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

F.-J. Haug

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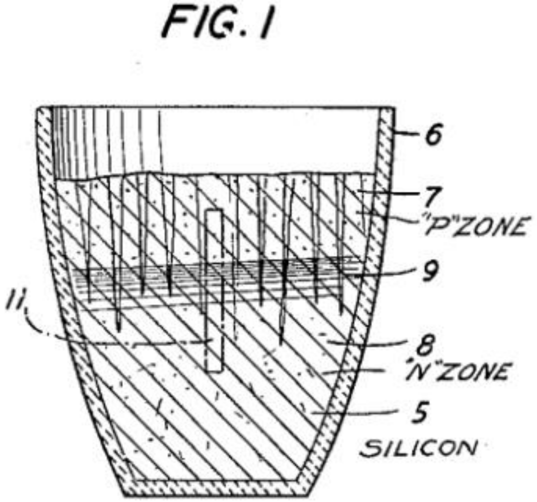
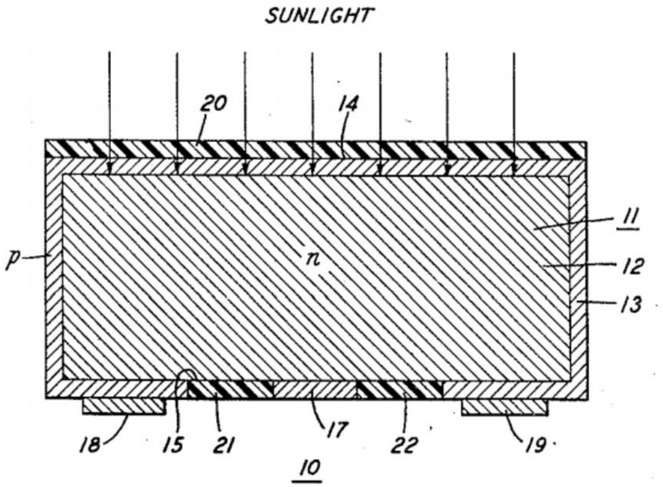
The early days of c-Si solar cells

Ohl (1941)



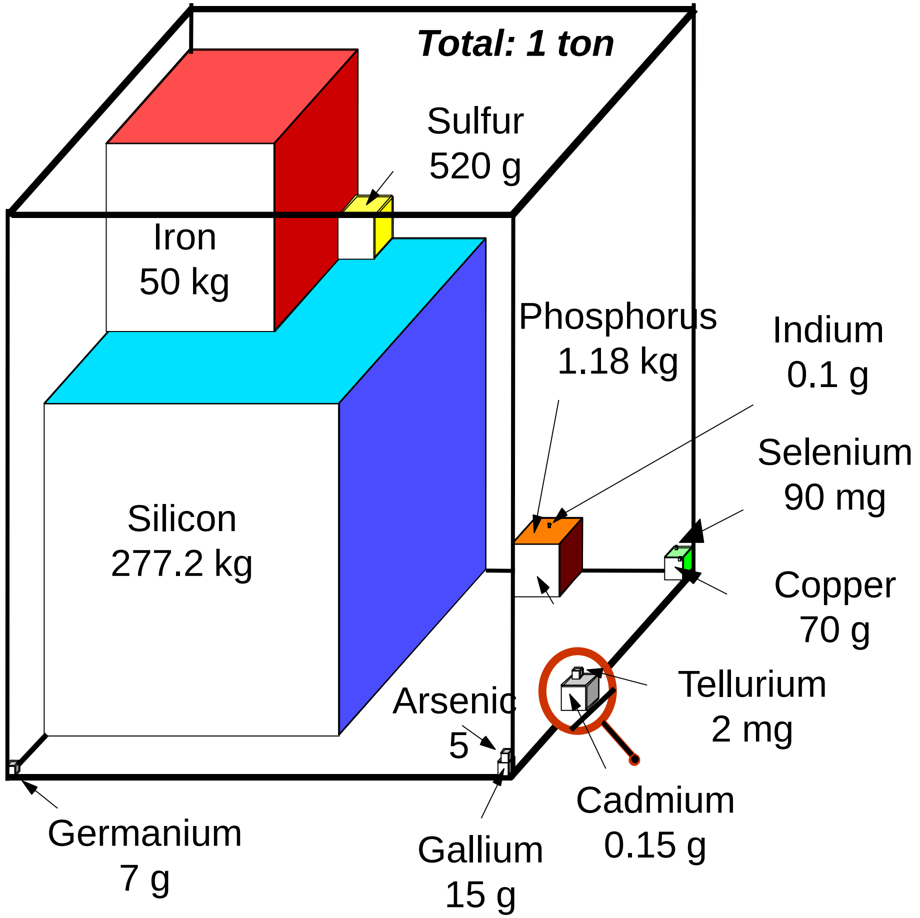
vertically solidified p-n junction
Cut vertical slab
attach Cu electrodes

Pearson, Chapin, Fuller (1952)

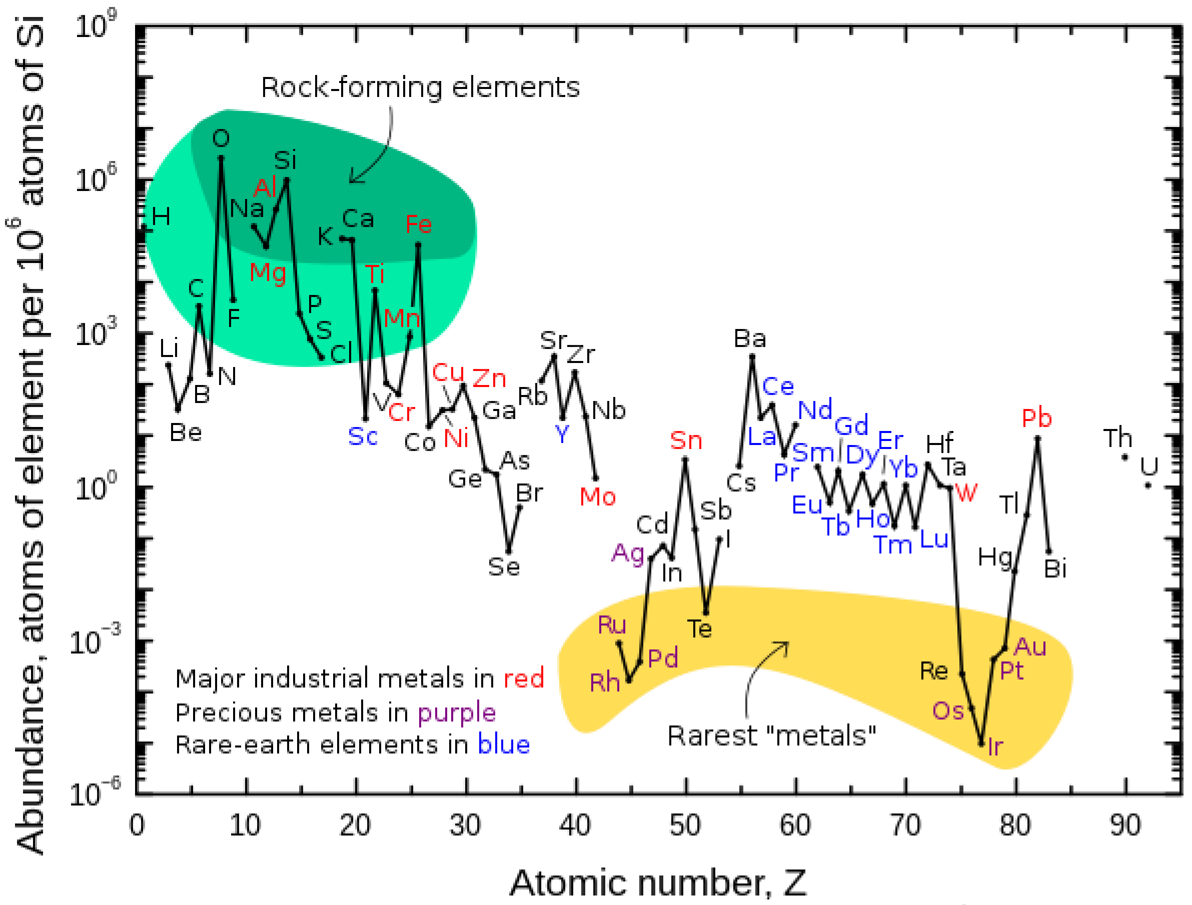


n-wafer
p-diffusion
rear etch
Rh rear contact configuration
Efficiency: approximately 6%

Why silicon?



Availability of various materials in 1 ton of earth crust



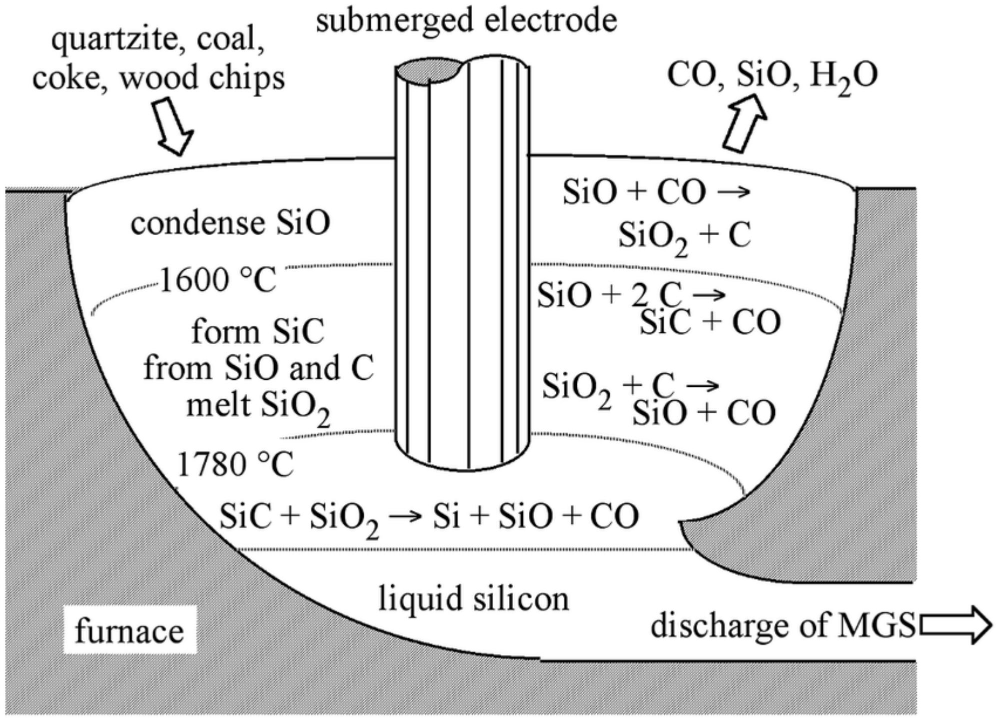
US Geological Survey

Silicon: benign and abundant resource, well understood material

Large Area Electronic Materials – Crystalline Silicon II

F.-J. Haug

How to make Si (metallurgical grade, MG)



CNBM International

Overall reaction $SiO_2 + C \rightarrow Si + CO_2$ (1 kg Si: 34 mol => at least 1.5 kg CO2 per kg Si

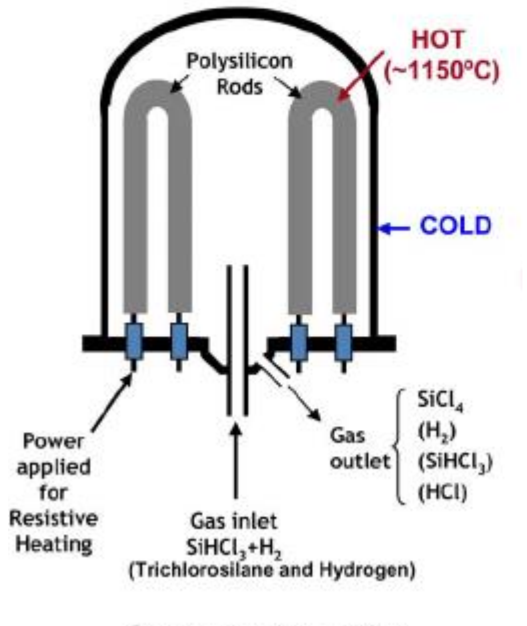
Split into sub-reactions in within furnace

Si only produced in arc zone (>1800°C)

Fe or Ca can enhance reaction (but must be removed later since recombination active)

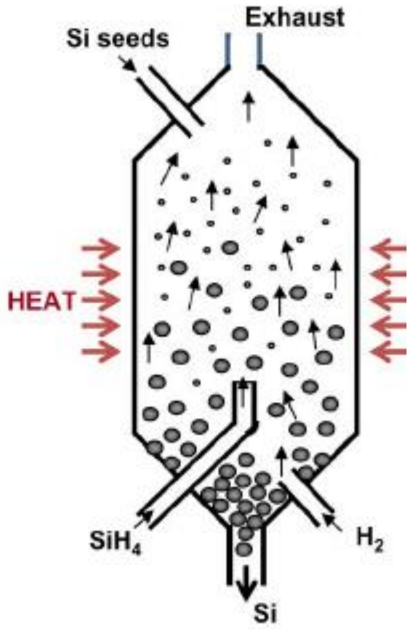
Purification of Si

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



Siemens Reactor

Alternative: FBR



Fluidized Bed Reactor

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)

Melt silicon (1417°C)

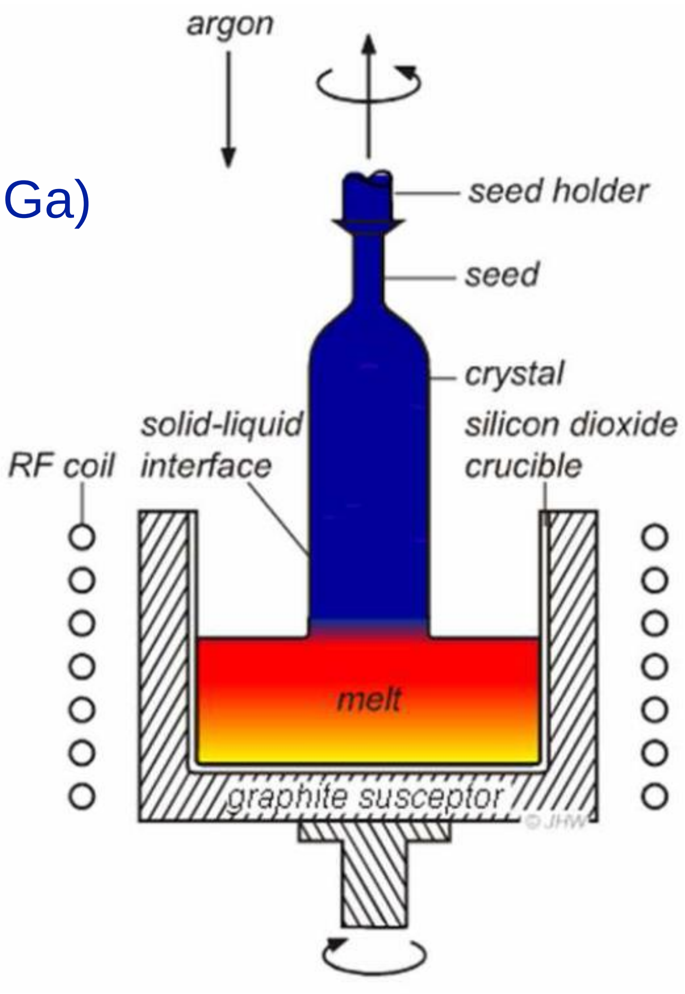
Add dopants (for solar cells historically B, now Ga)

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)

Generally acceptable for solar cells,
Main issue: B-O complex
=> flood with inert gas (Ar), replace B by Ga

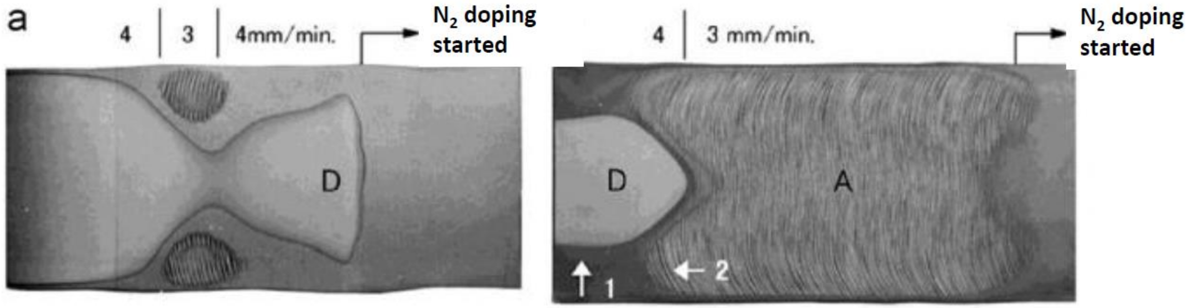


Single crystal growth (float zone method)

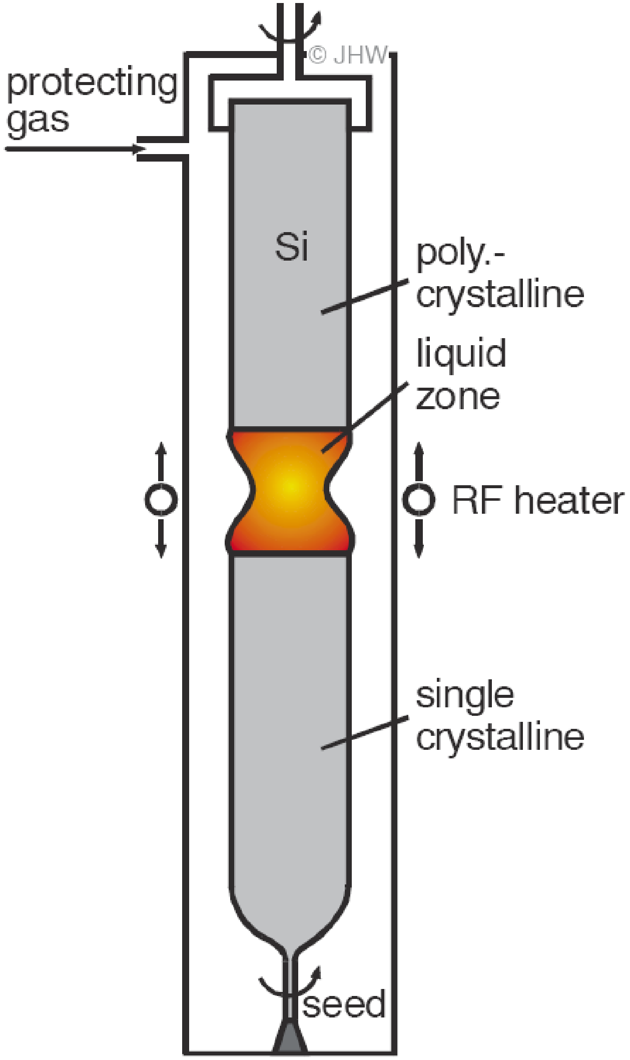
Pull RF coil along polycrystalline rod within quartuz tube
Accumulate impurities by segregation in melt

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 el. J. Cryst Growth 2011

Cast silicon (multicrystalline)

