GROWTH OF BULK CRYSTALS FROM THE MELT or SOLUTION

Tomasz Słupiński
IF PAN, SL3.2 MBE Lab.
tslupinski@ifpan.edu.pl

Photo (by T.S.):
Crystal of GaAs:Te grown by Czochralski method,
glued on goniometer of cutting saw.

22.02.2022

PLAN

1. Phase diagrams, the congruent melting point
2. Czochralski method
3. Other methods:
    - zone melting (Float Zone): Si
    - Bridgmann and variants (HB, VB, VGF)
    - Kyropoulos: Al_2O_3 - saphfire
4. Transport of heat in melt growth
5. Control and modelling of growth
6. Doping, growth striations, growth instabilities
7. (Very) Few rules and examples of growth from a solution
8. Comparison: melt growth vs. solution growth

Some thermodynamic terms

Molten phase (melt, pol. "roztop", "faza roztopiona")
- liquid having the same chemical composition as intended
  crystal

Growth from the melt – realization of phase transition liquid phase -
crystalline solid phase, where chemical compositions of liquid and
solid are the same (not counting impurities < ~0.1 % at.)

Phase equilibria decide about a possibility to grow a particular crystal
from its melt   (**phase diagrams**)

Example: diamonds

p-T phase diagram of Carbon

for one component material,
Carbon, we have 2 thermodynamic
parameters which describe
thermodynamic state:
pressure and temperature
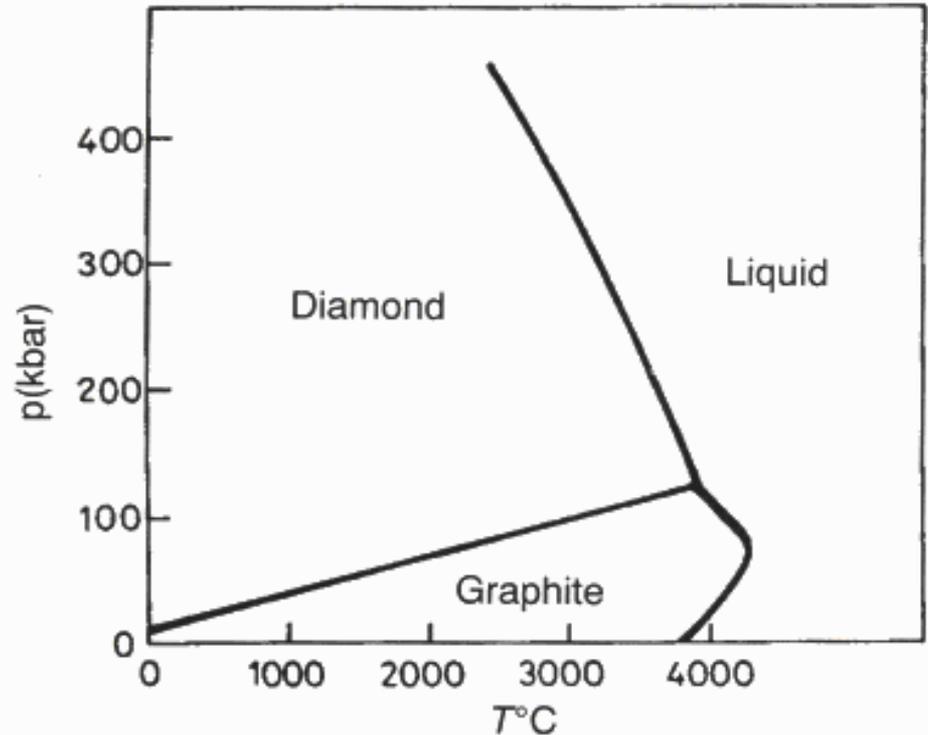
- technically, it is not possible to realize phase transition liquid-solid:
 too high pressure (~100 kbar) and too high temperature (~3500K),
  There are no container materials which can withstand such high requirements.
 Industrially, diamonds (small grains) are grown from Carbon solutions in molten metals, e.g. Ni.

Example 2: SiO$_2$ with α-quartz structure (piezoelectric)

p-T one component (SiO$_2$) phase diagram

Necassary conditions for a possibility of growth of a crystalline phase from melt:

- **no other phase transitions of 1-st type** between liquid and final required phase, or between melting point and RT (such phase transitions in solid phase introduce defects)

alpha-quartz cannot be grown from the melt. It can be grown by a solution method using SiO$_2$ solution in supercritical H$_2$O.
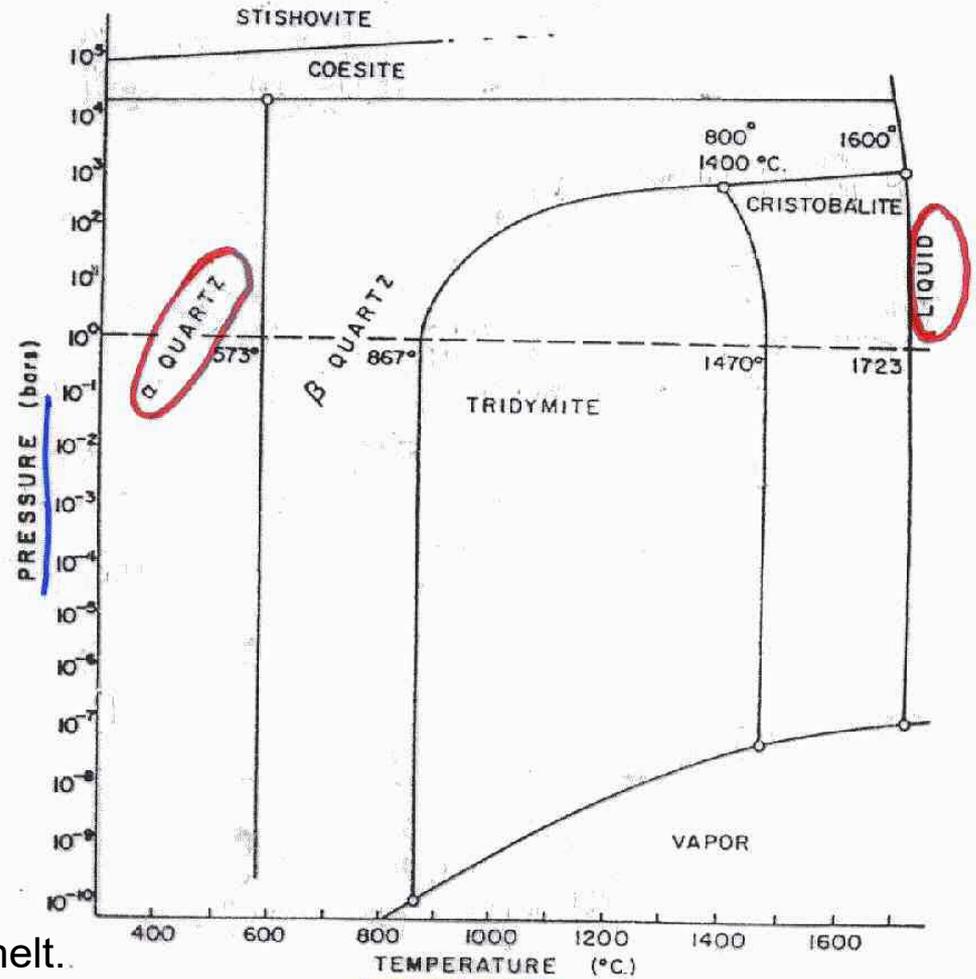

Figure 27. P-T diagram for system SiO$_2$ drawn to scale. From Roy and White (1975).

Another necessary condition (and often sufficient) for a possibility to crystallize from the melt

An existence of **thermodynamic equilibrium** point between liquid and solid at the same chemical compositions of both phases **r** =

= existence of the **congruent point** on T-x phase diagram
(temperature, T – composition, x.   Pressure is taken as fixed)
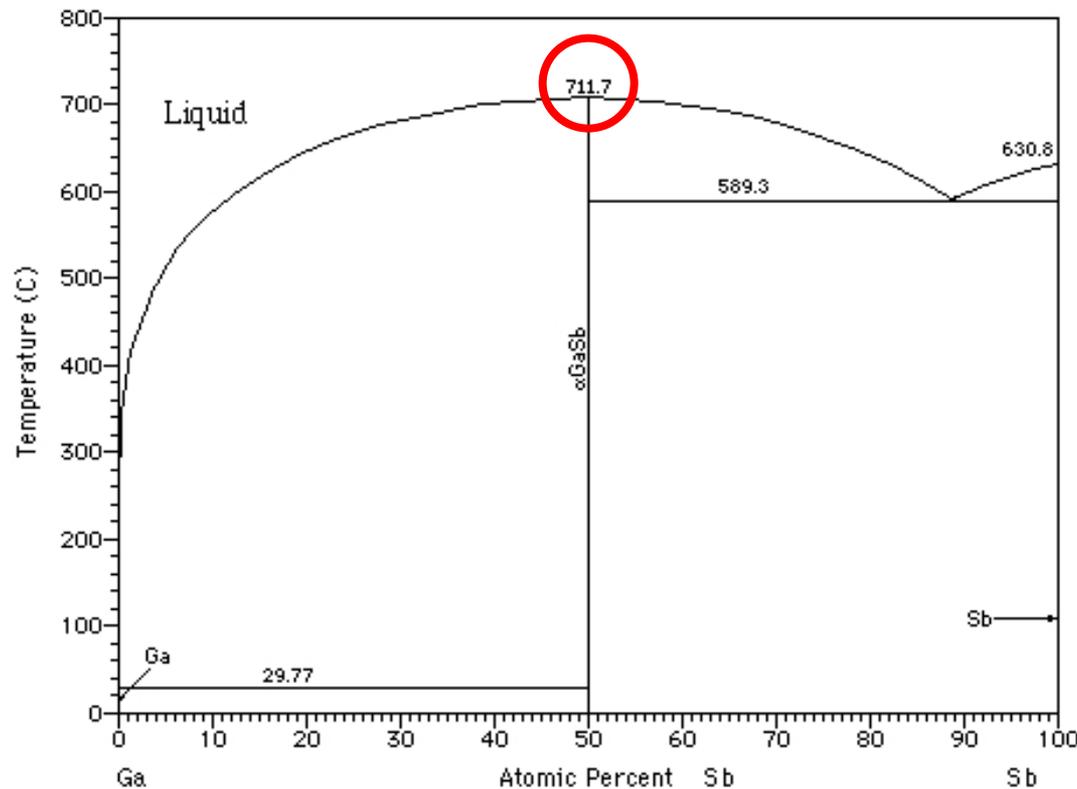
2 components is described by 3 thermodynamic parameters:
p, T and x=Sb/Ga ratio

Another example: SiC
- no congruent point
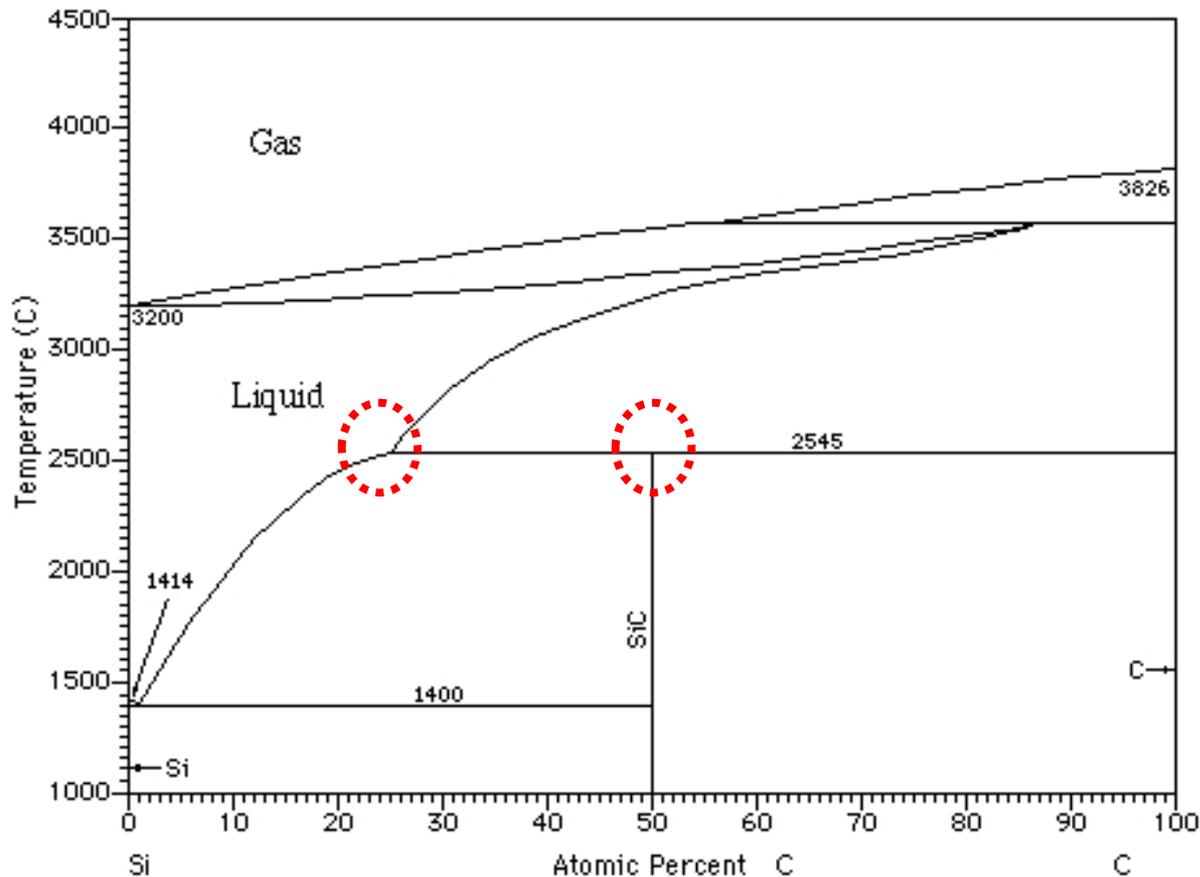
SiC single crystals can be grown from solution in Silicon, or from the vapour phase.
SiC is very hard material (used in mechanical cutting tools).
High perfection SiC single crystals are used for high power, high frequency electronic devices.

# Yet another example: $Si_{1-x}Ge_x$ alloy (solid solution)
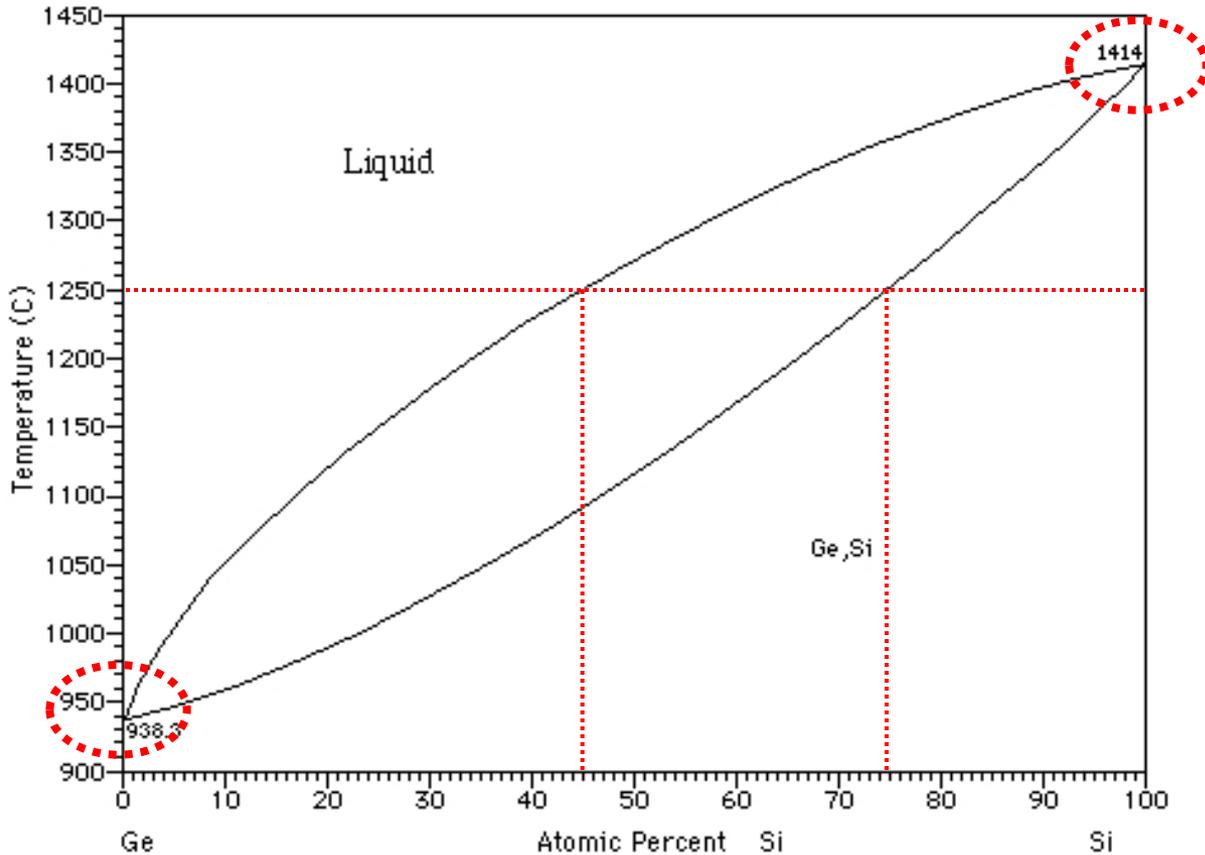
Using simple melt-growth methods, only Ge or Si can be grown with constant composition.

GaAs
(and similar for InP, InAs, GaP, GaSb, ….)

Q, by the way:

What is the width of GaAs solid phase?

What effects determine this width ?

A:

Non-stechiometric defects in crystal,
e.g. w GaAs typu As_{Ga}, some few-atomic As_{Ga} clusters, etc.
It is regarded that at equilibrium at high temperatures GaAs crystals can contain $r \sim 10^{-6}$ - $\sim 10^{-5}$, (composition $Ga_{1-r}As_{1+r}$), also vacancies, interstitial atoms, etc.

