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NeoGrowth Silicon: Low oxygen, high purity, proven crystal growth method for 450mm + silicon optics

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- » Introduce NeoGrowth crystal growth
 - Principles of operation
 - Distinctions relative to other methods
- » Properties of NeoGrowth silicon
 - Dislocations
 - Impurities and lifetime
 - Doping

NeoGrowth Silicon: What is it?



U.S. Patent

Apr. 19, 2016

Sheet 1 of 9

US 9,315,917 B2

- >> Basics: most similar to pedestal growth
 - Continuous, Float Zone like process with balanced input and freezing of liquid
 - Non-contact solidification: no containing crucible
 - Large area seeding process with a seed having a cross-section close to that of the finished ingot
 - Capable of extremely low thermal stresses even at high growth speed
 - Capable of producing circular or squarish cross-sections
- >> Stoddard et al, Progress in Photovoltaics, 1/2018
- >> Stoddard et al, Journal of Crystal Growth vol 452

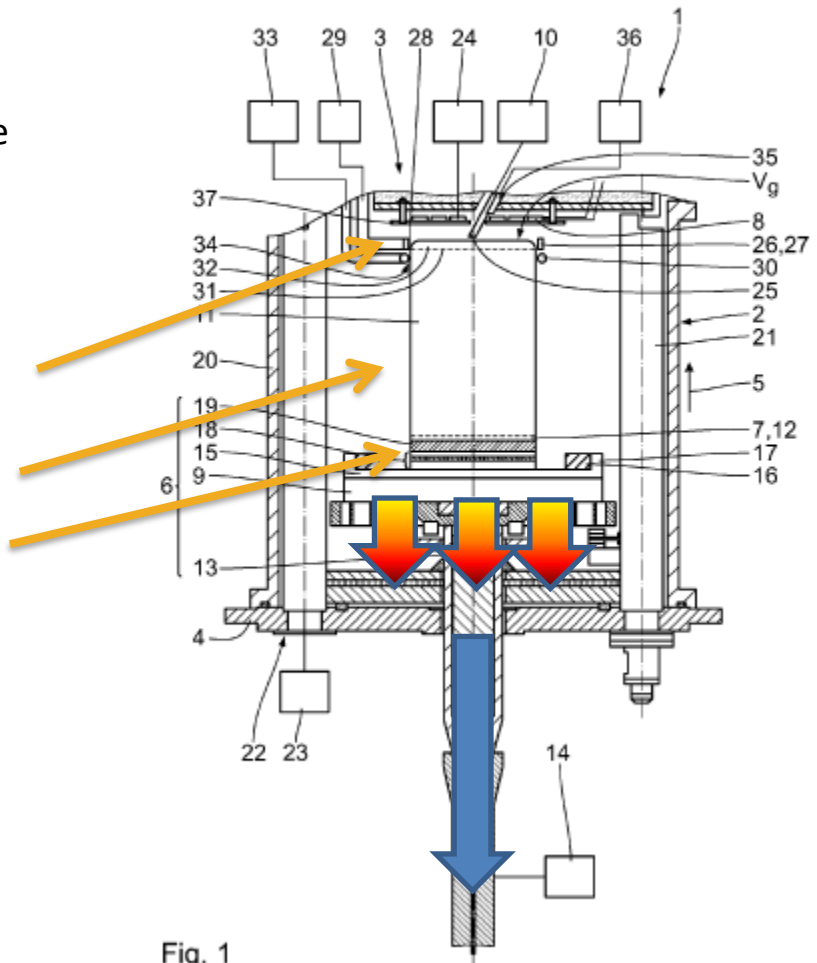


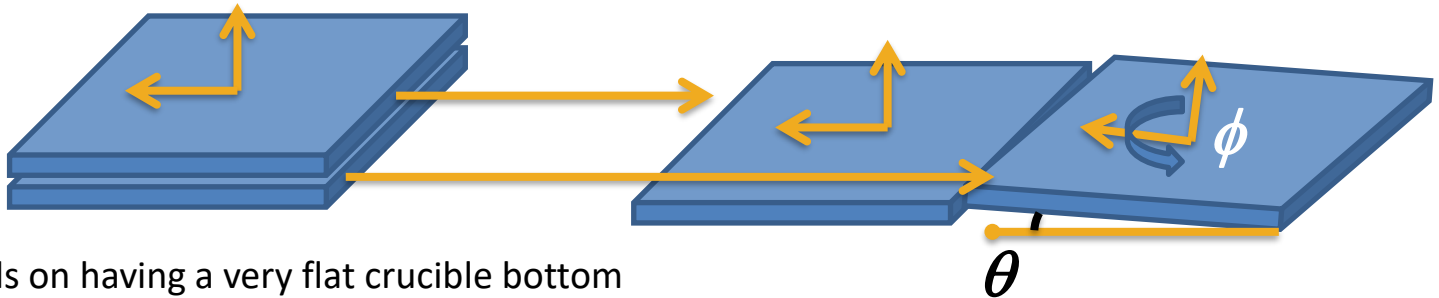
Fig. 1

CM-Si Challenges: Seeding



>> Seed boundaries

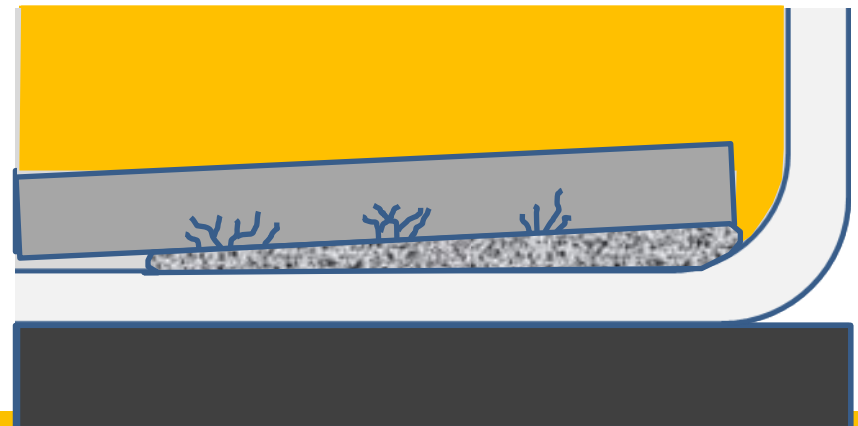
- Angle mismatch of >0.1 degrees can lead to sub-grain boundary