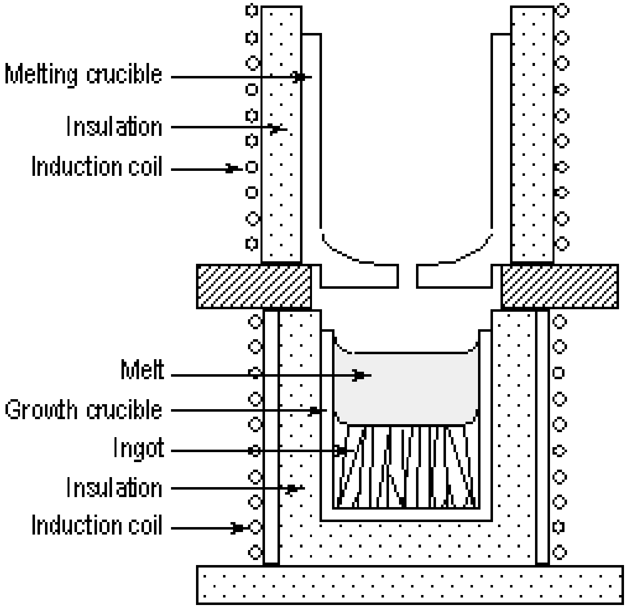
Casting into graphite or quartz molds

Molds possibly coated with Si_3N_4

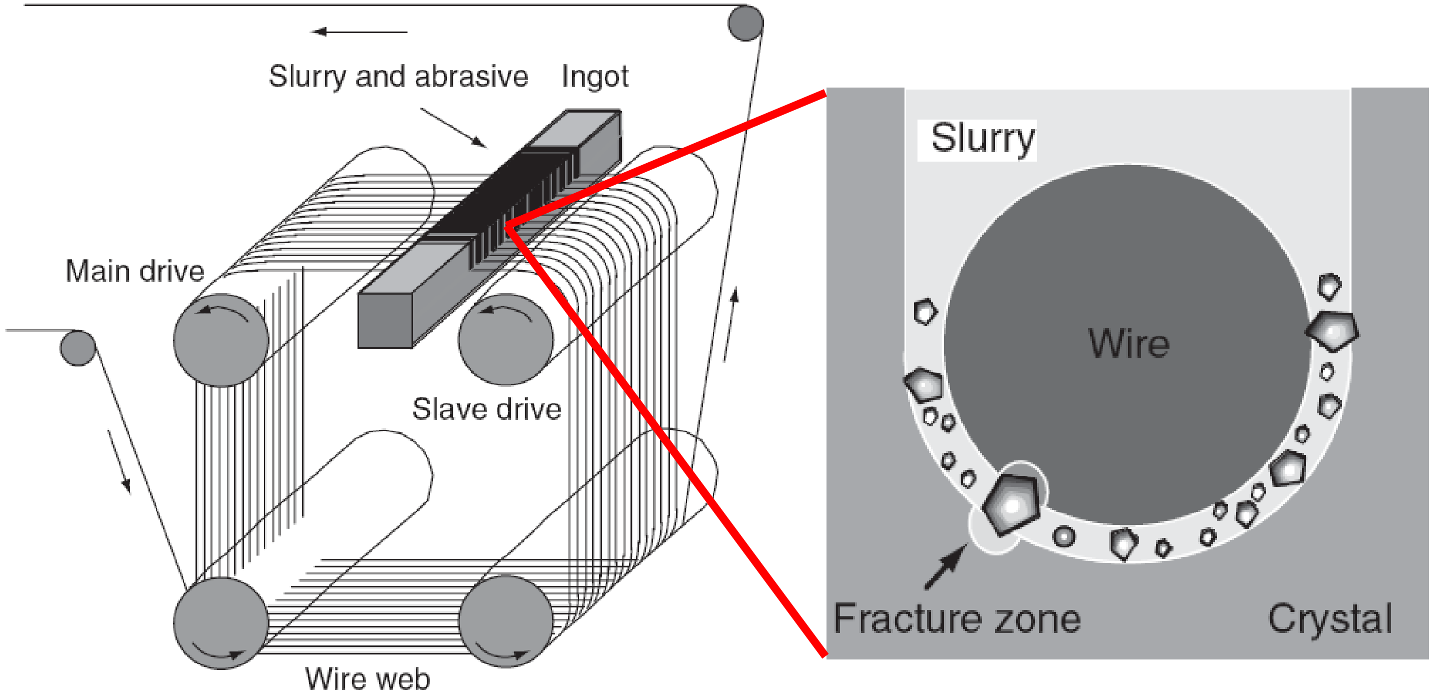
Place wafers at bottom and sides for nucleation of “enhanced mc-Si”

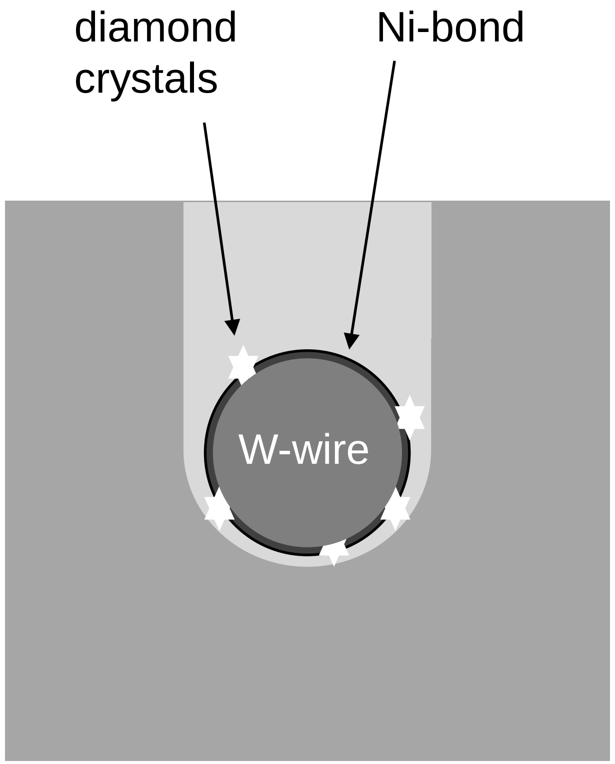
typically 690 mm x 690 mm, 240 kg

Solidification takes ca. 30 to 60 h



Wafer sawing





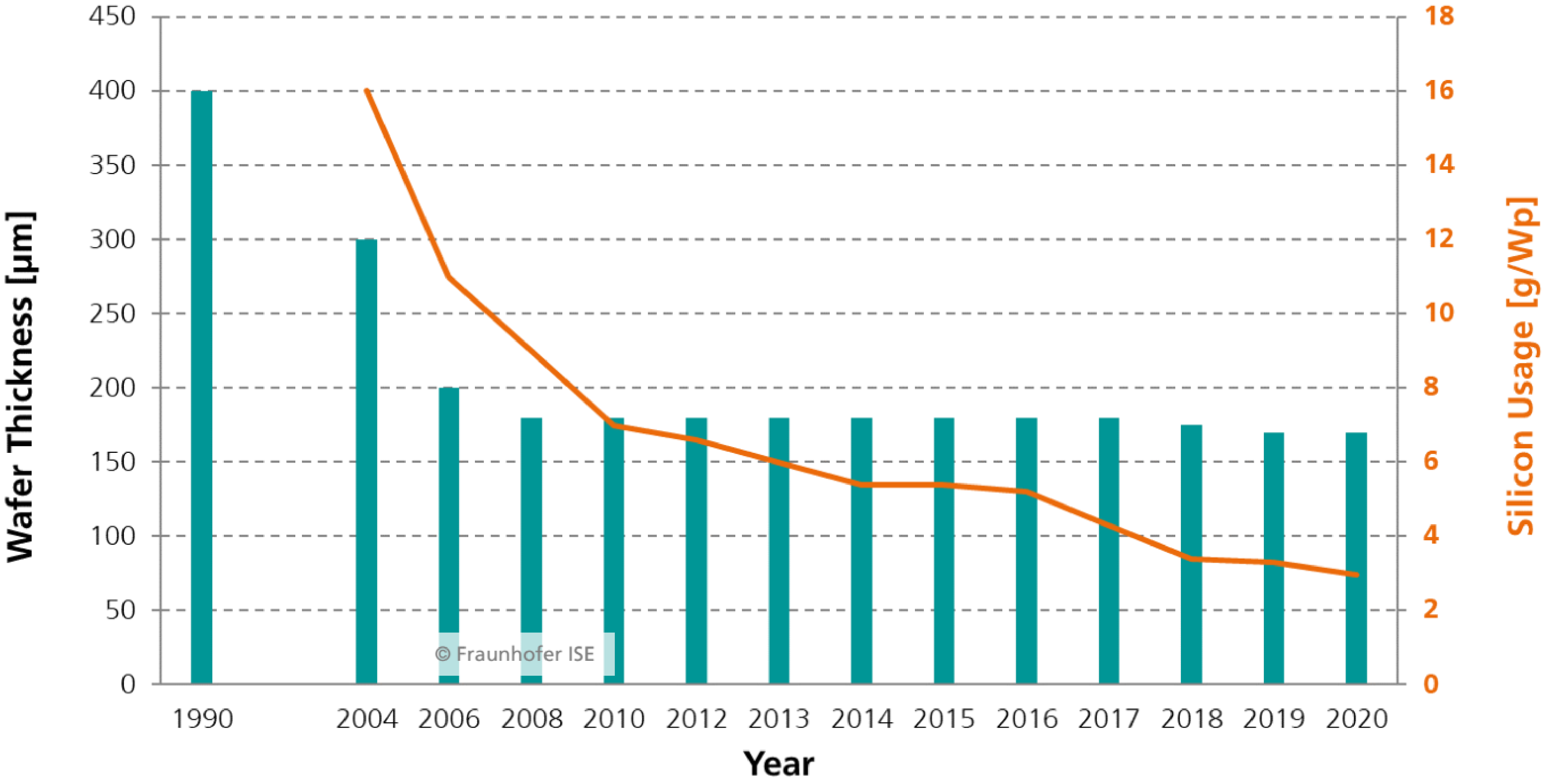
Originally: cutting with wire and SiC slurry

- 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

Wafer thickness



Photovoltaics report 2021,
Fraunhofer ISE

Summary

FZ-Si:

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

Cz-Si:

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

mc-Si:

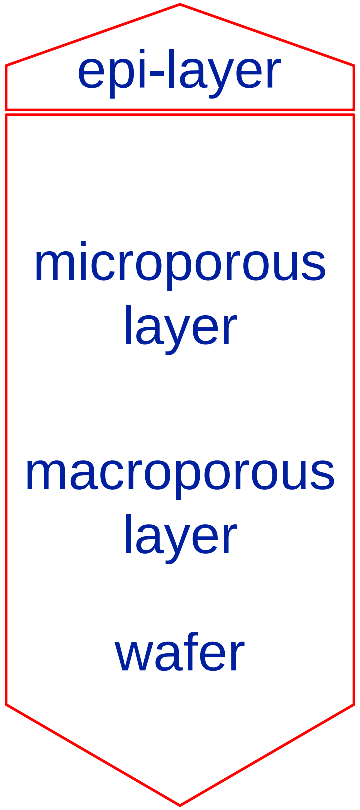
- volume production, >50% of market, usually p-type
- low cost cells, ca. 17-19%, records up to 22%

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

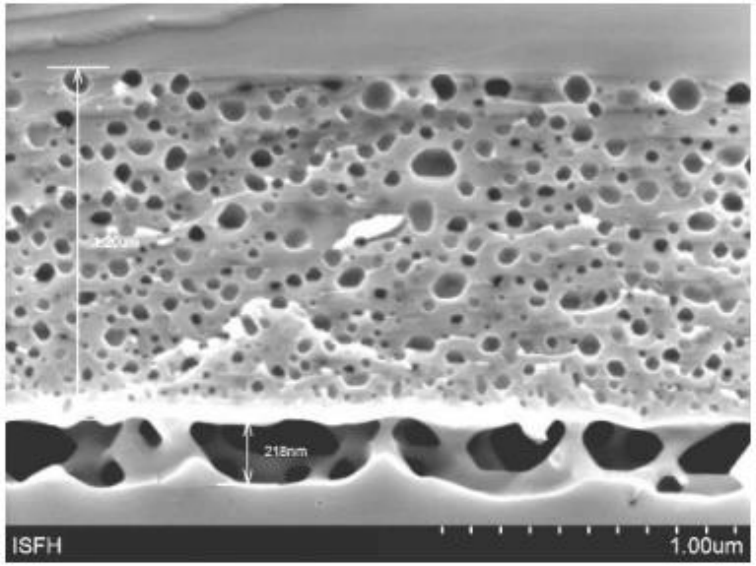
Kerf-free wafering

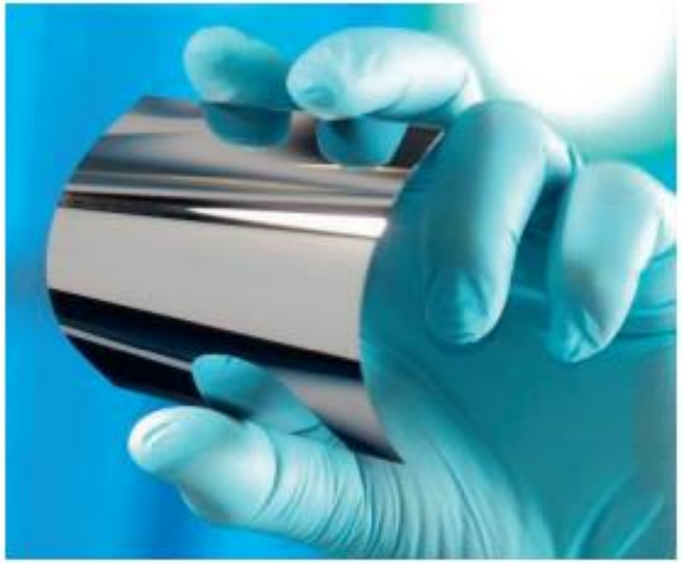

epi-layer

microporous layer

macroporous layer

wafer



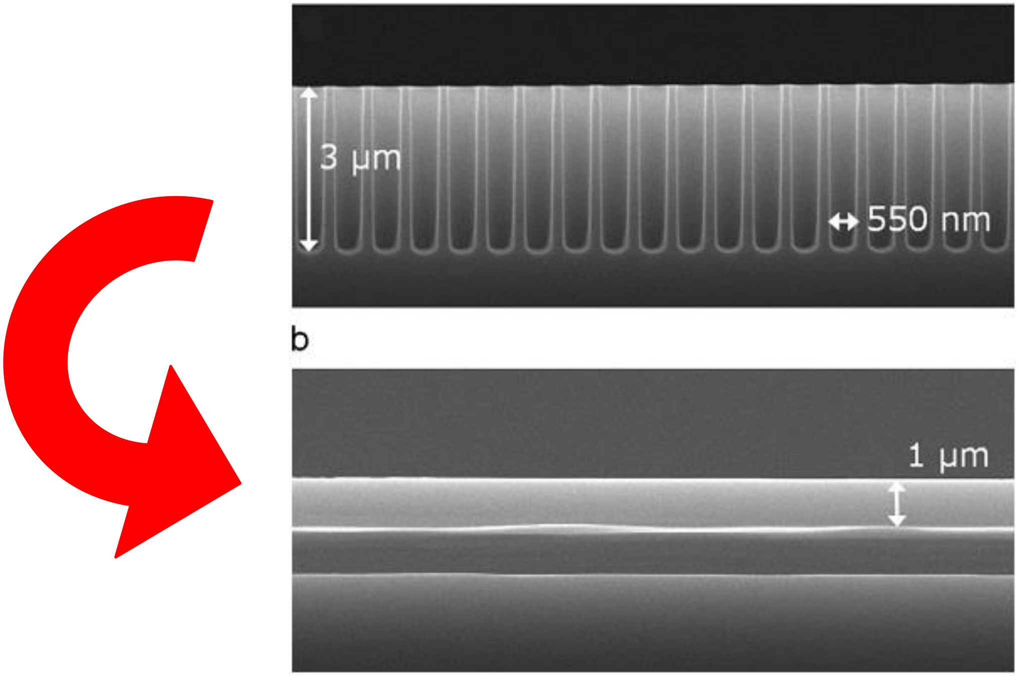


apply front of “standard” c-Si cell fabrication
remove from substrate (and glue to substrate)
process back (with a process that does not harm the glue)

F. Haase, JAP (2013)

Kerf-free wafering

60 min
1150°C



DRIE etch

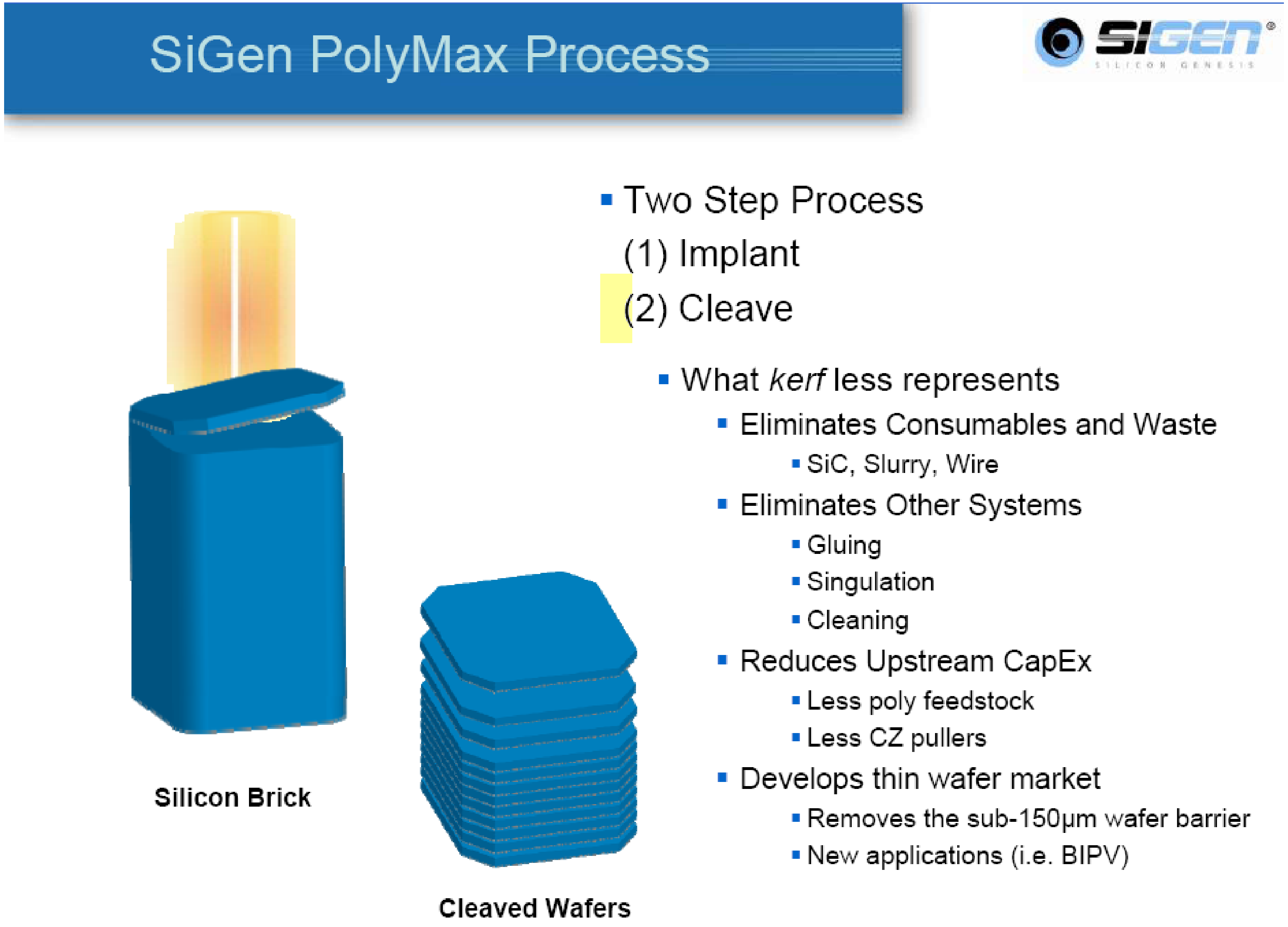
wafer

free standing membrane
void
wafer

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

I. Gordon, SEM (2011)

Kerf-free wafering



SiGen PolyMax Process

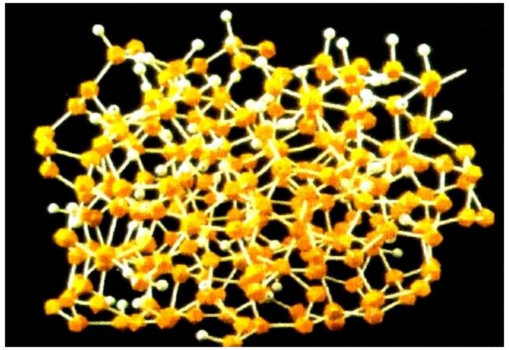
- Two Step Process
  (1) Implant
  (2) Cleave
  - What *kerf* less represents
    - Eliminates Consumables and Waste
      - SiC, Slurry, Wire
    - Eliminates Other Systems
      - Gluing
      - Singulation
      - Cleaning
    - Reduces Upstream CapEx
      - Less poly feedstock
      - Less CZ pullers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

