



Manufacture of High Resistivity, Low Oxygen Czochralski Silicon

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Olli Anttila

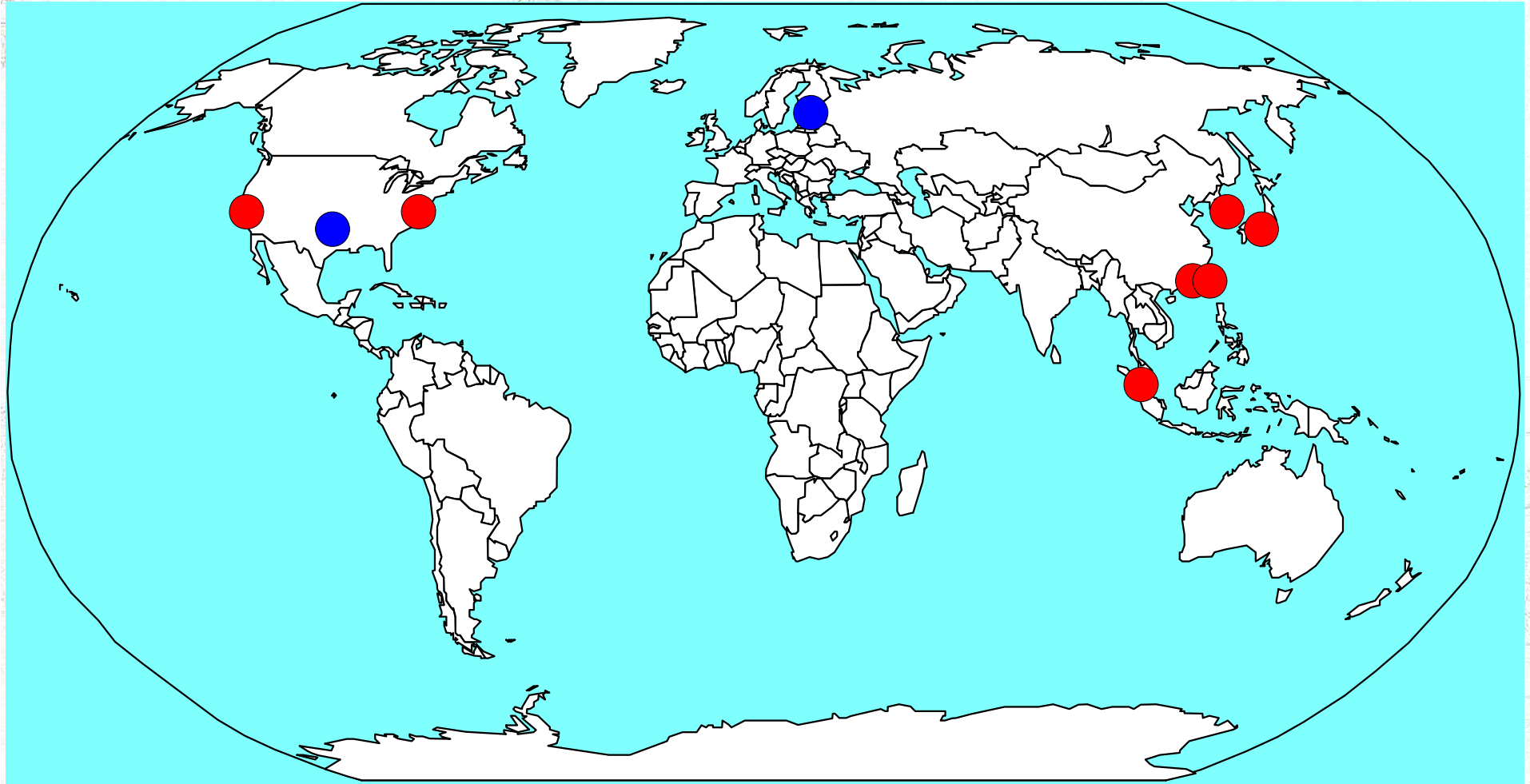
Okmetic Fellow, Okmetic Oyj

Manufacture of High Resistivity, Low Oxygen Czochralski Silicon

Outline

- Background
- Crystal growth and wafer manufacturing
- Wafer characteristics
- High resistivity CZ
 - Metals and lifetime
 - Dopants
 - Oxygen
 - Magnetic field
- Silicon melt behavior
- Conclusions

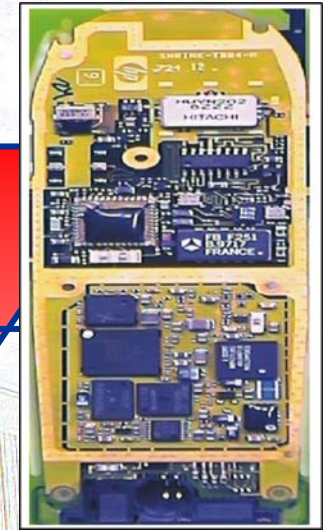
Okmetic Worldwide Presence



Market Overview



Electronic Equipment
\$ 1000 billion / + 8% *)



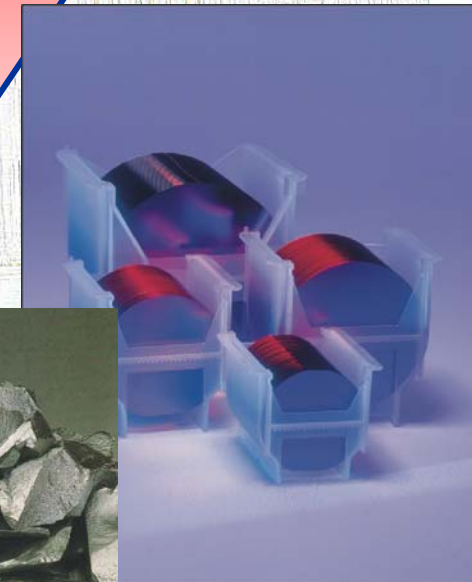
Semiconductors
\$ 250 billion / +15 % *)

Silicon Wafers
\$ 8 billion / +13 % *)



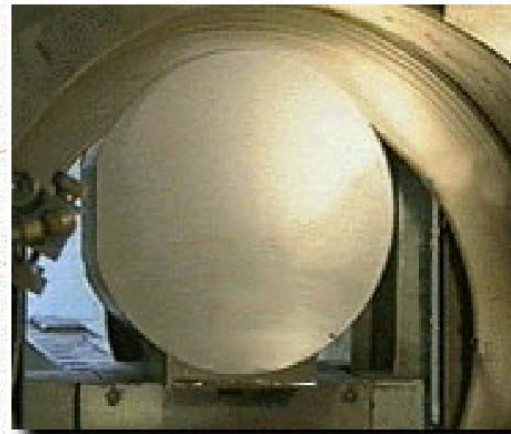
Polysilicon
\$ 0,7 billion
+14 % *)

*)
1970-2003
CAGR



Silicon wafers: Key process steps

- **Crystal Growth**
 - bulk and some surface material properties
- **Wafer slice**
 - final thickness typically 500-600 μm
- **Wafer etch**
 - remove damage
 - final backside



Silicon wafers: Key process steps

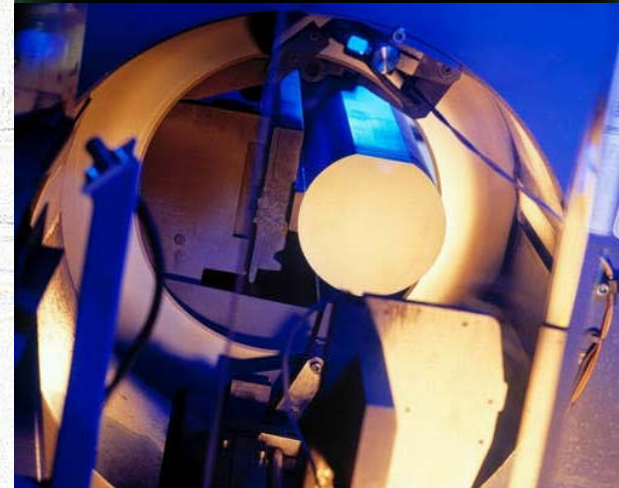
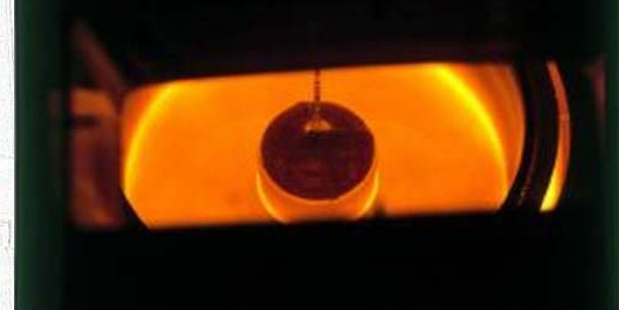
- **Polish**
 - to obtain excellent flatness and surface properties

