



# Manufacture of High Resistivity, Low Oxygen Czochralski Silicon

June 2005

Olli Anttila

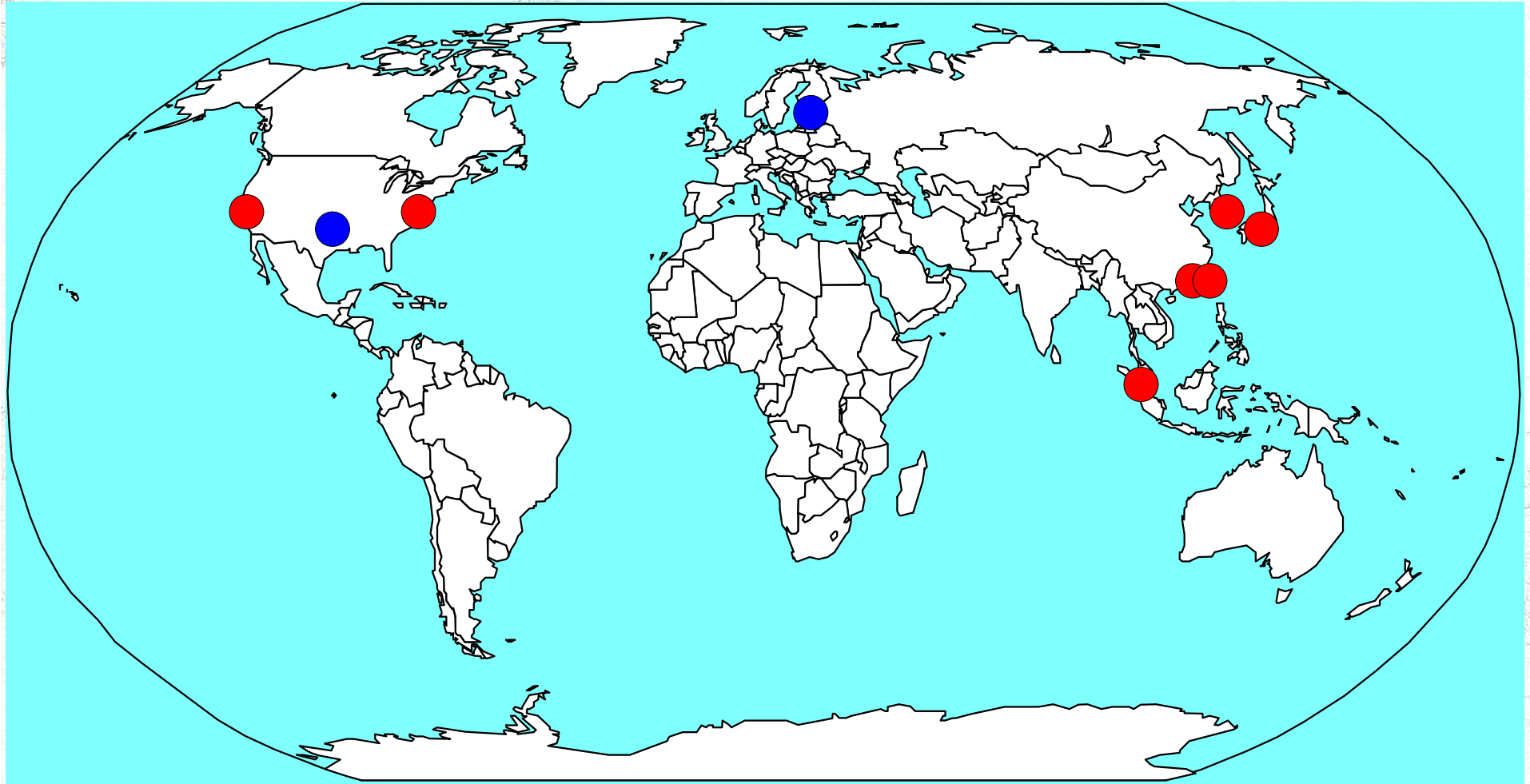
Okmetic Fellow, Okmetic Oyj

# 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

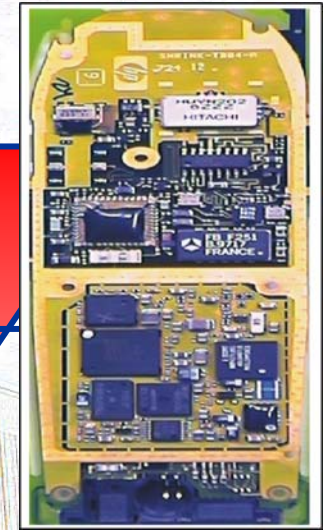
# Okmetic Worldwide Presence



# Market Overview



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



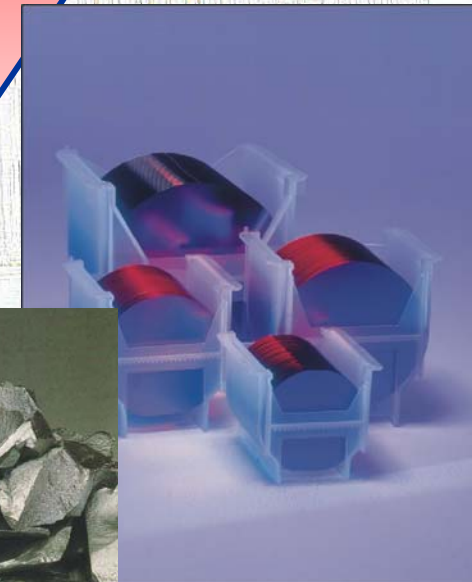
**Semiconductors**  
\$ 250 billion / +15 % \*)

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



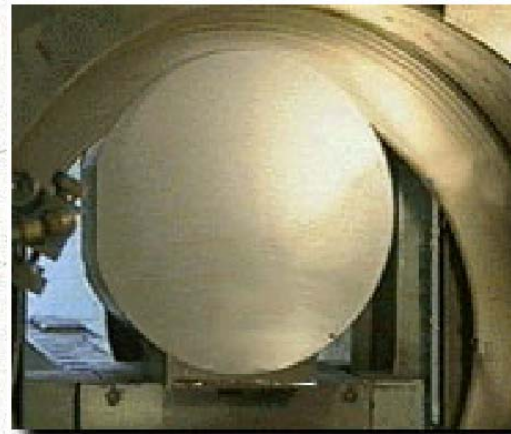
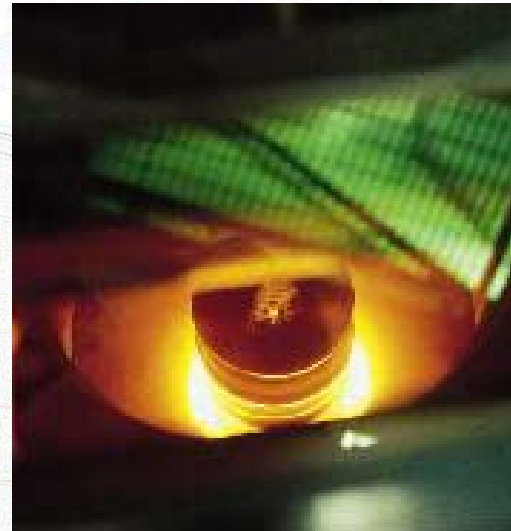
**Polysilicon**  
\$ 0,7 billion  
+14 % \*)

\*)  
1970-2003  
CAGR



# Silicon wafers: Key process steps

- **Crystal Growth**
  - bulk and some surface material properties
- **Wafer slice**
  - final thickness typically 500-600  $\mu\text{m}$
- **Wafer etch**
  - remove damage
  - final backside



