

Modern PV-Technologies

3.2: c-Si solar cell cells

F.-J. Haug

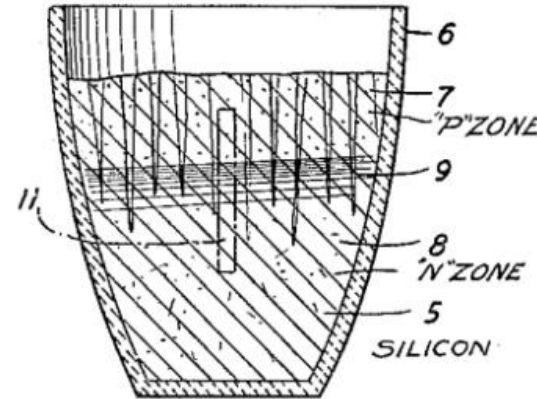
Ecole Polytechnique Fédérale de Lausanne
PV-Lab

The early days of c-Si solar cells

Ohl (1941)

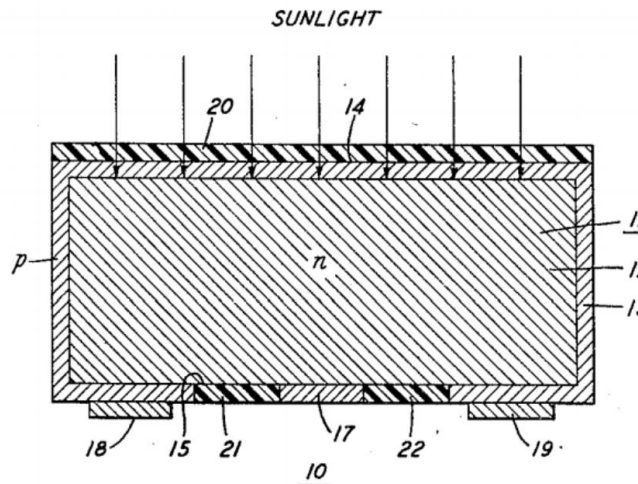


FIG. 1



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

Pearson, Chapin, Fuller (1952)



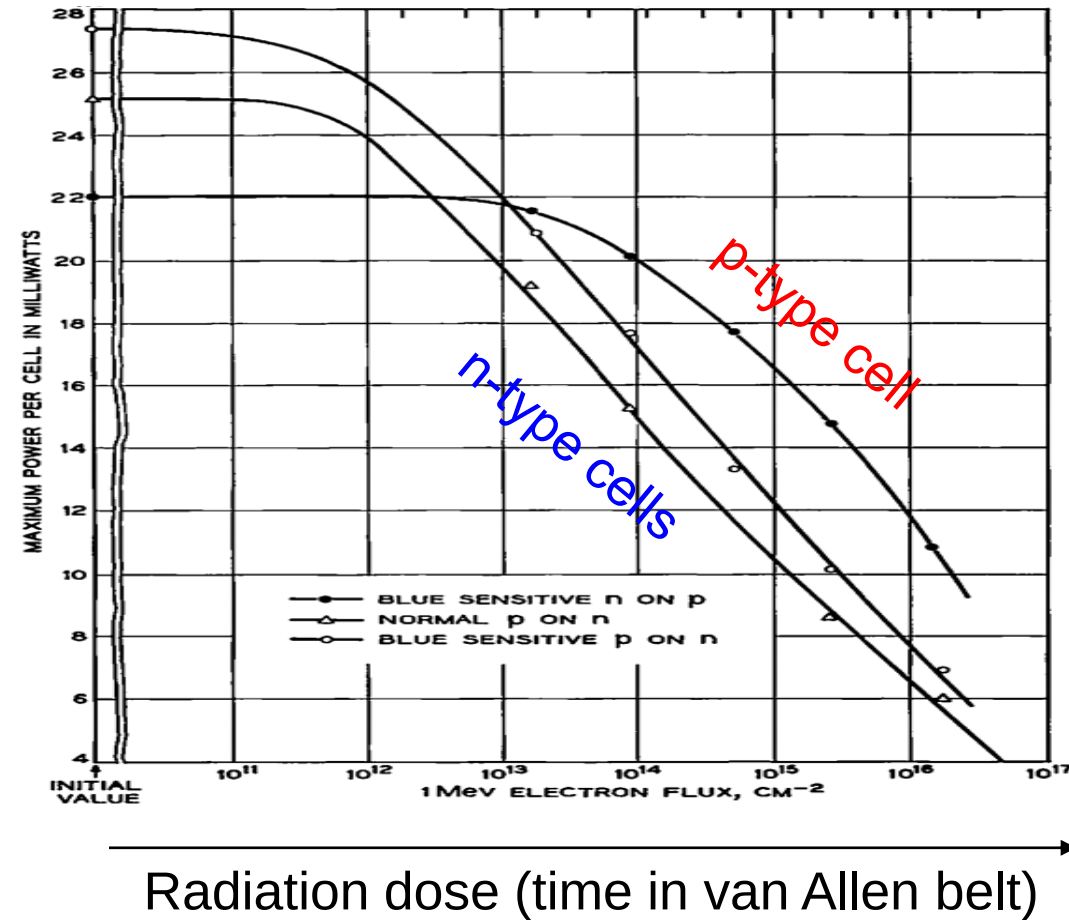
n-wafer
p-diffusion
rear etch
Rh rear contact configuration
Efficiency: approximately 6%

EPFL c-Si cells for space

Telstar I & II



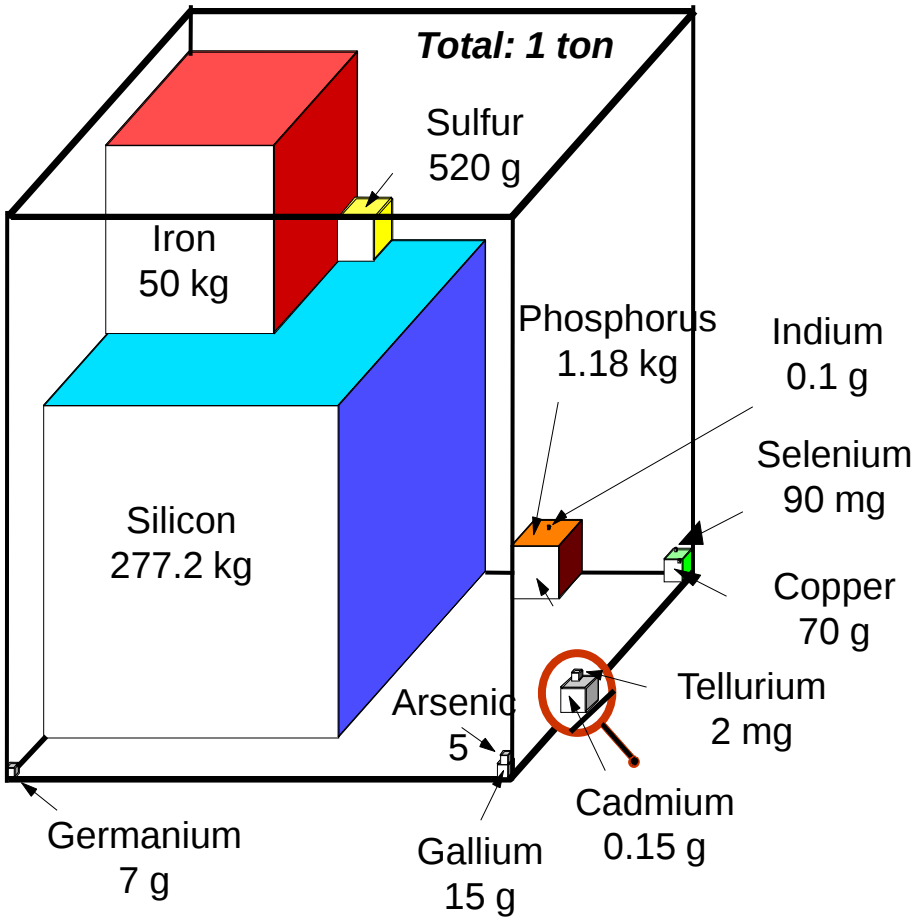
first trans-Atlantic satellite communication



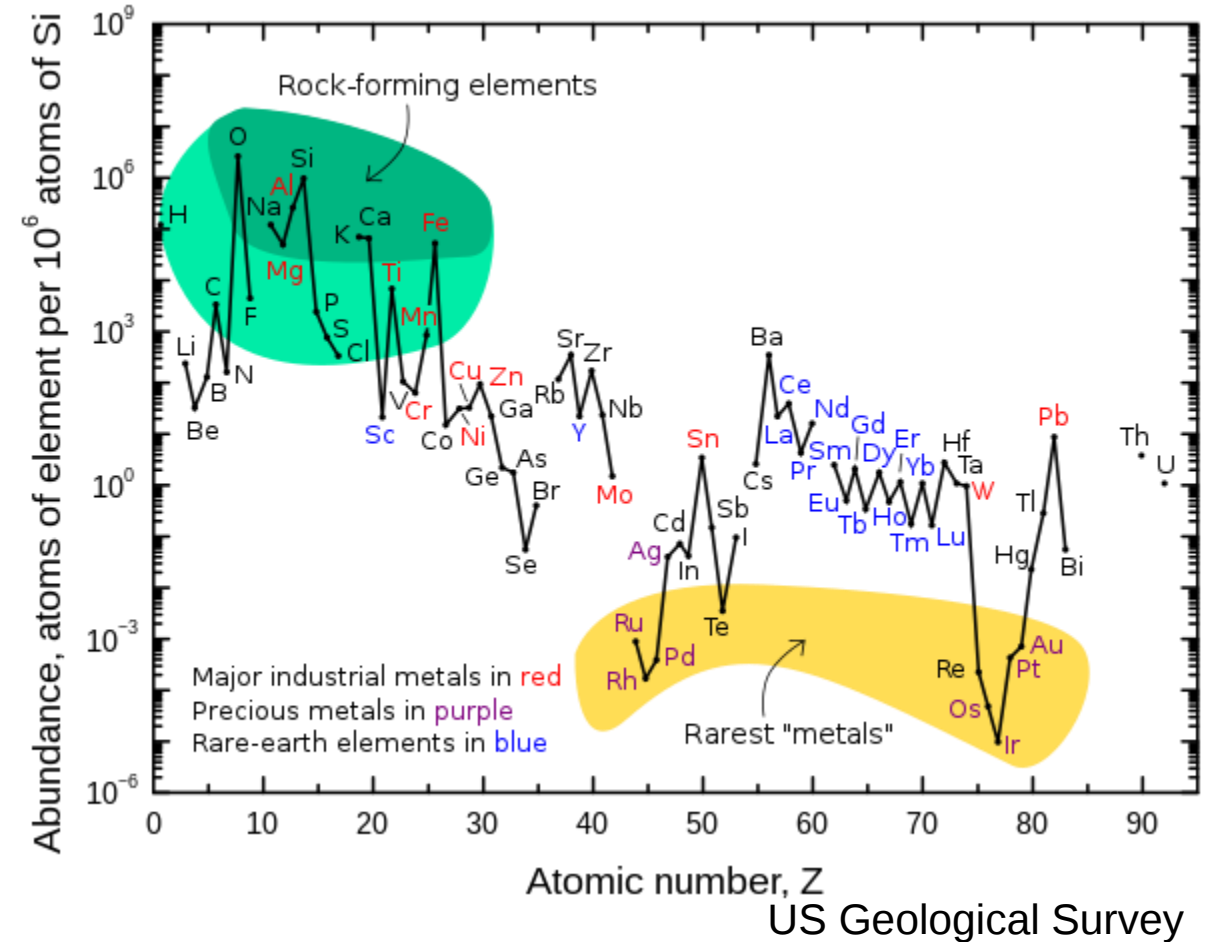
Radiation dose (time in van Allen belt)

Rosenzweig, BST (1962)

EPFL Why silicon?

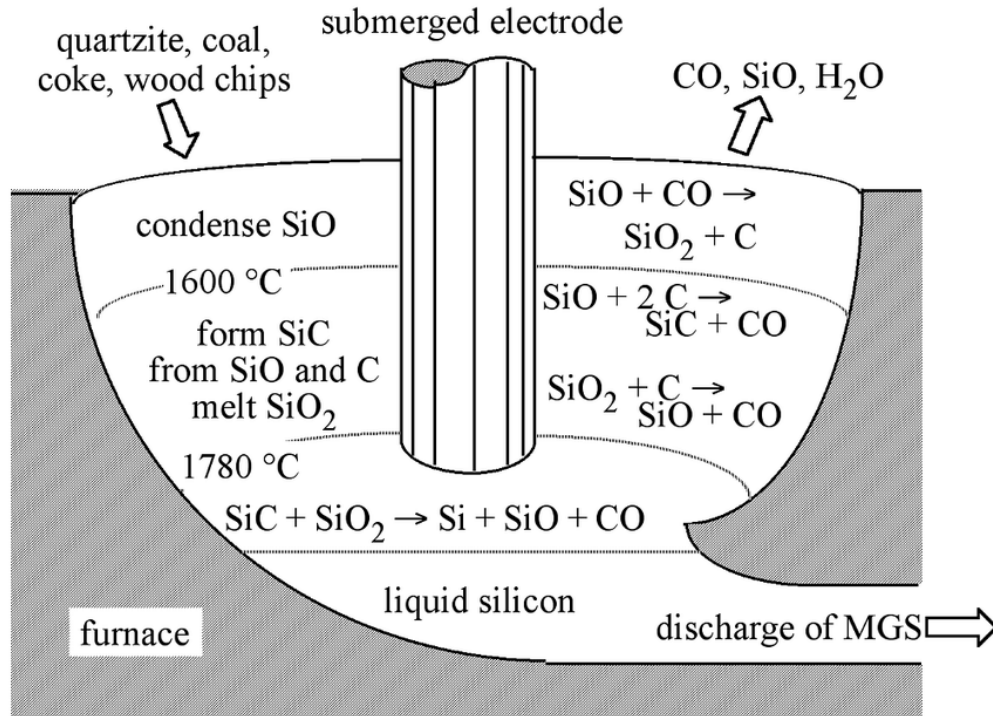


Availability of various materials in 1 ton of earth crust



Silicon: benign and abundant resource, well understood material

How to make Si (metallurgical grade, MG)

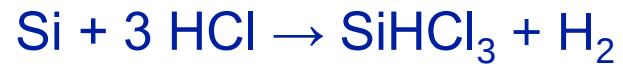


CNBM International

Overall reaction $\text{SiO}_2 + \text{C} \rightarrow \text{Si} + \text{CO}_2$ (1 kg Si: 34 mol $\Rightarrow$ 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)

EPFL Purification of Si

Reaction to Tri-Chloro-Silane (TCS) :



Purification by fraction distillation

Impurity level < ppb



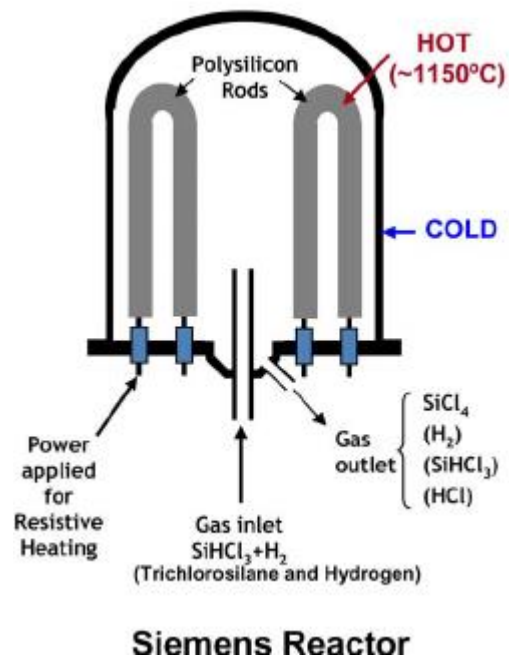
Solidification of pure Si

Siemens process:

React MG Si to SiHCl_3 (TCS)

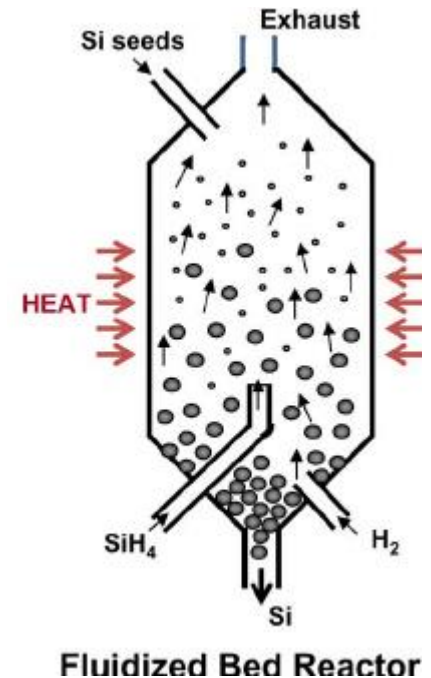
Purify by fractional distillation

React back to poly-Si



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

Alternative: FBR



so far: marginal

Single crystal growth (Czochralski method)

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:

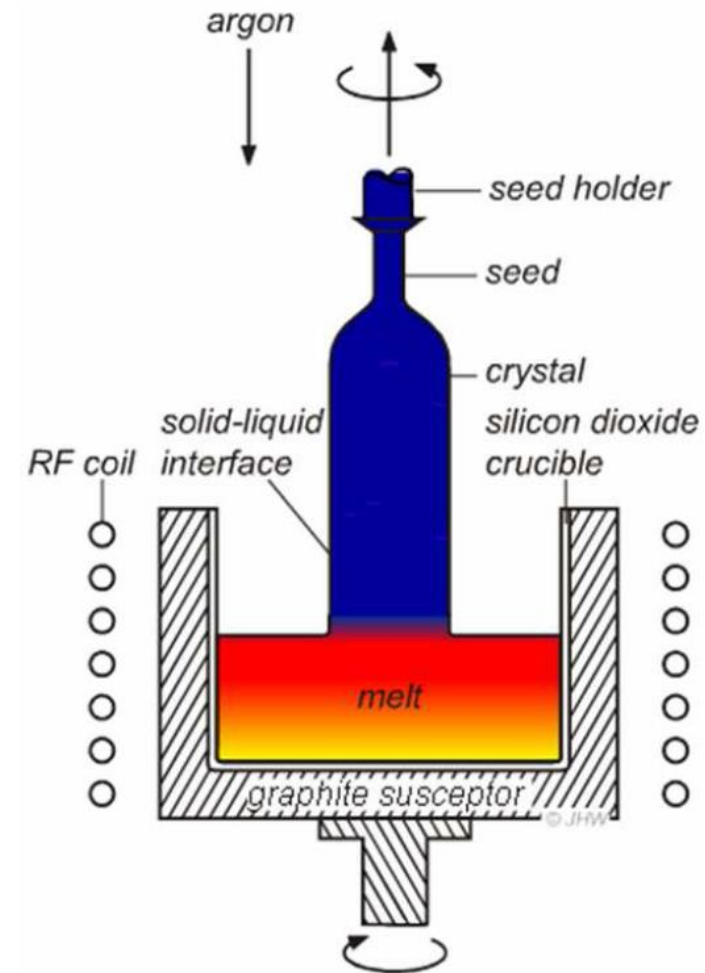
- O ($>10^{18} \text{ cm}^{-3}$, from atmosphere)
- C ($>10^{18} \text{ cm}^{-3}$, from crucible)