Silicon Brick

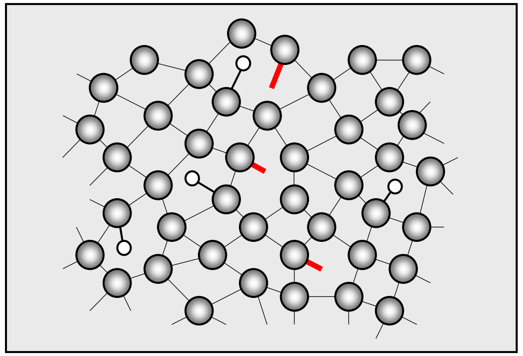
Cleaved Wafers

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)



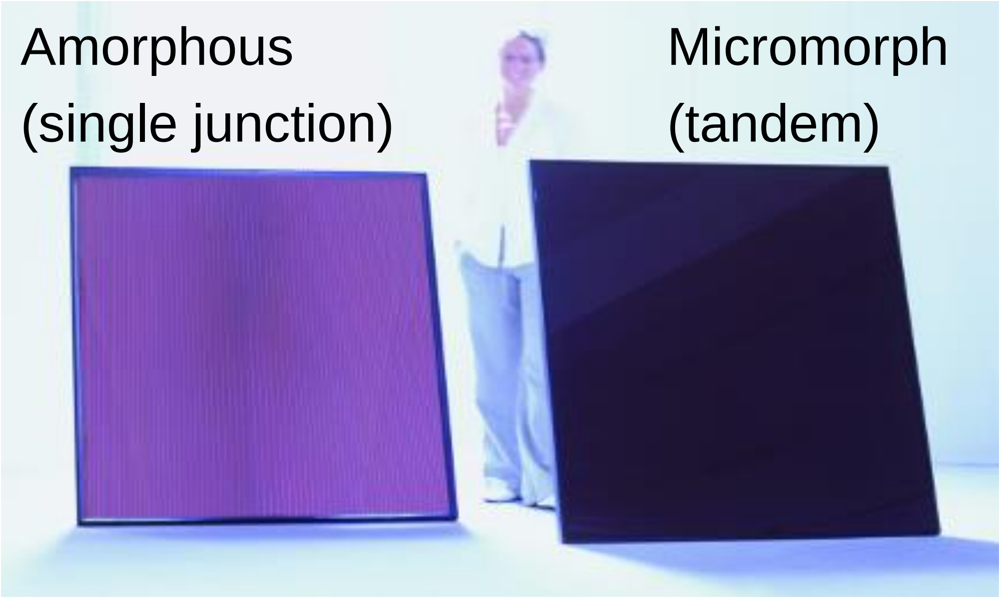
Defect equilibrium (frozen in at T_{growth})
$Si\text{-}H \leftrightarrow D^0 + H$

Passivation of 99.9999%,
but: about N_D~10^{16} cm^{-3} remain

a-Si commercialization

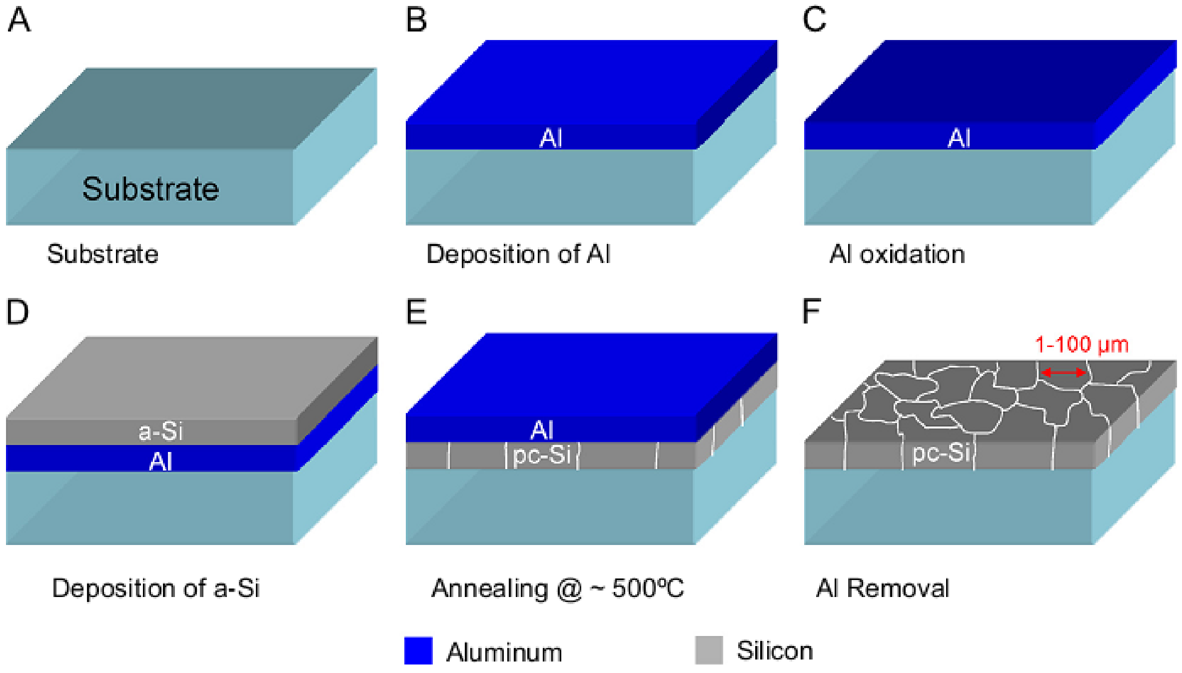
Strong business during early 2000s
Applied Materials, Oerlikon (equipment manufacturers)
Kaneka, UniSolar, Sharp, Mitsubishi, Bosch, etc. (Solar module eff. ca. 10%)

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



Source
Oerlikon Solar
(TEL Solar)

Al-induced crystallization (AIC)



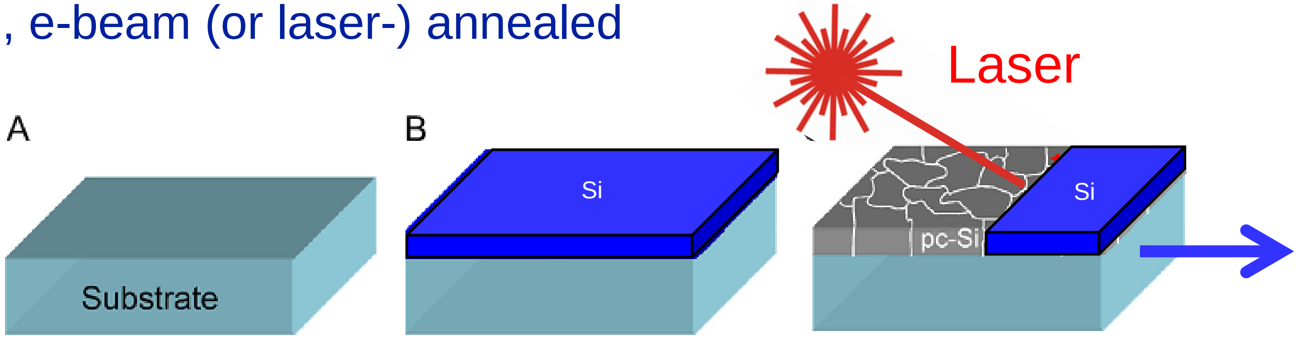
Melt Al, dissolve Si-film in liquid Al (eutectic at 577°C)
Growth of Si at interface to glass, epitaxy around nucleation sites

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

D. van Gestel, SEM (2013)

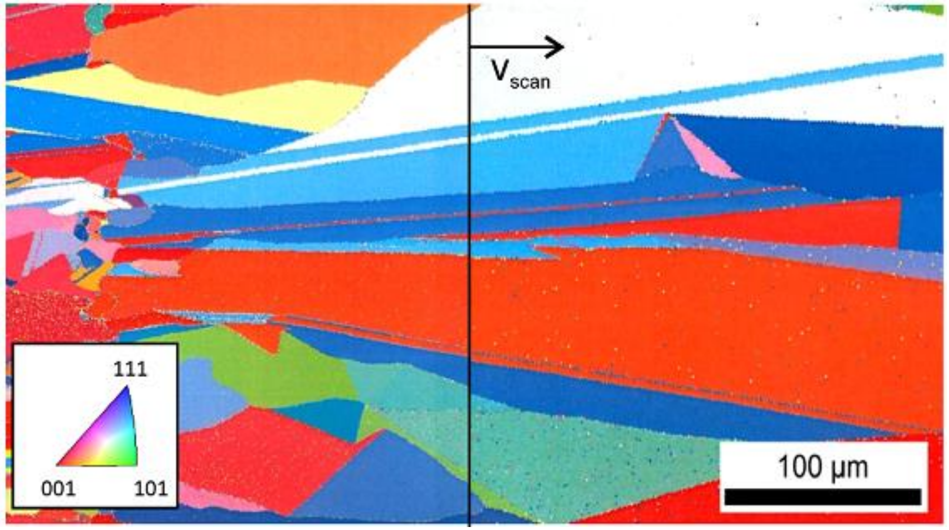
Liquid phase crystallized silicon

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



Deposition of Si

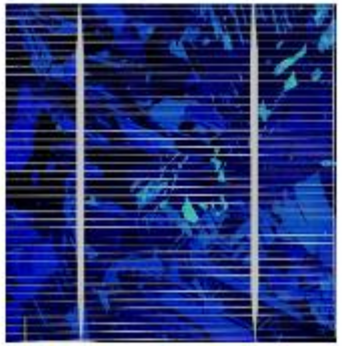
Orientation map by EBSD



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

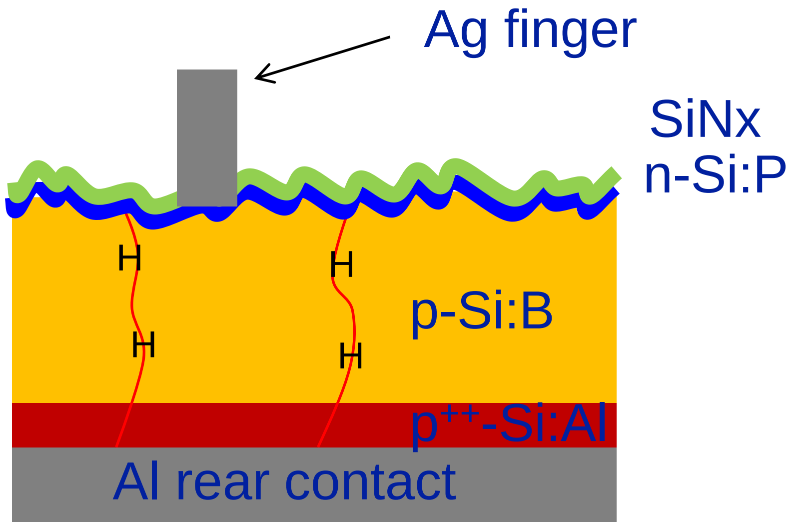
C. Becker, SEM (2013)
J. Haschke, SEM (2014)

c-Si processing



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

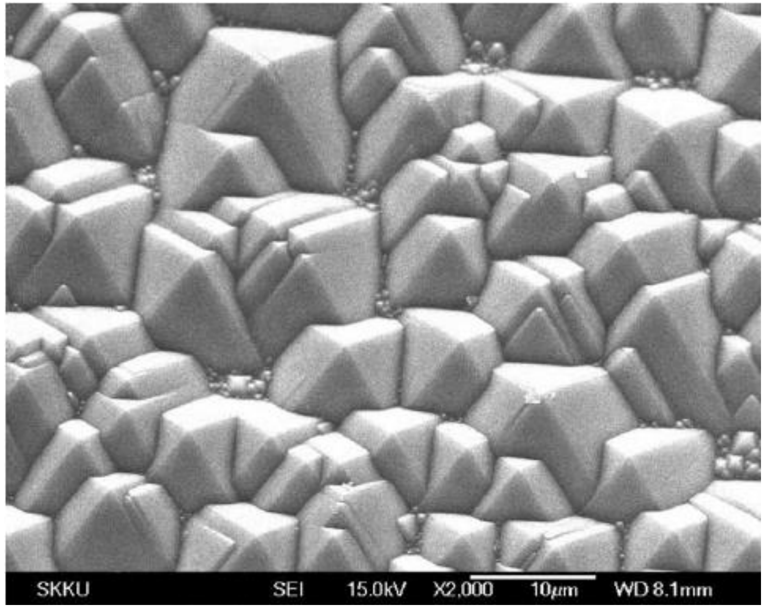
Metallization (screen printing)

Firing

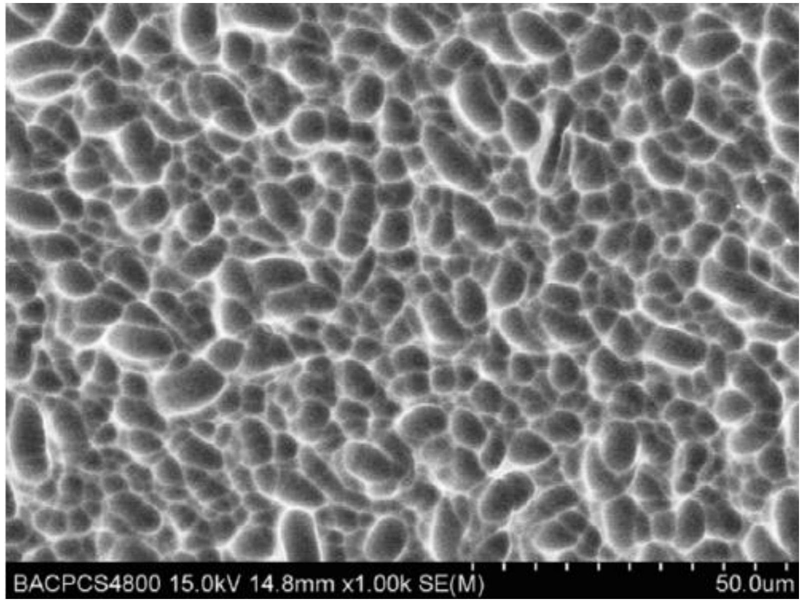
- release H from SiNx:H
- sinter Ag/glass through SiNx:H
- melt and solidify Si-Al eutectic

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

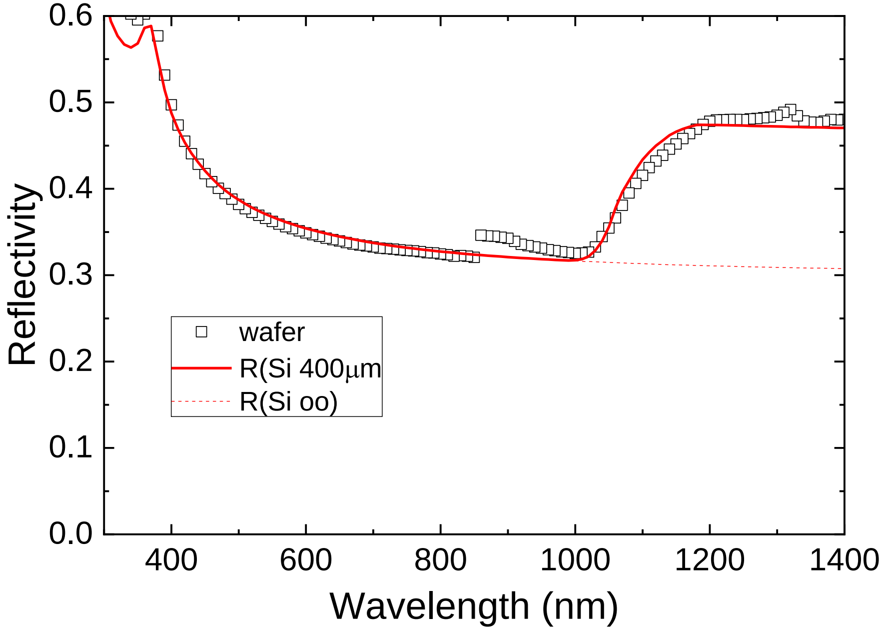


Issue: no longer applicable for diamond wire

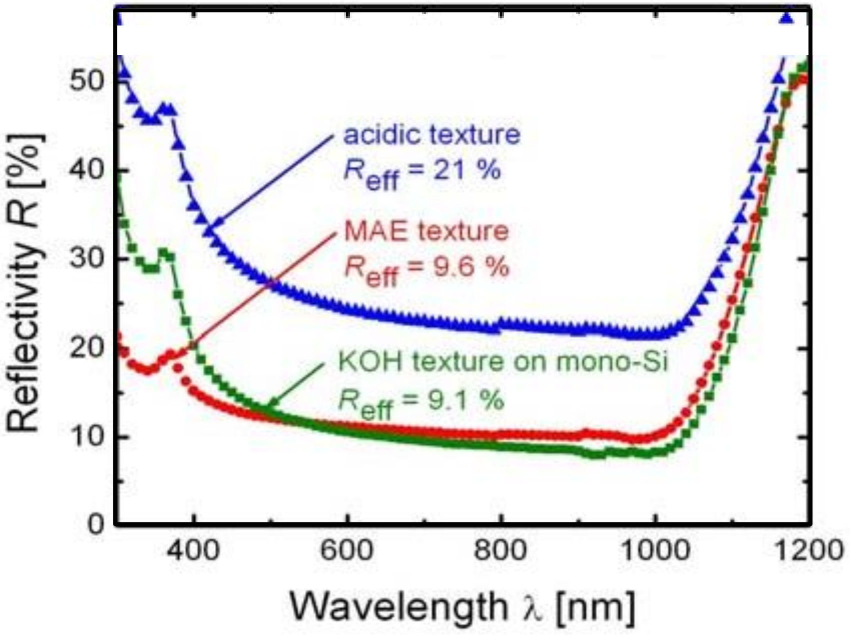
e.g. Gangopadhyay, SEM (2016)
e.g. Zhou, SEM (2013)

Reduction of reflectivity by texture

Bare silicon (n ≈ 3.5)

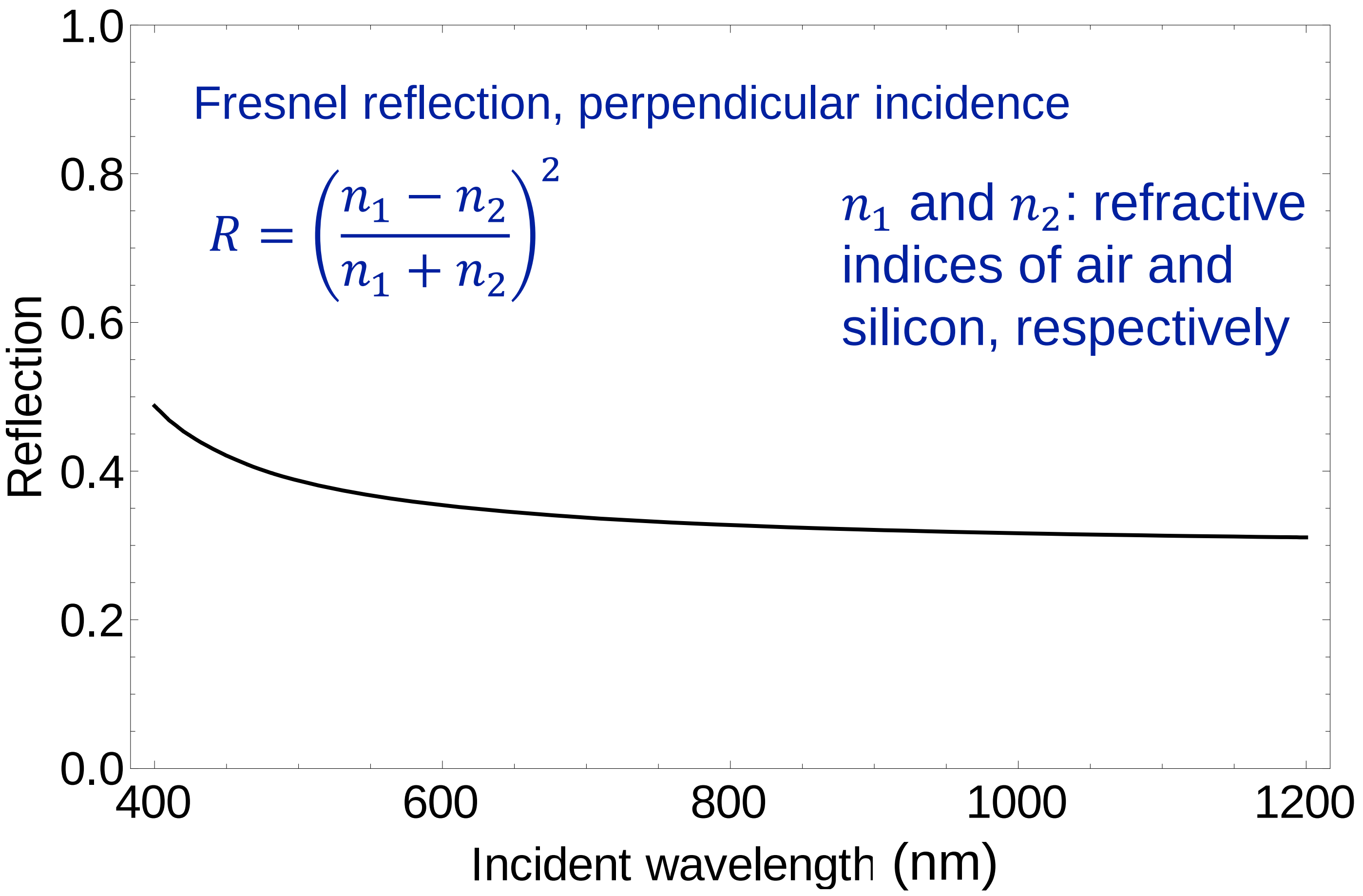


Textured silicon



e.g. Lipinki, PVSEC (2009)