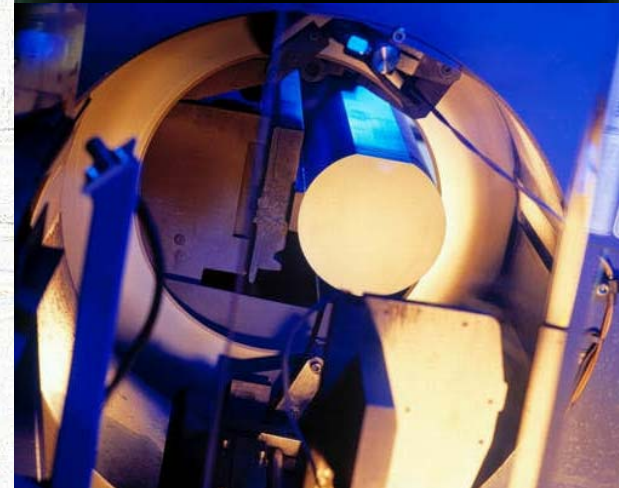
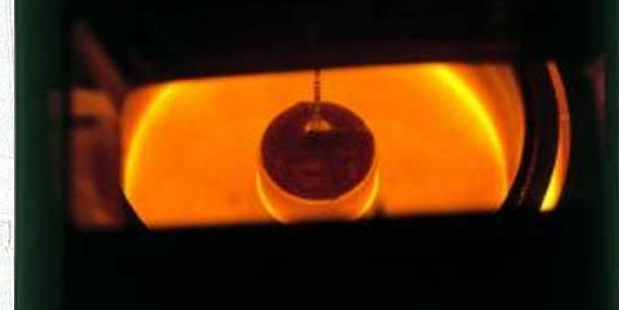
# Silicon wafers: Key process steps

- **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

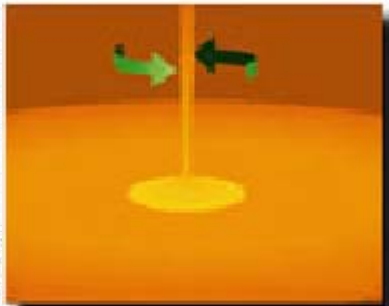
- Polished Cz-silicon wafers for microelectronics
- MEMS silicon wafers for micromechanics
- Epitaxial wafers
- SOI-wafers
- Diameters: 100...200 mm
- Dopants: boron, phosphorus, arsenic and antimony
- Resistivity: 0.002...> 2 kOhm-cm
- Orientations: 1-0-0, 1-1-1 and 1-1-0
- oxygen: < 6...18 ppma
- epi: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



# Czochralski (CZ) Crystal Growth



1. Polysilicon charge in silica crucible.



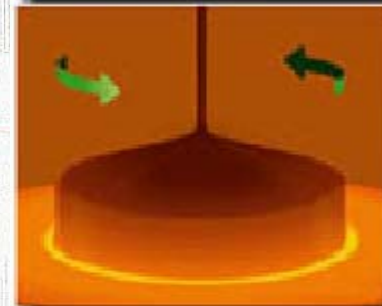
3. Shoulder growth, after neck is complete.



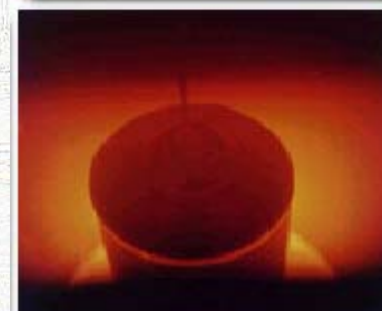
5. Body growth.



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



4. Start of body, after completion of shoulder.



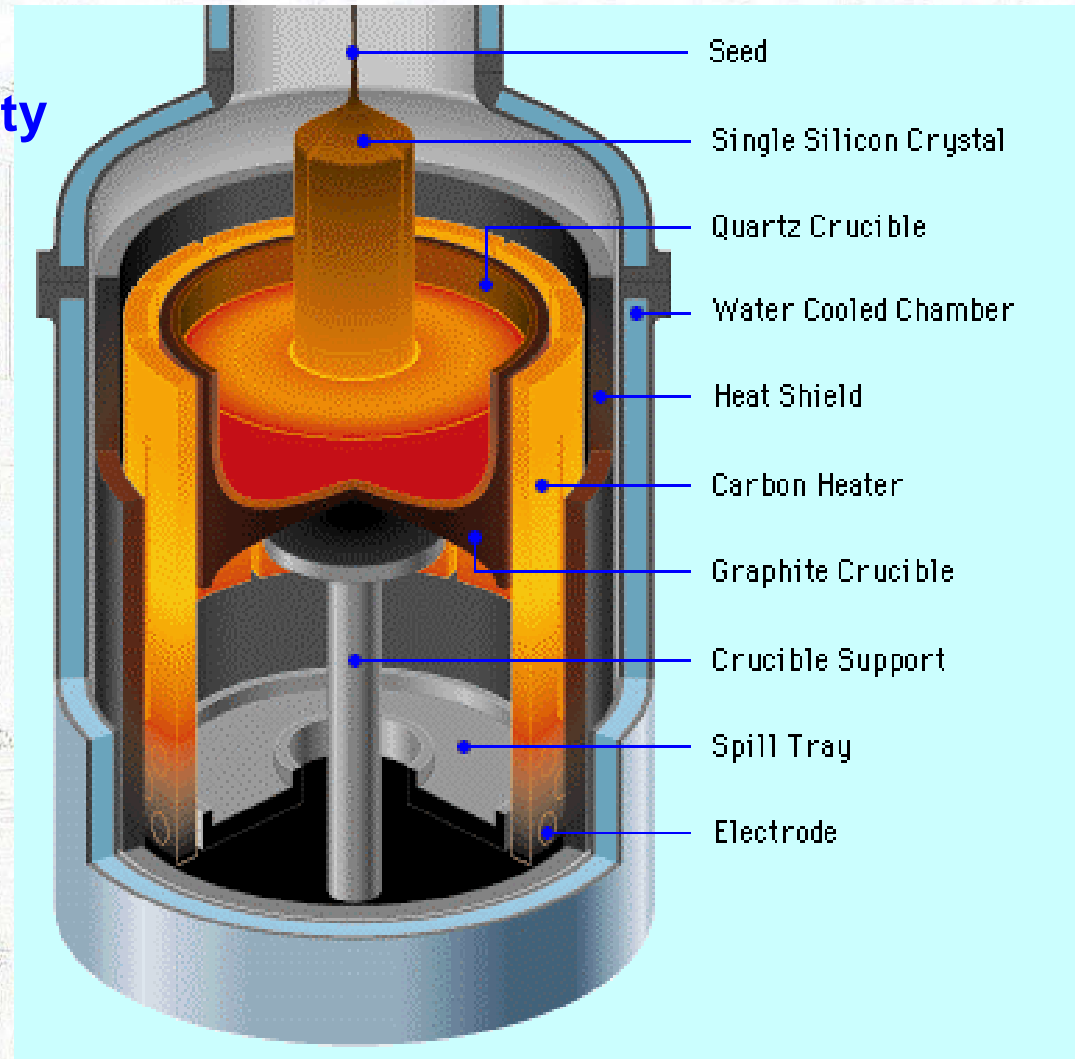
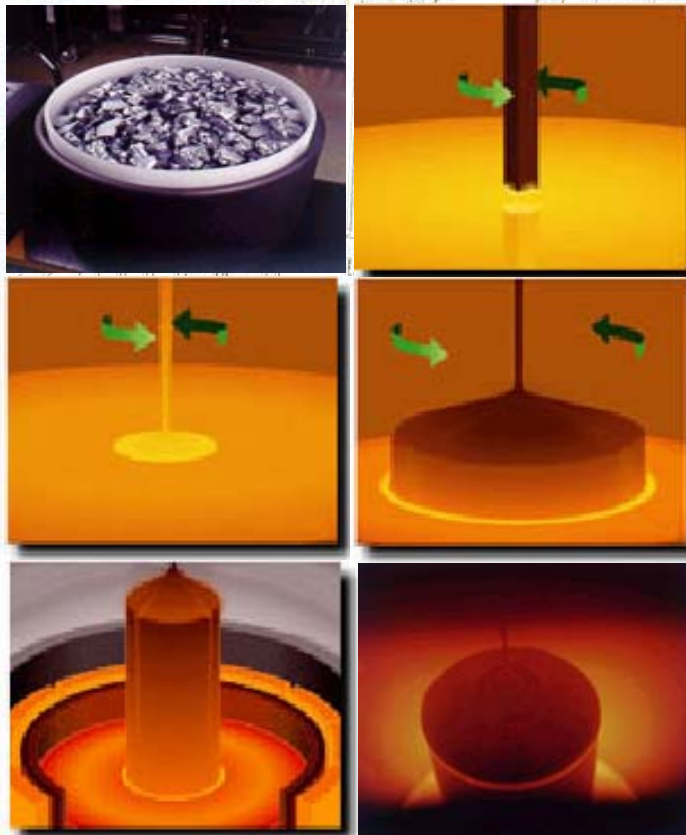
5. Conical tail growth after completion of body.