Generally acceptable for solar cells,

Main issue: B-O complex

=> flood with inert gas (Ar), replace B by Ga

=> use P-doped n-Si (TOPCon)

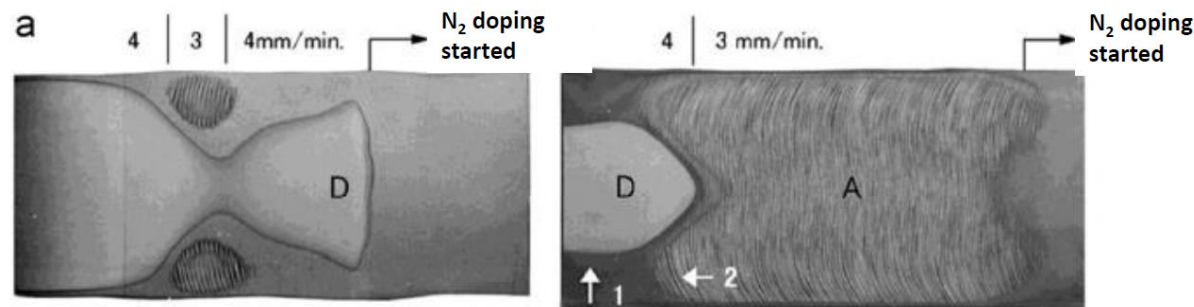


Single crystal growth (float zone method)

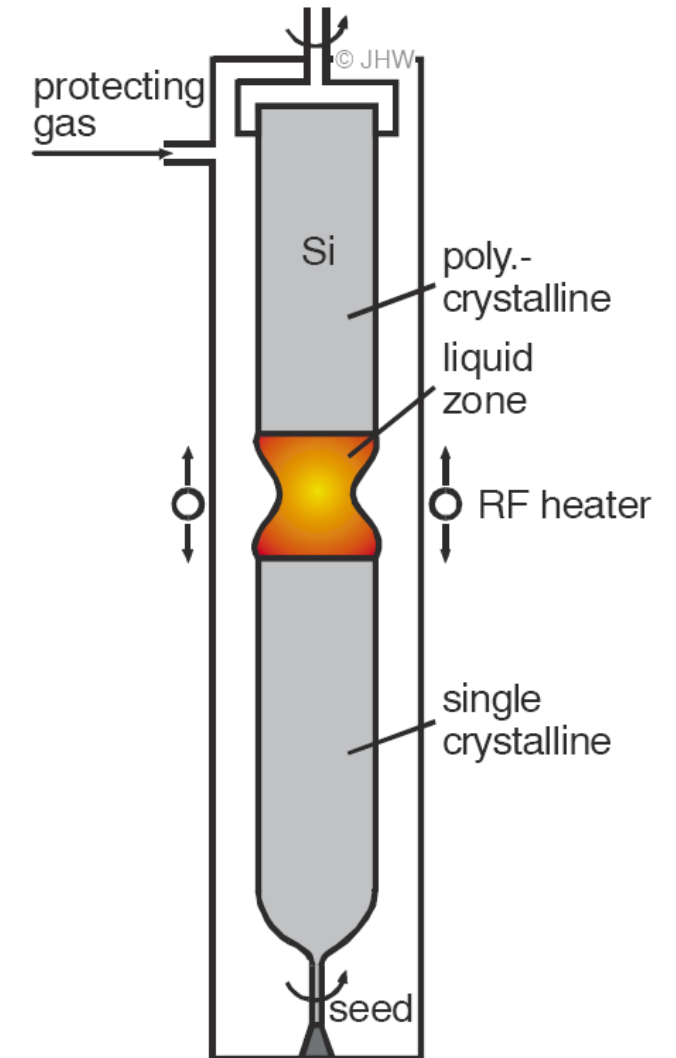
Pull RF coil along polycrystalline rod within quartz tube
Accumulate impurities by segregation in melt

Add desired dopants (B or P)

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



Limited by surface tension (dia. ca. 150 mm)



Abe et al. J. Cryst Growth 2011

Cast silicon (multicrystalline)

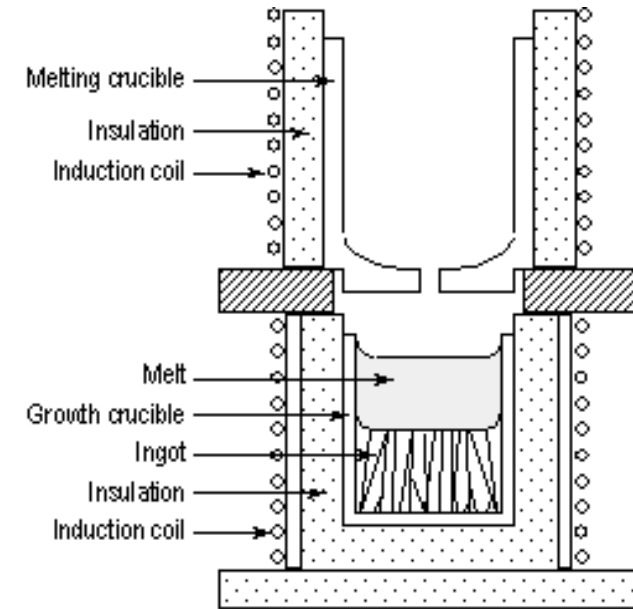
Casting into graphite or quartz molds

Molds possibly coated with Si_3N_4

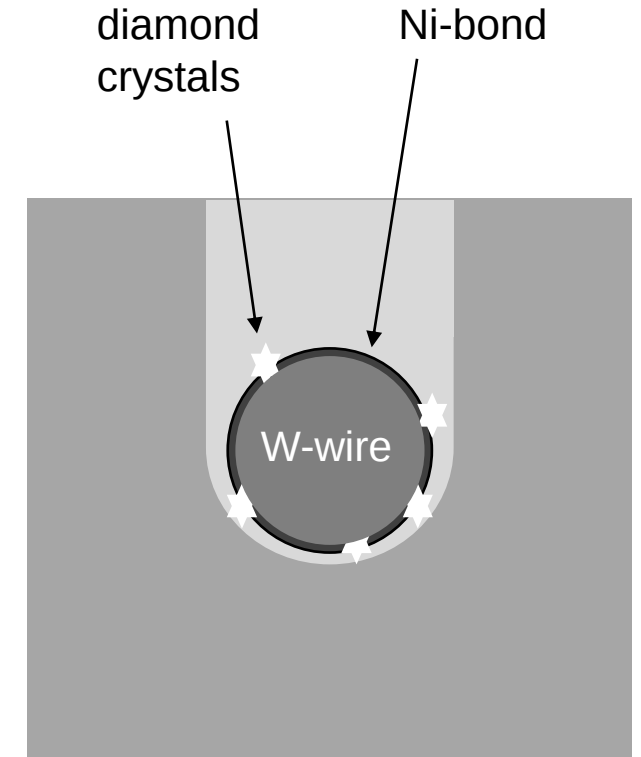
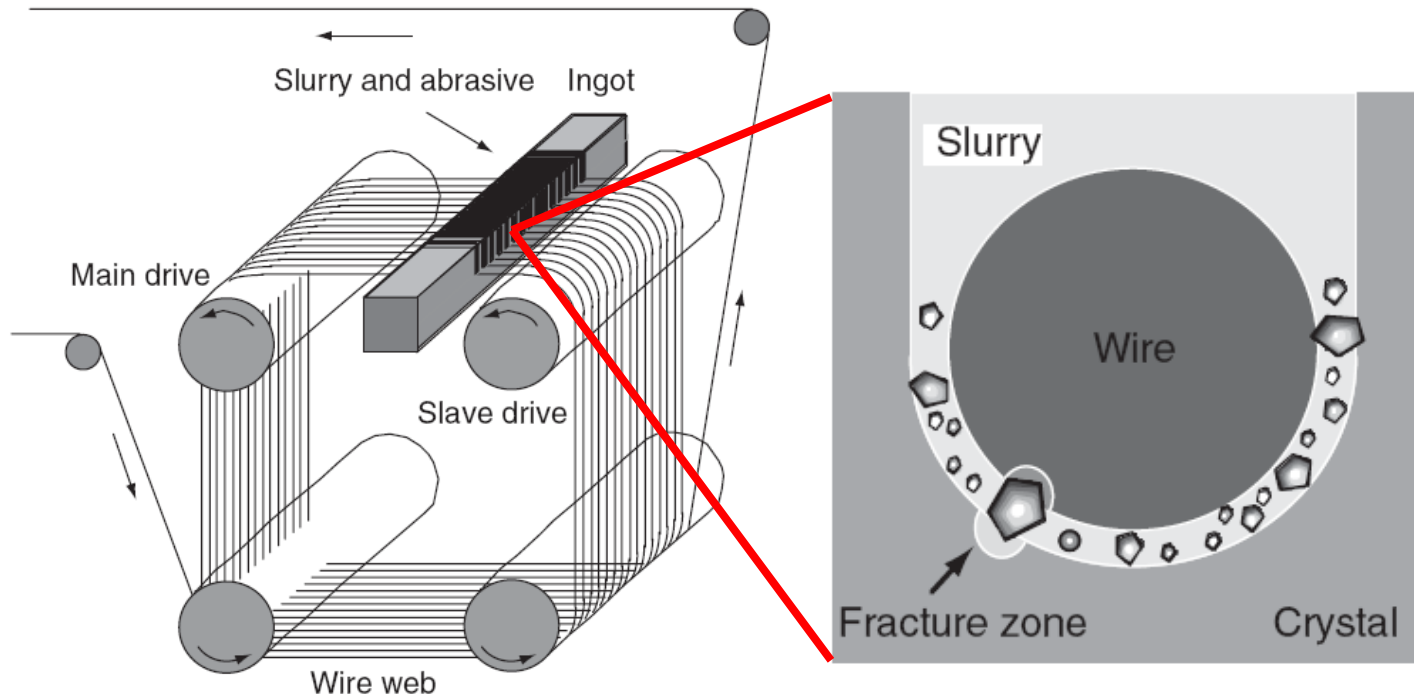
Place wafers at bottom and sides
for nucleation of “enhanced mc-Si”

typically 690 mm x 690 mm, 240 kg

Solidification takes ca. 30 to 60 h



EPFL Wafer sawing



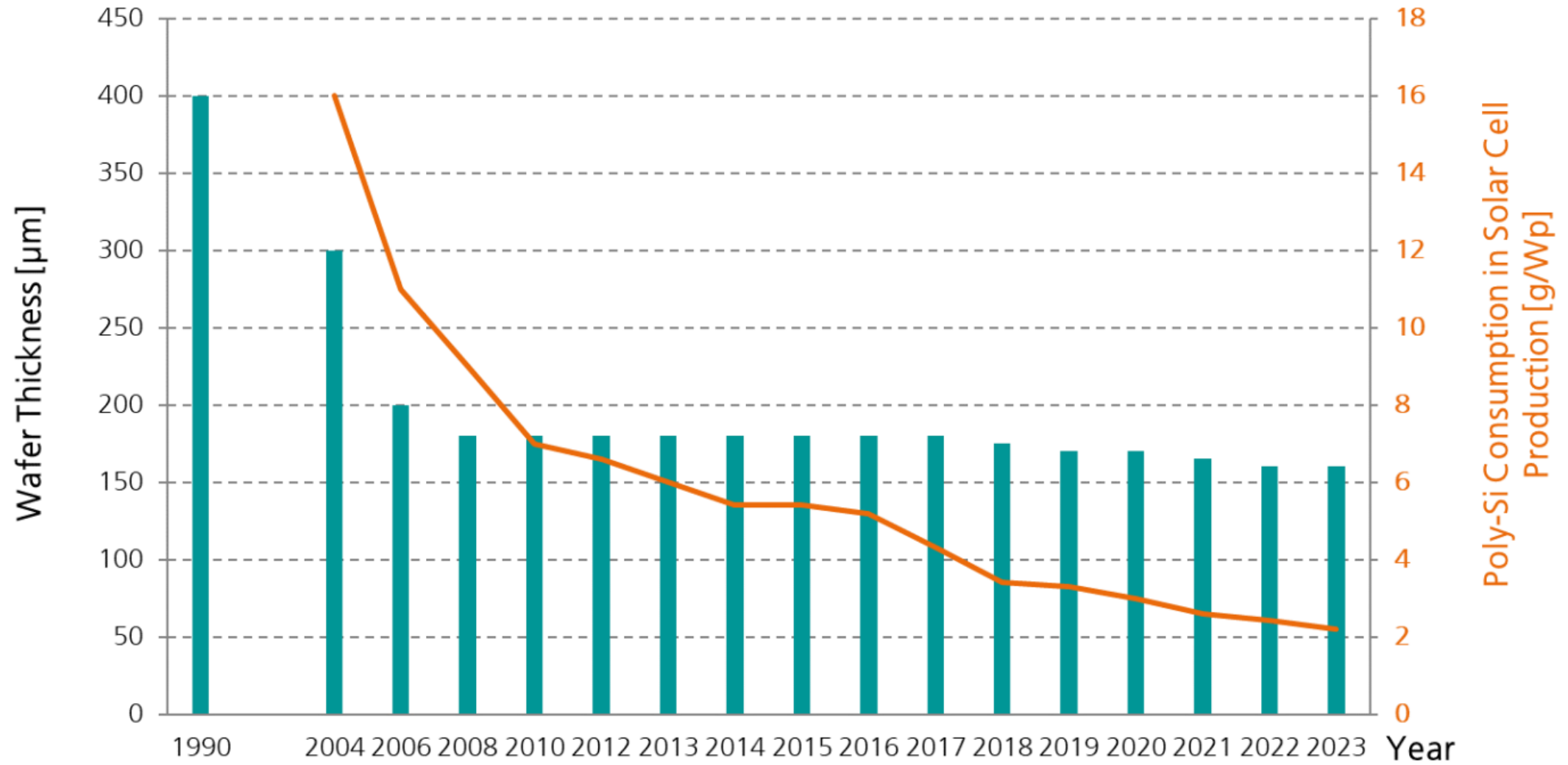
Originally: cutting with wire and SiC slurry

- rolling movement of SiC particles
- fracture by impact
- removal with half of wire speed

New standard: diamond-bonded wire

- scratching abrasion
- no fractures
- faster, less kerf-loss, easier recycling

EPFL Wafer thickness



Photovoltaics report 2024,
Fraunhofer ISE

FZ-Si:

- highest efficiencies, usually n-type
- record cells > 25%,

Cz-Si:

- high efficiency volume production, both types
- high quality products >20%

mc-Si:

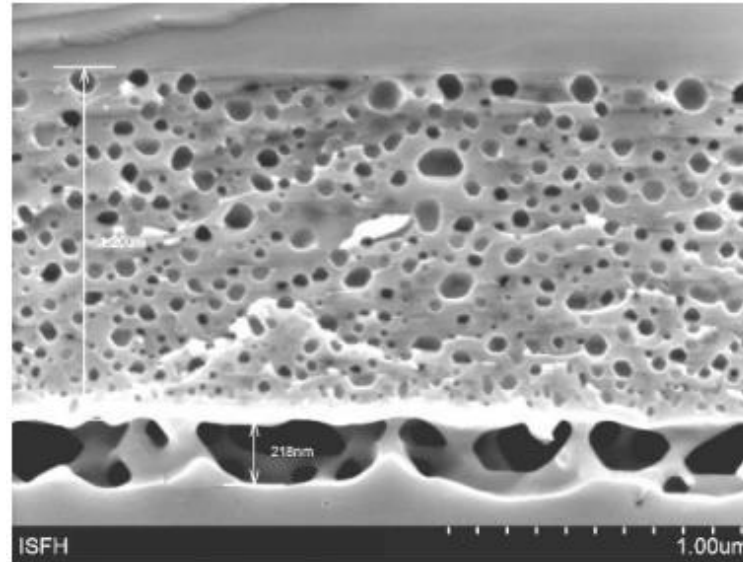
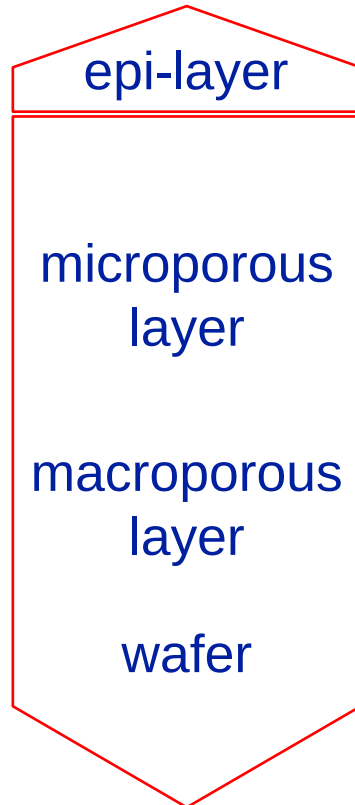
- phasing out from production (~10% of market in 2021), usually p-type
- low cost cells, ca. 17-19%, records up to 22%

Other types of c-Si

- Wafer pulling from melt
ribbon, cylinder, octagon, etc.
Edge defined Film Growth (EFG)
- Direct wafer solidification
offered by 1366 Inc., 20 s per wafer
cells with ca. 19% demonstrated



EPFL Kerf-free wafering

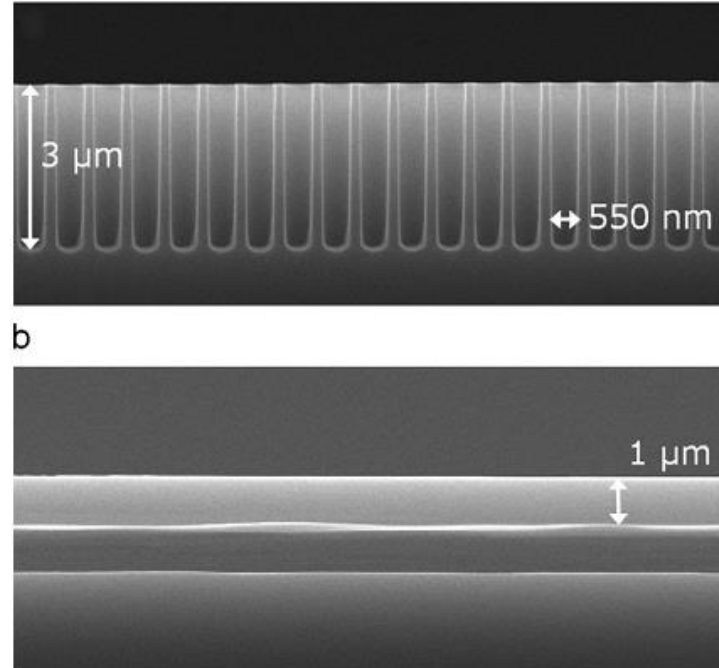


apply front of “standard” c-Si cell fabrication
remove from substrate (and glue to substrate)
process back (with a process that does not harm the glue)

