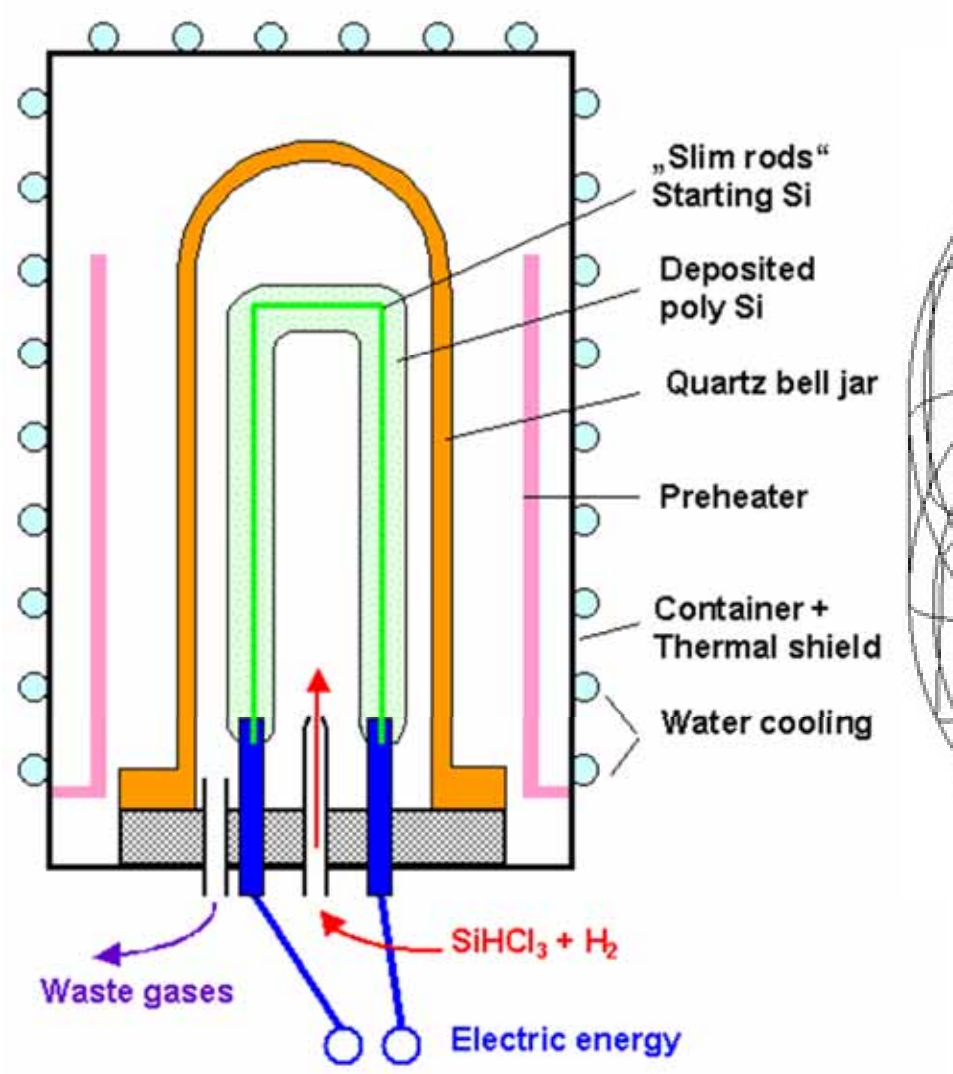
To go back to silicon we just run the same reaction backwards!

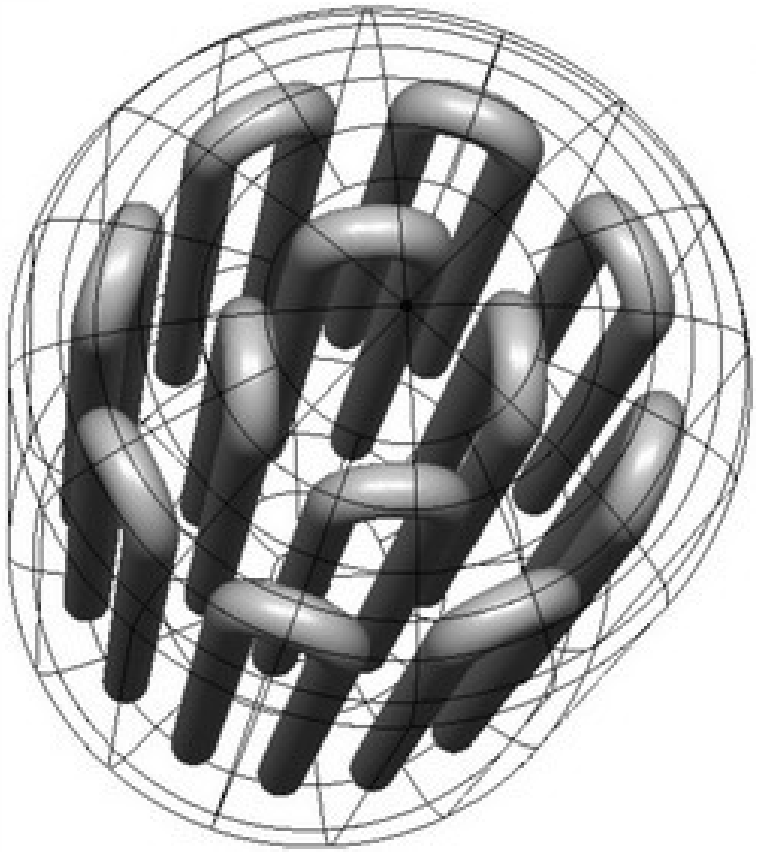
$$H_2 + SiHCl_3 \rightarrow 3HCl + Si$$

The reaction is run in a Siemens reactor that looks like this.

Inside the Siemens Reactor

Sandia National Laboratories





Siemens Polysilicon

Sandia National Laboratories

Siemen's reactor

Before polysilicon growth – slim rods

As grown polysilicon rods after a reactor run

Source: GR Fisher, Proc. IEEE, vol. 100, pp. 1454 – 1474, April 2012

80% of the worlds polysilicon is produced using the Siemen's process developed in the 1950's.

Insides of Siemens Reactor

Sandia National Laboratories

Before

After

Si from Siemens Process – Chunk poly

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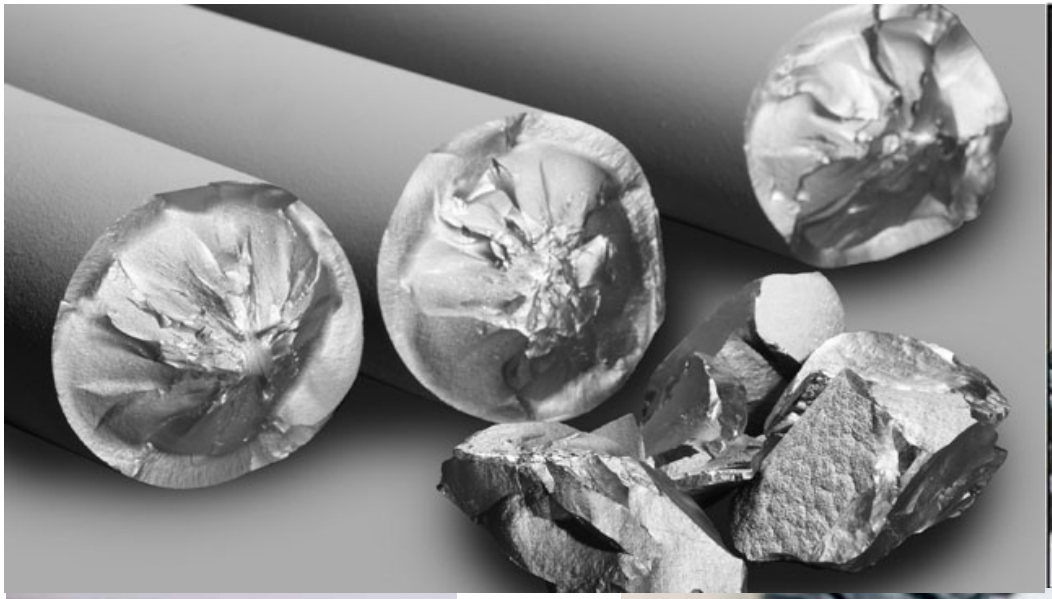
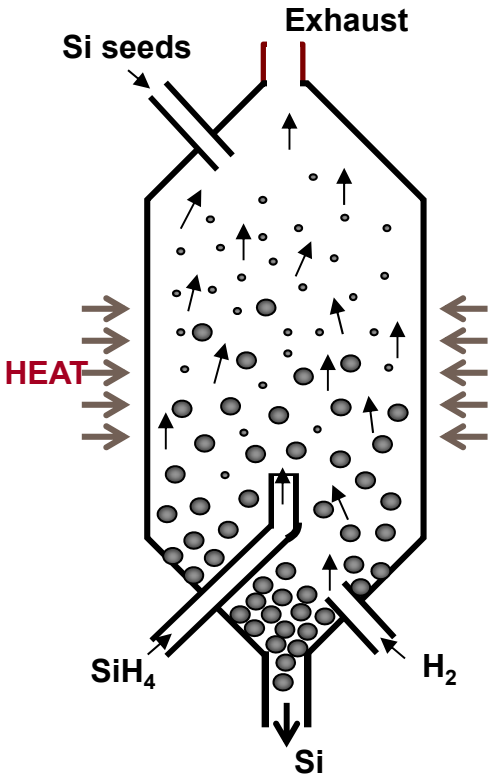
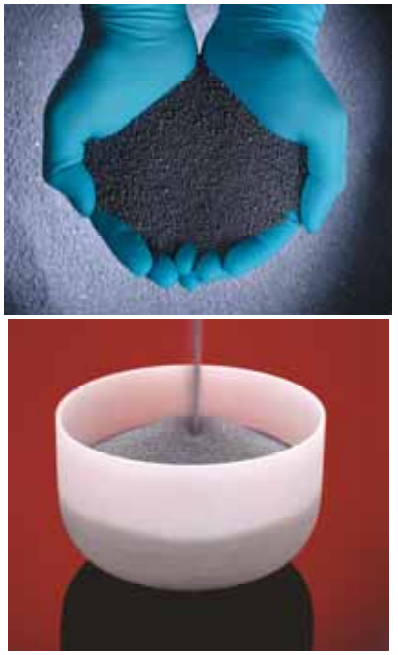