# Czochralski (CZ) Crystal Growth

Atmosphere: low pressure,  
high purity argon.

Hot zone: isostatic high purity  
graphite and graphite felt.



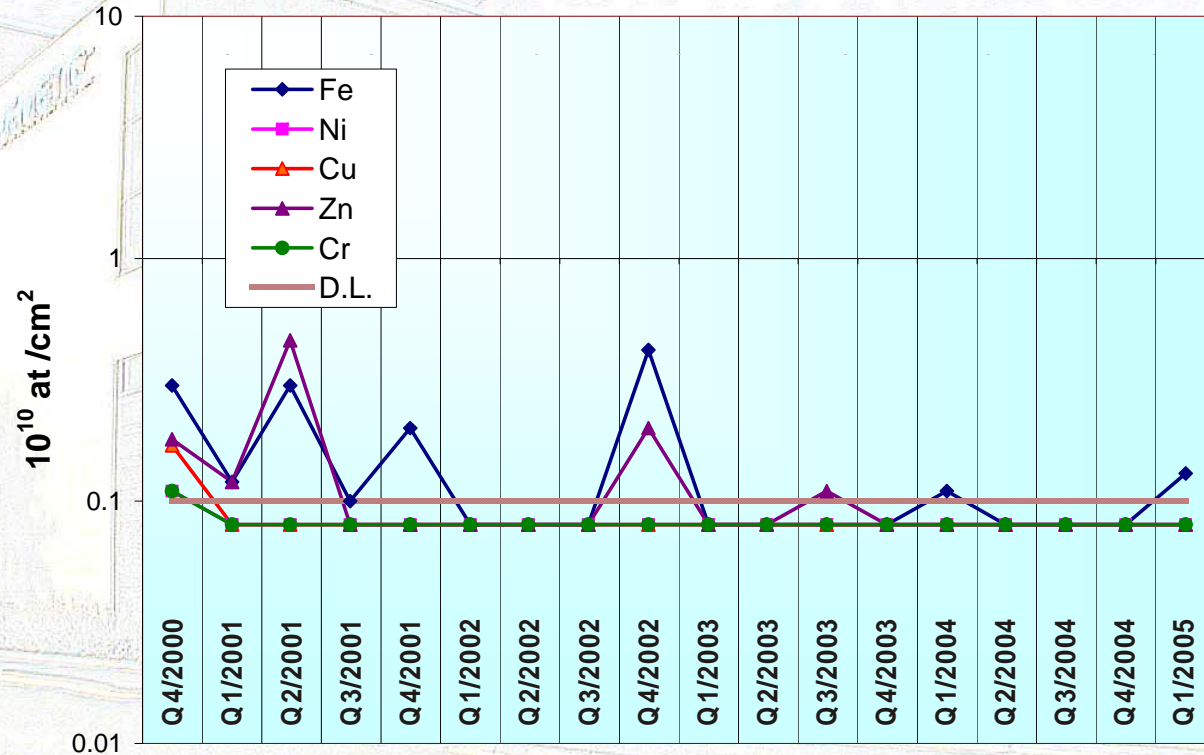
# Manufacture of High Resistivity, Low Oxygen Czochralski Silicon

## 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

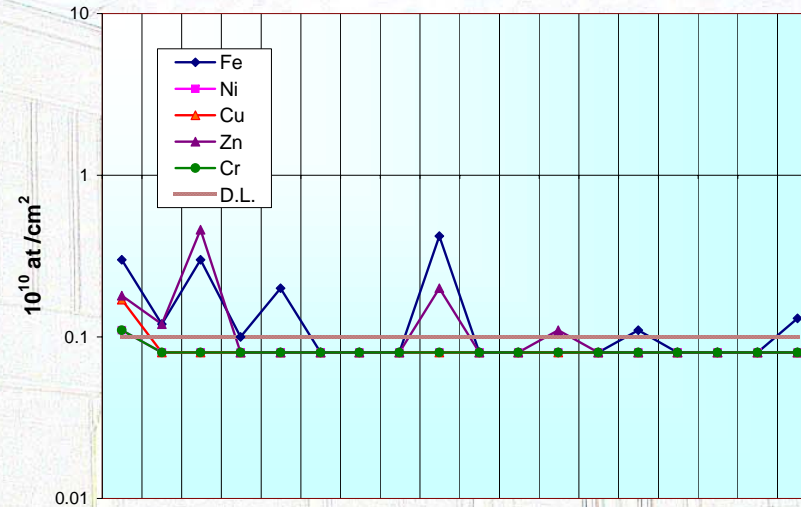
VPD-TXRF, Vantaa plant, Q4/2000 - Q1/2005, average values



Metal levels have been stable at or below detection limit of  $1E9$  at /cm<sup>2</sup>. Values include contamination from handling during sampling and measurement.

# Process Capability: Metals

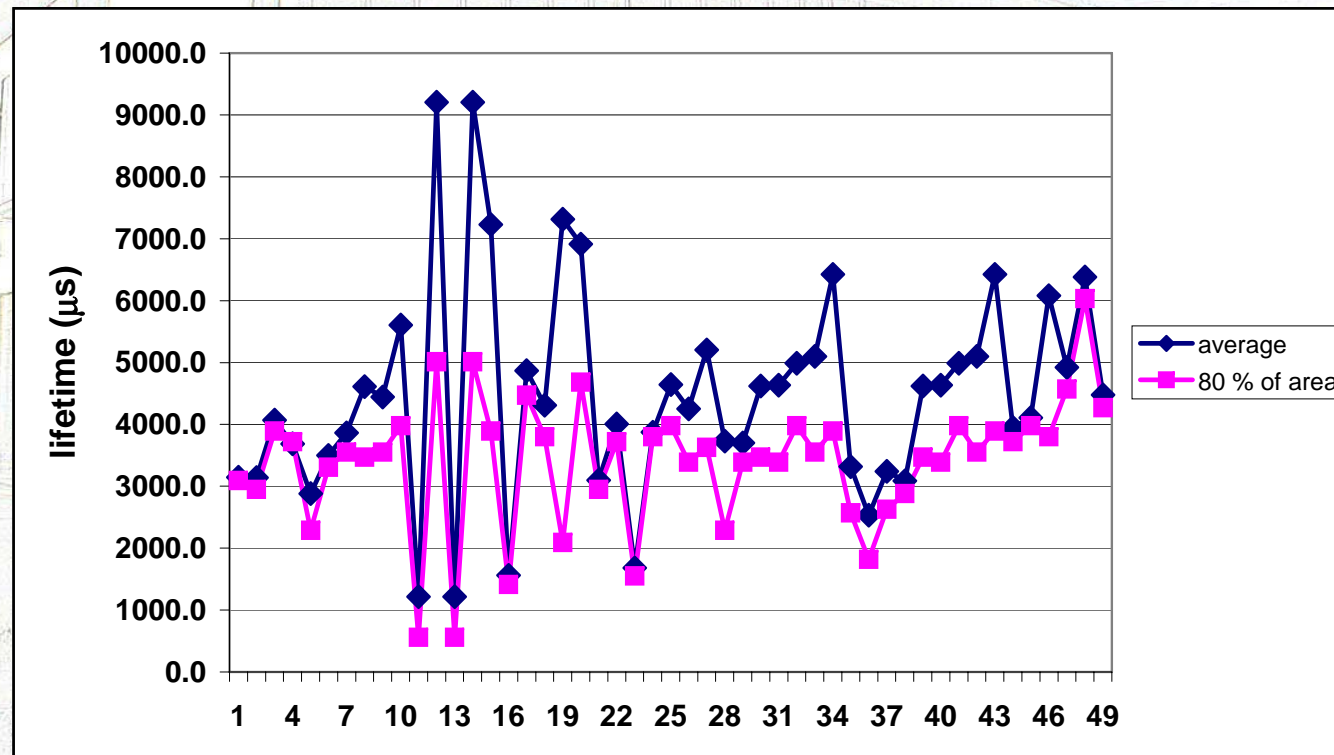
VPD-TXRF, Vantaa plant, Q4/2000 - Q1/2005, average values