- **Final Clean and Package**
 - remove particle, metallic, ionic, and organic contamination
 - ensure dependable storage behavior



Okmetic Products

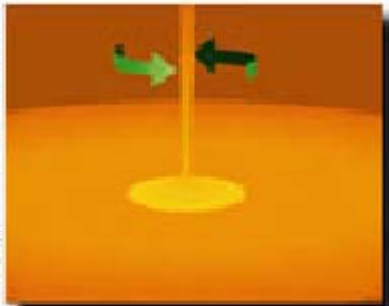
- Polished Cz-silicon wafers for microelectronics
- MEMS silicon wafers for micromechanics
- Epitaxial wafers
- SOI-wafers
- Diameters: 100...200 mm
- Dopants: boron, phosphorus, arsenic and antimony
- Resistivity: 0.002...> 2 kOhm-cm
- Orientations: 1-0-0, 1-1-1 and 1-1-0
- oxygen: < 6...18 ppma
- epi: high uniformity
high resistivity available



Czochralski (CZ) Crystal Growth



1. Polysilicon charge in silica crucible.



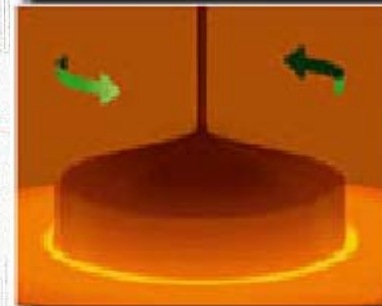
3. Shoulder growth, after neck is complete.



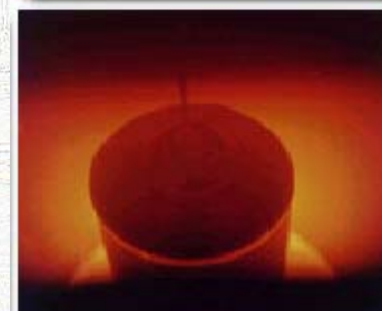
5. Body growth.



2. Start of neck. Seed is dipped to $> 1400\text{ }^{\circ}\text{C}$ melt.



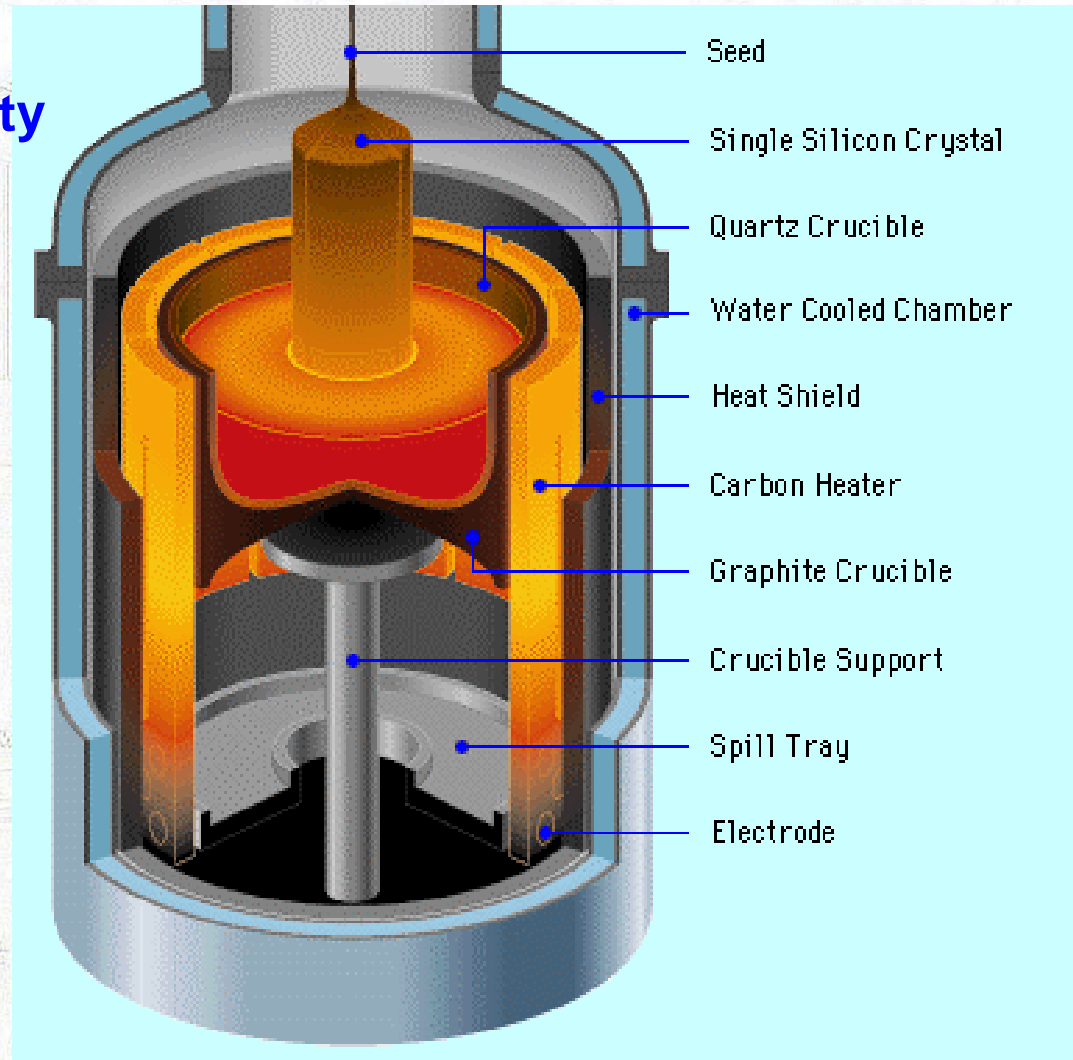
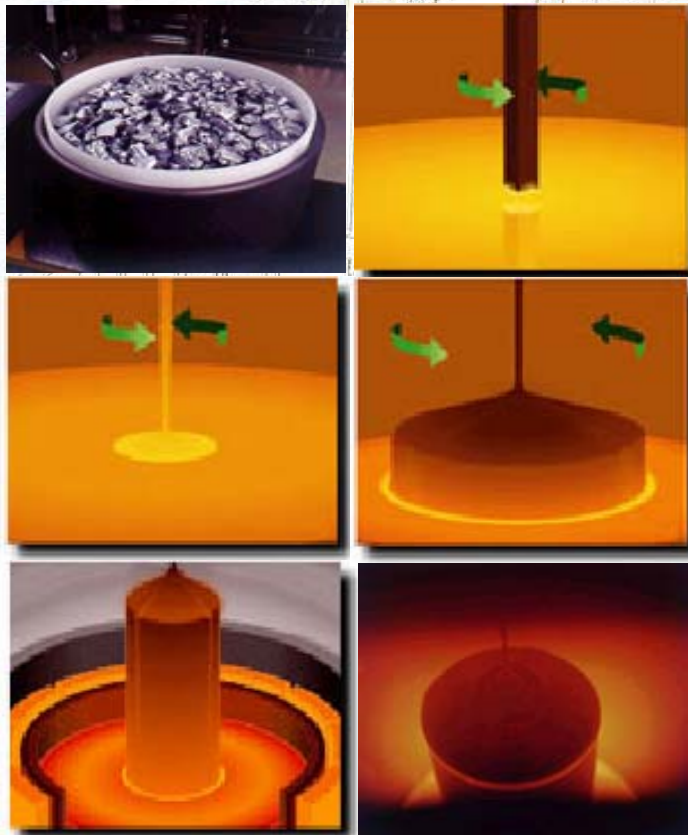
4. Start of body, after completion of shoulder.



5. Conical tail growth after completion of body.

Czochralski (CZ) Crystal Growth

Atmosphere: low pressure, high purity argon.
Hot zone: isostatic high purity graphite and graphite felt.