In the technology of (pure) crystals we want to control numbers of such defects. Also numbers of impurities of other elements build into the crystal lattice.
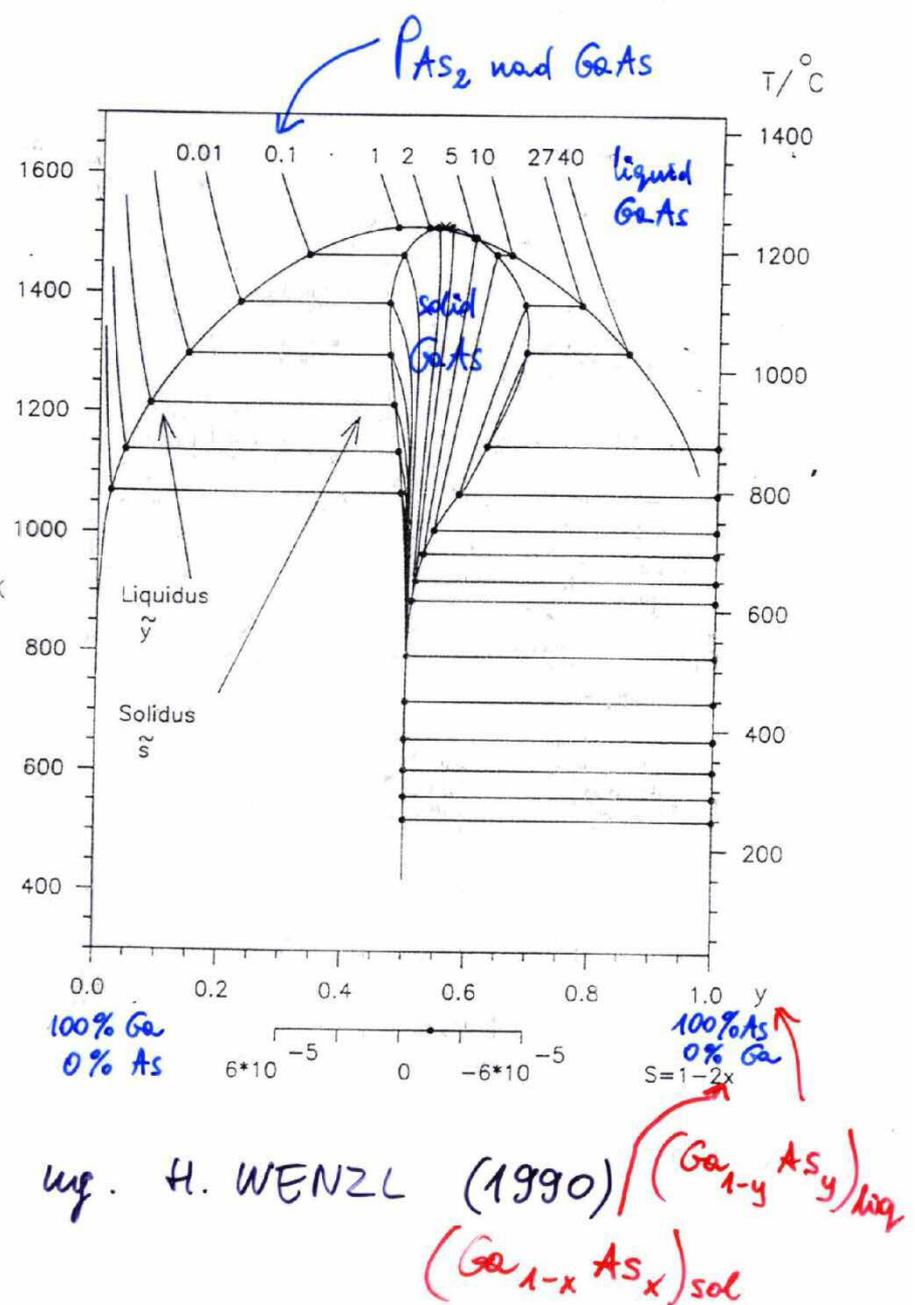
Many different crystals are produced, e.g.:

- Electronics, photonics, photovoltaics :   **Si**,   (very large amounts of Si)
                                              GaAs, **InP**, **GaSb, GaP, InSb**
                                              Ge,
                                              Al_2O_3, [**GaN**], [**SiC**]

- detectors of radiation: **Si**, **Ge**, **CdTe**, **metals**

- surface wave devices: **$LiNbO_3$** - piezoelectric,

- rezonators: [**SiO_2**]

- materials for lasers: **Al_2O_3**, **YAG** …

- optical elements: **CaF_2**, **$LiNbO_3$** [**ADP**, **KDP**], …

- hard materials: **Al_2O_3**, [**C**]

- and so on ....   (symbol **[**…**]** methods other than from the melt)

Table 1.1 Estimated annual production rates[a]

Crystal	Rate (tonnes/year)[c]	Growth methods[b]
Silicon	4000	Czochralski, floating zone (VPE)
Metals	4000	Bridgman, strain anneal
Quartz	800	Hydrothermal
III–V compounds[d]	600	Czochralski, Bridgman (VPE, LPE)
Alkali halides	500	Bridgman, Kyropoulos
Ruby	500	Verneuil
Germanium	400	Czochralski, Bridgman
Garnets	200	Czochralski
Lithium niobate	100	Czochralski
Phosphates	50	Low-temperature solution
Lithium tantalate	20	Czochralski
Cubic zirconia	15	Skull melting
TGS	10	Low-temperature solution
Diamond	10	High-temperature solution
II–VI compounds	5	Vapour, Bridgman

[a]The data are for the whole world.

- ok 1986

source: C. Brice (1986) book

CRYSTAL GROWTH PROCESSES

Table 1.4 Methods ranked by various criteria*

By mass		By value		By number of materials	
Melt	(60)	Melt	(40)	Melt	(70)
Solid	(20)	Vapour	(20)	Solution	(25)
Solution	(9)	Solid	(20)	Vapour	(20)
Hydrothermal	(7)	Solution	(10)	Solid	(3)
Vapour	(4)	Hydrothermal	(10)	Hydrothermal	(2)

*The figures in parenthesis are percentages of the total population. In the ranking by number of materials, the total exceeds 100% because some materials are grown by more than one method: roughly 15% are grown by two methods and 5% by three methods. If the entries for solution growth are divided between low-temperature and high-temperature methods, the entries for low temperature growth are about 6, 6 and 12. Note that the data relate to materials grown commercially of which there are about 200. For research purposes crystals of several thousand materials have been grown mostly from solution.

source: C. Brice (1986)

Important:

1. Growth methods from the melt allow relatively quickly produce large volumes of single crystals, at a relatively low price comparing to other methods. But not all materials can be grown (as shown in examples above).

2. Wafers, substrates, cut from such crystals are used in electronics/photonics etc. as templates, or seed crystals, to deposit epitaxial layers having a particular functionality e.g. of electronic device.

3. In electronics, single crystals are necessary, in polycrystalline materials the precise control od current flow or optical properties is partially lost comparing to single crystals (it was realized already by Shockley, ~1948, during works on transistor)
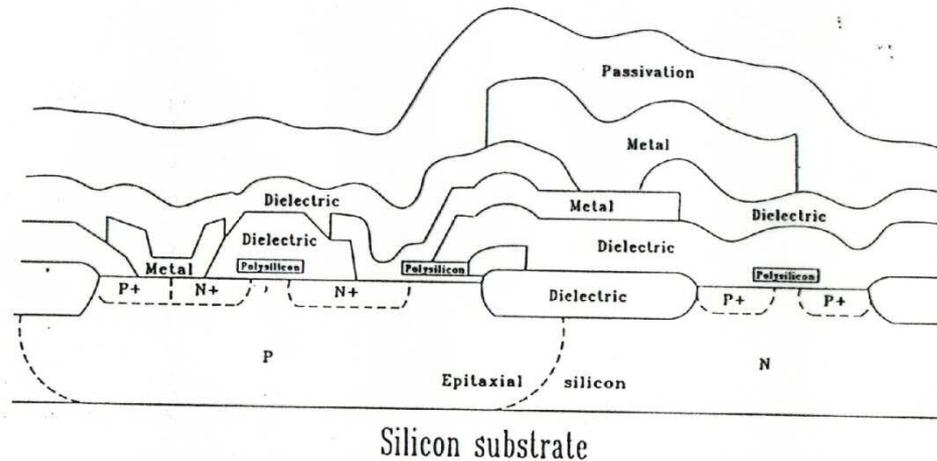

Figure 2. Sketch of cross section of a typical CMOS structure (circa 1984).

MRS BULLETIN/DECEMBER 1993

Si wafers for electronics, photovoltaics, etc

Diameter of wafers [mm]

Annually, world production of single crystals wafers of Si was ~ 5 km^2 (acc. to SEMI, 2007). At present is is much larger, mainly due to the photovoltaics.
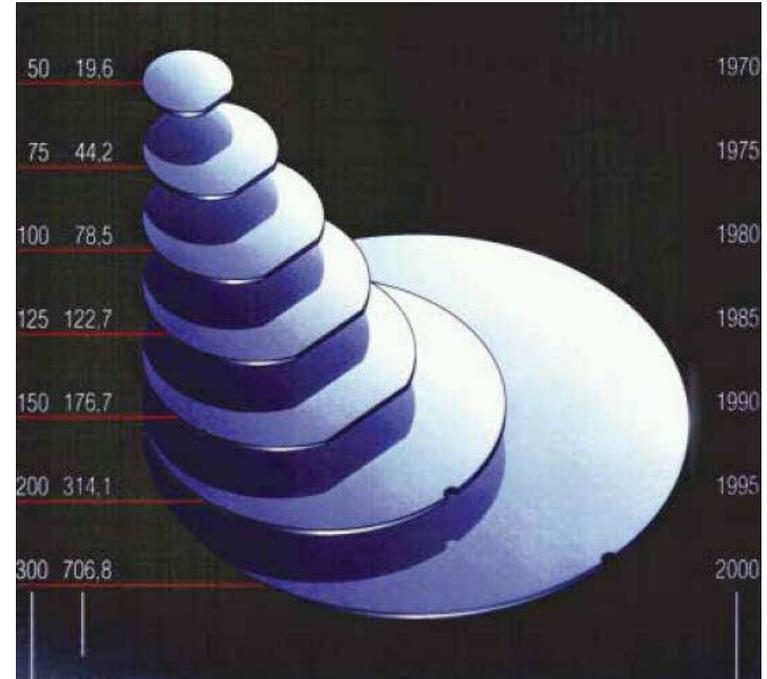
photos from: PVA TePla, Denmark
(producer of equipment for Si crystals growth)

90% world production of Si wafers for IC in 5 firms

k wafers Si per month
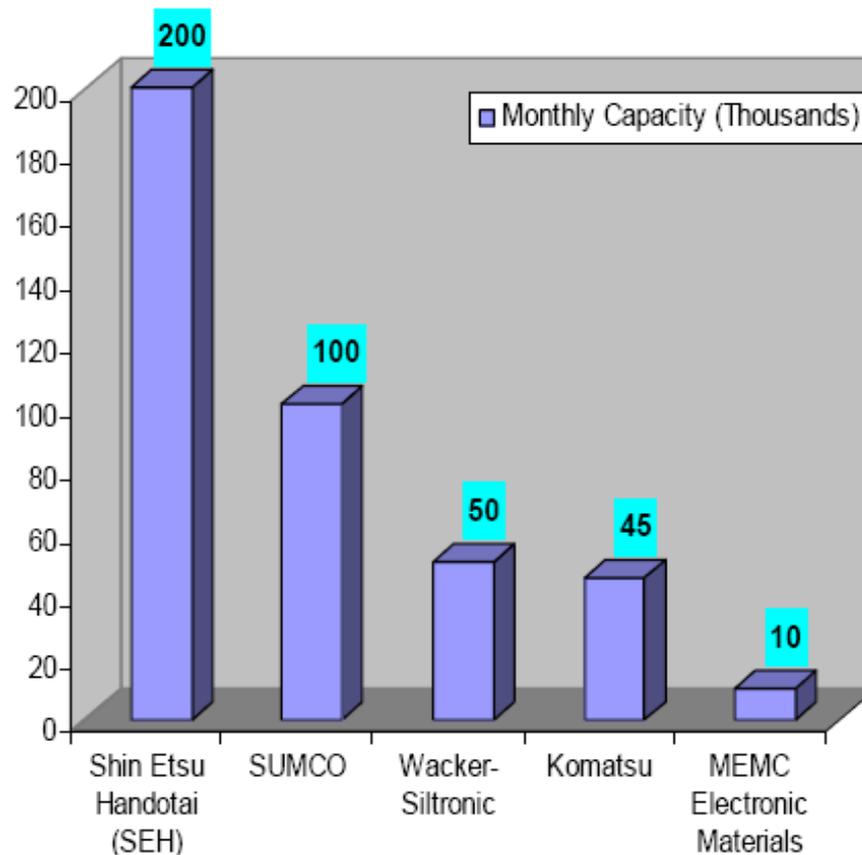
Source: Cusack i in.; Penn St. U. , ~2005

In recent years >2010 very strong growth of Chinesse Si crystals producers for photovoltaics.

III-V compounds single crystals wafers used for the epitaxy of III-V semiconductor layers, also for II-VI :   GaAs, InP, GaP, InAs, GaSb, InSb
(and GaN – not shown)
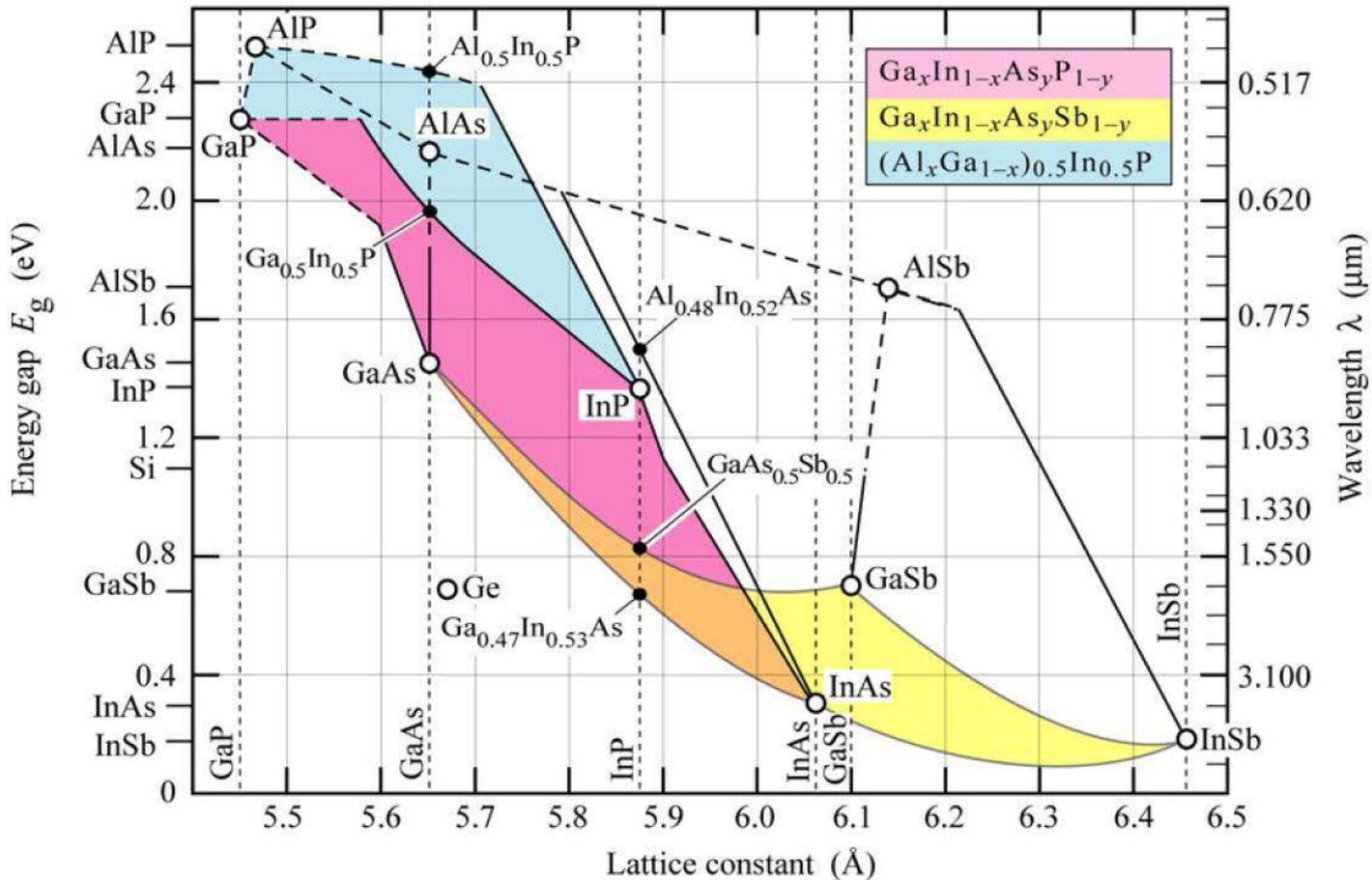
Fig. 17.9 Lattice constant versus energy gap at room temperature for various III–V semiconductors and their alloys (after Tien, 1985).

source: F. Schubert,   book "Doping in III-V semiconductors"

Example of epitaxial structure of 3-junction solar cell grown on Ge single crystal wafer

3-junction monolitic solar cell,
max. efficiency ~36% (a.d. 2005),

(mainly used in space stations, efficient but expensive in production)
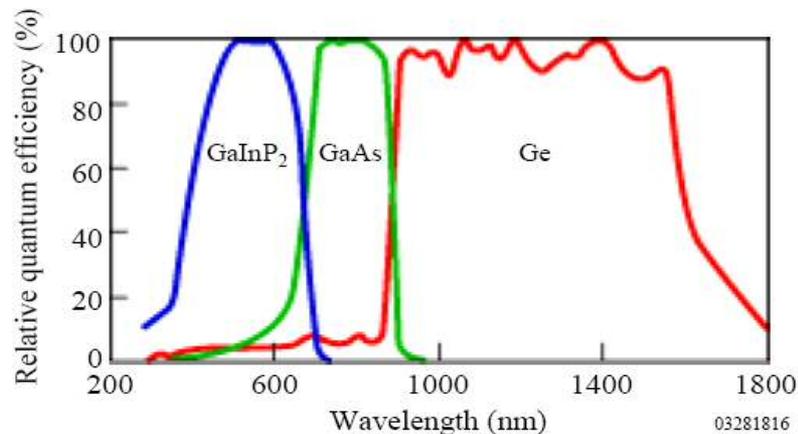
Figure 19. Quantum efficiency of each layer of the GaInP/GaAs/Ge triple-junction solar cell.
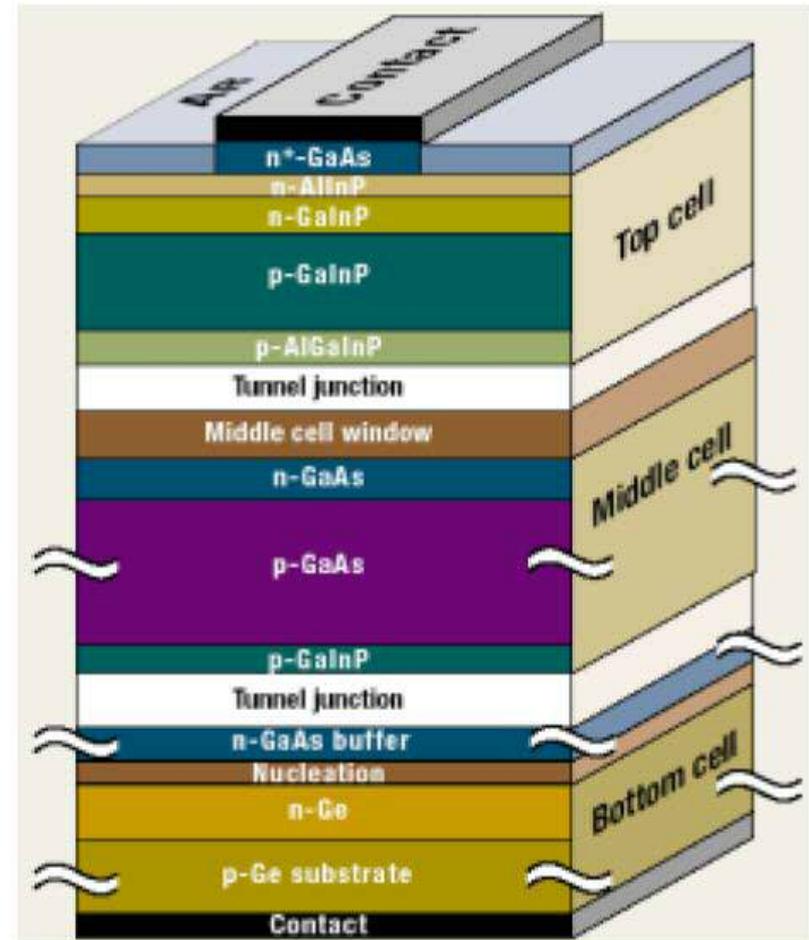
source: Spectrolab Inc.