F. Haase, JAP (2013)

EPFL Kerf-free wafering

60 min
1150°C



DRIE etch

wafer

free standing film

void

wafer

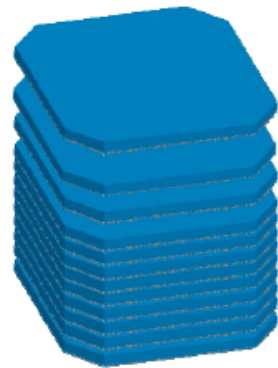
single-crystal film for “standard” c-Si cell fabrication

I. Gordon, SEM (2011)

SiGen PolyMax Process



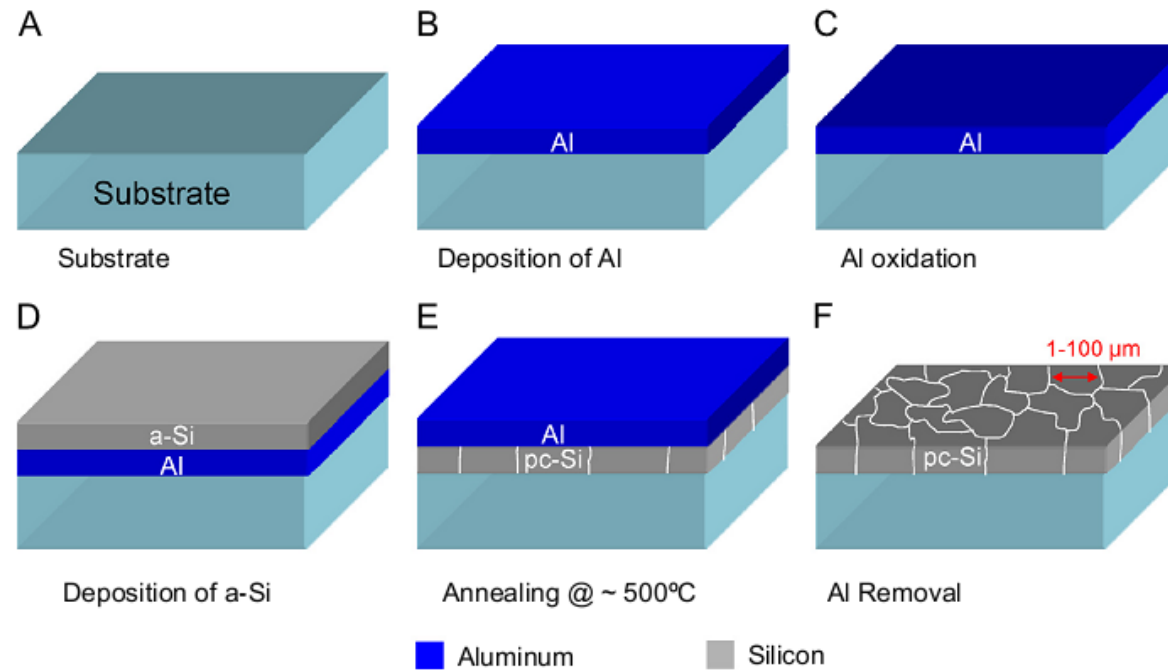
Silicon Brick



Cleaved Wafers

- Two Step Process
 - (1) Implant
 - (2) Cleave
- 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-150 μ m wafer barrier
 - New applications (i.e. BIPV)

Al-induced crystallization (AIC)



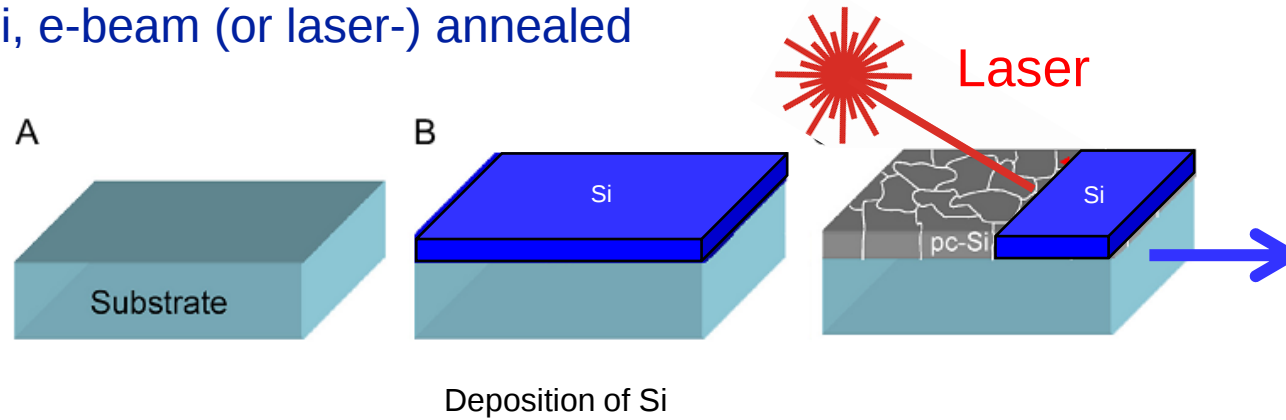
Melt Al, dissolve Si-film in liquid Al (eutectic at 577°C)
Growth of Si at interface to glass

Issue: impurities, unintended Al doping (ca. $2-3 \times 10^{18} \text{ cm}^{-3}$, saturation solubility in c-Si)
Potential: large grained substrates for epitaxial thickening

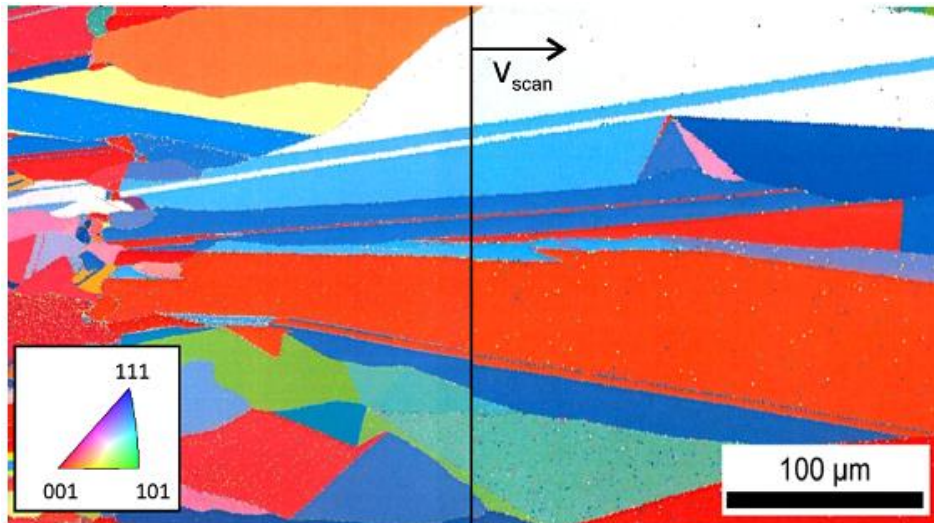
D. van Gestel, SEM (2013)

Liquid phase crystallized silicon

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



Orientation map by EBSD



Under research
(e.g. HZB, Germany
11.5% solar cells)

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

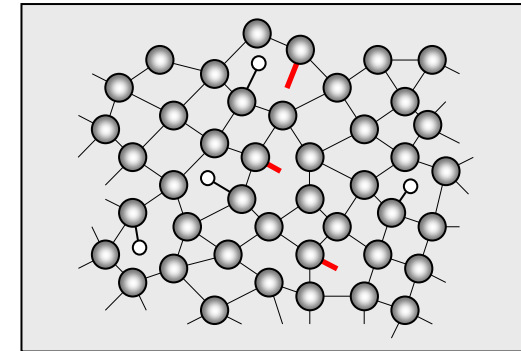
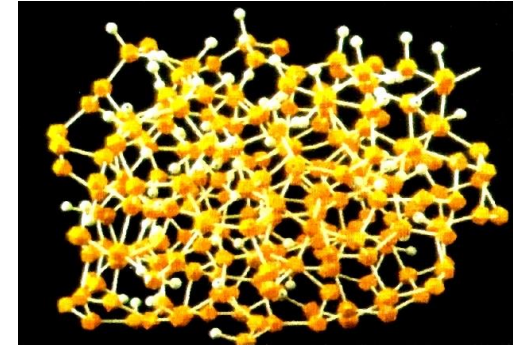
Coordination defects in evaporated a-Si
($N_D \sim 10^{20} \text{ cm}^{-3}$, one defect in 1000 Si atoms)

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

Defect equilibrium (frozen in at T_{growth})



Passivation of 99.9999%,
but: about $N_D \sim 10^{16} \text{ cm}^{-3}$ remain



Strong business during early 2000s

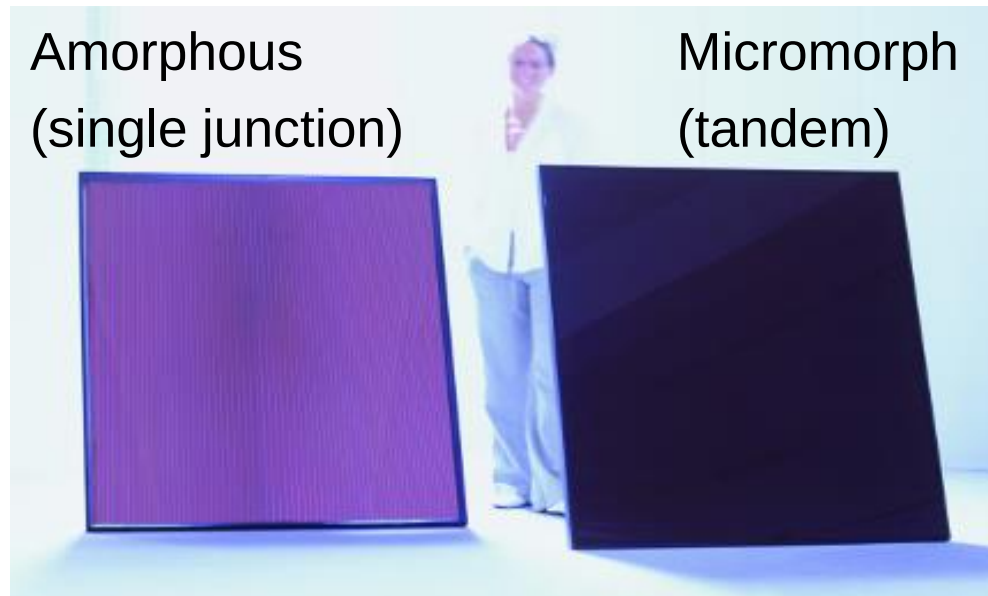
Applied Materials, Oerlikon (equipment manufacturers)

Kaneka, UniSolar, Sharp, Mitsubishi, Bosch, etc. (Solar module eff. ca. 10%)

Today:

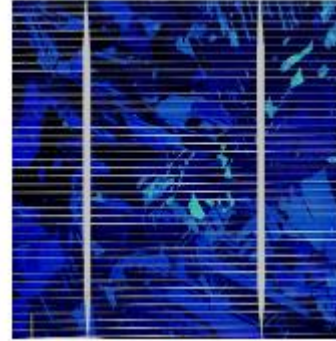
Kaneka is left on JP market, but focusses research on HIT concept

Niche markets survive (solar watches, etc.)



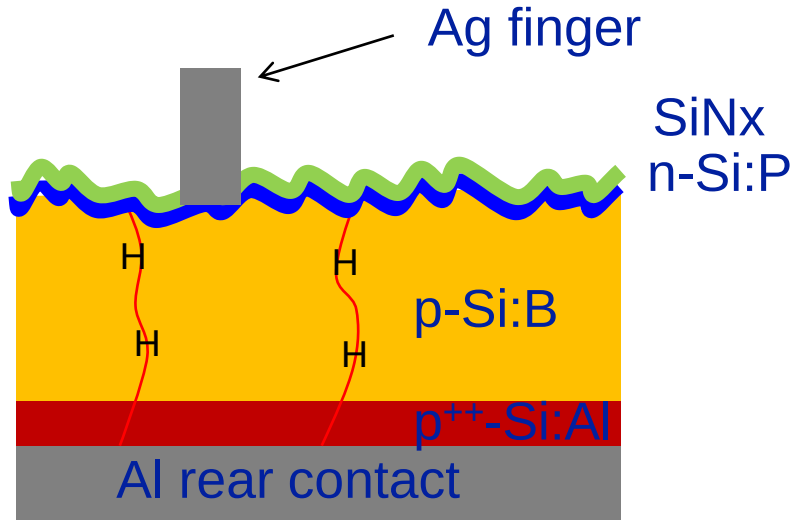
Source
Oerlikon Solar
(TEL Solar)

EPFL c-Si processing



Simple process: (multi-) crystalline Si-cell

Cells with BSF (back surface field):
 $V_{oc} \approx 660 \text{ mV}$



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)

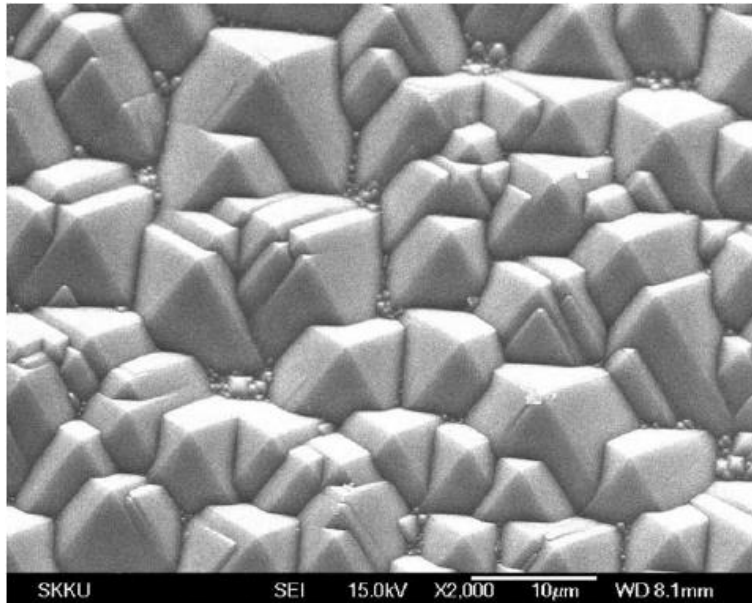
Apply SiNx:H AR coating

Metallization (screen printing)

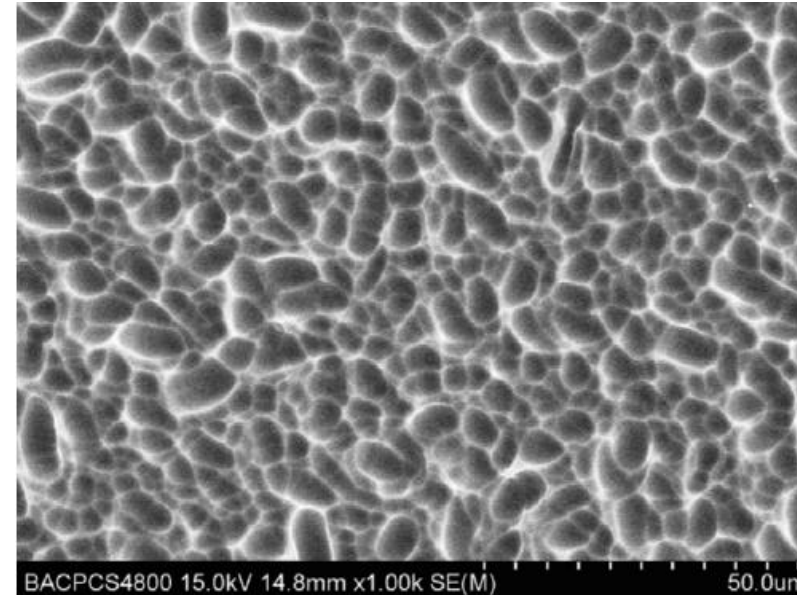
Firing

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

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



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



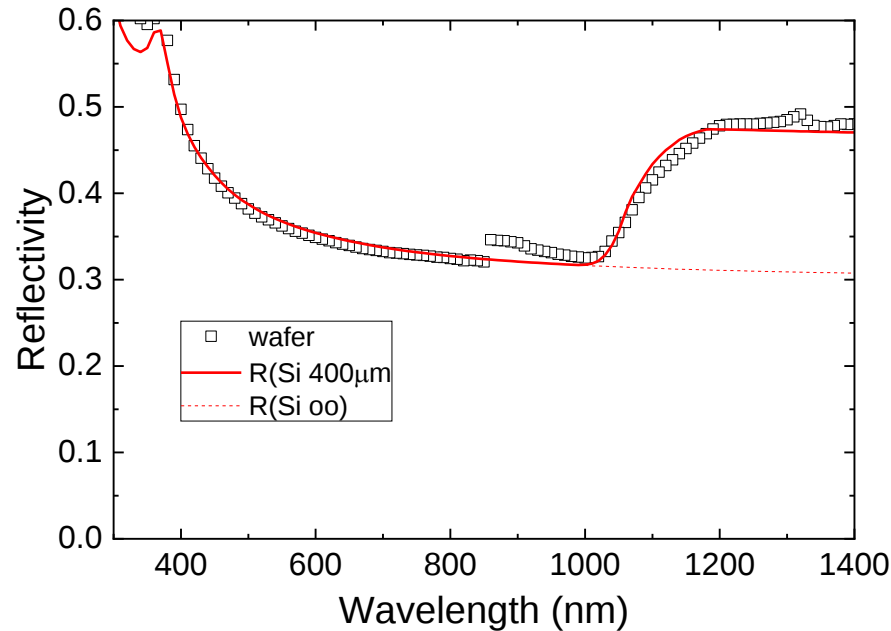
Issue: no longer applicable for diamond wire

e.g. Gangopadhyay, SEM (2016)