Graphics: Graham Fisher
MEMC Electronic Materials

Fluidized Bed Reactor Production



Hot wall reactors
Higher throughput



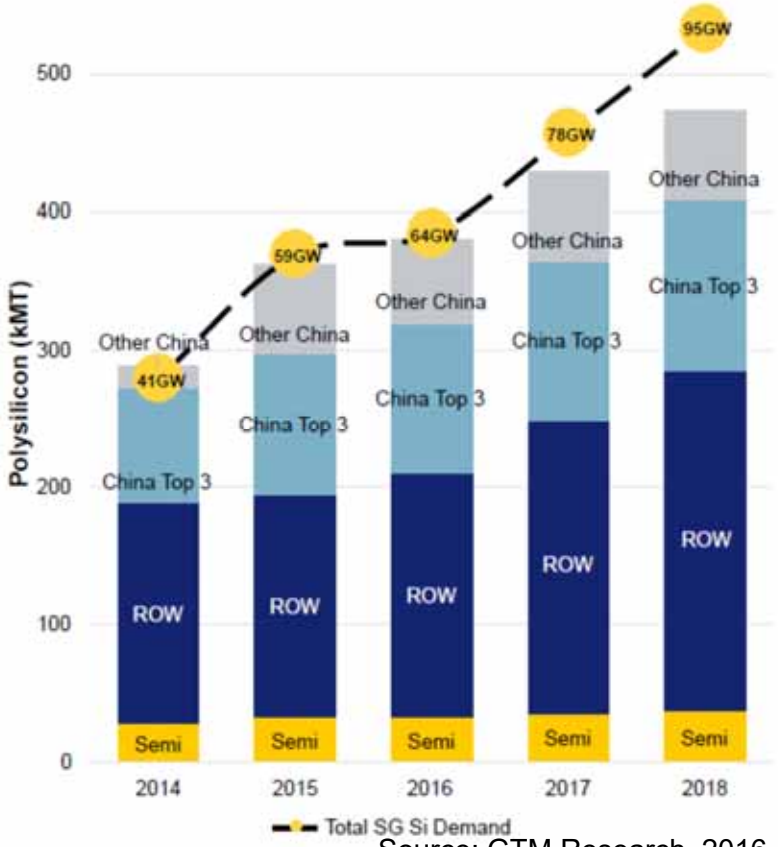
Granular polysilicon has a higher packing density in the crucible and, because it flows, can to used to recharge hot crucibles lowering cost and improves throughput of crystal growth processes.

Poly-Si Production – Large Chemical Plants

Sandia National Laboratories

Large capital outlays
10000 ton capacity plant ~$500M

Growth in Polysilicon Production



Source: GTM Research, 2016

Source: Polysilicon & wafer rankings
PV Magazine, March 2017

Over 90% of polysilicon is consumed by the PV Industry
Size of the PV market in 2017: 75 GW; 2017: 100 GW, Si used <5g/W

Crystal Growth and Wafer Manufacturing

- Czochralski(CZ) growth remains the dominant process for monocrystalline crystal growth
- Significant advances in Continuous CZ process
- Directional solidification (DS) for multicrystalline wafers

Solar vs. Semiconductor Silicon

Sandia National Laboratories

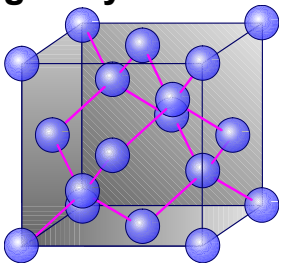
Polysilicon

Semiconductor Applications

Solar Applications

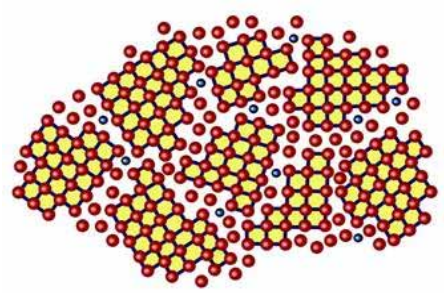
Monocrystalline silicon

Single crystal ~meters



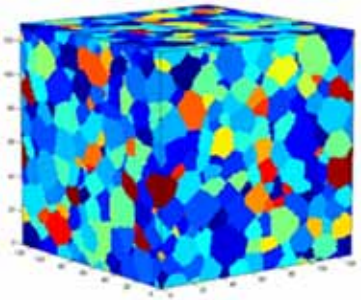
Polysilicon

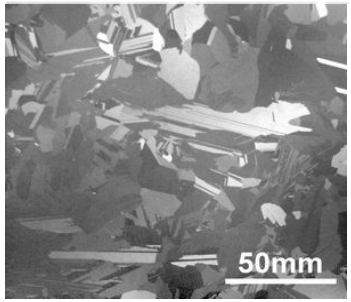
Grain size ~µm - mm



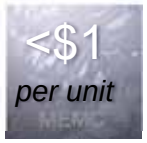
Multicrystalline silicon

Grain size ~mm - cm





Solar Wafers



$/W Cost Metric $/in^2

Semi Wafers

Semiconductor vs. Solar

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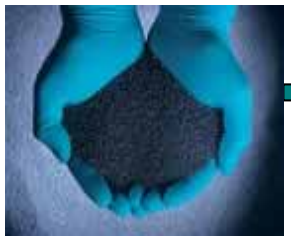
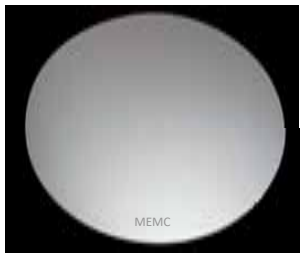
Semiconductor/Electronics Food Chain