Czochralski method of bulk crystal growth

T = const

zarodek
monokrystaliczny

seed crystal

faza ciekła

liquid

tygiel

crucible

elementy grzejne

heaters
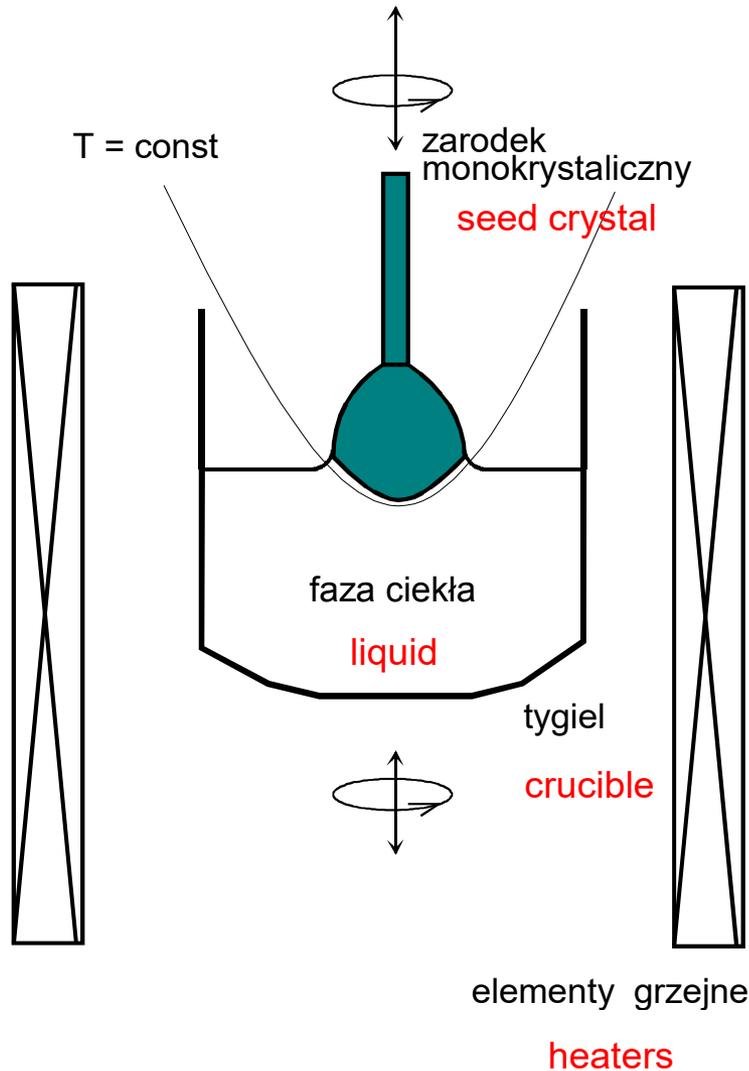
- growing crystal does not in contact with
  any other material, like crucible,
  (= less defects of crystal structure)

- growth and properties of crystal depends
  on **temperature field** in growth zone and
  in cooling zone

- control of diameter of crystal (cylindrical
  part), achieved by regulation of temperature
  field,
  control of process is difficult and nonlinear

- high growth rates ~1 - ~100 mm/h
  depending on material.

- use of single crystal seed forces the
  oriented crystal growth.

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Origin of the method: Jan Czochralski (worked in 1916-8 in Berlin as a metalurgy engineer and researcher, studies of metallic single crystals e.g. Sn, Zn, Cu in shapes of wires pulled out from the molten phase).

J. Czochralski noted a possibility to get single crystals if capillary pipe for initial crystallization was used.

The method was developed much in research group which invented the transistor (Bell Laboratories, 1946-51, first single crystals of Ge i Si: Teal, Little, Buehler)

Many informations can be found in books by Prof. P. Tomaszewski of Wroclaw Inst. of Low Temperatures Physics.

PAWEŁ TOMASZEWSKI

JAN CZOCHRALSKI
I JEGO METODA

JAN CZOCHRALSKI AND HIS METHOD
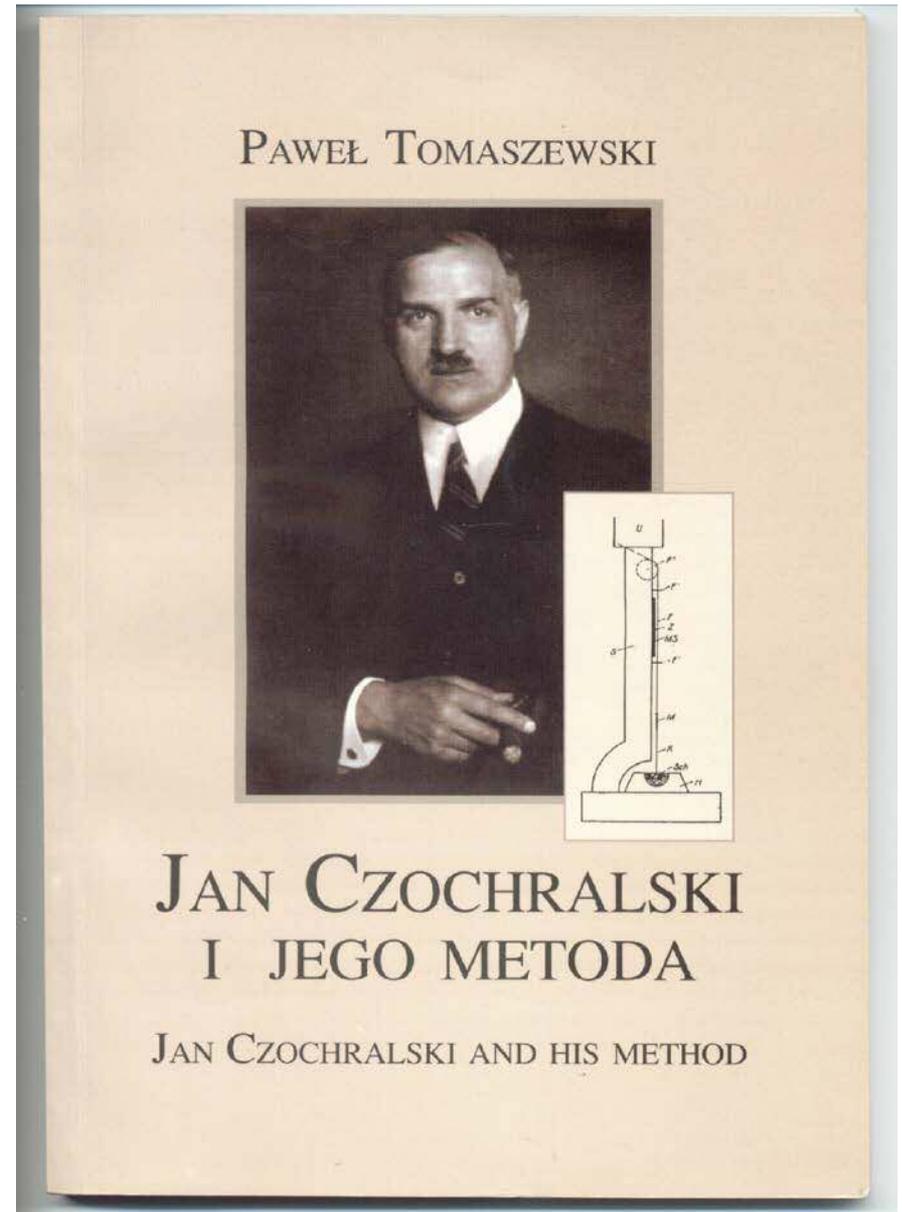
of condensers charged slowly to about 100 volts and discharged rapidly through two ignitron tubes in series with a small coil. The field thus produced in its interior remains above 70 percent of its peak value for about 400 μsec. A voltage proportional to the magnetic field is displayed as X deflection on an oscilloscope. This voltage is obtained from an integrating circuit fed from a probe coupled into the main coil. The X deflection is then calibrated in terms of field by means of a second probe coil of known characteristics situated within the main coil. The second probe coil is then removed and replaced by the germanium sample. This is supplied with a fixed current and the voltage drop across it (which is proportional to its resistance) is displayed as Y deflection. The oscilloscope therefore plots the resistance *vs.* magnetic field, and the trace is photographed.

I15. Growth of Germanium Single Crystals. G. K. Teal and J. B. Little, *Bell Telephone Laboratories* (*To be read by title*).—The growth in the number of ideas of possible conduction mechanisms of practical value that might be realized in germanium has emphasized the importance of developing specific methods of producing germanium single crystals in which the relevant properties of the material are controlled. In the present study germanium single crystals of a variety of shapes, sizes, and electrical properties have been produced by means of a pulling technique distinguished from that of Czochralski and others in improvements necessary to produce controlled semiconducting properties. Germanium is a solid that expands markedly on solidifying and is very sensitive to factors, such as physical strain, which give rise to twinning. The method of pulling the germanium single crystal progressively from the melt at such a rate as to have a stationary interface between the solid and the liquid only slightly above the liquid surface is very well suited to the material since it avoids the constraints inherent in solidifying the germanium within inflexible walls and provides a simple planar thermal gradient in the neighborhood of the interface thereby minimizing thermally induced strains. Single crystal rods up to 8 inches in length and $\frac{3}{4}$ inch in diameter and having a high degree of crystalline lattice perfection have been produced. Measurements in these Laboratories have shown the bulk lifetimes of injected carriers in these materials to be greater than 200 microseconds.

Phys. Rev. **78** (1950) 637

The first announcment Bell Labs concerning growth of Ge single crystals for an invention of first transistors. Authors (Teal and Little) invokes ideas of Chochralski to which they added many improvements necessary for semiconducting properties of Ge.

First crystals of Ge „pulled out" from the melt(Bell Labs)

historical report,   IEEE Trans. on Electr. Dev. ED-**23** (1976) 621

Fig. 2.   An early germanium single crystal grown in the type I crystal puller equipment by G. K. Teal and John Little.

TEAL: SINGLE CRYSTALS OF GERMANIUM AND SILICON

Fig. 17.   Three germanium single crystals grown while slowly rotating in the type II crystal pulling machine.

IEEE TRANSACTIONS ON ELECTRON DEVICES, JULY 1976

DONOR OR ACCEPTOR

ORIENTED SINGLE CRYSTAL SEED

GERMANIUM SINGLE CRYSTAL

CRUCIBLE

Ge LIQUID

Fig. 9.   Schematic of grown junction single-crystal technique of making p-n junctions and junction transistor structures.

APPROXIMATE CONCENTRATIONS OF DONORS AND ACCEPTORS

n

p-n JUNCTION

p

2 PARTS Sb/10^8 Ge

2 PARTS Sb + 4 PARTS Ga/10^8 Ge

Fig. 10.   Germanium single-crystal p-n junction made by the grown junction technique.

Ge single crystal wires
pulled out from melt
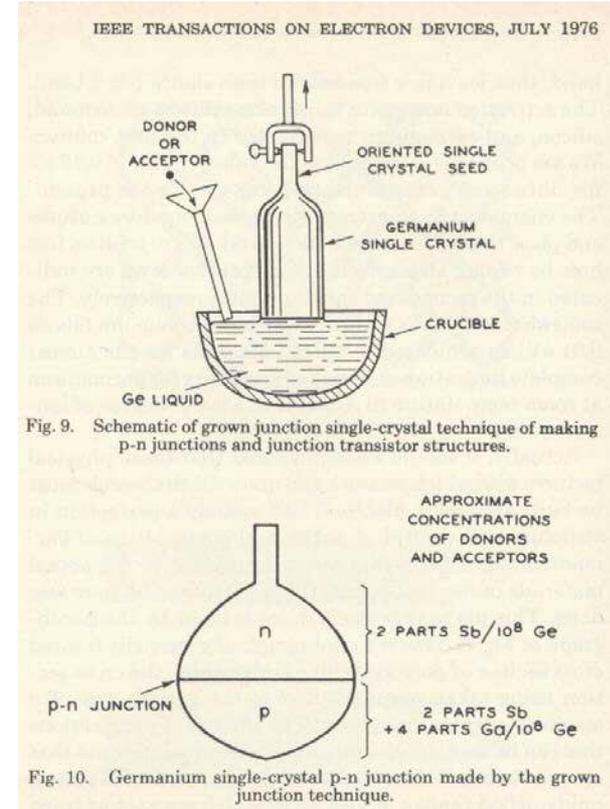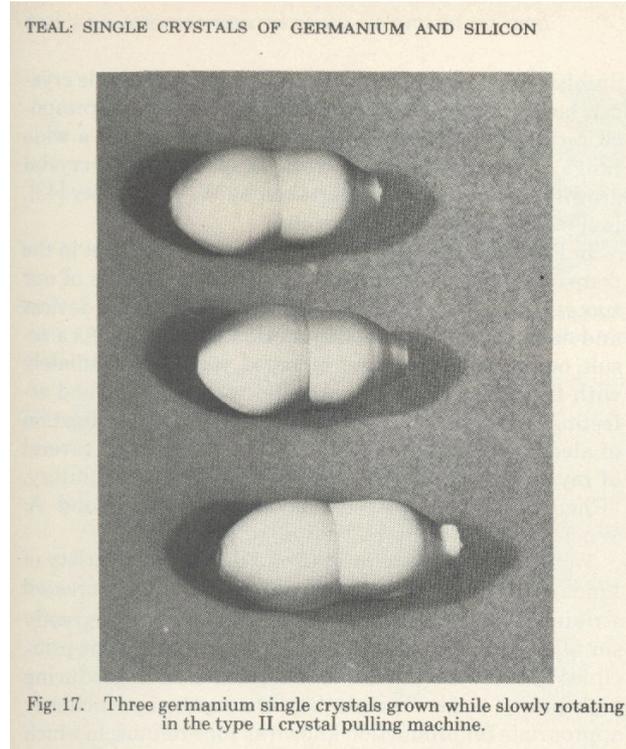
One of the first model p-n junctions
were produced by Czochralski method
changing doping elements during crystal pulling.

Schematic of current Chochralski method apparatus for Si

Seed

Single Silicon Crystal

Quartz Crucible

Water Cooled Chamber

Heat Shield

Carbon Heater

Graphite Crucible

Crucible Support

Spill Tray

Electrode
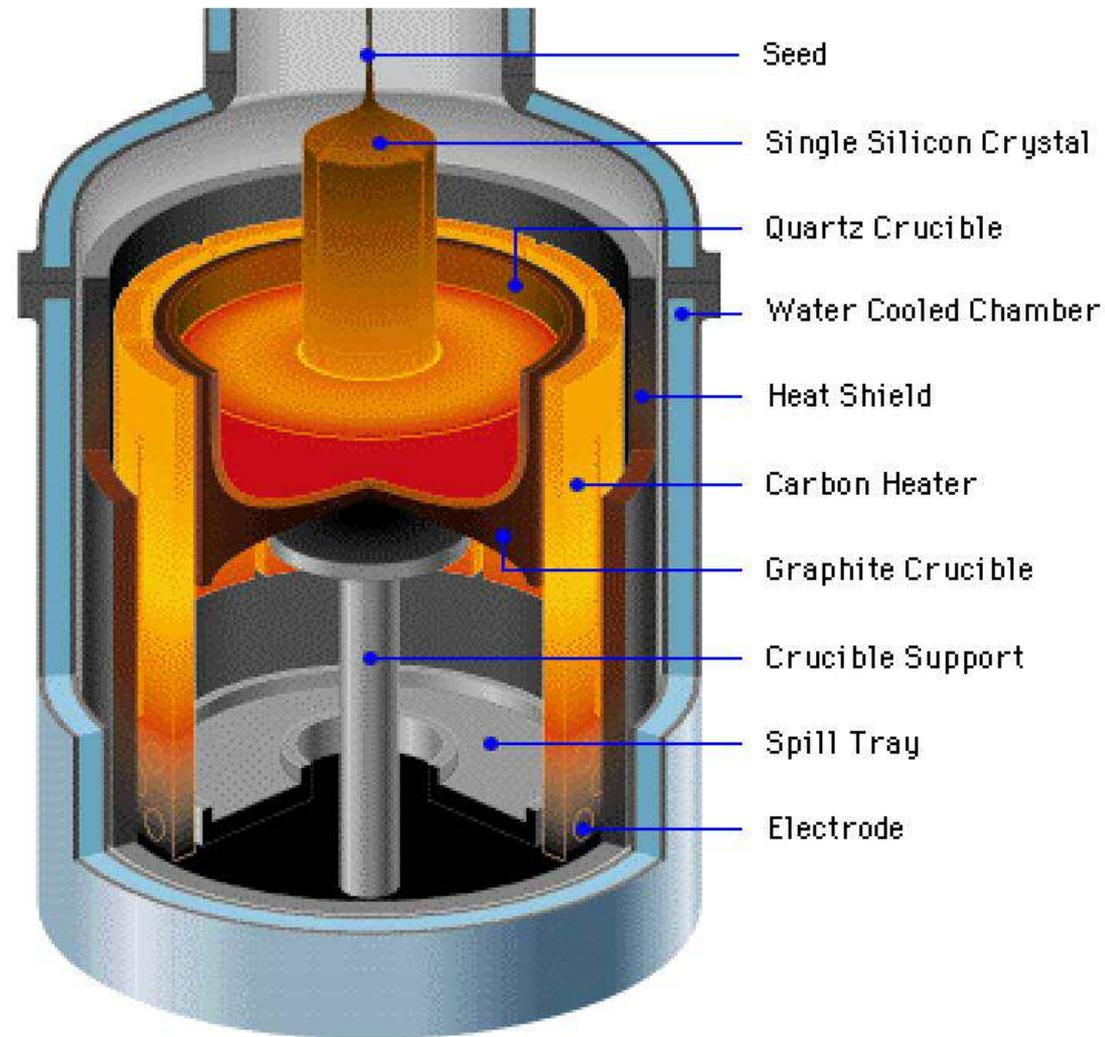
source: SUMCO

Steps of Cz. crystal pulling
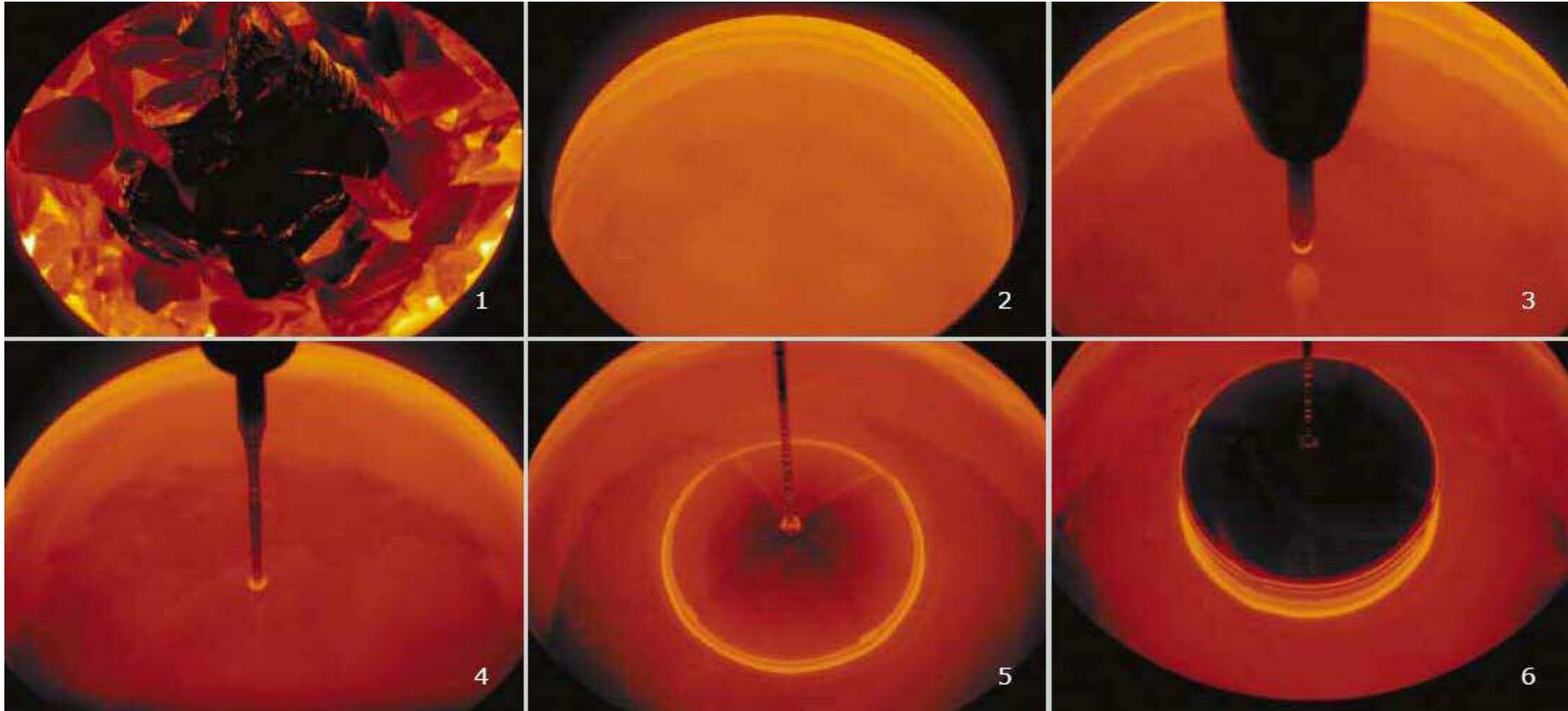
(1) melting, (2) stabilization of temperature, (3) seed-melt contact,
(4) extension of seed crystal pulled out, (5) increasing the diameter , (6) growth of cylindrical part.
Growth is controlled by adjusting the heating power (location of melting temperature isotherm).