- Two seeds cut to square from the same block can meet this requirement for ϕ



- θ depends on having a very flat crucible bottom
 - small chips, coating variations, crucible bumps and corners can cause problems

>> Liquid silicon undercutting also causes significant problems

- The liquid can come down the edges or between seeds
- As it pushes in, it is cooled and solidifies
- Expansion on solidification causes stress
 - Heavy dislocations in seed
 - Lifts and misaligns seeds, creating small angle GB's between seeds

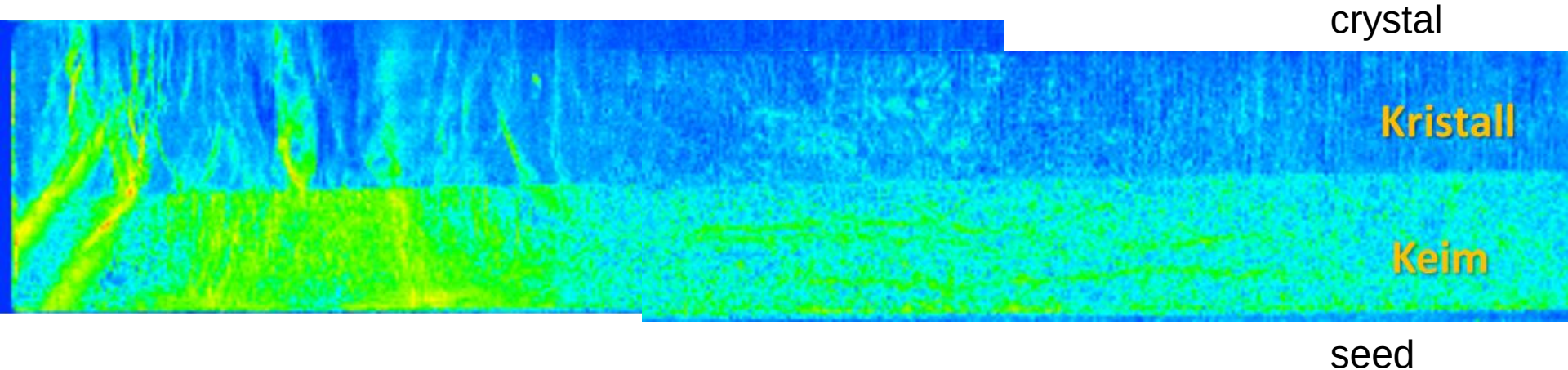


CM difficulties: crucible and coating

>> The crucible is an unavoidable source of impurities

- Dissolved oxygen, nitrogen, metals
- Nitride particles

vertical cross section



>> Uneven support of the seeds and weight loading of heavy feedstock cause seed dislocations

- Good news: most do not propagate
- Bad news: many still do

>> Czochralski Growth

- High oxygen concentration (15-25 ppma)
- Small cross-section
- Batch doping limitations
- Long times for seed-in, stabilization, tail
- That Czech name

>> Float Zone

- Feedstock limitations (high density polysilicon rods)
- Diameter limitations (200 mm max)
- High Frequency Inductive heater

>> So how about some details on NeoGrowth?