Polysilicon


Ingot

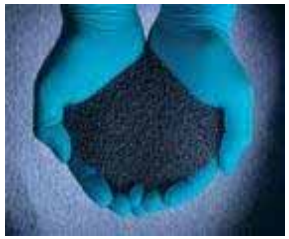


Wafers


Semiconductors

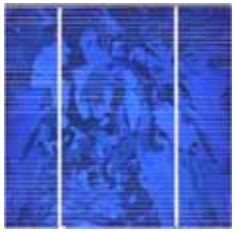

Electronics

Solar Food Chain


Polysilicon

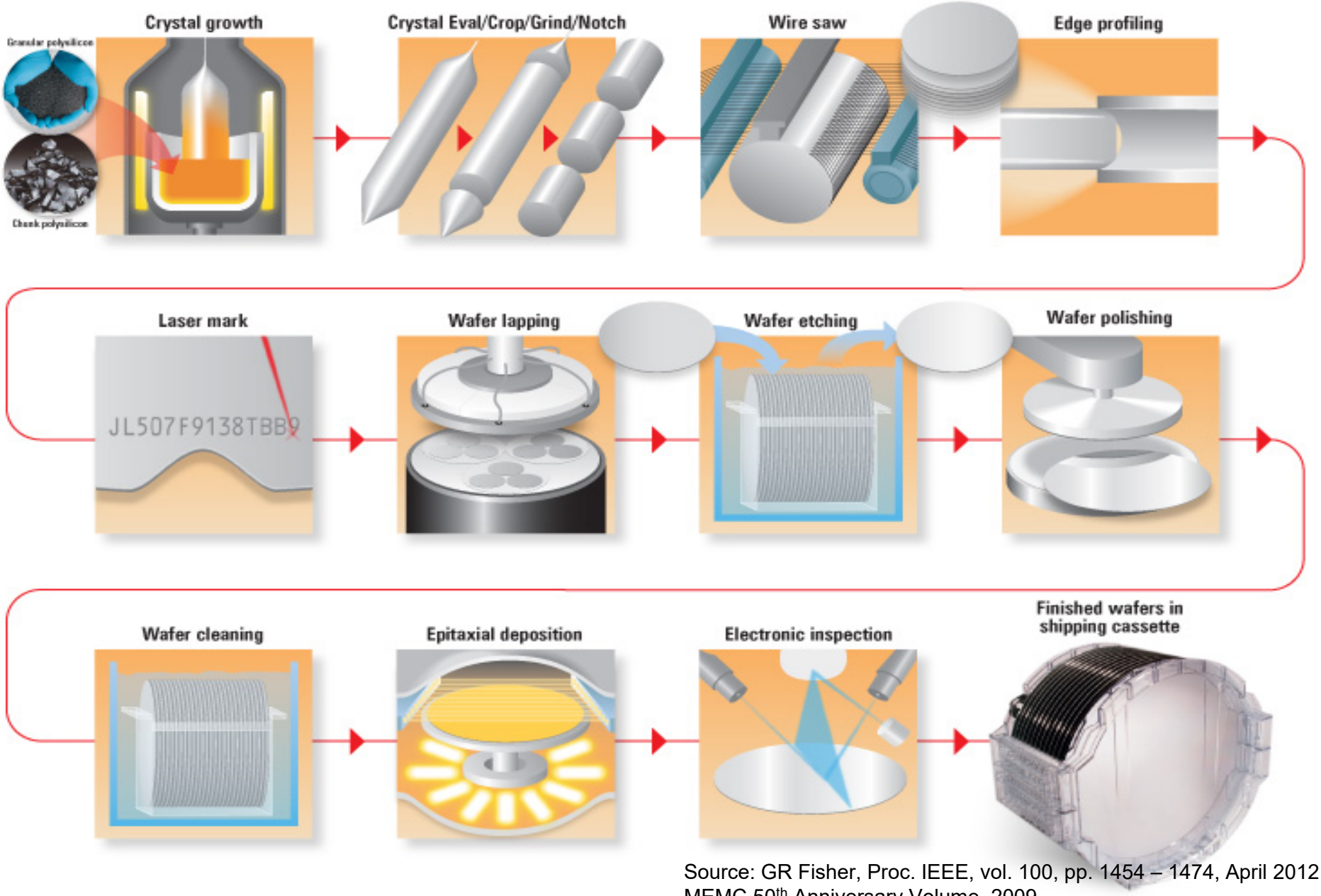

Ingot

Wafers


Cells

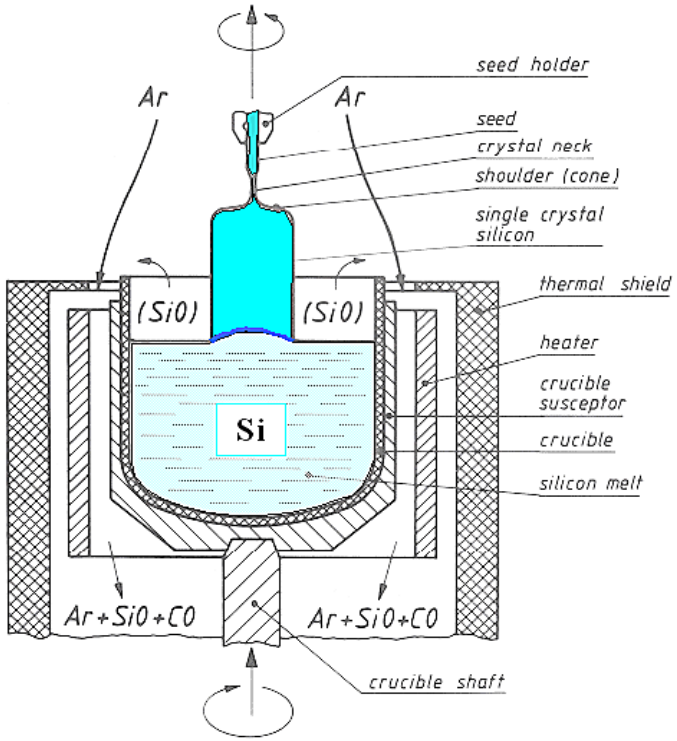

Solar Modules

Monocrystalline Si Wafer Manufacturing Process

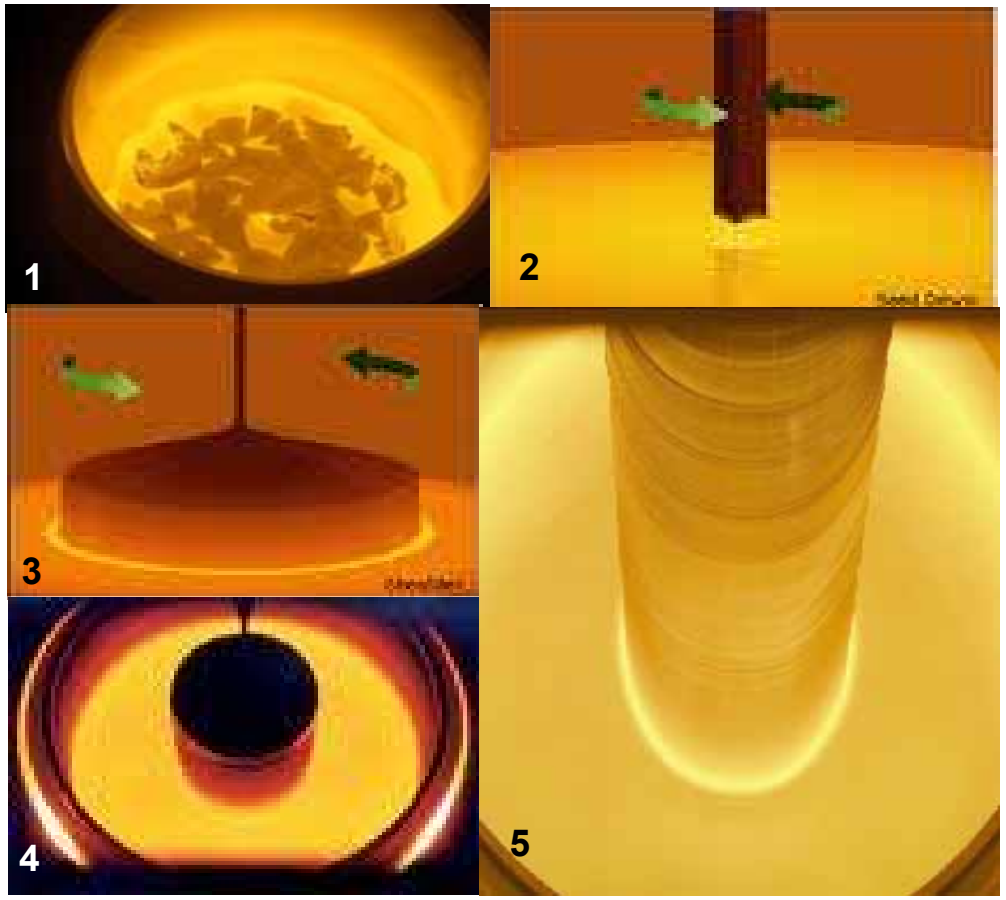


Source: GR Fisher, Proc. IEEE, vol. 100, pp. 1454 – 1474, April 2012
MEMC 50th Anniversary Volume, 2009

Crystalline Si Czochralski Crystal Growth



Crystal Puller



Various stages of Czochralski crystal growth,
1 Meltdown, 2 Seed Dip, 3 Top, 4 Shoulder, 5 Body

Source: GR Fisher, Proc. IEEE, vol. 100, pp. 1454 – 1474, April 2012

Czochralski Method for Silicon Crystal Growth

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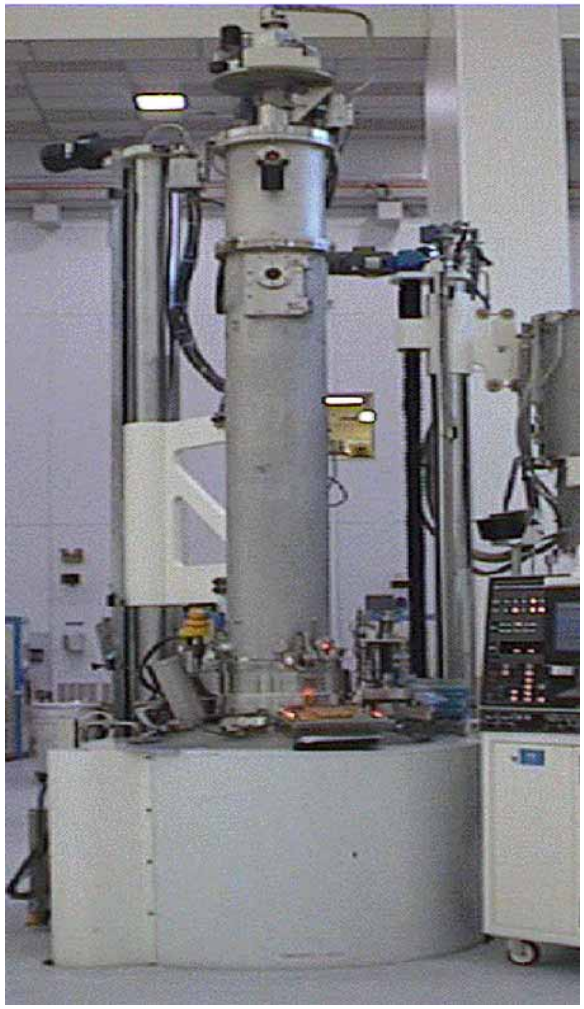
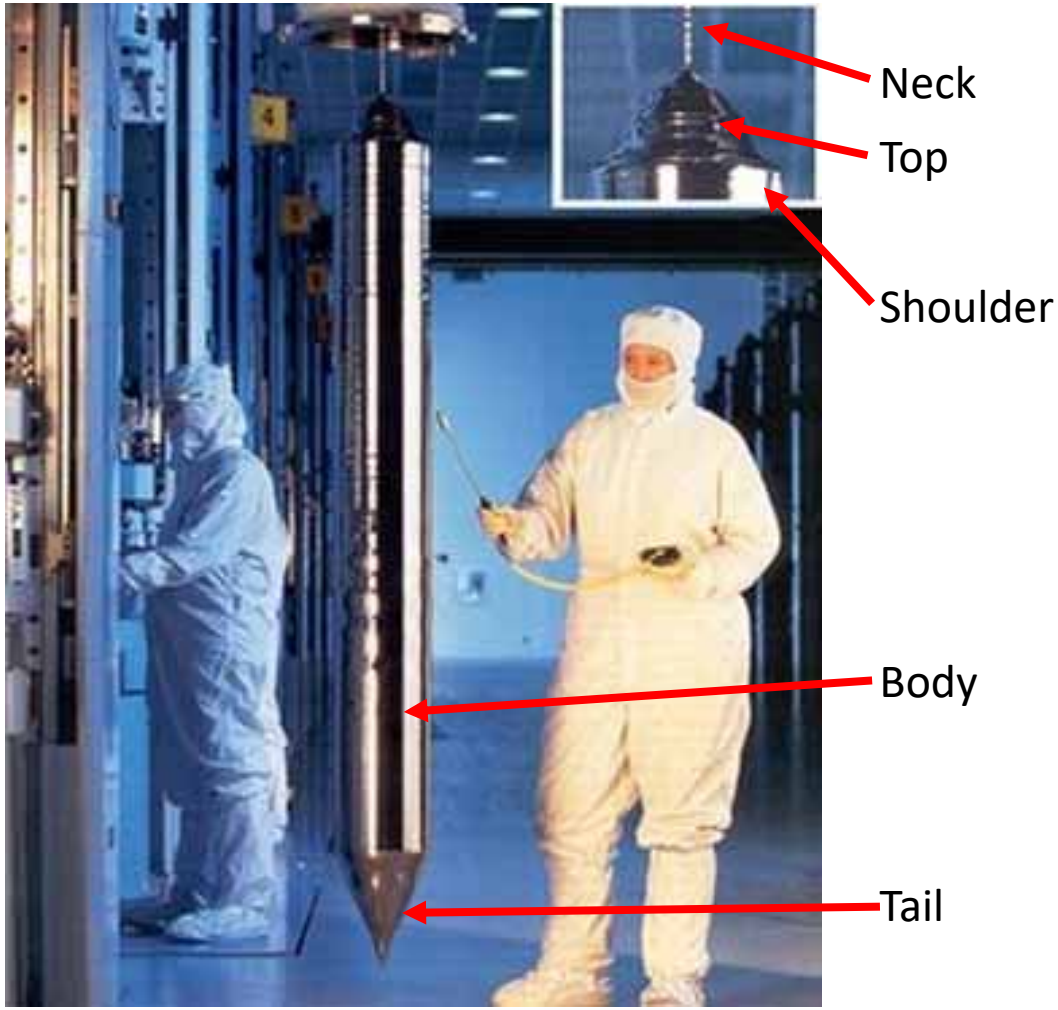


