EPFL

Modern PV-Technologies
3.2: c-Si solar cell cells

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PV-Lab

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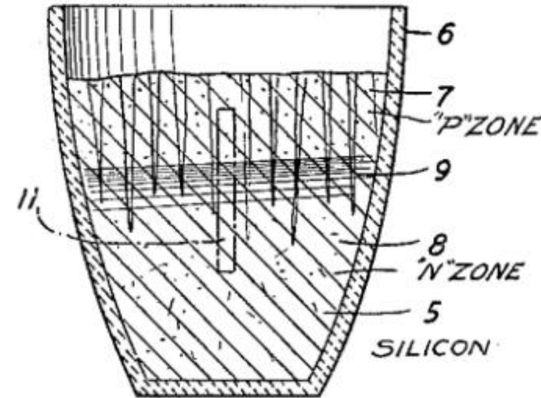
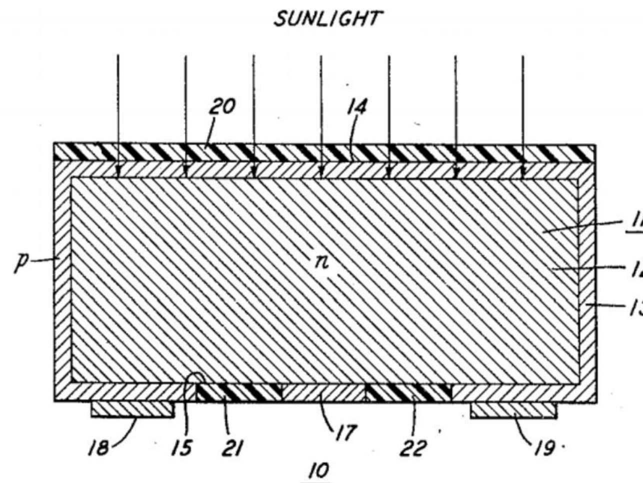
The early days of c-Si solar cells

Ohl (1941)



vertically solidified p-n junction
Cut vertical slab
attach Cu electrodes

Pearson, Chapin, Fuller (1952)

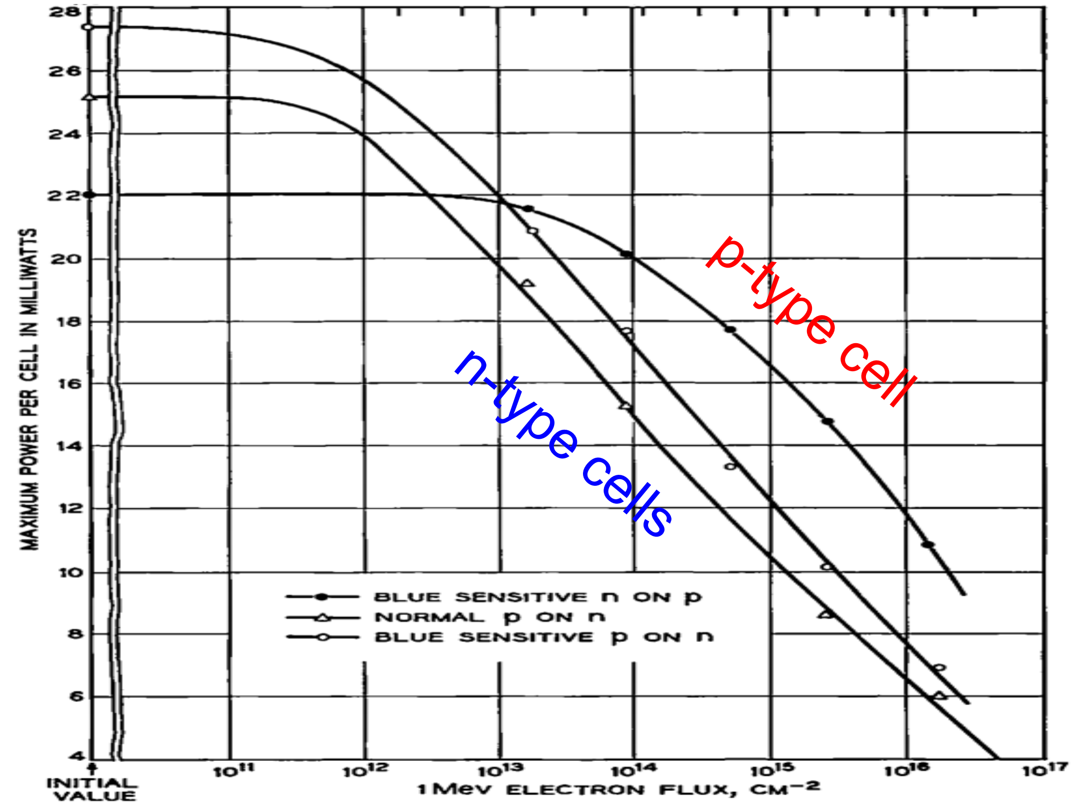


n-wafer
p-diffusion
rear etch
Rh rear contact configuration
Efficiency: approximately 6%

c-Si cells for space

Telstar I & II

first trans-Atlantic satellite communication

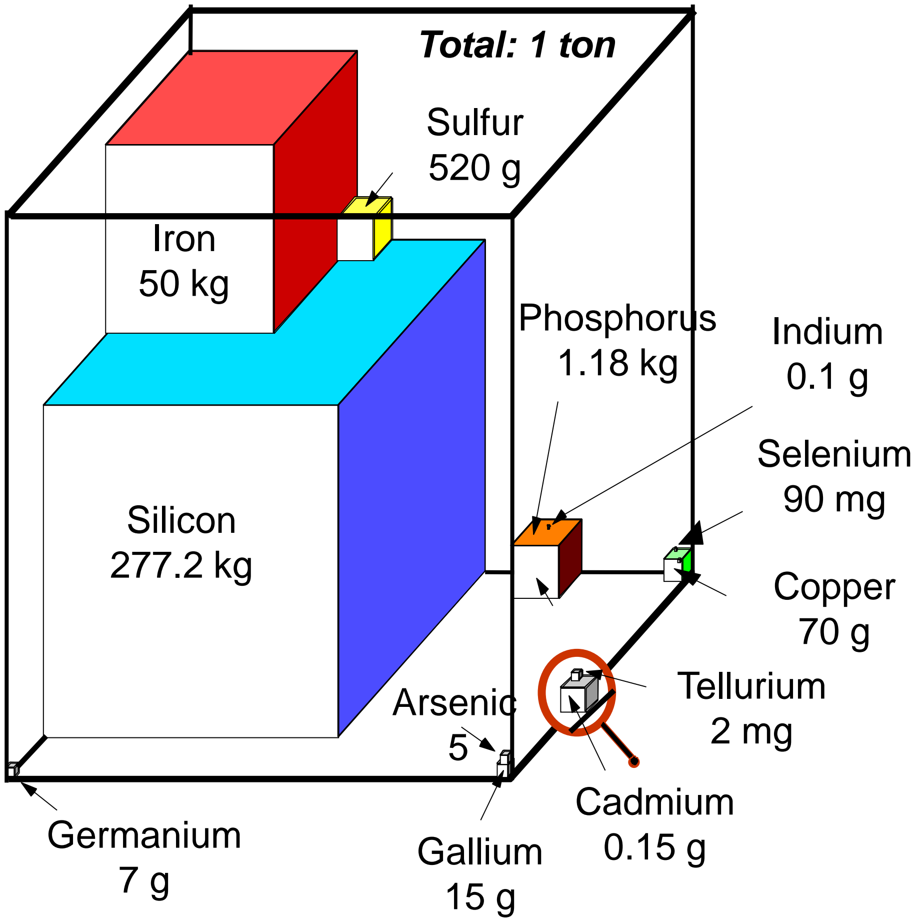


Radiation dose (time in van Allen belt)

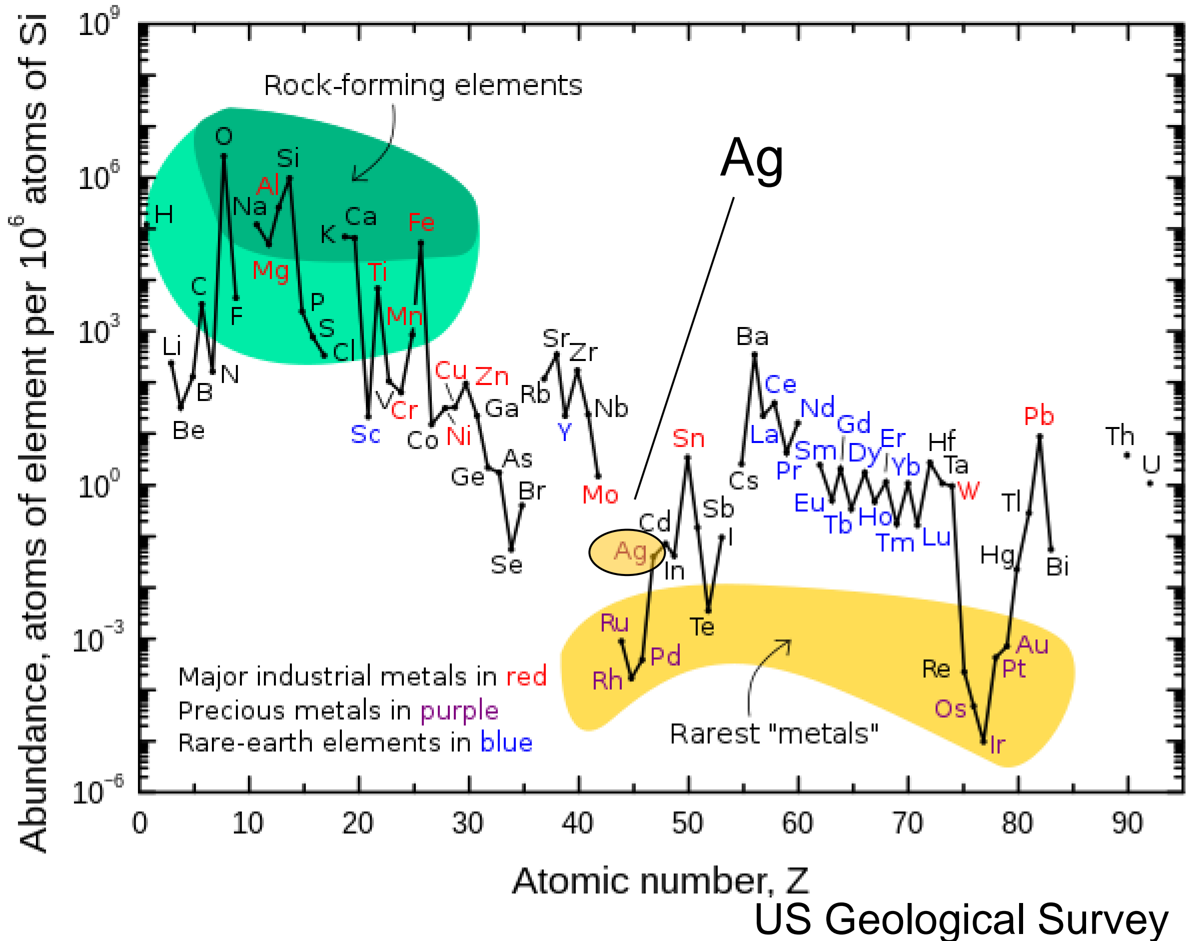
Explanation: radiation causes defects in lower part of the gap
=> Less recombination of minority carriers s are electrons

Rosenzweig, BST (1962)

Why silicon large scale applications?



Availability of various materials in 1 ton of earth crust



US Geological Survey

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Silicon: benign and abundant resource, well understood material

Attention: Ag is critical for metallic contacts; similarly abundant to In

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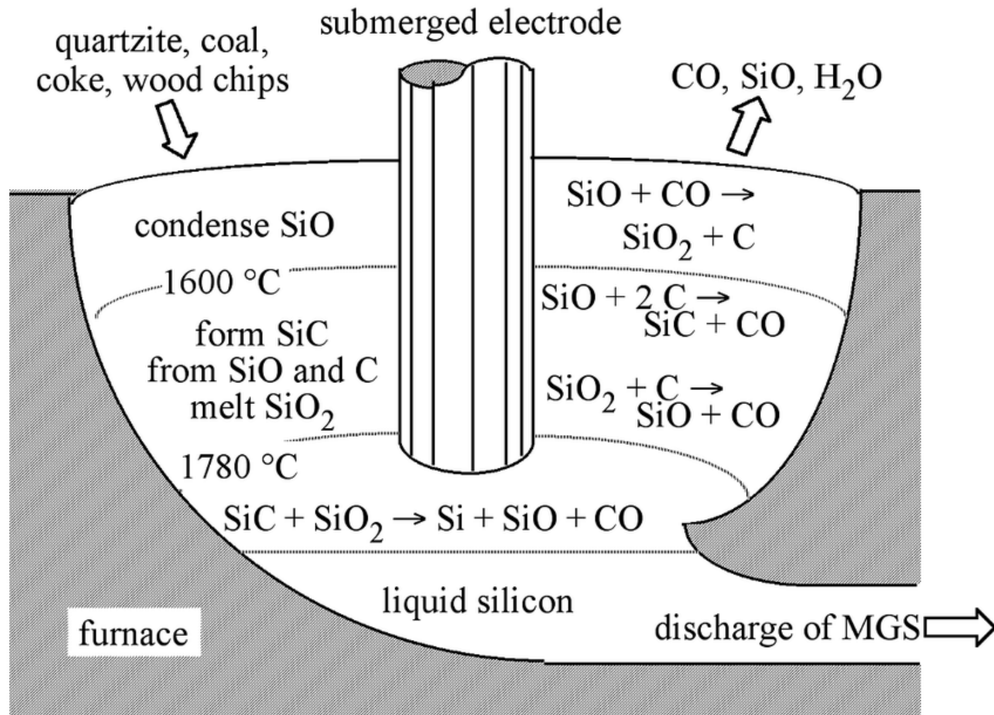
How to make Si (metallurgical grade, MG)

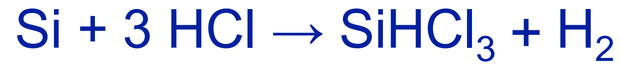


CNBM International

Overall reaction SiO_2 + C → Si + CO_2 (1 kg Si: 34 mol => at least 1.5 kg CO2 per kg Si
Split into sub-reactions in within furnace
Si only produced in arc zone (>1800°C)
Fe or Ca can enhance reaction (but must be removed later since recombination active)

Purification of Si

Reaction to Tri-Chloro-Silane (TCS) :



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

Purification by fractional distillation

Impurity level < ppb

https://silicongases.com/trichlorosilane

Solidification of pure Si

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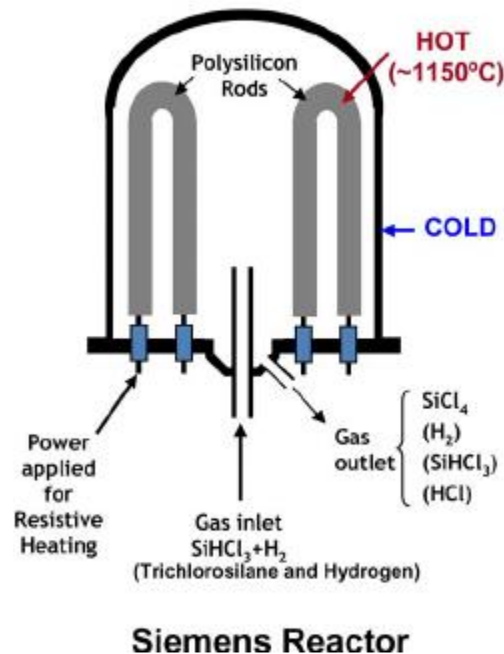
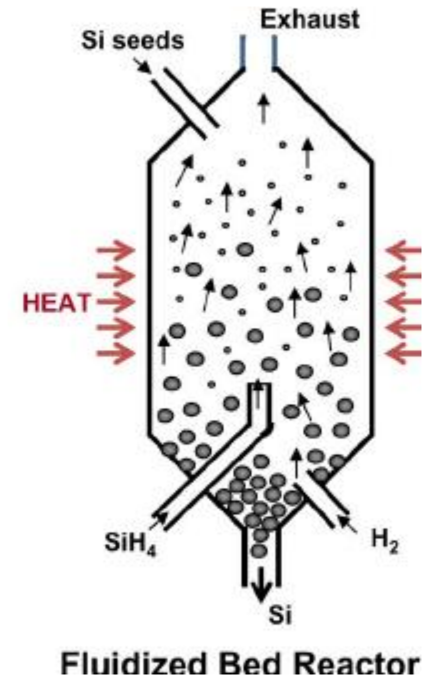
Siemens process:
- React MG Si to $SiHCl_3$ (TCS)
- Purify by fractional distillation
- React back to poly-Si



Alternative: FBR



Energy intensive (must heat rods to >1100°C, keep cool walls)

so far: marginal

Fisher, Silicon Crystal Growth and Wafer Technologies (2012)

Single crystal growth (Czochralski method)

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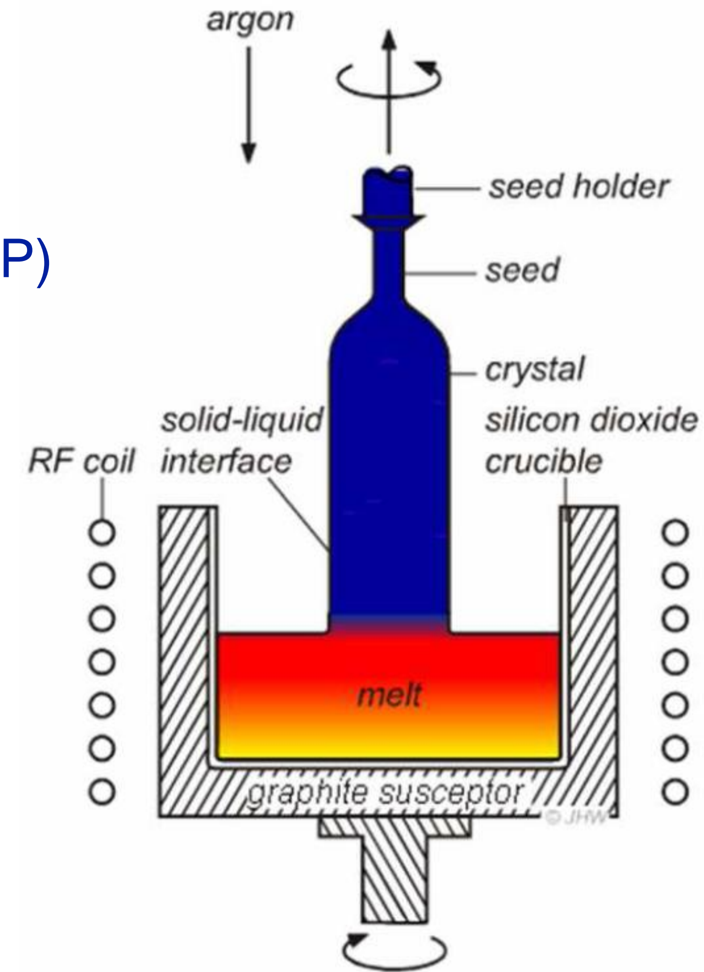
Melt silicon (1417°C)

- Add dopants
  (for solar cells historically B, later Ga, now P)
- Insert seed crystal
- Pull ingot under rotation and cooling

Main impurities:

- O (>10^{18} cm^{-3}, from atmosphere)
- C (>10^{18} cm^{-3}, from crucible)
- V_{Si} (fast pulling, forms VO_2 defect clusters)

Historically main issue: B-O complex
=> flood with inert gas (Ar), replace B by Ga
=> use P-doped n-Si (SHJ, TOPCon)



Single crystal growth (float zone method)