NeoGrowth melt supply

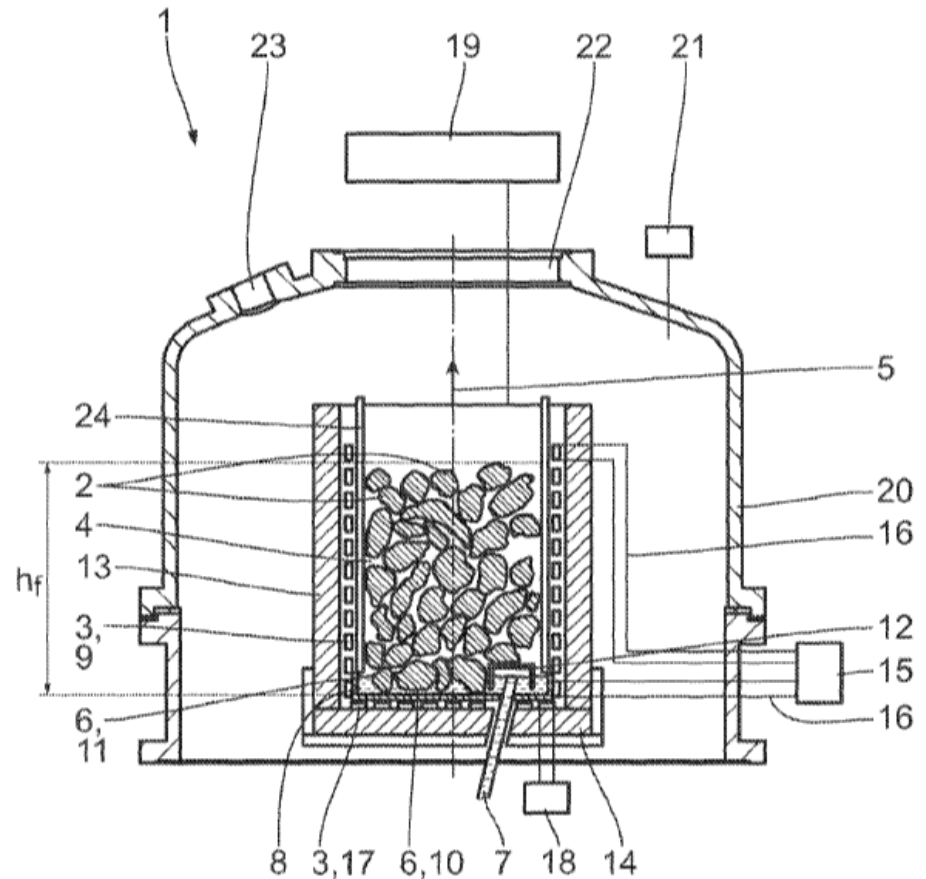


>> Requirements for melt supply

- Mass flow must match crystal growth rate in order to prevent build up or diminishing of melt puddle height
- Smooth flow preferred to avoid melt vibrations
- Through-flow of unmelted bits of feedstock material must be avoided

>> Nice to have

- Feedstock flexibility
- Reusability over multiple runs
- Minimal liquid contact with foreign material



NeoGrowth Properties



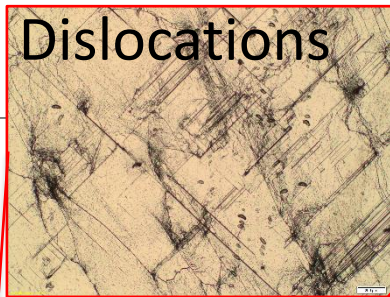
- >> We have grown crystals at 230mm, 300mm and 450mm diameter in square and circular cross-sections
- >> Dislocations present from seeding do not cause structure loss
 - Maintaining low thermal stress during growth prevents the evolution into dislocation clusters and small-angle grain boundaries
- >> We have not yet been able to grow a dislocation-free crystal, but that has not been a main goal
- >> We have found a tendency for twins to form at the nodes of the crystal unless great care is taken
- >> Height
- >> Growth rate



NeoGrowth and Dislocations

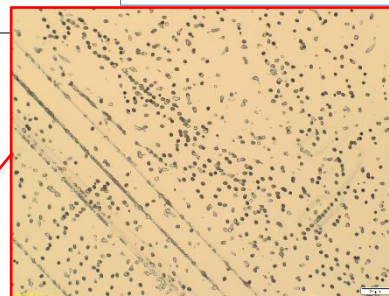


Huge amount of twins/SF's and dislocations in last-to-freeze



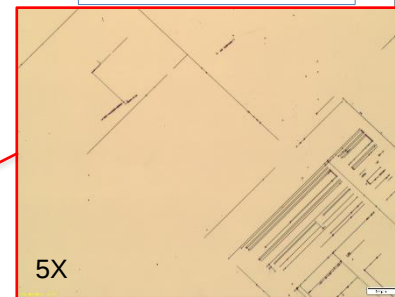
5X

Some defect 'slip-back' near top

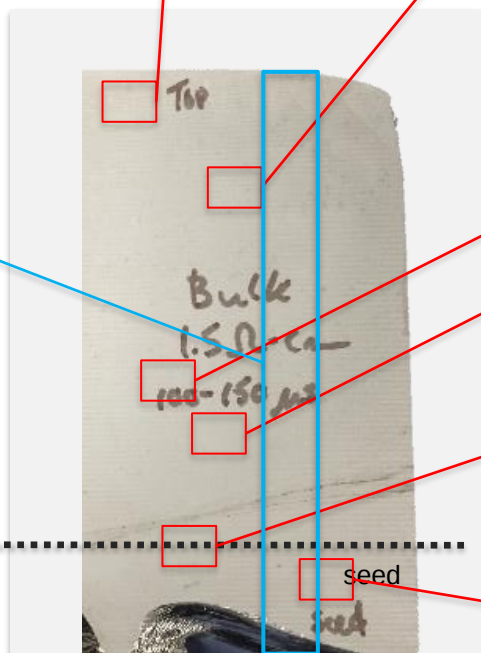


50X

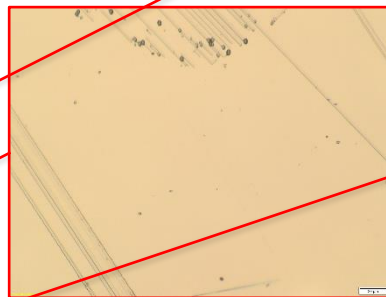
Twins/SF's: some decorated by dislocations