Crystal Puller



Product

Typical Factory Floor

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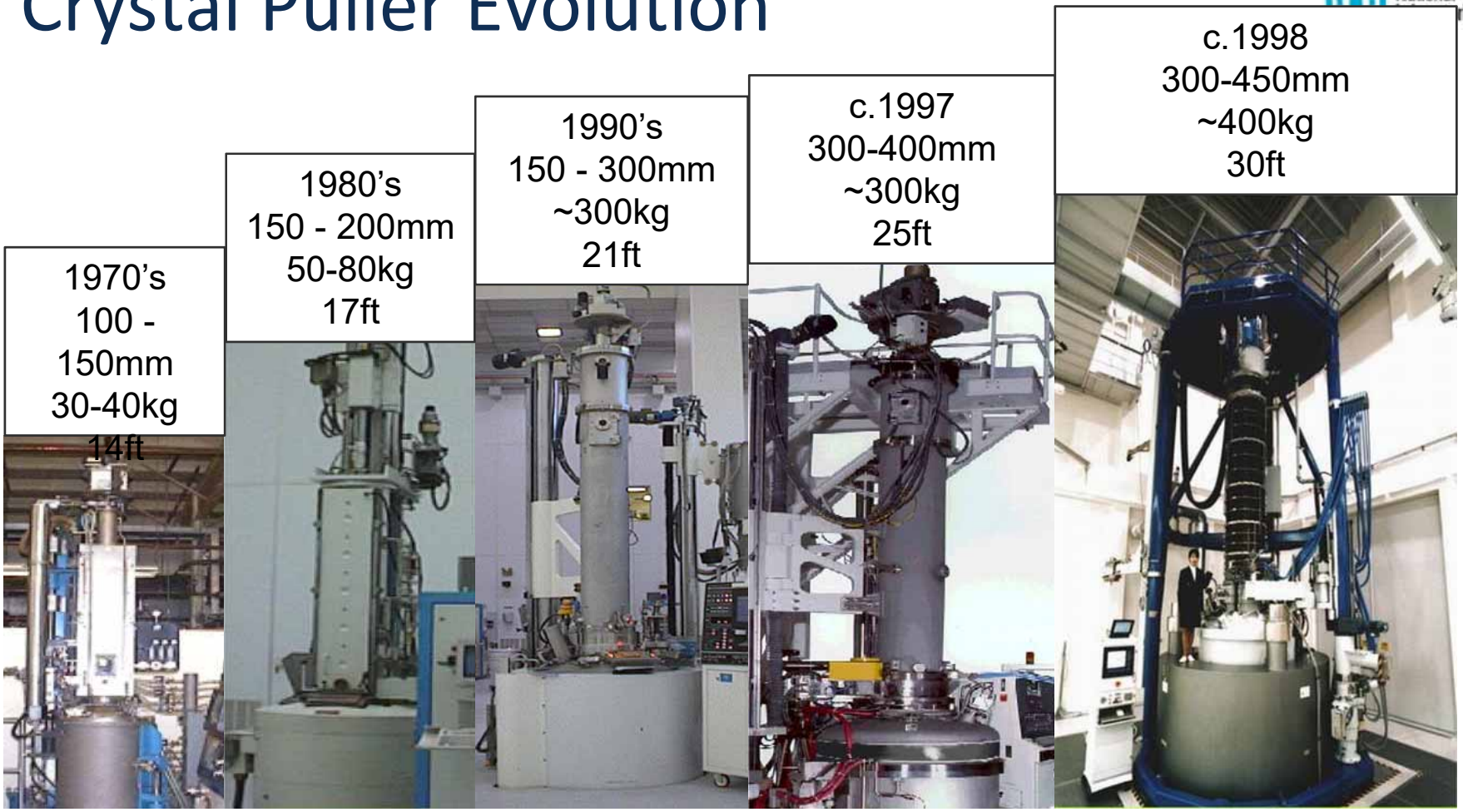
Early days of Czochralski(CZ) growth crystals were small and easy to handle. Current generation crystal are large, heavy and need specialized handling equipment.

Source: MEMC 50th Anniversary Volume, 2009

Crystal Puller Evolution



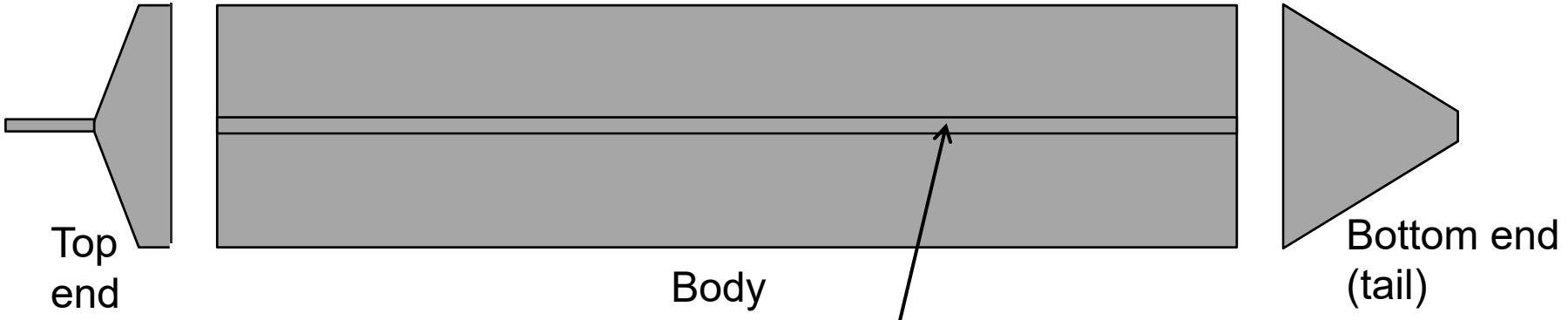
Examples of progress in Czochralski crystal pullers from 1970 through current diameter capability. Showing approximate period, crystal diameters, typical polysilicon charge weight and approximate height of the equipment above the working floor. Later models have services (water, argon, vacuum) below floor level. (Right hand photo shown is courtesy of Super Silicon Institute (SSI).)

Source: GR Fisher, Proc. IEEE, vol. 100, pp. 1454 – 1474, April 2012

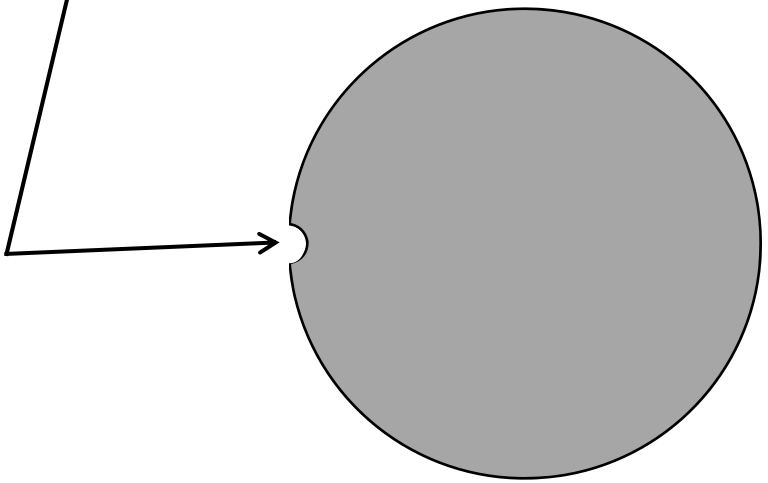
Continuous Czochralski Crystal Growth

Sandia National Laboratories

Wafer Slicing



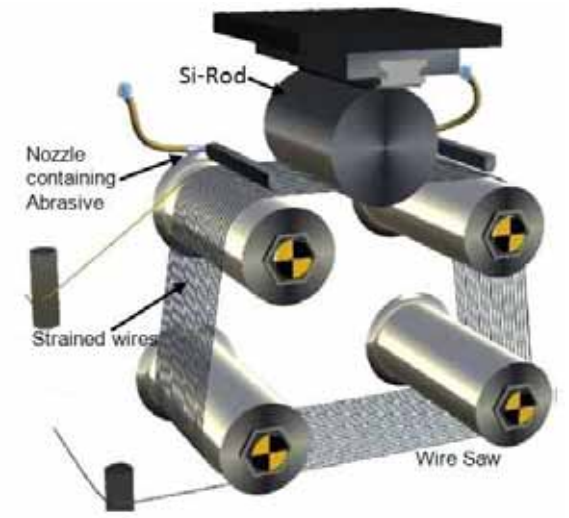
Before getting the ingot ready for slicing, top and tail ends are removed. Orientation of the crystal lattice determined by x-ray diffraction.