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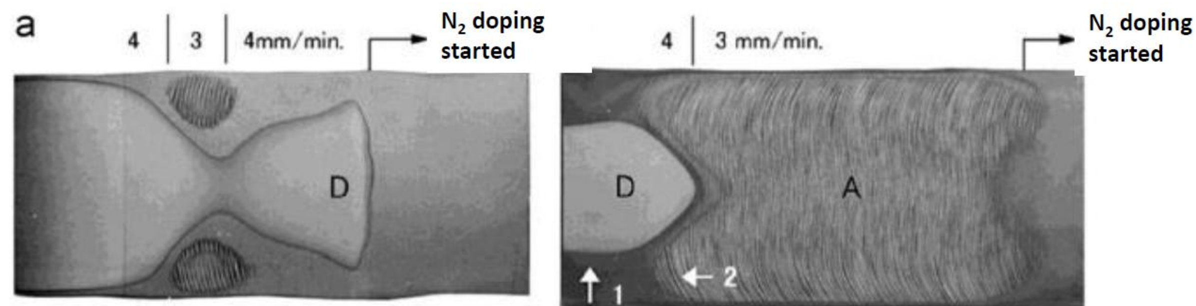
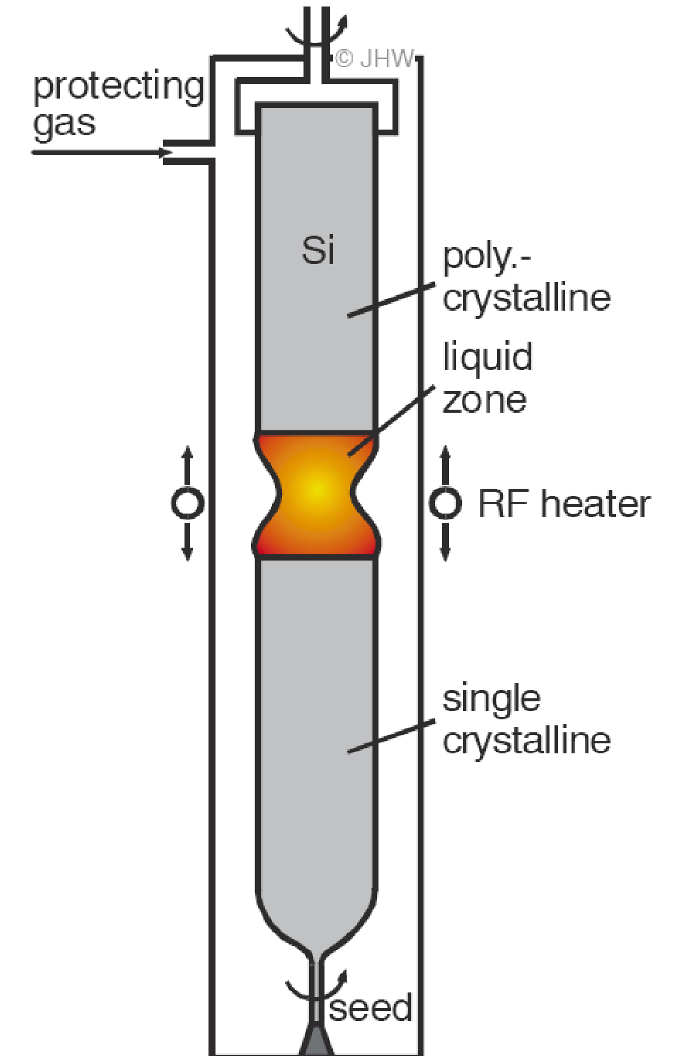
Pull RF coil along polycrystalline rod within quartz tube
Accumulate impurities by segregation in melt

Add desired dopants (B or P)

Add nitrogen (below doping level)
to control micro-defects



Wafer size limited by surface tension (dia. ca. 150 mm)



Abe et el. J. Cryst Growth 2011

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Cast silicon (multicrystalline)

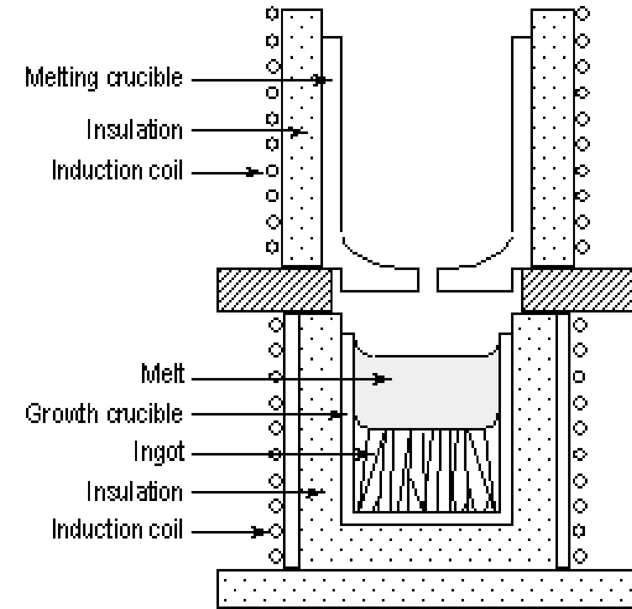
Casting into graphite or quartz molds

Molds possibly coated with Si_3N_4

Place wafers at bottom and sides
for nucleation of "enhanced mc-Si"

typically 690 mm x 690 mm, 240 kg

Solidification takes ca. 30 to 60 h



Wafer sawing

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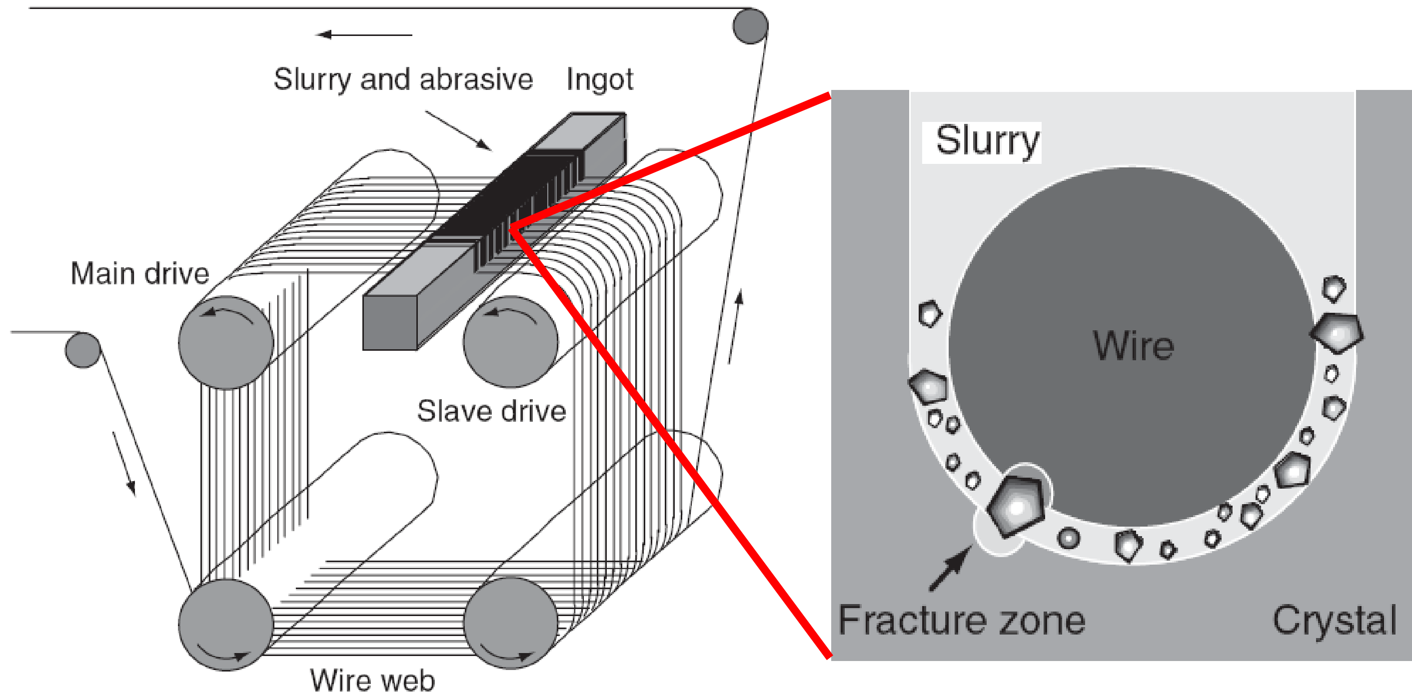
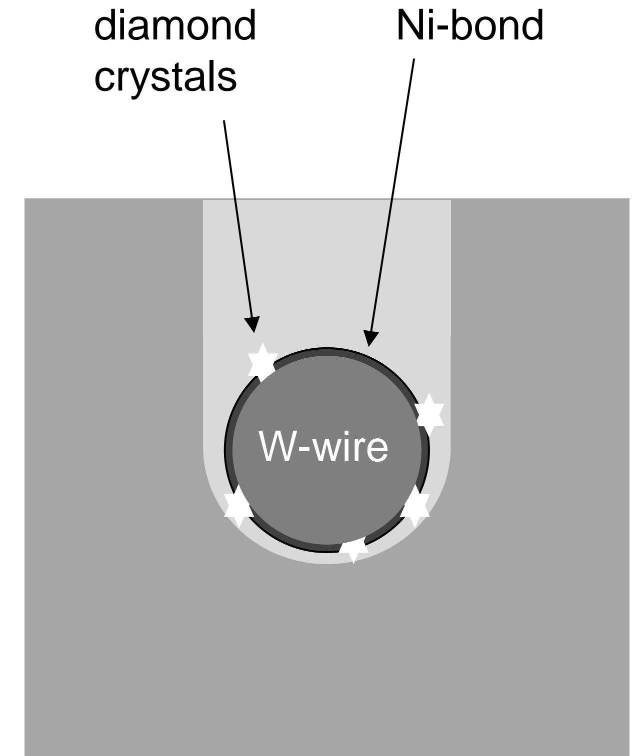
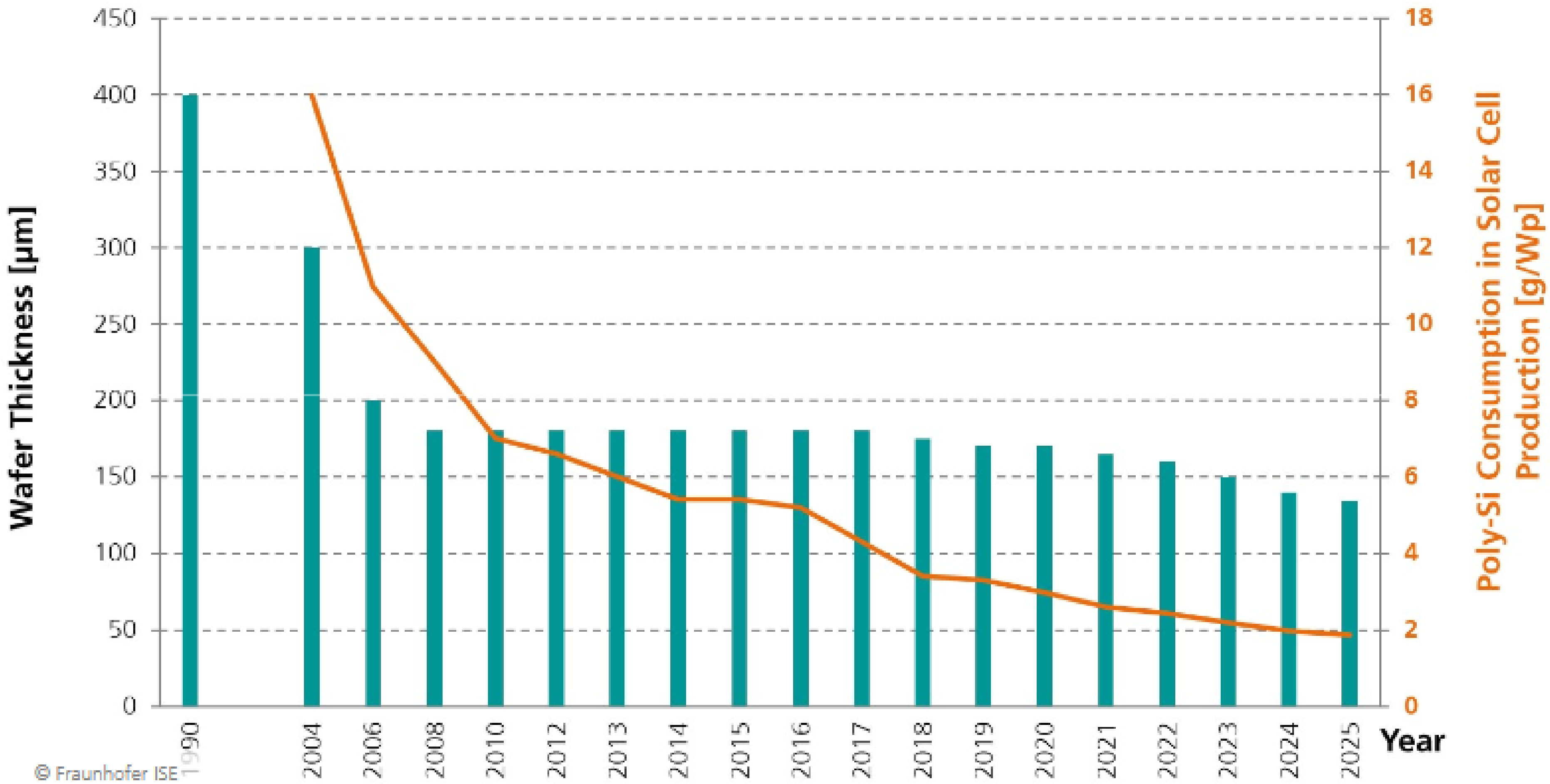




Originally: cutting with wire and SiC slurry
- rolling movement of SiC particles
- fracture by impact
- removal with half of wire speed

New standard: diamond-bonded wire
- scratching abrasion
- no (few) fractures
- cut with full wire speed
- narrower kerf-loss,
- easier recycling of Si/lubricant

Wafer thickness



Photovoltaics report 2025, Fraunhofer ISE

Summary

FZ-Si:

- highest efficiencies, usually n-type
- historic record cells up to ca. 25%,

Cz-Si:

- high efficiency volume production
- recent world records >26%

mc-Si:

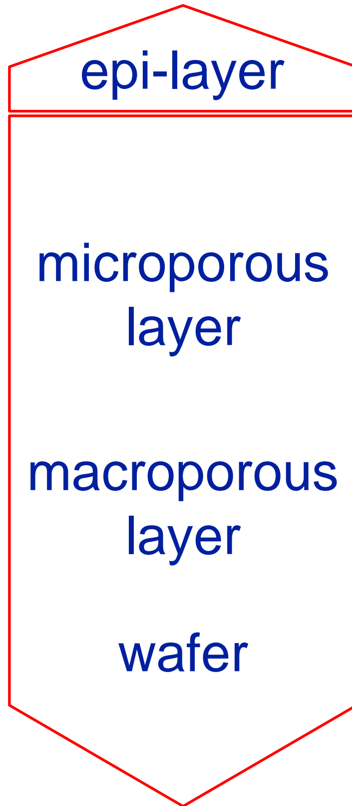
- phased out from production (~10% of market in 2021, was usually p-type)
- low cost or raw material, best cells up to 22%

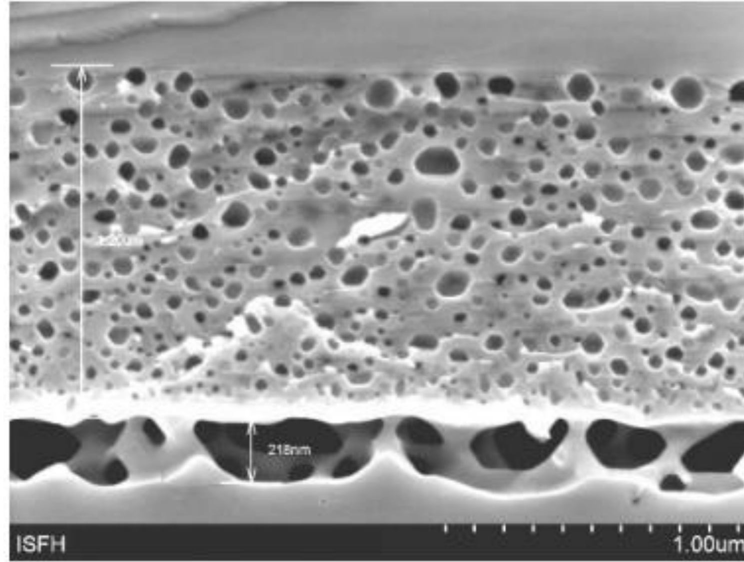
Other types of c-Si

- Wafer pulling from melt
  ribbon, cylinder, octagon, etc.
  Edge defined Film Growth (EFG)

- Direct wafer solidification
  (like H_20, solid floats on liquid phase)
  pioneered by 1366 Inc., 20 s per wafer
  cells with ca. 19% demonstrated

Kerf-free wafering





apply front of “standard” c-Si cell fabrication
remove from substrate
re-use wafer

F. Haase, JAP (2013)

Kerf-free wafering

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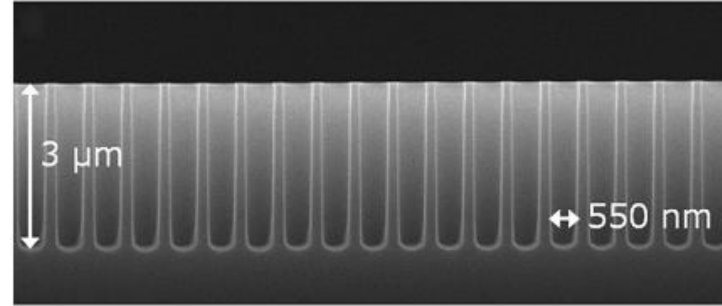
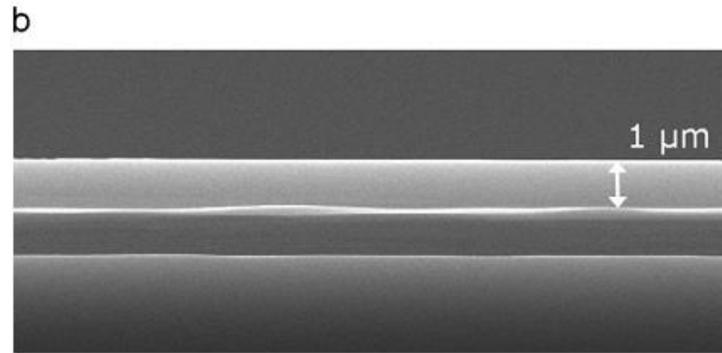
60 min
1150°C



DRIE etch

wafer



free standing film
void
wafer

single-crystal film
glue to substrate
process rear (with a process that does not harm the glue)

I. Gordon, SEM (2011)

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Kerf-free wafering

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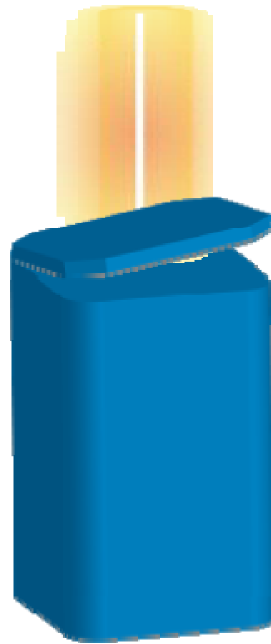
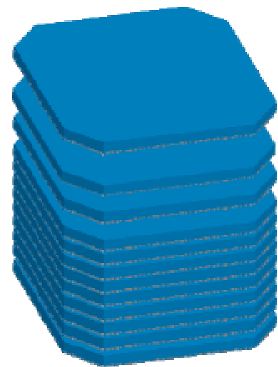
SiGen PolyMax Process