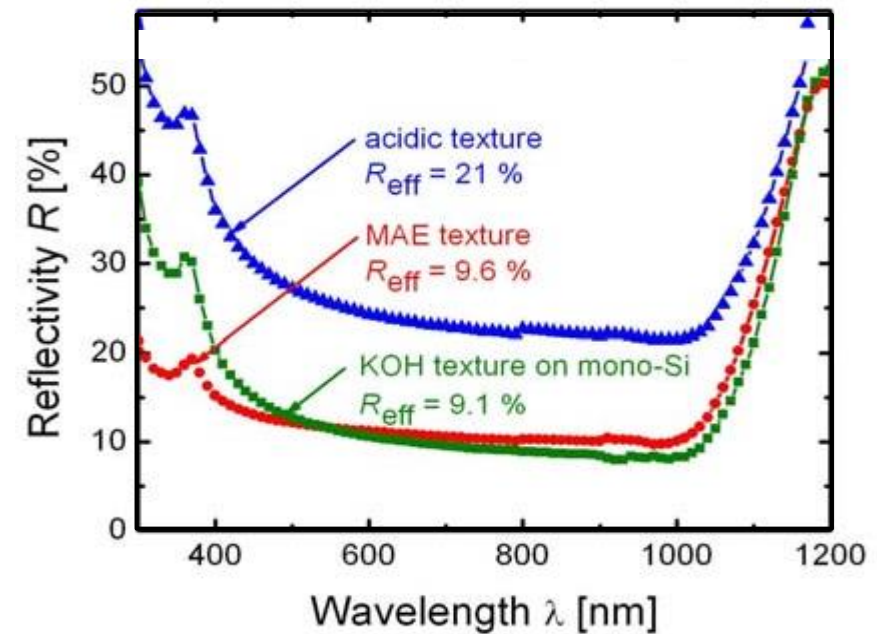
e.g. Zhou, SEM (2013)

Reduction of reflectivity by texture

Bare silicon ($n \approx 3.5$)

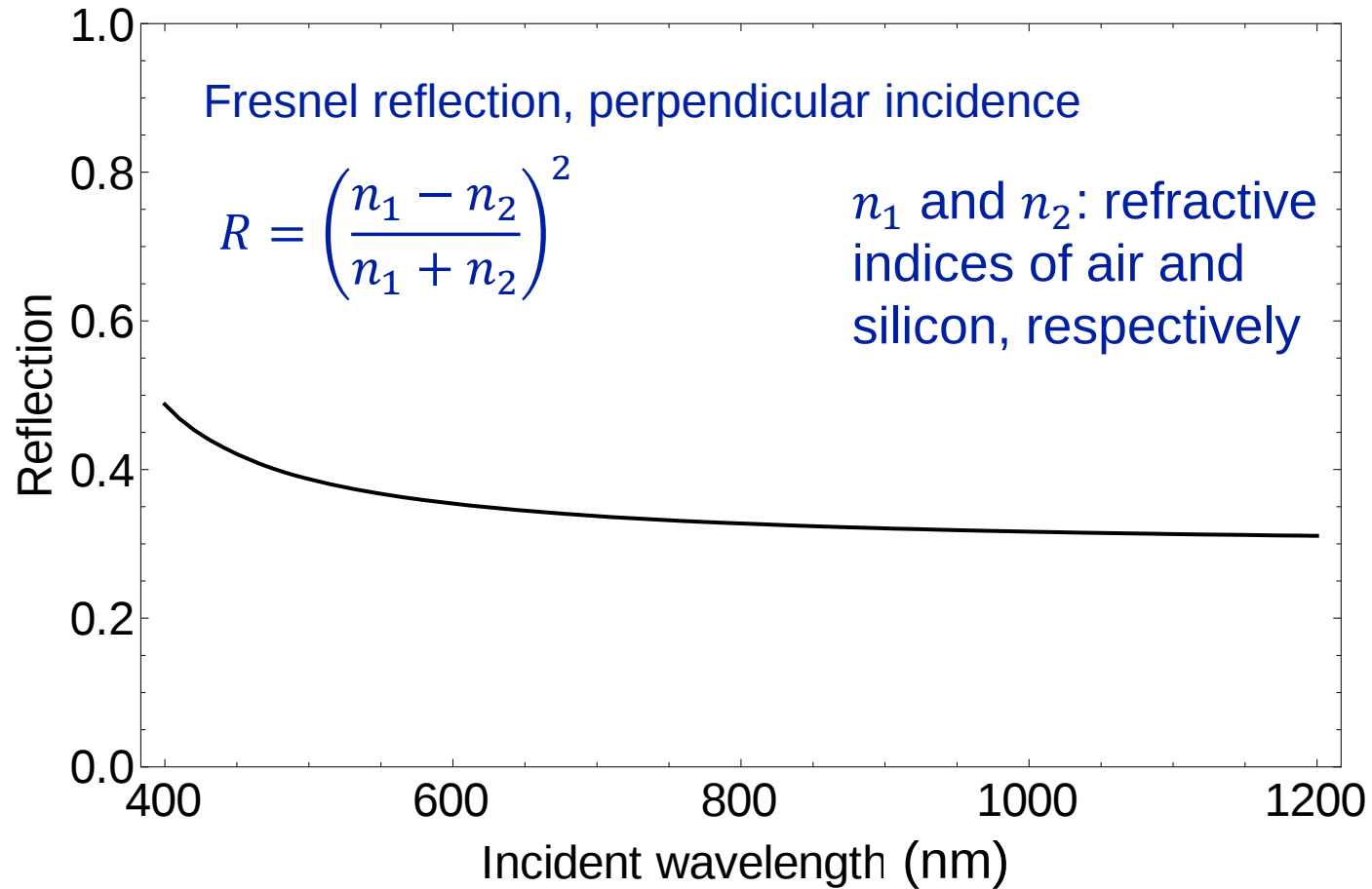


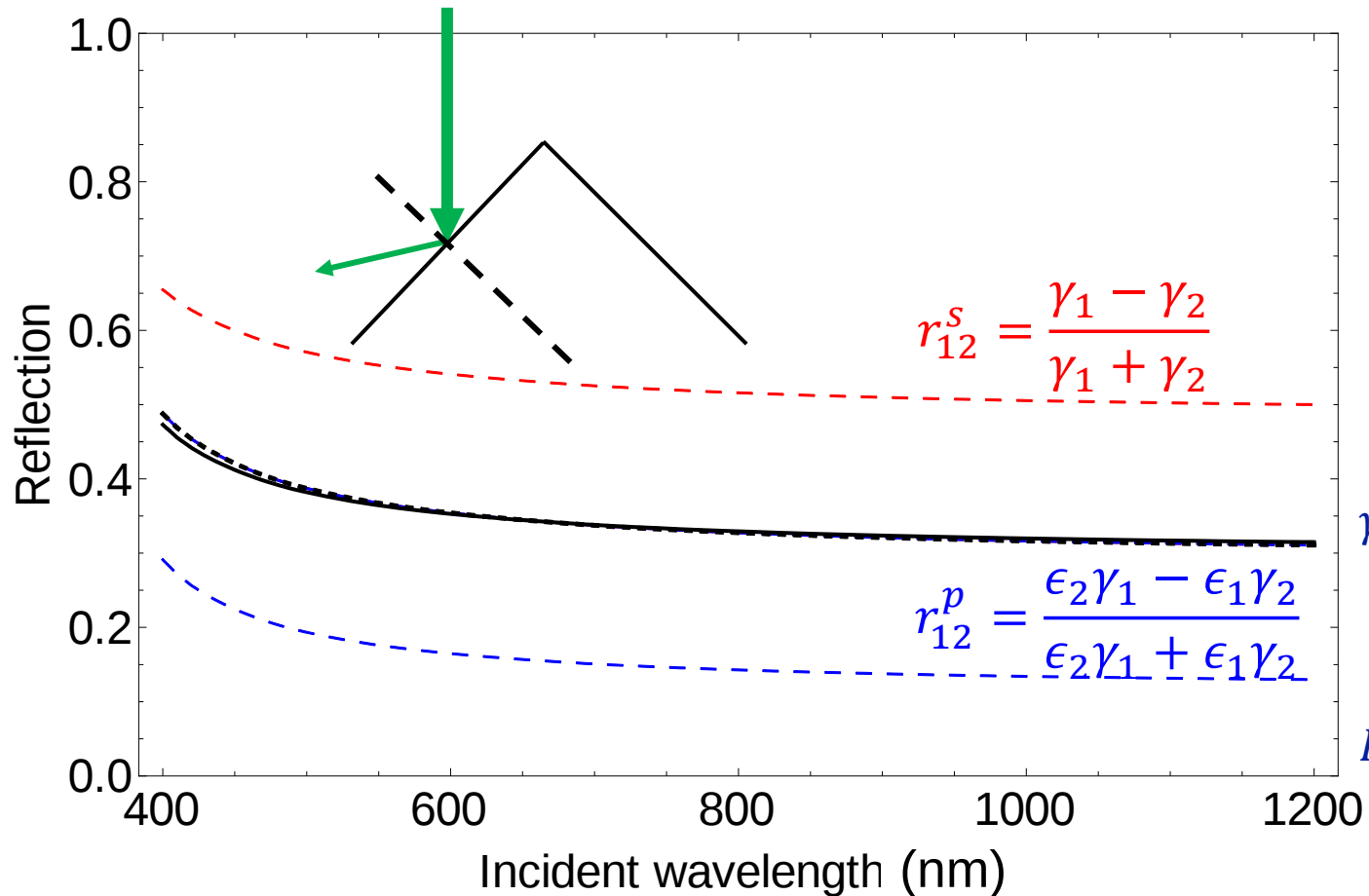
Textured silicon



e.g. Lipinki, PVSEC (2009)

AR effect by double rebound





Distinguish
polarization
directions:
s (“senkrecht”)
p (parallel)

propagation constants

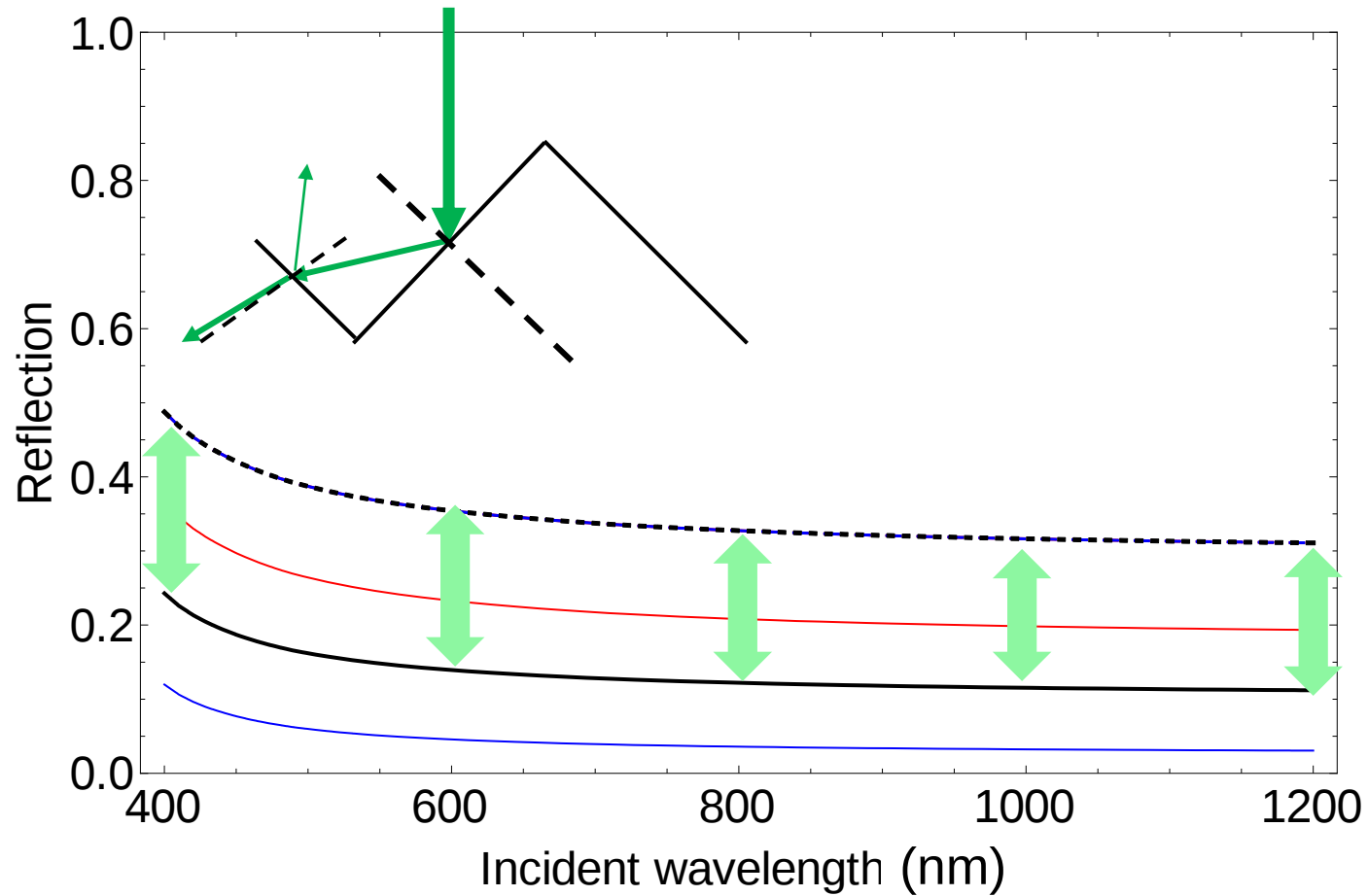
$$\gamma_i = k_0 \sqrt{\epsilon_i - \sin^2 \theta}$$

unpolarized average

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

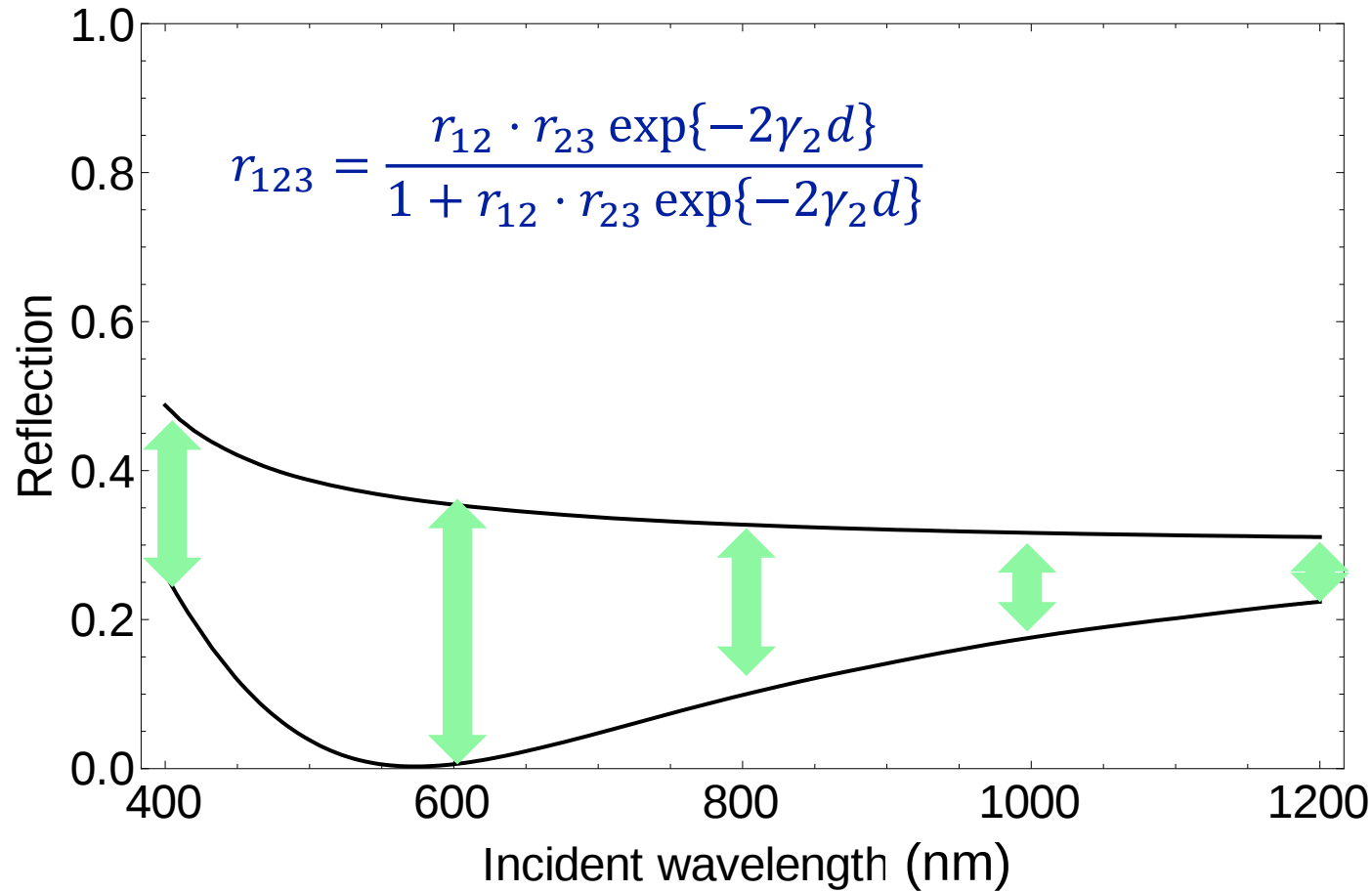
Practically no difference in polarisation-averaged reflection

Reflection with rebound ($\theta > 45^\circ$)