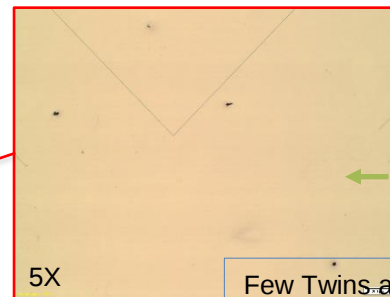
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500 µm



5X

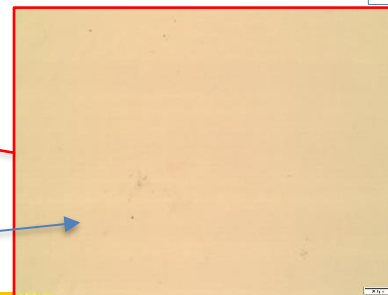


5X

seed/melt interface

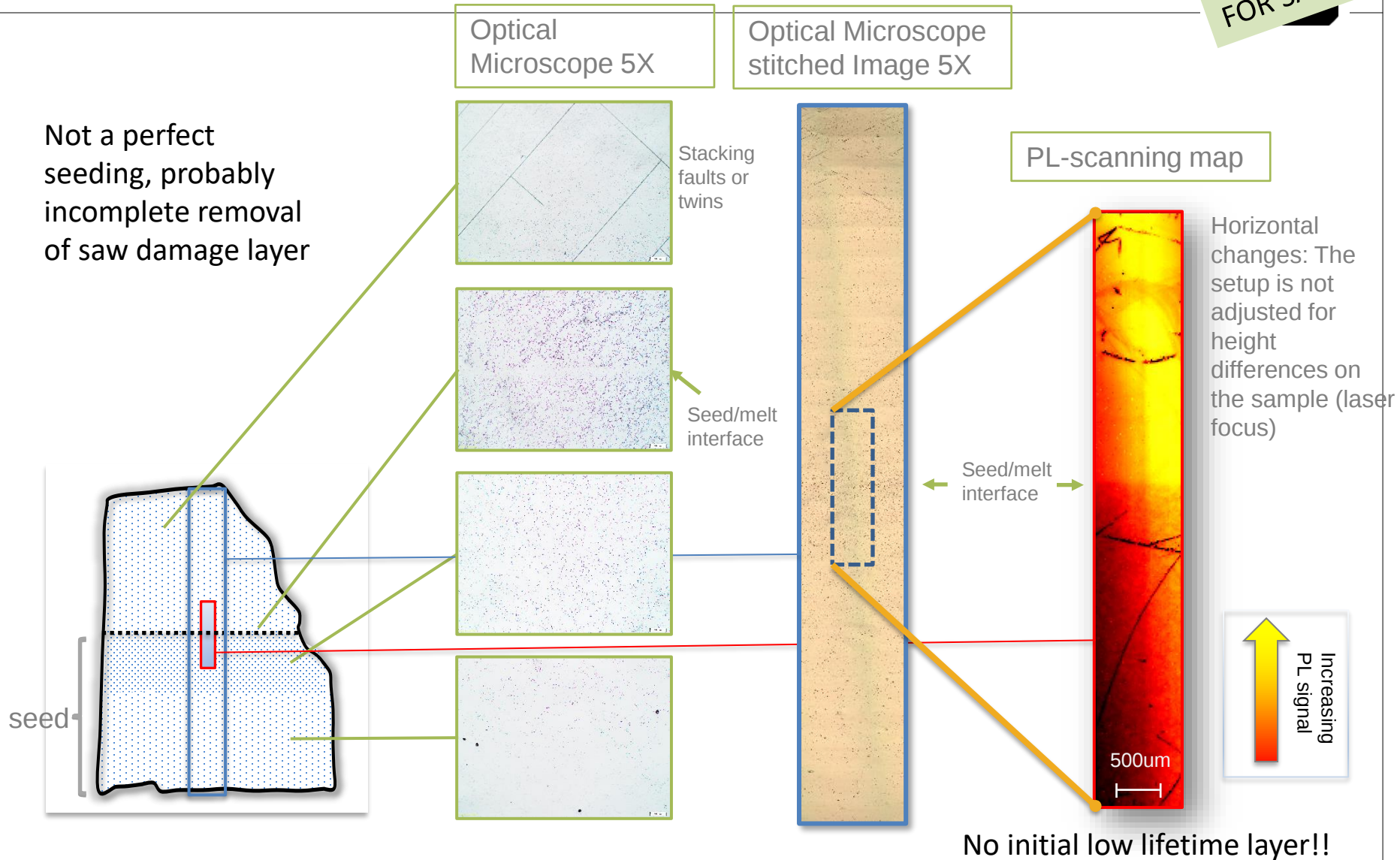
Few Twins and Disl initiated at the seed/melt interface

No dislocations are visible in the seed!!