Silicon Brick



Cleaved Wafers

- Two Step Process
  (1) Implant
  (2) Cleave

< insert here: annealing

- What *kerf* less represents
  - Eliminates Consumables and Waste
    - SiC, Slurry, Wire
  - Eliminates Other Systems
    - Gluing
    - Singulation
    - Cleaning
  - Reduces Upstream CapEx
    - Less poly feedstock
    - Less CZ pullers
  - Develops thin wafer market
    - Removes the sub-150µm wafer barrier
    - New applications (i.e. BIPV)

Al-induced crystallization (AIC)

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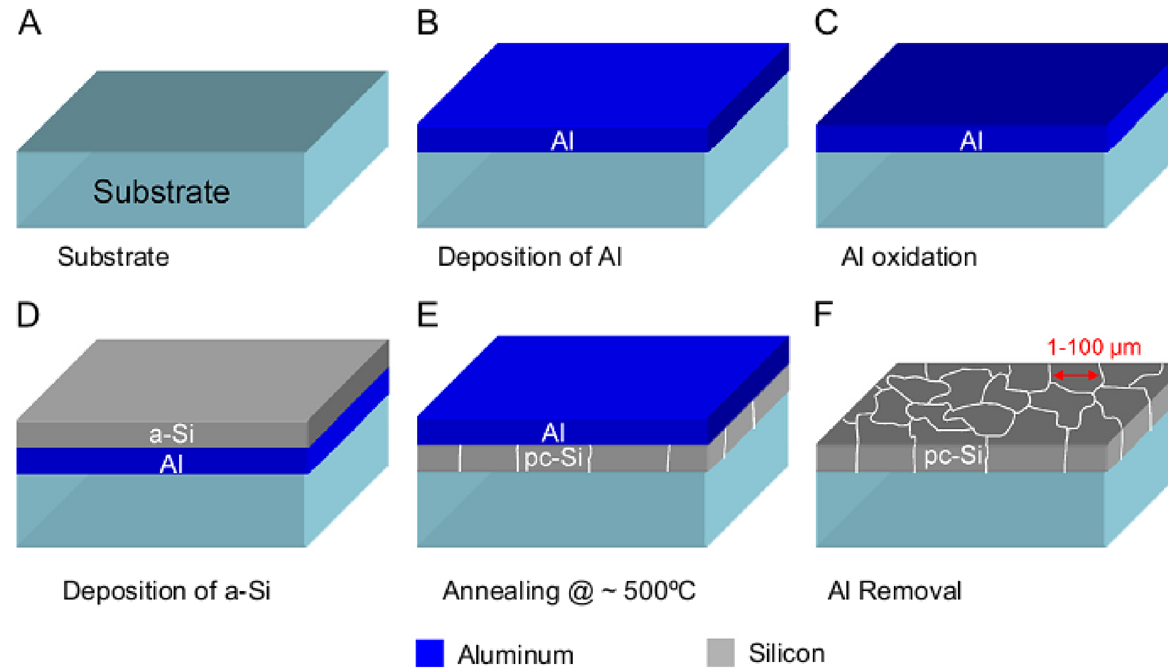

Deposit Al (B), deposit Si (D), melt Al & dissolve Si-film in liquid Al eutectic at 577°C (D-E), cool and segregate Si from supersaturated melt, grow Si at coldest interface, i.e. glass, remove Al

Issue: impurities, unintended Al doping (ca. 2-3 × 10^{18} cm^{-3}, saturation solubility in c-Si), Al is too costly to just etch and discard
Potential: large grained substrates for epitaxial thickening

D. van Gestel, SEM (2013)

Liquid phase crystallized silicon

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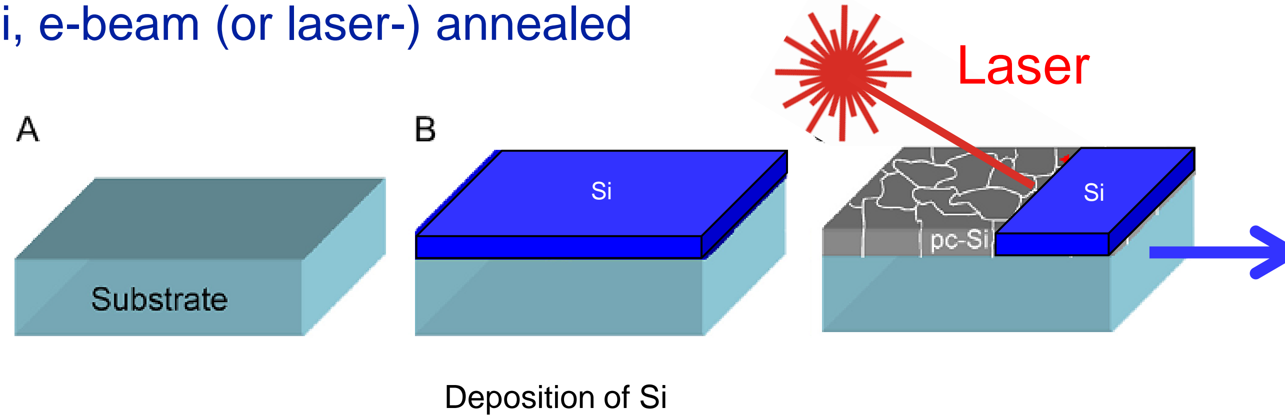
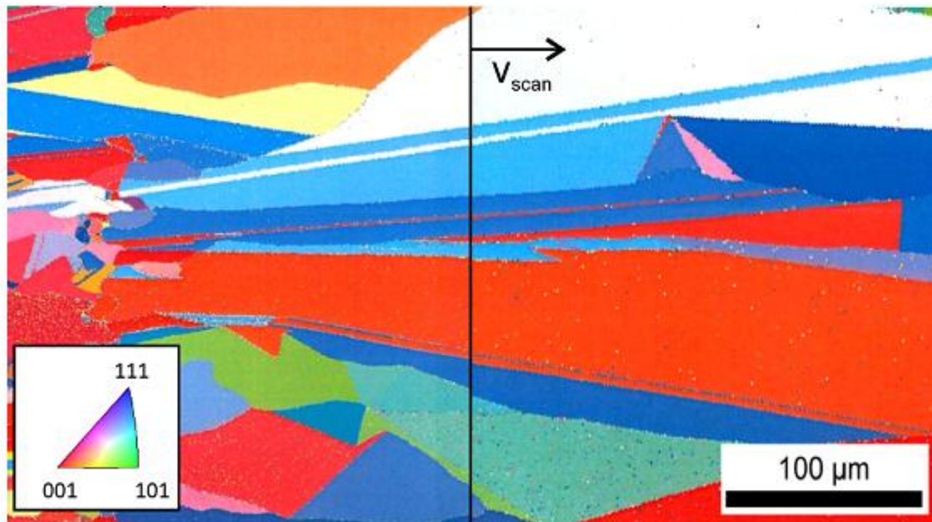
a-Si, e-beam (or laser-) annealed



Deposition of Si

Orientation map by EBSD



e.g. HZB, Germany
11.5% solar cells
Main issues: grain size, impurities

C. Becker, SEM (2013)
J. Haschke, SEM (2014)

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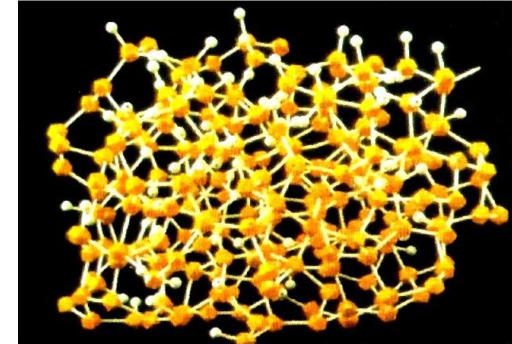
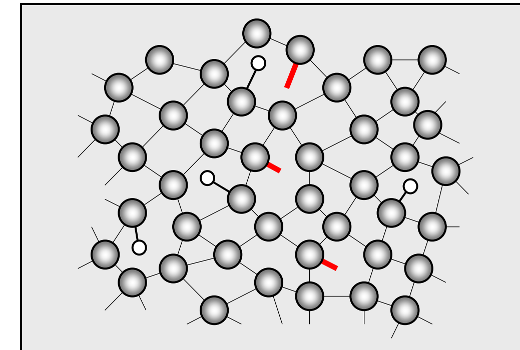
Amorphous silicon

Coordination defects in evaporated a-Si
(N_D~10^{20} cm^{-3}, one defect in 1000 Si atoms)



Passivation by hydrogen in PECVD a-Si:H
(similar to H-termination of c-Si by HF dip)



Defect equilibrium (frozen in during cooling)

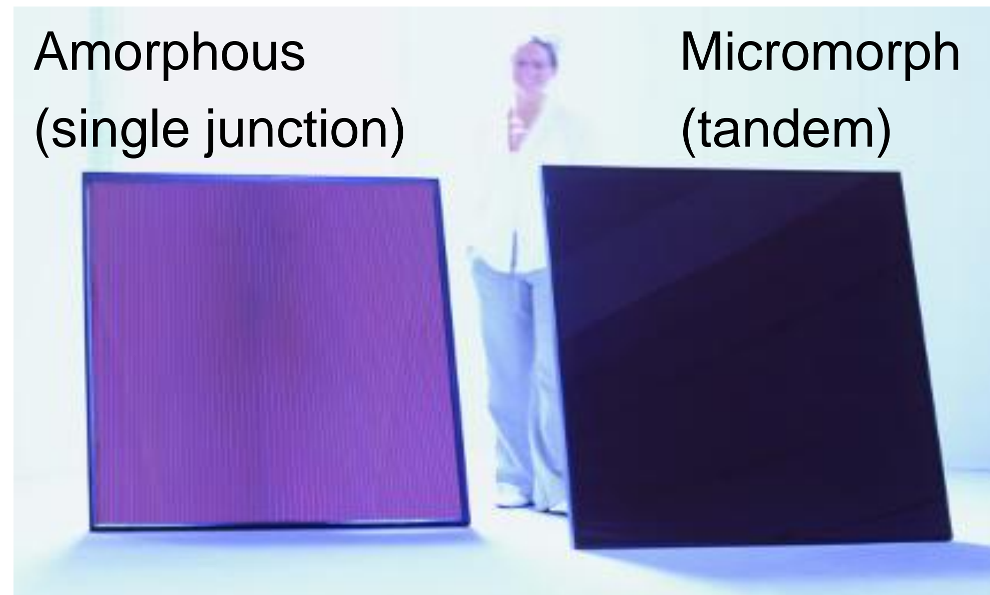
$$Si\text{-}H \leftrightarrow D^0 + H$$

99.9999% of all defects are passivated,
but: about N_D~10^{16} cm^{-3} remain

a-Si commercialization

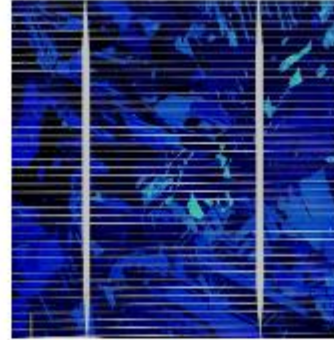
Strong business during early 2000s
Applied Materials, Oerlikon (equipment manufacturers)
Kaneka, UniSolar, Sharp, Mitsubishi, Bosch, etc. (Solar module eff. ca. 10%)

Today:
Kaneka is left in JP market, but focusses research on HIT concept
Niche markets survive (solar watches, etc.)



Source
Oerlikon Solar
(TEL Solar)

c-Si processing



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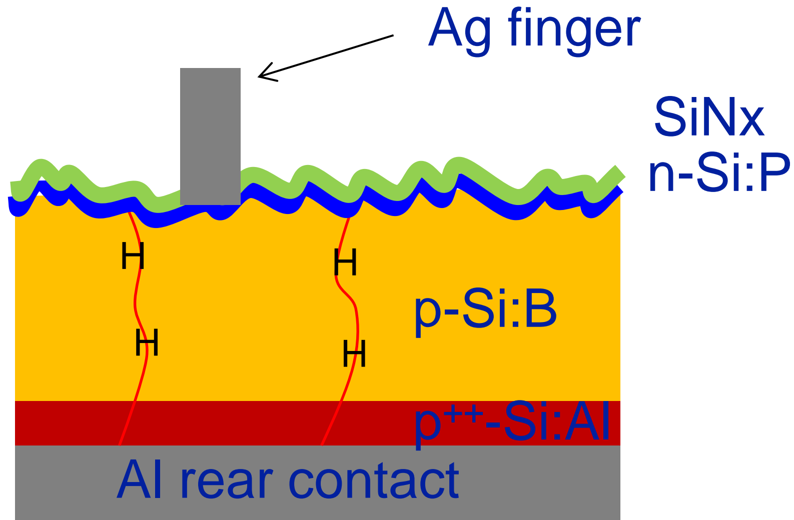
Simple process: (multi-) crystalline Si-cell

Cells with BSF (back surface field):
Voc ≈ 660 mV



large direct back contact (recombination!)
field effect passivation by strong doping
nitride passivation on front

fabrication sequence:

Saw damage removal,
Texture etch

P-diffusion ($POCl_3$)
(also impurity gettering/removal)

Apply SiNx:H AR coating

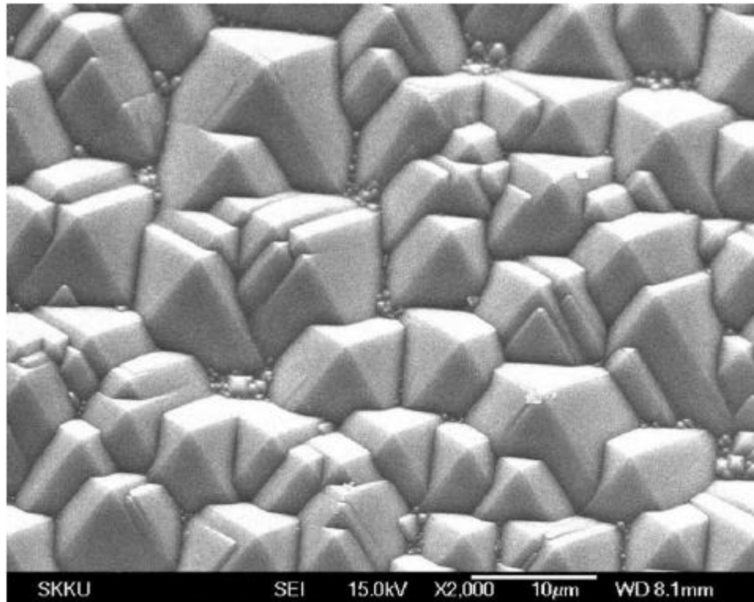
Metallization (screen printing)

Firing

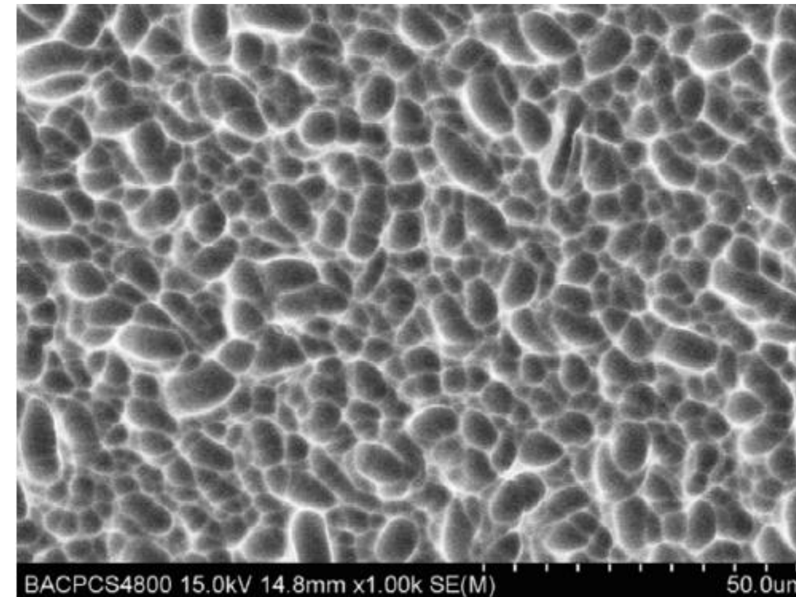
- release H from SiNx:H
- sinter Ag/glass through SiNx:H
- melt and solidify Si-Al eutectic

Surface texture

Caustic etch of Si(100)
anisotropic exposure of
111 oriented facets



Acidic etch of mc-Si
preferential etch of
SiC saw damage fractures



Issue: no longer applicable for diamond wire

e.g. Gangopadhyay, SEM (2016)
e.g. Zhou, SEM (2013)

Reduction of reflectivity by texture

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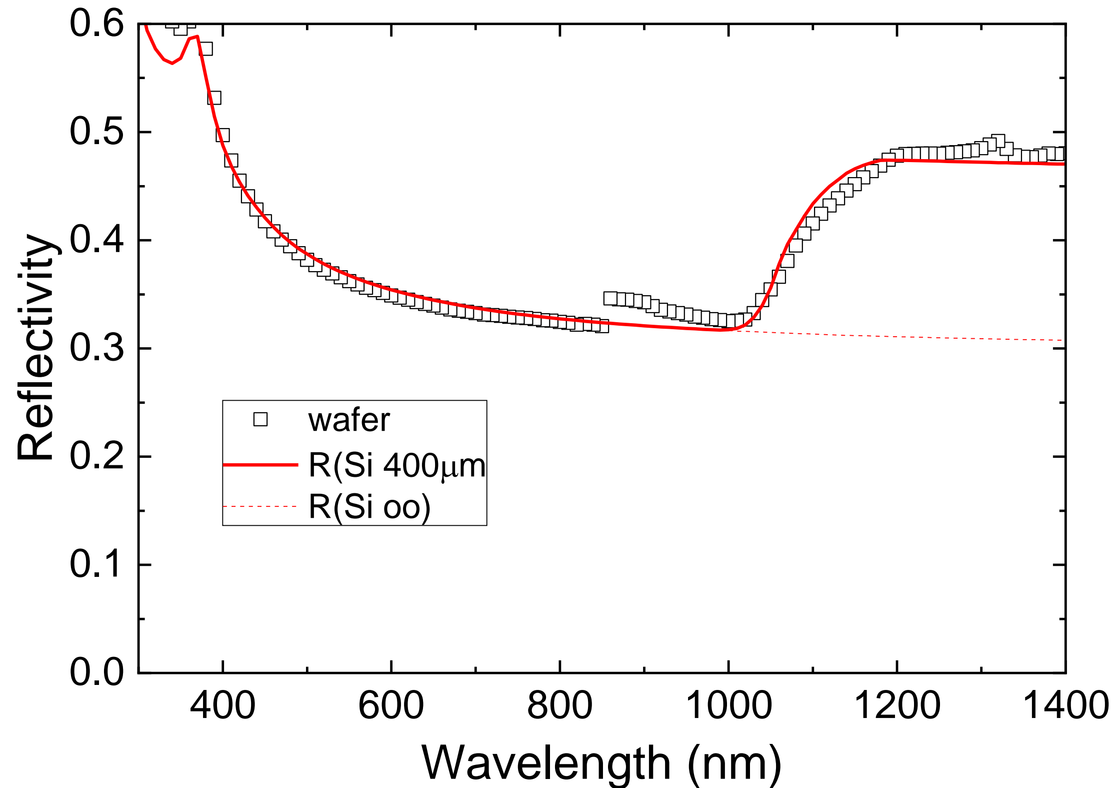
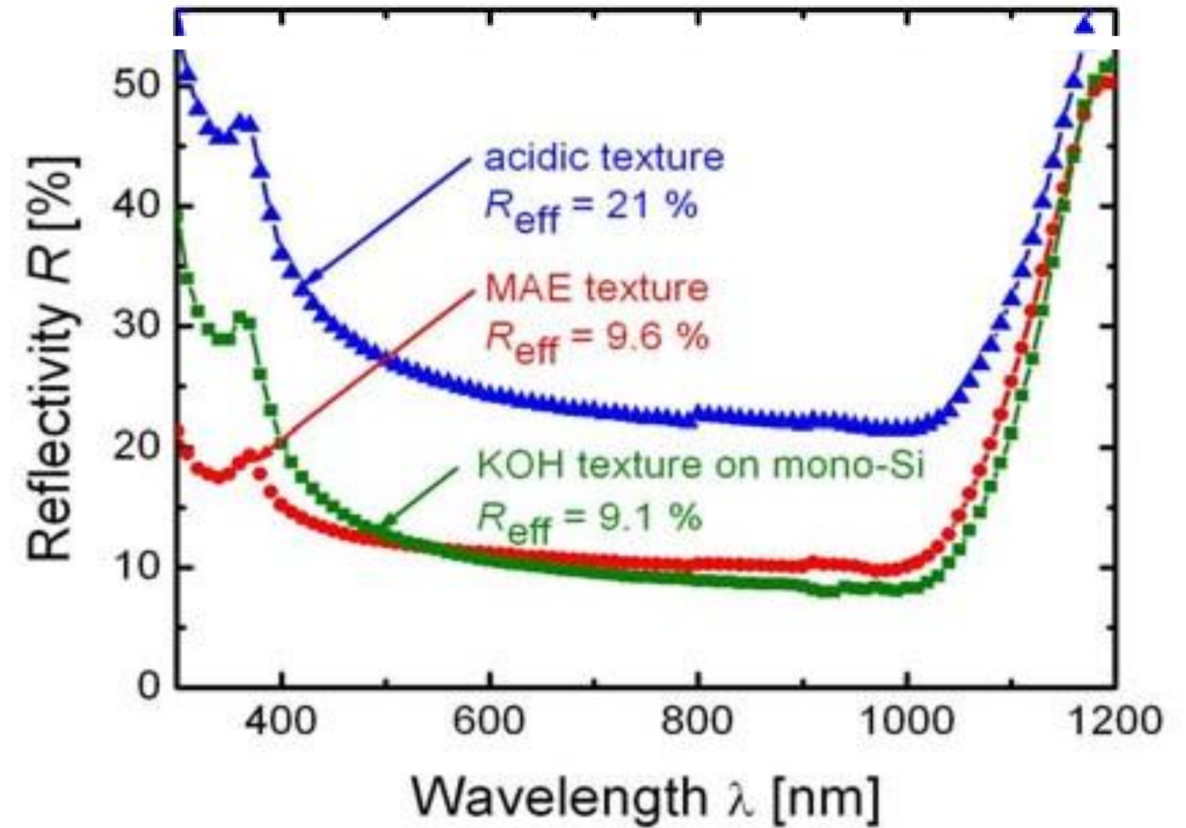
Bare silicon (n ≈ 3.5)