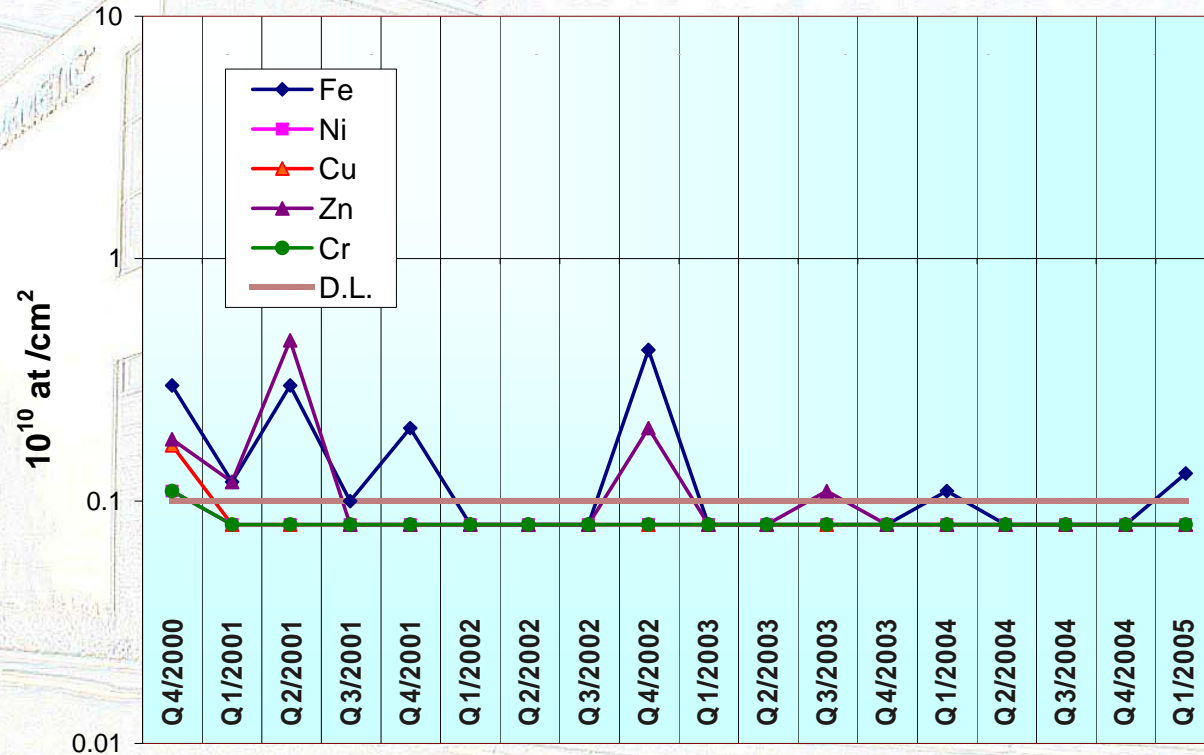
Manufacture of High Resistivity, Low Oxygen Czochralski Silicon

Outline

- Background
- Crystal growth and wafer manufacturing
- **Wafer characteristics: lifetime and metals**
- **High resistivity CZ**
 - Metals and lifetime
 - Dopants
 - Oxygen
 - Magnetic field
- Silicon melt behavior
- Conclusions

Process Capability: Metals

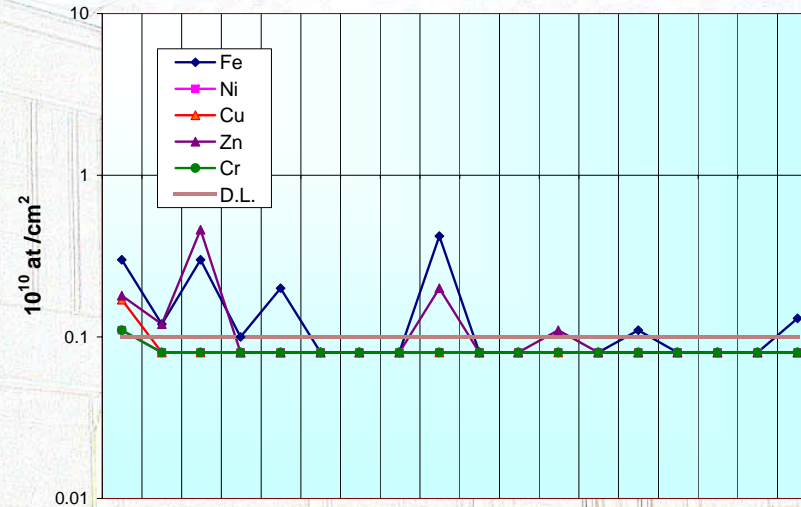
VPD-TXRF, Vantaa plant, Q4/2000 - Q1/2005, average values



Metal levels have been stable at or below detection limit of $1E9$ at /cm². Values include contamination from handling during sampling and measurement.

Process Capability: Metals

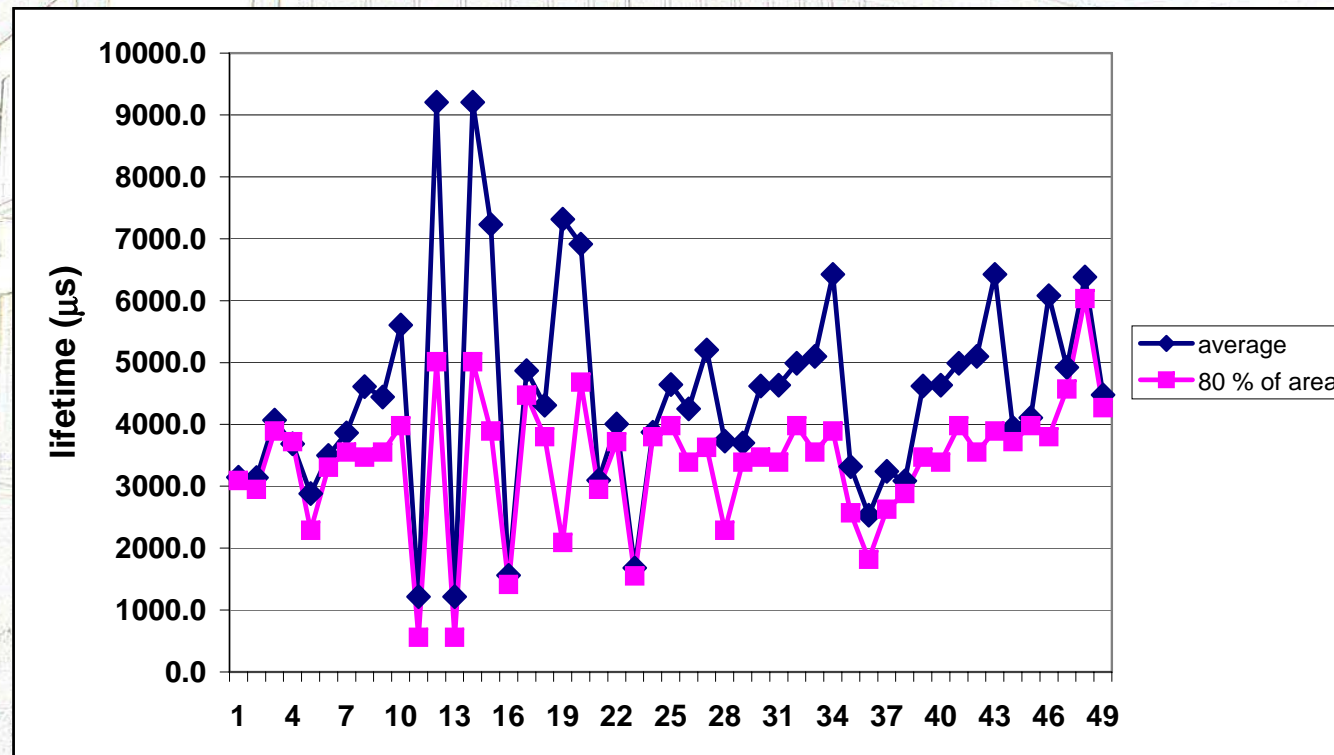
VPD-TXRF, Vantaa plant, Q4/2000 - Q1/2005, average values



Imagine that a coin is made to slide on a wafer, leaving a tail of 10^9 /cm² metal atoms. This equals the typical contamination level of a state-of-the-art clean. Then on another wafer, and another, over and over again. After a while, the coin wears and it gets thinner. How far should we make the coin go, before it is all used up???

Lifetime as-oxidized, during past 24 months

- specification > 500 Ωcm
- both n- and p-type
- no specific emphasis on surface passivation



CZ vs. FZ MATERIAL

for high frequency and detector applications

- **FZ comes naturally oxygen lean**
- **high resistivity readily available with FZ**

So, why look into CZ

- **CZ available in larger diameters**
- **lower wafer cost**
- **better compatibility with advanced CMOS processes**
- **oxygen brings significant improvement in thermal slip resistance**
- **oxygen gives significant radiation hardness advantage?**

CZ vs. FZ MATERIAL

for high frequency and detector applications

Does CZ fulfill the requirements?

- dopant control?
- oxygen related donors?
- metallic contamination? **!YES!**
- recombination lifetime / diffusion length? **!YES!**
- COP's?