source: PVA TePla

Control of diameter

Shoulder
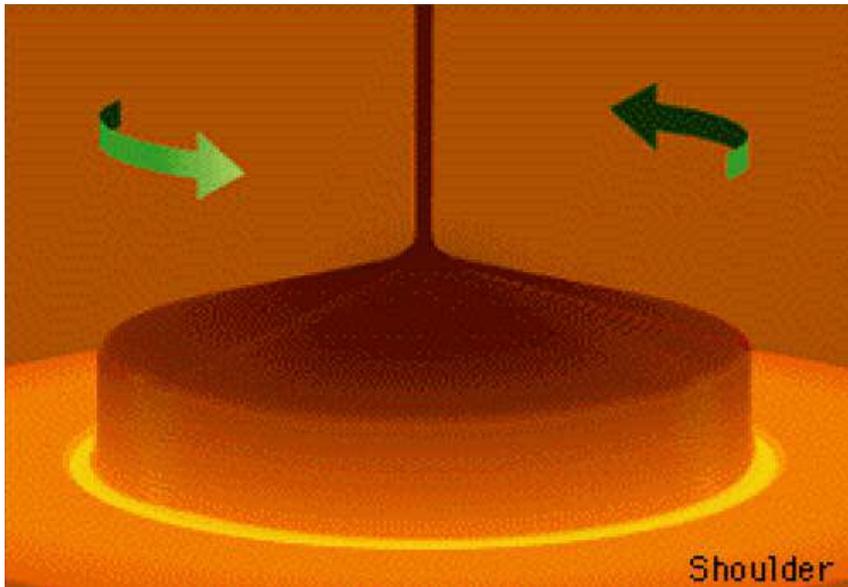
- a curvature of meniscus is seen (brighter ring)

Source: SUMCO

Diameter is controlled by a location of melting isotherm, its cross section with surface of melt in the crucible.

Methods of diameter control:
- experimental adjustment of time profile of heater's temperature

- control in a closed loop ofregulation based on actual measured diameter of crystal. This is difficult regulation task.

Actual diameter can be determined by optical means (detecting lighter ring of meniscus) using automated methods of image recognition. Another method is continuous weighting of crystal or crucible. Some difficulties arise due to meniscus forces.

Role of meniscus in Czochralski method
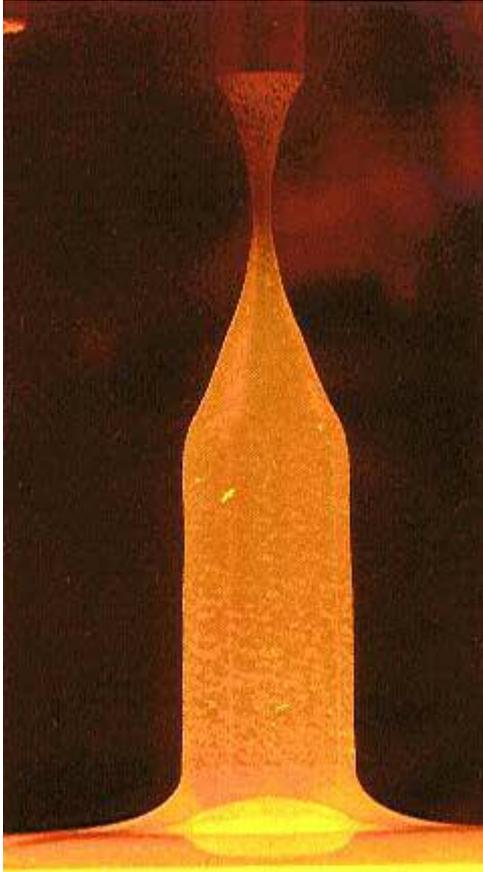
- Radiative heat transport depends on "lookinhg angle" of meniscus, related to tilt angle of meniscus. A source of instability: if crystal diameter shrinks, the meniscus "looks" at hotter parts of heater around and the crystal gets a tendency to shrinking more.

- meniscus facilitates optical methods of actual diameter detection

- meniscus gives capilar forces which sometimes hinder to determine actual diameter from weight signal

source of photo: MaTeC GmbH

1-dim heat transpoty near the liquid - solid interface in Cz. method
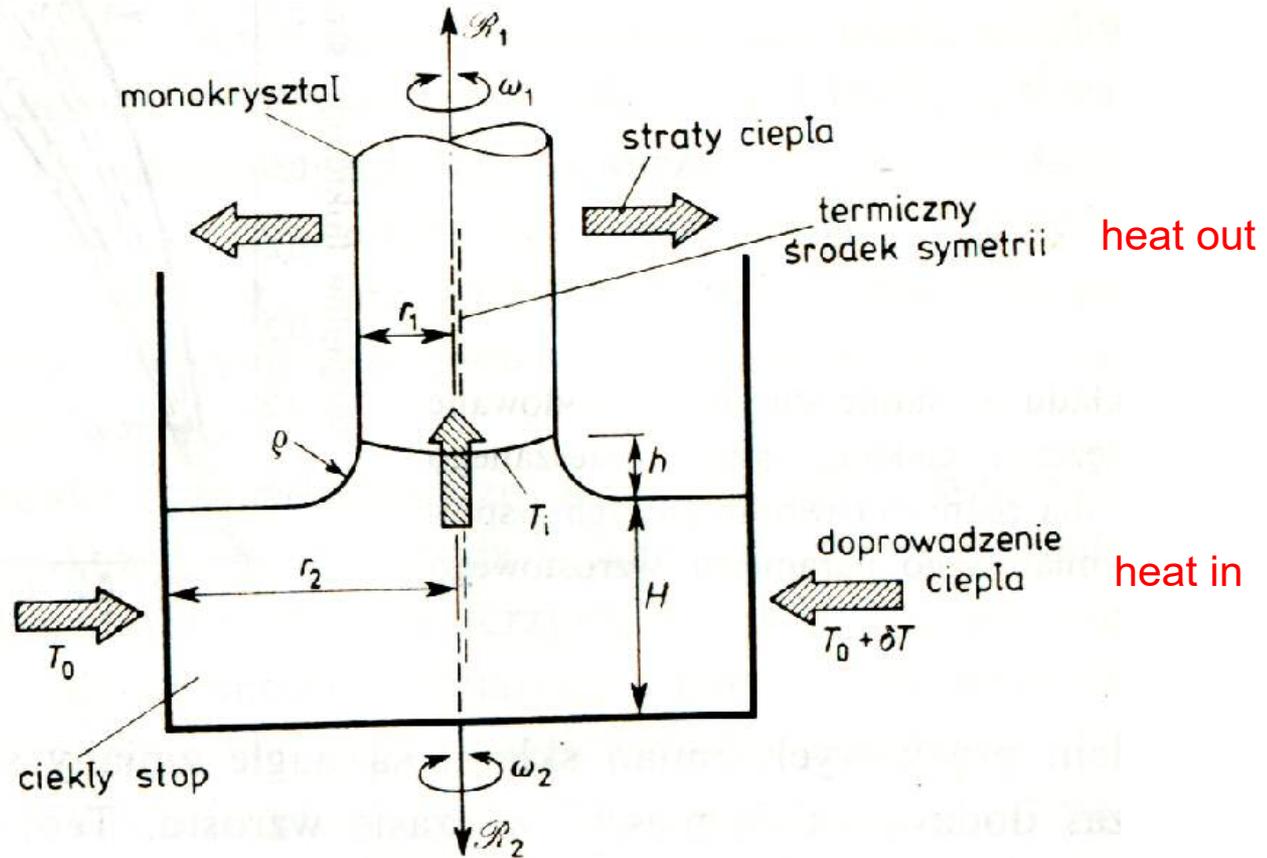
source: Prof. J. Żmija book, „Otrzymywanie monokryształów"

1-dim heat transport equation

$$-\kappa_{sol}\frac{\partial T_{sol}}{\partial z} + \kappa_{liq}\frac{\partial T_{liq}}{\partial z} = L \cdot \rho_{sol} \cdot V_{growth}$$

K – thermal conductivity
L – heat of crystallization
V_{growth} – linear growth rate

$$\frac{\partial T}{\partial z}$$ - temperature gradients

- in increase of growth rate (forced by a mechanics of Cz apparatus) requires an increase of temperature gradients   (but it may lead to an increase of defects in crystals, e.g. dislocations, cracks etc. due to thermal stresses)

- there exists a possibility to change of crystal diameter by changing the growth velocity (due to heat of crystallization released),

 Maximum possible growth rate for a crystal of given material:
  - in multi-component crystals (also in one-component doped crystals) is usually limited by effects of transport of component in liquid phase (to avoid defects incrystals), not the heat transport.
  - in one component crystals (like Si, Ge, etc.) usually limited by thermal stresses when crystal goes trough a high thermal gradient zone. Possible formationof dislocations, cracks etc.

Role of convection in the melt on the distribution of temperature
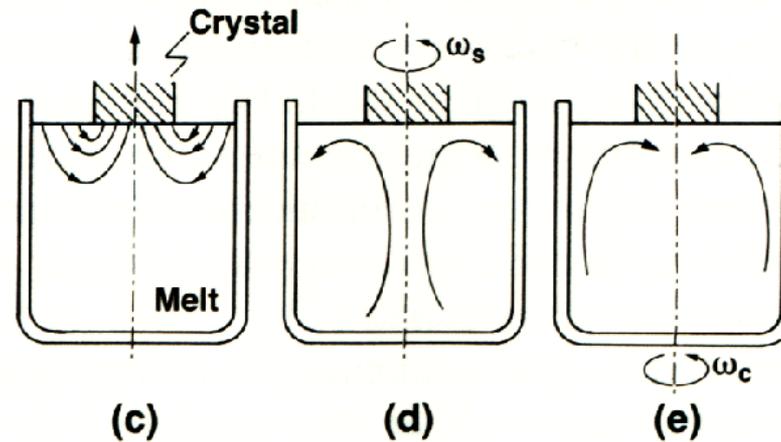
Fig. 5.17. Basic convection patterns of melt in Czochralski crucible. (After Kobayashi.[78])

Strong effect for melts with high viscosity and low thermal conductivity, e.g. oxides materials
   In IF PAN, effects and oxide crystals widely studied by Prof. Marek Berkowski, IF PAN.

Weak role for melts with high thermal conductivity and small viscosity of liquid,
   e.g. metals, semiconductors:

Role rescribed by Prandtl dimensionless number:

$$Pr = \frac{\mu \cdot c_P}{\kappa}$$

κ – thermal conductivity
c_P – specific heat
μ - viscosity

Application of magnetic field in high perfection Si for in Cz. method integrated cirquits wafers

movable opposite magnet coils
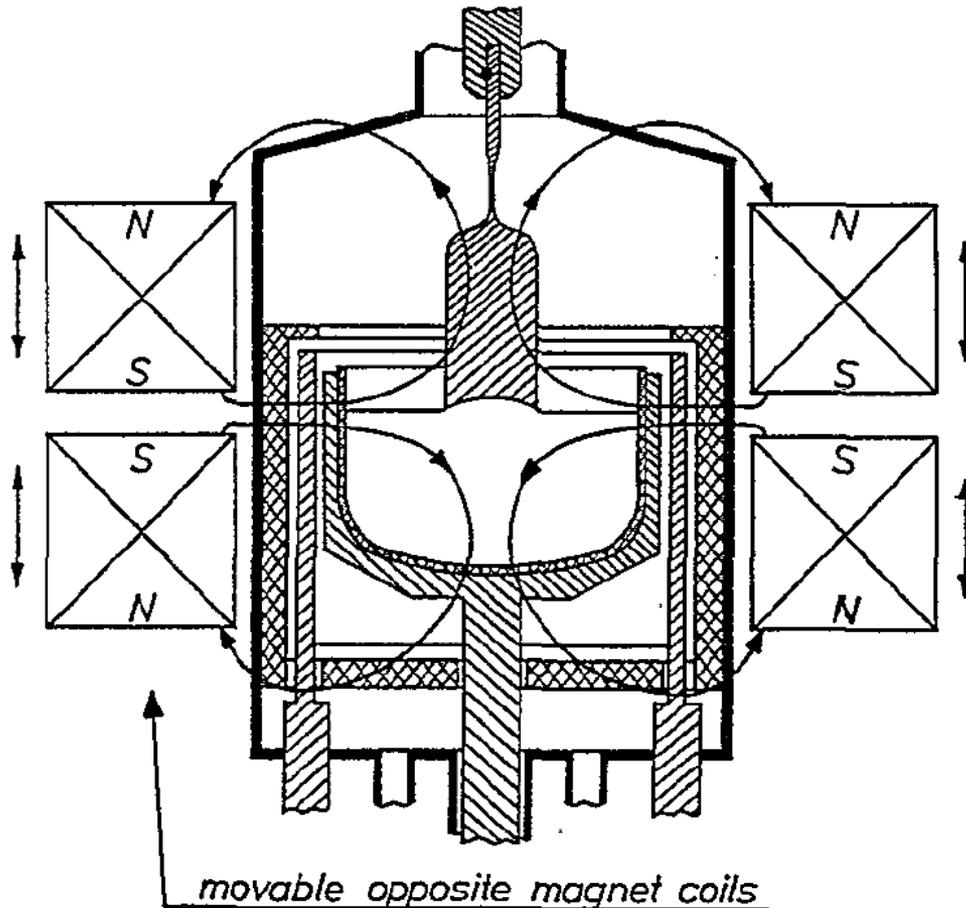
- field damping of oscillatory flows in the crucible due to field induced increase of effective viscosity of ionized melt.

- it results in a smaller concentration of defects in Si crystal, smaller transport of Oxygen from SiO_2 crucibles used for Si melts, more homogeneous distribution of defects. Oxygen in Si crystals, originating from a dissolutio of SiO_2 crucibles, plays a detrimental role in Si crytals due to a tendency to form few-atomic Oxygen clusters, which introduce local strains, also some forms of clusters give thermally ustable electric donors.

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magnetic coil

(Google Grafika: Czochralski)

Cz. puller apparatus, Kayex company

Si single crystal for wafers

T. Słupiński, IF PAN

KAYEX® Vision300™
SILICON CRYSTAL GROWING FURNACE

Industrial type
Czochralski puller for
Si 12-inch, 30 cm
diameter crystals

Meeting the
productivity
demands of the 21ST
century.

HAMCO®
SEMICONDUCTOR MATERIALS PROCESSING EQUIPMENT

KAYEX®
CZ Crystal Growers

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Isotope ^{29}Si Cz. crystal grown using SiC seed
(SiC used not to dissolve Si seed of several isotopes)
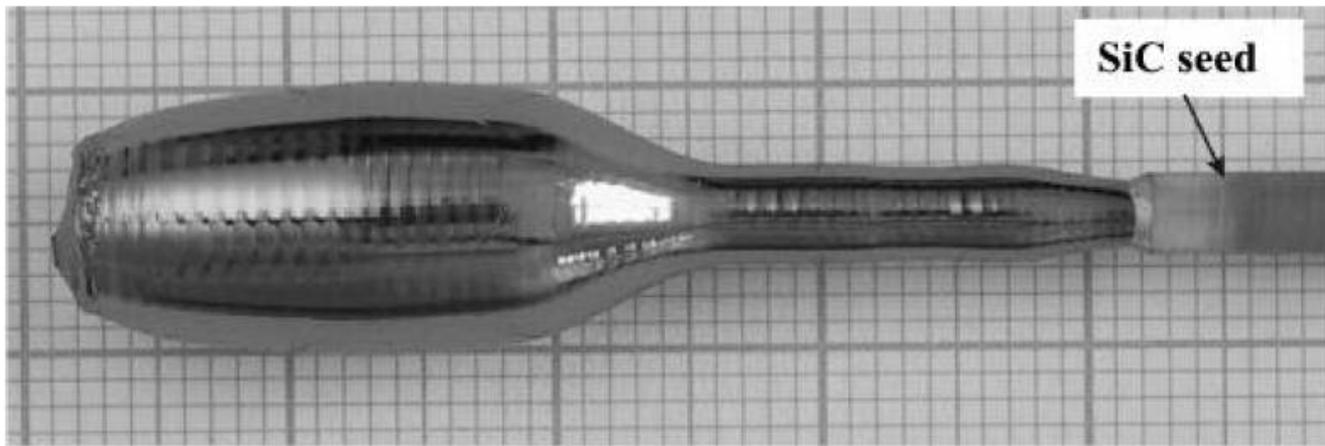
Fig. 2 ^{29}Si crystal grown by mini-CZ technique from the 4g charge using SiC seed.

Table 1 Isotopic composition and chemical purity of ^{29}Si and ^{30}Si before (granulate) and after (crystal) growth process measured by spark-mass-spectral-method

Content of Si isotope, at%	natural Si	^{29}Si		^{30}Si	
		granulate	crystal	granulate	crystal
^{28}Si	92,23	2,15	2,5±0,9	0,2	0,7±0,11
^{29}Si	4,67	97,58	97,2±1,0	0,7	0,62±0,14
^{30}Si	3,10	0,27	0,32±0,14	99,1	98,68±0,21
Chemical purity, not less wt%		99,9970	99,99934	99,9918	99,9992

Abrosimov i in., Inst. of Crystal Growth, Berlin
Cryst. Res Technol. **38**, 654 (2003)

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Sapphire Al_2O_3 using Czochralski method

ITME, Warszawa

High melting temperature: 2050 ^{o}C
induction heating
crucible: Ir, W, Mo
gas atmosphere: Ar, N_2, vacuum
linear growth rate: 1-3 cm/h

For industrial applications (e.g. GaN/InGaN LED diodes)
Al_2O_3 for wafers is grown by Kyropoulos method (slightly
simpler equipment for crystal growth comparing to Cz.)