Textured silicon



e.g. Lipinki, PVSEC (2009)

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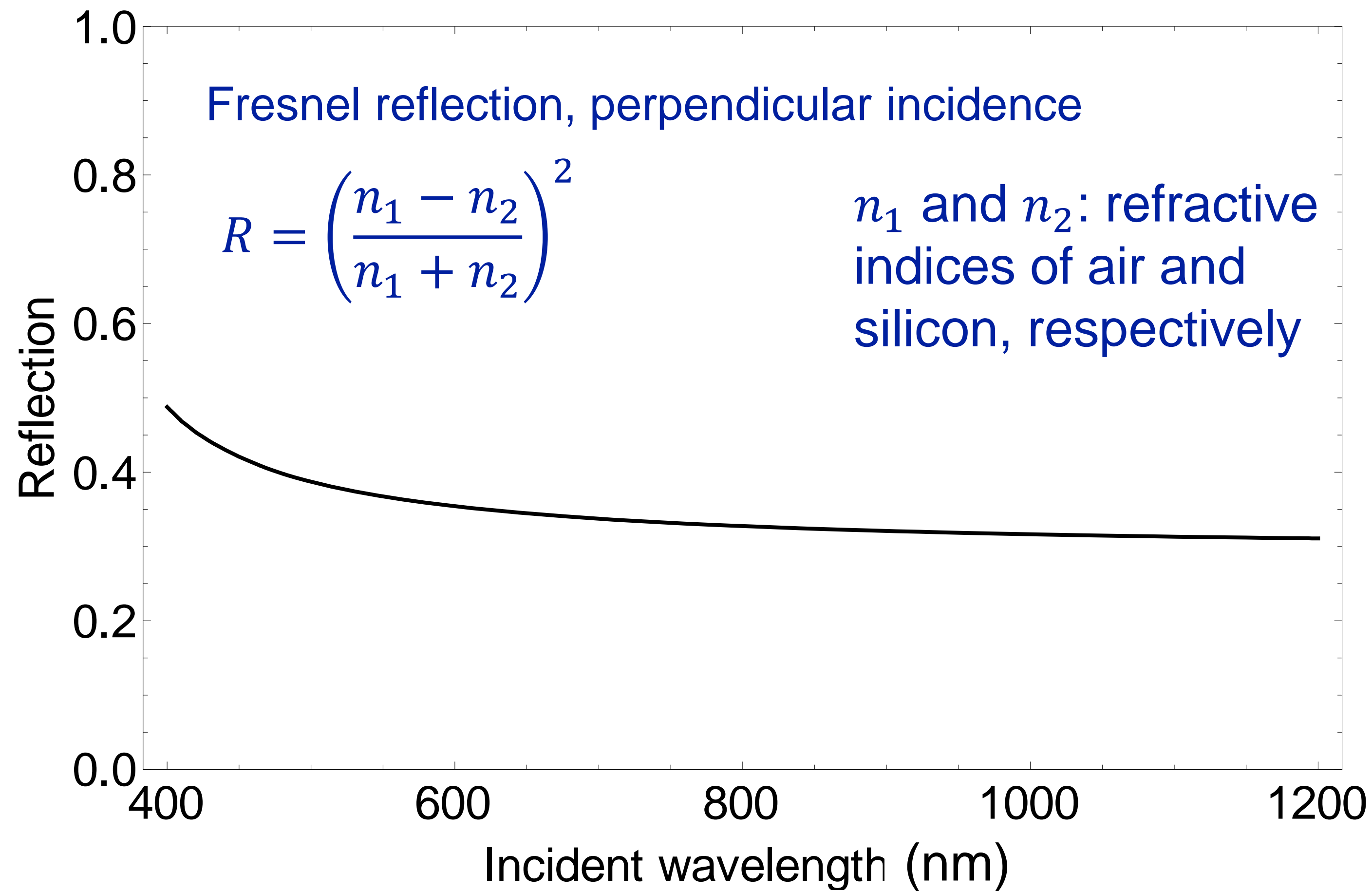
AR effect by texture



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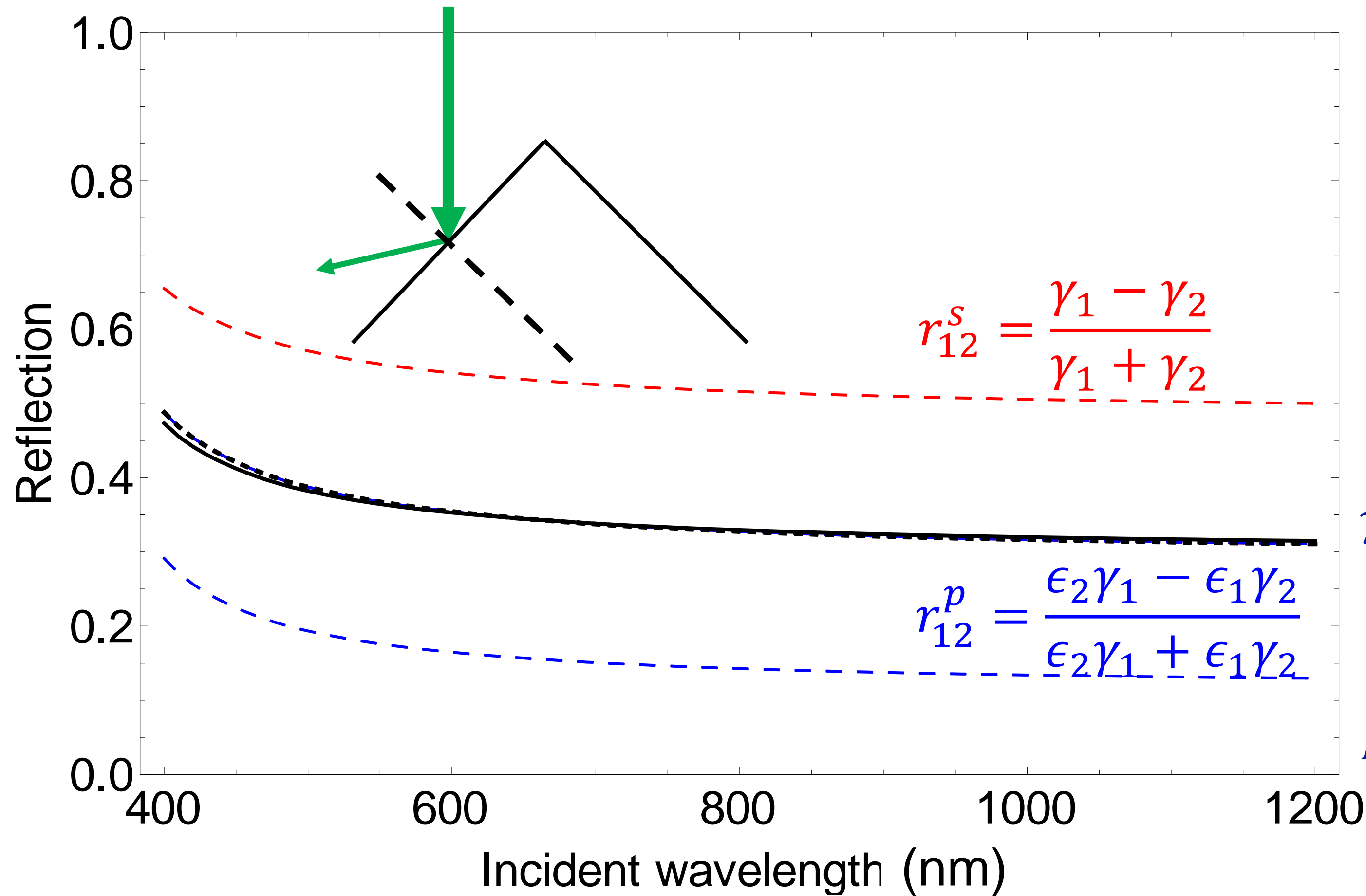
Reflection from a facet



$$r_{12}^{s} = \frac{\gamma_1 - \gamma_2}{\gamma_1 + \gamma_2}$$

$$r_{12}^{p} = \frac{\epsilon_2\gamma_1 - \epsilon_1\gamma_2}{\epsilon_2\gamma_1 + \epsilon_1\gamma_2}$$

Distinguish polarization directions:
s ("senkrecht")
p (parallel)

propagation constants

$$\gamma_i = k_0\sqrt{\epsilon_i - \sin^2\theta}$$

unpolarized average

$$R = \frac{1}{2}\left(|r_{12}^{s}|^2 + |r_{12}^{p}|^2\right)$$

Practically no difference in polarisation-averaged reflection

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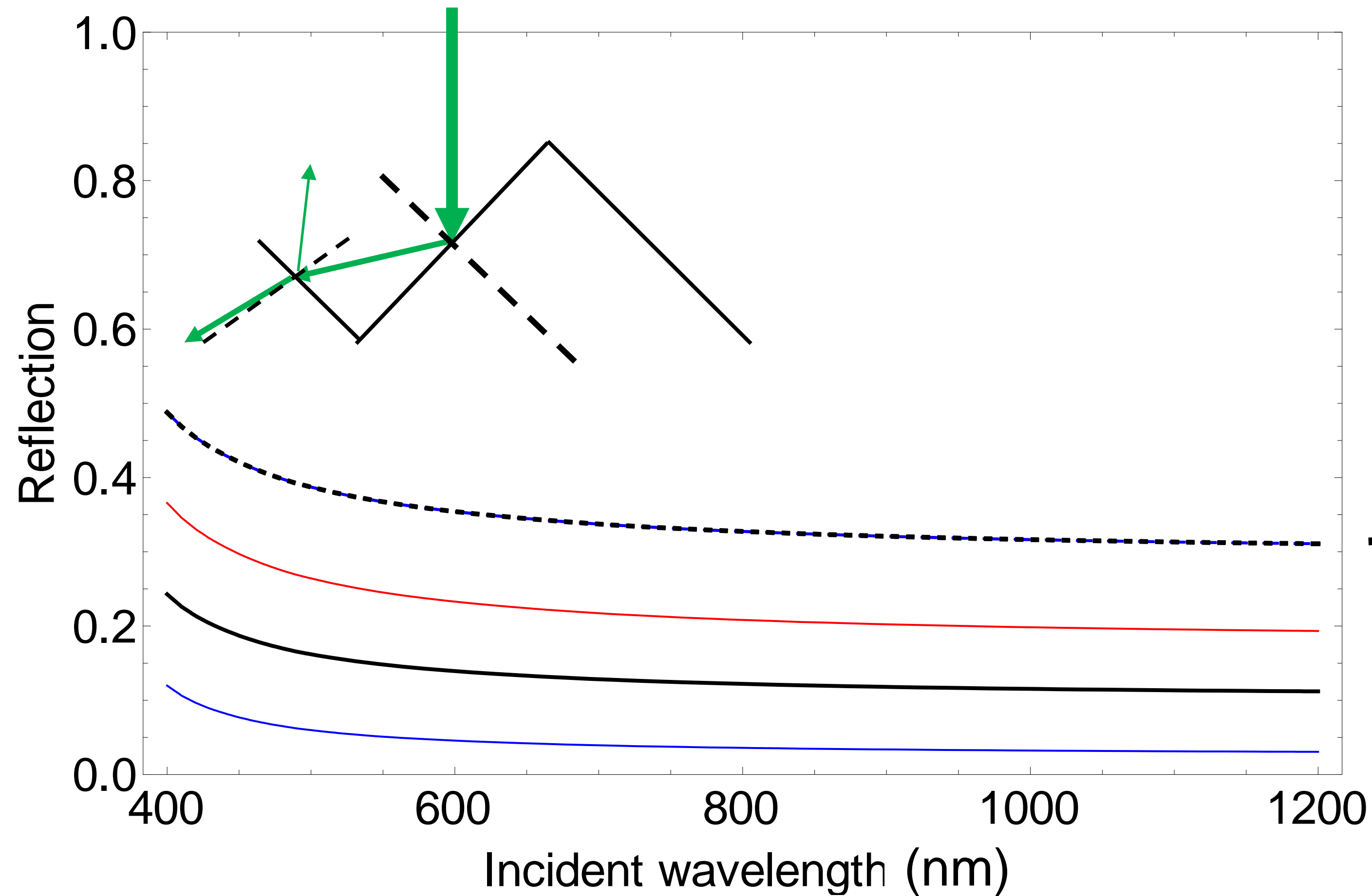
Reflection after second rebound ($\theta > 45°$)



Reduction from ca. 30% to ca. 10%

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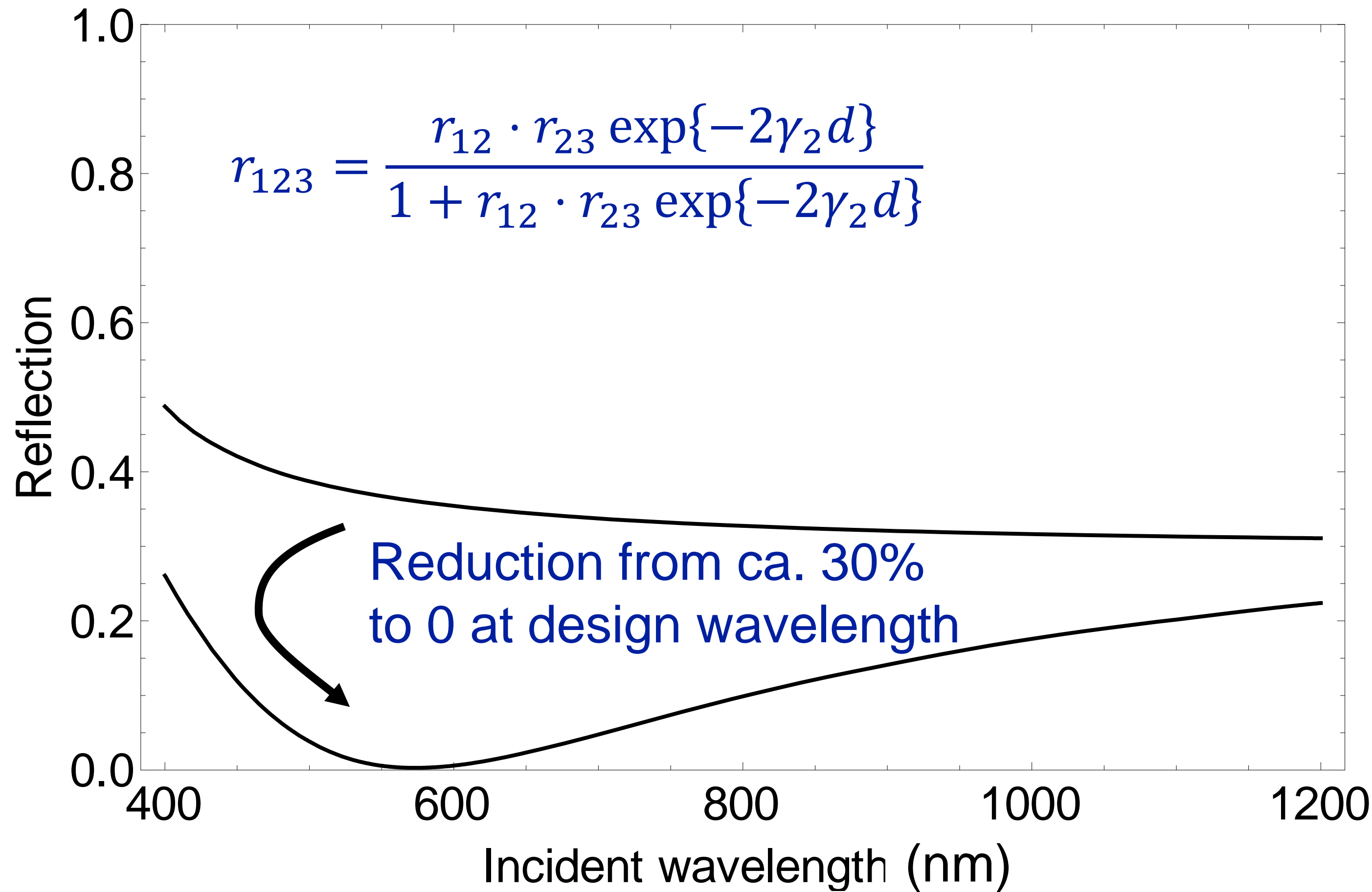
Flat Si with AR coating: e.g. 75 nm of ITO