AR effect by double rebound

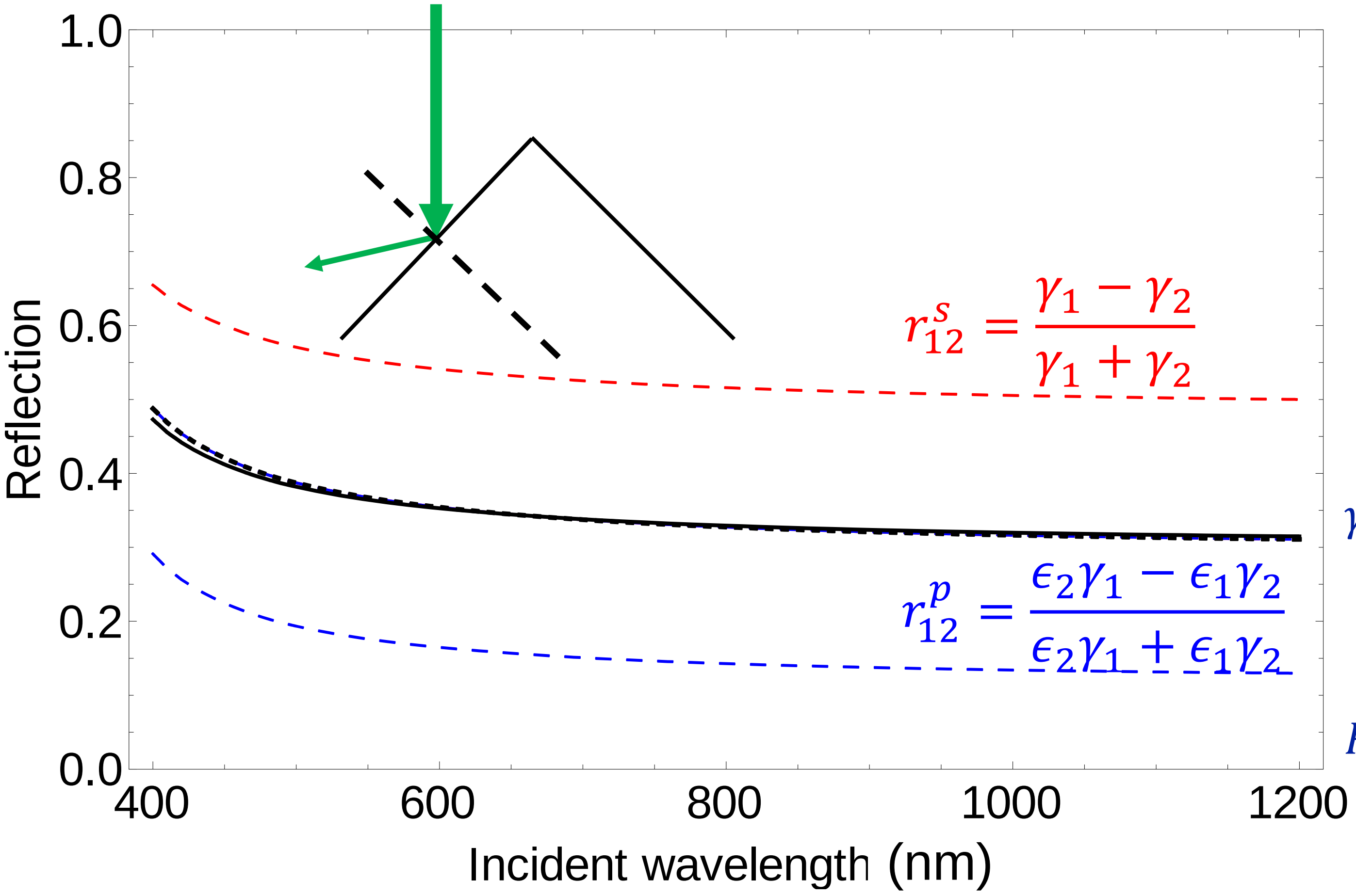


Fresnel reflection, perpendicular incidence

$$R = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2$$

n_1 and n_2: refractive indices of air and silicon, respectively

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

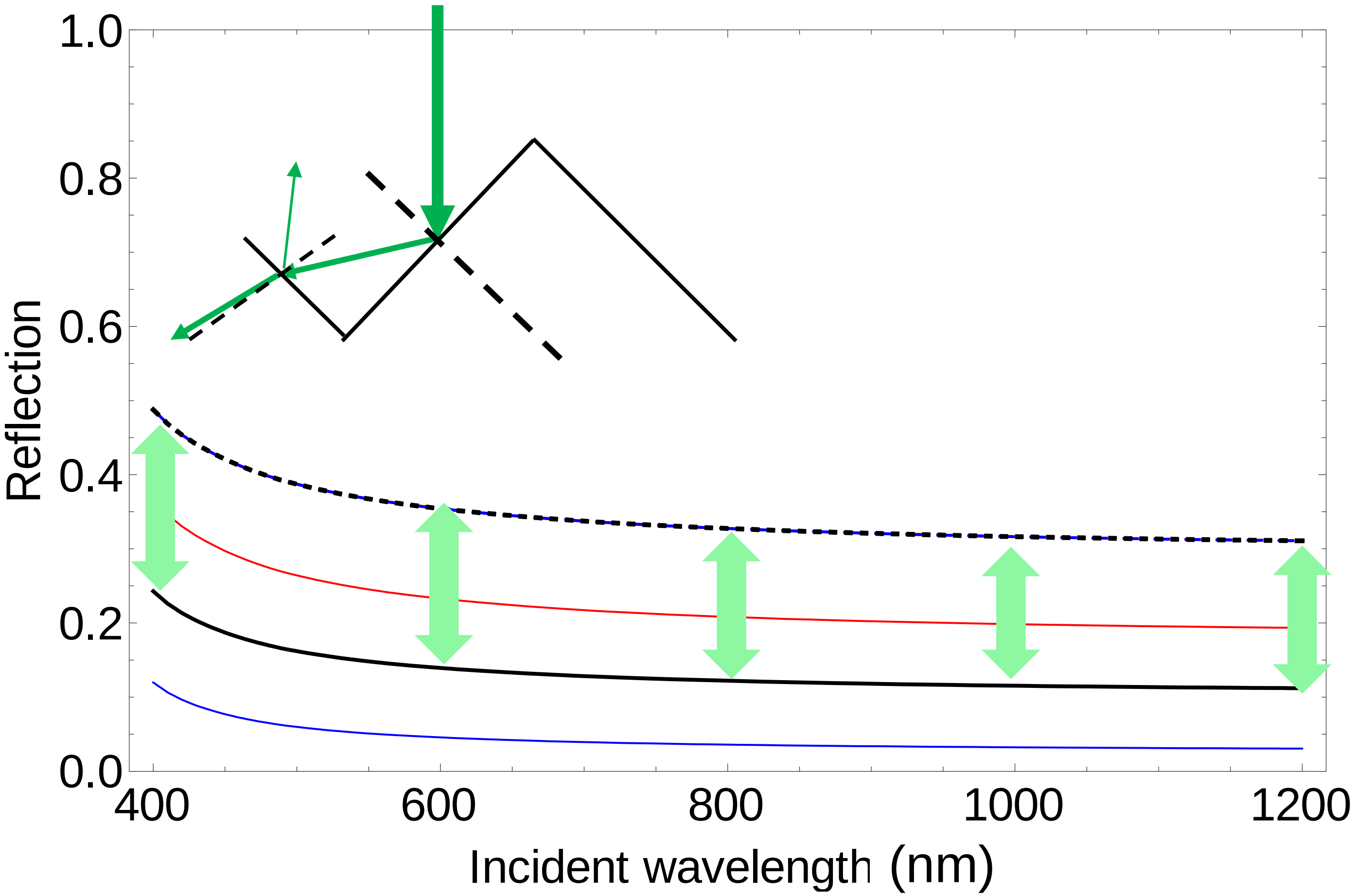
$$\gamma_i = k_0\sqrt{\epsilon_i - \sin^2\theta}$$

unpolarized average

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

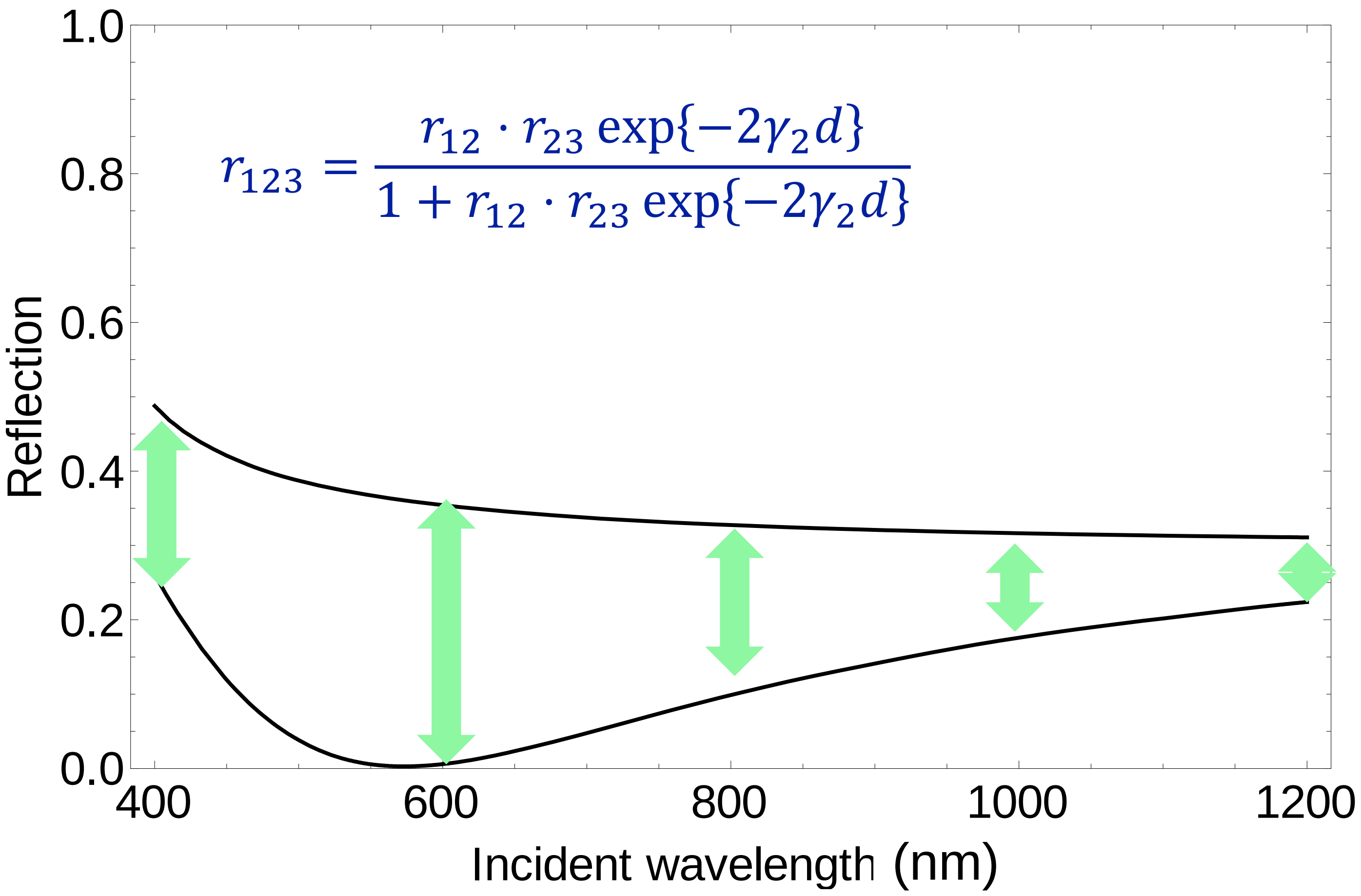
Practically no difference in polarisation-averaged reflection

Reflection with rebound ($\theta > 45°$)



Reduction from 30% to 10%

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

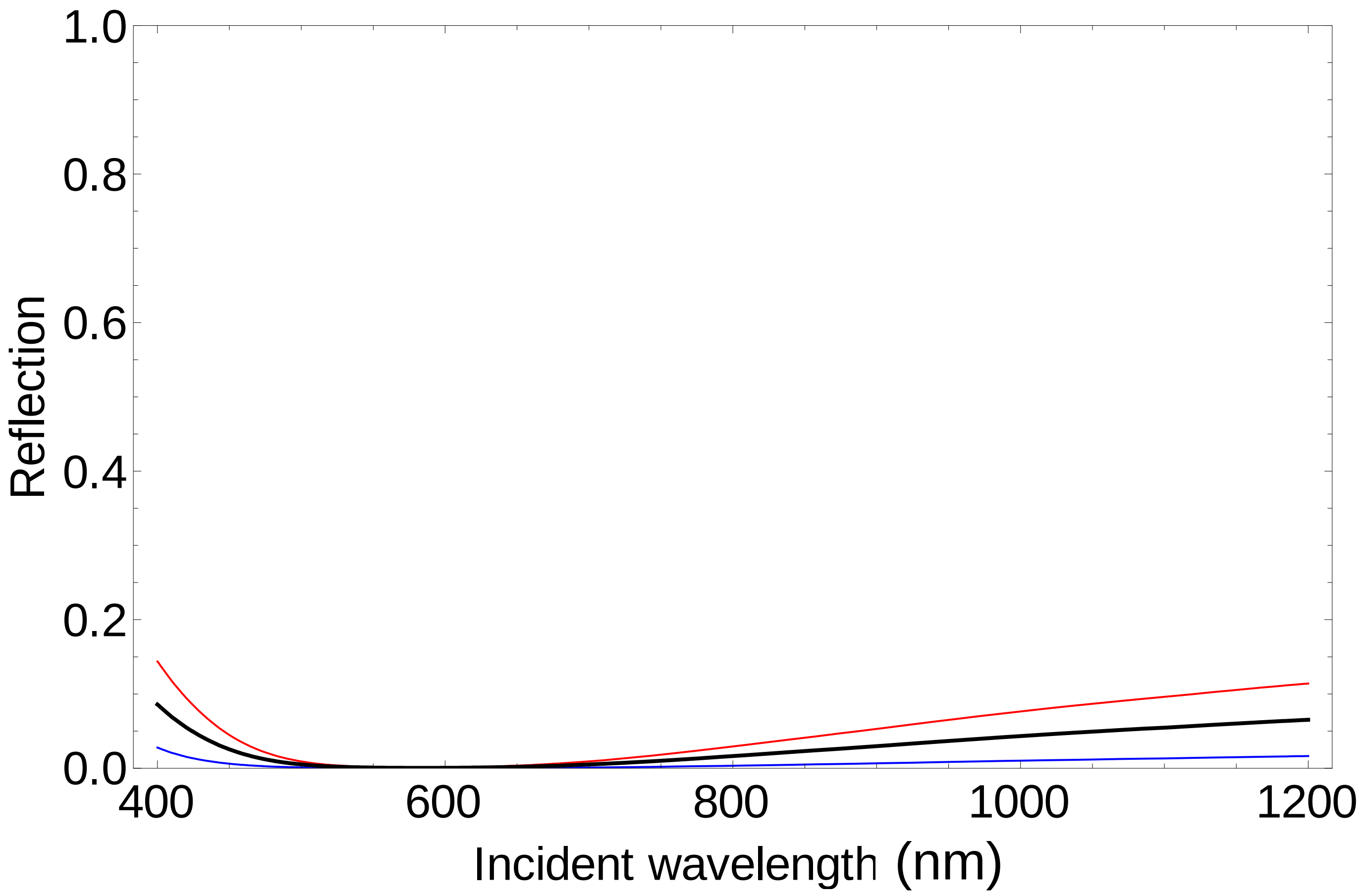


$$r_{123} = \frac{r_{12} \cdot r_{23} \exp\{-2\gamma_2 d\}}{1 + r_{12} \cdot r_{23} \exp\{-2\gamma_2 d\}}$$

ITO: transparent
contacts for
HIT solar cells

similar with SiNx

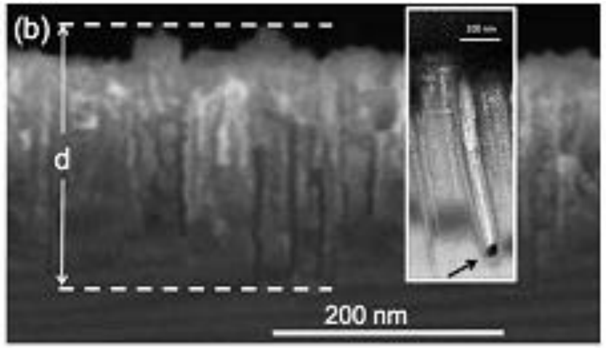
Effect of double rebound and AR coating

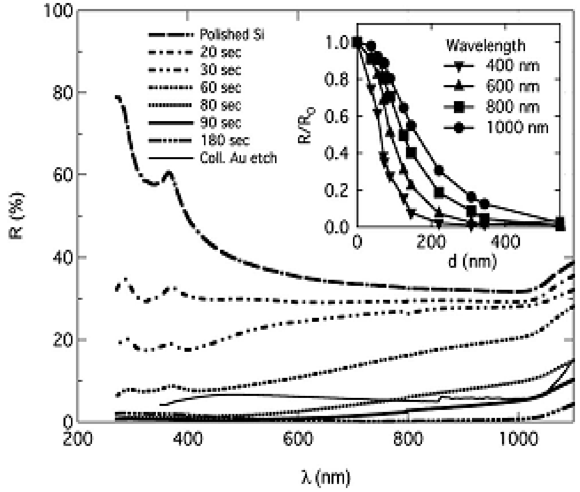


integrated over ROI :
< 3% absorption

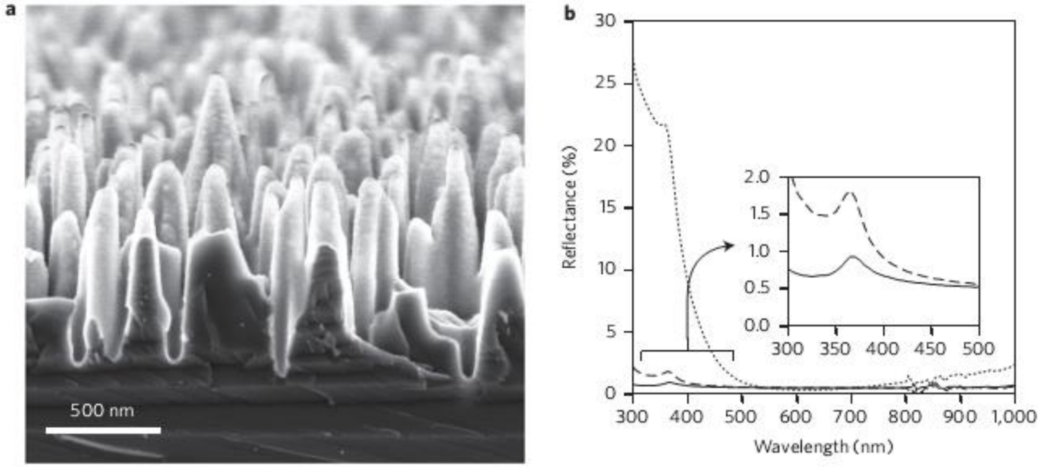
What else?