Imagine that a coin is made to slide on a wafer, leaving a trail of  $10^9$  /cm<sup>2</sup> 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  $\Omega\text{cm}$
- 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  $10^9$  /cm<sup>2</sup> 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

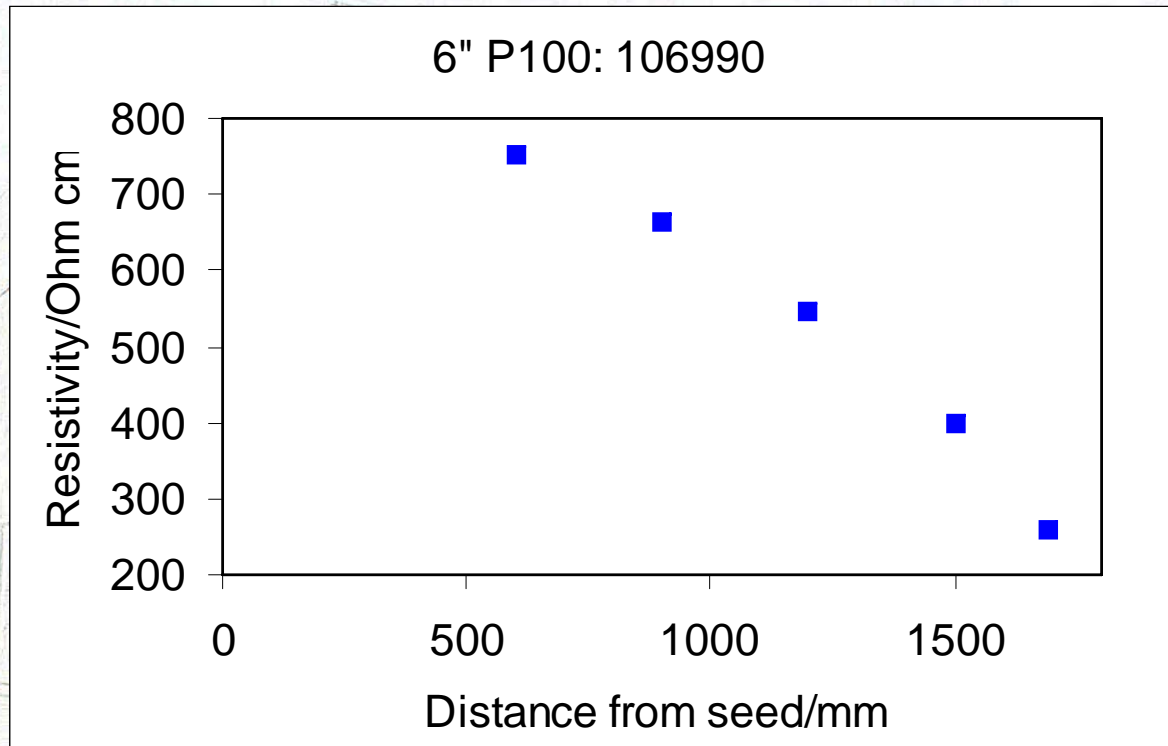
## for high frequency and detector applications

Does CZ fulfill the requirements?