Metals in silicon



Imagine that a coin is made to slide on a wafer, leaving a trail of 10^9 /cm² metal atoms. This equals the typical contamination level of a state-of-the-art clean. Then on another wafer, and another, over and over again. After a while, the coin wears and it gets thinner. How far should we make the coin go, before it is all used up???

From the Earth to the Sun, 150 million km!!

Another quiz:

Common metallic contaminants in grown crystal appear typically at 10 ppqa (parts per quadrillion atomic) level. That is 0. and how many zeros??

CZ vs. FZ MATERIAL

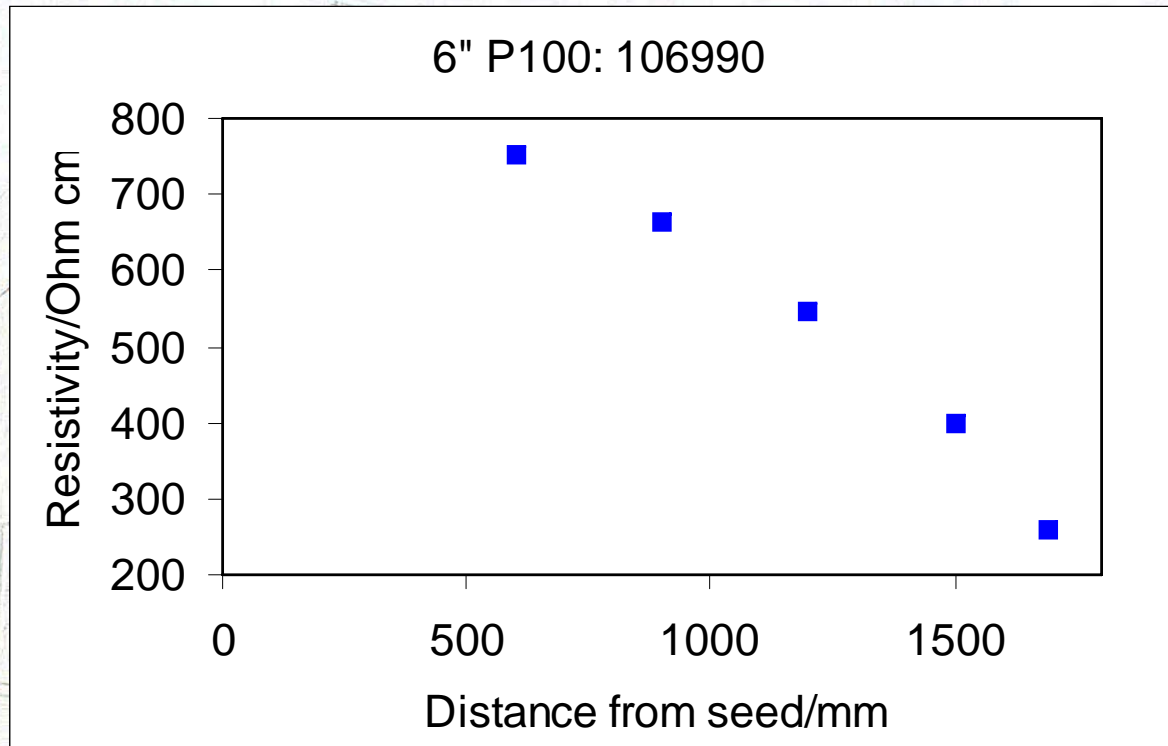
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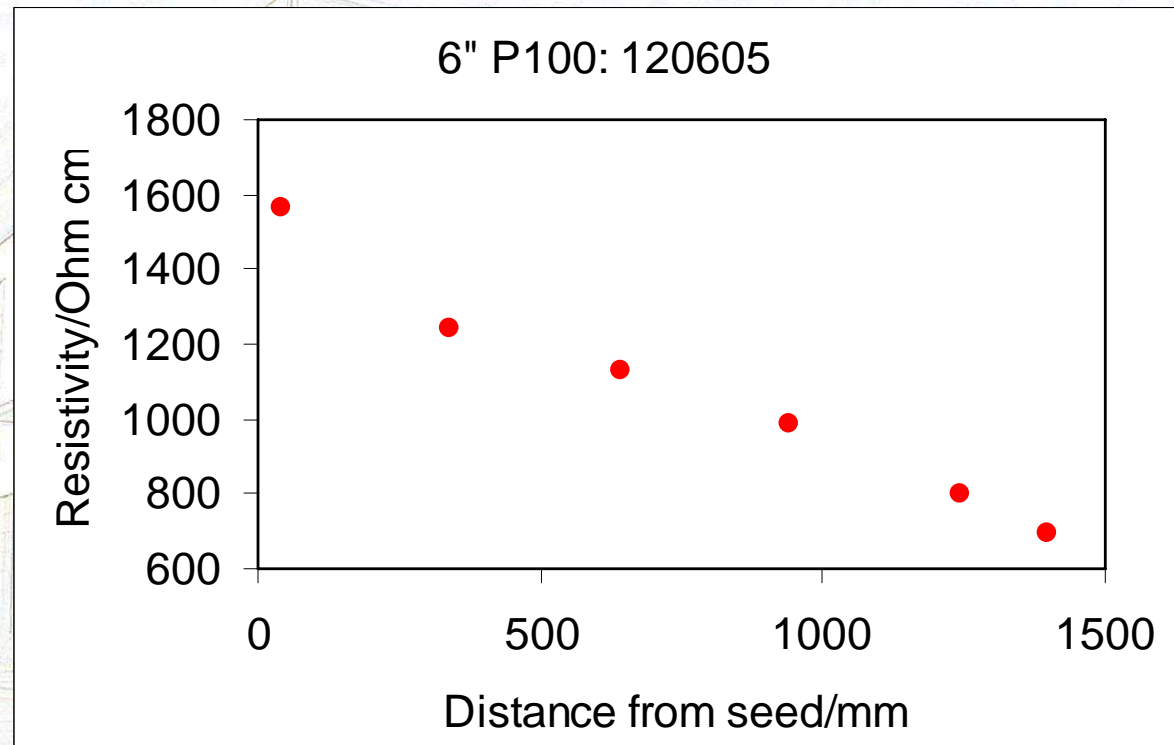
HIGH RESISTIVITY MATERIAL: 6" P100

normal crucible quality



- Intentional doping at about 1600 Ohmcm level at seed end.
- Typical seed-to-tail resistivity ratio is about 1.5; here much larger.
- High crucible boron (& Al) content results in < 1 kOhmcm material.

HIGH RESISTIVITY MATERIAL: 6" P100 synthetic crucible

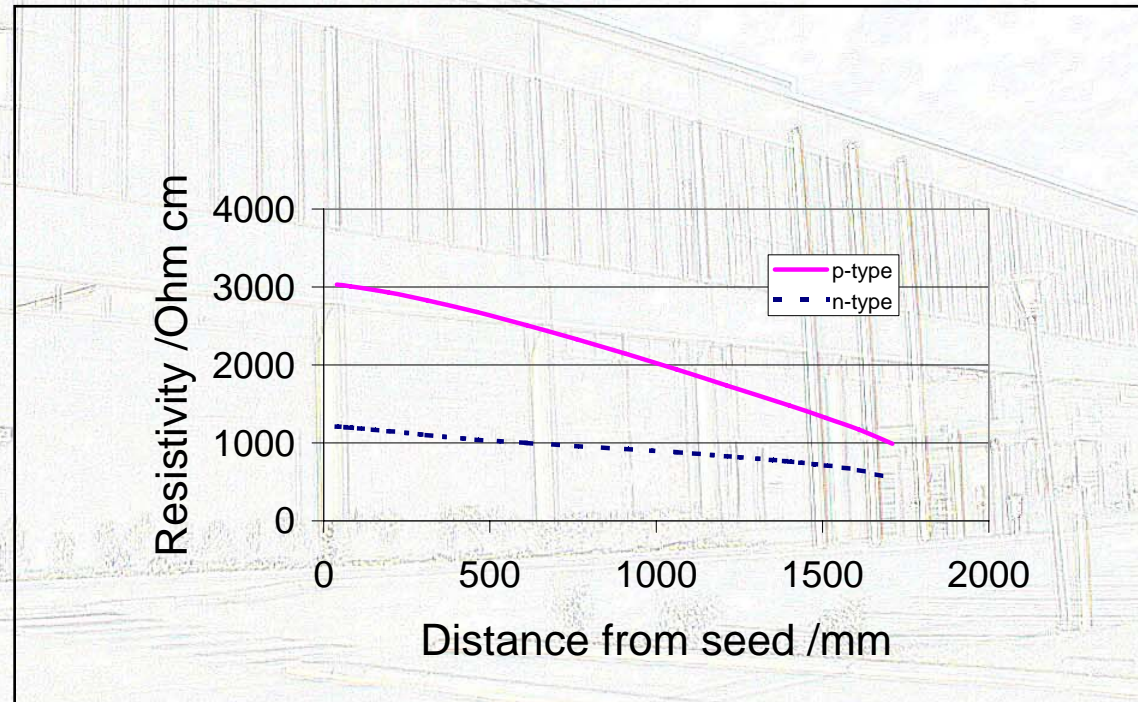


- special SiO₂ coating
- resistivity at seed end is higher due to oxygen donors
- boron contamination in some critical graphite parts

HIGH RESISTIVITY MATERIAL: 150 mm

Appr. attainable *reproducible* resistivity vs. crystal length

- MCZ growth
- high purity silica crucible
- polysilicon grade comparable to high resistivity FZ
- high level of control on hot zone purity



CZ vs. FZ MATERIAL

for high frequency and detector applications

Does CZ fulfill the requirements?