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



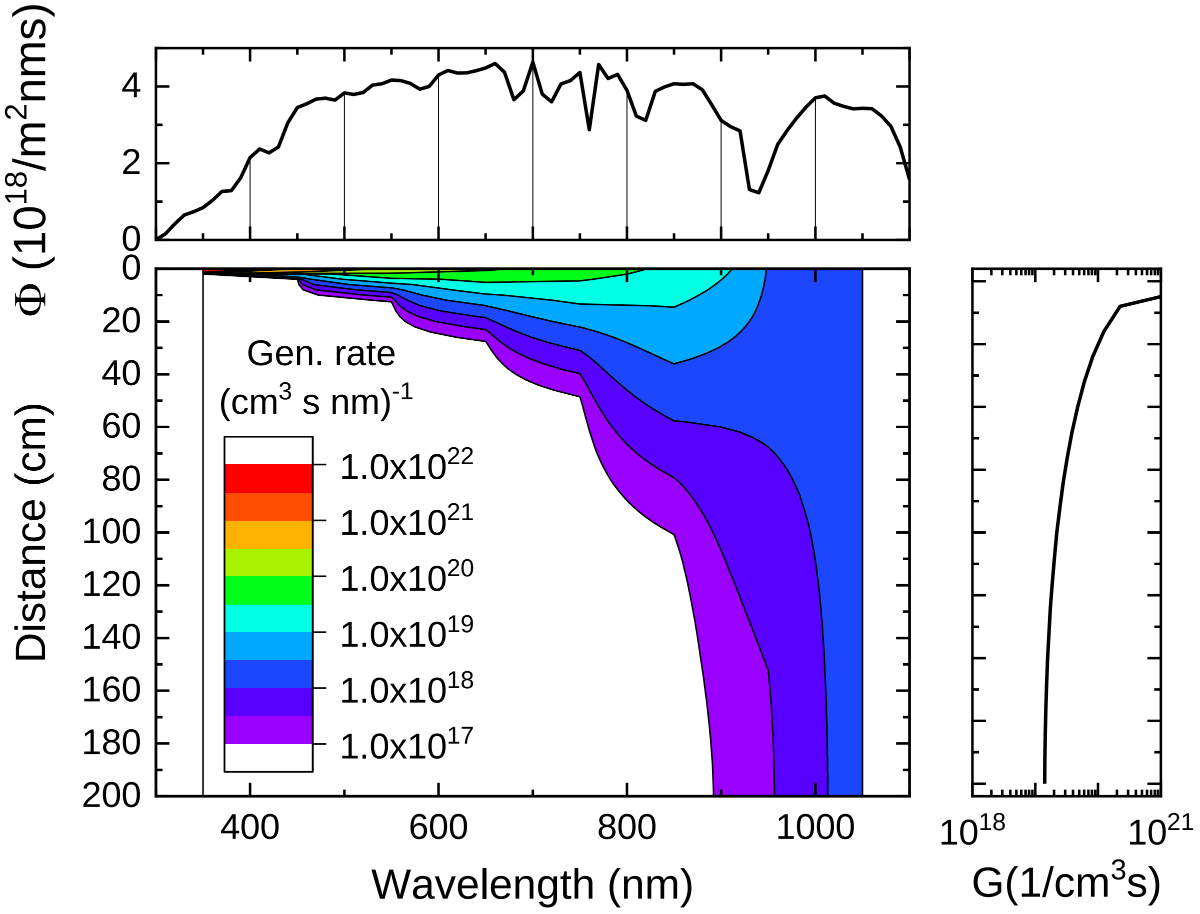


- “black silicon”
  => extreme texture,
  multiple fwd. reflections
  (difficult to passivate,
  works with rear contacts)



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

Generation rate



Short λ: strong absorption
=> Large $G(x)$ at front

Long λ: weak absorption
=> Almost uniform $G(x)$ in bulk

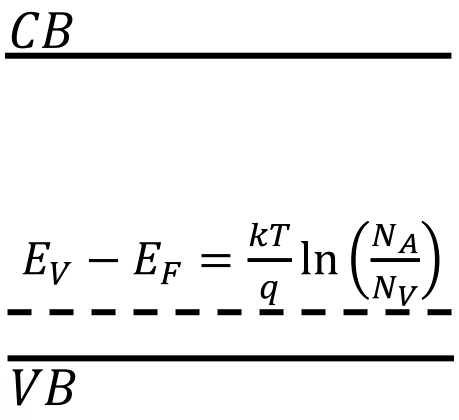
QFL splitting

When no carriers are extracted
(e.g. semiconductor w/o contacts or solar cell at Voc):

Recombination rate R = Optical generation rate G

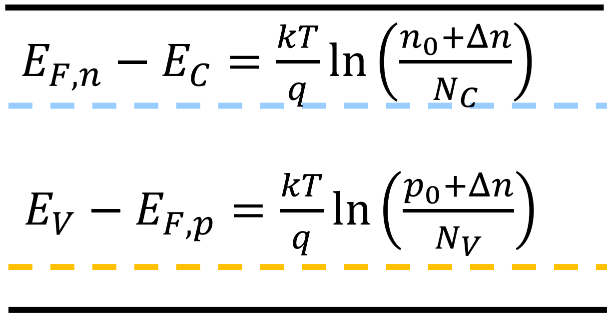
$\Delta n = G\tau$ (excess minority carrier density in steady state)

Dark:
thermal equilibrium,
unique Fermi level



$$E_V - E_F = \frac{kT}{q}\ln\left(\frac{N_A}{N_V}\right)$$

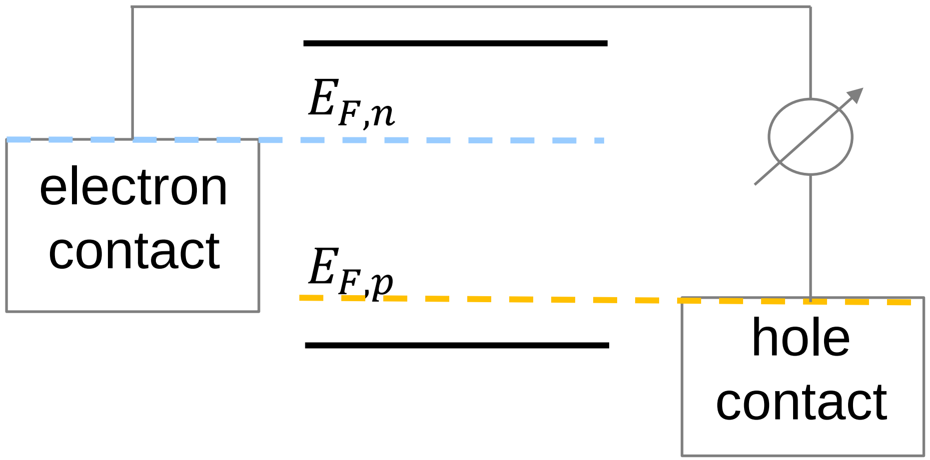
Illuminated:
Define independent
quasi Fermi levels (QFLs)



$$E_{F,n} - E_C = \frac{kT}{q}\ln\left(\frac{n_0+\Delta n}{N_C}\right)$$

$$E_V - E_{F,p} = \frac{kT}{q}\ln\left(\frac{p_0+\Delta n}{N_V}\right)$$

With idealized contacts:
QFL splitting equal to
achievable voltage



Implied open circuit voltage (iVoc)

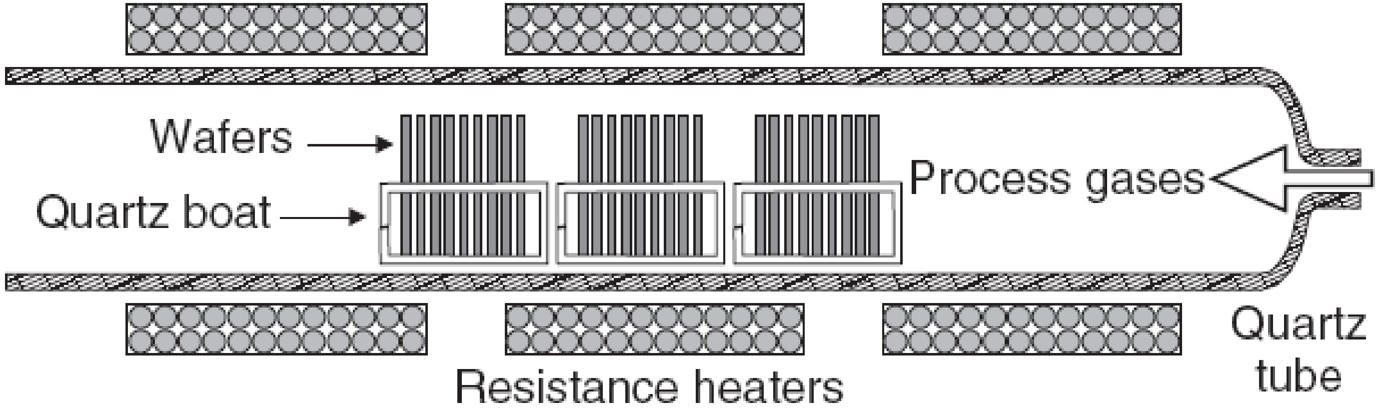
For ideal contacts: QFL splitting equal to external voltage

Assume
- $N_A = 10^{16}$ cm^{-3} (= p_0)
- $G \approx 10^{19}$ cm^{-3}s^{-3}
- $\tau \approx 1$ ms (minority carrier lifetime)

$$\Delta n = G\tau \approx 10^{16} \text{ cm}^{-3}$$

$$iV_{oc} = \frac{kT}{q} \ln \frac{np}{n_i^2} \approx 720 \text{ mV}$$

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

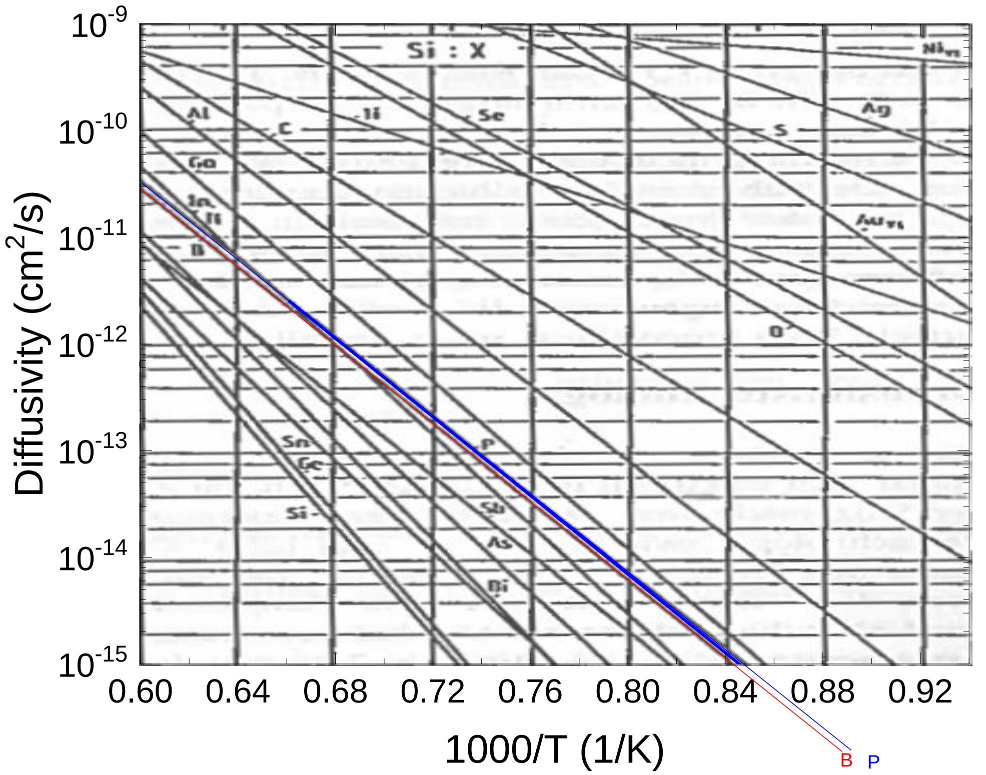
Fick's second law, often simplified for constant diffusivity D:

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

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

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

Issue: D is not constant!



Diffusion equation

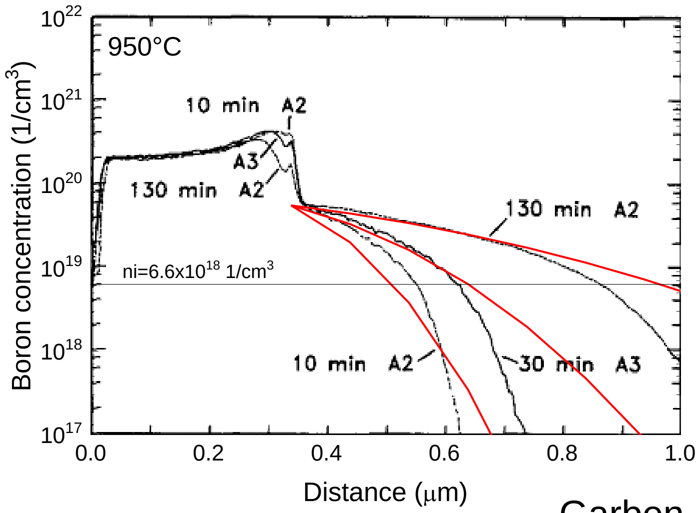
$$c(x) = c_0\,\mathrm{erfc}\left(\frac{x-x_0}{2\sqrt{Dt}}\right)$$

Constant D only approximately for high T

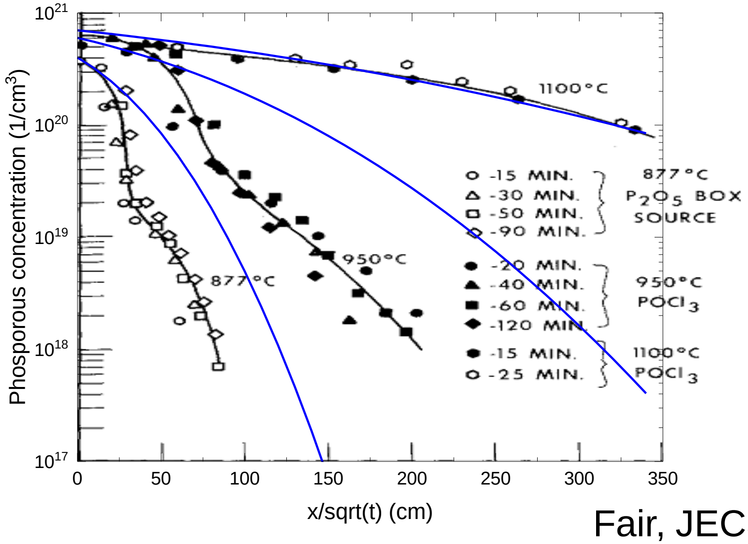
Generally:

- 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)

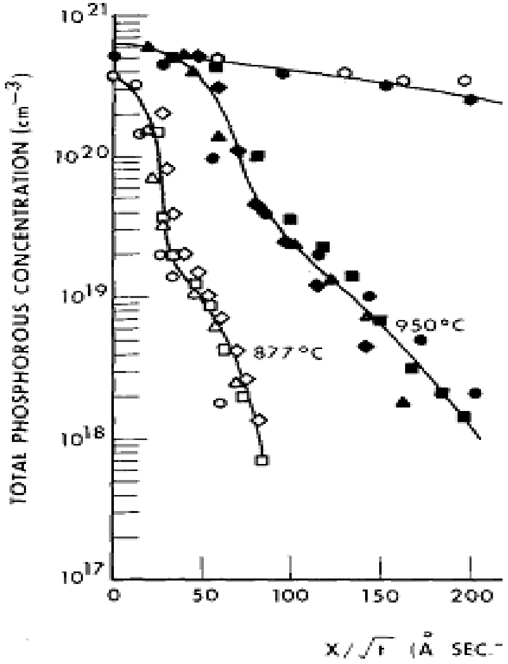
Boltzmann-Matano analysis

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 :

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

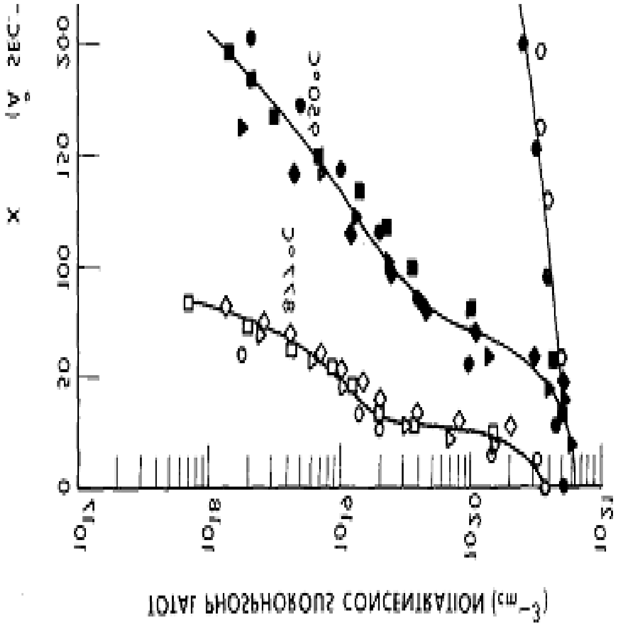
plot $c(x)$

derive
dc/dx



plot $x(c)$

integrate
xdc



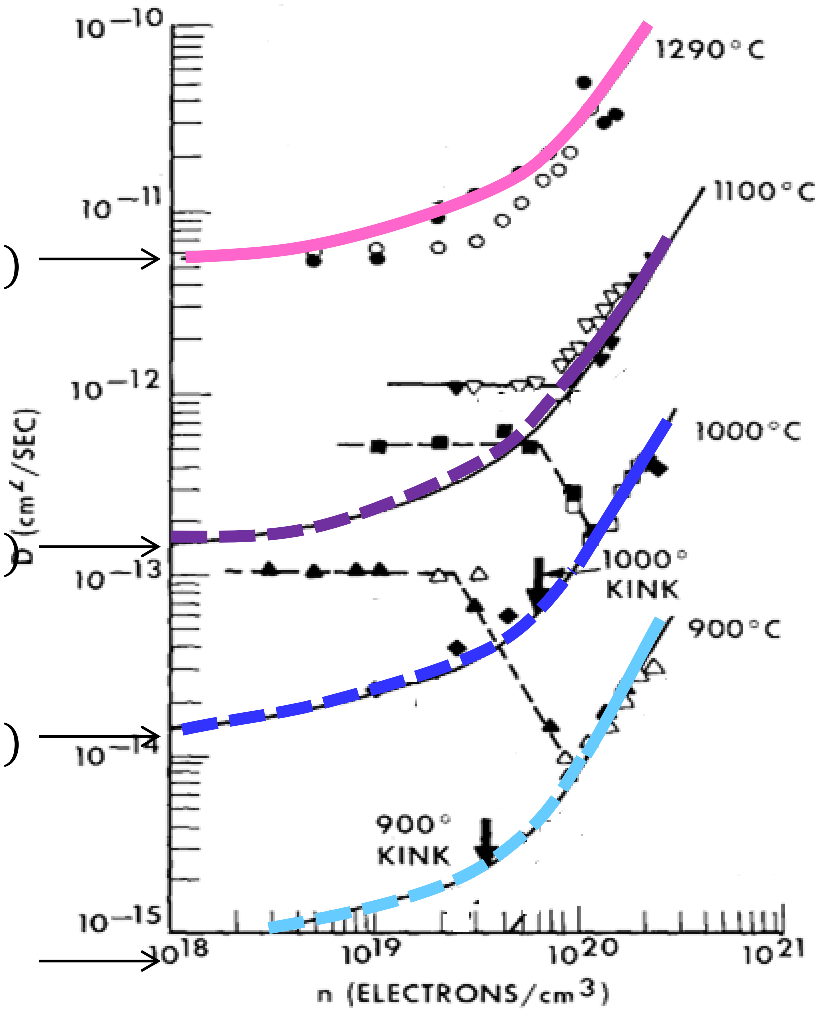
Boltzmann-Matano analysis (II)