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

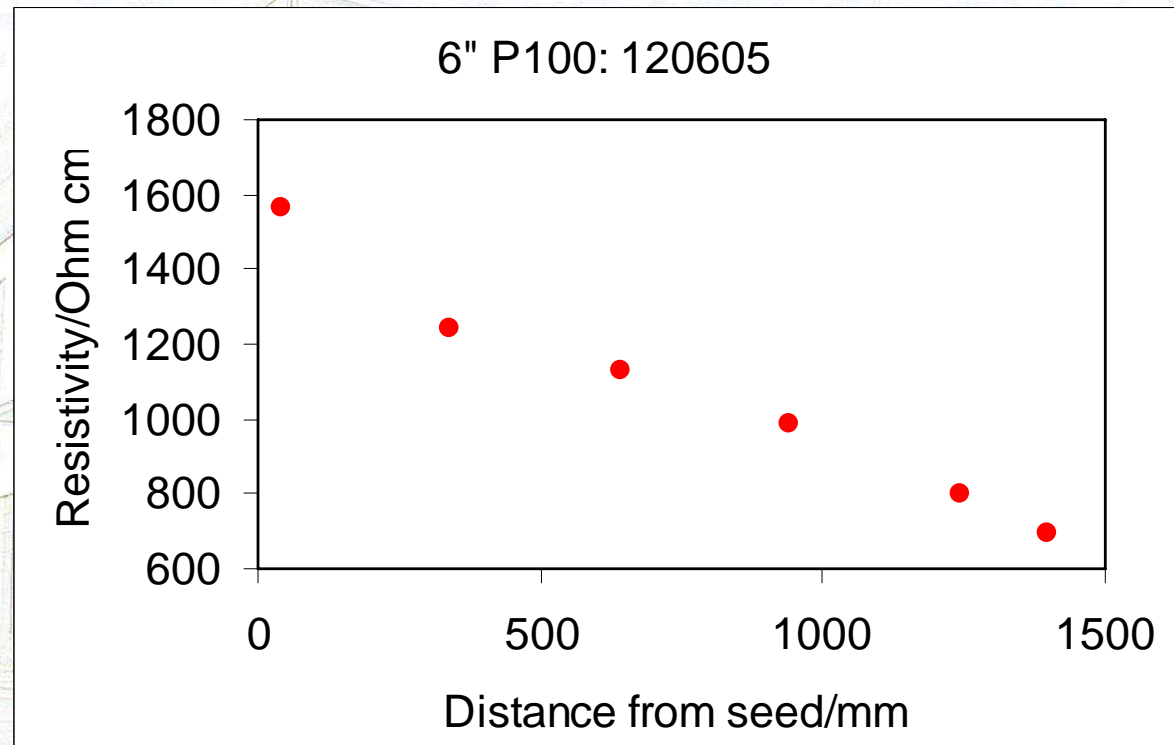
# HIGH RESISTIVITY MATERIAL: 6" P100

*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

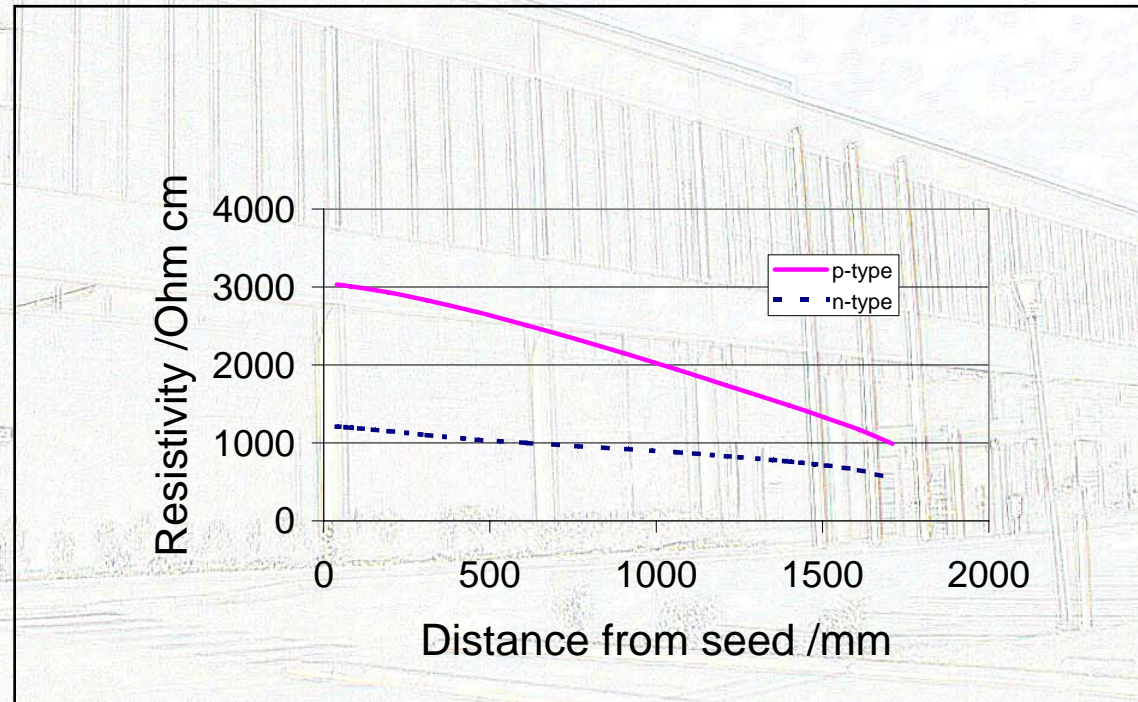


- special SiO<sub>2</sub> coating
- resistivity at seed end is higher due to oxygen donors
- boron contamination in some critical graphite parts

# 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?

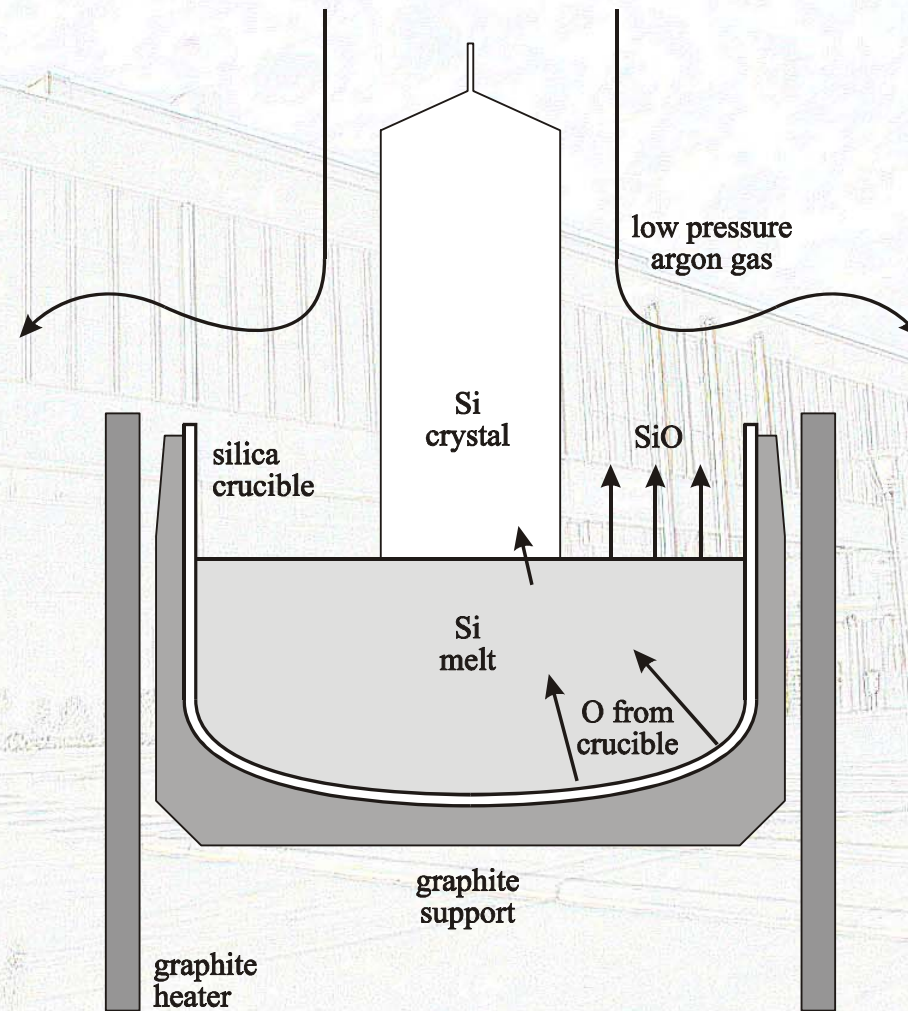
- dopant control? **!YES?**
- oxygen related donors?
- metallic contamination? **!YES!**
- recombination lifetime / diffusion length? **!YES!**
- COP's?

# 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



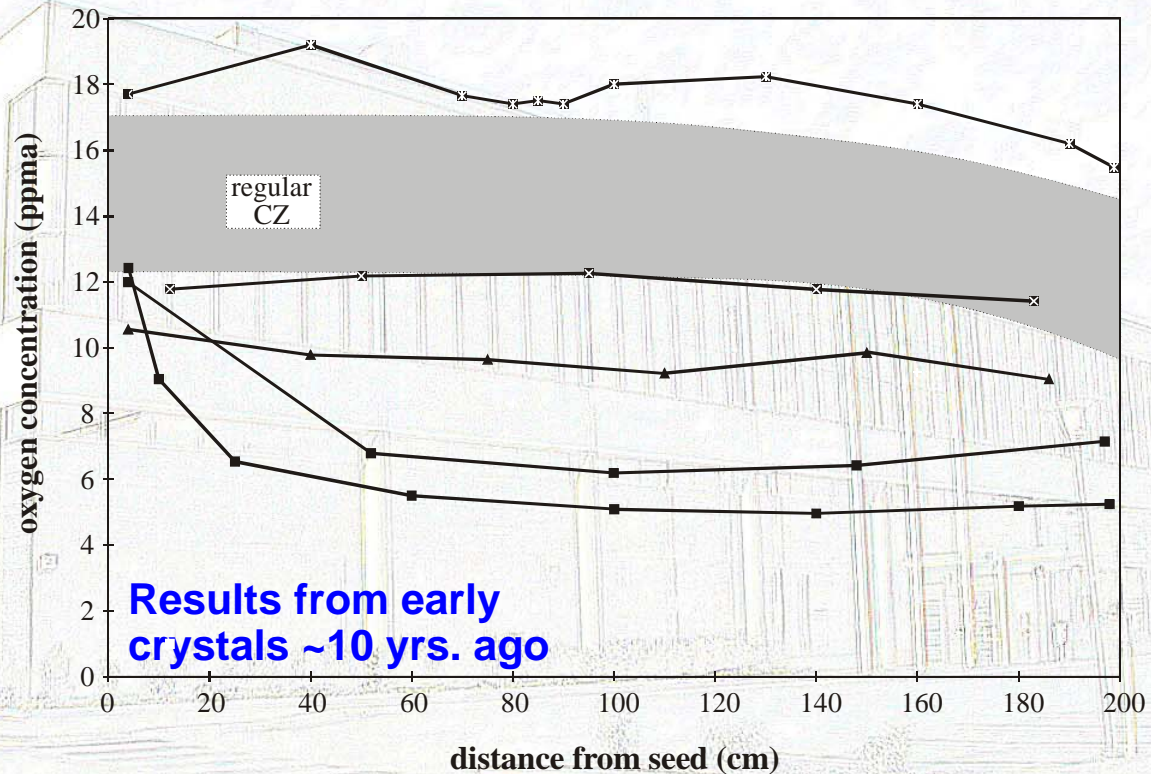
# MCZ Puller

- 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.