50X

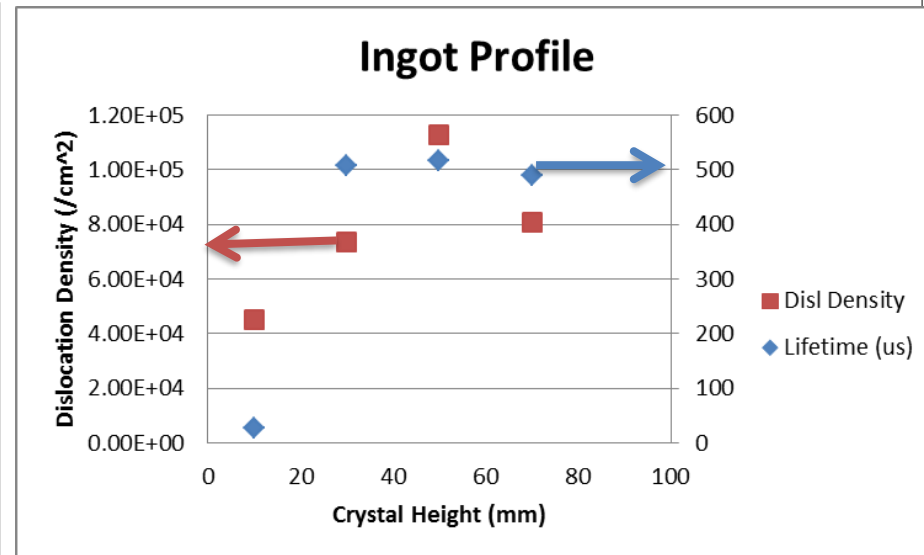
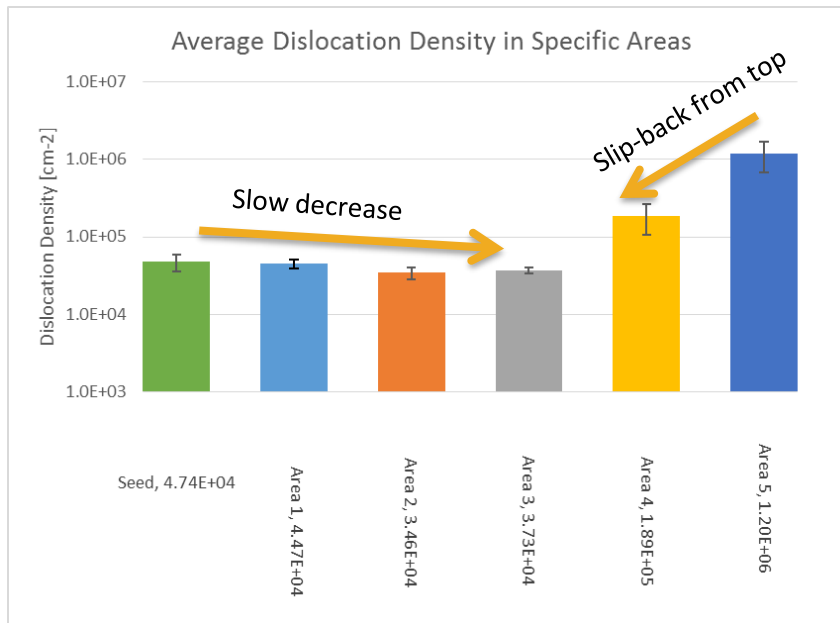
NeoGrowth seeding interface



Dislocation evolution



- >> Cool-down stress can change things, but we often see a slow decrease in dislocation density as ingot growth proceeds (left, typical)
- >> Up to low 10^5 disl/cm², we see no significant correlation of dislocation density and MCL