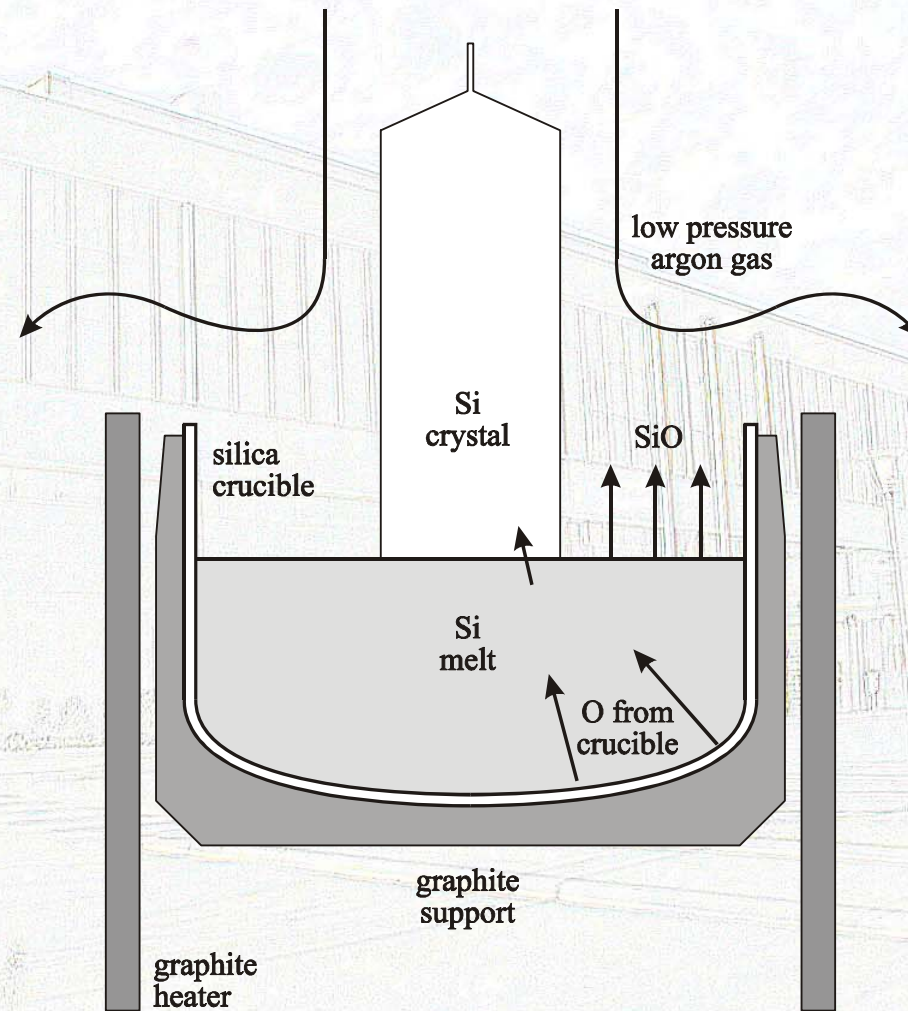
- dopant control? **!YES?**
- oxygen related donors?
- metallic contamination? **!YES!**
- recombination lifetime / diffusion length? **!YES!**
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HIGH RESISTIVITY CZ MATERIAL

- **low interstitial oxygen mandatory**
 - oxygen donors created during crystal growth and device process
 - critical temperature appr. 450 °C
 - donors annihilated > 600 °C
 - back-end-of-the-line (BEOL) temperatures between 400 and 500 °C to be avoided
 - e.g., at 420 °C, only 10-30 min allowed, depending on O_i and resistivity
 - typical O_i 5-8 ppma for high res. material

Oxygen control parameters

- Gas flow
- pressure
- purge tubes (gas flow pattern)
- crucible rotation
- crystal rotation
- temperature distribution
- magnetic field

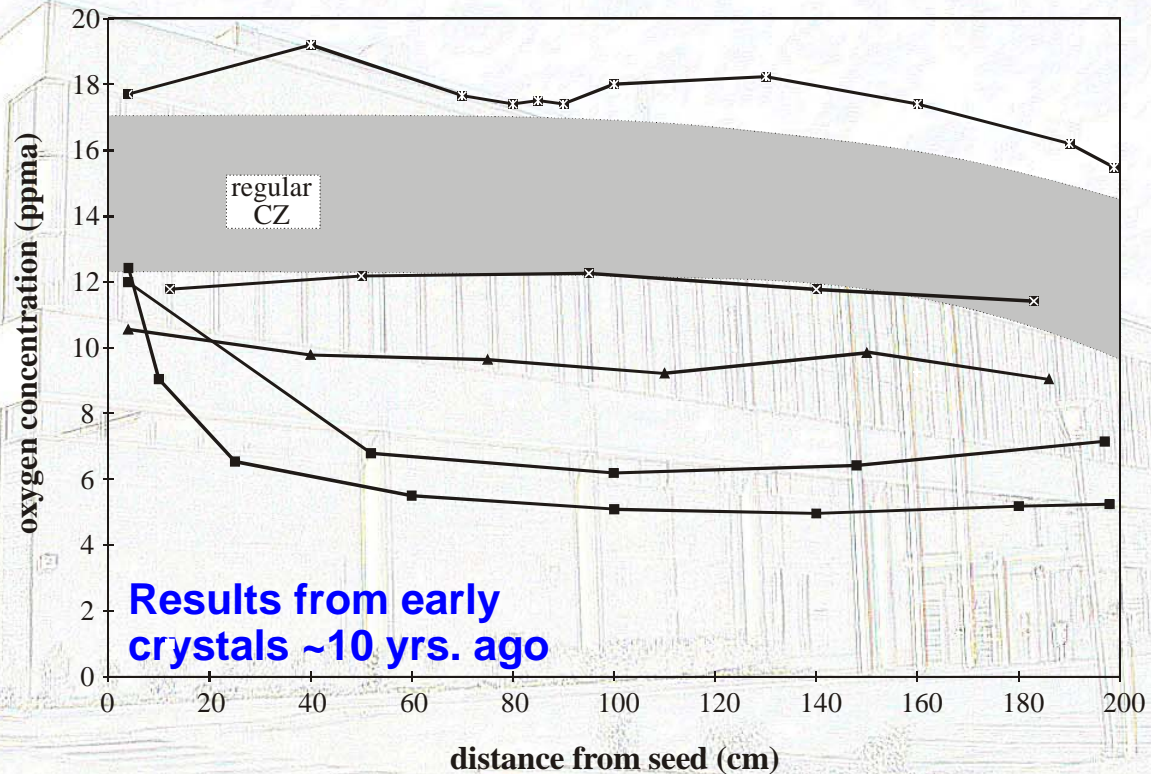


MCZ Puller

- Vacuum system operating at above 1400 °C offers electrical power control, mechanical movements and gas flows. Argon purge pressure is typically 20-30 mbar.
- The I.D. of the magnet > 1 m, max. power range 100 kW.