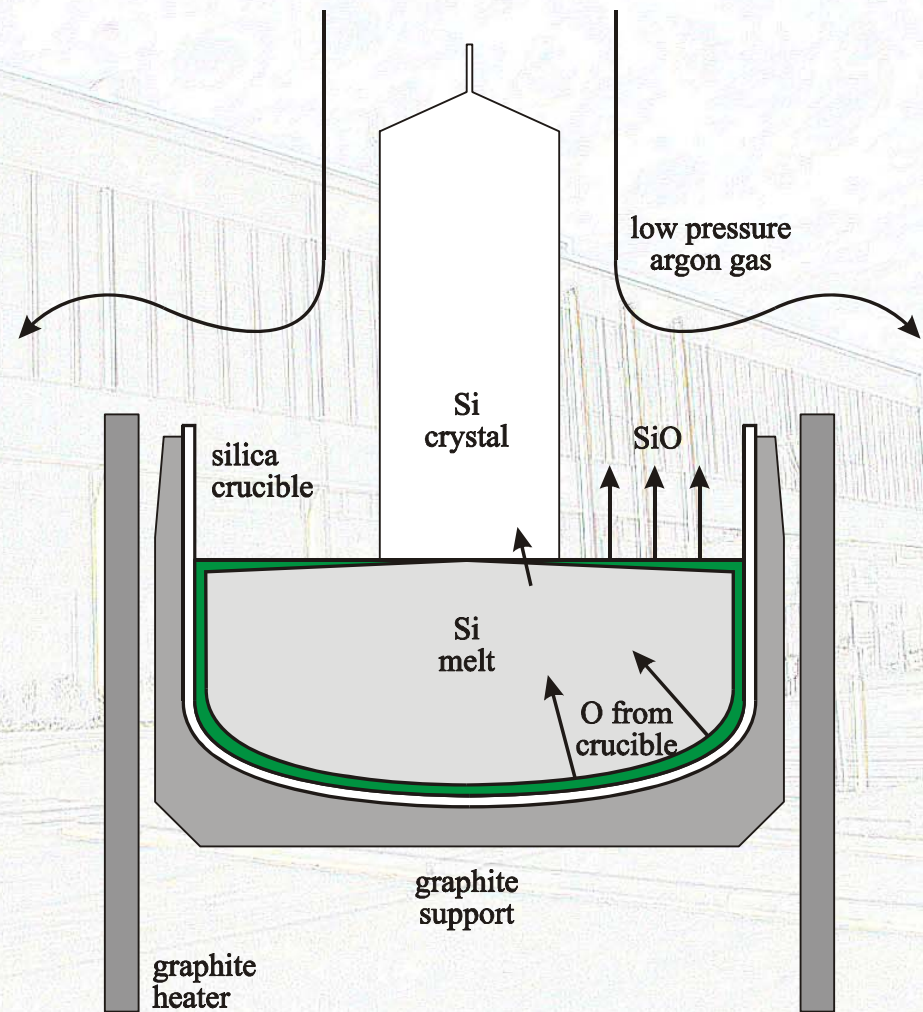
# MCZ stabilizes the melt and has some influence on oxygen level



- 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**



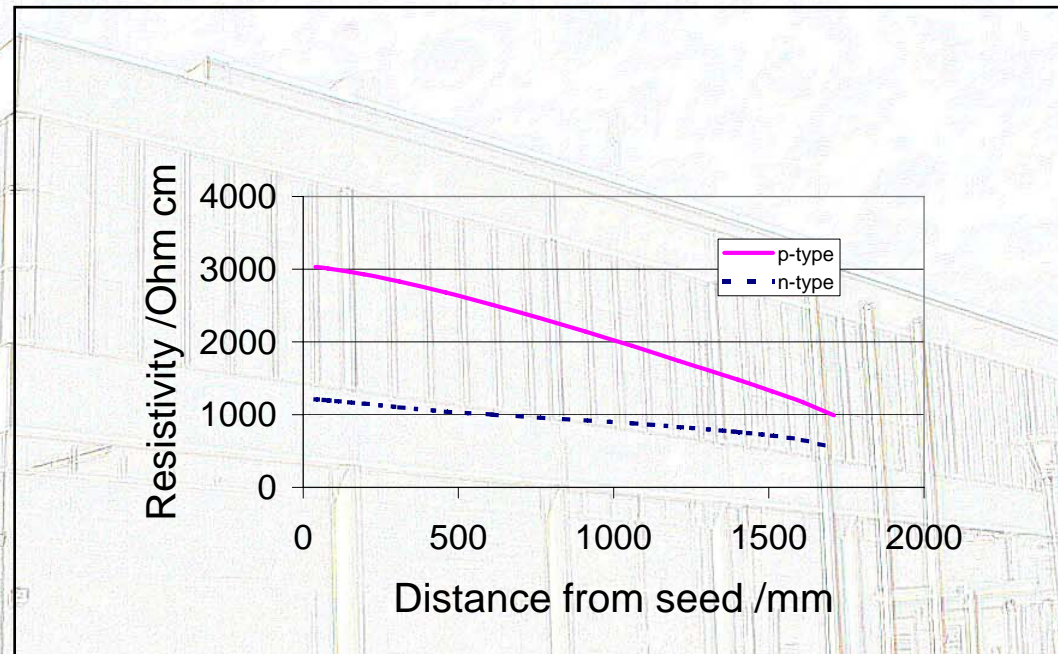
# CZ vs. FZ MATERIAL

## 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.

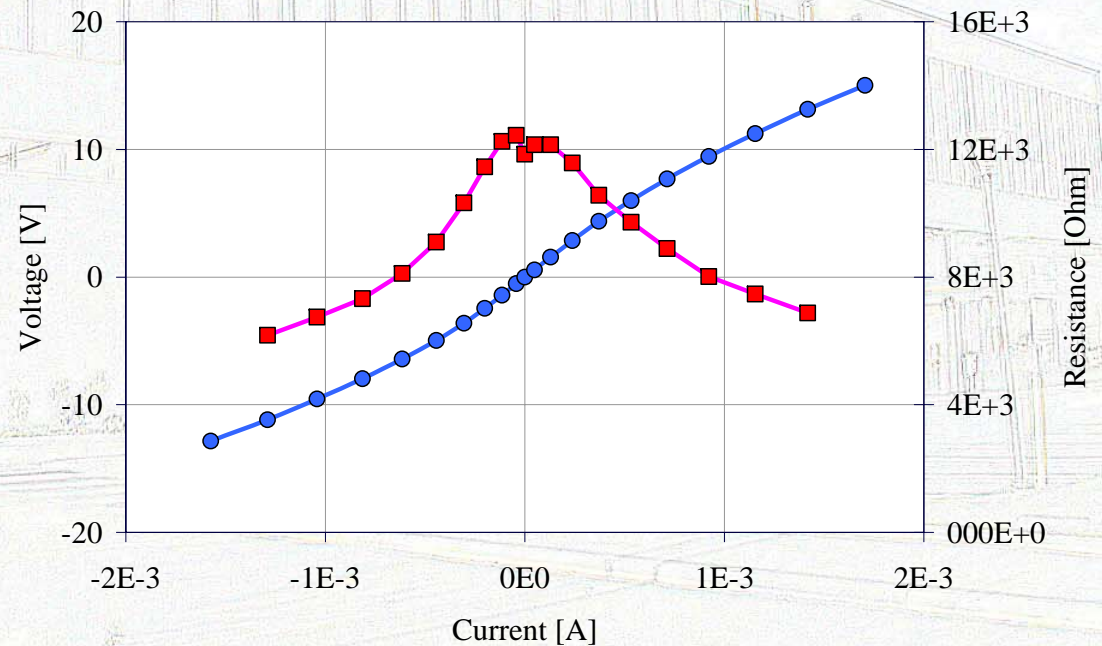
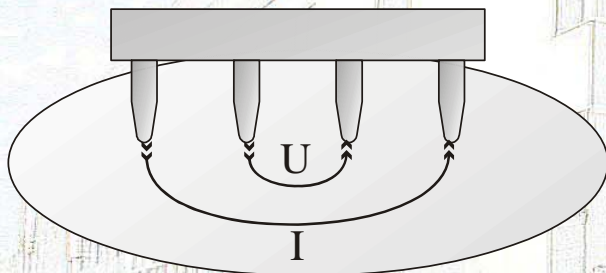
# HIGH RESISTIVITY MATERIAL: 150 mm