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Kyropoulos method
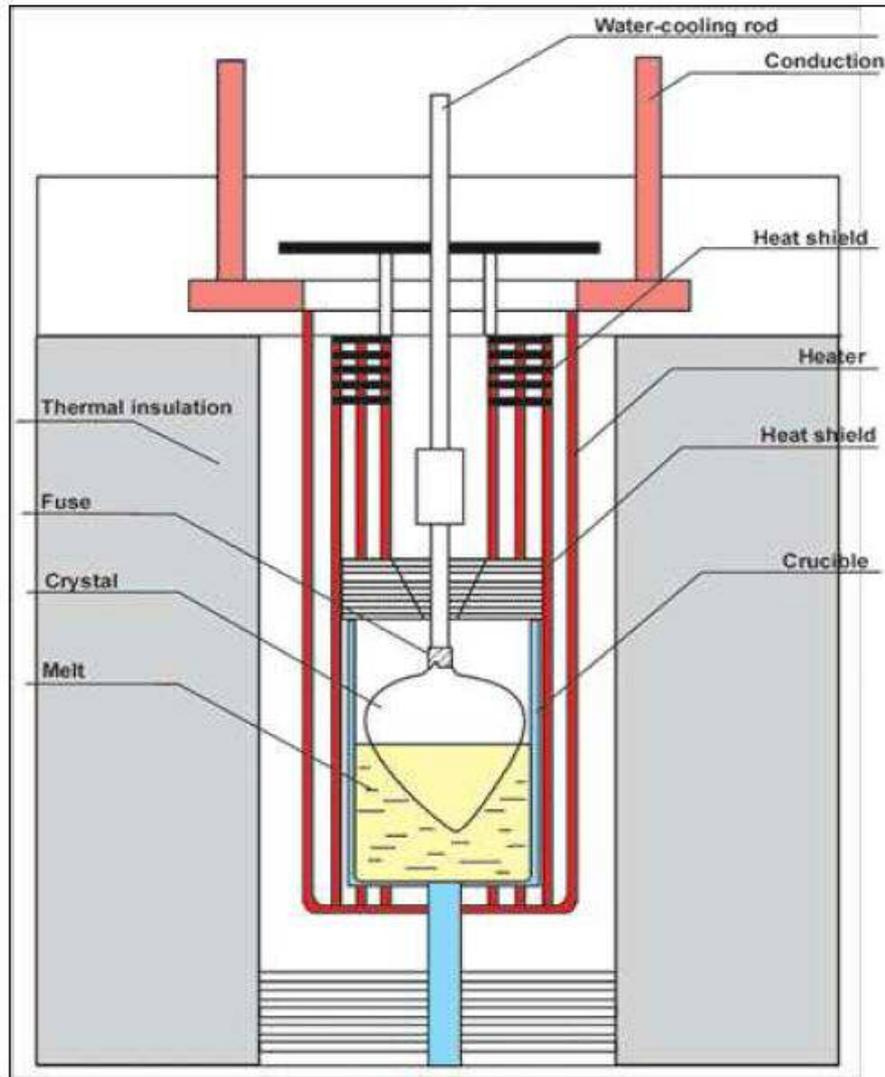
- similar configuration like in Cz.

- crystallization solely by a lowering of melt temperature around the seed crystal

- cheaper method than Cz. and good enough for applications in wafers, optical windows etc.

Monocrystal PLC, Rosja

LEC, liquid encapsulated Czochralski method for some III-V materials which evaporates at elevated temperatures (GaAs, InAs, InP, GaP)
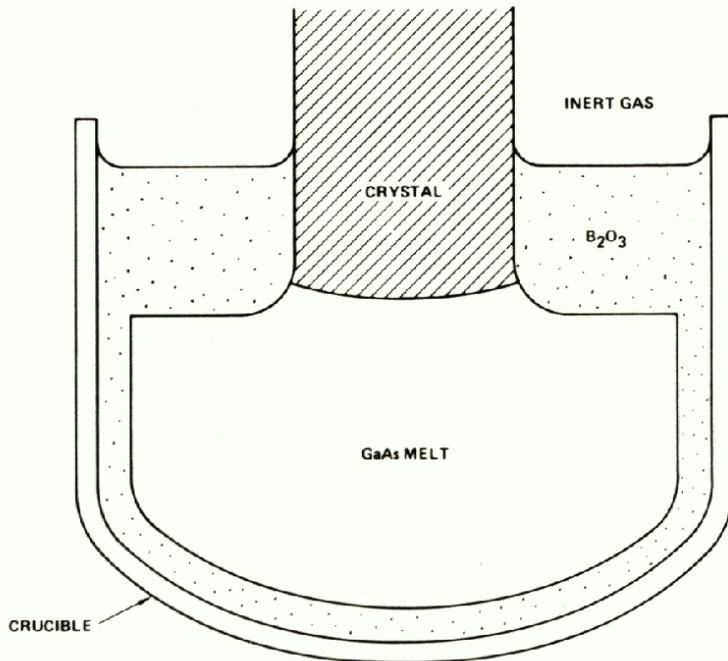
Figure 2.2 LEC crucible configuration during growth

Liquid Encapsulated Czochralski (LEC);   Metz, Miller, Mazelski (1962)
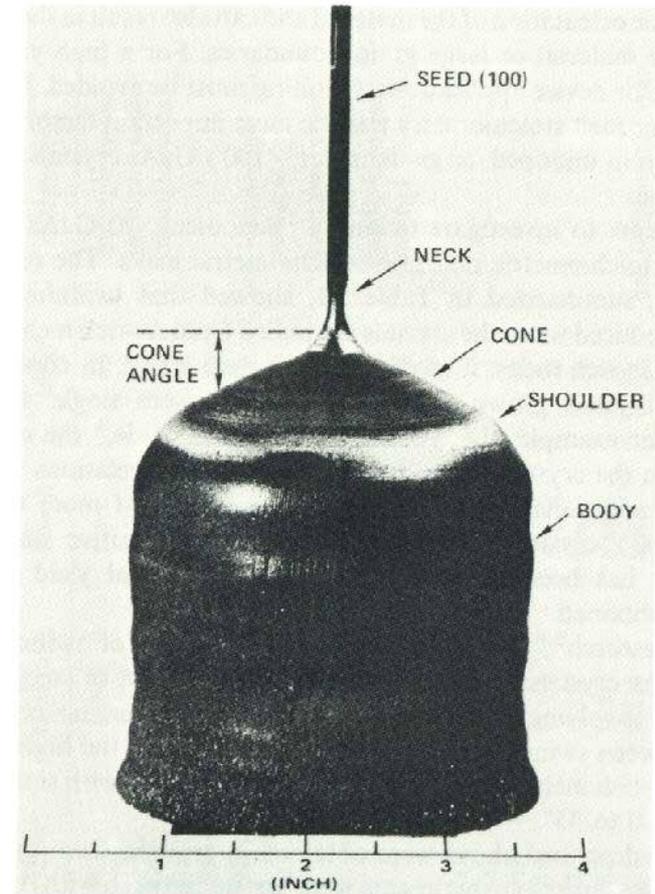
Figure 2.3 LEC GaAs (100) crystal and seed

Pressure-type apparatus for LEC method

Several furnaces in Warsaw in:
   IMiF Łukasiewicz RN (previously ITME),
     Wólczyńska street

   Faculty of Physics, U. of Warsaw
     (previous lab of yours today's lecturer)
     - not operating at present

Czochralski apparatus at U. of Warsaw

Zone-melting techniques: Float Zone for Si

advantages for Si:
- lowered content of Oxygen impurity
  (no SiO_2 crucibles used)

FZ Si:
  - higher uniformity than Cz. Si
    (wafers applied in high current/high power devices
    tyristors, triacs, power IGBT transistors ,...)

  - longer minority carrier lifetimes

Rotation

Polycrystalline silicon rod

RF heating coil

Molten zone

Single–crystal silicon product rod

Silicon seed crystal
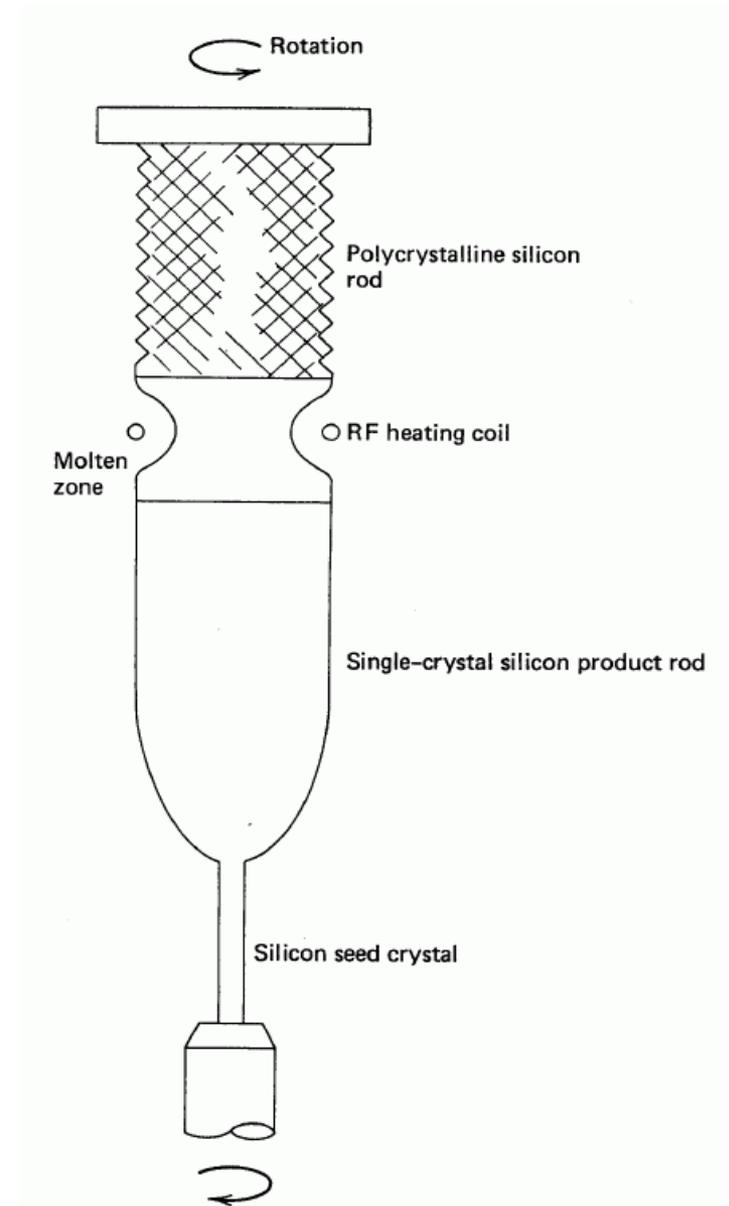
Float Zone method

Fig. 1a. FZ set-up

Fig. 1b. FZ growth

Fig. 1c. Finished FZ ingot

Fig. 1d. Frozen particula

source: T.F. Ciszek et al., NREL

Float Zone method

6" crystal growth

source:
PVA TePla
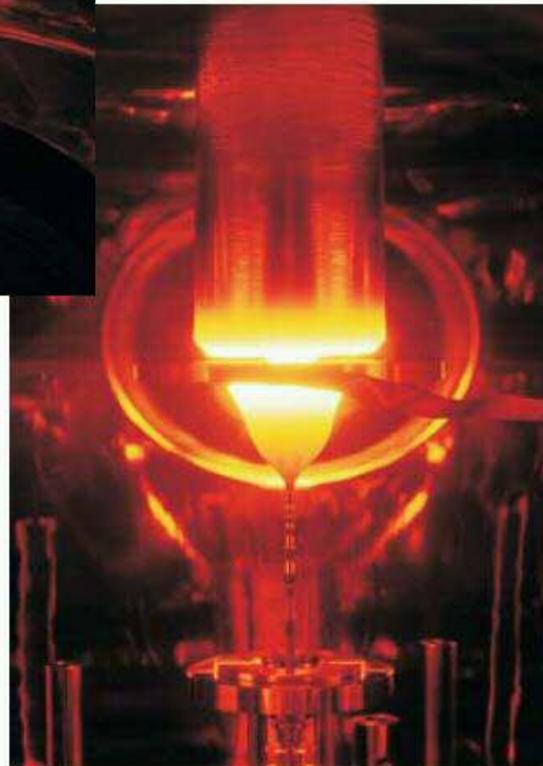
Initial melt zone

- around 3% world production of Si uses FZ, the rest by Cz.

(source: TopSil, Annual Rep. 2007)

Comparison of Si

Growth method	Czochralski	Float Zone
Diameter	50-150 mm	
Crystal Orientation	<100>, <111>	
Orientation Accuracy	< 0.5°	
Type and Dopant	undoped, n and p-type	
Dopant	Phosphorous, Boron	
Bulk resistivity	1-100	1-30000
Oxygen concentration (new ASTM)	< 18 ppma	< 0.02 ppma
Bulk lifetime	> 20 μs	> 1000 μs
Wafer thickness	200-1300 μm	

Bridgman methods: HB, VB and VGF

Seed selection or seed crystal

V

Melt

Horizontal Bridgman 1923

Melt

V

Seed selection or seed crystal
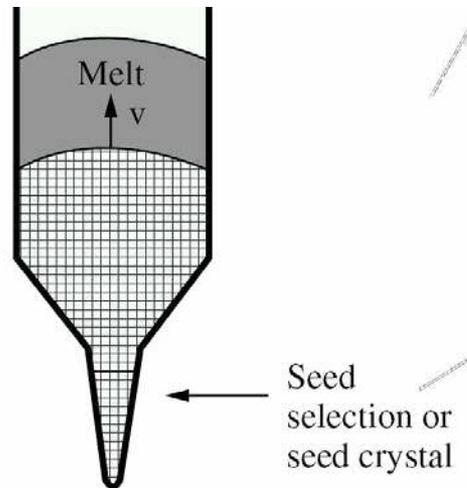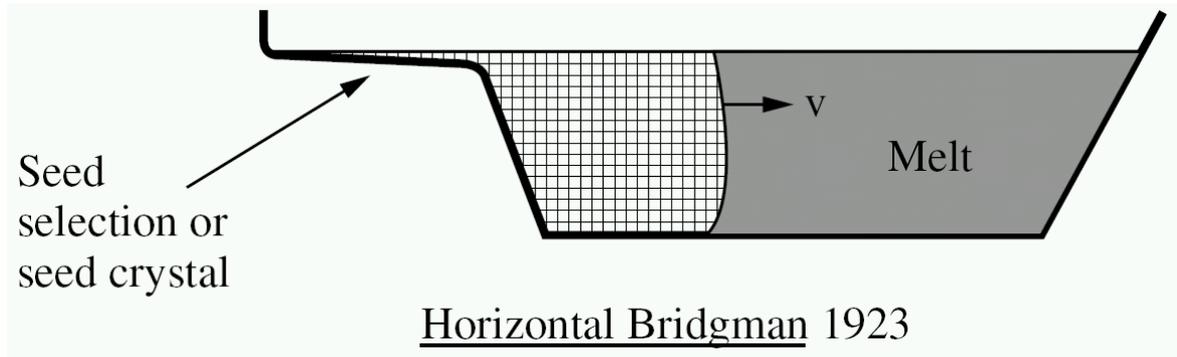
Tammann 1914 / Stöber 1925
Bridgman 1923 / Stockbarger 1936
Vertical Gradient Freeze VGF

Melt and crystal in contact with a
crucible material,

easy automation of method

cheaper method than Cz or FZ,
but often lower

Vertical Gradient Freeze (VGF) method
uses multiple section heaters and
in industrial scale in large part took over
the market of Cz. GaAs.

VGF (Vertical Gradient Freezing)
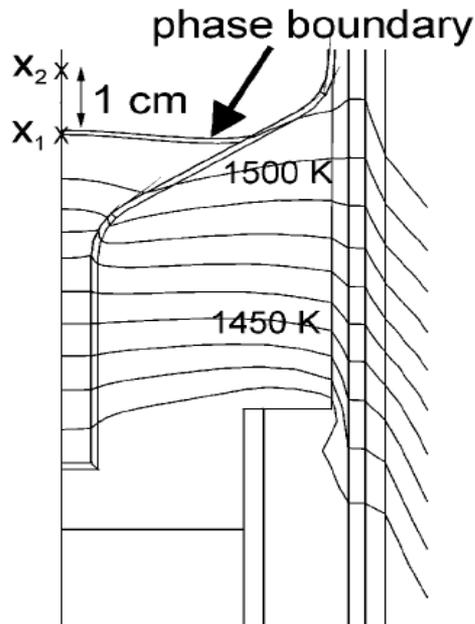
(a) $\lambda_{support}$=3 W/mK
max. σ_{vM}=3.02 MPa

(b) $\lambda_{support}$=5 W/mK
max. σ_{vM}=1.93 MPa

Calculated temperature distributions in the grown crystal

source: Muller, Birkman; JCG (2002)
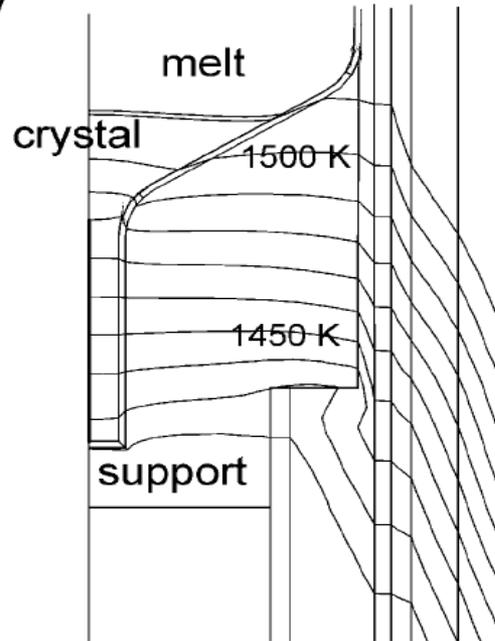
Many independently controled heaters allows for a precise control of temperature field during crystal growth.

Small temperature gradients lower the thermal stresses in crystal (and lower the number of dislocations).

High degree of process control automation possible.

Modeling of thermal conditions in crystal growth zone
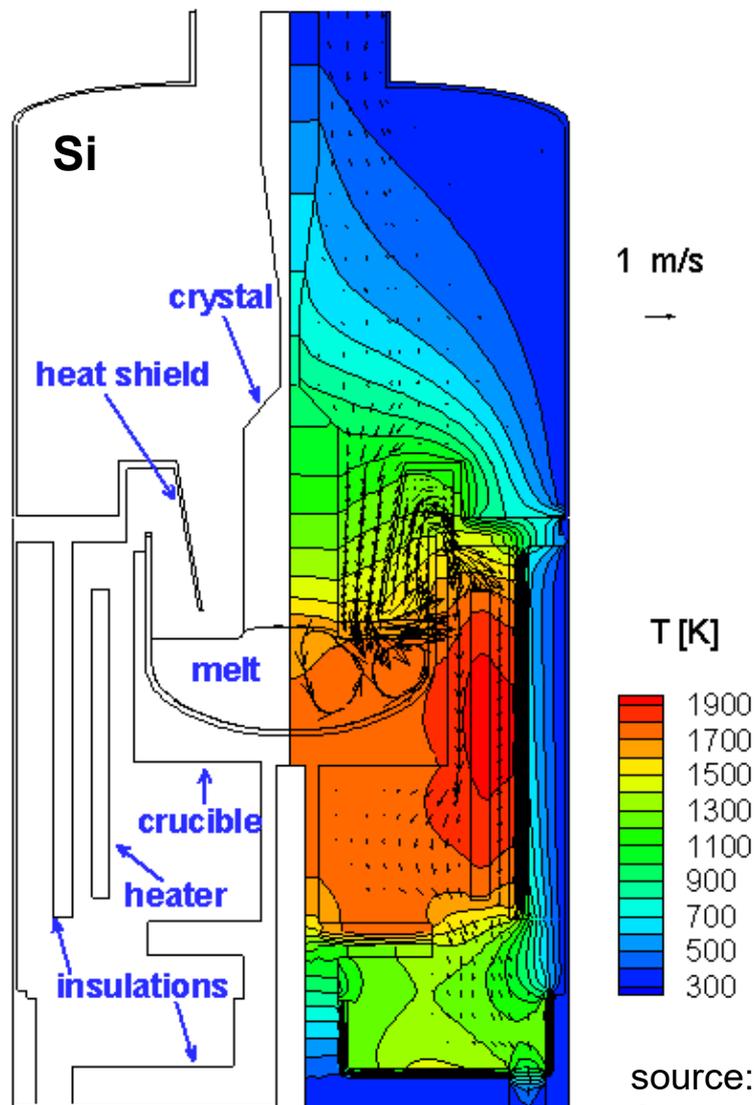
- temperature distribution
- thermal stresses in crystal,
- optimalization of thermal design of apparatus
- studies of liquid flows in the crucible,
- etc.