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

$$D_P = D^0 + D^- + D^=$$

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

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



$D_i^0(1100°C)$ →

$D_i^0(1100°C)$ →

$D_i^0(1000°C)$ →

$D_i^0(900°C)$ →

Fair, JECS (1977)

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

Defect pairing

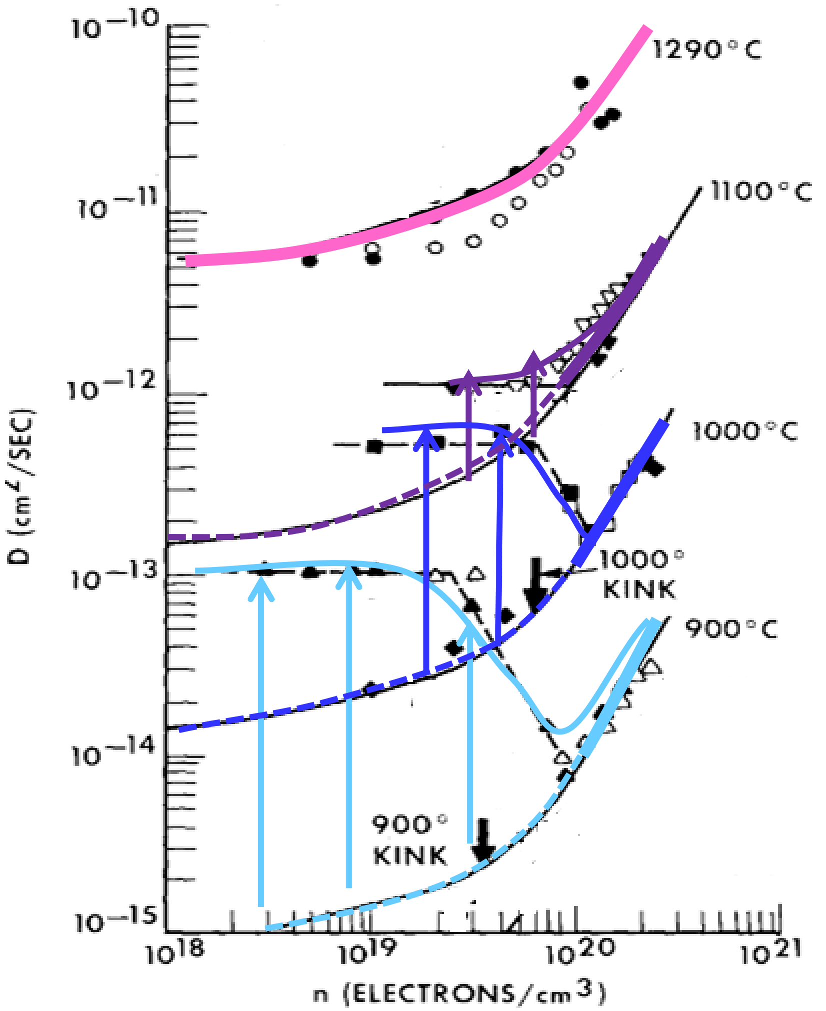
For low c, low T:

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

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



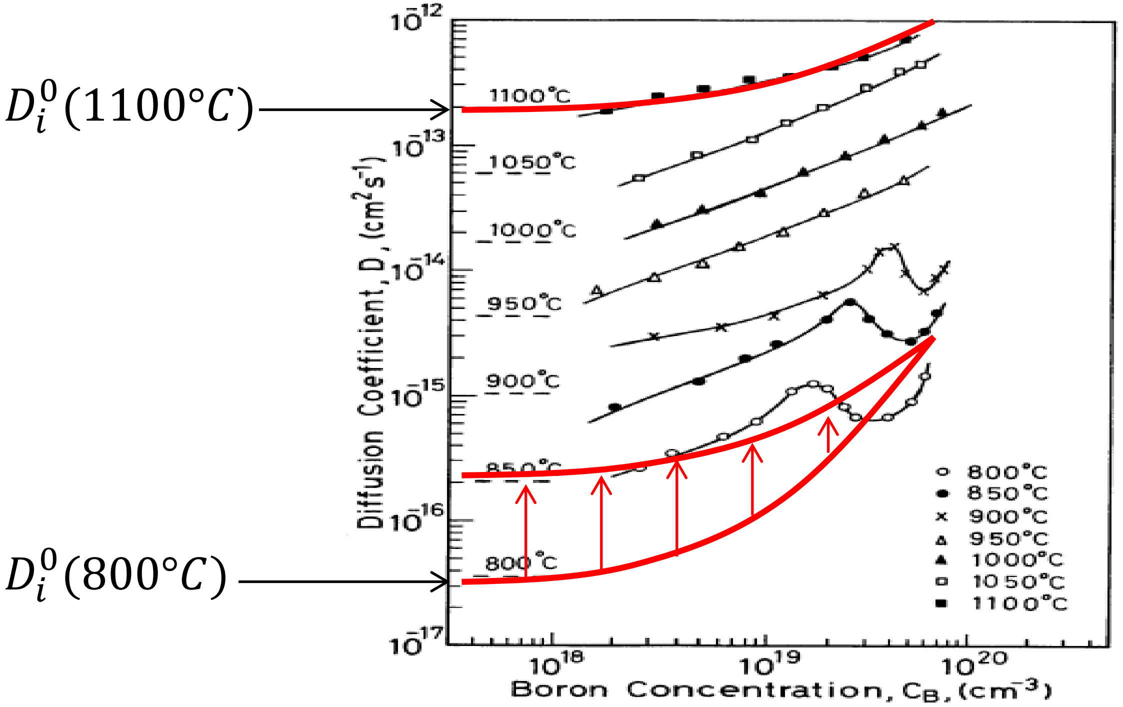
Fair, JECS (1977)

Boron diffusivity

Similar for boron, but only linear charge enhancement

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

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


$D_i^0(1100°C)$

$D_i^0(800°C)$

Matsumoto, JJAP (1983)

Modelling

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

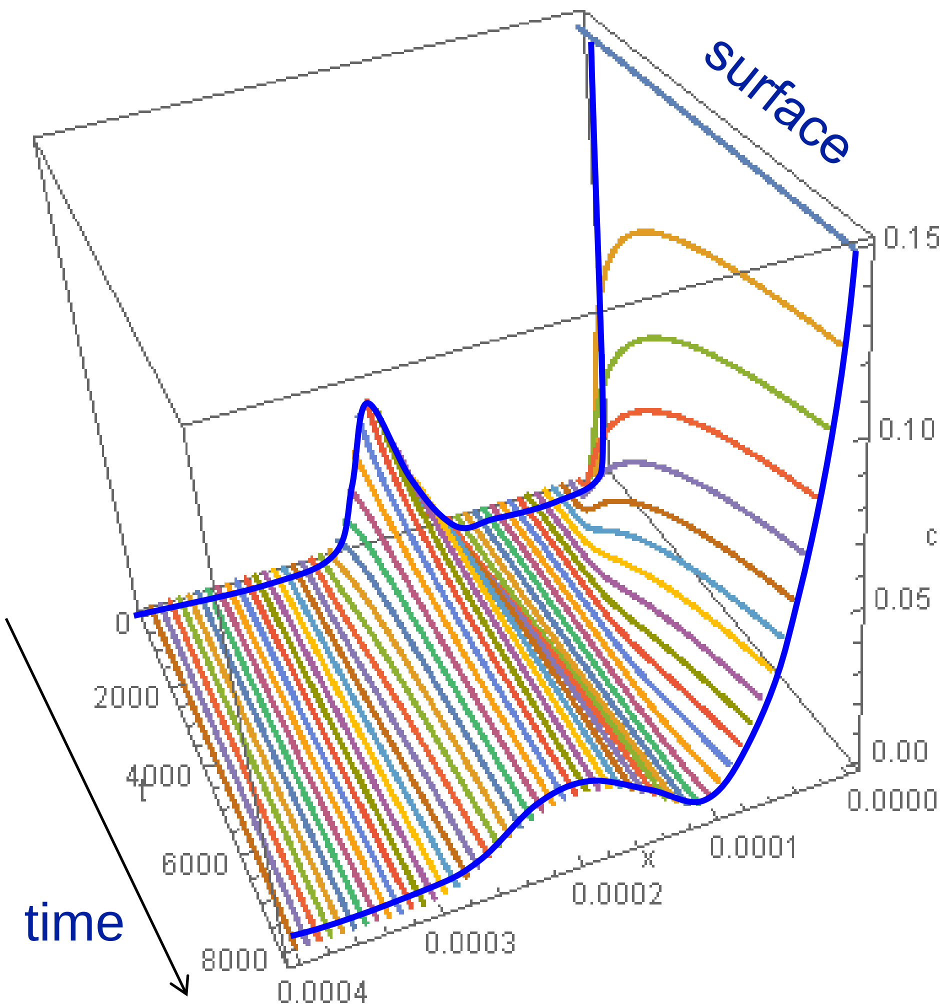
$$\frac{d}{dt}c = \frac{d}{dx}\left(hD(c)\cdot\frac{d}{dx}c\right)$$

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

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

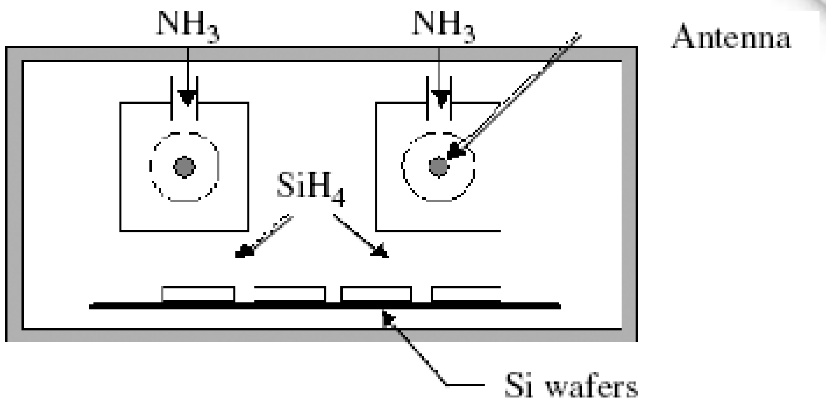
$$h = 1 + \frac{c_B}{2n_i} / \sqrt{\frac{c_B^2}{n_i^2}+1}$$

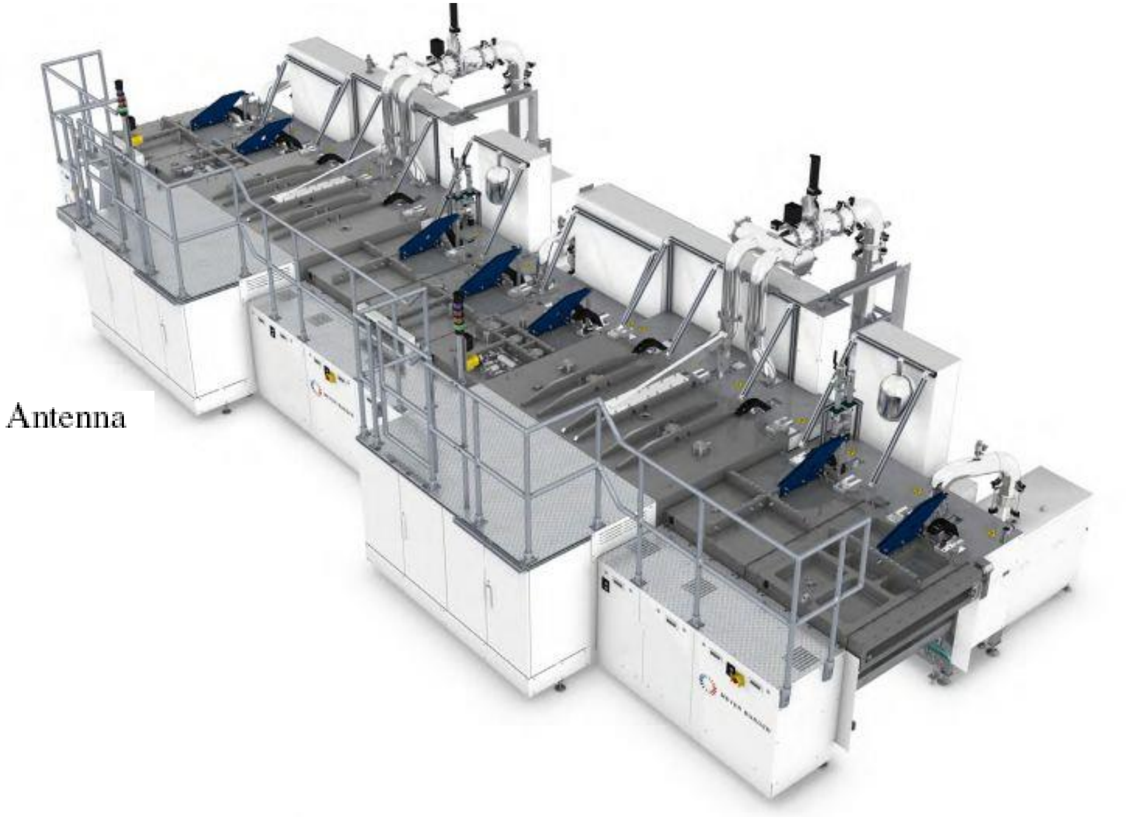
Example: diffusion from surface and broadening of Gaussian implant at x=200 nm



Next: Si_3N_4 front ARC by MW-PECVD

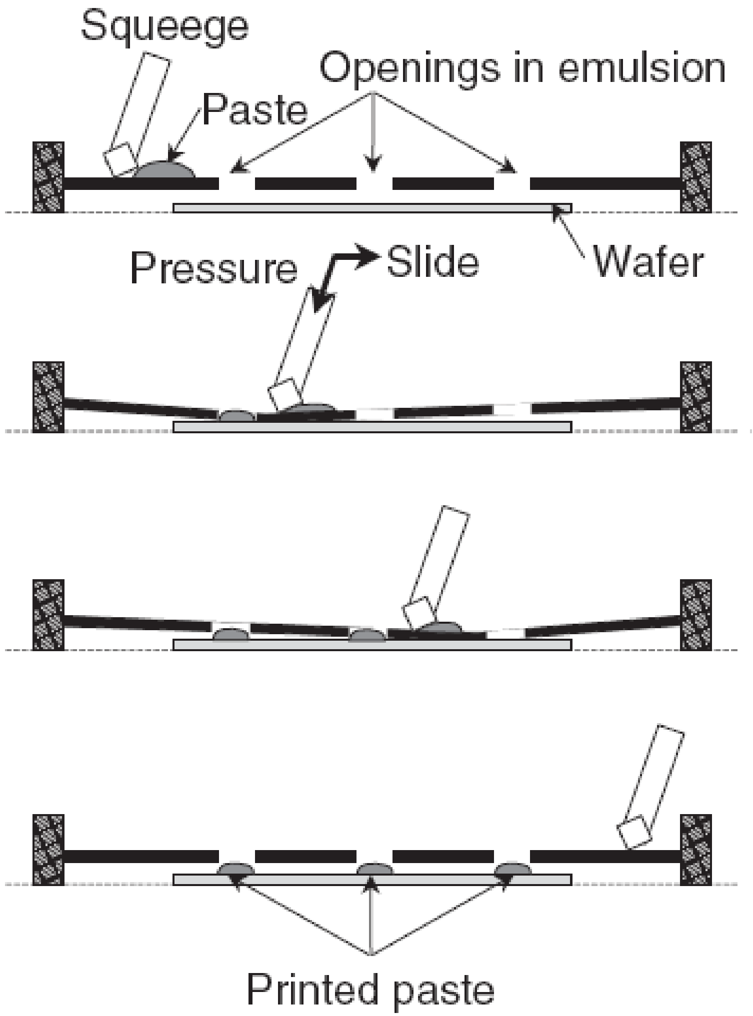
Plasma enhanced chemical vapour deposition (PE-CVD)
Microwave plasma in atmosphere of NH_3 and SiH_4



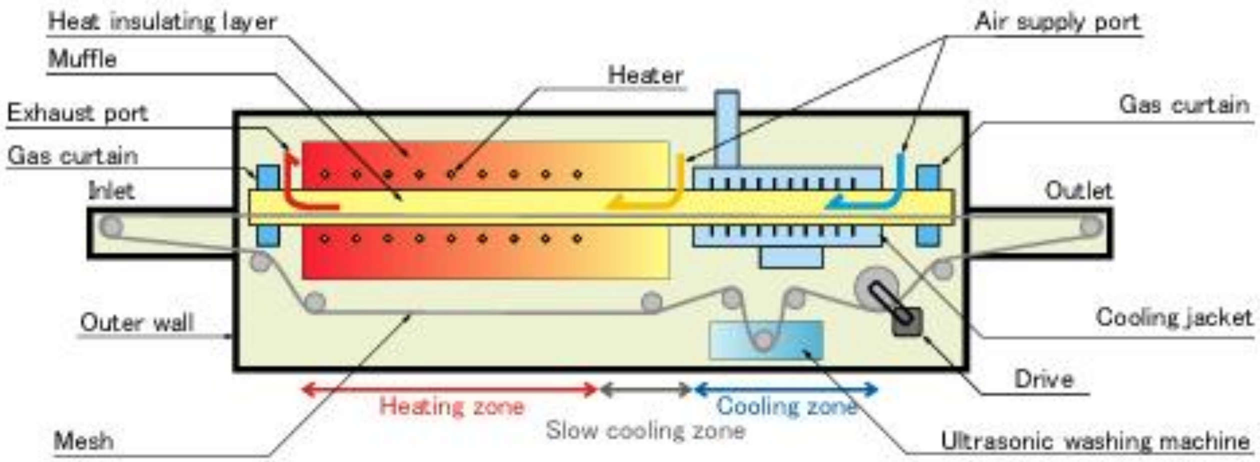


e.g. Meyer Burger AG (Roth&Rau)

Next: metallization by screen printing



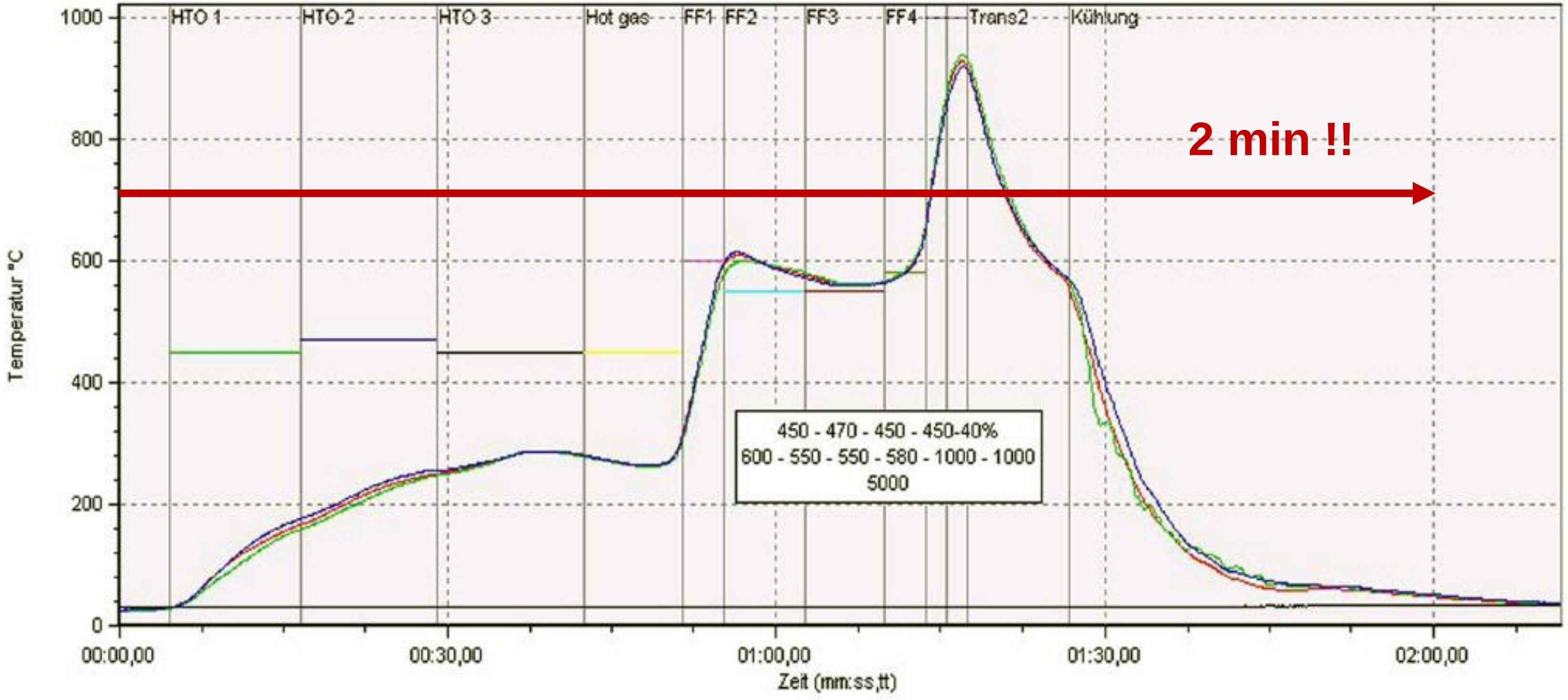
Finally: Contact firing



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

Firing-through profile

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



2 min !!