A is notch is cut on outside aligned with the crystal lattice. Later when the wafers are cut from the ingot, each one has a notch which indicates the orientation of the crystal lattice.

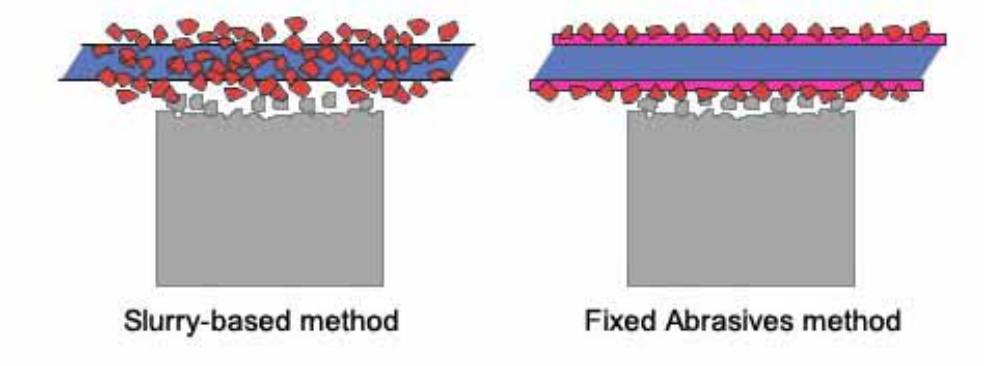
Wafer Slicing

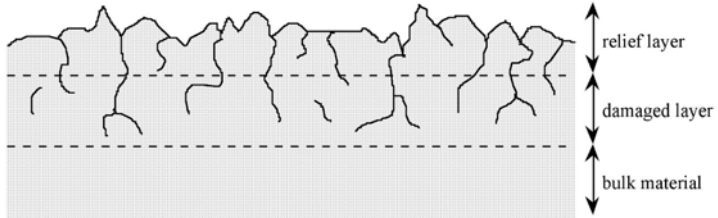
Sandia National Laboratories

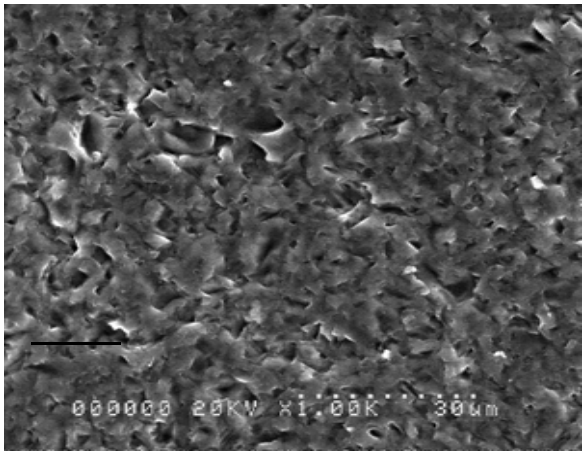


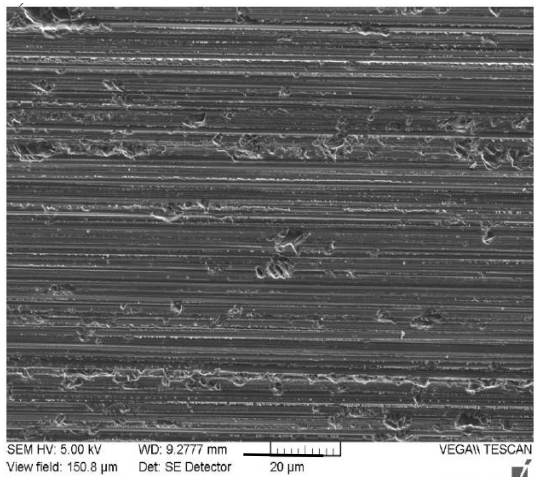
Solar wafers 180 - 220 μm thick, typical Semiconductor wafer ~900μm

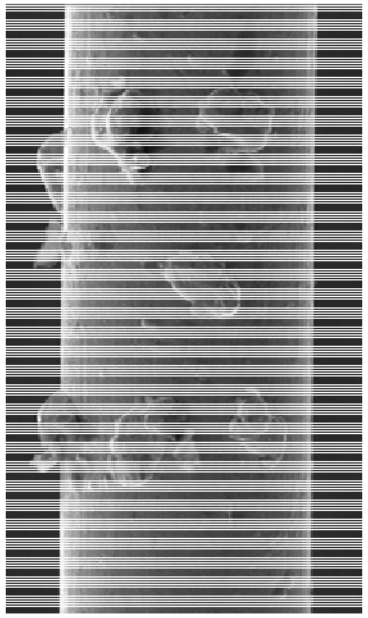
Wafer Slicing









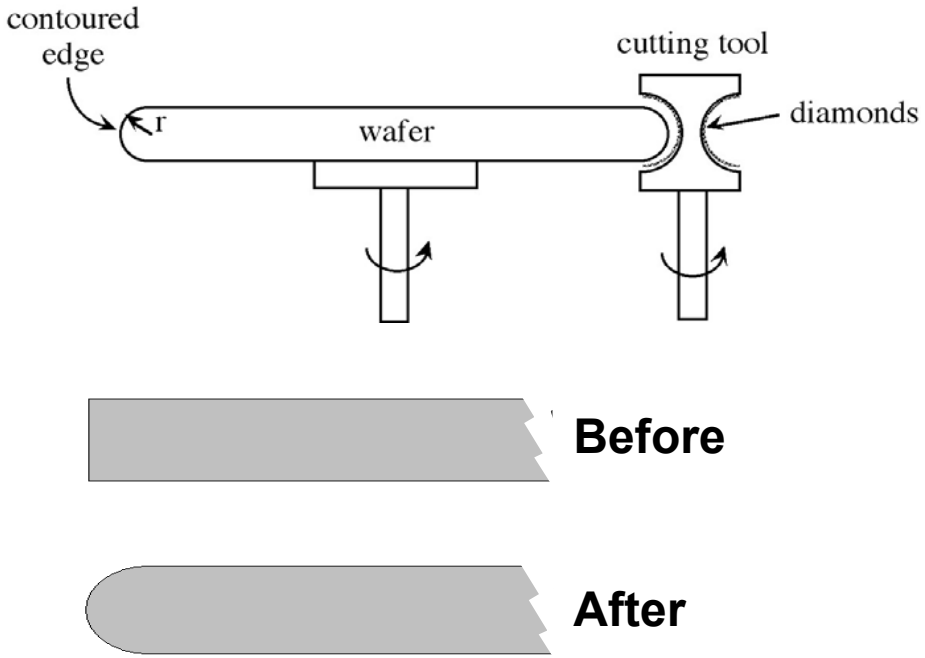


Edge Profiling

Sandia National Laboratories

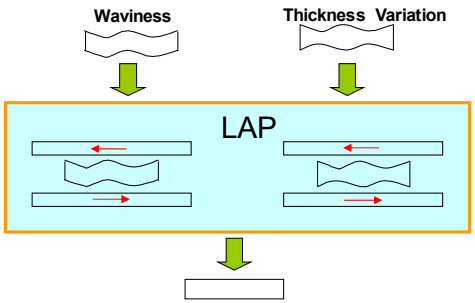
Purpose

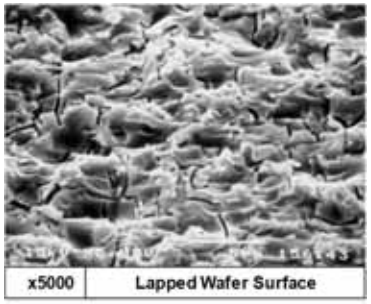
- Produce a rounded wafer edge that is tougher and more resistant to chipping during handling
- Minimize edge surface roughness
- Minimize depth of damage on edge

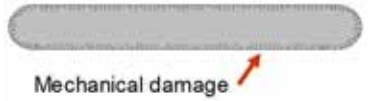


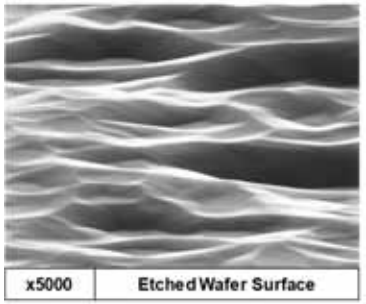
Lapping, Etching and Polishing

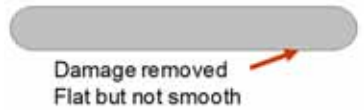
Lapping removes saw damage and produce a flat wafer. Etching and chemical mechanical polishing processes further improve the surface to almost atomically smooth.