Growth of crystals from the melt is described by coupled equations of heat transport, mass or component transport and by equations of liquid and gas flows in the growth apparatus.

Models are solved using FEM methods. Important role of proper knowledge of material parameters for the results.

source:
Semiconductor Technology Research, Inc.

Example of LEC method simulated

distribution of
the Von Mises
stress in the crystal

InP crystal

B_2O_3

InP melt

crucible
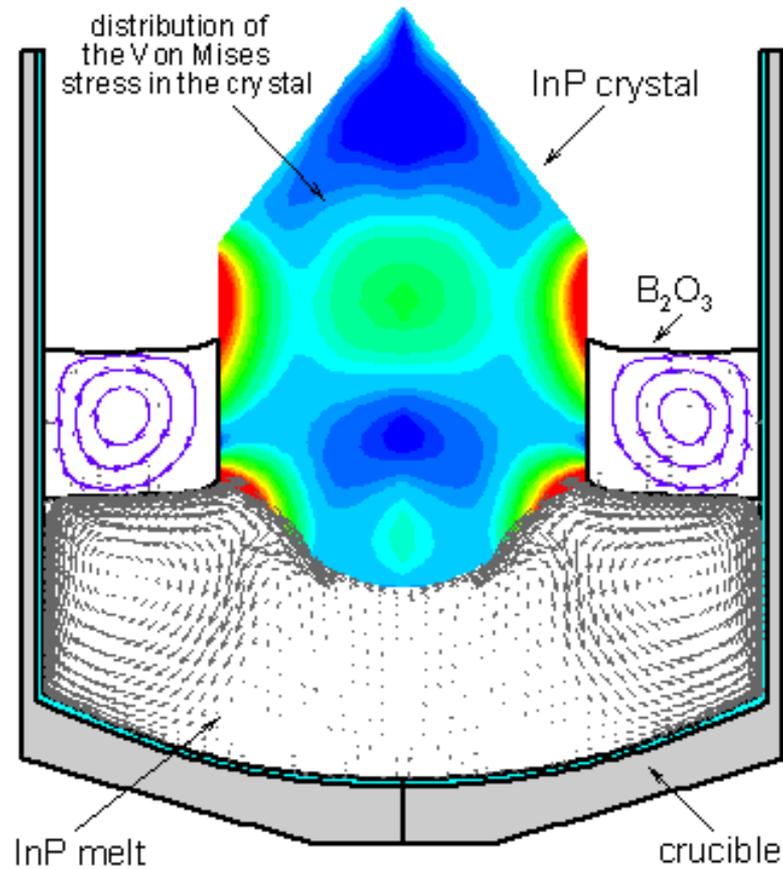
source:
Semiconductor Technology Research, Inc.

Photovoltaics – very rapid growth in 2000-2022, mostly Si

Beneixama, Spain (started in August, 2007)
– one of the first high power PV farms in EU (20 MW)

In an area of 500,000 m², 30 million kilowatt hours of clean energy are produced annually.

At present (2022) about 5 GW PV power installed in PL.
India plans to install soon 100 GW.
Since ~2010 China took over of most PV production.
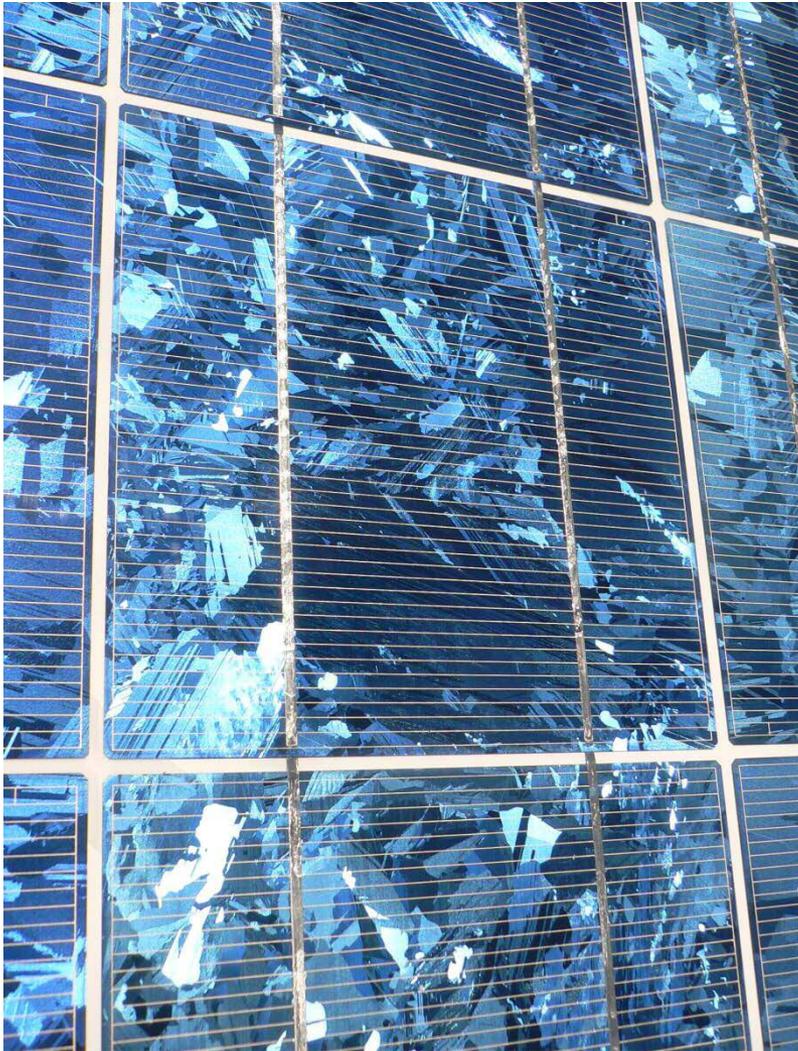
Multicrystalline solar cell,
- efficiency ~15-20 %
(slightly lower than in mono-crystalline Si cells, but slightly cheaper in production).

mono-crystalline Si cells:
- efficiency ~ 20% or even slightly more

Top solar cells efficiency chart
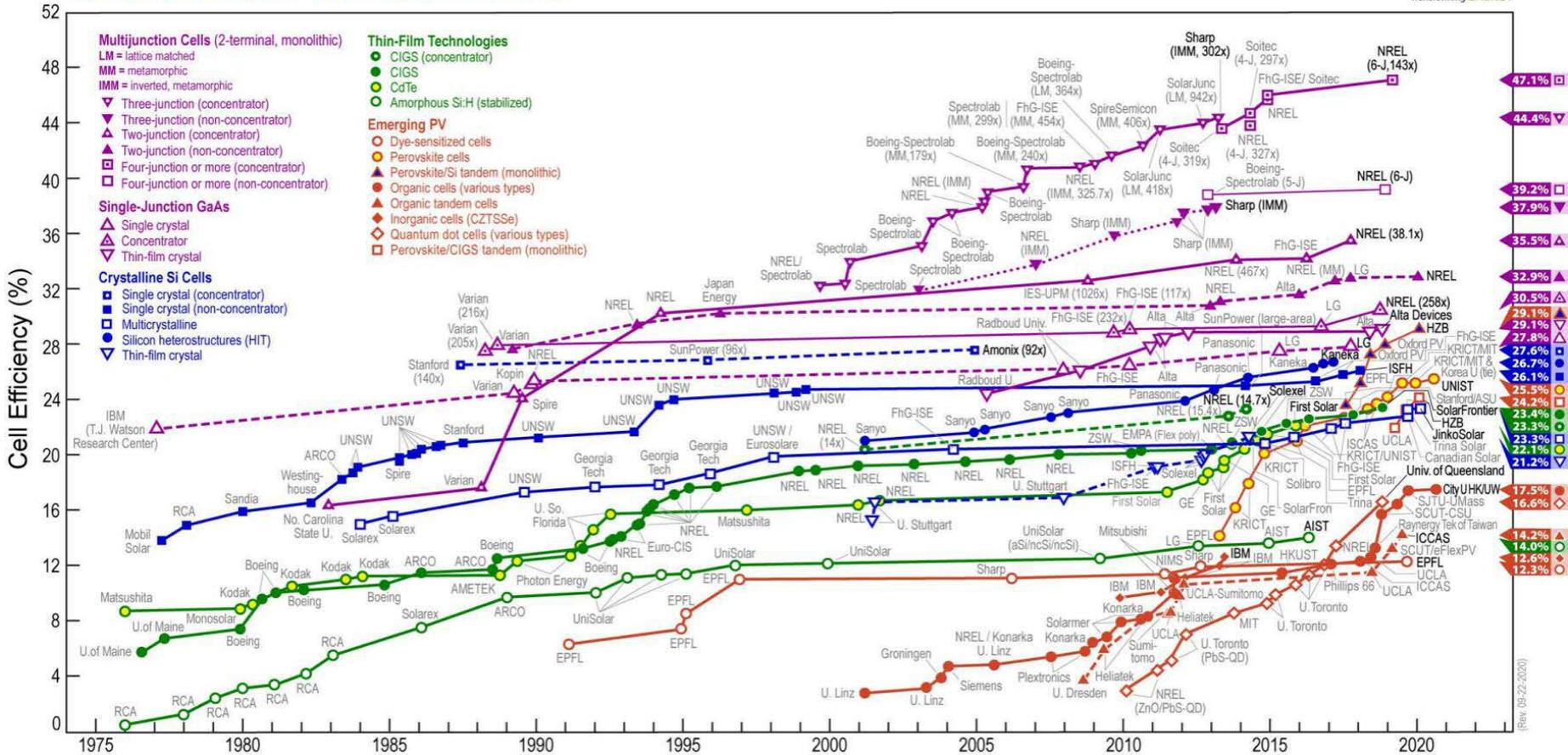
source: National Renewable Energy Laboratory, USA
https://www.nrel.gov/pv/cell-efficiency.html

GROWTH of CRYSTALS
from solutions -
- some rules and few
selected methods

Tomasz Słupiński
IF PAN
SL3.2 – MBE lab.
tslupinski@ifpan.edu.pl

Photo (by T.S.):
instabilities of liquid-solid interface
during GaAs(1-x)Px crystal growth visible in
growth striations at selectively etched cross section of crystal

22.2.2022

Outline

1. Doping of crystals, segregation of components

2. Transport of components, growth striations

3. Constitutional supercooling effect

4. Methods of growth from solutions

5. Selected examples:
   - hydrothermal method for SiO_2
   - ammonothermal method for GaN
   - growth from metallic solutions, e.g.: GaN from Ga+Na solution,
     (another example: GaN from Ga solution, IHPP PAN „Unipress")

6. Comparison of melt and solution growths

Idea of segregation of component, example of $Si_{1-x}Ge_x$
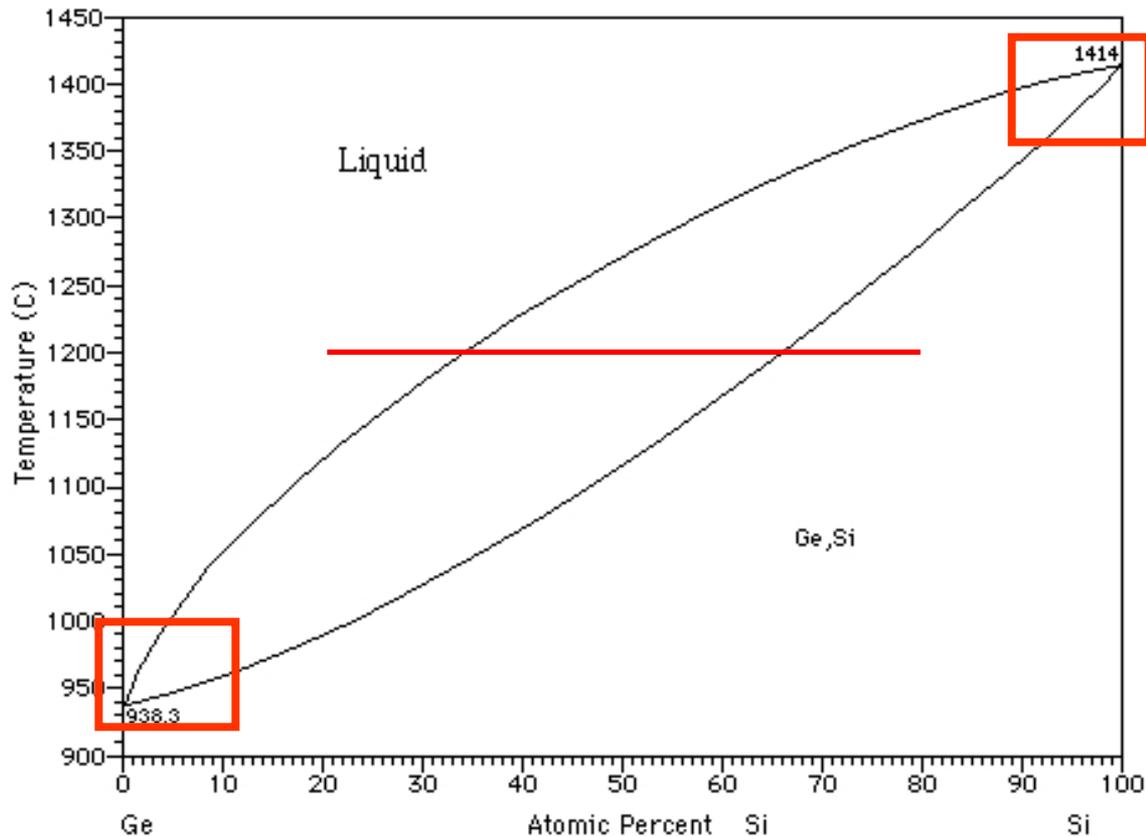
Typically, from the melt only **Ge** and **Si** are grown.

In case of solid solution $Si_{1-x}Ge_x$ growth many complications follow - a consequence of different compositions of solid solution and liquid solution being in an equilibrium at given temperature, e.g. 1200 deg C

Impurity segregation effect
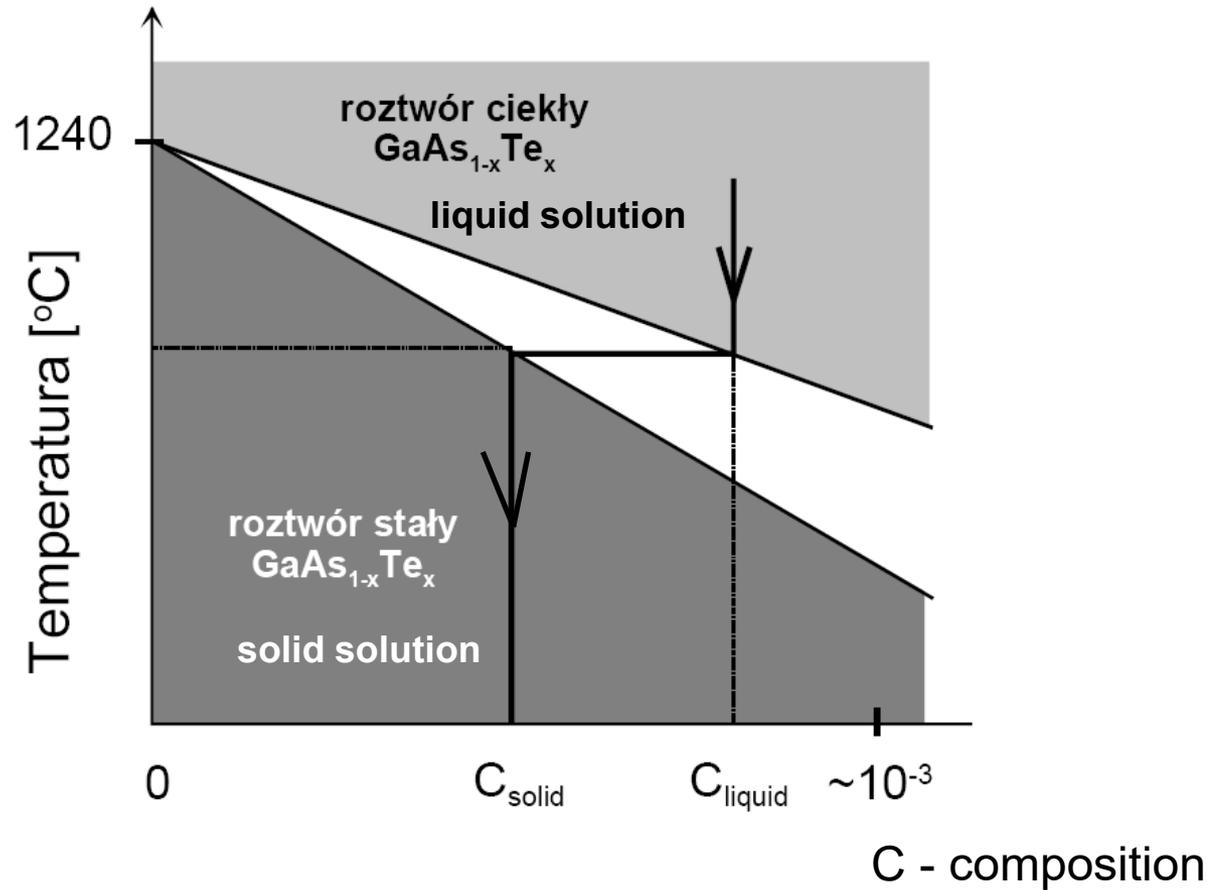
Segregation coefficent (equilibrium): $$k_0 = \frac{C_{solid}}{C_{liquid}}$$

Segregation of impurities
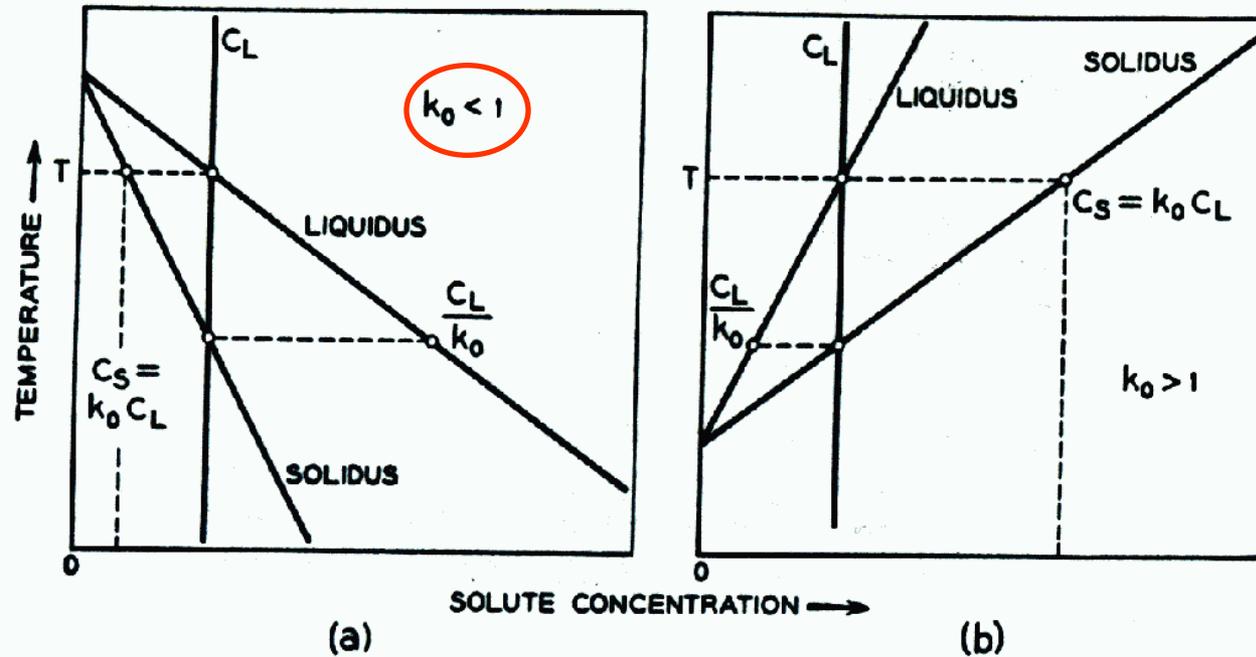
FIG. 1. Portions of constitutional diagrams in which the freezing point of the solvent is, (a) lowered, (b) raised, by the solute.