Reduction from 30% to 10%

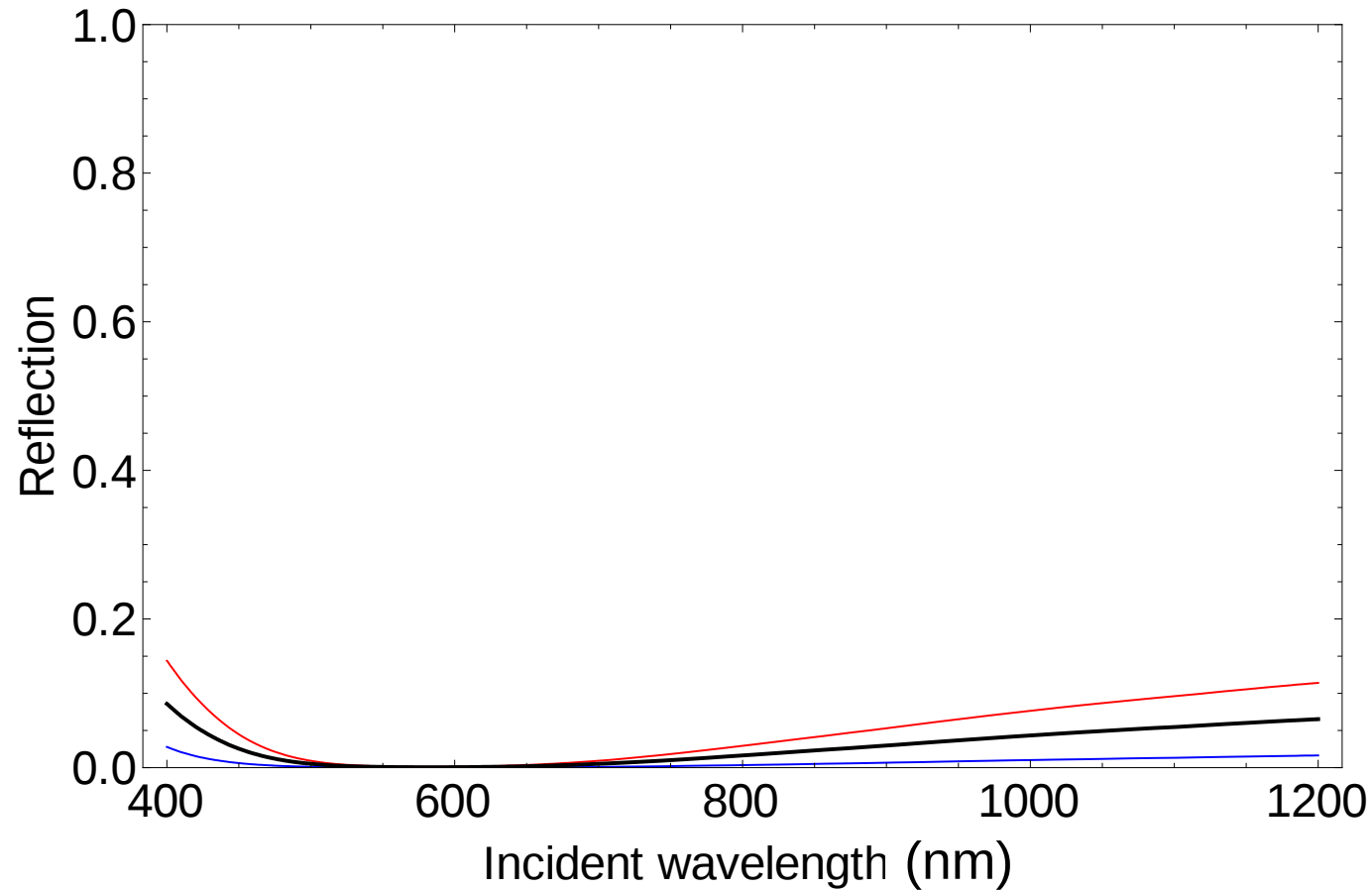
Flat Si with AR coating: e.g. 75 nm of ITO



ITO: transparent
contacts for
HIT solar cells

similar with SiNx

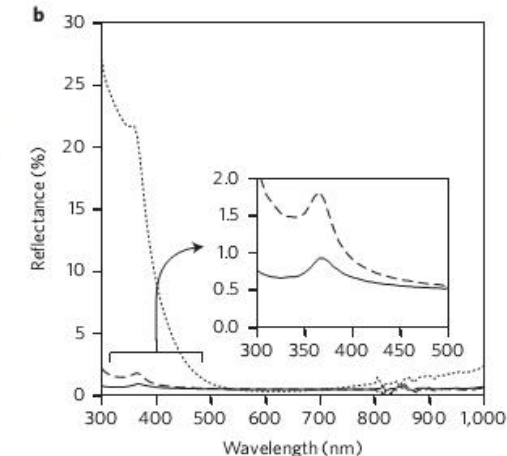
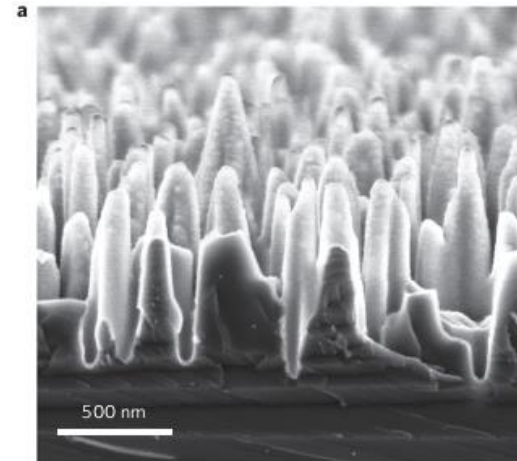
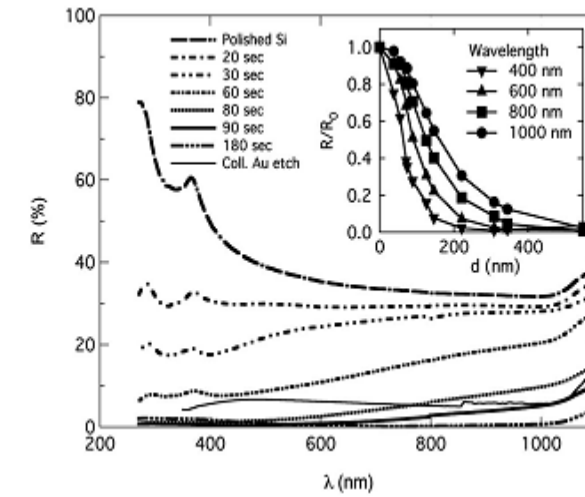
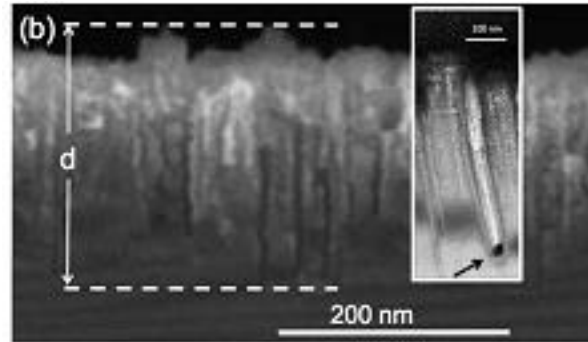
Effect of double rebound and AR coating



integrated over ROI :
< 3% reflection

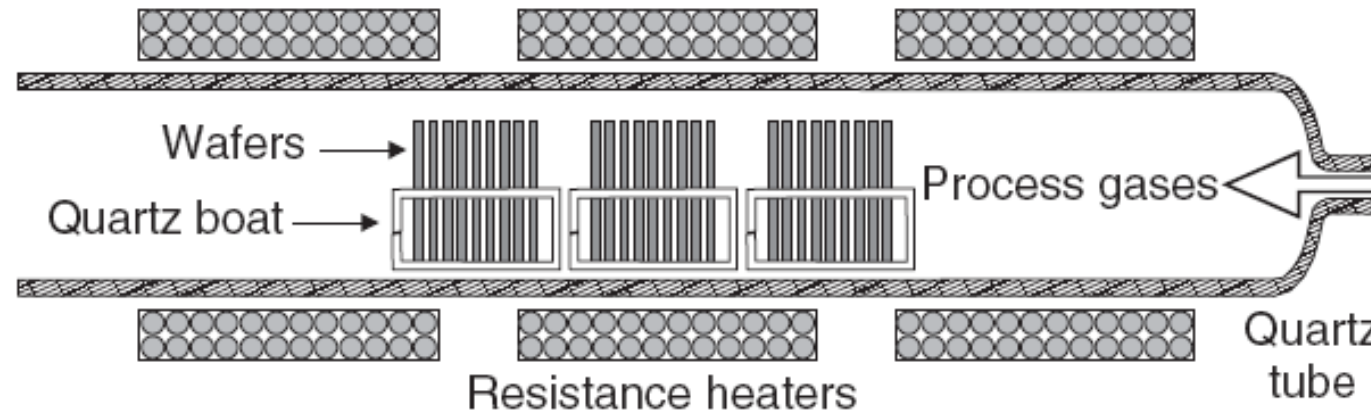
What else?

- 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

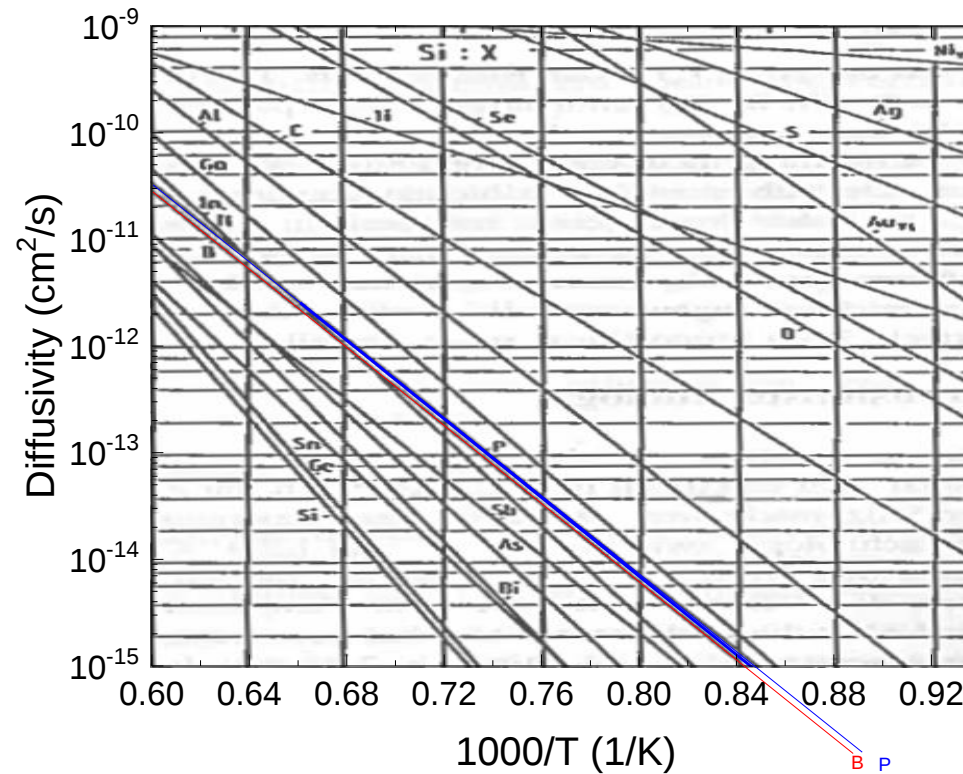
Fick's second law, often simplified for constant diffusivity D :

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

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

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

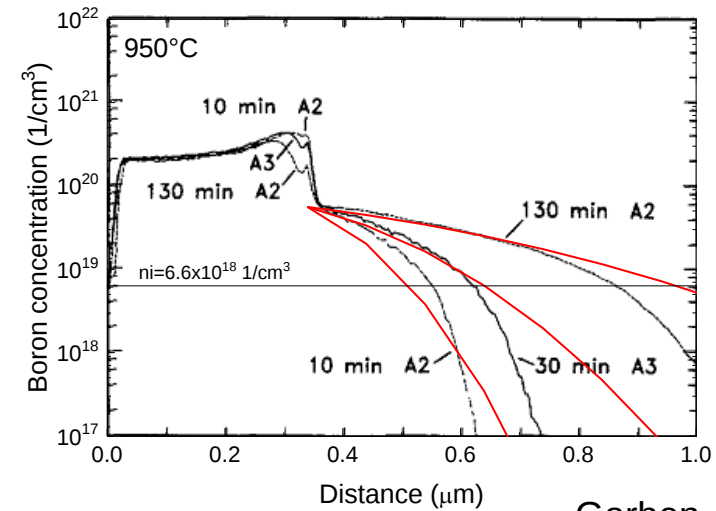
Constant D only approximately for high T

Generally:

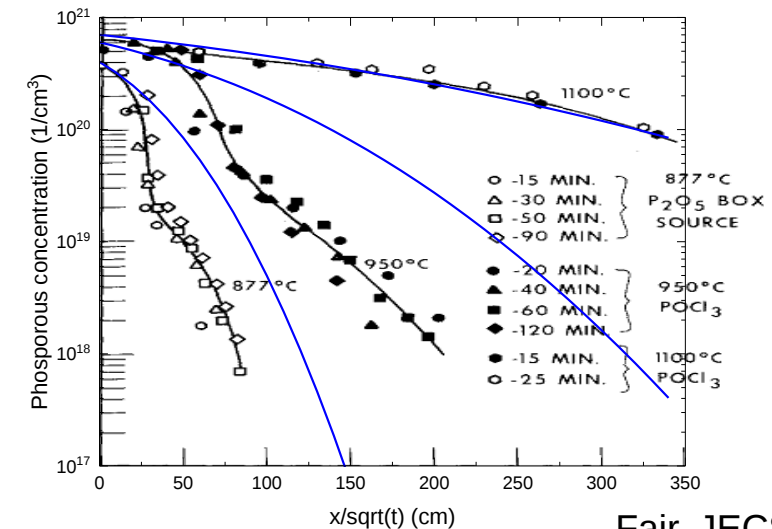
- high D close to interface
- low D deeper in bulk

Special for P:

sudden decay (“kink”) $\Rightarrow$ low D
eventually high D (tail region)



Garben, JECS (1986)



Fair, JECS (1977)

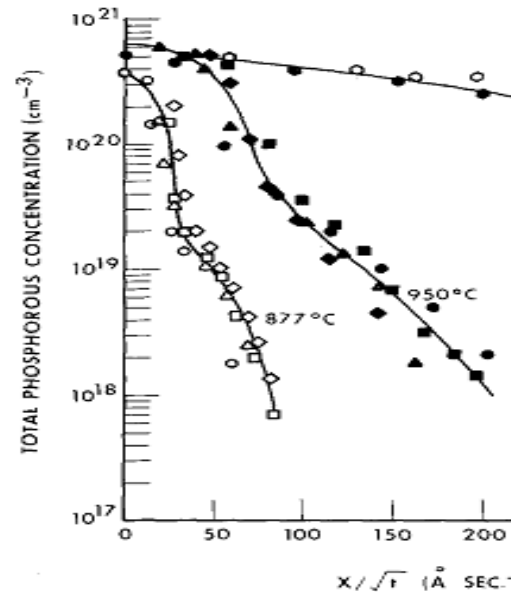
Boltzmann-Matano analysis

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

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

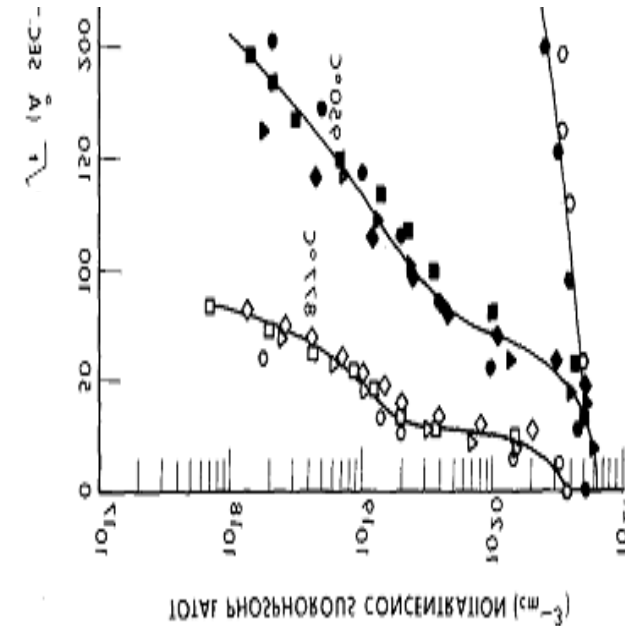
plot $c(x)$

derive
 dc/dx



plot $x(c)$

integrate
 $x dc$



Matano, Jap. J. Phys. (1933)

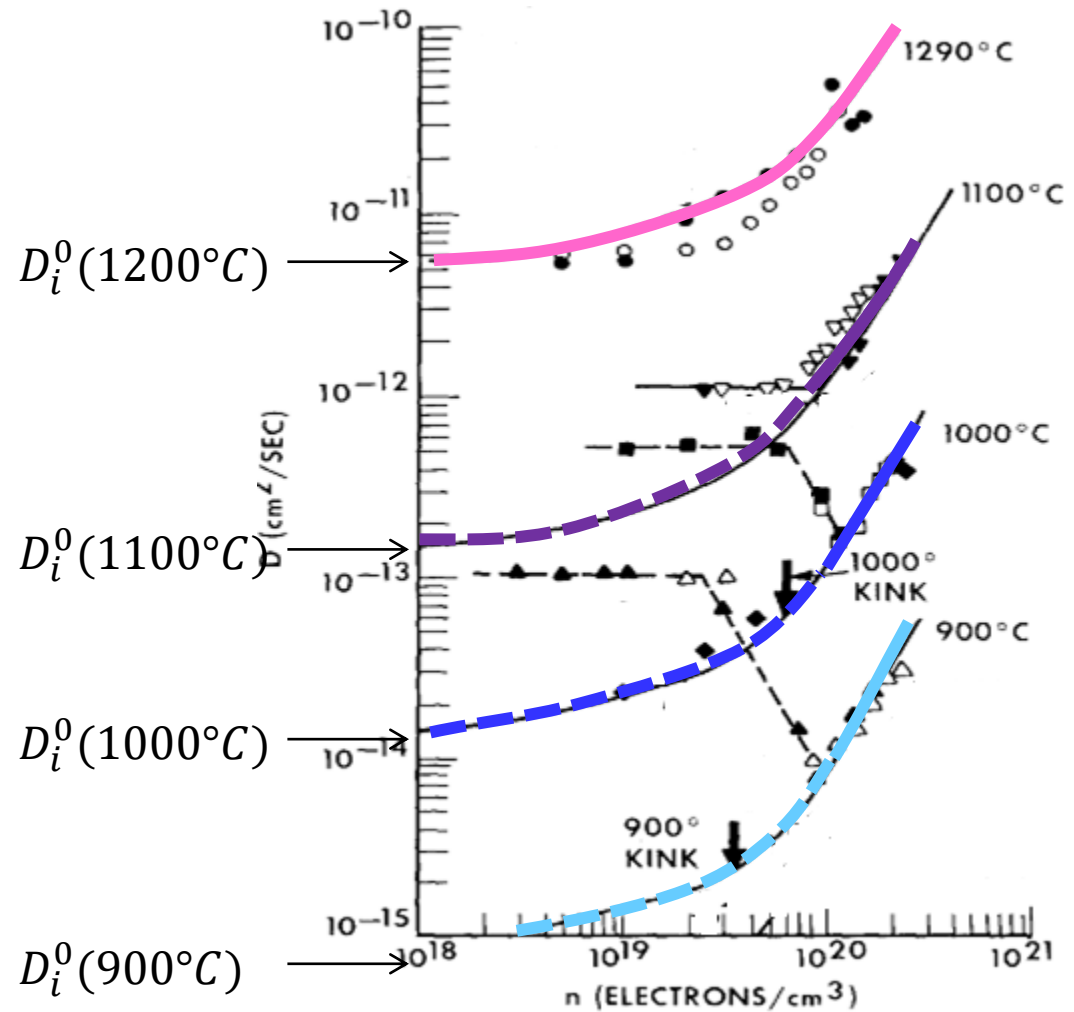
For high c , high T :