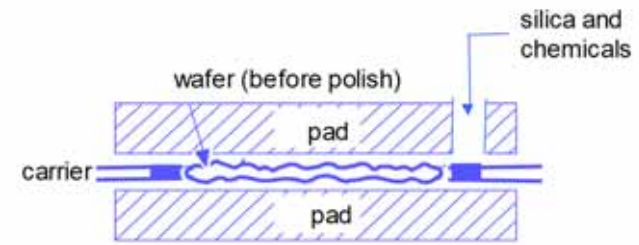












Finished Semiconductor Wafer

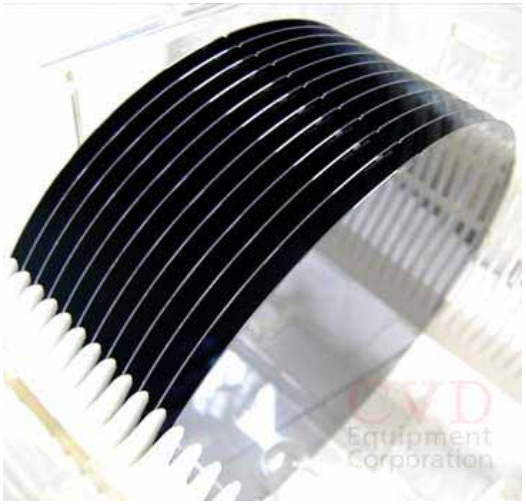
Sandia National Laboratories

Flat to within 250nm

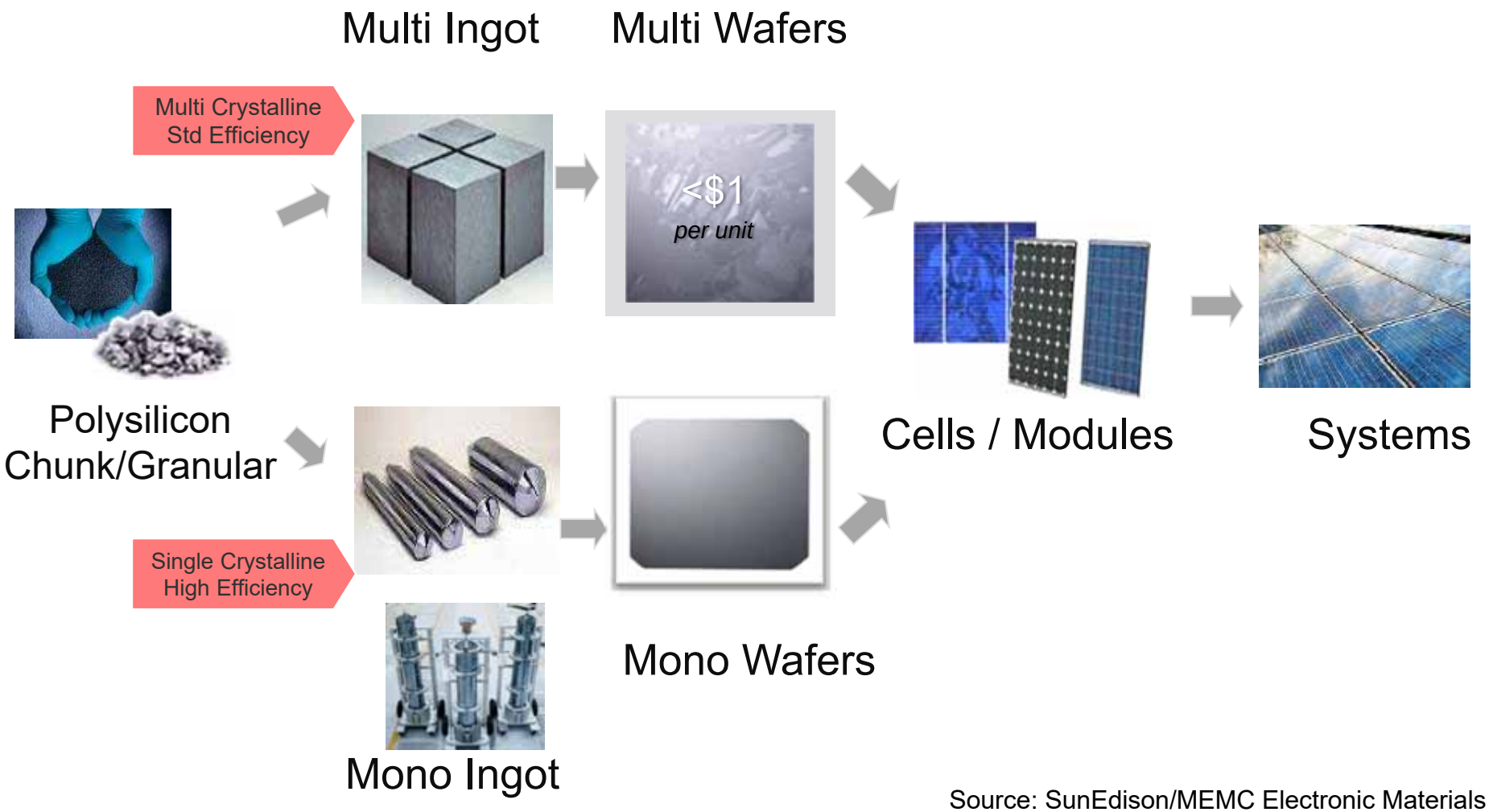
- equivalent to a football field flat to within 2 thousandth of an inch

Clean <10^{10} unwanted impurity atoms/cm^2

Purity <10^{11} metal atoms/cm3



Silicon PV Food Chain



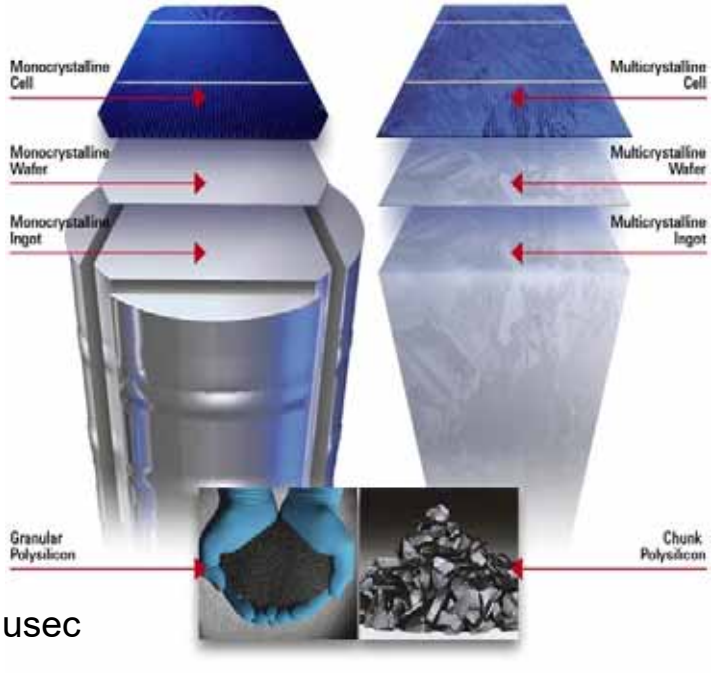
Source: SunEdison/MEMC Electronic Materials

Mono vs. Multi Silicon Wafers

Sandia National Laboratories

Mono Characteristics

- P-type/N-type
- Resistivity ~ 0.5-3ohm-cm
- Nominal thickness ~ <=200um
- Oxygen < ~ 20ppma
- Carbon < ~ 1ppma
- Dislocation-free
- Lifetime > 10usec on block
- Passivated lifetime > 100-1000 usec
- Single orientation = lower reflectivity texturing