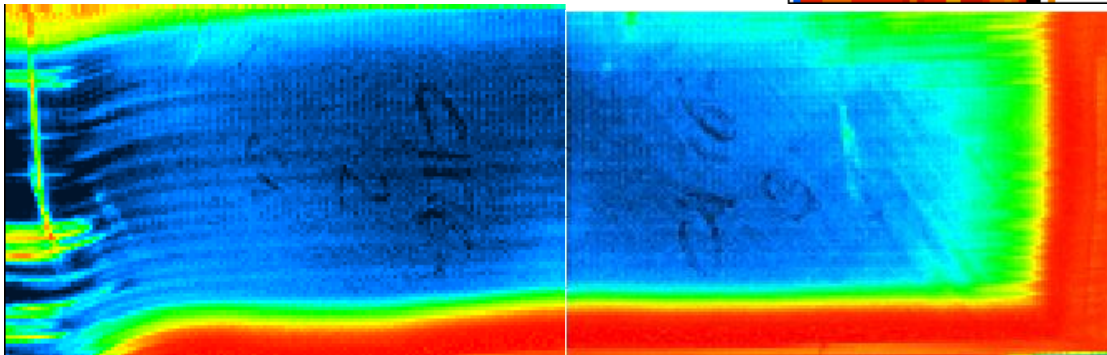
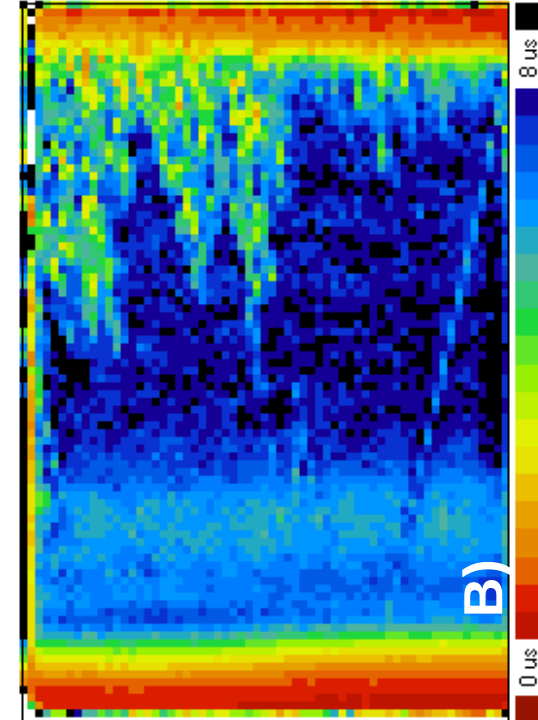
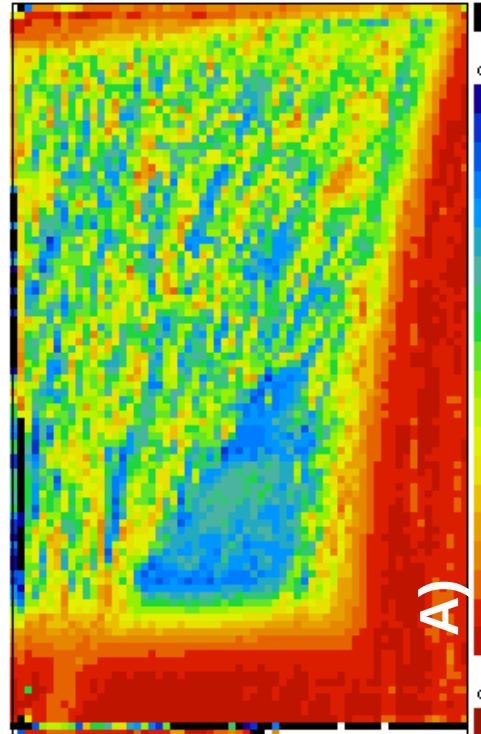