- 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

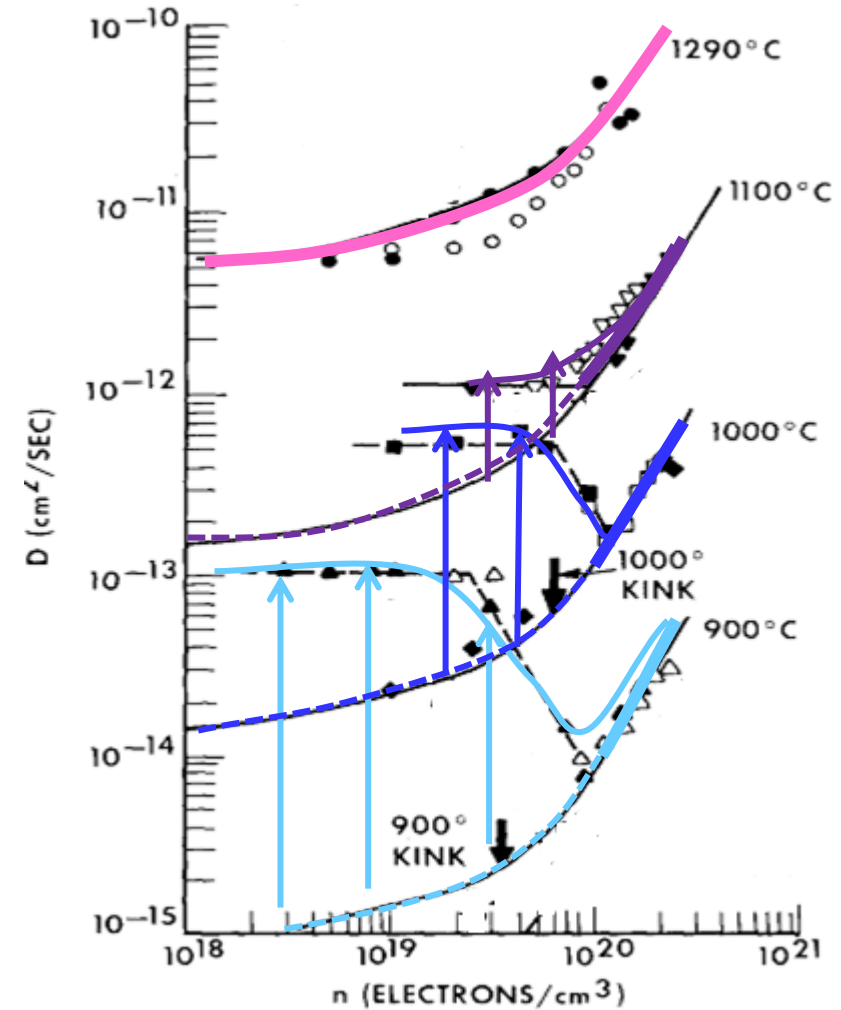
For low c , low T :

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

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



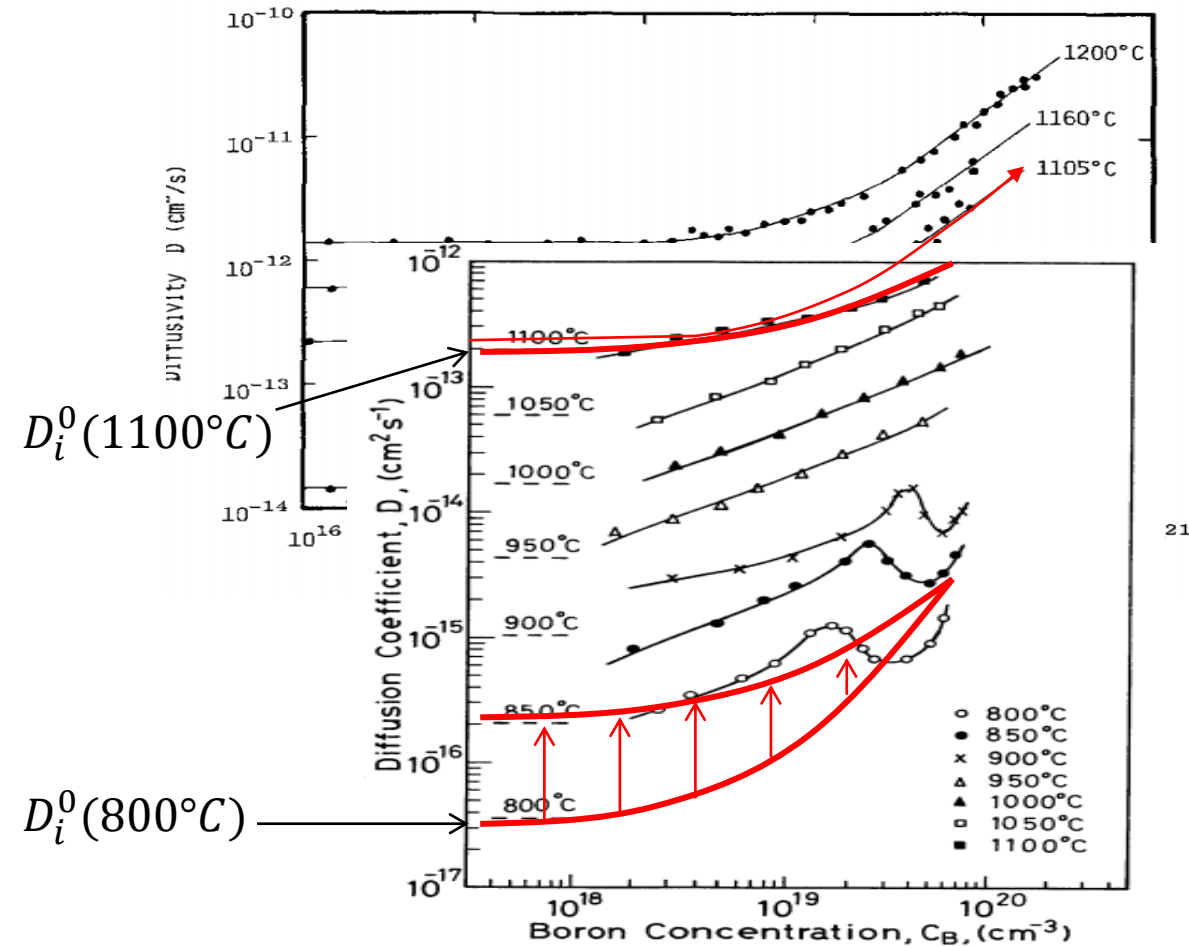
Fair, JECS (1977)

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)

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

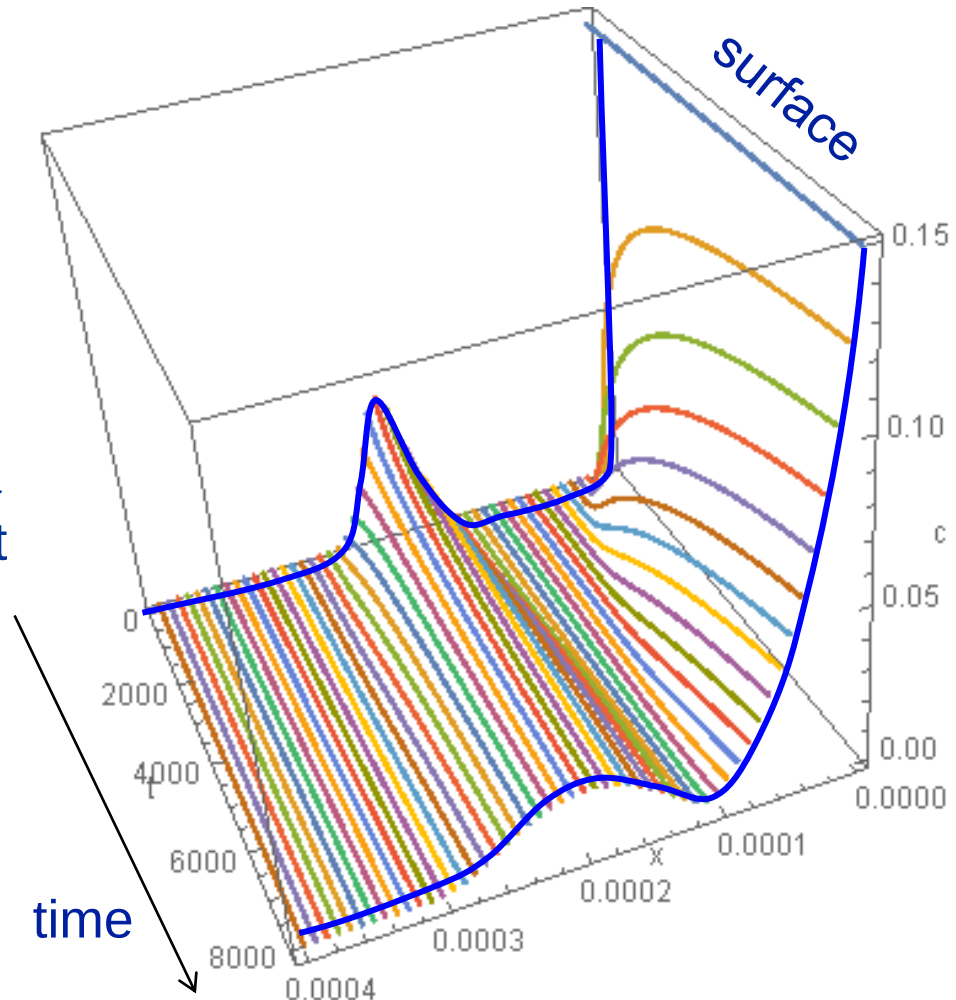
$$\frac{d}{dt} c = \frac{d}{dx} \left(h D(c) \cdot \frac{d}{dx} c \right)$$

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

Final addition: field enhancement h
 $\Rightarrow$ drift term due to doping gradient

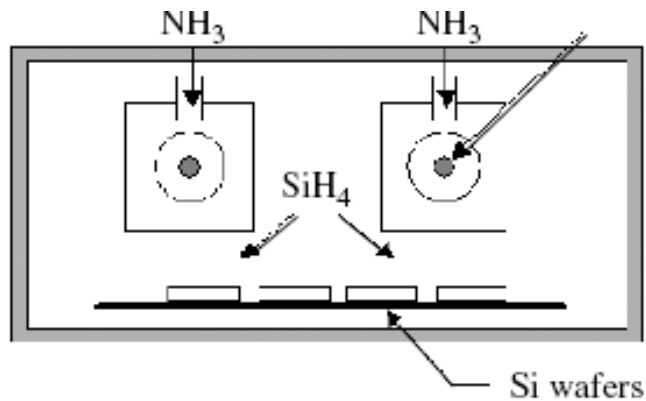
$$h = 1 + \frac{c_B}{2n_i} / \sqrt{\frac{c_B^2}{n_i^2} + 1}$$

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



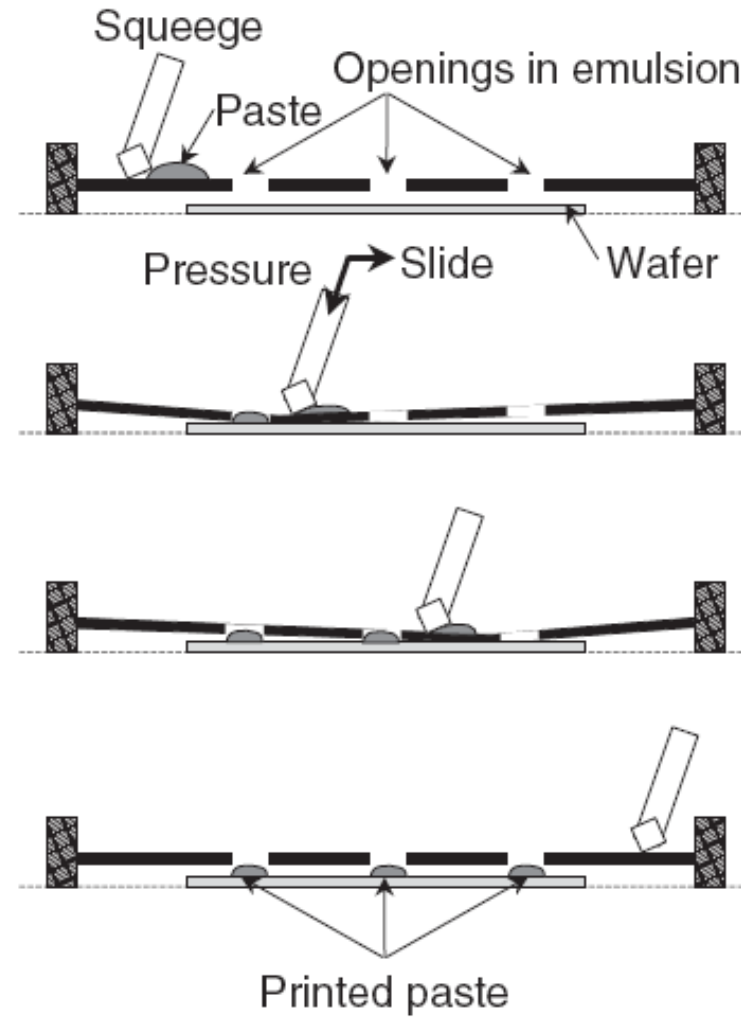
Next: Si_3N_4 front ARC by MW-PECVD

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

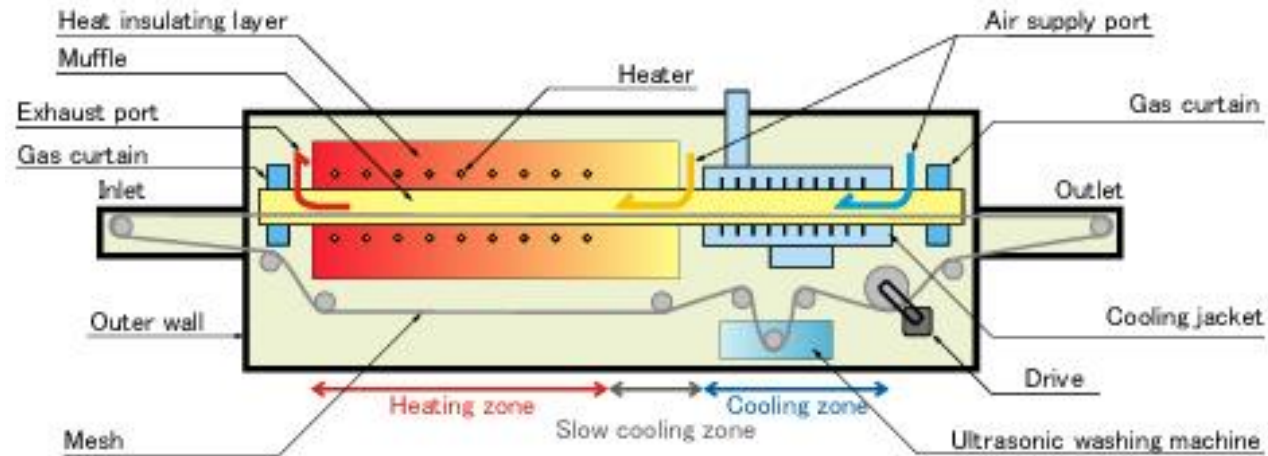


e.g. Meyer Burger AG (Roth&Rau)