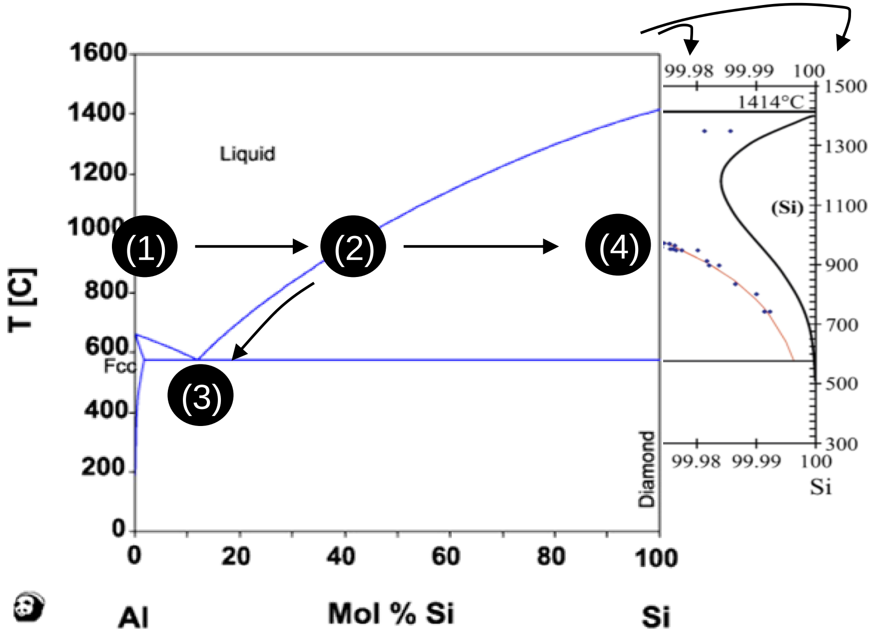
Real profile, measured by thermocouple bonded to a wafer

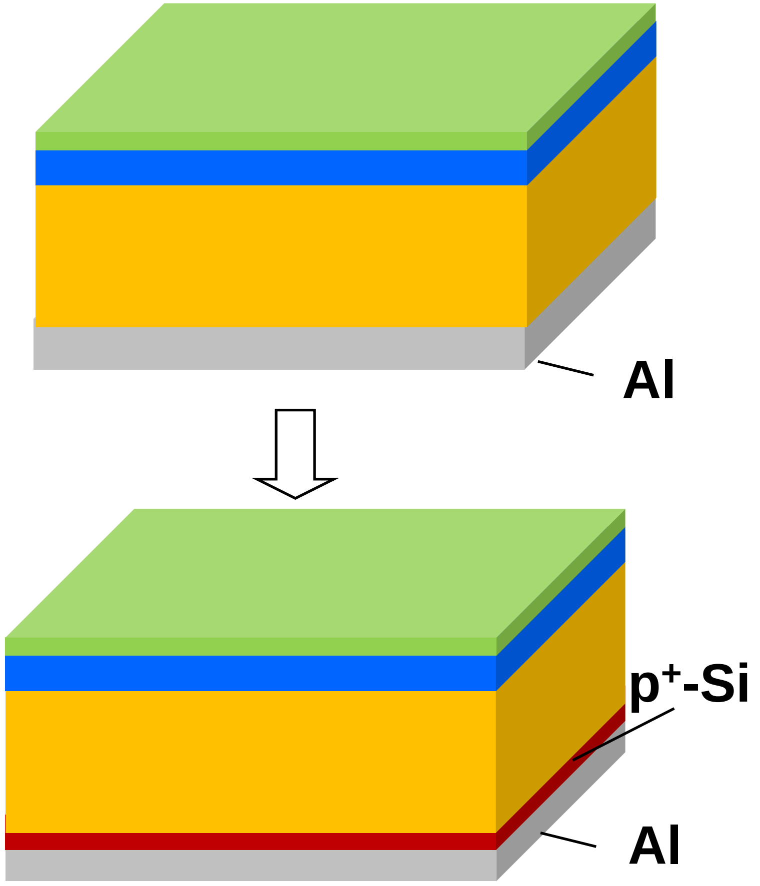
Formation of Al back-surface field (BSF)

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)

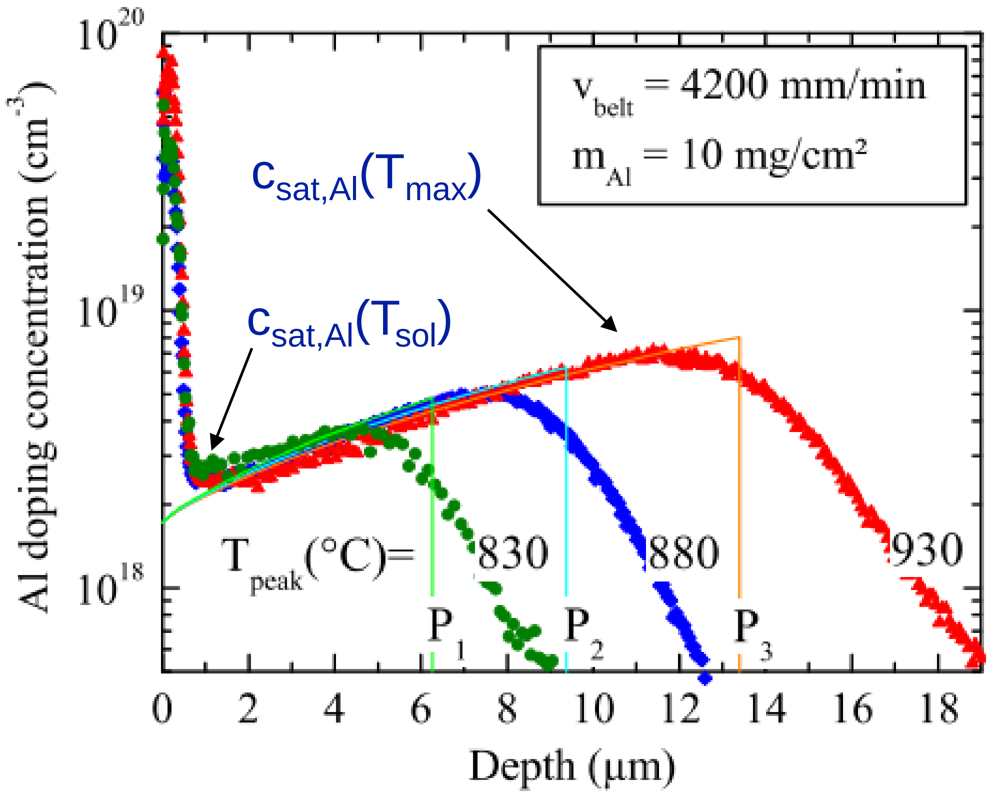
=> $N_A=c_{sat,Al} \approx (0.015 \times 2.5\times10^{22} \approx 4\times10^{18})\text{cm}^{-3}$





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

Al-BSF



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 $c_{sat,Al}$

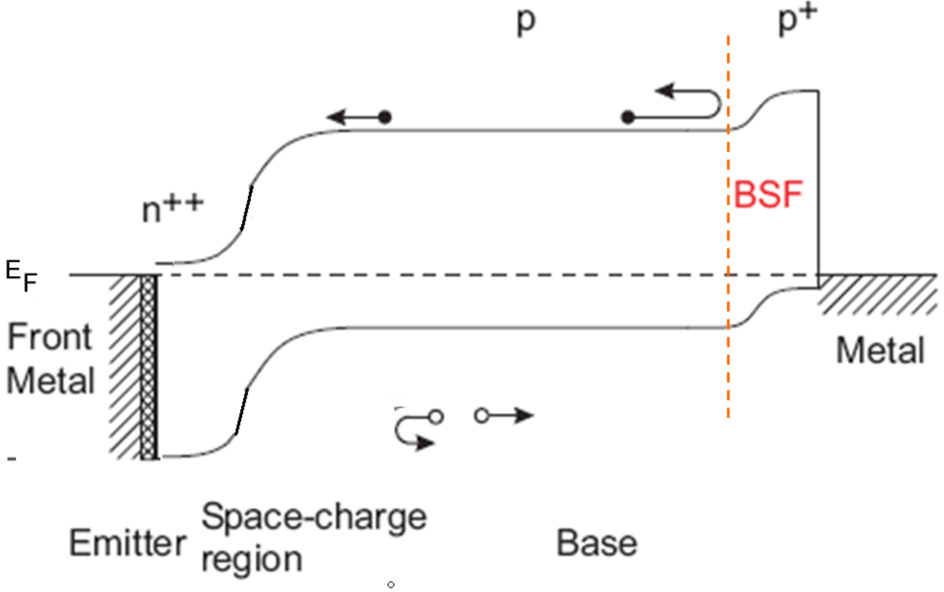
Lowest concentration at surface

$N_A = c_{sat,Al} \approx 3 \ldots 6 \times 10^{18}$ cm^{-3}

Krause, SEM (2011)

Back-surface field

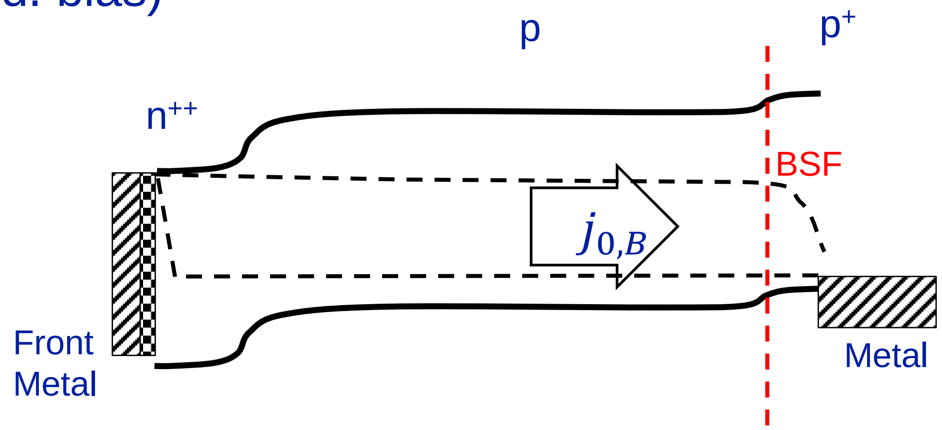
Dark, equil.



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

Function principle of Al back-surface field

Operation (light, fwd. bias)



note: $j \sim \nabla E_F$ and E_F is flat at pp$^+$ junction
Effect of drift field (∇E_C) is compensated by diffusion ($\sim \nabla n$)

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)

Front contact between Ag paste and n$^+$-region

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

Front grid less than 10% coverage

=> needs contact resistance $\rho_c < 10$ mΩ cm^2

- deep junction required
- high n+ doping required

=> yields high $j_{0,e}$ (emitter saturation current) because of Auger effect

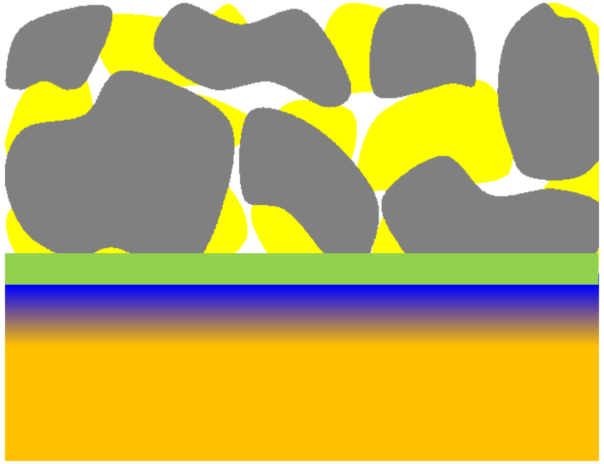
=> limits efficiency

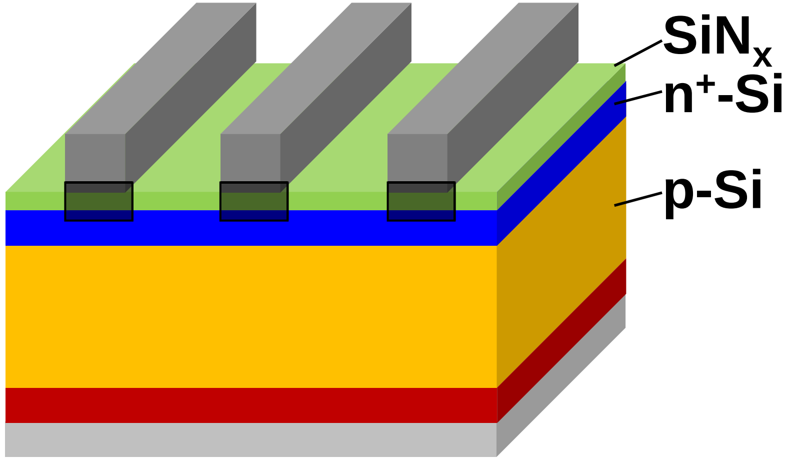
Ballif et al., Appl. Phys. Lett. 82, 1878 (2003)

How does Ag contact n$^+$ Si through the SiN$_x$?

Paste:

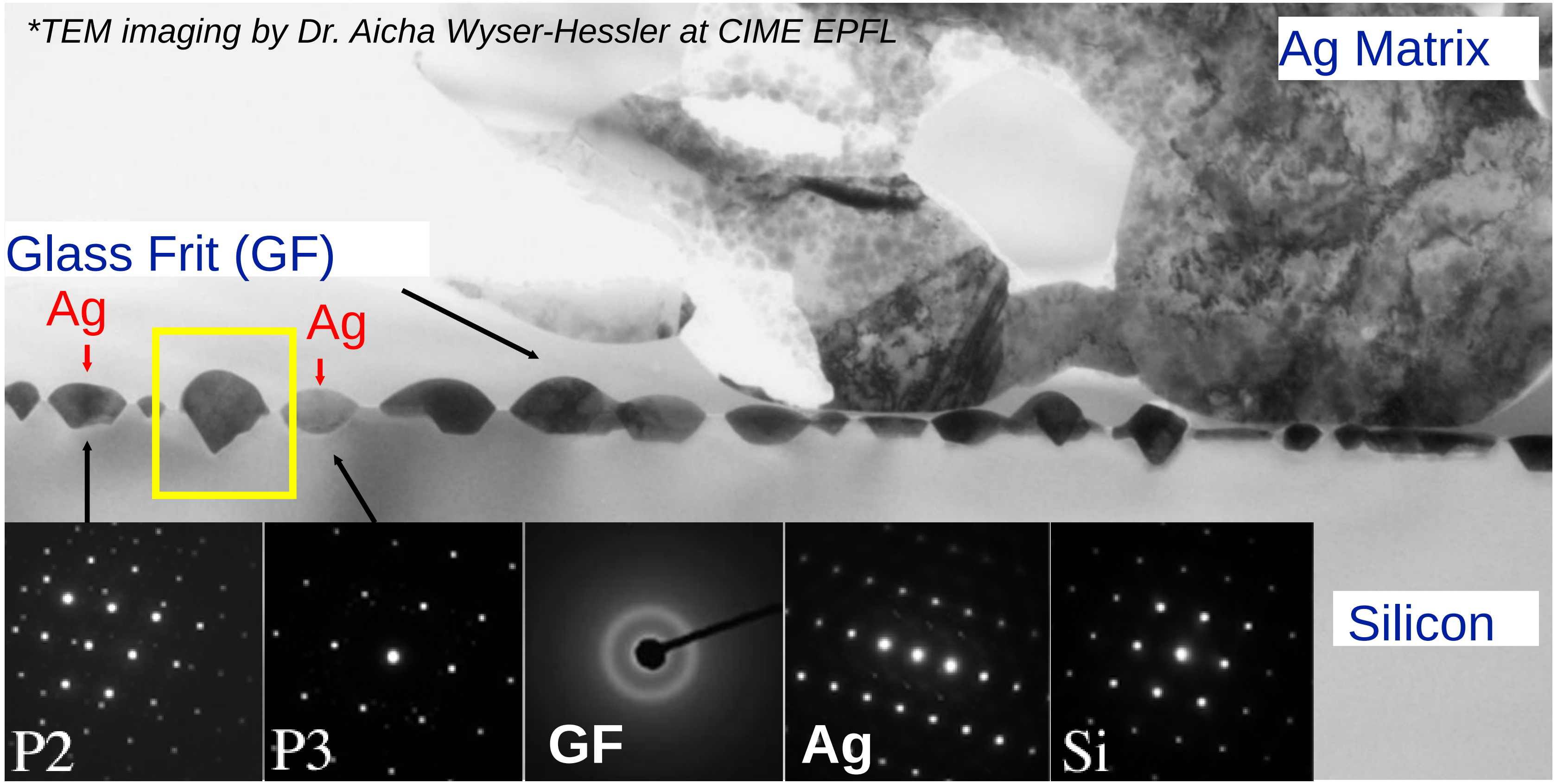
- Ag powder (1-10 µm, flakes and grains)
- Glass frit (GF) (lead borosilicate)
- Organic materials → control rheology





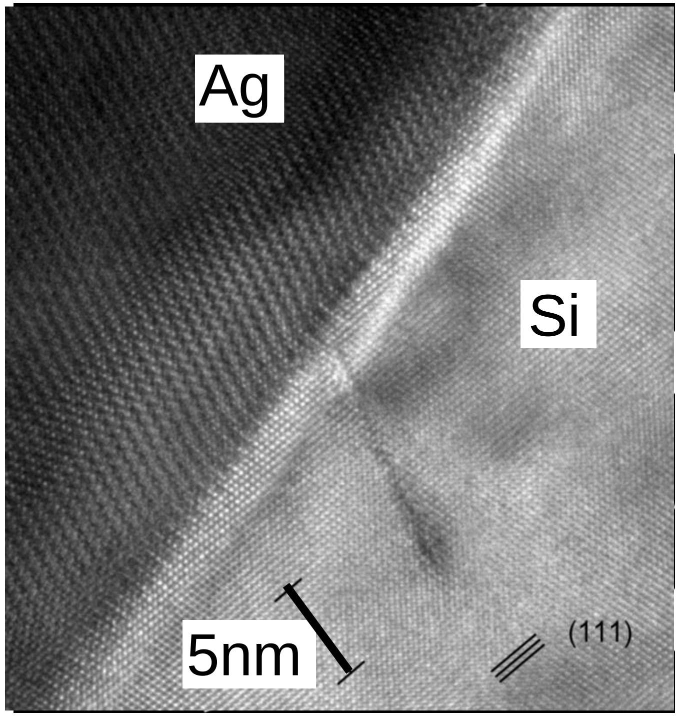
What happens during annealing at 700-800°C