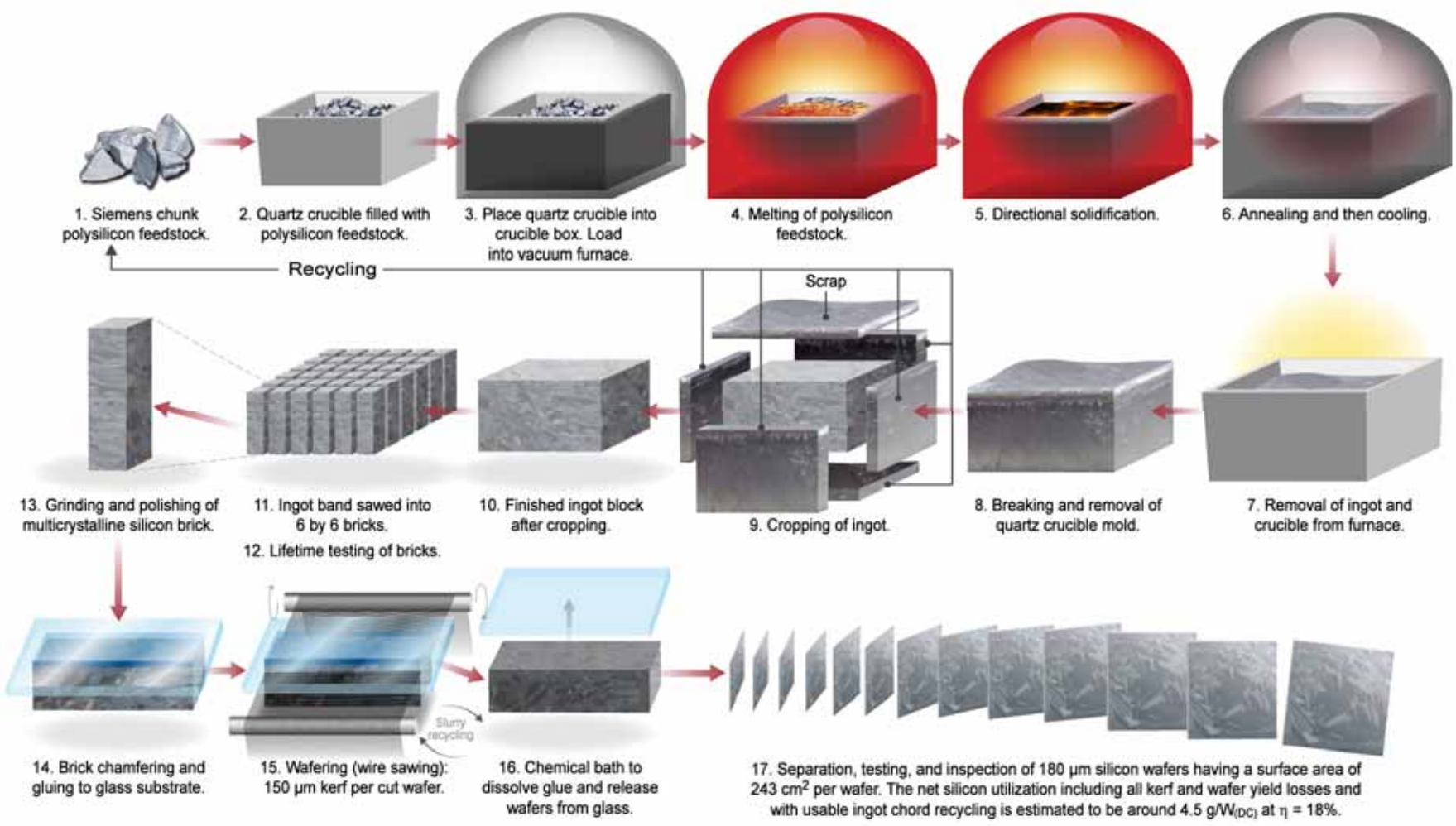
Multi Characteristics

- P-type
- Resistivity ~ 0.5-3ohm-cm
- Nominal thickness ~ 200um
- Oxygen < ~ 10ppma
- Carbon < ~ 10ppma
- Dislocations ~ E5/cm3
- Lifetime > 2usec on block
- Passivated lifetime > 10usec
- Multi orientation = higher reflectivity texturing

Choice depends on application and cost requirements

Multicrystalline Si Wafer Manufacturing Process

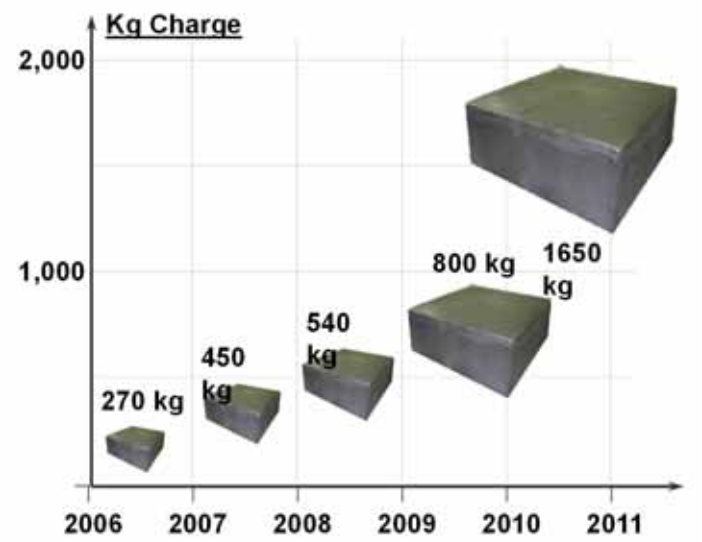
Sandia National Laboratories



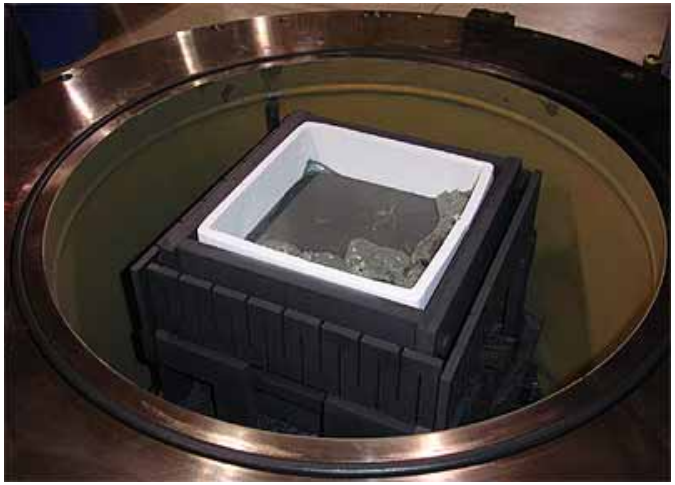
Graphic: courtesy of NREL, 2015

mc-Si Directional Solidification

Casting furnace



A . Deshpande, 2012 NREL Silicon Workshop
Images Courtesy of MEMC



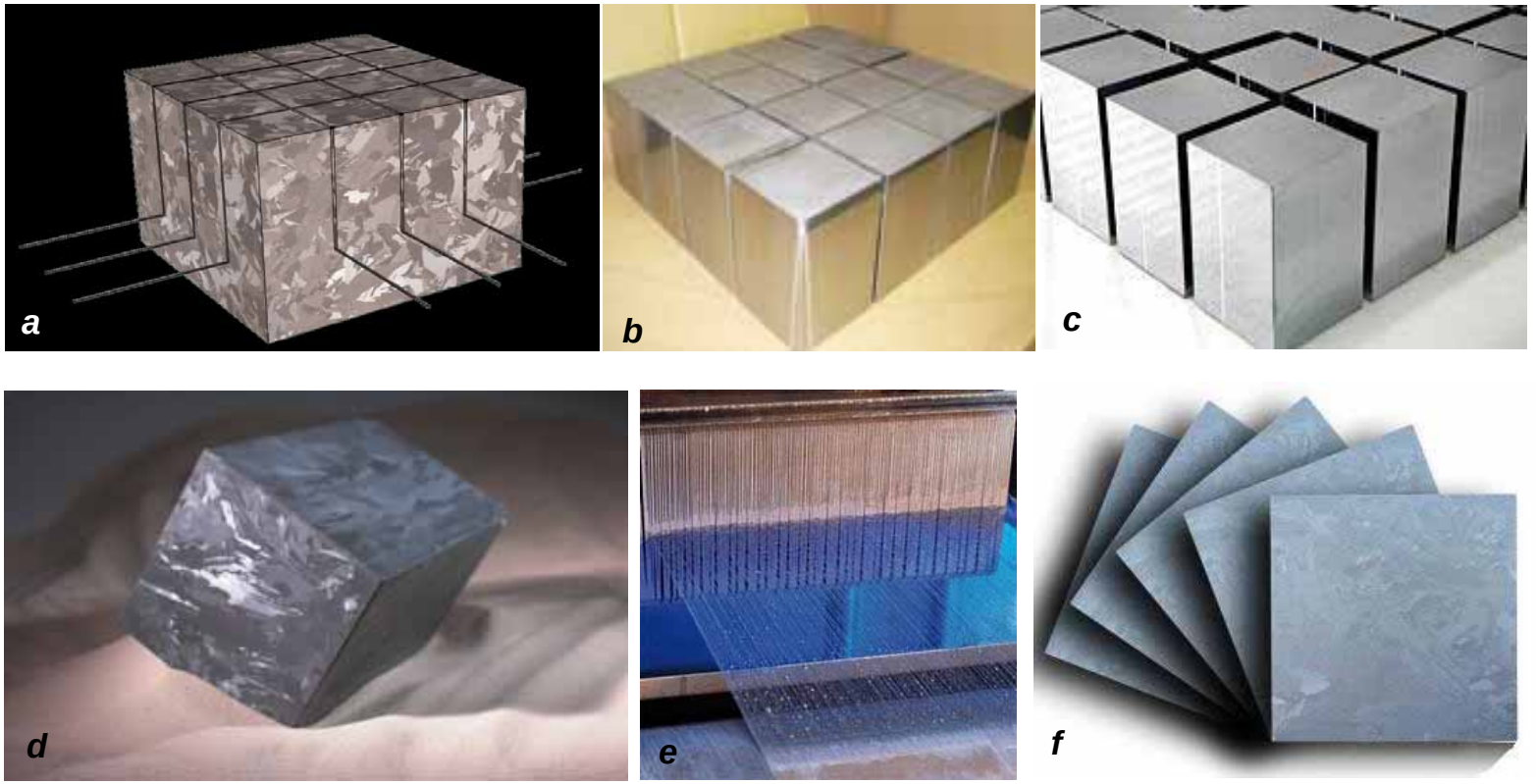
Open furnace after casting

Finished casting

DSS allows for large cast

Fabrication of Solar Wafers

Sandia National Laboratories

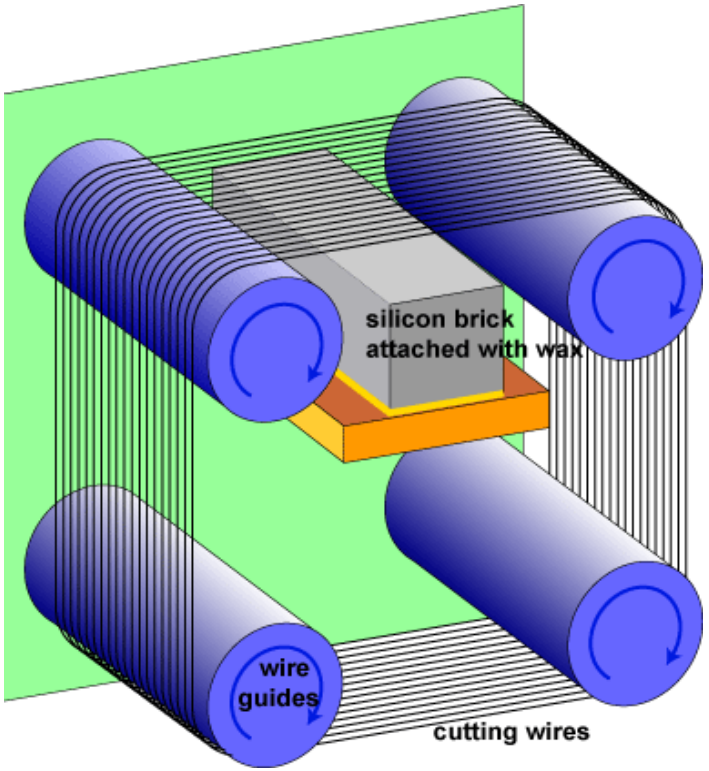


(a & b) Sawn into bricks ; (c) Bricks are ground; (d)chamfered, then (e)sawed into wafers, (f) polished wafers