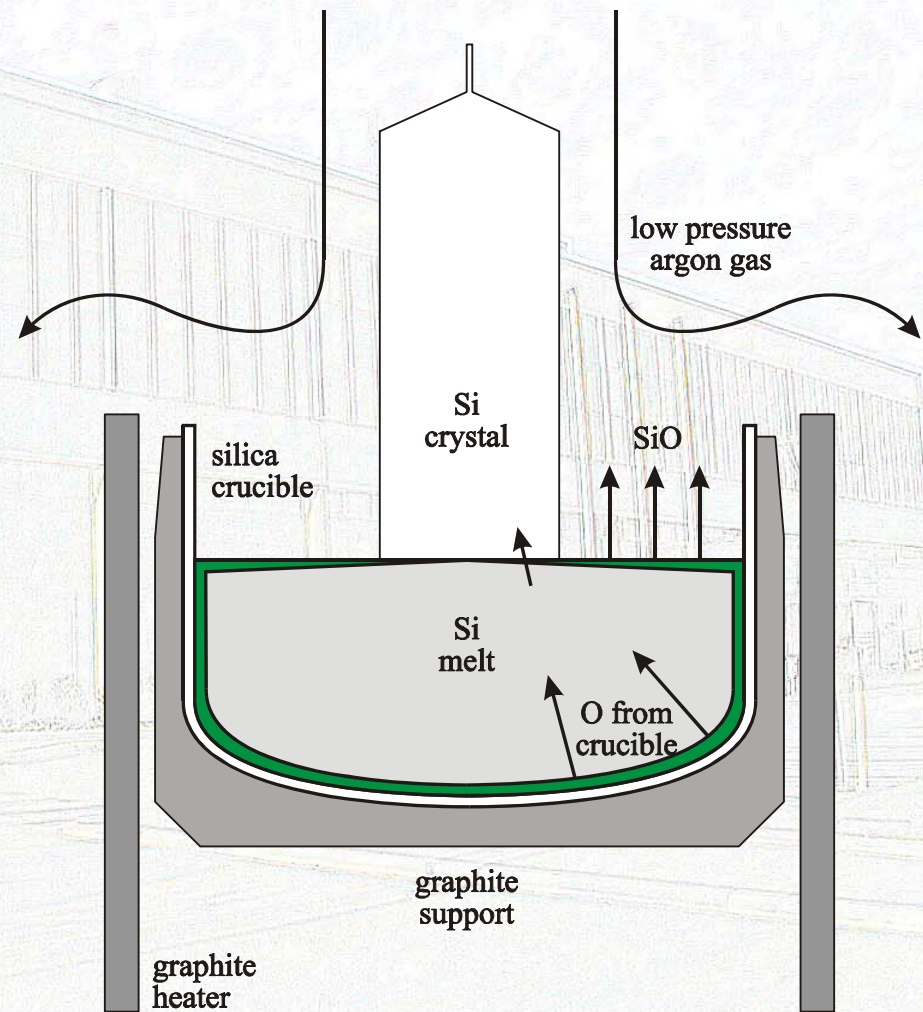
MCZ stabilizes the melt and has some influence on oxygen level



- magnet used by Okmetic results to somewhat *higher* oxygen level than regular CZ
- better melt stability *widens oxygen range*; more aggressive control parameters can be used

Magnetic field changes oxygen behavior

- thicker laminar layer next to crucible wall => *slower oxygen dissolution*
- thicker laminar layer at gas interface => tendency to *increase oxygen in the melt*
- balance between these two effects defines oxygen level
- slow crucible erosion => long crucible lifetime, low dopant emission rate
- **price to pay: more difficult control of radial variations! Both dopants and oxygen**



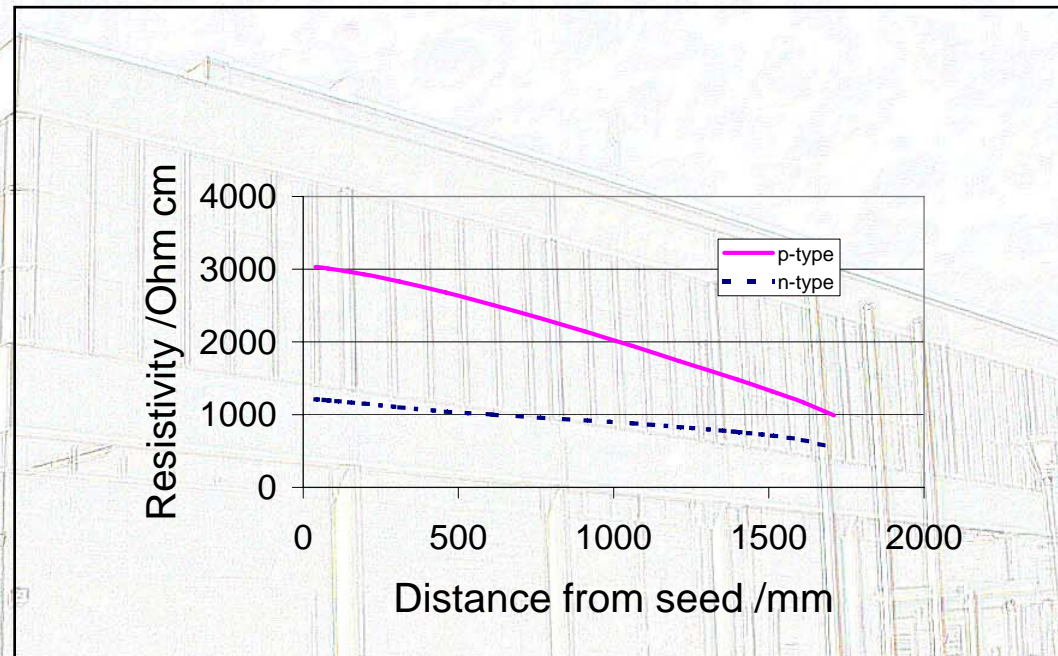
CZ vs. FZ MATERIAL

for high frequency and detector applications

Does CZ fulfill the requirements?

- dopant control? **!YES?**
- oxygen related donors? **!YES?**
- metallic contamination? **!YES!**
- recombination lifetime / diffusion length? **!YES!**
- **COP's?** remains unresolved at this point, and should be addressed later, if needed; typical density $< 1E6$ /cc.

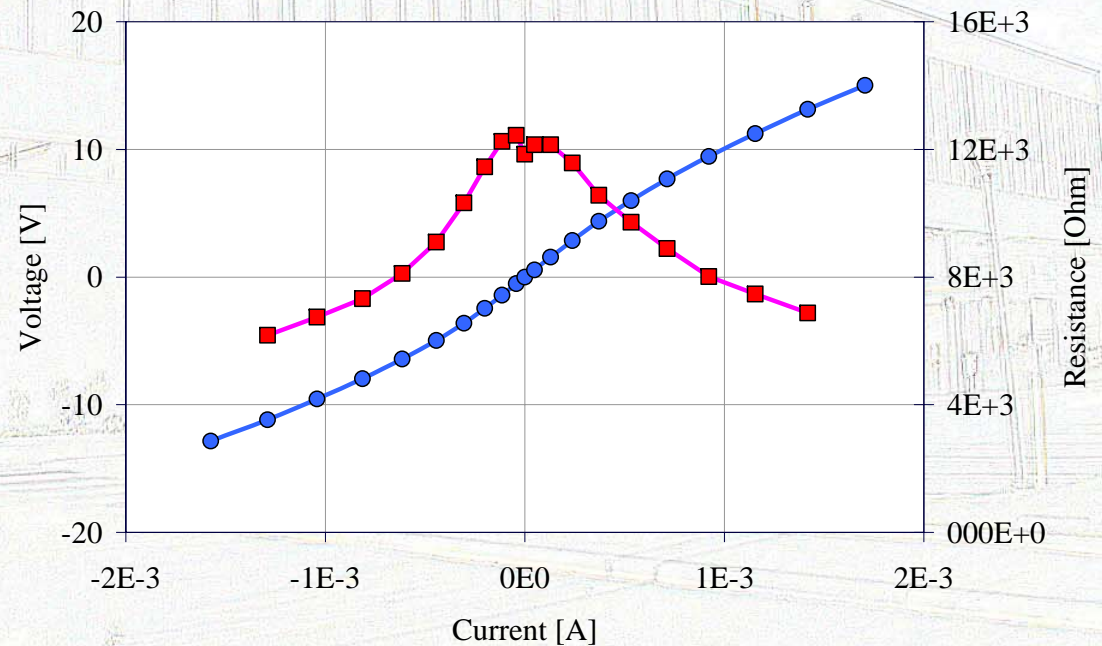
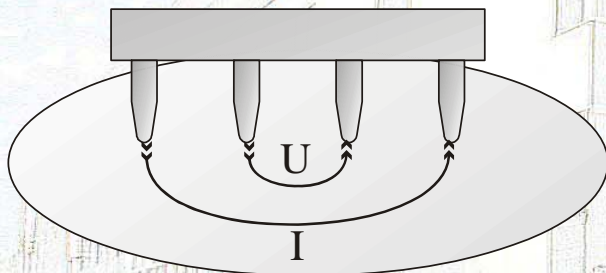
HIGH RESISTIVITY MATERIAL: 150 mm