Segregation effect of impurities in crystallization (i.e. an offset of compositions of solid and liquid phases being in the thermodynamic equilibrium follows already from the simplest models of solutions, like ideal solution model where entalpy of mixing is zero: $\Delta H_{mixing} = 0$. It is a very common effect in phase transitions.
E.g. M. Skłodowska-Curie has separated radioactive elements using effect of segregation at liquid-solid phase transition.

Consequence (1) of segregation effect for crystal growth: a gradient of concentration of impurities along the crystal
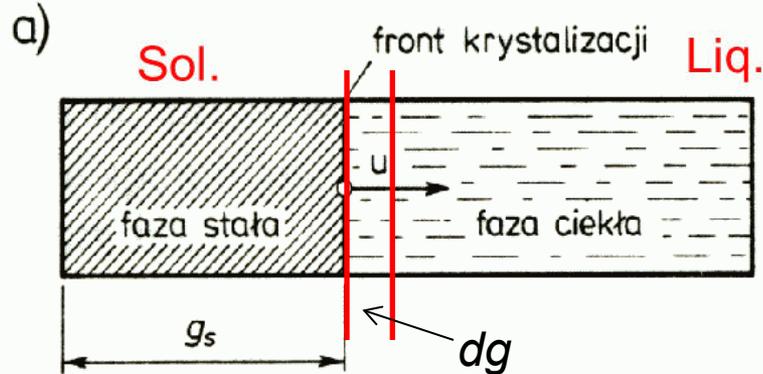
g – fraction of liquid solidified,
$g = 0...1$ - molar fraction
(or sometimes fraction of mass)
$C^s(g)$, $C^l(g)$ – molar composition of solid (s) and liquid (l)
$N^l(0)$ – starting amount of liquid
k – segregation coefficent
dg – infinitezimal fraction of melt solidified

Eq. of balance of amount of impurities during crystallization:

$$C^l(g) \cdot (1-g) \cdot N^l(0) = C^l(g+dg) \cdot (1-g-dg) \cdot N^l(0) + C^l(g) \cdot k \cdot dg \cdot N^l(0)$$

amount of impurity in liquid part

amount of impurity in liquid after crystallizing of dg fraction

amount of impurity in part dg crystallized

$$-\frac{dC^l}{C^l} = (k-1) \cdot \frac{dg}{1-g}$$

$$\boxed{C^s(g) = C^l(0) \cdot k \cdot (1-g)^{k-1}}$$

- this model assumed easy diffusion (strong mixing) of impurities in liquid phase and no diffusion at solid phase. It is satisfied if crystallization goes enough slowly, and then k – equilibrium segregation coefficent.
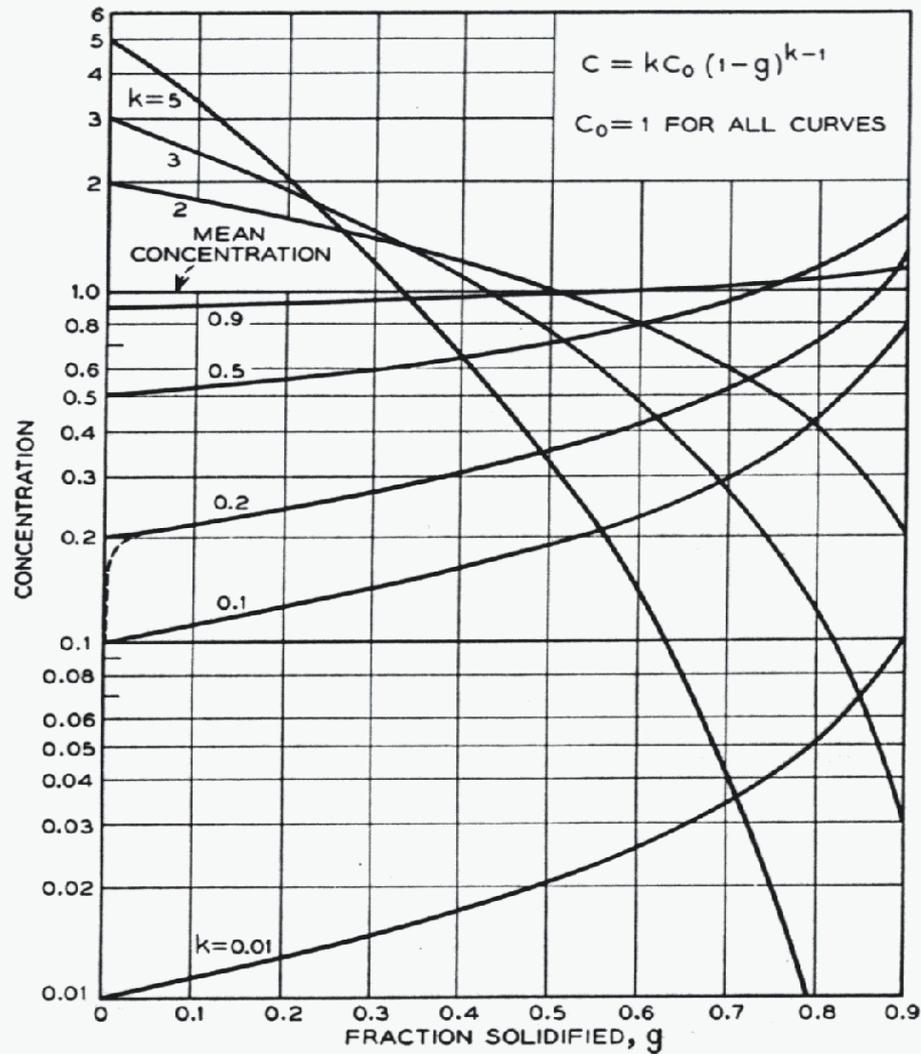
FIG. 3. Curves for normal freezing, showing solute concentration C in the solid *versus* fraction solidified g, calculated from Eq. (2.1) for various values of the distribution coefficient k.

Pfann; Solid St. Physics. Vol. 4 (1958)

T. Słupiński, IF PAN

Example: GaAs:Te   and   GaAs:Te,Ge
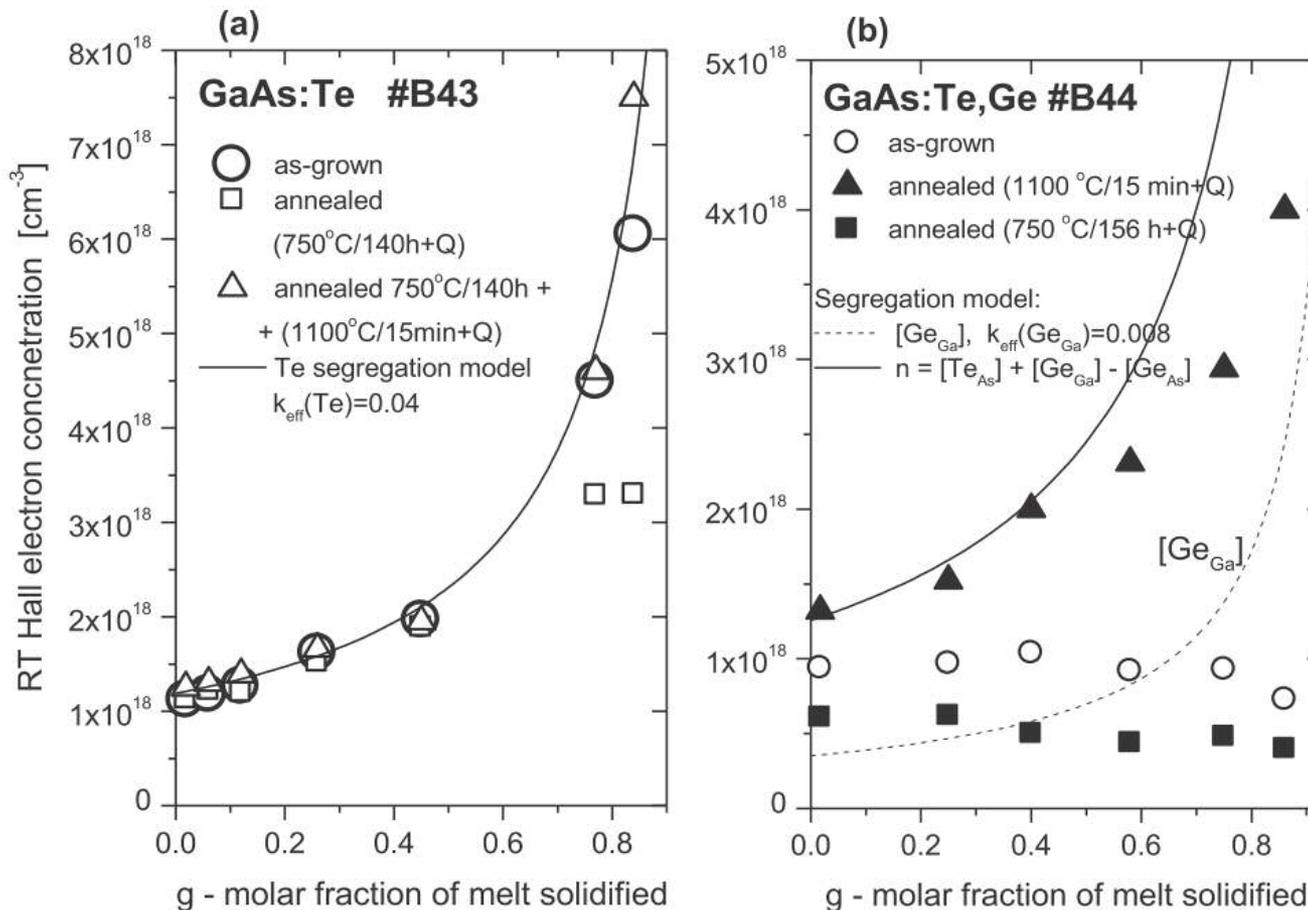
Deviation from normal segregation in as-grown crystals in double-doped GaAs:Te,Ge and restoration of normal segregation at high annealing temperature was interpretted as a result of chemical interaction of Te-Ge donor impurities, involving their mutual electrical deactivation when Ge-Te molecules are formed.

T. Slupinski, J. Przybytek, D. Wasik,   J. Cryst. Growth **468**, 433 (2017)

(electrical doping limit effect or deactivation/reactivation of impurities are very actual topics even in Silicon material and devices)

T. Słupiński, IF PAN

Segregation in zone melting

b) front krystalizacji **Liq.** front topienia
faza stała · u · u · faza stała
l strefa topienia
Sol. l_w **Sol.**

$$C/C_0 = 1-(1-k)e^{-kx/l}$$
$$C_0 = 1 \text{ FOR ALL CURVES}$$
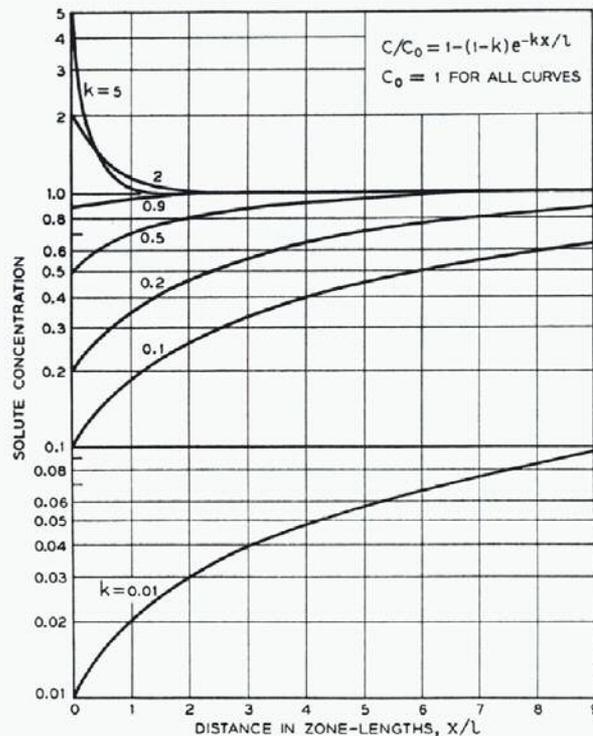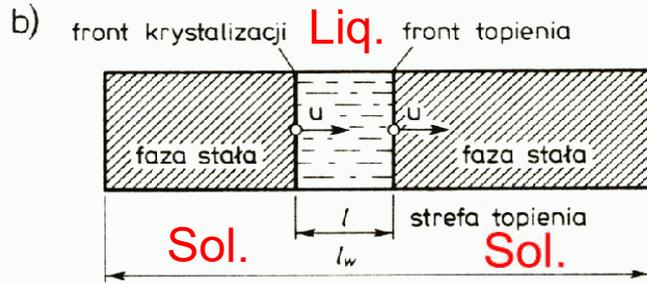
FIG. 8. Curves for single-pass zone melting, showing solute concentration in the solid *versus* distance in zone lengths from beginning of charge, for various values of the distribution coefficient k.

Multiple pass of molten zone is a method of puryfying crystals (widely used in early days of semiconductor materials – 1950's). At present e.g. Silicon is purified as some compound by a distillation (i.e. segregation at liquid – vapour phase transition)
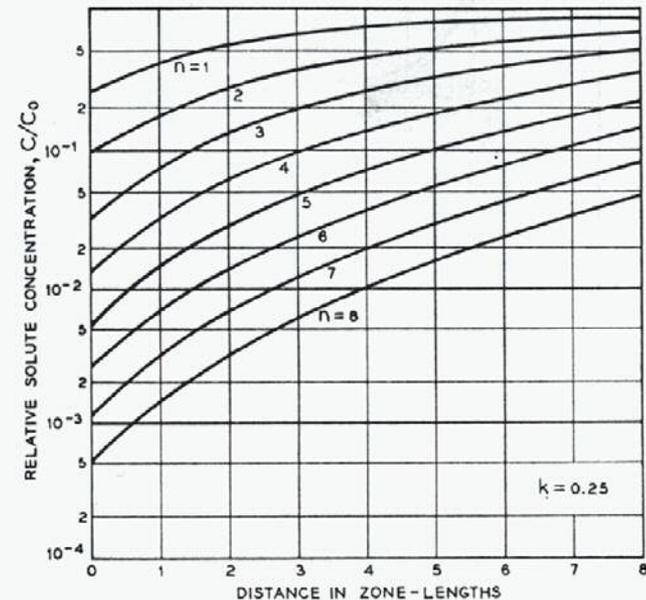

FIG. 10. Curves showing solute concentration against distance in zone lengths, with number of passes as a parameter, for a semi-infinite ingot. $k = 0.25$ (after Lord).

$x/L = L/L_w$ - length of molten zone / length of whole container

Consequence (2):   Segregation of component in case of weak mixing in liquid phase

For k < 1 (less impurities incorporated into solid than present in a liquid phase), a layer enriched in impurities exists in liquid during crystal growth

- **diffusion layer** of effective thickness δ
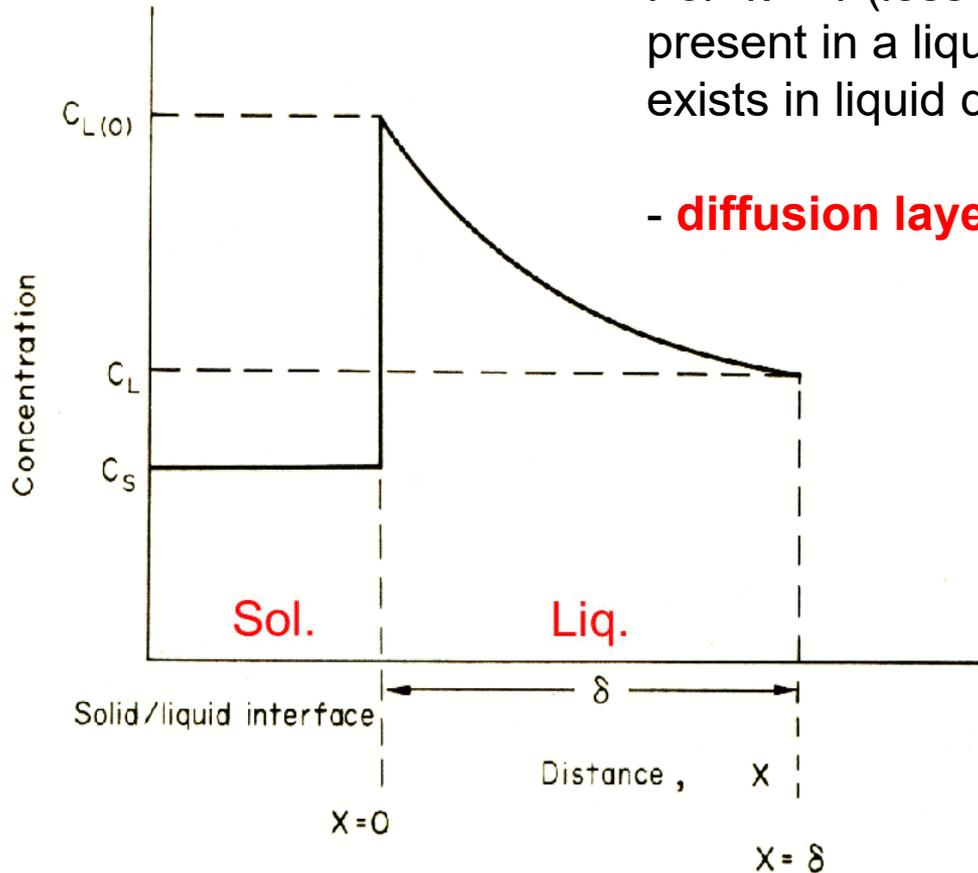
$$k_0 = \frac{C^s}{C^l_{(o)}}$$ - equilibrium segregation coefficent (from phase diagram)

$$k = \frac{C^s}{C^l}$$ - effective segregation coefficent (includes effects of mixing in liquid phase)

FIG. 4.2. Concentration profile and the diffusion layer at a solid/liquid interface.