Cross-section [110], typical TEM* view



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

High-resolution TEM



HR TEM image

Ag crystallite properties

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

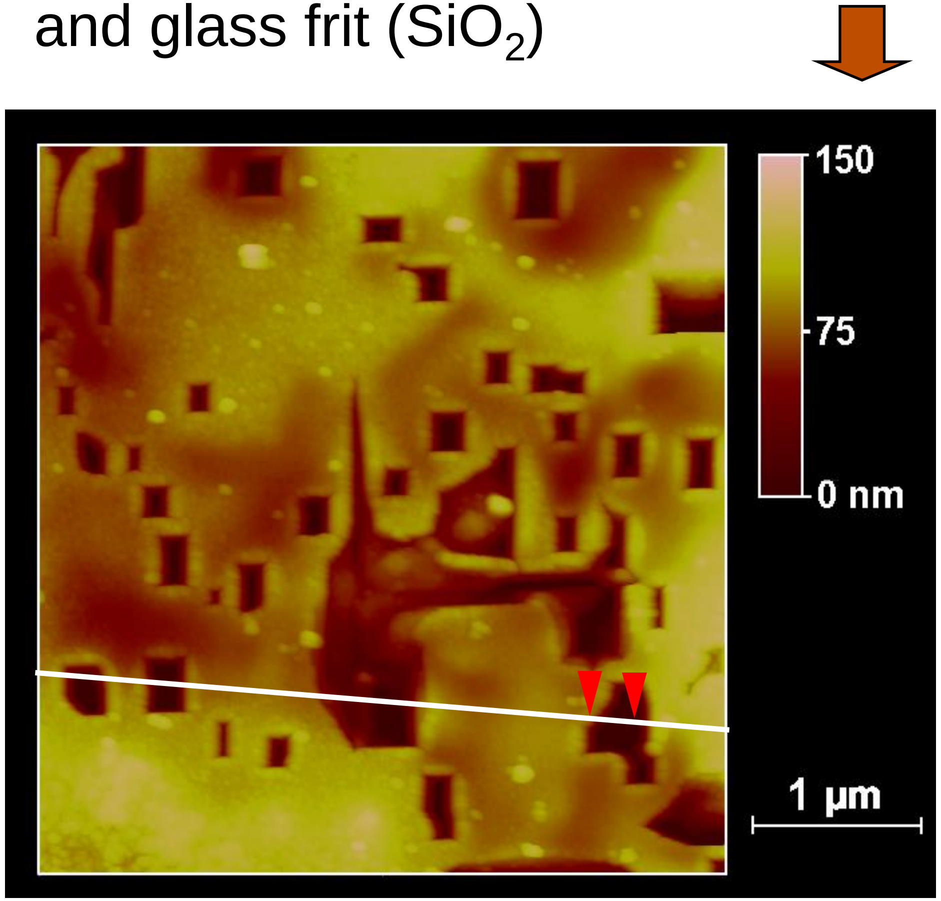
HR-TEM Ag/Si interface

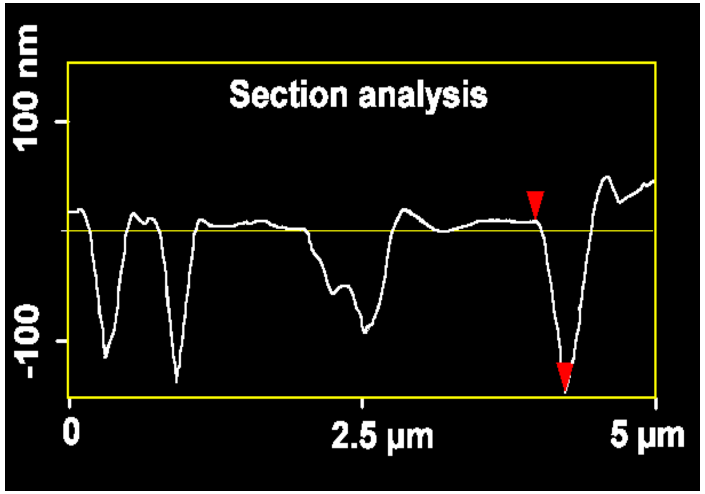
- No amorphous phase
- No oxide (HR-EDS)

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

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

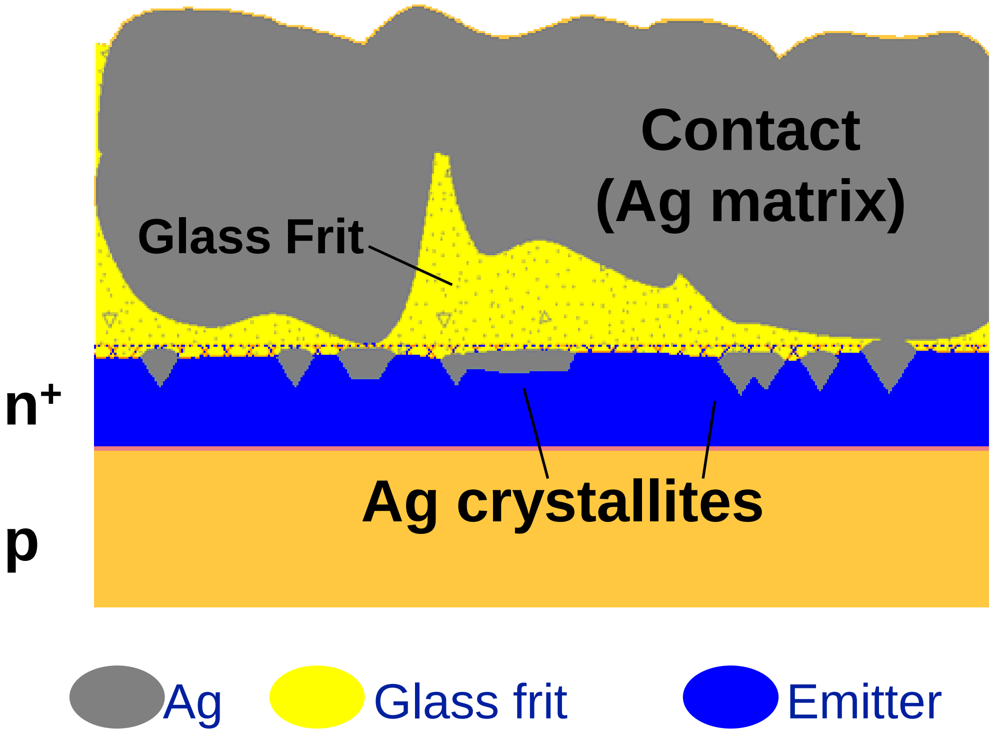
Model for contact formation

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



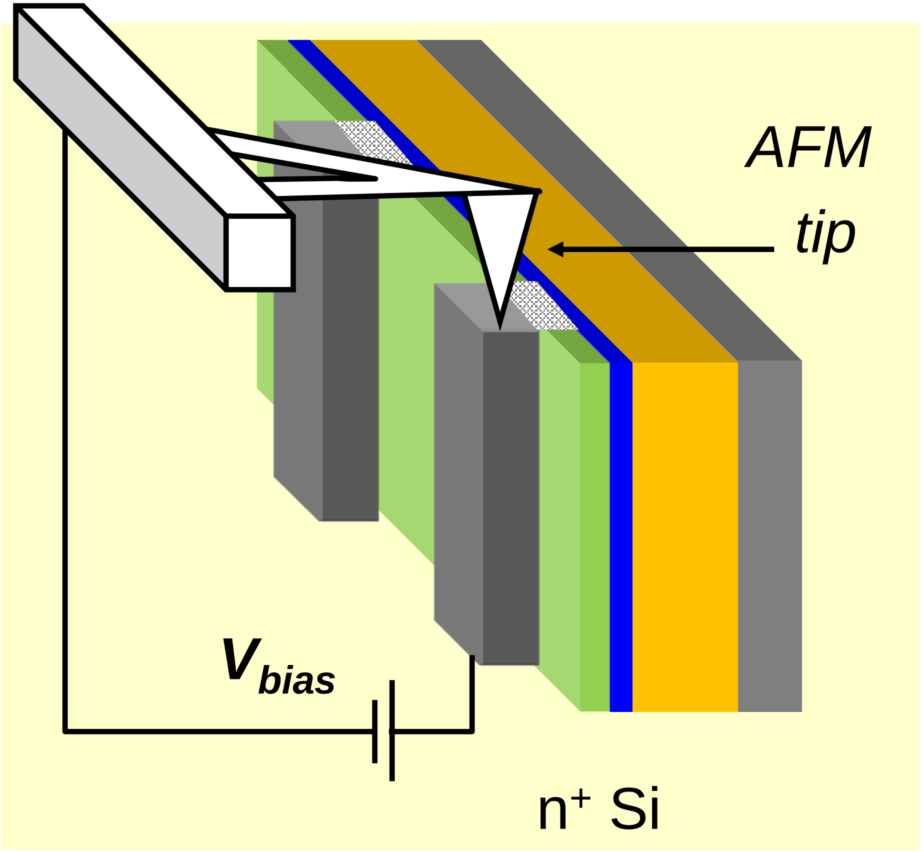
***n.b.: alternatively, etching of pyramids into the wafer was proposed**

Electrical properties

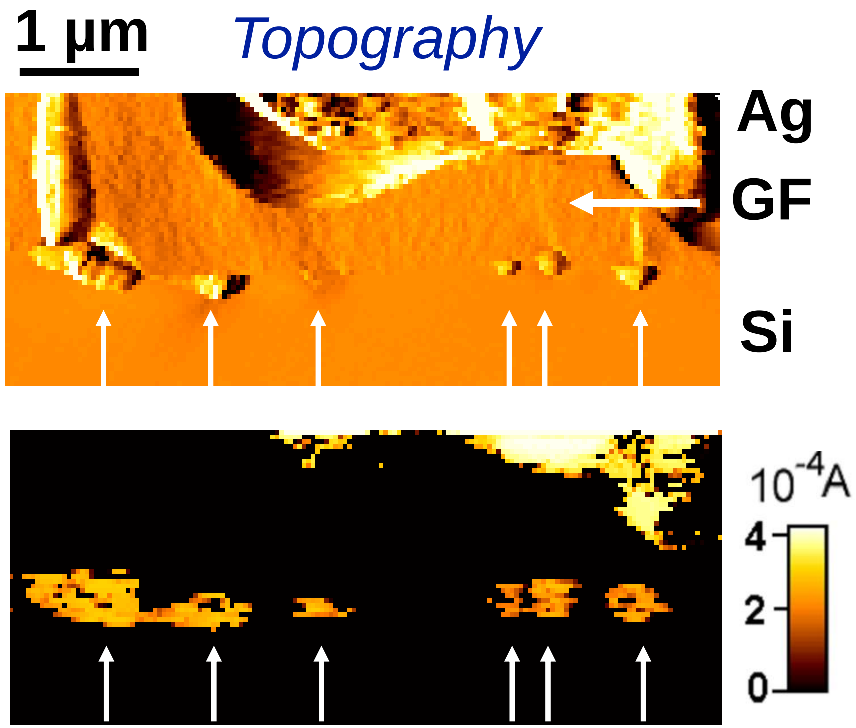
Insulating glass frit layer

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

Conductive AFM on cross-sections of contact



Conductive AFM on cross-sections of contact



AFM current, V_{bias} = 0.2 V

On Ag crystallites

→ I = 0.3 mA

→ $R_{contact}$ = 700 Ohm

→ $R_c < 10^{-7}$ Ohm cm^2

<< 10^{-3} Ohm cm^2

(observed macro)

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

Model for current flow

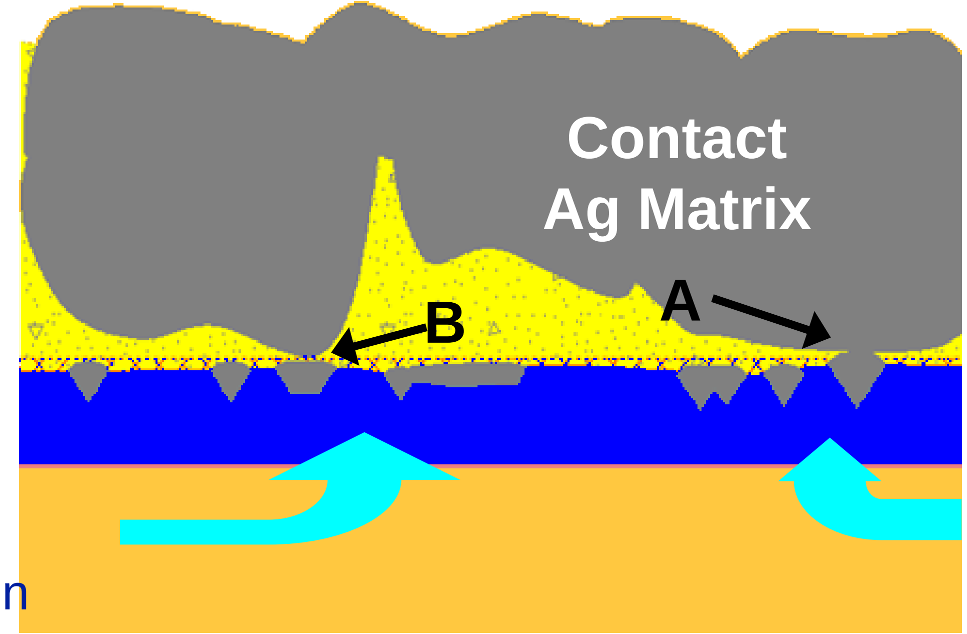
Glass frit

- 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

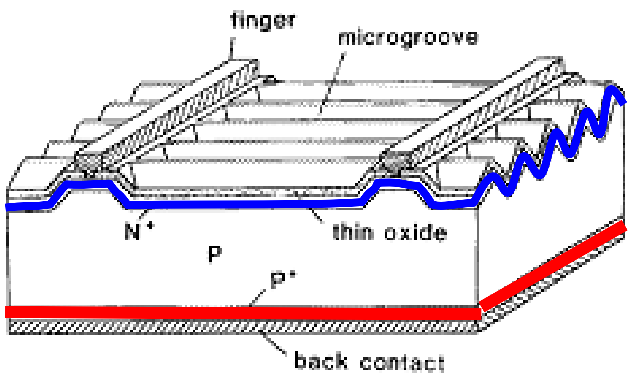
Alternative/refined models in literature

Cell generations (UNSW)

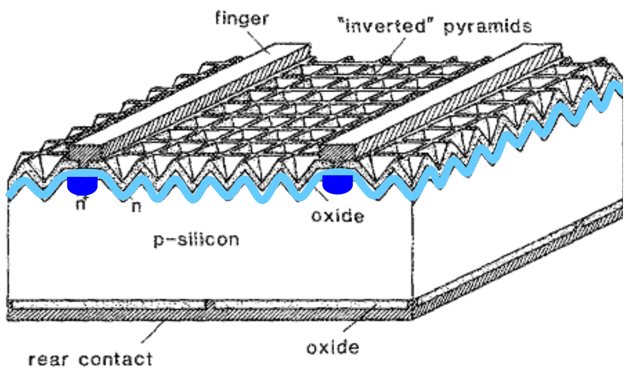
PESC (Passivated Emitter Solar Cell):
Voc = 670 mV
eff=20%

PERC (Passivated Emitter and Rear):
Voc = 696 mV
eff=22.8%

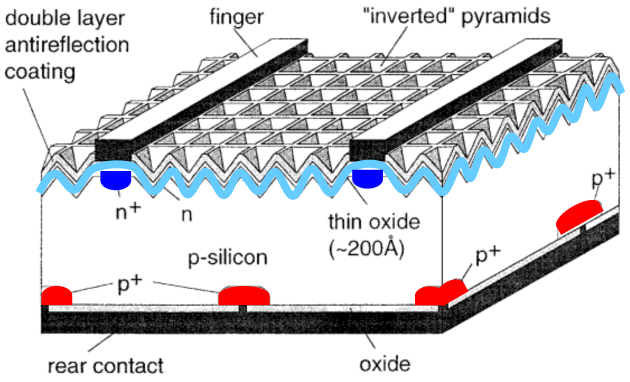
PERL (Passivated Emitter, Rear Locally diffused):
Voc = 706 mV
eff=24.7%



Blakers, APL (1986)



Blakers, APL (1989)



Zhao, PPV (1999)

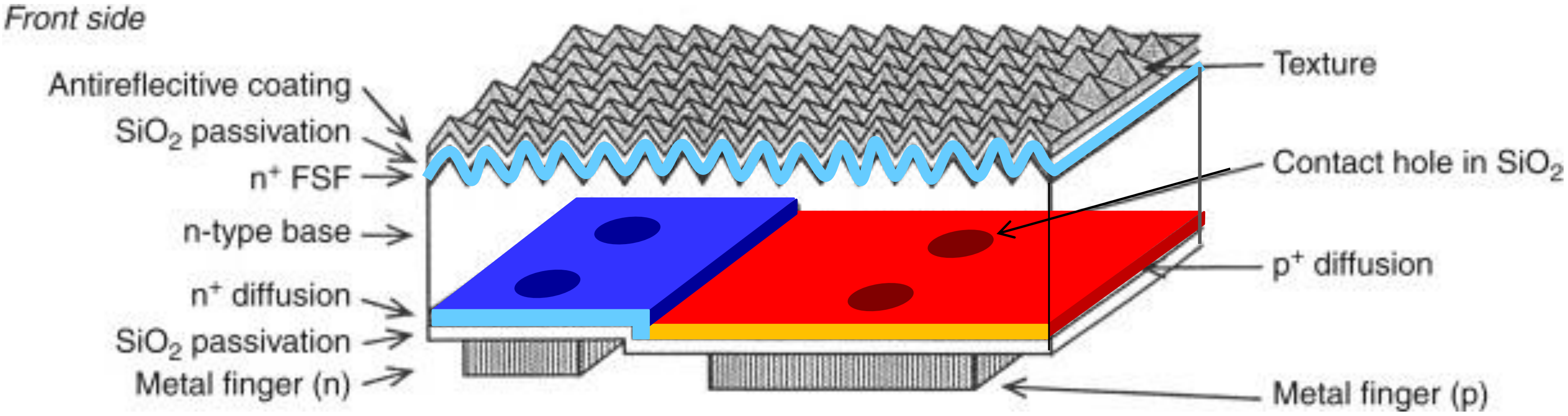
“First we fixed the front, then we fixed the back” (M. A. Green)

A design with improved optics (U Stanford)

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

Early commercialized by SunPower with diffused junctions

adapted to HIT type by Sanyo/Panasonic and Kaneka
=> current world record, 26.7%

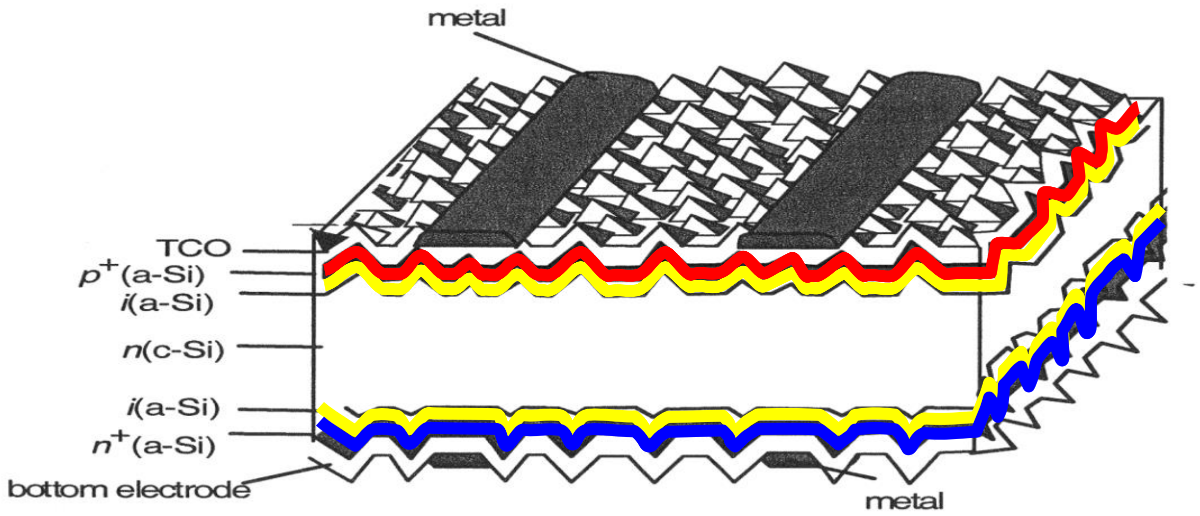


Mulligan, EU-PVSEC (2004)

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)



Tanaka, JJAP (1992)
Taguchi, JPV (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)