- > 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  $\Omega\text{cm}$  p-type
- proper value only at very low current (avalanche injection!)
- measurement stability major issue



# 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

## 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 m<sup>2</sup>/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

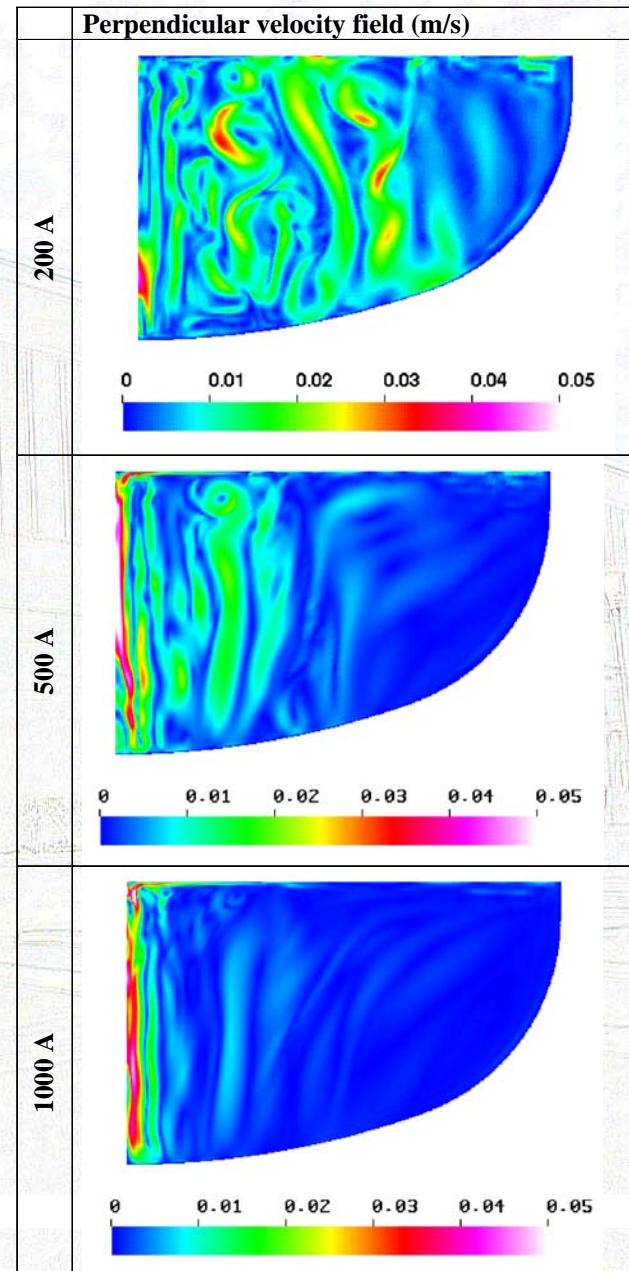


# Magnetic field effect

- 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

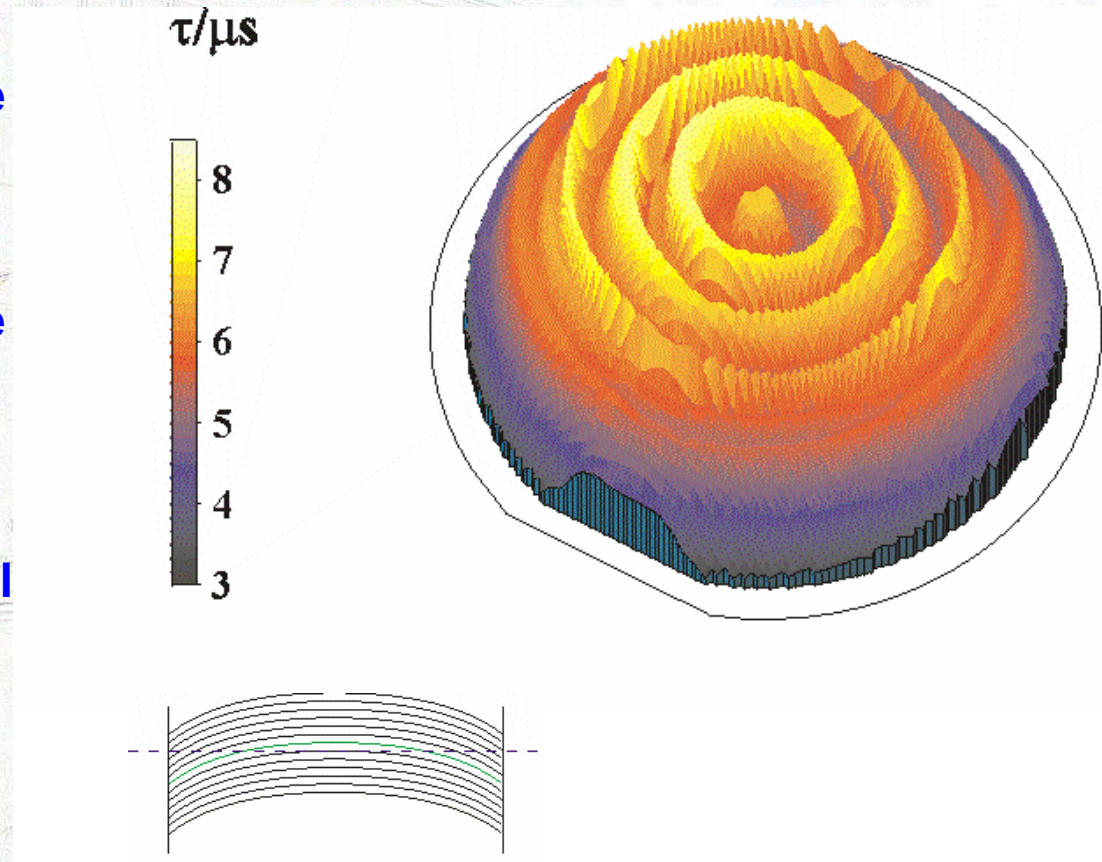




# The melt behavior is not quite so smooth...

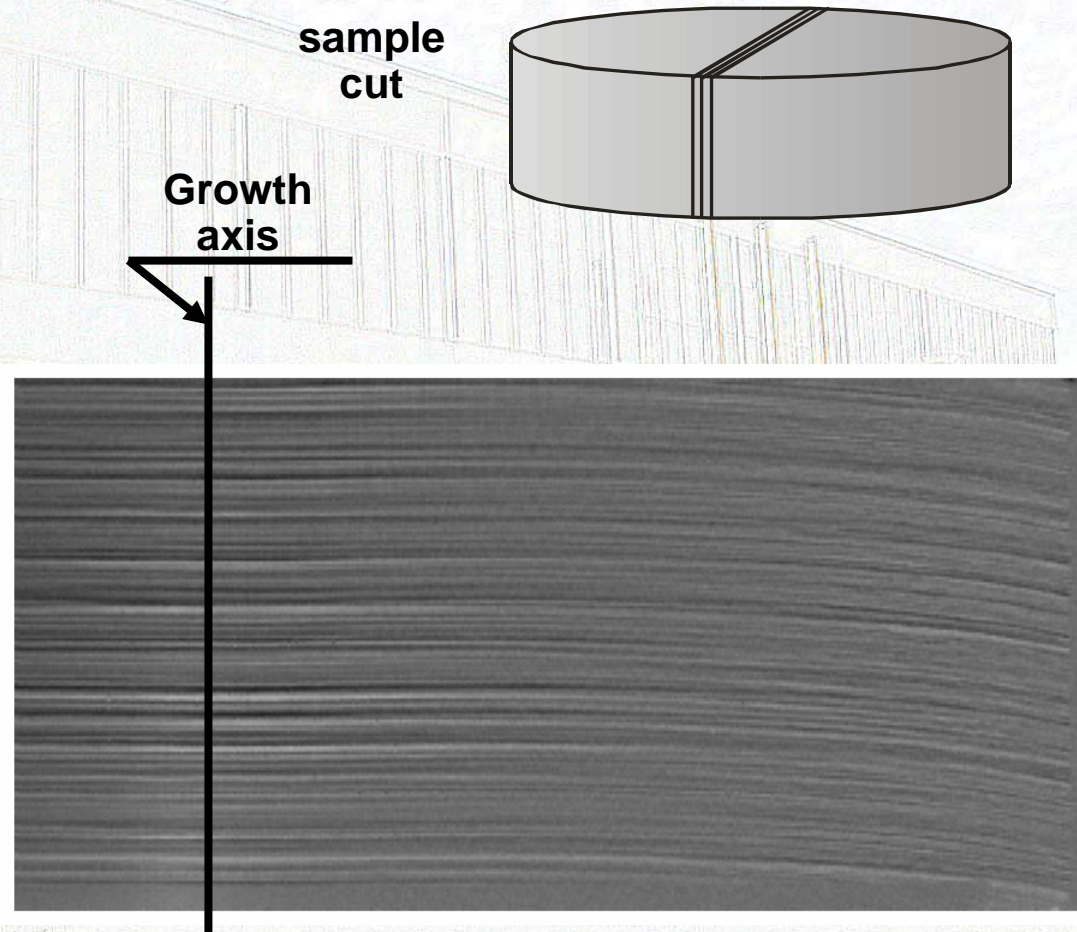
Recombination Lifetime After Oxygen Precipitation  
125 mm N(100), 850 °C / 4h + 1000 °C / 12 h O<sub>2</sub>