A word about dislocation cascades

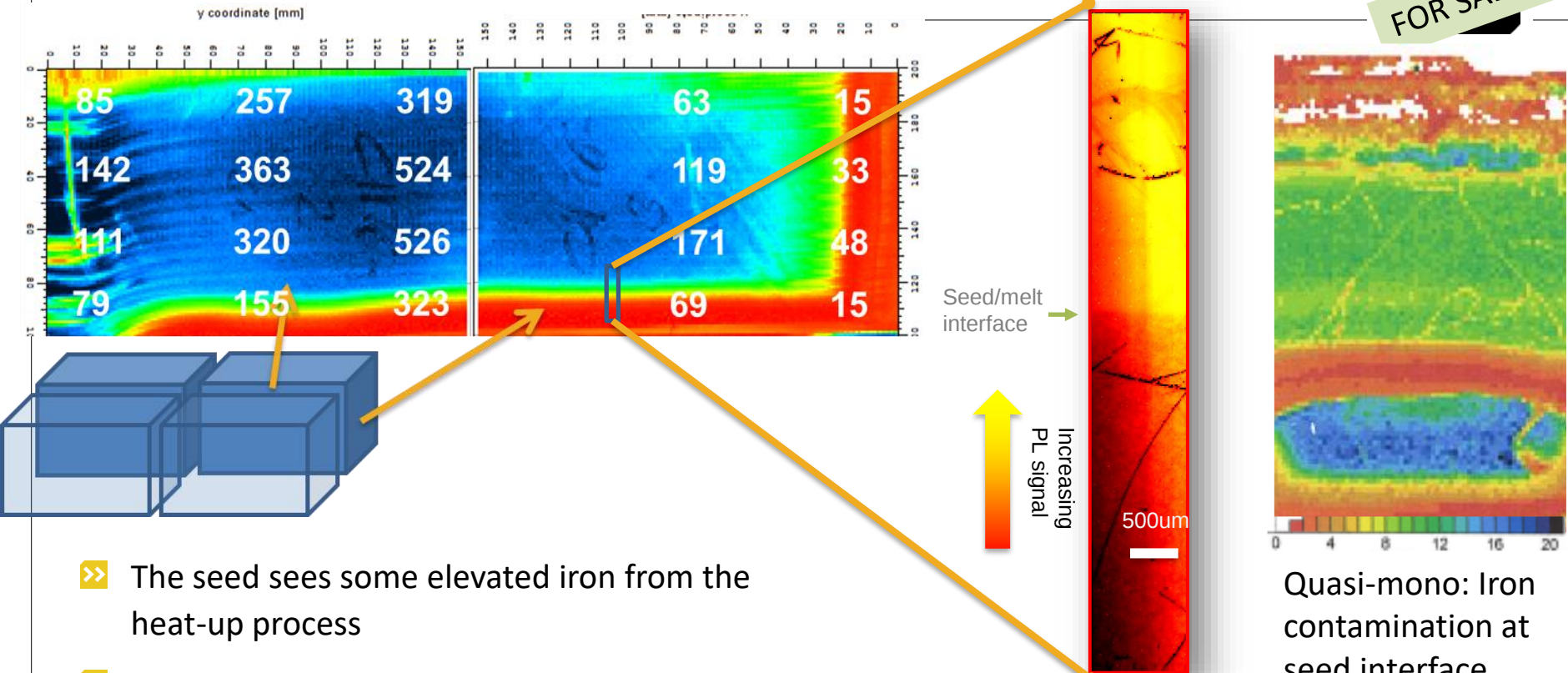


Mono² Bricks

- >> One of the biggest limitations of the Mono² / quasi-mono process is the presence of dislocation cascades
 - Generated at seed tile boundaries
 - Generated higher from inclusions and built-up stress
- >> NeoGrowth has no seed tile boundaries
- >> NeoGrowth has no inclusions
- >> NeoGrowth has very low simulated stress even at >50 cm (< 5MPa)



Impurities



- >> The seed sees some elevated iron from the heat-up process
- >> The grown material has exceedingly high purity
- >> The exterior of the ingot sees some post-growth iron deposition from the hot zone ambient
 - Hot zone material quality is crucial
- >> Minority carrier lifetime post diffusion measured as high as 1.7 ms at 1.5 ohm-cm

NeoGrowth: No iron contamination at seed interface

Quasi-mono: Iron contamination at seed interface

The Light Elements



>> Oxygen source in melter apparatus, but good argon sweeping keeps levels low

>> The only carbon source is gaseous:

- $\text{SiO} + \text{C} \rightarrow \text{SiC} + \text{CO}$
- Carbon is controlled through the atmospheric conditioning

FTIR Concentrations (atoms/cm³)

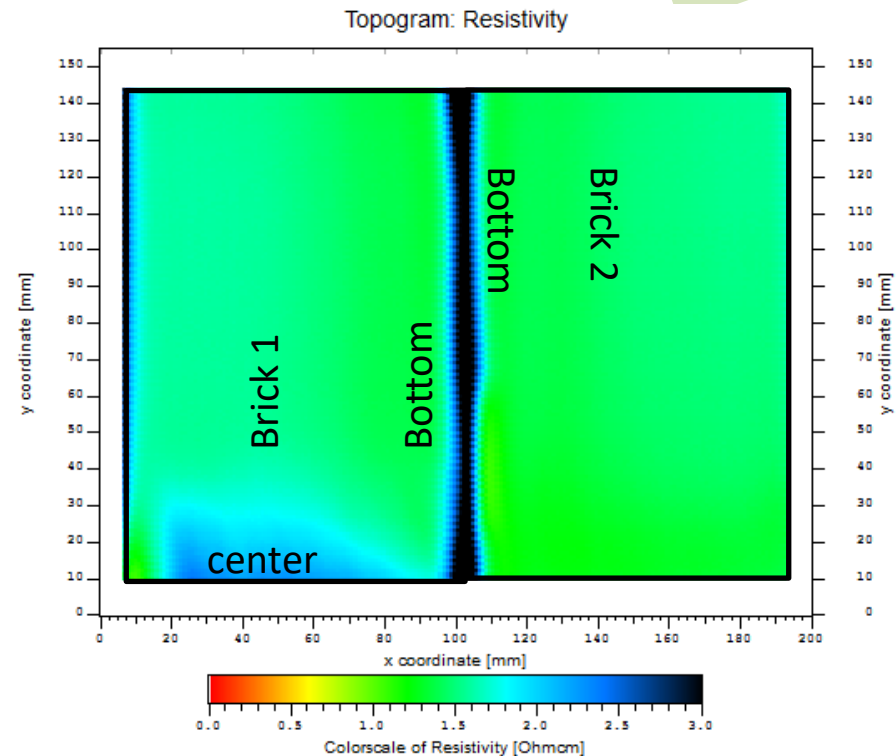
[O _i]	Center	Half-way	Edge
Top	4.00E+17	3.73E+17	3.87E+17
Middle	5.05E+17	3.88E+17	3.47E+17
Bottom	5.73E+17	4.85E+17	4.18E+17
[C _s]	Center	Half-way	Edge
Top	9.43E+16	1.65E+17	9.76E+16
Middle	7.80E+16	9.55E+16	1.27E+16
Bottom	7.11E+16	3.27E+16	< 1E+16