- > 2 kOhmcm P-type material manufacturable
- 100 mm material allows somewhat higher values
- n-type resistivity about factor 2 lower
- oxygen < 8 ppma

Measurement of Resistivity 4-Point Probe

- ~ 2000 Ωcm p-type
- proper value only at very low current (avalanche injection!)
- measurement stability major issue



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Characteristic data

- + crucible diameter ~0.5 m
- + crystal diameter 100-300 mm (300 mm)
- + about 100 kg in the beginning of process (several 100's of kg)
- + melting temp 1412 °C
- + kinematic viscosity very low 2.8 E-7 m²/s
- + Prandtl number very low 0.011
- + crystal rotation 10-30 rpm
- + crucible rotation 2-20 rpm
- + typical Grashof number high **1E10**
- + typical crystal Reynolds number
some 10's of thousands

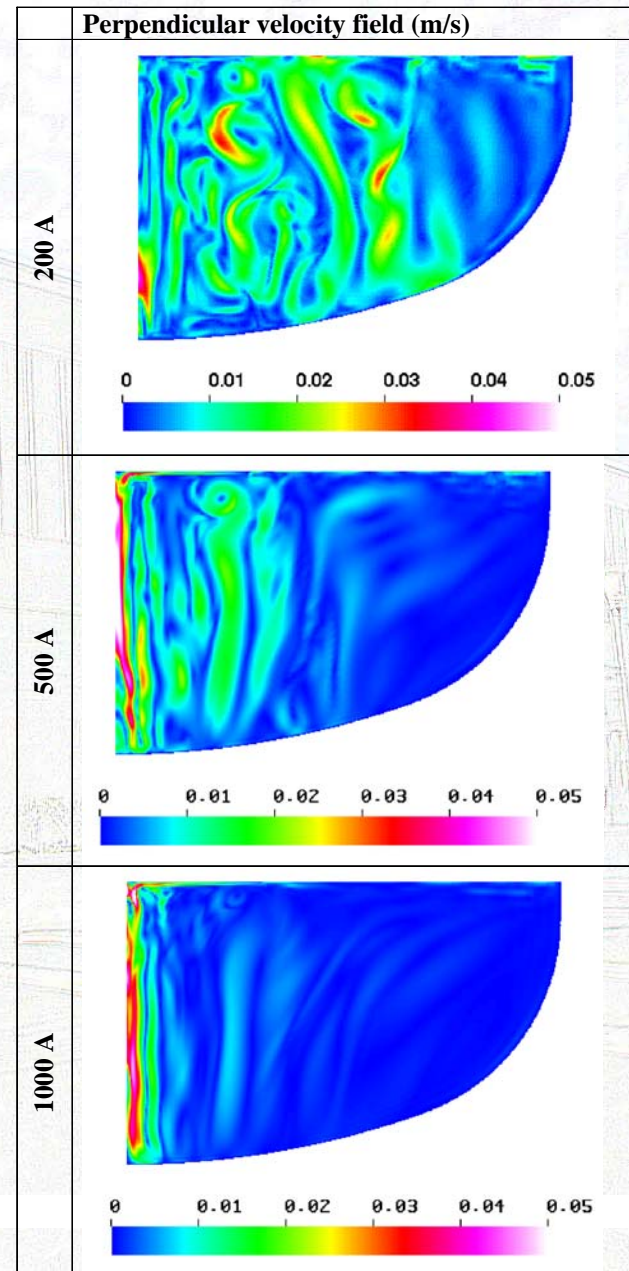


Magnetic field effect

- Strongest field at crucible corner
 - flow suppressed by strong field
- => growth effectively from smaller, less unstable melt
- under crystal, minor impact

dopant, oxygen distribution is not uniform even with MCZ

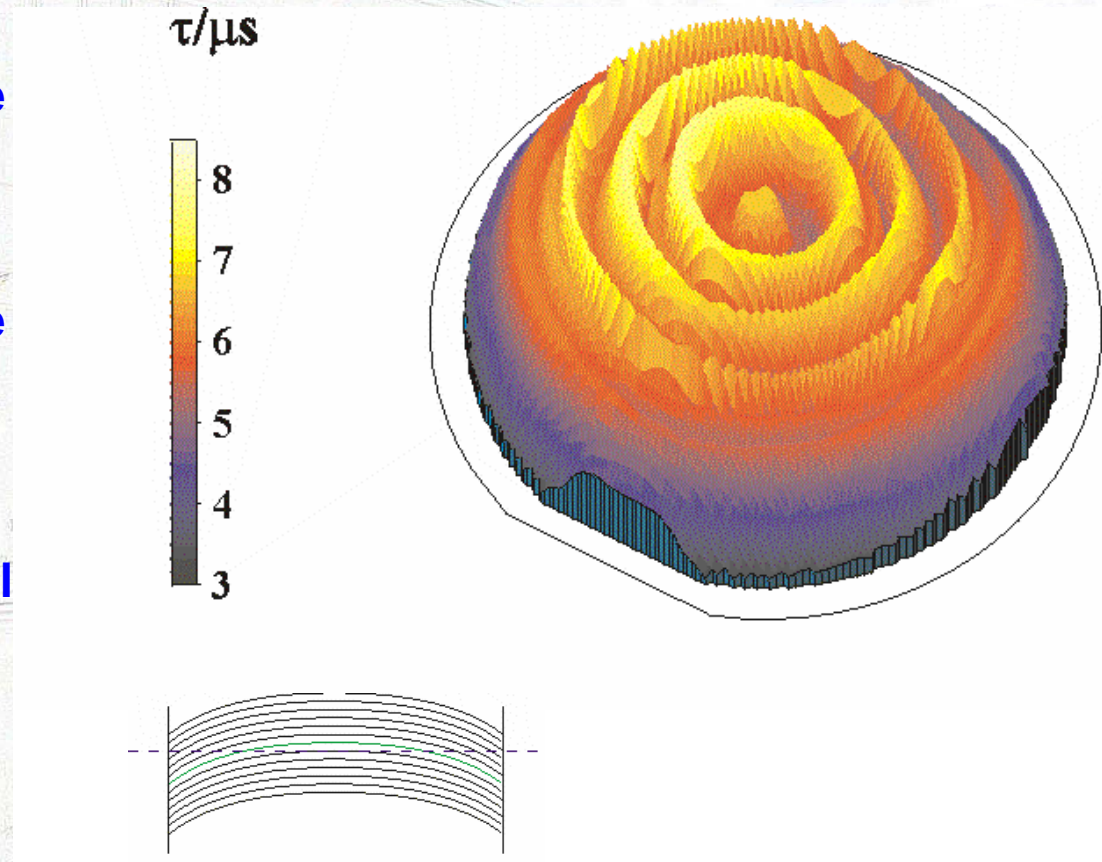
Melt flow is buoyancy driven turbulent



The melt behavior is not quite so smooth...

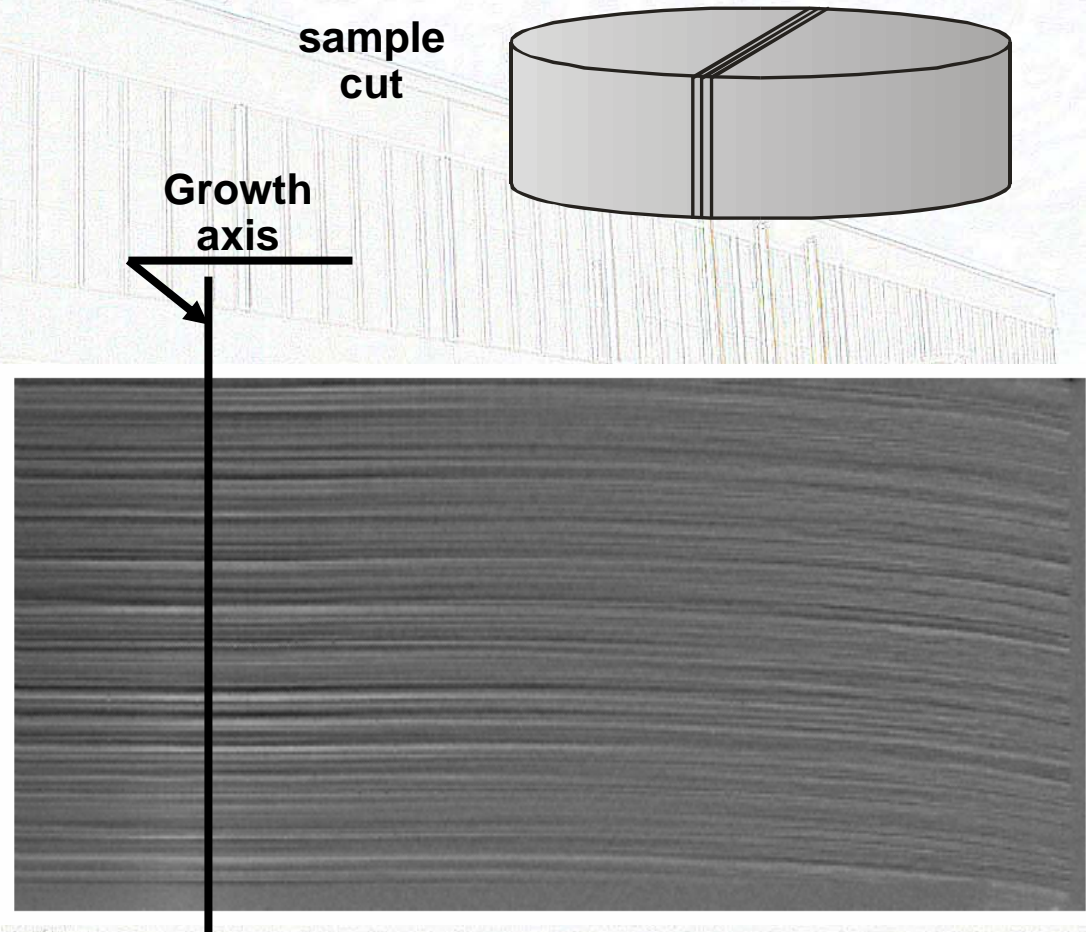
Recombination Lifetime After Oxygen Precipitation
125 mm N(100), 850 °C / 4h + 1000 °C / 12 h O₂