- 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



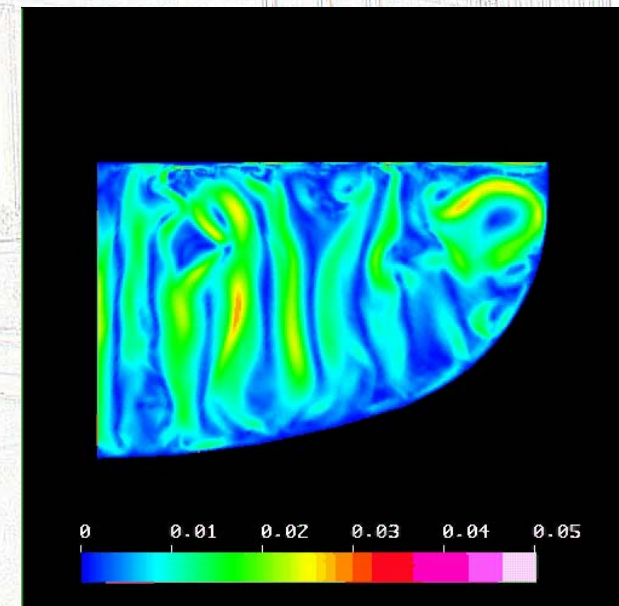
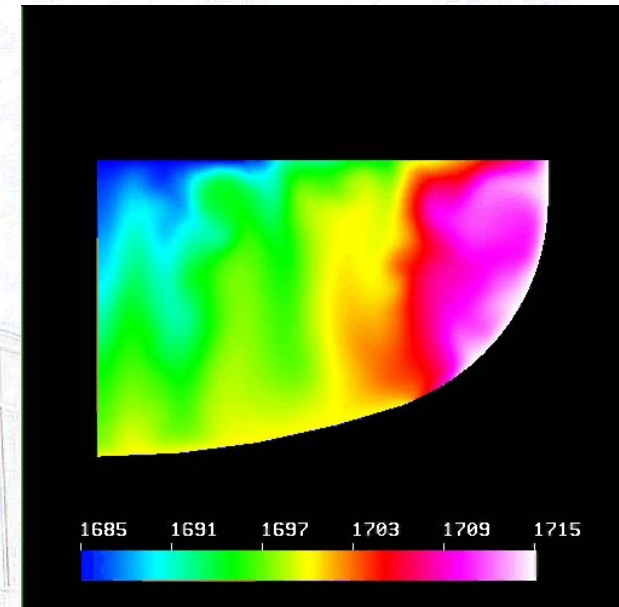
## LPS measurement on 150 mm N(100) 5 Ohmcm crystal

- 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:

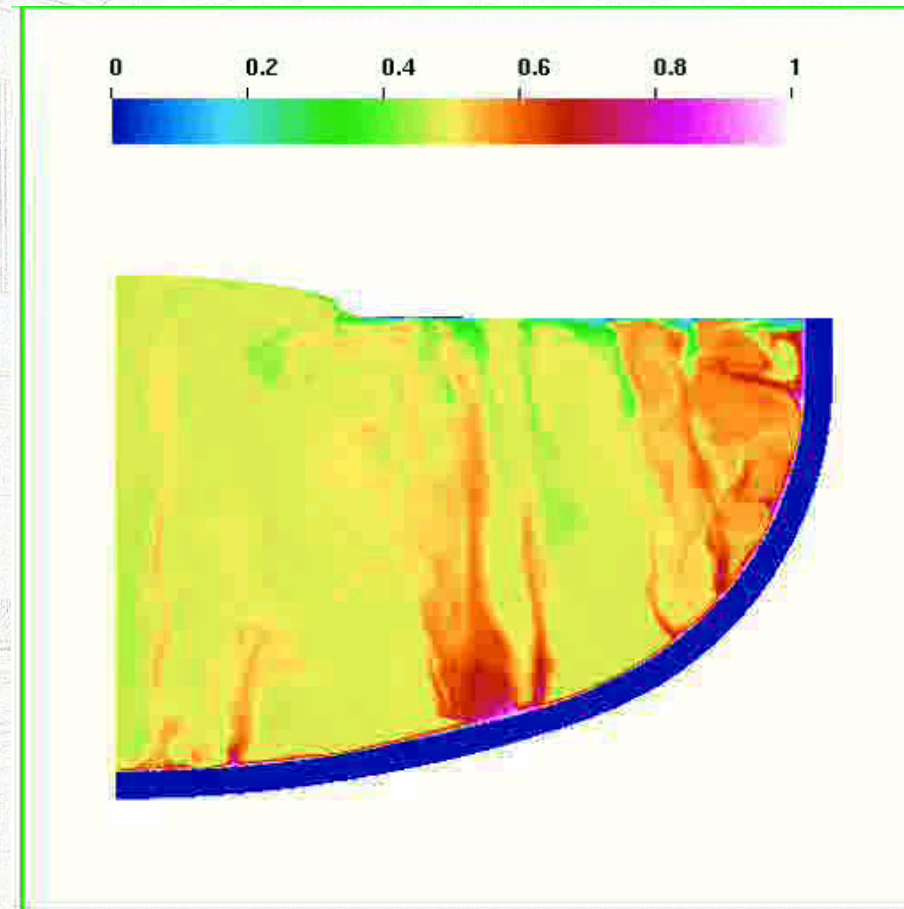
“I am an old man now, and when I die and go to Heaven there are two matters on which I hope for enlightenment. One is quantum electrodynamics, and the other is the turbulent motion of fluids. And about the former I am really rather optimistic.”

– 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**



# Manufacture of High Resistivity, Low Oxygen Czochralski Silicon

June 2005

Olli Anttila

Okmetic Fellow, Okmetic Oyj