Doping



- >> Doping does not follow Scheil's equation because there is a constant supply of fresh feedstock
- >> Low segregation coefficient dopants perform well: dope once at the beginning and slowly deplete the melt concentration
- >> Evaporation can be an issue, depending on the ambient pressure
- >> Zone height variations will also change the doping by changing the melt concentration

$$C(x) = C_0 * k * e^{-krx A/V}$$



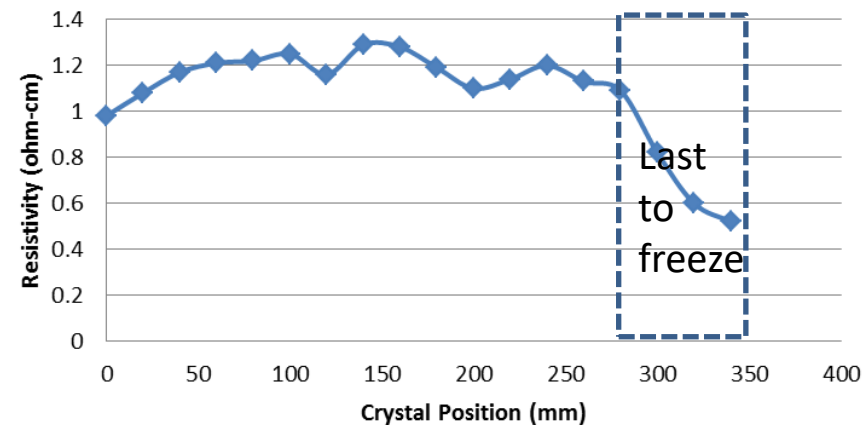
- k is the segregation coefficient
 - $r = \rho_s/\rho_l$ is the ratio of densities
 - x is the linear crystal position
 - A is the cross-section of crystal growth
 - V is the liquid volume
- Or $A/V = 1/h$ where h is the zone height

Doping

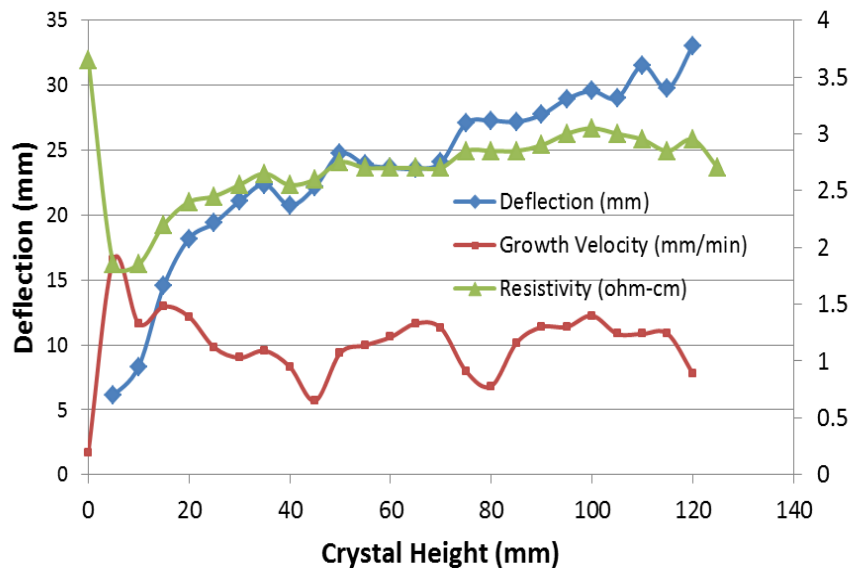


- >> Ambient pressure has a big effect on dopant evaporation
 - High pressure: dope once and done
 - Low pressure: have to redope
- >> Zone height also has a significant effect

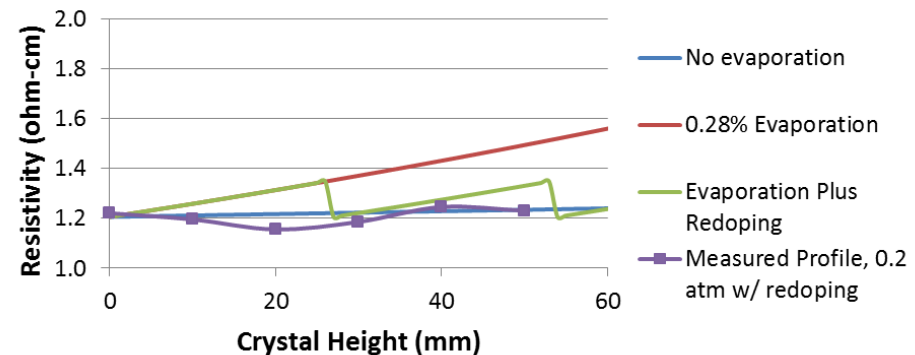
NeoGrowth Doping: High Pressure



Resistivity with varying zone height



Low pressure, Constant Zone Height



Challenges



>> Early Challenges Overcome

- Stability of melt puddle
- Uniformity of melt flow
- Argon purge design for low carbon

>> Current challenges

- Maintaining low stress to avoid dislocation multiplication narrows the process window
- Twins coming from the nodes are pernicious
 - Problem solved at 230 mm, but not fully resolved at 450 mm

>> Opportunities

- Dislocation-free seeding seems possible, but not yet repeatable
- Potential to increase the process stability via melt edge contact

Conclusions



- » NeoGrowth method demonstrated to have good promise for solar substrates
 - Low dislocations, oxygen, metals
 - High throughput drives low cost
 - Good doping and high lifetime
 - Possible extension to dislocation-free technique
 - Technique and equipment are part of the sale of SolarWorld Americas

- » Excellent crystal growth advice now available from The Stoddard Consultancy

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Questions?