Next: metallization by screen printing



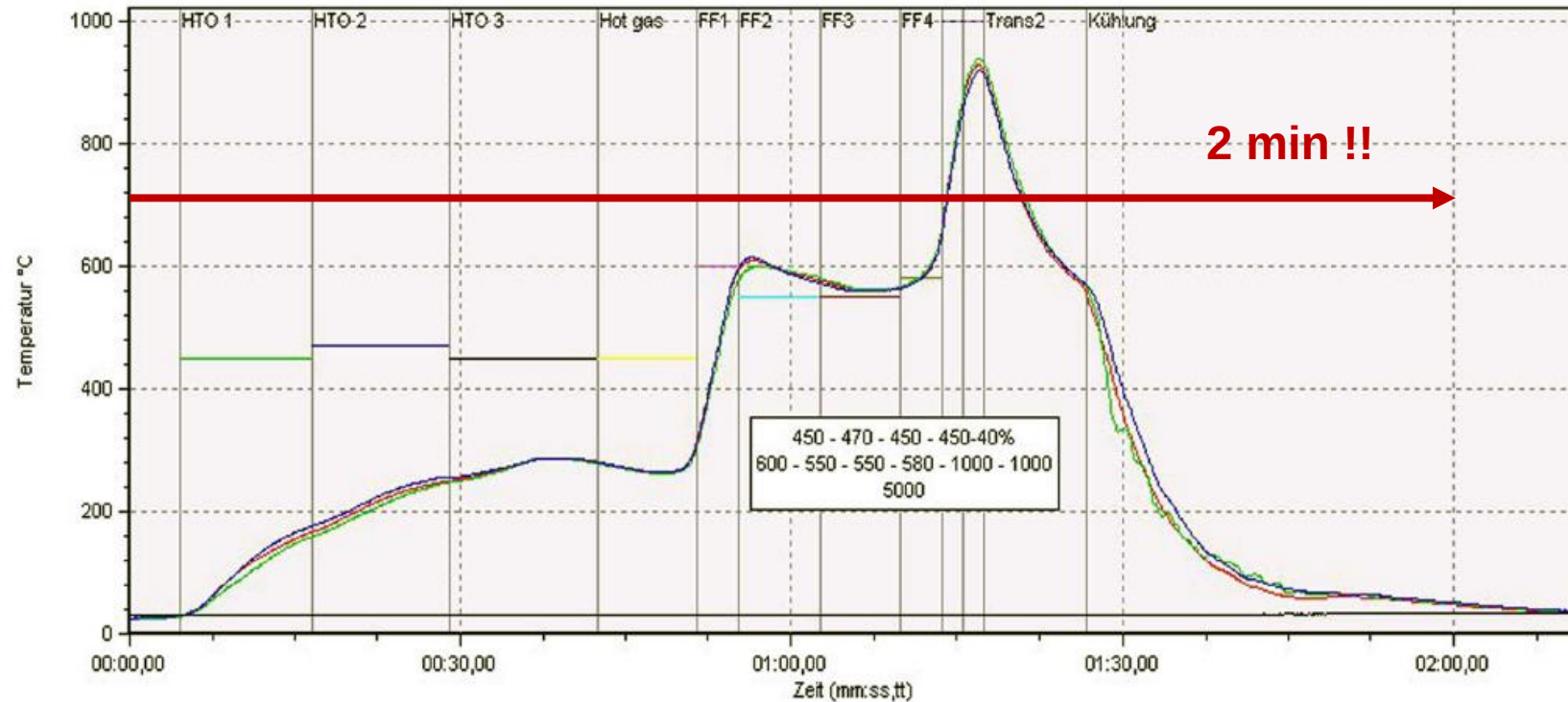
EPFL Finally: Contact firing



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

EPFL Firing-through profile

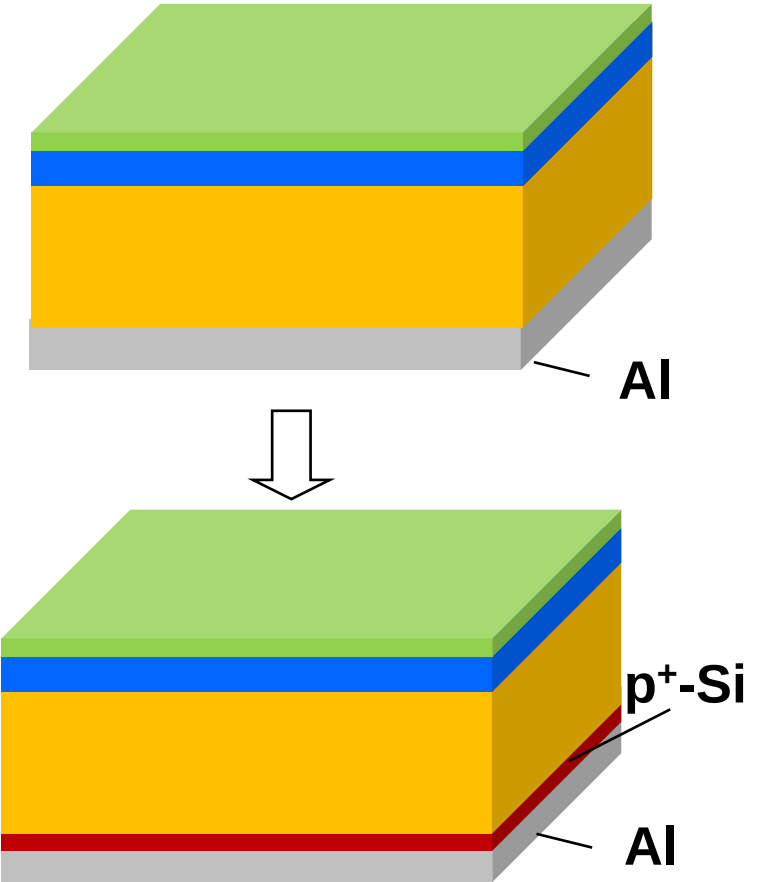
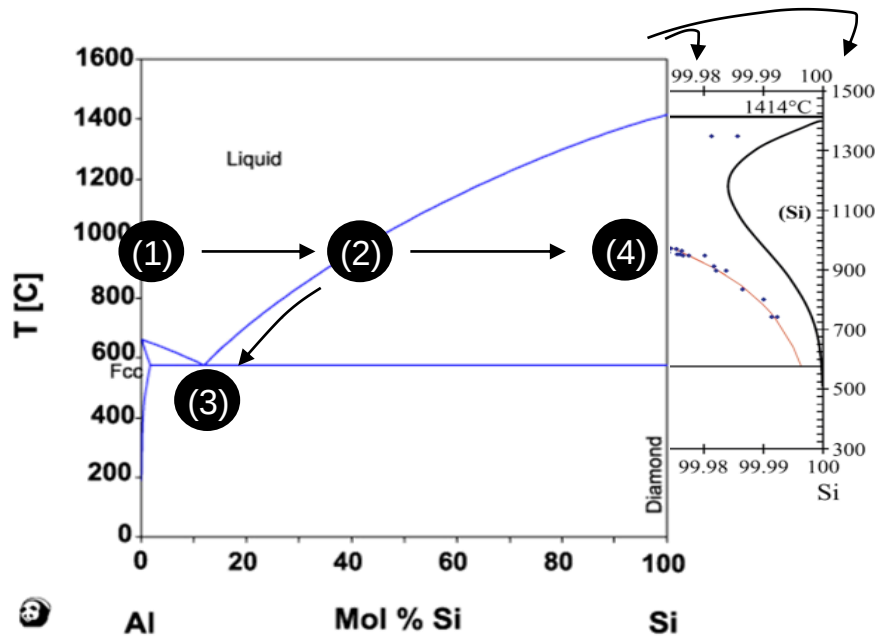
Peak temperature at 870-900°C
Profile of T and thermal load important !



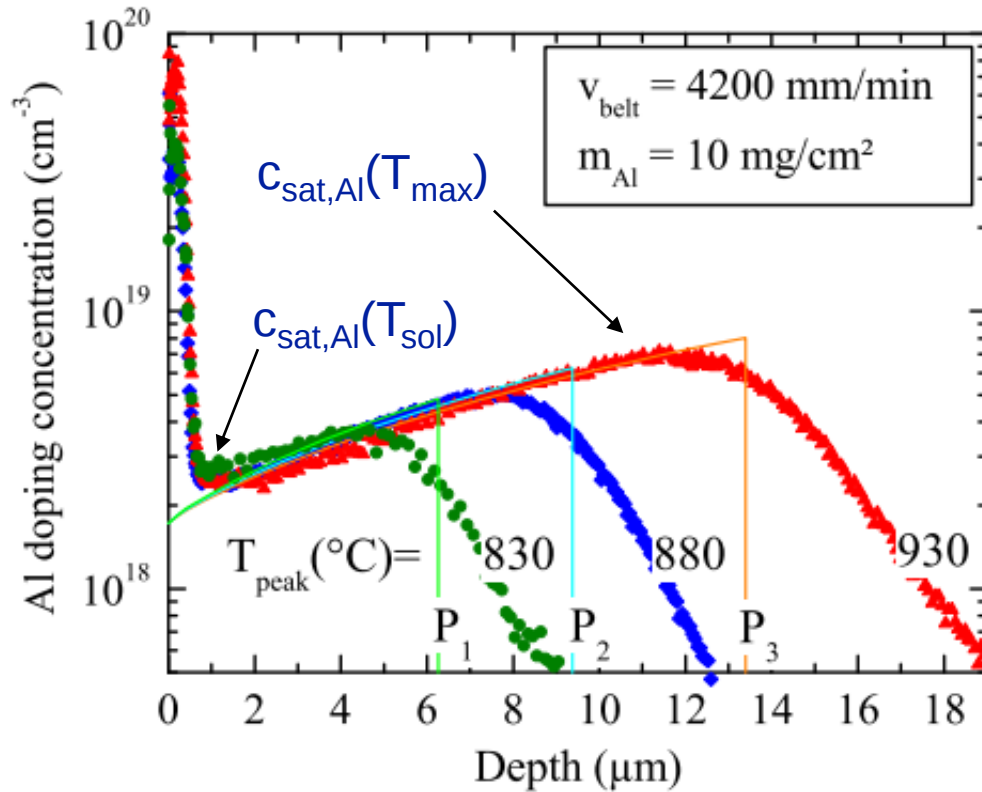
Real profile, measured by thermocouple bonded to a wafer

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)
 => $N_A = c_{sat,Al} \approx (0.015 \times 2.5 \times 10^{22} \approx 4 \times 10^{18}) \text{ cm}^{-3}$



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



Retrograde depth profile:

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

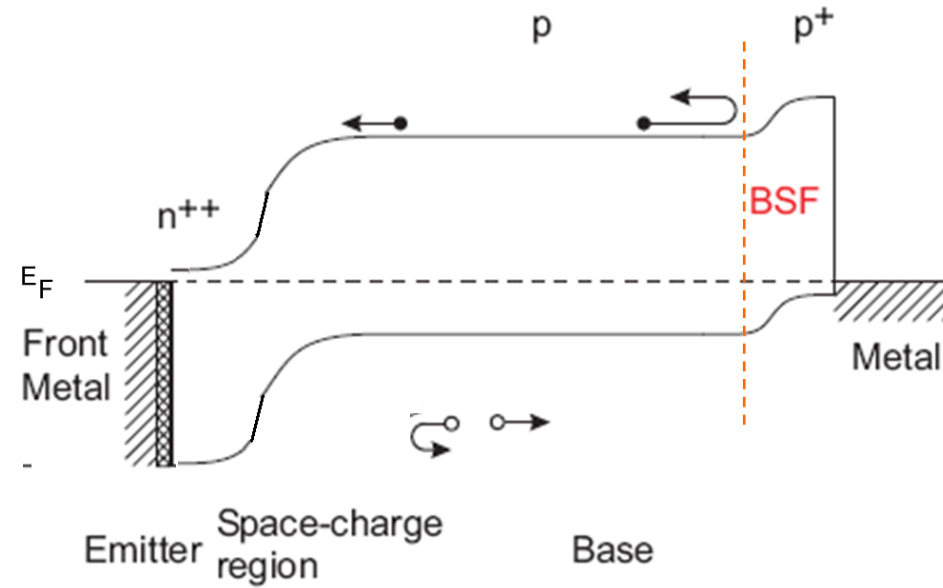
during cooling:

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

Lowest concentration at surface

$$N_{\text{A}} = c_{\text{sat,Al}} \approx 3 \dots 6 \times 10^{18} \text{ cm}^{-3}$$

Krause, SEM (2011)



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

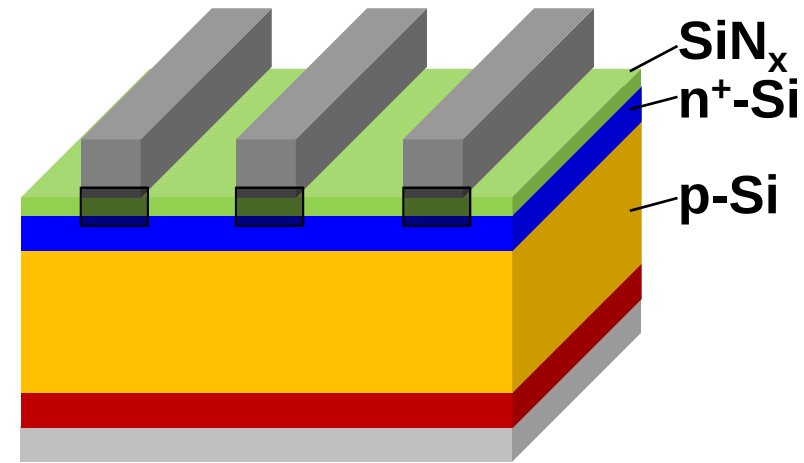
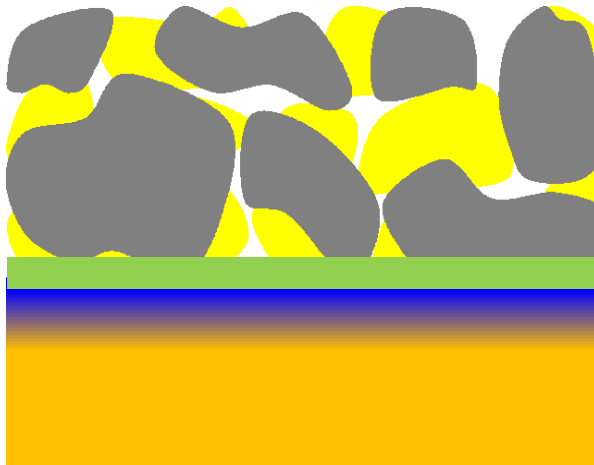
On the true role of the highly doped region:
«The doped region mostly gives a **reduction** of minority carriers (and hence of recombination)»

Cuevas, JPV (2013)

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

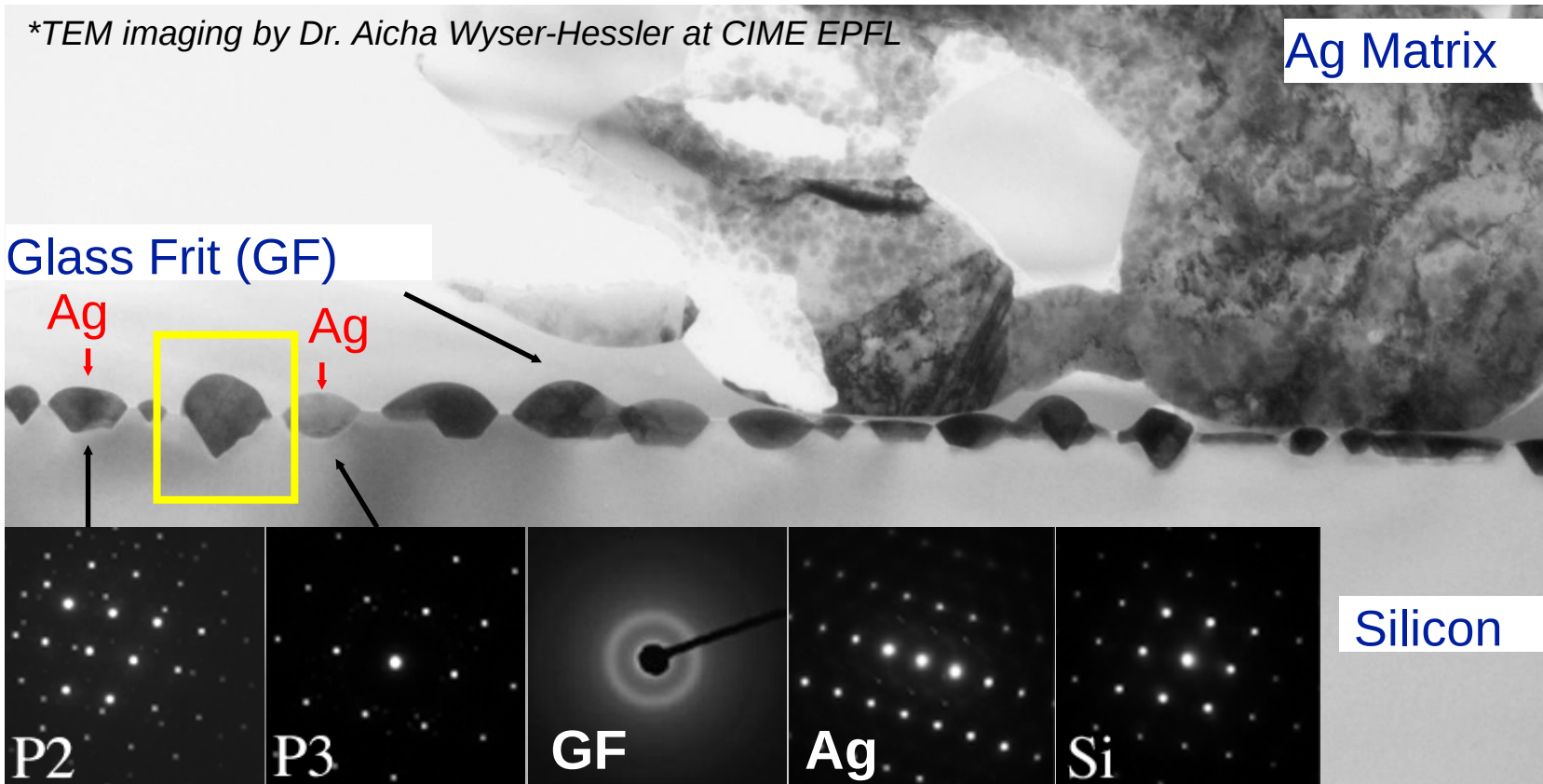
Paste:

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



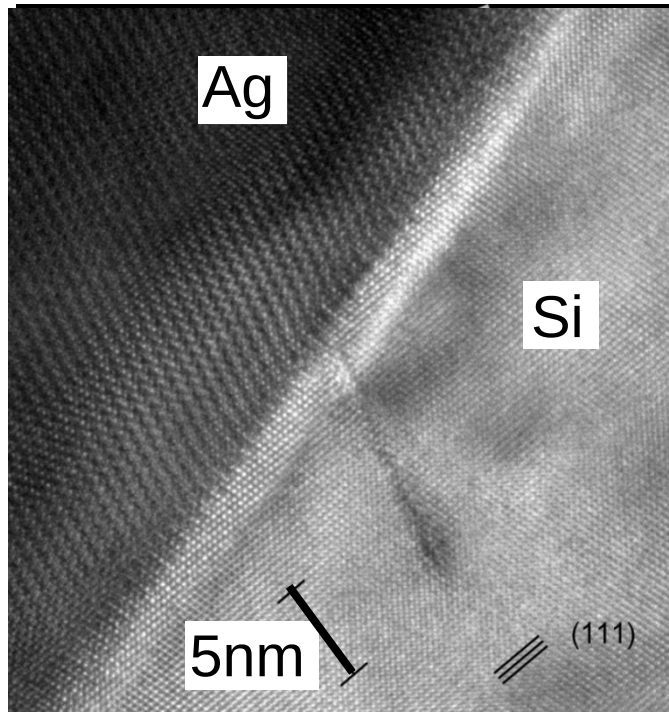
What happens during annealing at 700-800°C

Cross-section [110], typical TEM* view



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





HR TEM image

Ag crystallite properties

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

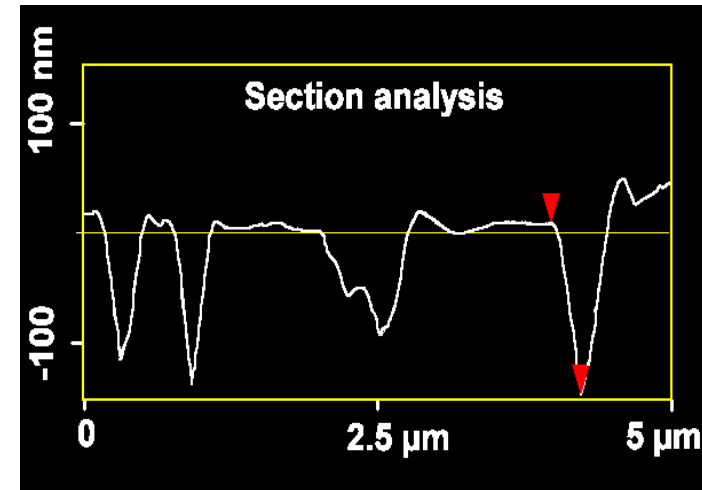
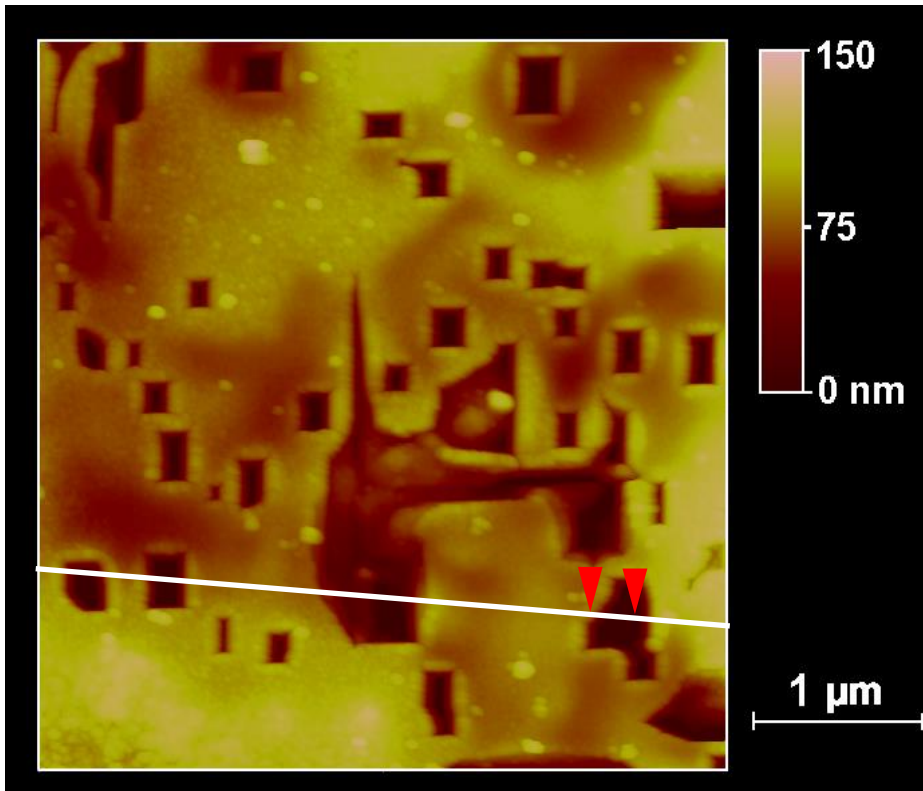
HR-TEM Ag/Si interface