ITO: transparent contacts for HIT solar cells

similar with SiNx

Combination of double rebound and AR coating

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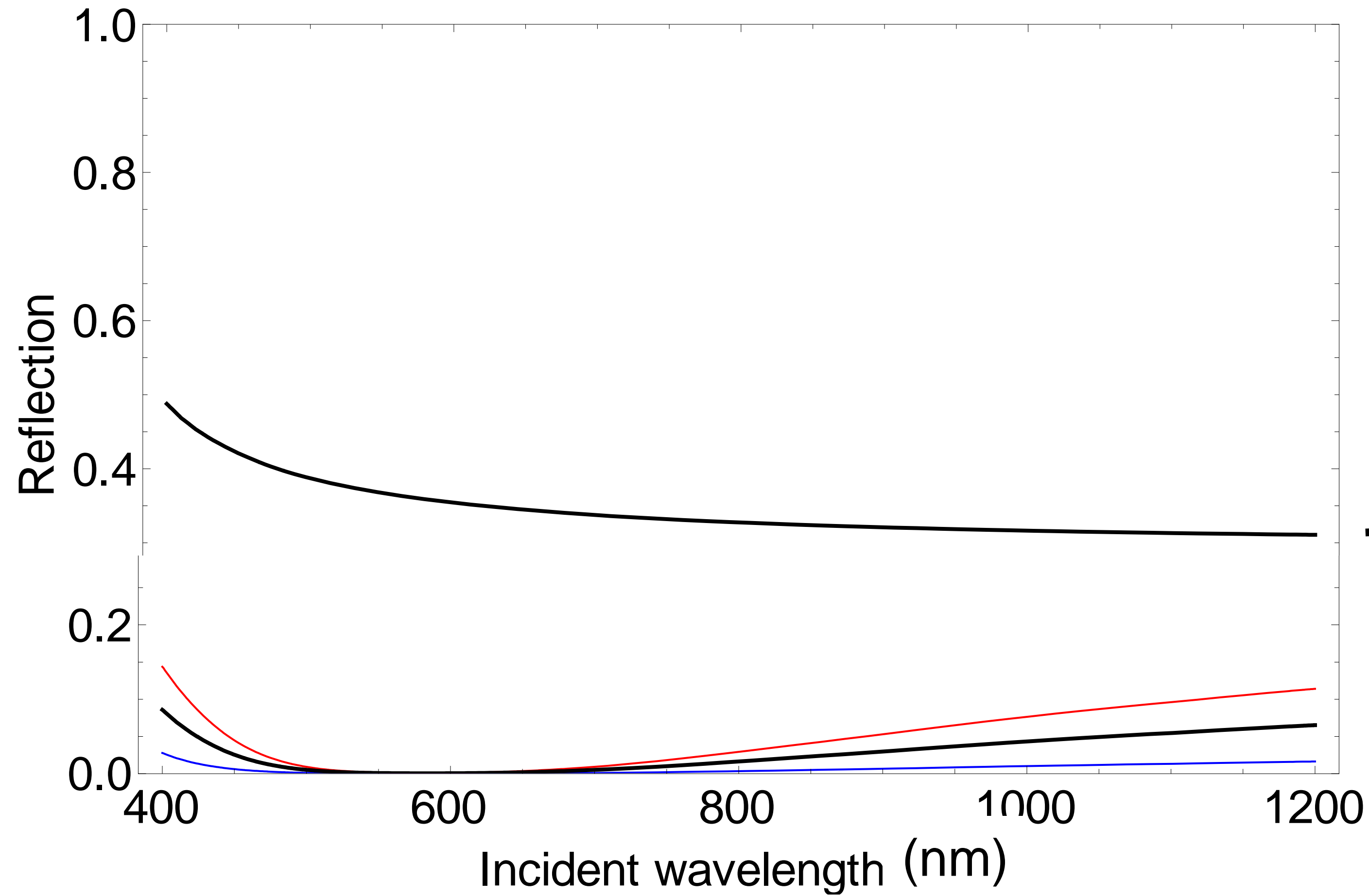
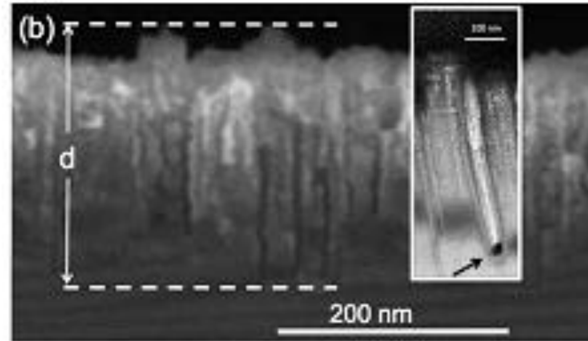
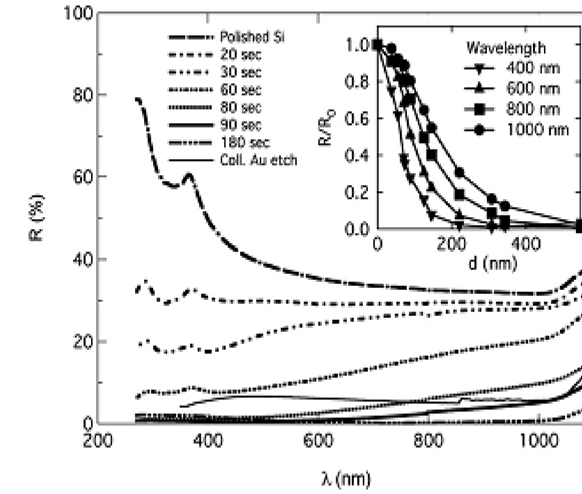


Reduction
from ca. 30%
To <.3% (average)

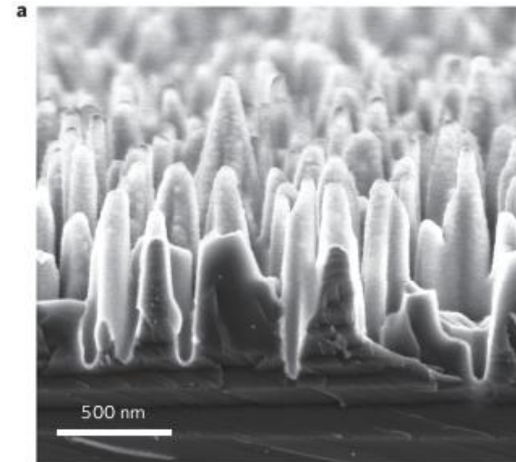
What else?

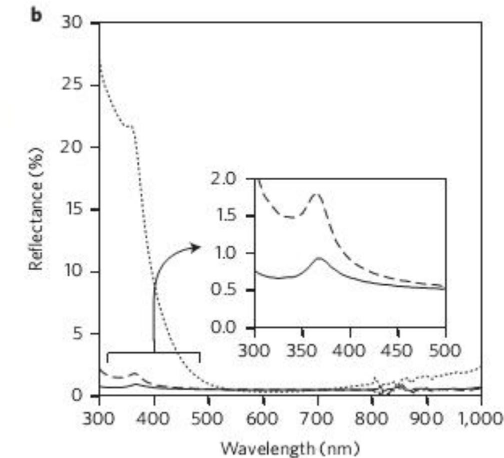
- Porous silicon
  => index grading
  perfect AR
  (difficult to
  passivate and contact)





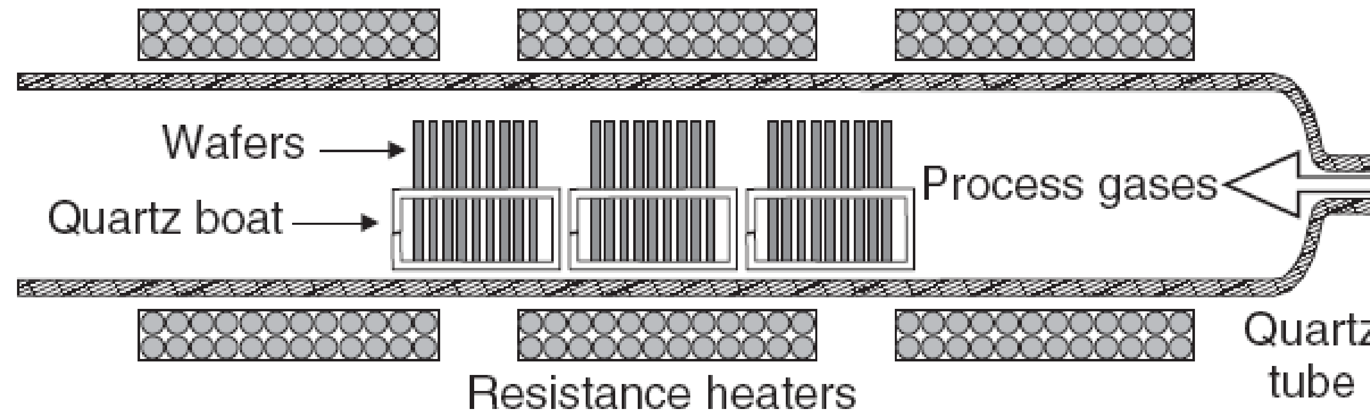
- “black silicon”
  => extreme texture,
  multiple fwd. reflections
  (difficult to passivate,
  works with rear contacts)





Branz, APL (2009)
Savin, nature nanotech. (2015)

Front contact: phosphorous diffusion



Furnace with atmosphere of $POCl_3$

Formation of phosphorus-silicate glass (PSG)

Diffusion of P from PSG (ca. 15 min at 850°C)

Cl removes metallic impurities

Possibly combined with “drive in” diffusion

e.g. Centrotherm Inc.

Diffusion equation

F.-J. Haug

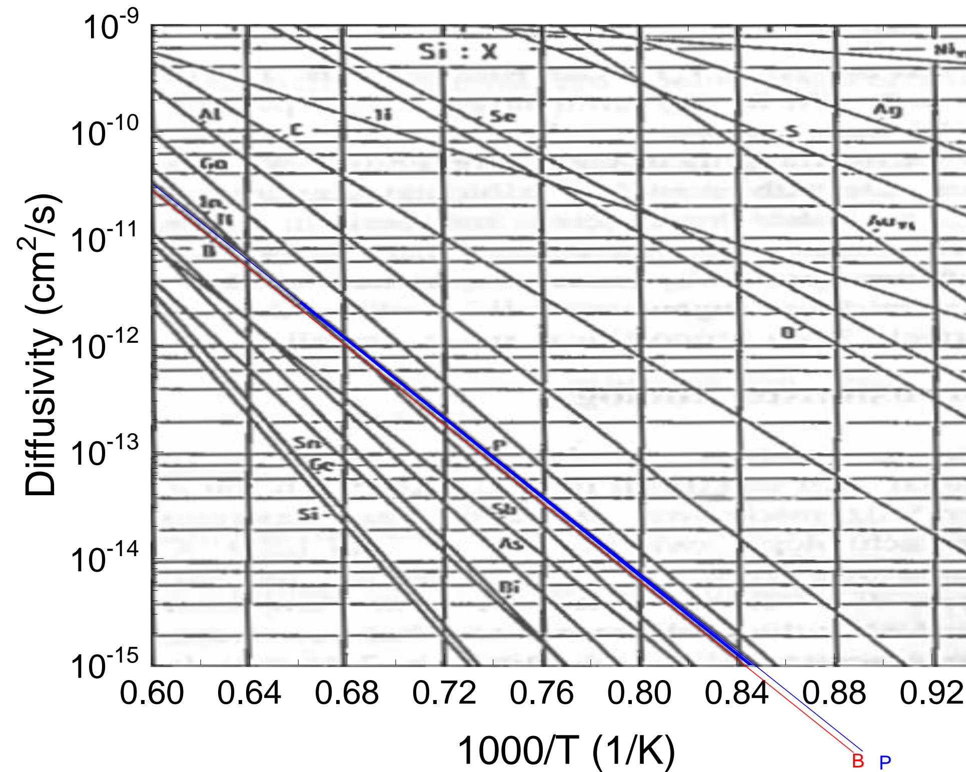
Fick's second law, often simplified for constant diffusivity D:

$$\frac{d}{dt}c = \frac{d}{dx}\left(D\frac{d}{dx}c\right)$$

Solution for inexhaustible reservoir c_0 at $x = x_0$:

$$c(x) = c_0 \operatorname{erfc}\left(\frac{x - x_0}{2\sqrt{Dt}}\right)$$

Issue: D is not constant!



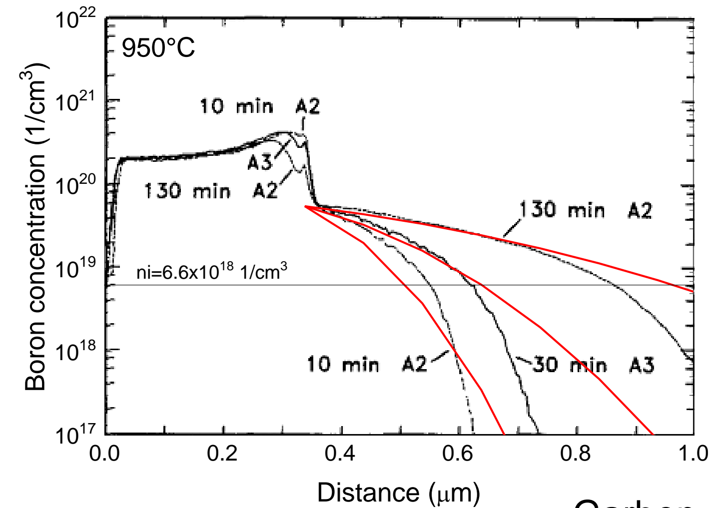
Diffusion equation

$$c(x) = c_0 \operatorname{erfc}\left(\frac{x - x_0}{2\sqrt{Dt}}\right)$$

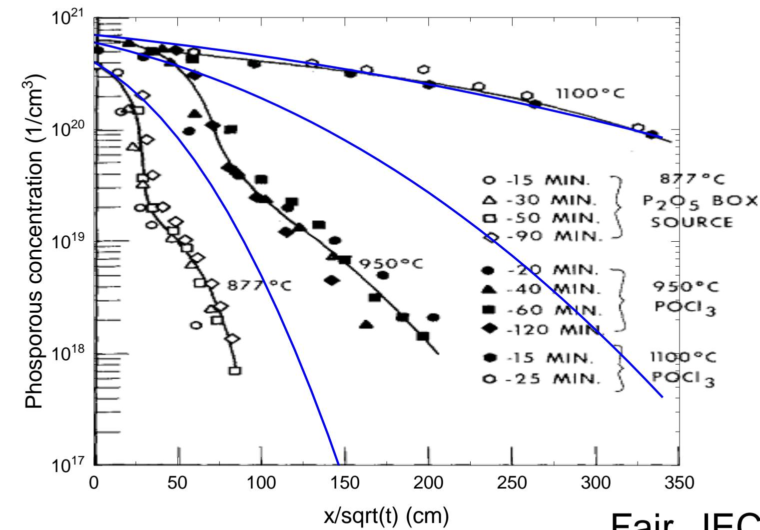
Constant D only approximately for high T

Generally:
- high D close to interface
- low D deeper in bulk

Special for P:
sudden decay ("kink") => low D
eventually high D (tail region)



Garben, JECS (1986



Fair, JECS (1977)

Boltzmann-Matano analysis

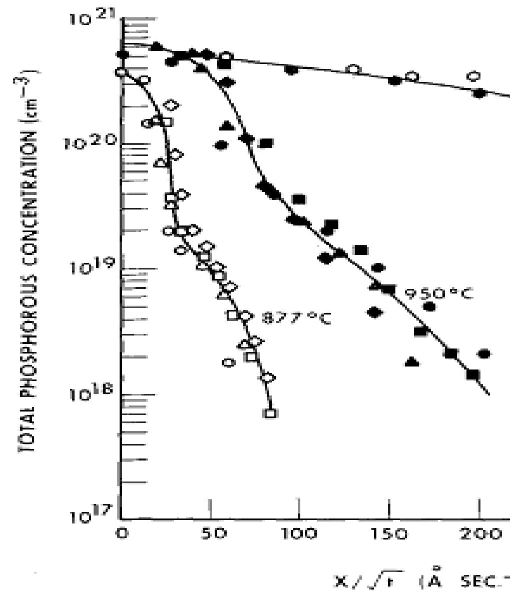
F.-J. Haug

When D does not explicitly depend on time (ramp time negligible w.r. to dwell time):
Boltzmann substitution to eliminate time derivative
=> Differentiate and integrate, and solve for D :

$$D = \frac{\int x \cdot dc}{2t \cdot dc/dx}$$

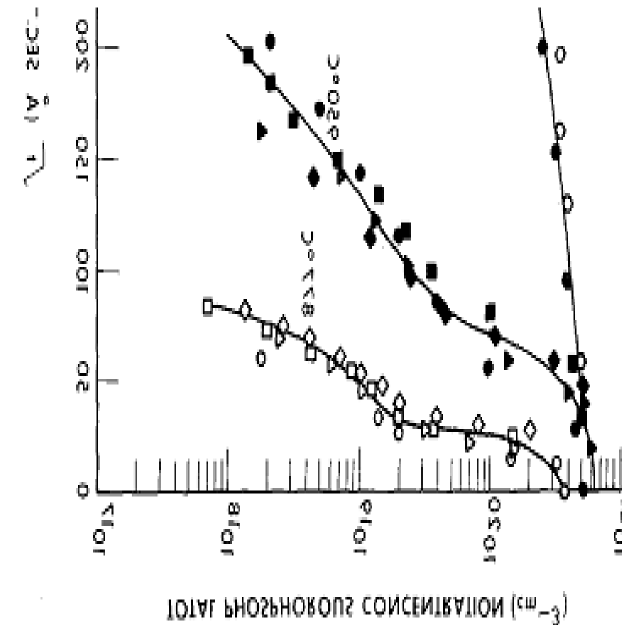
plot $c(x)$

derive dc/dx



plot $x(c)$

integrate xdc



Matano, Jap. J. Phys. (1933)

EPFL
PV-lab
IEM NEUCHATEL

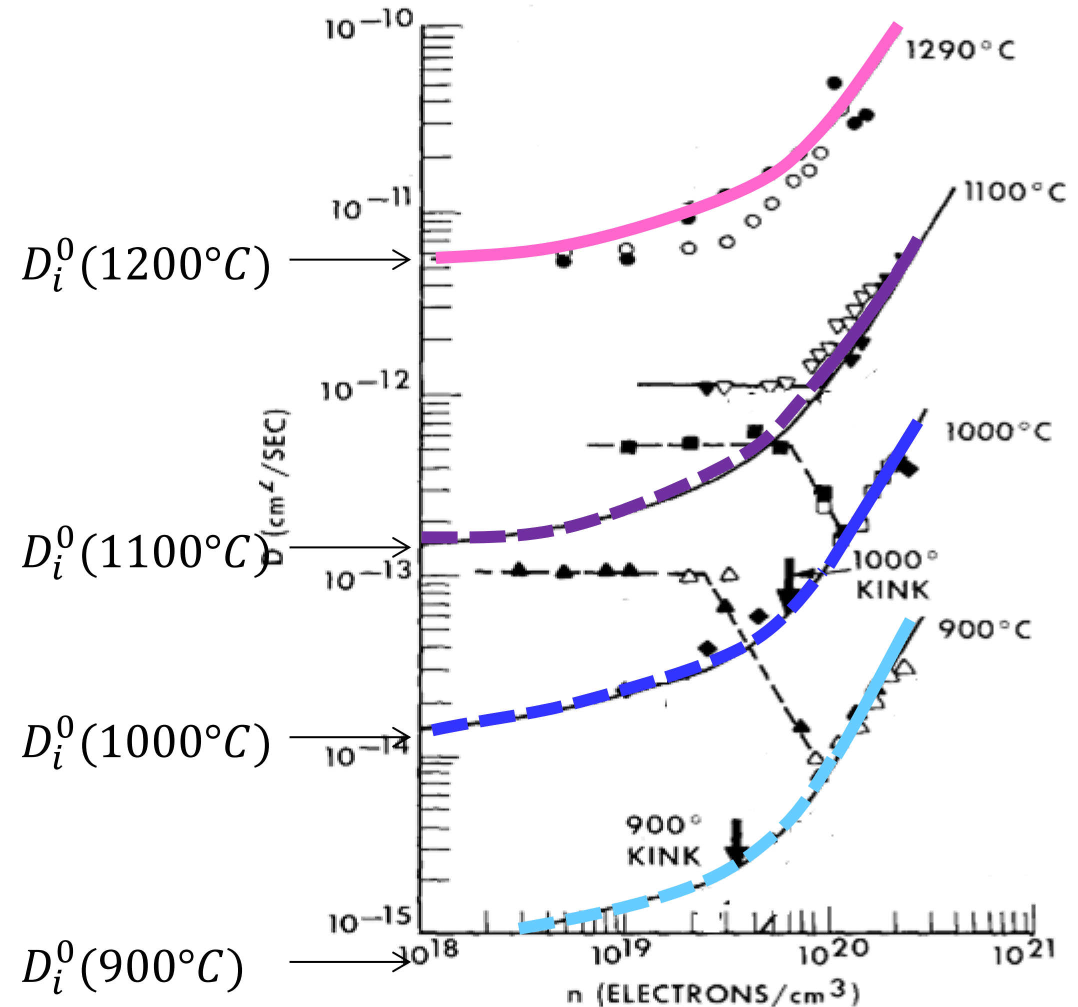
Boltzmann-Matano analysis (II)