- shorter lifetime where more precipitates
- ring diameters give time scale, together with freezing interface curvature
- quasiperiodic behavior, time scale ~1 min
- ~ open hot zone, early 90's
- behavior is *not* external pull rate related



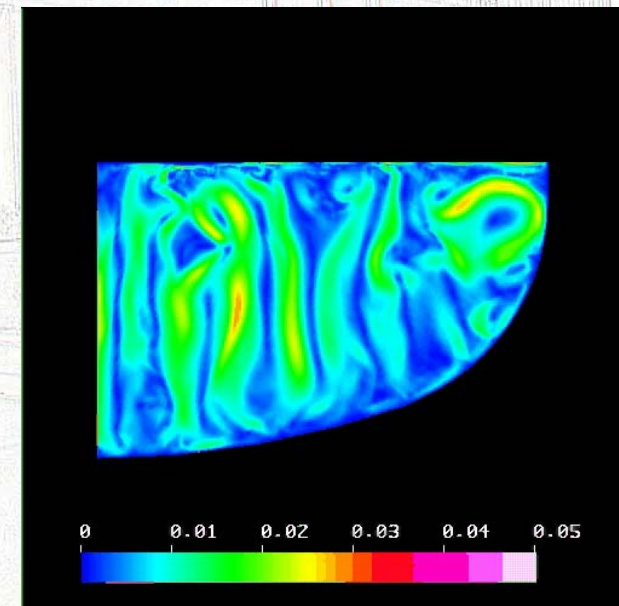
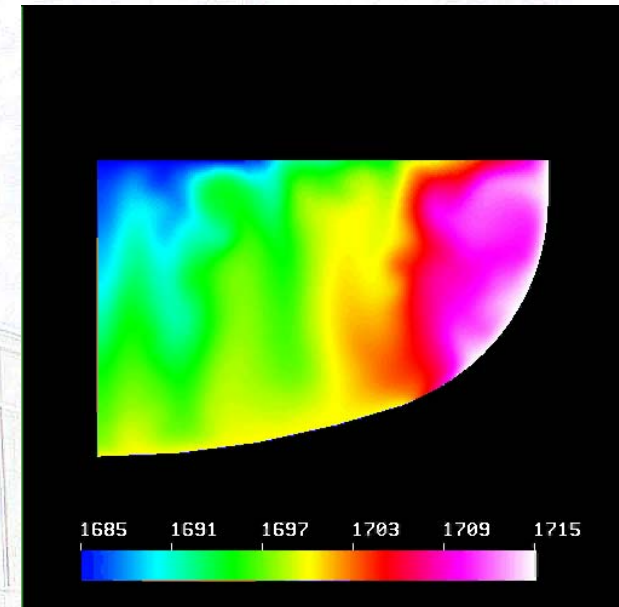
LPS measurement on 150 mm N(100) 5 Ohmcm crystal

- area shown 100 x 50 mm
- sample as-grown and donor kill annealed
- freezing interface shape nicely visible
- time dependent freezing velocity can be measured if spectral response of measurement is known



Silicon Melt Modeling: Temperature Distribution and Velocity Field

- crucible rotation 5 rpm
- time dependent, chaotic behavior
- heat to the crystal largely from the bottom



Turbulence

It was at a meeting of the British Association in London in 1932 that I remember Hoarce Lamb remarked:

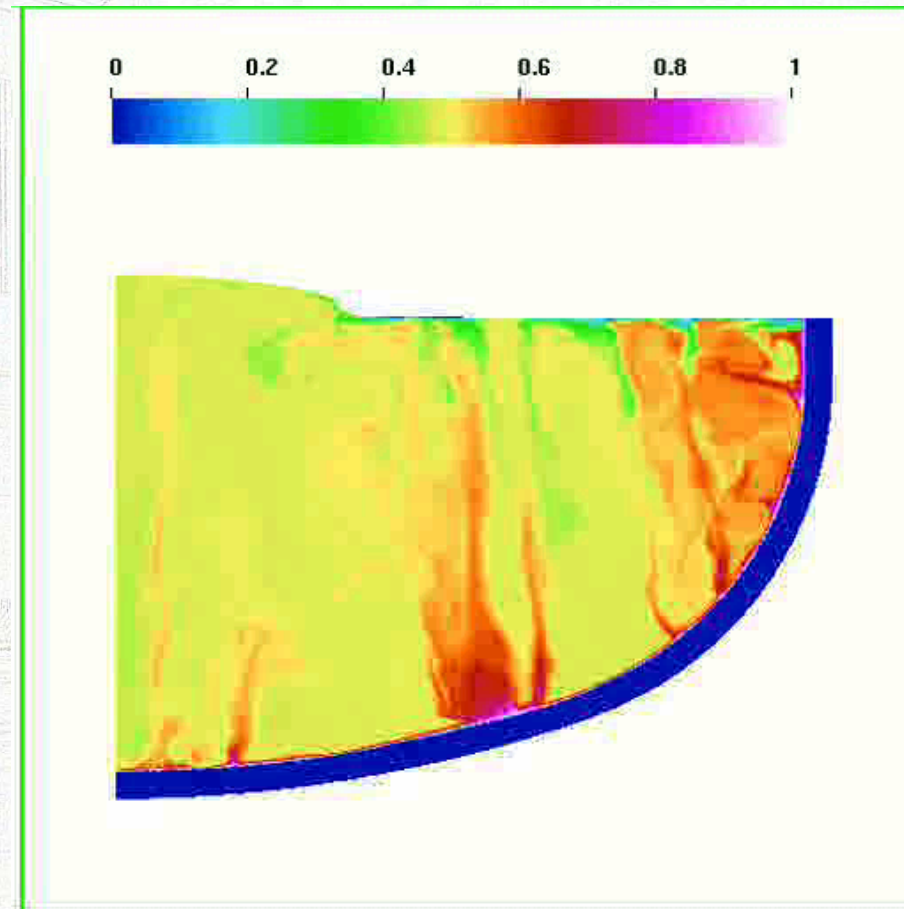
“I am an old man now, and when I die and go to Heaven there are two matters on which I hope for enlightenment. One is quantum electrodynamics, and the other is the turbulent motion of fluids. And about the former I am really rather optimistic.”

– Sir Sydney Goldstein

Annual Reviews of Fluid Mechanics, Vol. 1 (1969), p. 1

Modeling: Oxygen distribution in melt

- relatively large radial gradients in the melt
 - well mixed melt pool assumption
 - classical explanation for lower oxygen in tail needs reconsideration
 - oxygen slow diffuser, contrary to heat
- => no direct connection between oxygen and dopant striations



50 slpm@20 mbar

Conclusions

- **Main issues in high resistivity CZ material**

- **metallic contamination**
- **lifetime**
- **dopant level**
- **oxygen level**

have been solved to satisfactory / reasonable level

- **magnetic Cz and tight control of dopant contamination mandatory**
- **naturally appearing oxygen offers some advantages**
- **ample space for further developments**



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