A . Deshpande, MEMC Electronic Materials

Wafer Slicing

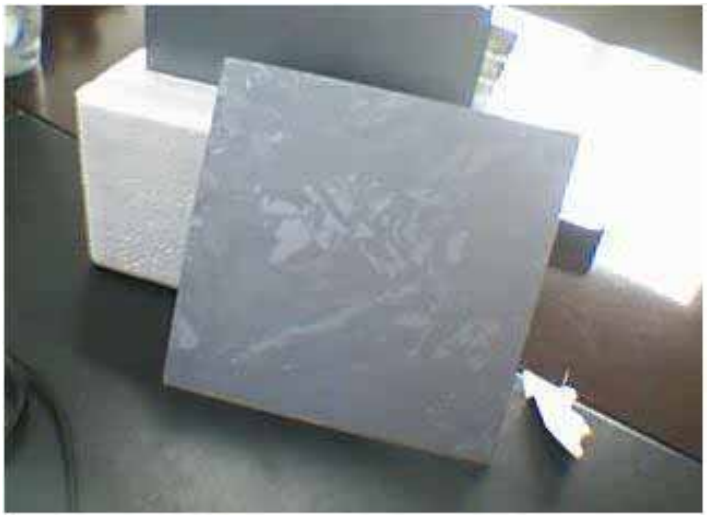
Sandia National Laboratories



Solar wafers 180 - 220 μm thick, typical Semiconductor wafer ~900μm

Finished Solar Wafer

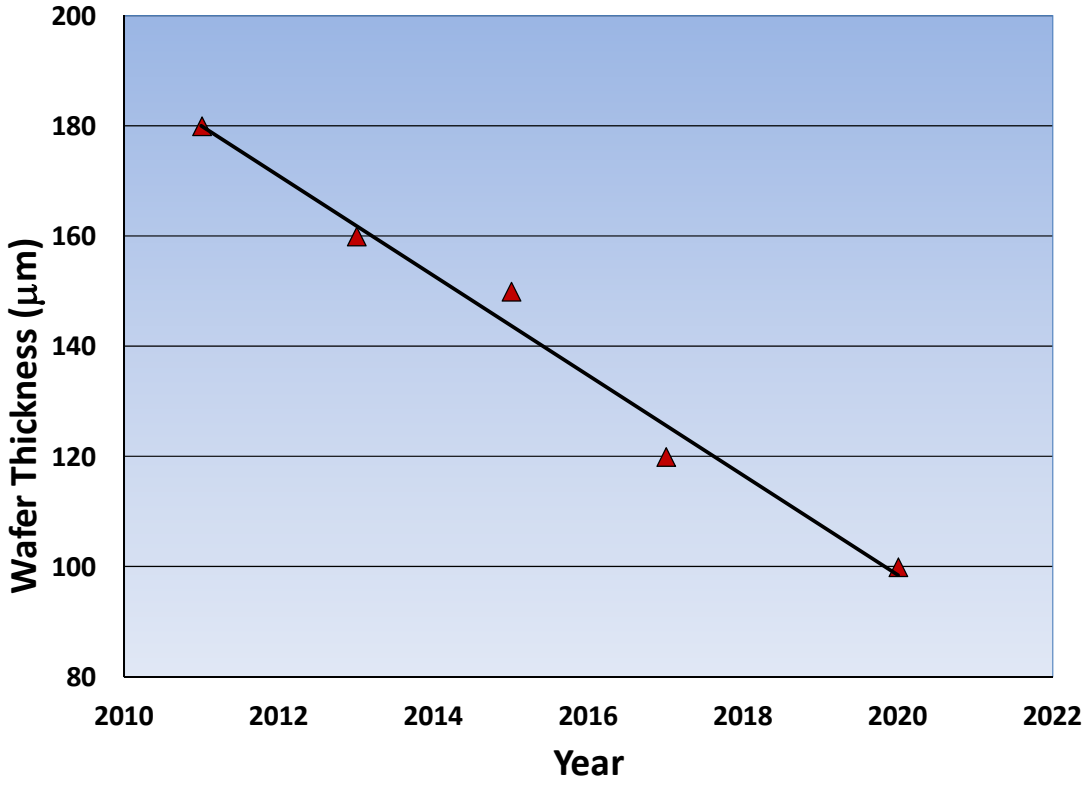
Sandia National Laboratories



For solar applications cost is key

Processing downstream from slicing is limited to cleaning and an etch to remove some saw damage and add texture.

Trends in Wafer Technology



Projected trend in minimum wafer thickness processed in mass production of solar cells
(International Technology Roadmap for Photovoltaics, SEMI PVGroup/ITRPV, 2011).

Wafers to Cell and Modules

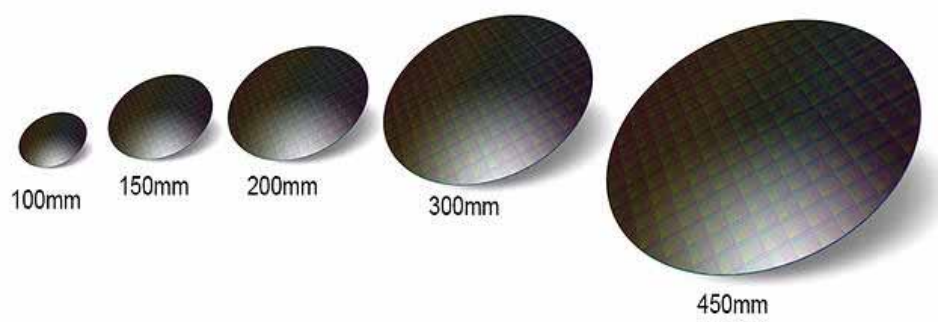
Sandia National Laboratories

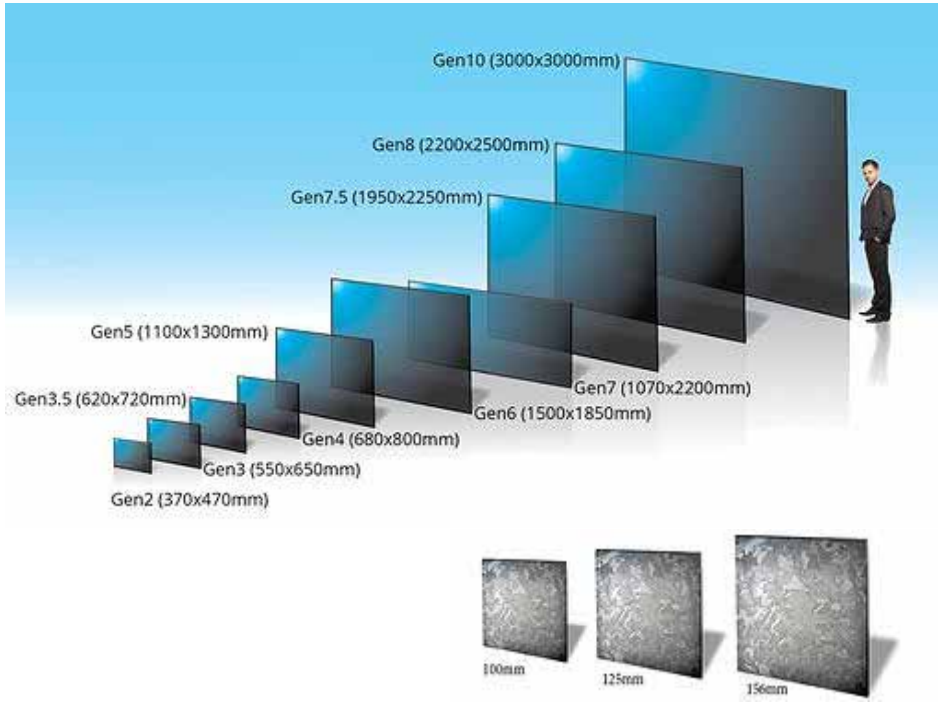
156 mm monocrystalline solar wafer and cell.

156mm multi-crystalline solar wafer and cell

Solar cell module
(from multi-crystalline wafers)

Scaling (size, volume, and performance)





Microelectronics
Si Substrates
20x scaling (30 yr)
50, 100, 150, 200, 300 mm

Flat Panel Displays
Glass Substrates
50x scaling (30 yr)
Gen1 (370x470mm)
Gen 8 (2200x2600 mm)

Solar Panels
Si Substrates
100 mm to 150 mm
2x scaling (20 yr)

Source: Brad Mattson, Sivapower
D. Mitzi, Solution Processing of Inorganic Materials, 2010

Summary

Sandia National Laboratories

- Continuing advances in Si materials technology making
  - Microelectronics cheaper
  - Si PV reaching grid parity with fossil fuel electricity generation
- Manufacturing scale and growing demand for Si for PV further driving down the cost of polysilicon
- Further opportunities to improve materials utilization in Si PV

Acknowledgements

- Graham Fisher, Mike Seacrist, Bob Standley, and a number of colleagues at MEMC Electronic Materials/SunEdison Semiconductor for discussions and for presentation material.