F.-J. Haug

For high c, high T:
- Diffusion of neutral P
- Diffusion of pairs
  (ionized P, charged defect)

$$D_P = D^0 + D^- + D^=$$
$$= D_i^0 + D_i^- \left(\frac{n}{n_i}\right) + D_i^= \left(\frac{n}{n_i}\right)^2$$

$$n = \frac{1}{2}\left(c_P + \sqrt{c_P^2 + 4n_i^2}\right)$$



Fair, JECS (1977)

Note: $n_i(T_{diff})$ not negligible to c_P

Defect pairing

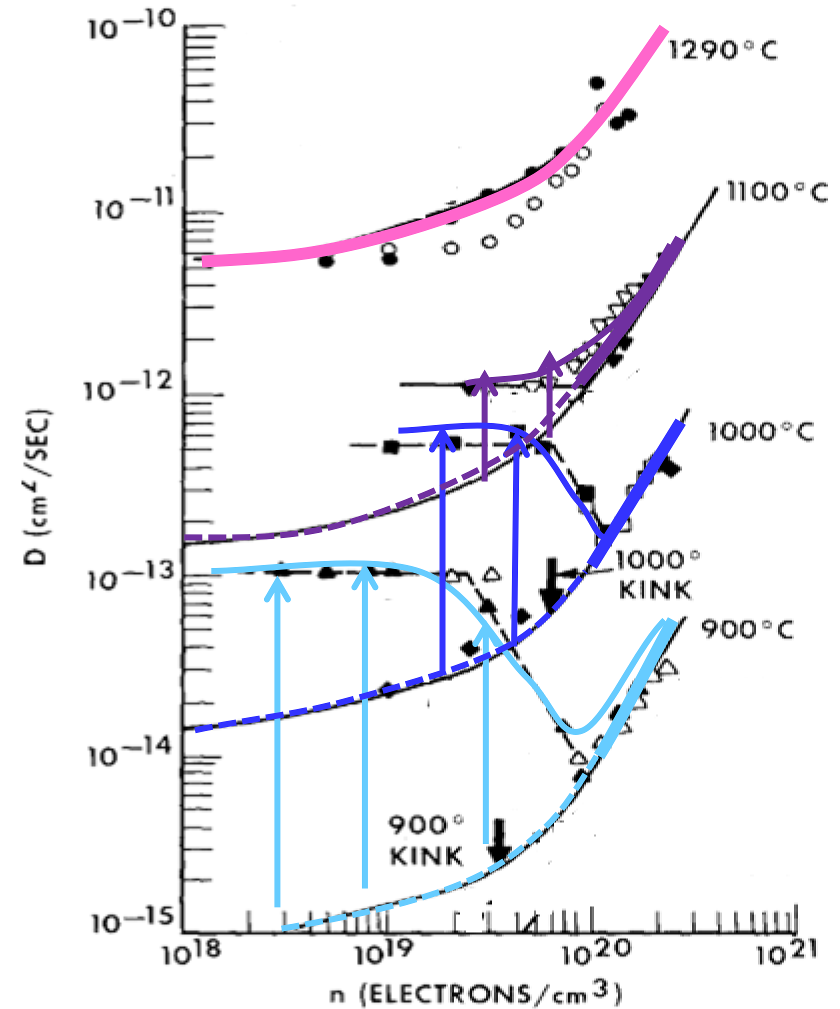
For low c, low T:

Deviation, found proportional to surface concentration

Reason: Additional defects injected by excess of c_{surf} (forced by reservoir) over c_{sat} in crystal (temperature dependent)

Describe by fractional pairing to vacancies and interstitials emitted from surface

$$D_P = f_V D_V^* + (1 - f_V) D_I^*$$



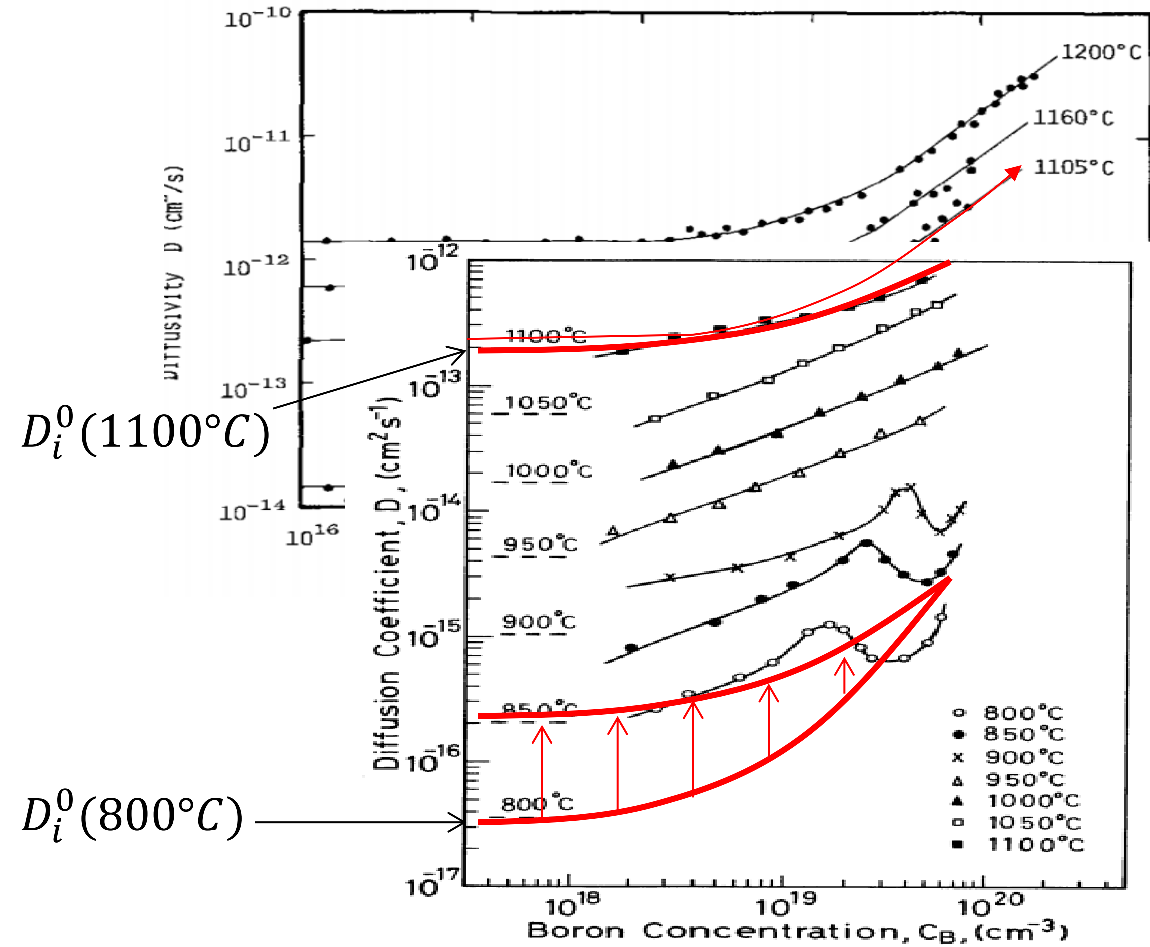
Fair, JECS (1977)

Boron diffusivity

Similar for boron,
but only linear charge
enhancement

$$D_B = D^0 + D^+$$
$$= D_i^0 + D_i^+\left(\frac{p}{n_i}\right)$$

$$p = \frac{1}{2}\left(c_B + \sqrt{c_B^2 + 4n_i^2}\right)$$



Matsumoto, JJAP (1983)

Modelling

Mathematica: 1D x-t model with method of lines:
discrete in x-direction,
continuous in time

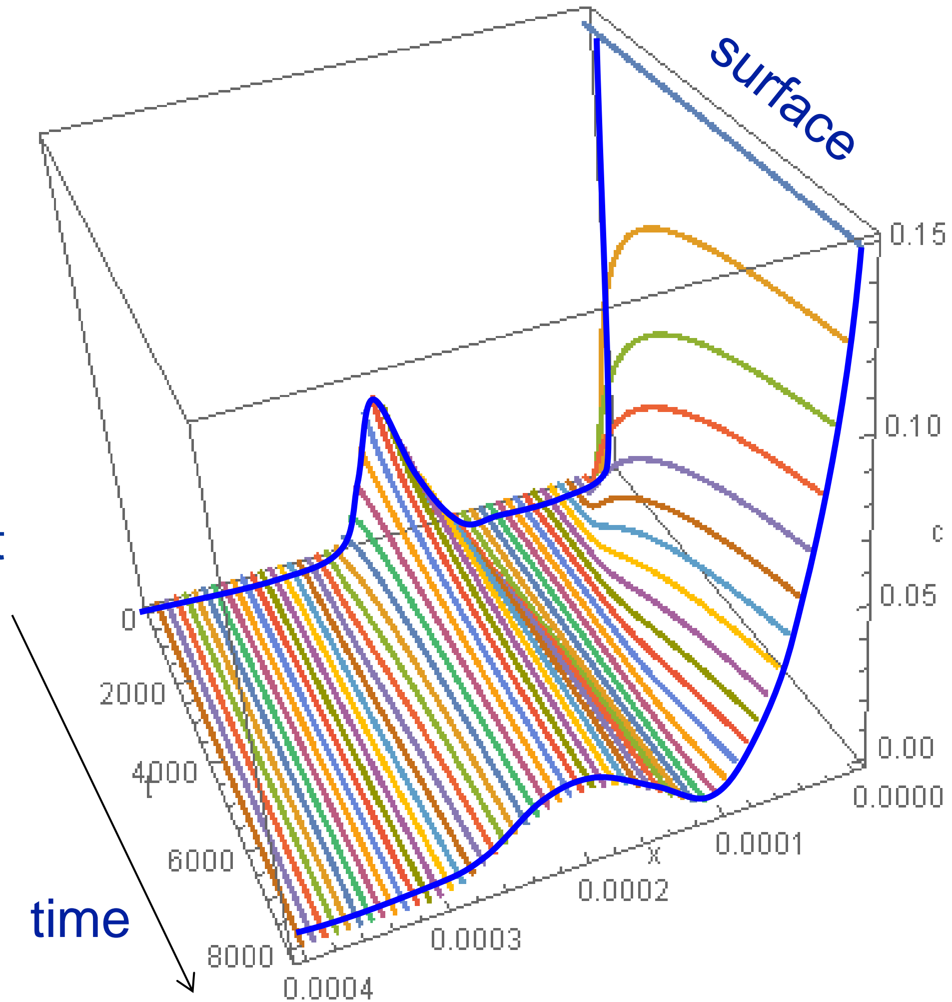
$$\frac{d}{dt}c = \frac{d}{dx}\left(hD(c)\cdot\frac{d}{dx}c\right)$$

$$\frac{dy}{dx} \approx \frac{\Delta y}{\Delta x}$$

Final addition: field enhancement h
=> drift term due to doping gradient

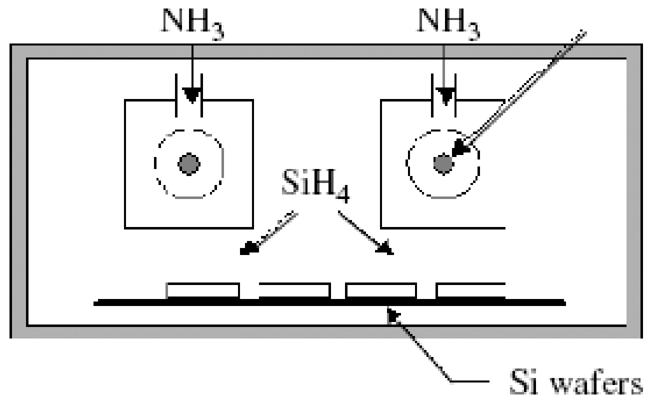
$$h = 1 + \frac{c_B}{2n_i} / \sqrt{\frac{c_B^2}{n_i^2} + 1}$$

Example: diffusion from surface
and broadening of Gaussian
implant at x=200 nm



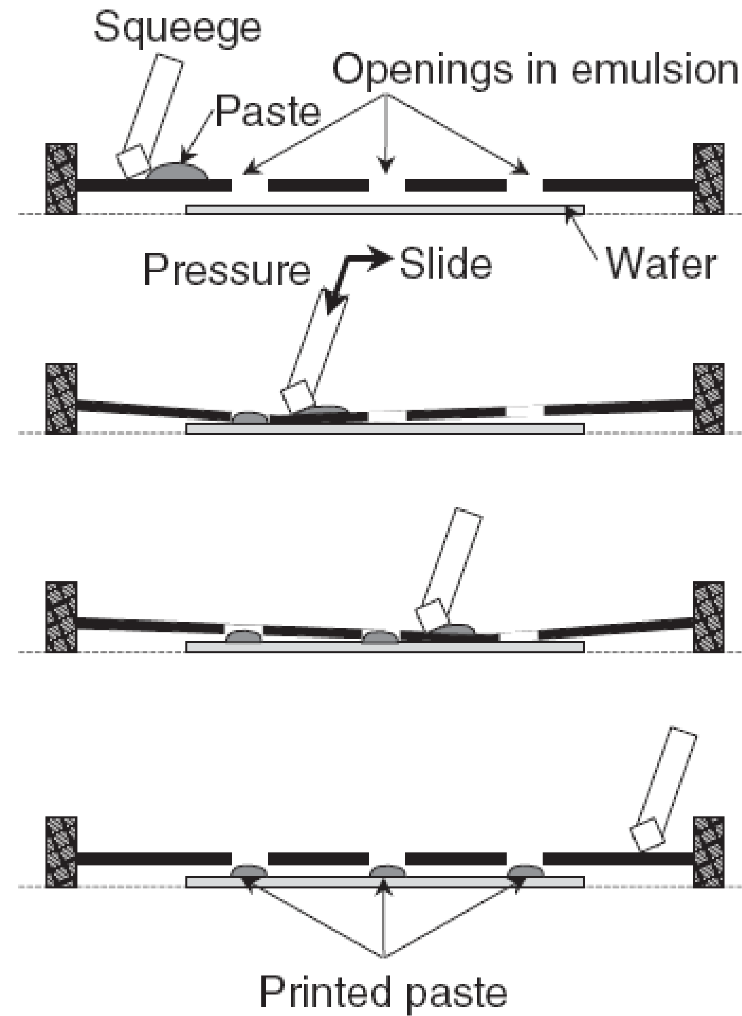
Next: Si_3N_4 front ARC by MW-PECVD

Plasma enhanced chemical vapour deposition (PE-CVD)
Microwave plasma in atmosphere of NH_3 and SiH_4

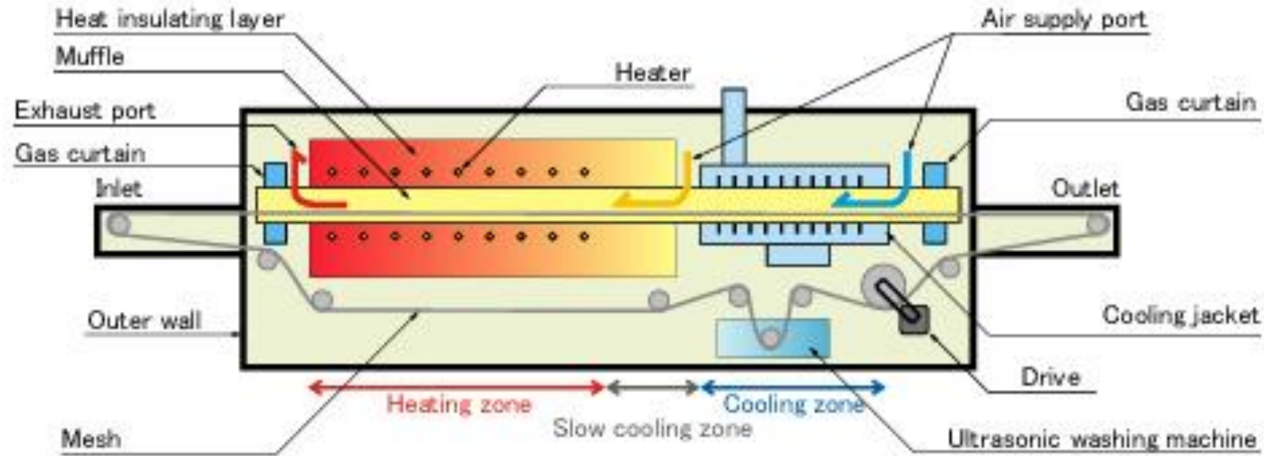


e.g. Meyer Burger AG (Roth&Rau)

Next: metallization by screen printing



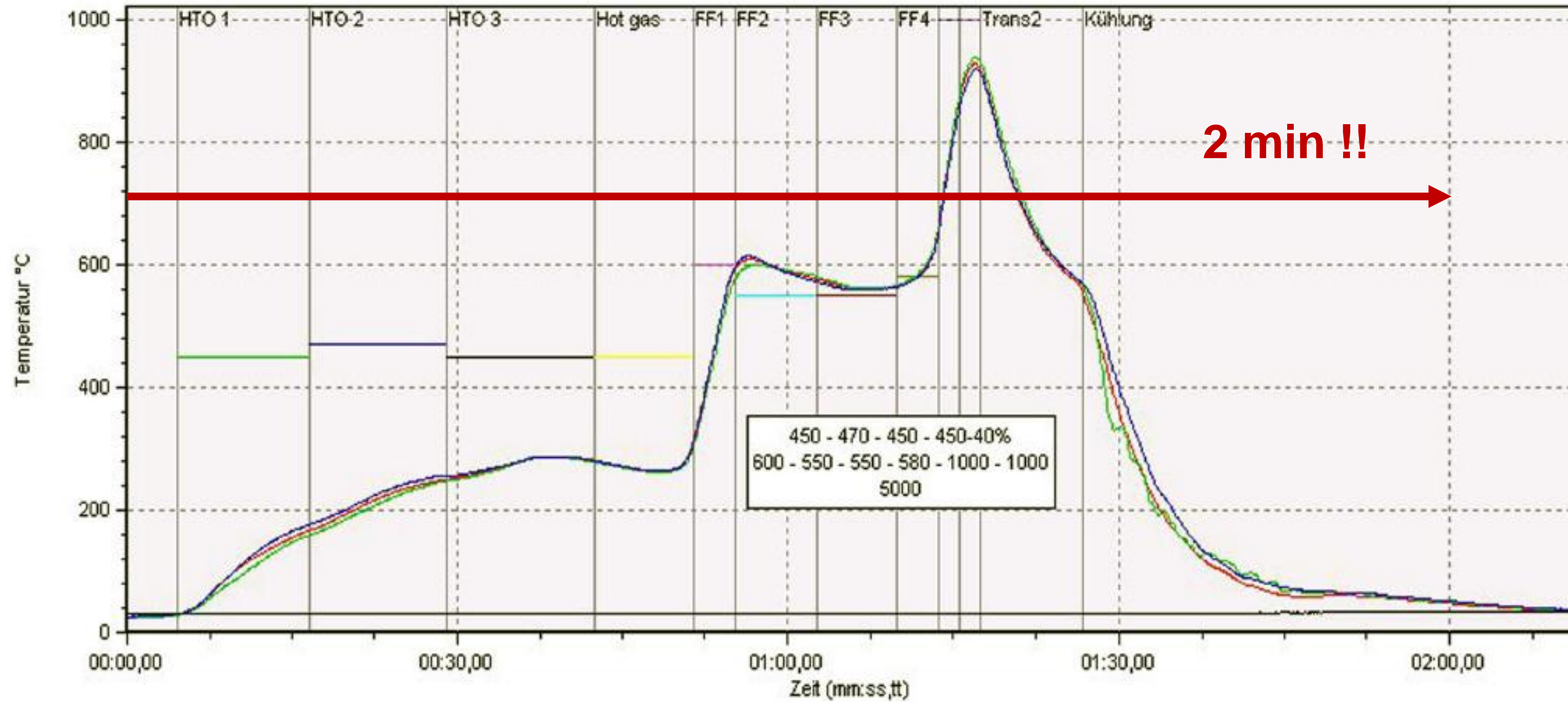
Finally: Contact firing



e.g. Noritake (JP)
e.g. LCI furnaces

Firing-through profile

Peak temperature at 870-900°C
Profile of T and thermal load important !