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

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

AFM of surface after etching

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



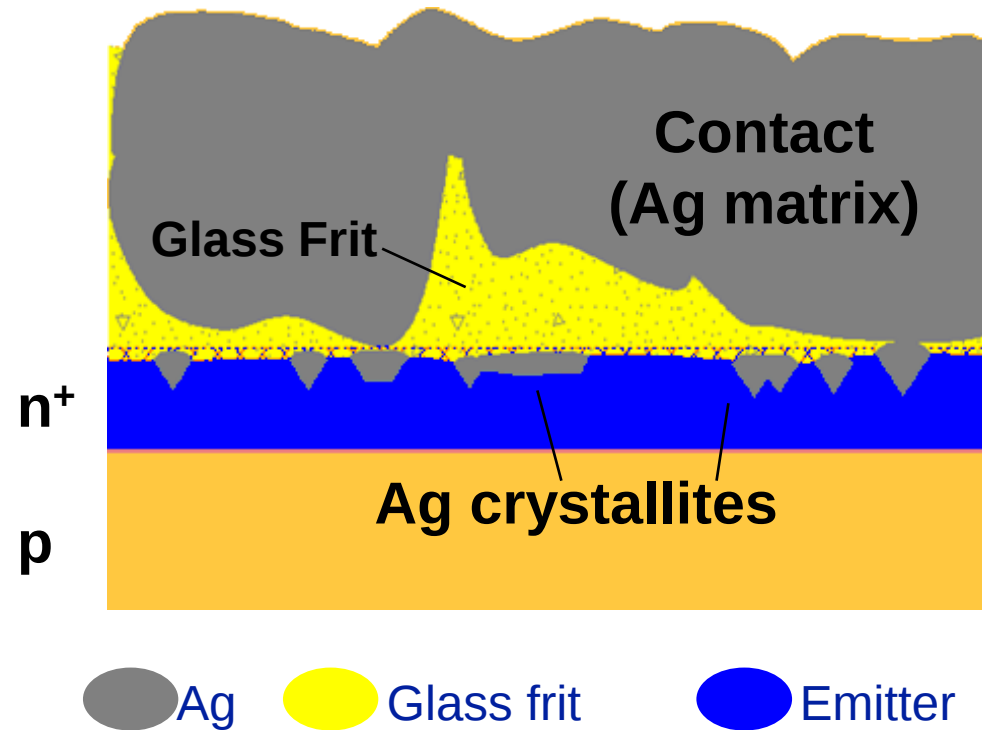
- ~100 nm dips
- Confirms TEM analyses

Heating

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

Cooling

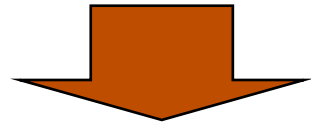
- Excess Si:
→ epitaxial regrowth on Si
- Excess Ag:
→ nucleation w. orientation of Si, growth towards surface
- Process stops with intermediate glass frit layer



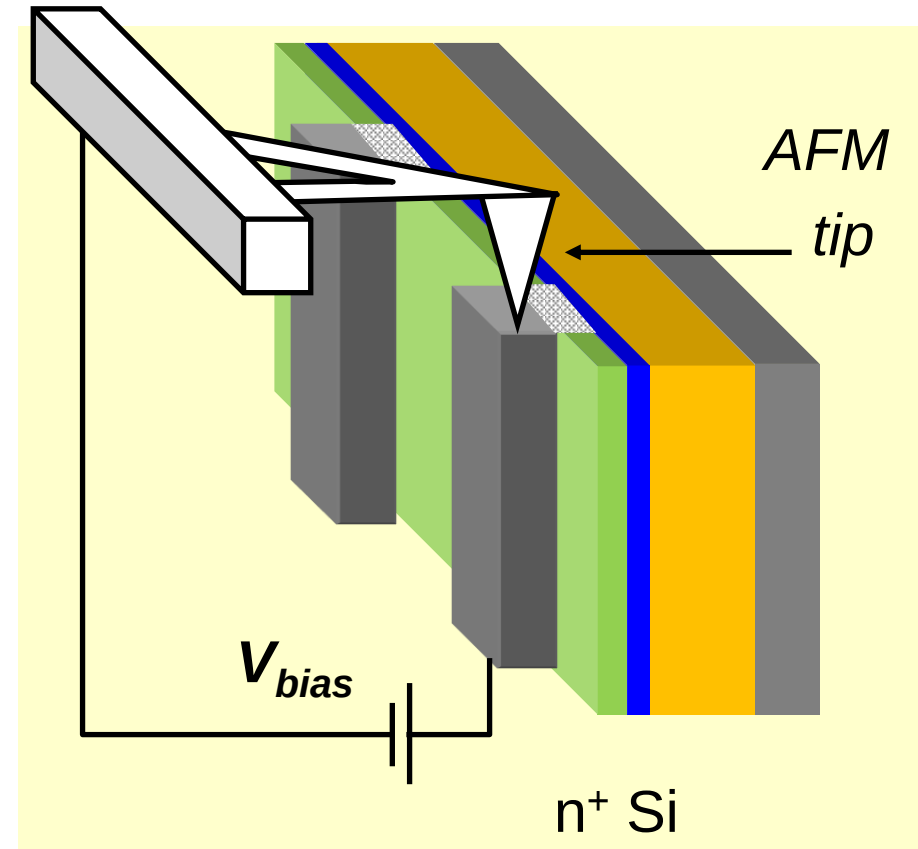
*n.b.: alternatively, etching of pyramids into the wafer was proposed

Insulating glass frit layer

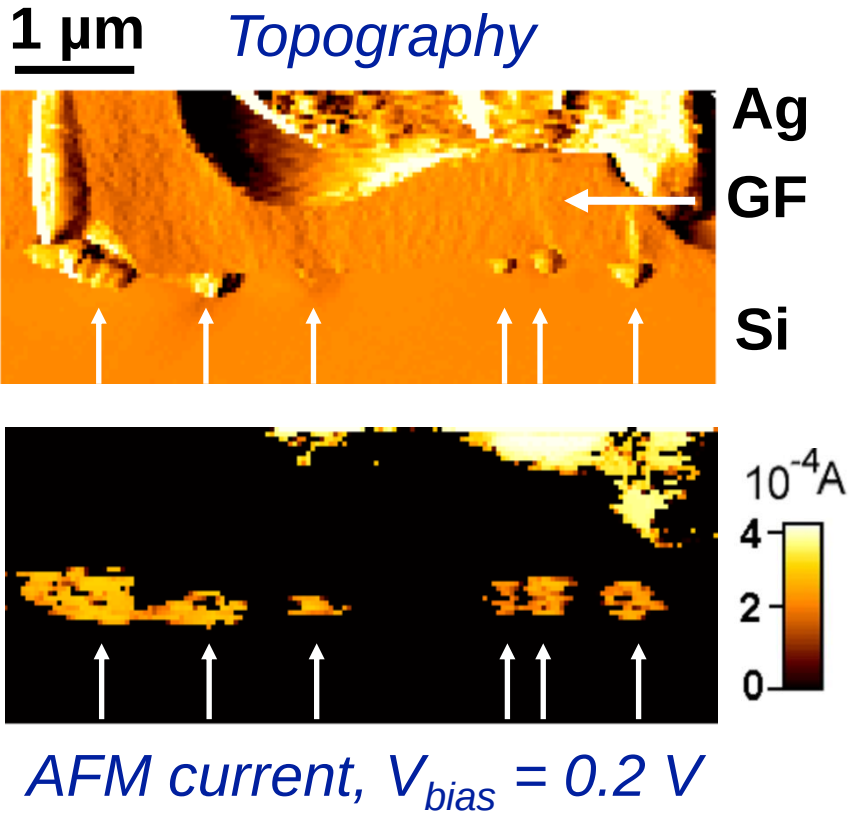
- where does current flow ?
- how to determine contact resistance ?



Conductive AFM on cross-sections of contact



EPFL Conductive AFM on cross-sections of contact



On Ag crystallites

$$\rightarrow I = 0.3\text{ mA}$$

$$\rightarrow R_{\text{contact}} = 700\text{ Ohm}$$

$$\rightarrow R_c < 10^{-7}\text{ Ohm cm}^2$$

$$<< 10^{-3}\text{ Ohm cm}^2$$

(observed macro)



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

Model for current flow

Glass frit

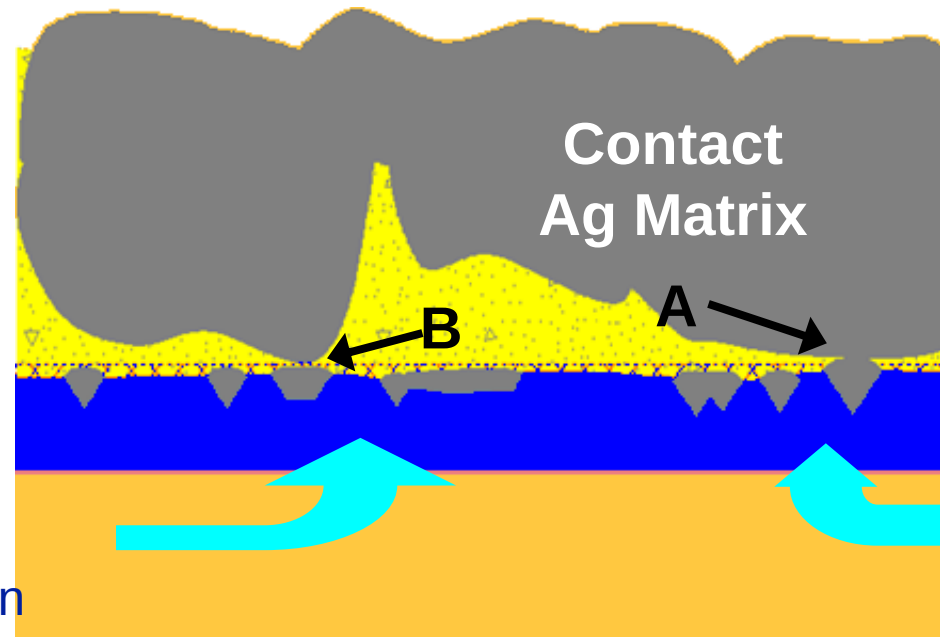
- No Ag or Pb precipitates
→ isolating



- 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

EPFL 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)

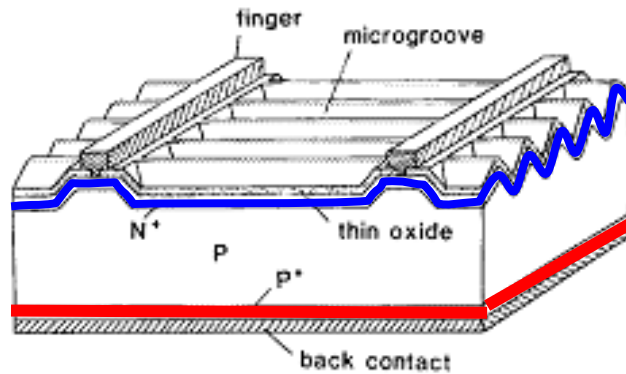
Cell generations (UNSW)

PESC (Passivated Emitter Solar Cell):

$V_{oc} = 670 \text{ mV}$

$j_{sc} = 38.3 \text{ mA/cm}^2$

eff=20%



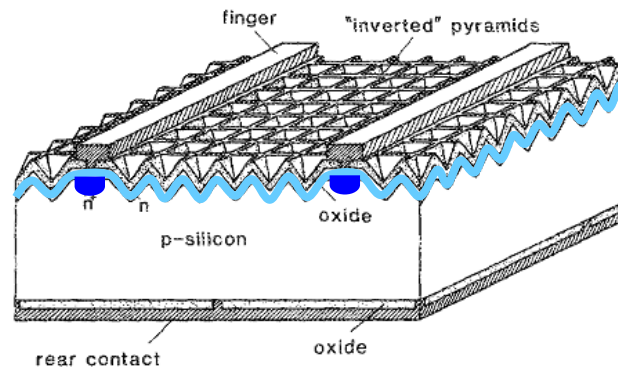
Blakers, APL (1986)

PERC (Passivated Emitter and Rear):

$V_{oc} = 696 \text{ mV}$

$j_{sc} = 40.3 \text{ mA/cm}^2$

eff=22.8%



Blakers, APL (1989)

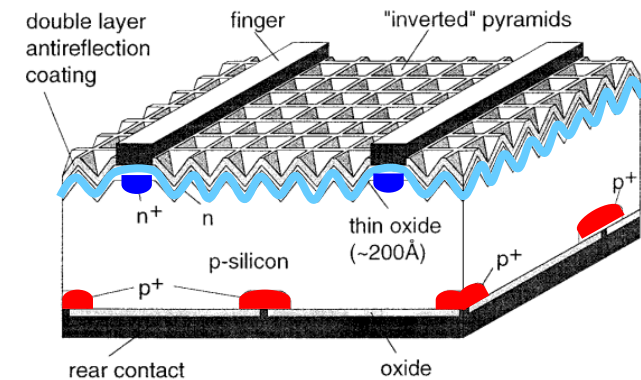
PERL (Passivated Emitter, Rear Locally diffused):

$V_{oc} = 706 \text{ mV}$

$j_{sc} = 42.9 \text{ mA/cm}^2$

eff=24.2 - 24.7%

(25% after AM1.5 update)



Wang, APL (1990)

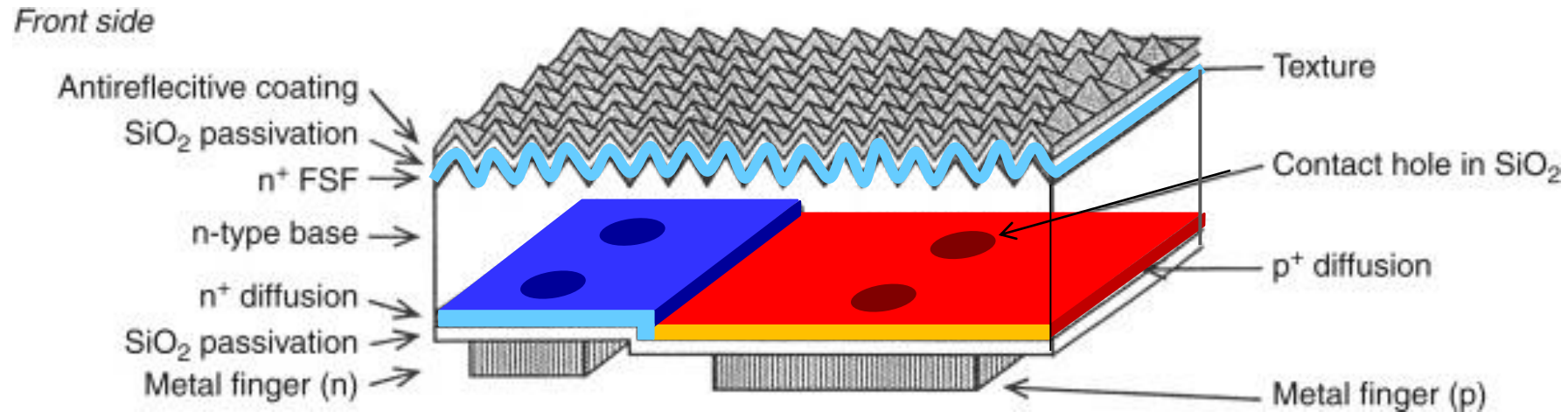
Zhao, PPV (1999)

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

EPFL 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)

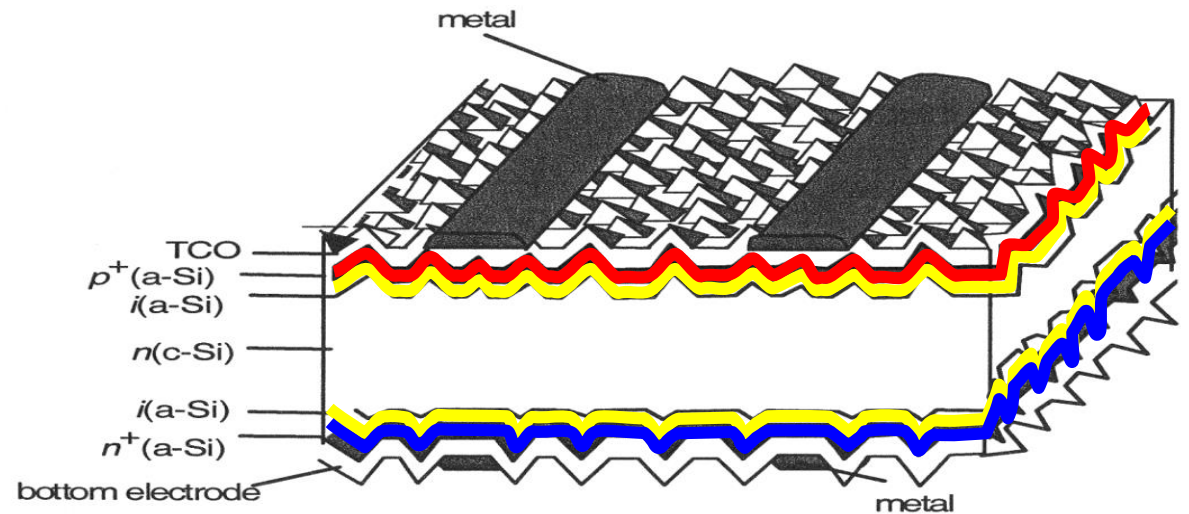
EPFL Cells with full passivation (Sanyo/Panasonic)

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)

- 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)