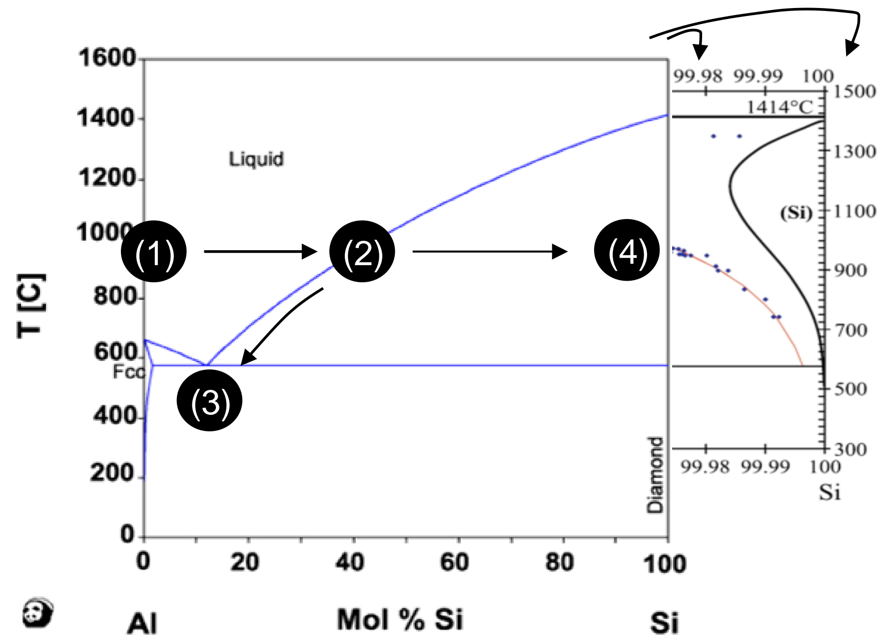
Real profile, measured by thermocouple bonded to a wafer

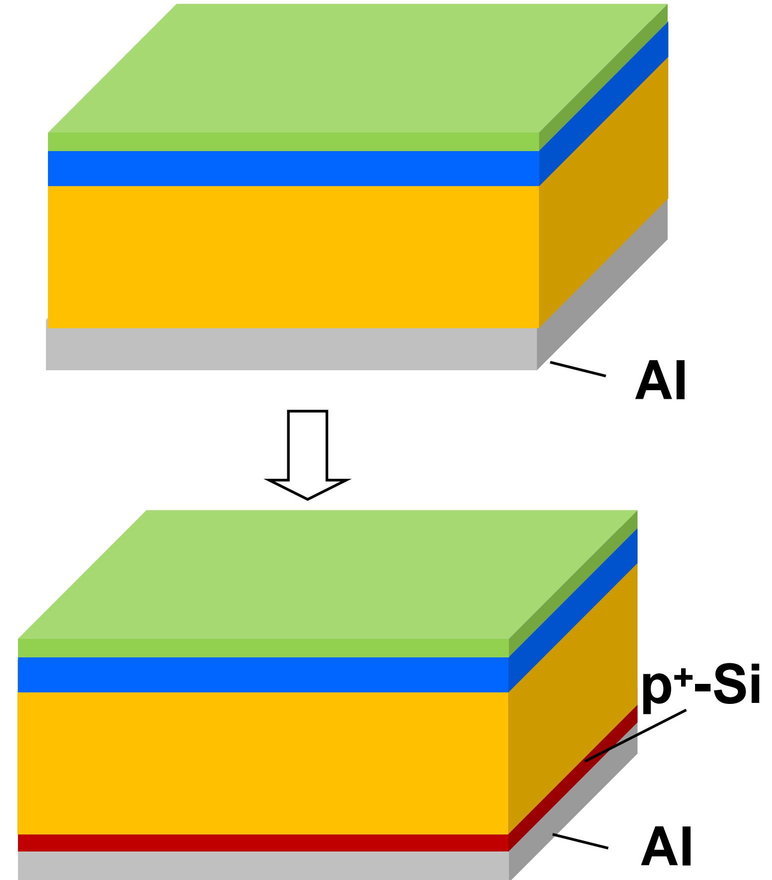
Formation of Al back-surface field (BSF)

1) Above 577°C: Al melts
2) Si dissolves in Al to form an eutectic liquid
3) Cooling: Si is expelled from melt ($c_{Si}>c_{sat}$)
4) epi re-growth of Si with $c_{sat,Al}$ Al dopants

=> Deep p+ doped regions (~10 micron)

=> $N_A=c_{sat,Al}\approx (0.015 \times 2.5\times10^{22} \approx 4\times10^{18})cm^{-3}$

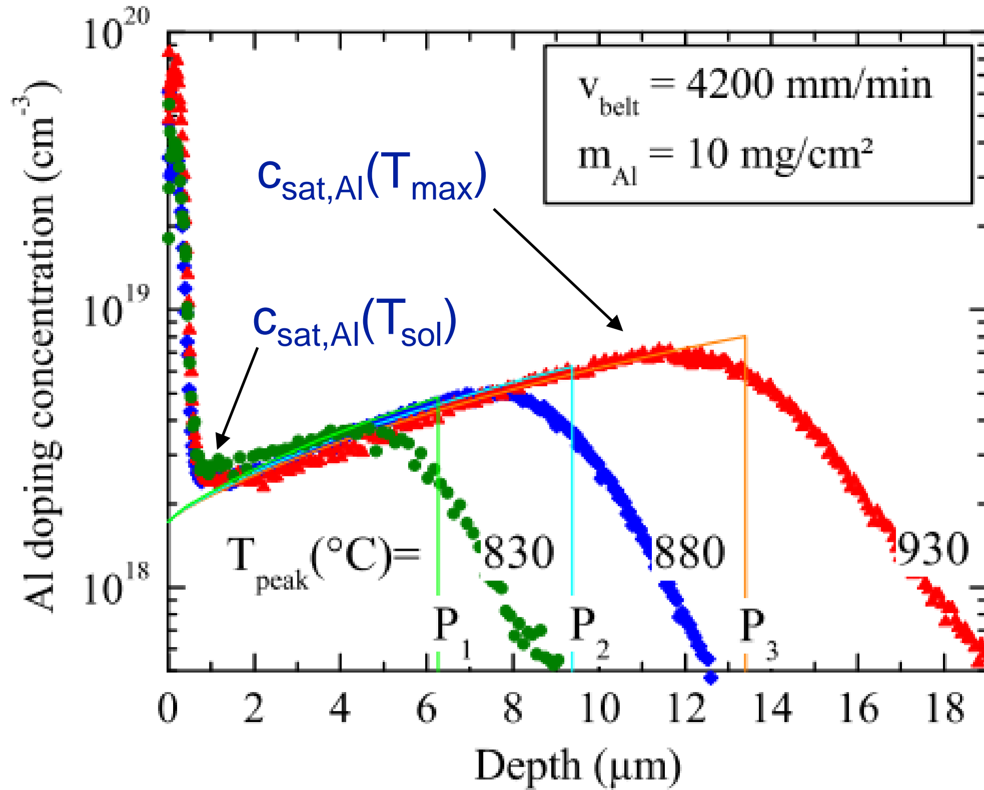




Del Alamo, SSE(1981)
Lauermann, PPV (2013)

Al-BSF

F.-J. Haug



Retrograde depth profile:

Highest concentration deep in bulk (where re-growth from liquid/solid interface started at highest T)

during cooling:

- solidification towards rear surface
- reducing $c_{sat,Al}$

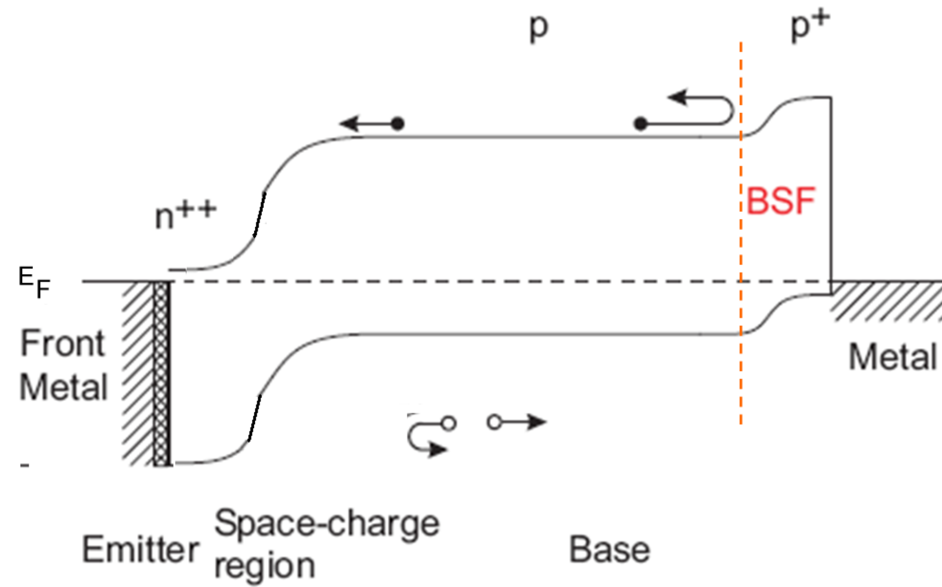
Lowest concentration at surface

$N_A = c_{sat,Al} \approx 3\ldots6 \times 10^{18}$ cm^{-3}

Krause, SEM (2011)

Back-surface field

F.-J. Haug



Layman's explanation: electrons (minority carriers in p-bulk) get "reflected" by the field

On the true role of the highly doped region:
«The doped region mostly gives a **reduction** of minority carriers (and hence of recombination)»

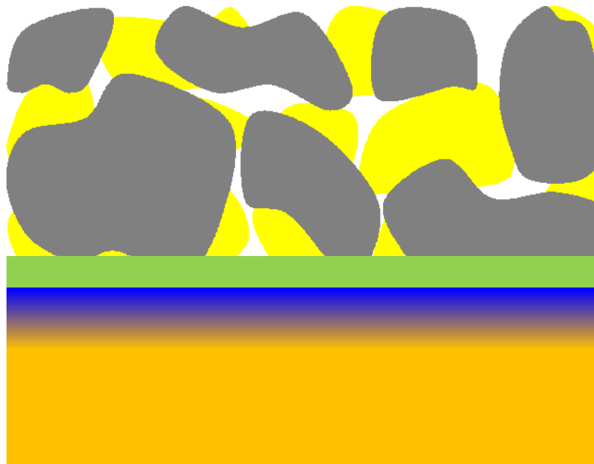
Cuevas, JPV (2013)

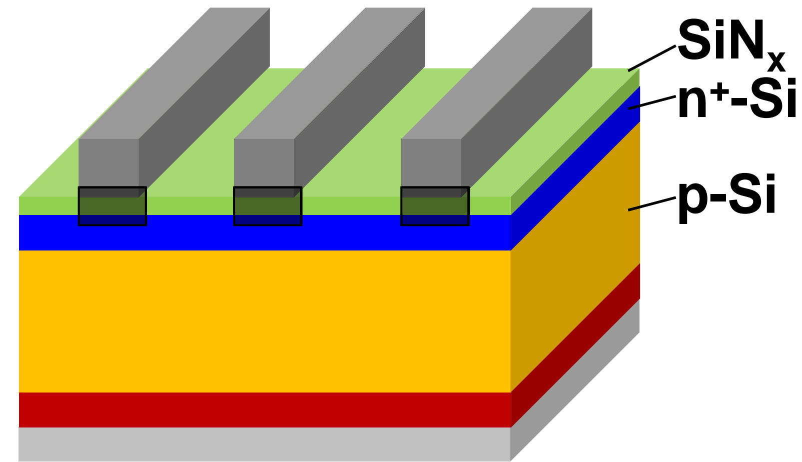
How does Ag contact n^+ Si through the SiN_x?

F.-J. Haug

Paste:

- Ag powder (1-10 µm, flakes and grains)
- Glass frit (GF) (lead borosilicate)
- Organic materials → control rheology





HOW?

Cross-section [110], typical TEM* view

*TEM imaging by Dr. Aicha Wyser-Hessler at CIME EPFL

Ag Matrix

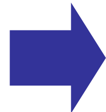
Glass Frit (GF)

Ag

Ag

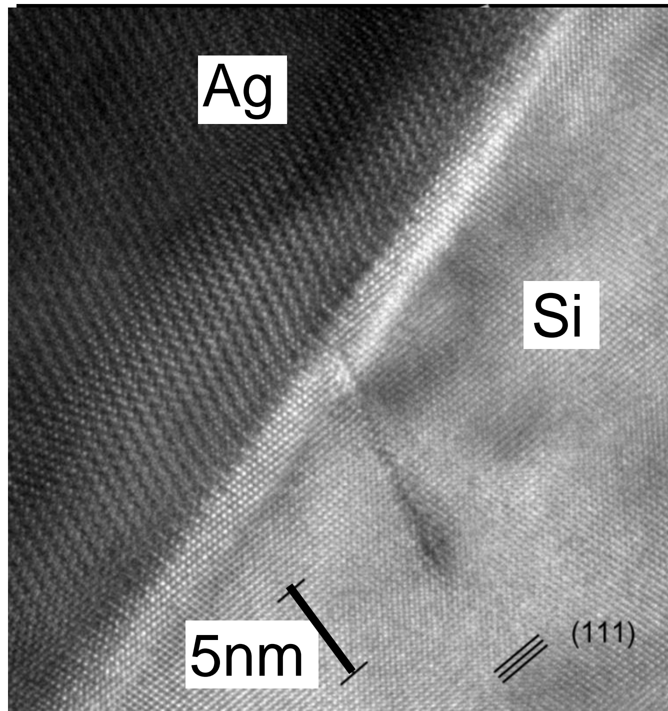
P2 P3 GF Ag Si

Silicon



- Ag crystallites present at interface
- Same [110] orientation as Si
- Separated from Ag matrix by glass frit

High-resolution TEM



HR TEM image

Ag crystallite properties

- Size 100 - 500 nm
- Depth ~ 100 nm in Si
- {111} faces in Si

HR-TEM Ag/Si interface

- No amorphous phase
- No oxide (HR-EDS)

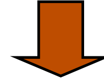
- local epitaxial growth of Ag in Si
- perfect metal-semiconductor Interface

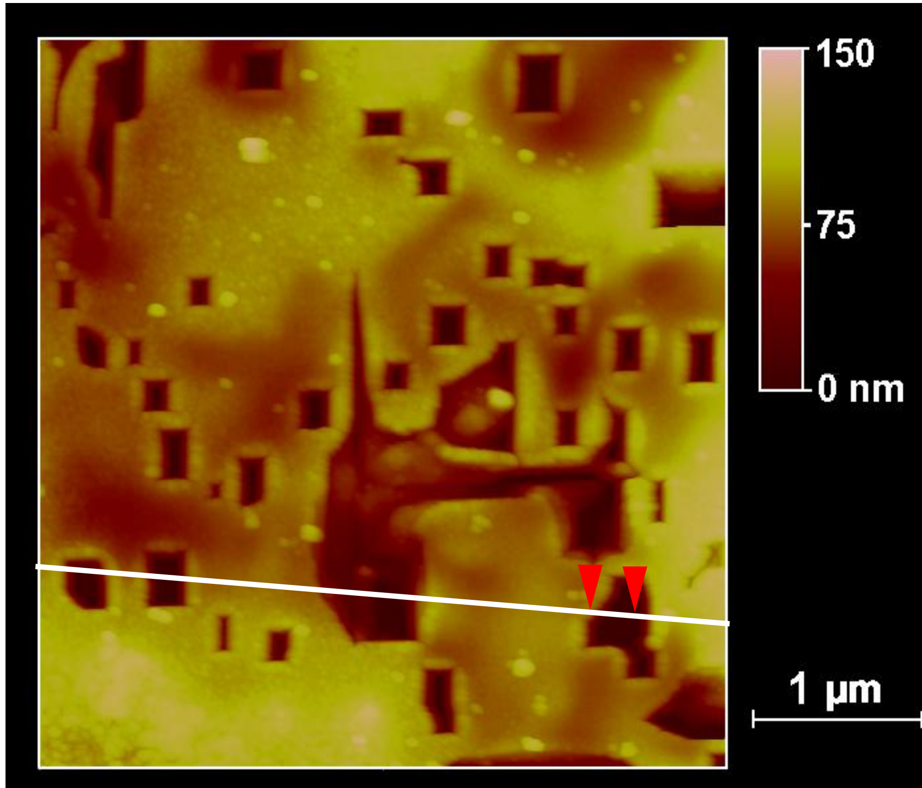
EPFL

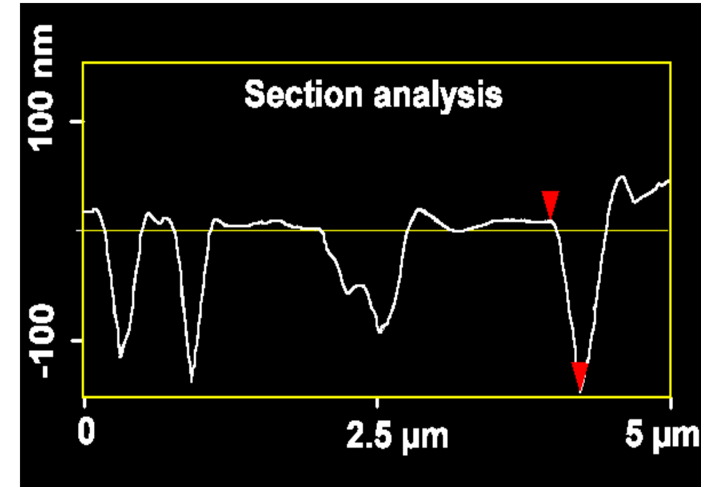
AFM of surface after etching

F.-J. Haug

Cycle HNO_3/HF to remove Ag (HNO_3) and glass frit (SiO_2)







- ~100 nm dips
- Confirms TEM analyses

Model for contact formation

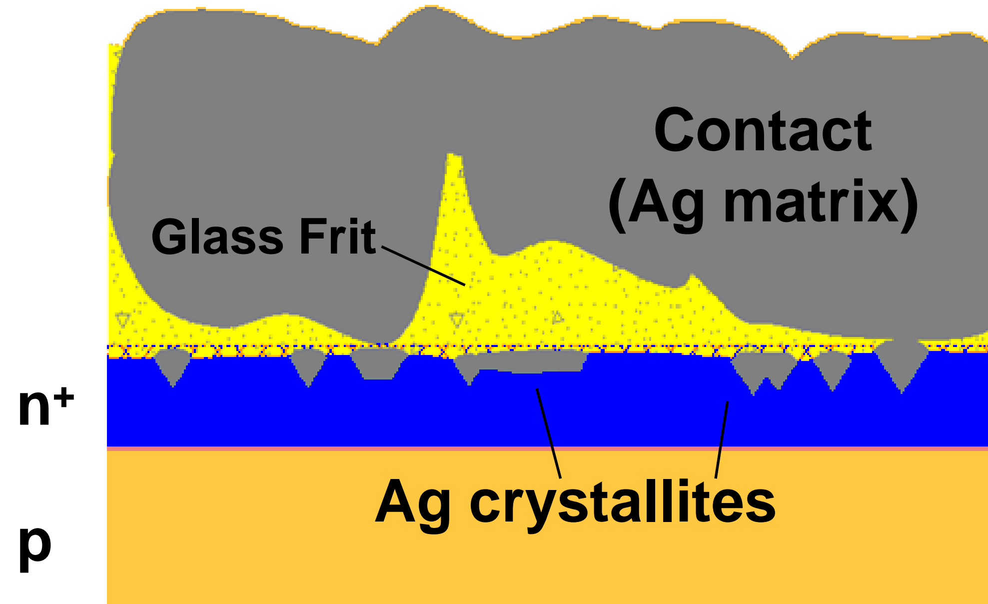
F.-J. Haug

Heating

- Sintering of Ag powder
- Glass frits becomes liquid and wets SiN
- Etching of SiN and Si, Si and Ag dissolved in GF

Cooling

- Excess Si:
  → epitaxial regrowth on Si
  Excess Ag:
  → nucleation w. orientation of Si, growth towards surface
- Process stops with intermediate glass frit layer



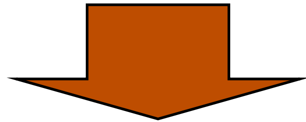
*n.b.: alternatively, etching of pyramids into the wafer was proposed

Electrical properties

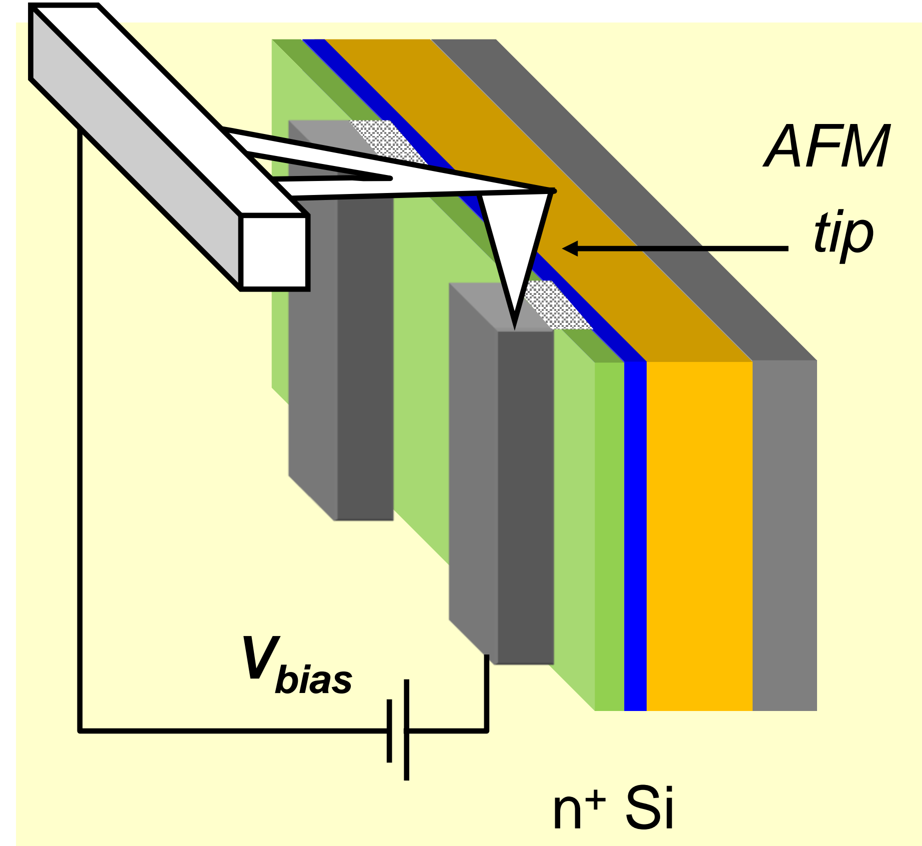
F.-J. Haug

Insulating glass frit layer

- where does current flow ?
- how to determine contact resistance ?

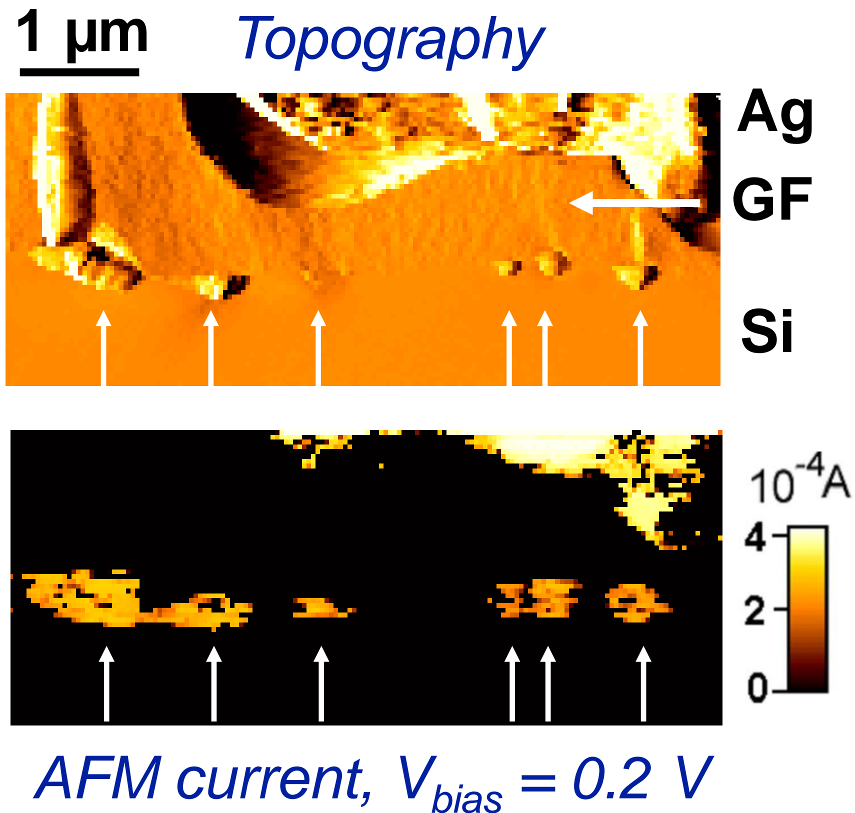


Conductive AFM on cross-sections of contact



Conductive AFM on cross-sections of contact

F.-J. Haug



AFM current, $V_{bias} = 0.2$ V

On Ag crystallites

→ $I = 0.3$ mA

→ $R_{contact} = 700$ Ohm

→ $R_c < 10^{-7}$ Ohm cm²

<< 10^{-3} Ohm cm²

(observed macro)

- High Si doping near Ag
- Only 1/10’000 of Si surface used for contacts

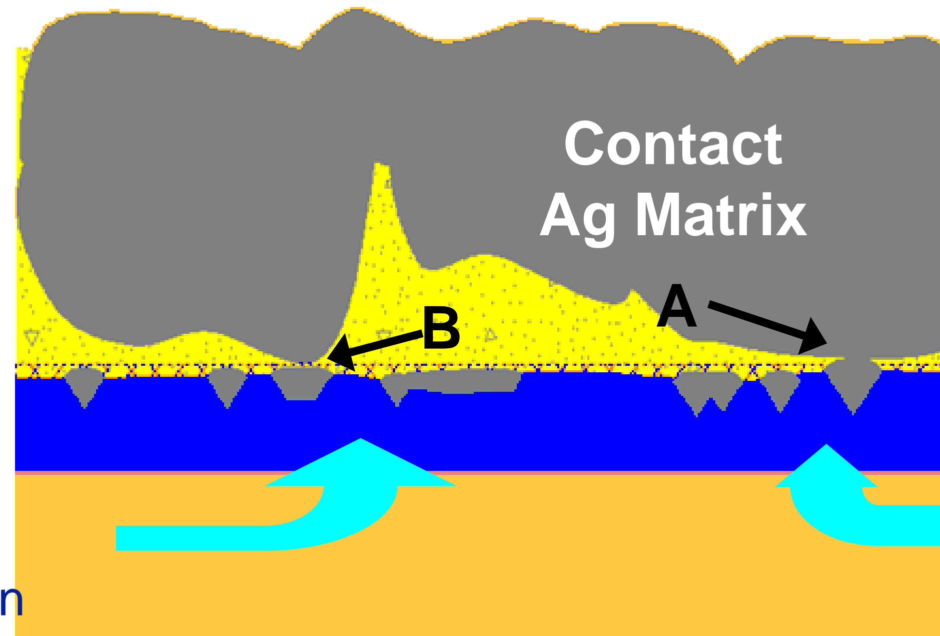
Model for current flow

F.-J. Haug

Glass frit

- No Ag or Pb precipitates
  → isolating

  - Only a few crystallites contribute to current flow



A: direct connections

B: tunnel effect through ultra-thin glass frit

→ High doping necessary ↔low « active » surface for contact
Deep junction ↔ Ag crystallites and impurity diffusion

→ Alternative/refined models in literature

Front contact between Ag paste and n^+-region

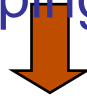
Rule of thumb: series resistance negligible in FF if $\rho_c < 0.1\ \Omega\ \text{cm}^2$

Front grid less than 10% coverage

=> needs contact resistance $\rho_c < 10\ \text{m}\Omega\ \text{cm}^2$

Additional requirements:

- deep junction (avoid shunting by Ag crystallites)
- high n+ doping required (low contact resistance, low sheet resistance)



Drawback: recombination losses by Auger effect

=> find best trade-off

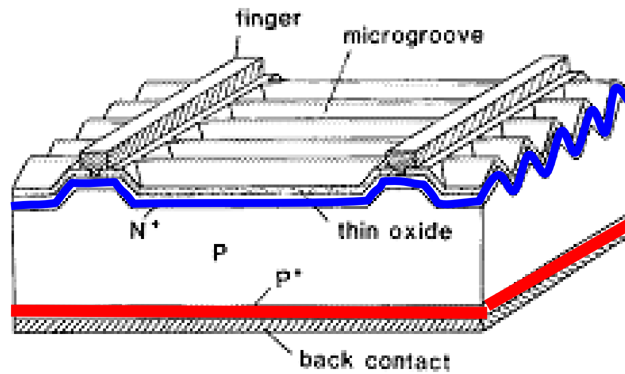
Ballif et al., Appl. Phys. Lett. 82, 1878 (2003)

Cell generations (UNSW)

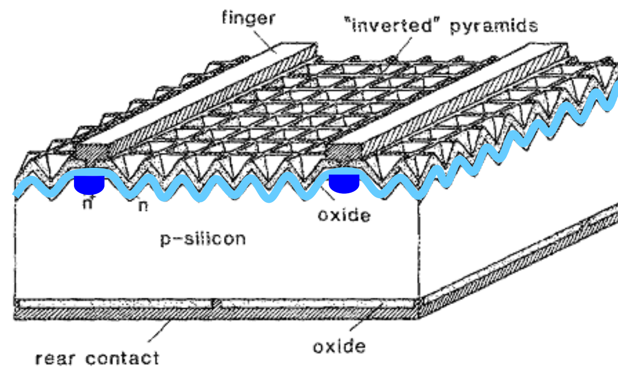
PESC (Passivated Emitter Solar Cell):
Voc = 670 mV
jsc=38.3 mA/cm^2
eff=20%

PERC (Passivated Emitter and Rear):
Voc = 696 mV
jsc=40.3 mA/cm^2
eff=22.8%

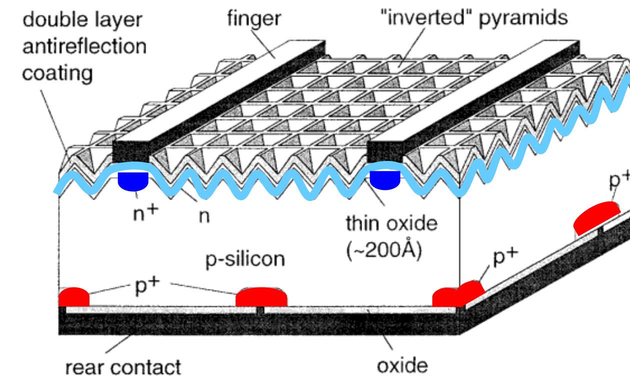
PERL (Passivated Emitter, Rear Locally diffused):
Voc = 706 mV
jsc=42.9 mA/cm^2
eff=24.2 - 24.7%
(25% after AM1.5 update)



Blakers, APL (1986)



Blakers, APL (1989)



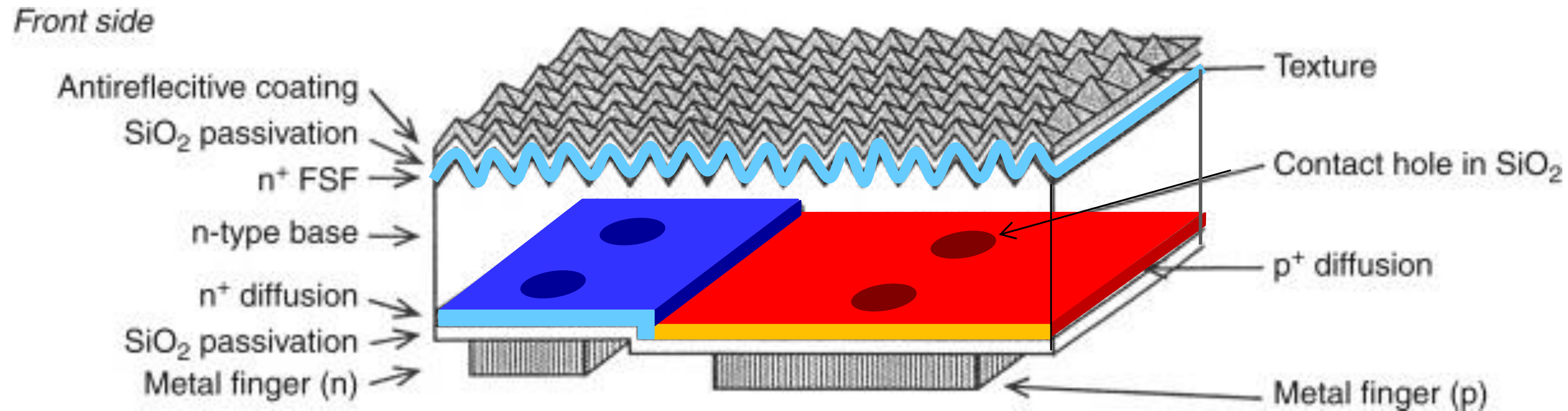
Wang, APL (1990)
Zhao, PPV (1999)

“First we fixed the front, then we fixed the back” (M. A. Green)

IBC design with improved optics (U Stanford)

IBC (Interdigitated Back contact): Avoid shadowing by front contacts

Early commercialized by SunPower with diffused junctions



Mulligan, EU-PVSEC (2004)

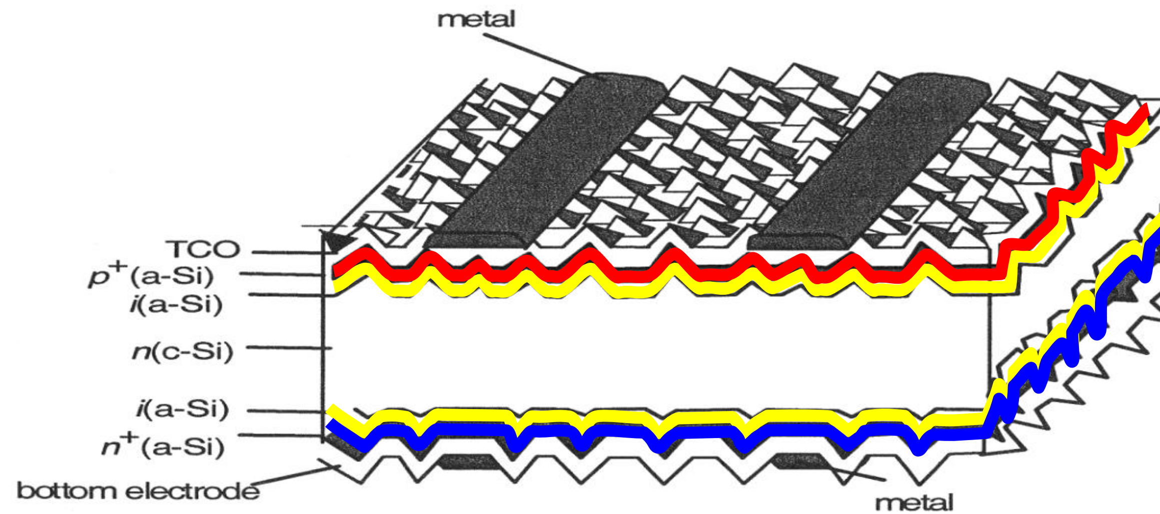
Cells with full surface passivation (Sanyo/Panasonic)

F.-J. Haug

HIT (Heterojunction w. Interlayer Technology):

First demonstrated in 1992
a-Si provides excellent passivation => highest Voc (up to 750 mV)

=> also used by Longi (current world record, 27.8%)



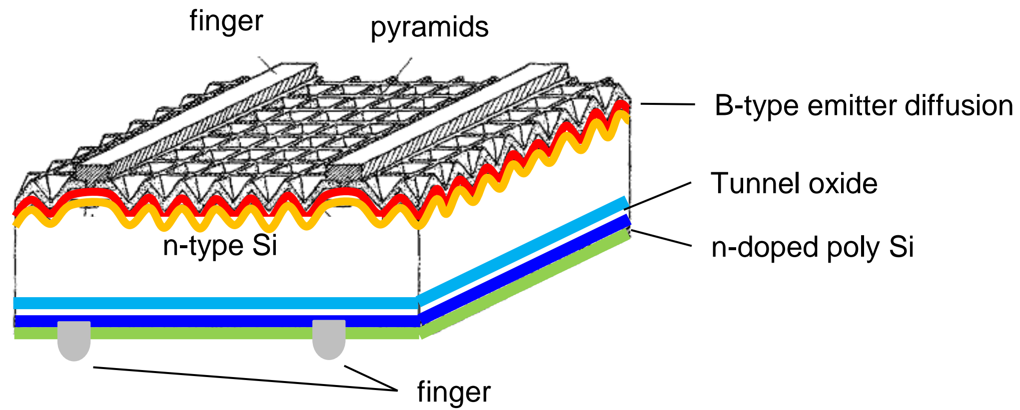
Tanaka, JJAP (1992)
Taguchi, JPV (2014)

PV-lab IEM NEUCHATEL

TOPCon cells

Tunnel oxide passivating contact
First published in 2008-2013 (Fraunhofer ISE)

Wafer type switched to n-type, use B-doped front emitter
SiO_2 provides excellent rear passivation, must be ultra-thin for tunnel transport



Most steps compatible with established PERC manufacturing

Borden, EU-PVSEC (2008)
Feldmann, SolMat (2014)

Summary

- Silicon is an abundant material
- Of all semiconductors, Si is probably best studied
- Silicon comes in many forms and shapes
- Si can rely on mature technology
- PV is business (and has no mercy)