Segregation coeff. (effective) depends on crystallization velocity!

$$k = \frac{k_0}{k_0 + (1-k_0) \cdot \exp(-u \cdot \delta / D)}$$

Burton, Prim, Slichter (1953)

u – linear growth rate
  (velocity of movement of growth front)
δ – effective thickness of diffusion layer
D – diffusion constant of impurity in liquid

RESULT:
A dependence exists between the growth
rate and an amount of impurity in a crystal
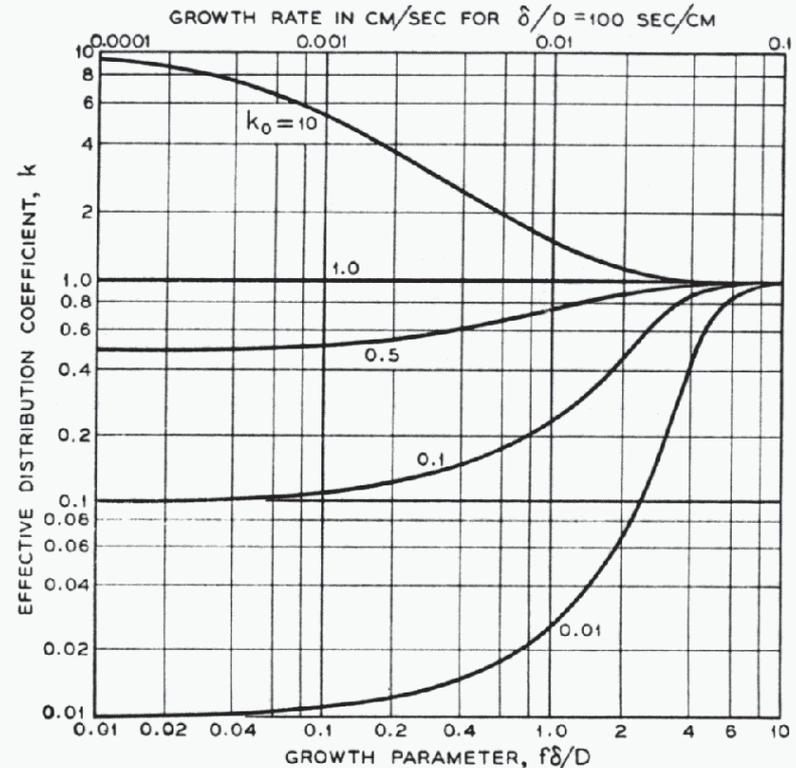
FIG. 4. Dependence of effective distribution coefficient k on normalized growth velocity $f\delta/D$, for several values of equilibrium distribution coefficient k_0.

Transport of heat in melt-growth
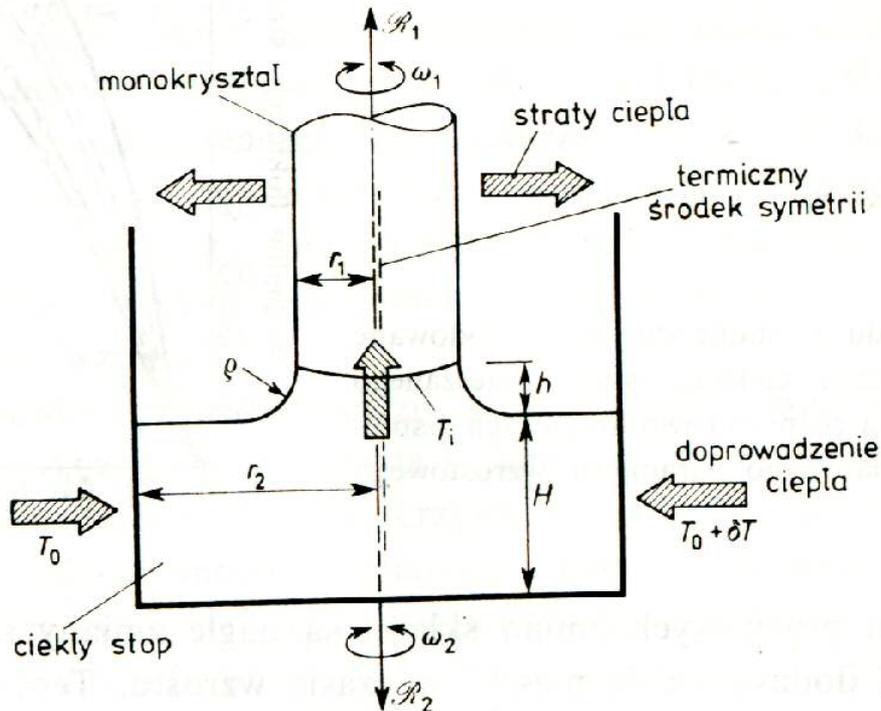
1-dim heat transport equation
(a case near the growth front):

$$-\kappa_{liq}\frac{\partial T_{liq}}{\partial z}+L\cdot\rho_{sol}\cdot V_{growth}=-\kappa_{sol}\frac{\partial T_{sol}}{\partial z}$$

κ – heat transport coeff.
L – heat of crystallization
V_{growth} – growt velocity linear
ρ_{sol} – density of crystal

$$\frac{\partial T}{\partial z}$$ - axial gradients of temperature

Near liquid – crystal interface, gradients of temperature exist.
Growth velocity is related to gradients of temperatures.

Convection in liquid phase
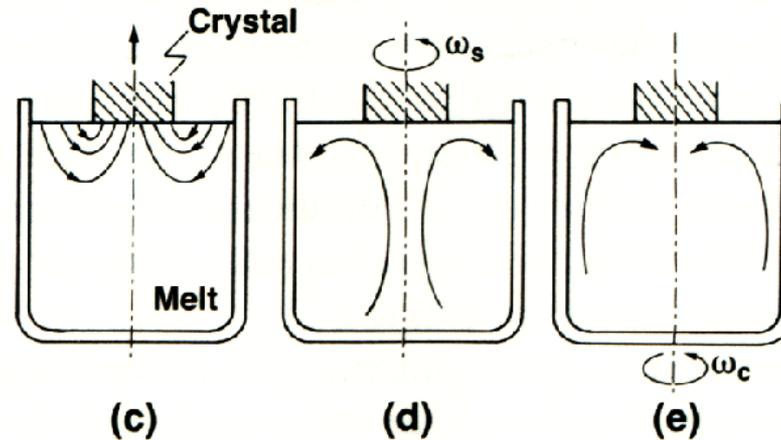
Fig. 5.17. Basic convection patterns of melt in Czochralski crucible. (After Kobayashi.[78])

Due to a non-laminar flow often experienced, the convection has oscillatory character, meaning:
temperature near the growth front oscillates in time
meaning:
growth velocity (linear) oscillates in time.

Fluctuation of growth front velocity cause the fluctuations of concentration of impurities. They are visible in a crystal as *growth striations*.

_____

T. Słupiński, IF PAN

Consequence (2) of segregation effect: growth striations

R.L. Parker, Results of crystal growth in Skylab   863

Fig. 11. Etched longitudinal cross-section of Te-doped InSb crystal regrown on Skylab 4. Space-grown region (bottom), earth-grown region (top).
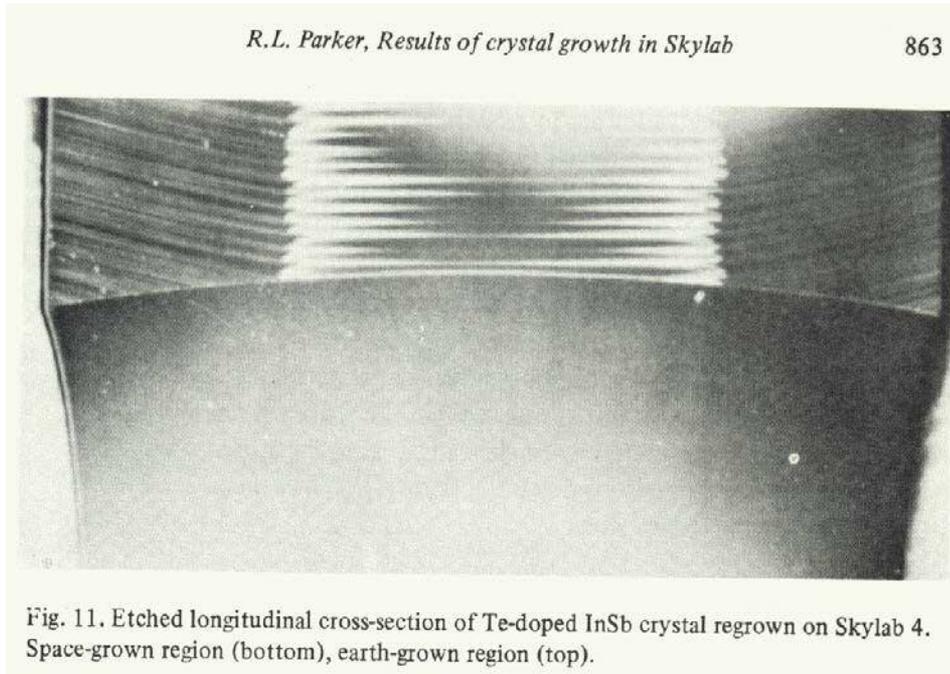
InSb:Te crystal growth experiment in Skylab space station

- This part of crystal was grown on Earth

———————————————

- and this – in space station,
  no gravitation conditions,
  so a lack of convection effect
  and NO growth striations.

Current Topics in Mat. Sci., vol. 2 (1976)

Growth striations (fluctuations of concentration of impurities in scale of ~ 1-10 μm) originate from an oscillatory character of convection in liquid, no gravitation - no growth striations.

Growth striations reveal information on the shape of growth front, e.g. its spatial or temporal stability.
Growth striations can be observed e.g. in x-ray topography or using a selective etching of polished cross section of crystal

Similarly, damping of oscillatory convection is possible in a magnetic field applied during crystal growth.

This metod of improving the uniformity of Si crystals is used for the highest grade silicon crystals growth for wafers for microprocessors.
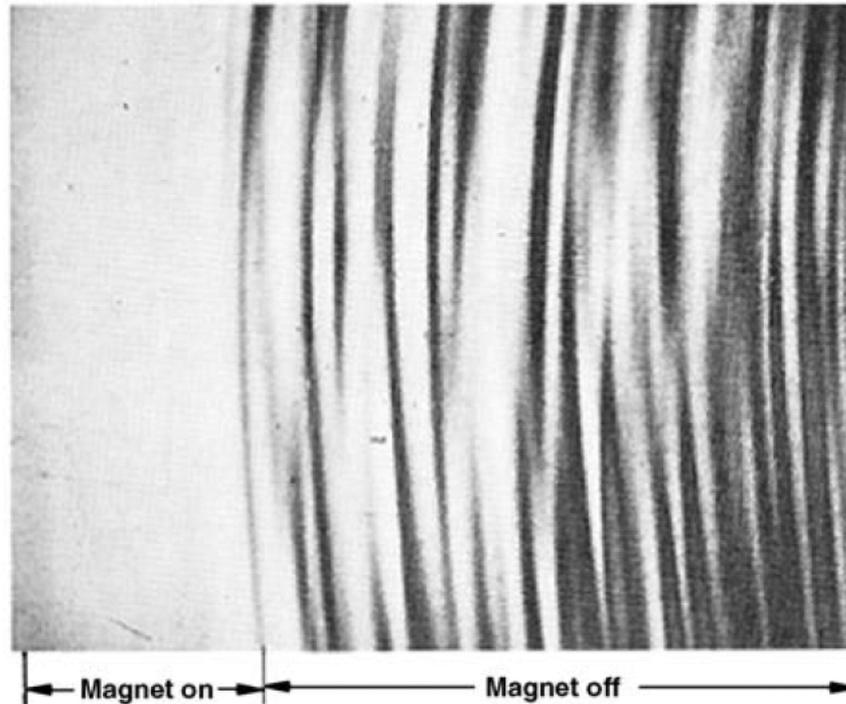

Fig. 3. Banding during crystal growth caused by convection in the melt.

K.A. Jackson, J. Cryst. Growth **264**, 519 (2004)

Growth striations example: onset of growth instabilities

growth of alloy crystal $GaAs_{1-x}P_x$, x=0.07
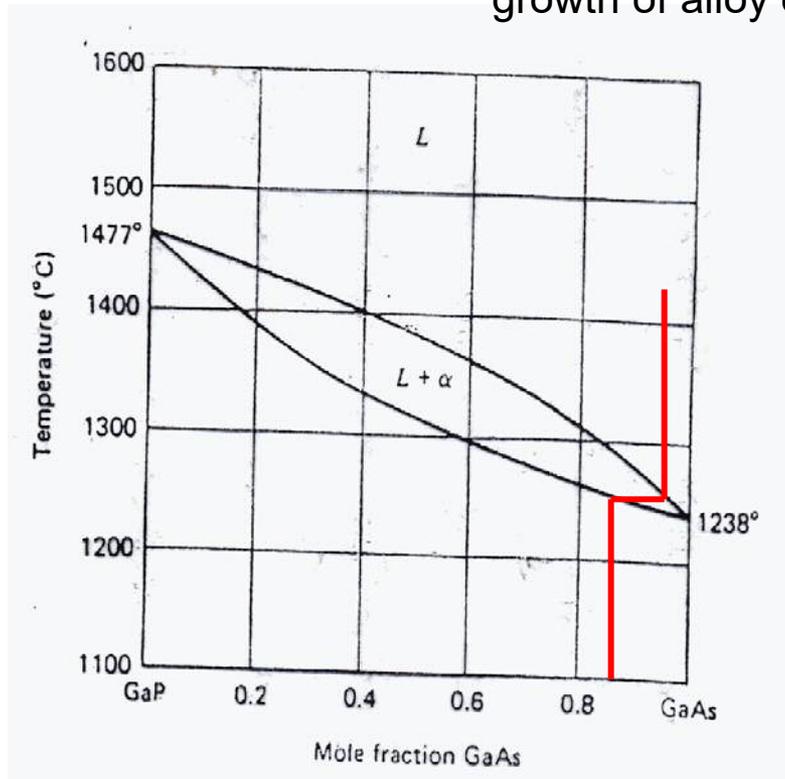
500 μm x 500 μm

Cross-section of crystal along the growth
Direction seen in Nomarski optical microscopy

Growth front instabillities occur in a case of too large linear growth rate forced in for a case
of $GaAs_{1-x}P_x$ alloy crystal growth in Czochralski method.
Non-acceptable nonuniformities (unwanted defects) exist in such crystals.
Often they lead to a polycrystalline growth.
– this example demonstrates an important role of component transport effect.

Origin of such instabilities is related to a presence of impurity and too high growth rate or too small gradients of temperature: constitutional supercooling effect

$k < 1$

Solid

Liquid

C_L

C

I

Permitted conc

C_S

II

C_∞

(a)

Actual conc

O

Z

II

I

Liquidus temperature

T

Actual temperature

I

II

(b)

O

Z

FIG. 3.9 (a) Actual concentration (full line) and permitted concentration (dot–dash) in the steady state. (b) Actual temperature (full line) and equilibrium temperature from the actual concentration and the phase diagram. The liquid is constitutionally supercooled in experiment I but not in experiment II. The two experiments have the same solute profile but different temperature gradients.

I, II – gradients of temperature near liquid-solid interface
I – unstable Sol-Liq interface.
II – stable interface for higher gradient

Equilibrium temperature (from phase diagram) for an actual concentration in the diffusive layer

Region of liquid supercooled too much for the value I of temp. gradient

To avoid the constitutional supercooling one should:
- lower growth rate
- increase *grad* T

T. Słupiński, IF PAN

Mid-lecture conclusions:

If the liquid phase has different composition than the growing crystal,
then effects of transport of component
are important.

Then, **transport of component determines possible growth rates,**
not a transport of heat.

This has fundamental consequences for growth of crystals from
solutions.

Some examples of crystal growth metods from liquid solutions

DEFINITION of terms used:

growth of crystal of chemical substance AB from a solution in C
concerns a situation when molar composition of AB (solute) in solvent
C is of the order of ~0.1% - ~10 % (usually)

- low-temperature solutions (e.g. H_2O, organic solvents, etc)

- high temperature solutions
(e.g. molten metals, liquid salts, supercritical fluids loke H_2O, NH_3 etc.)

Growth rates possible to achieve: ~1 – ~100 µm/h
(from economy point of view: the higher – the better)

Supersaturation is a factor which controls the growth of crystal and
growth rate
(to remind you: supercooling in a case of melt-growth)

To achieve supersaturation usually the dependence of solubility on temperature
is used.

_____

Dissolution zone – transport – crystallization zone
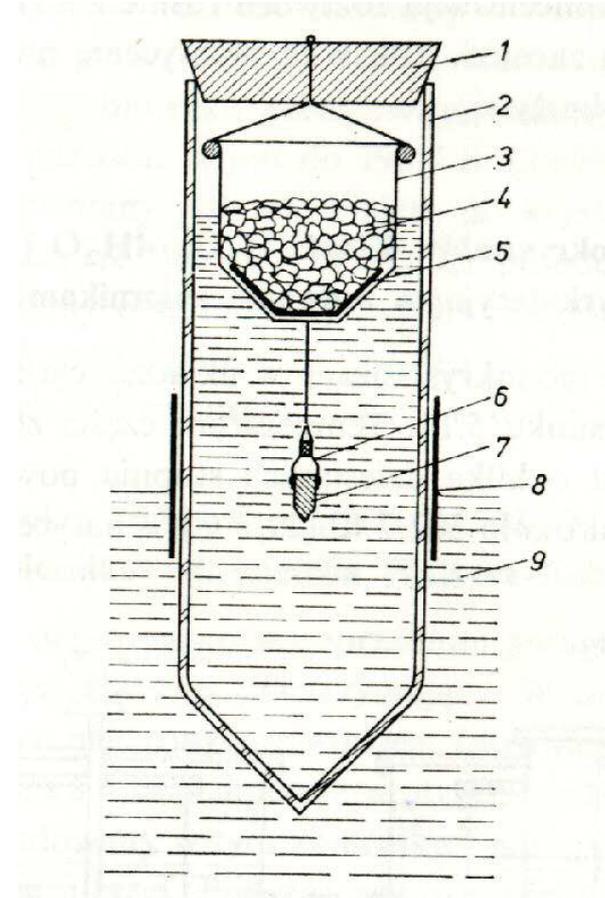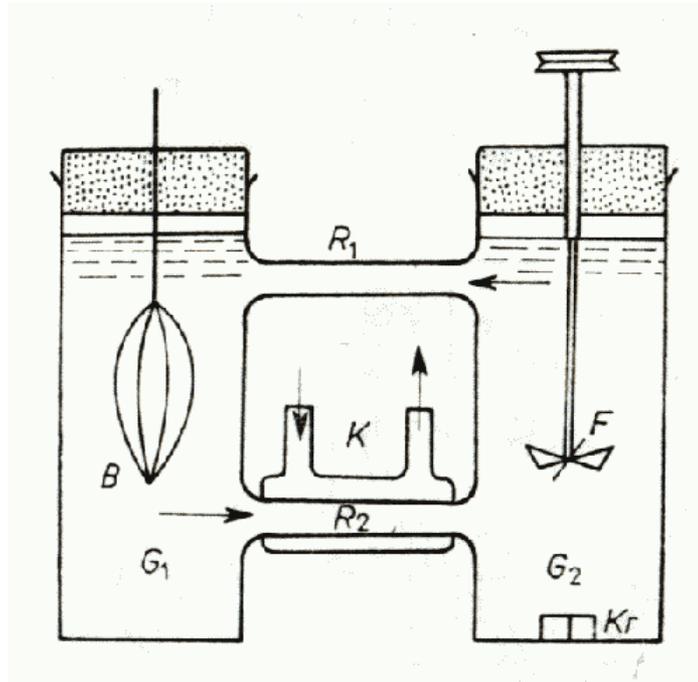
Example: hydrothermal growth of SiO_2 from solution in H_2O in supercritical state

- SiO_2 phase diagram shows that alpha-quartz phase (applied in pioezoelectric devices) cannot be grown from SiO2 liquid phase:

- other intermediate phases and solid-solid transitions willl defect (crack) the crystal.
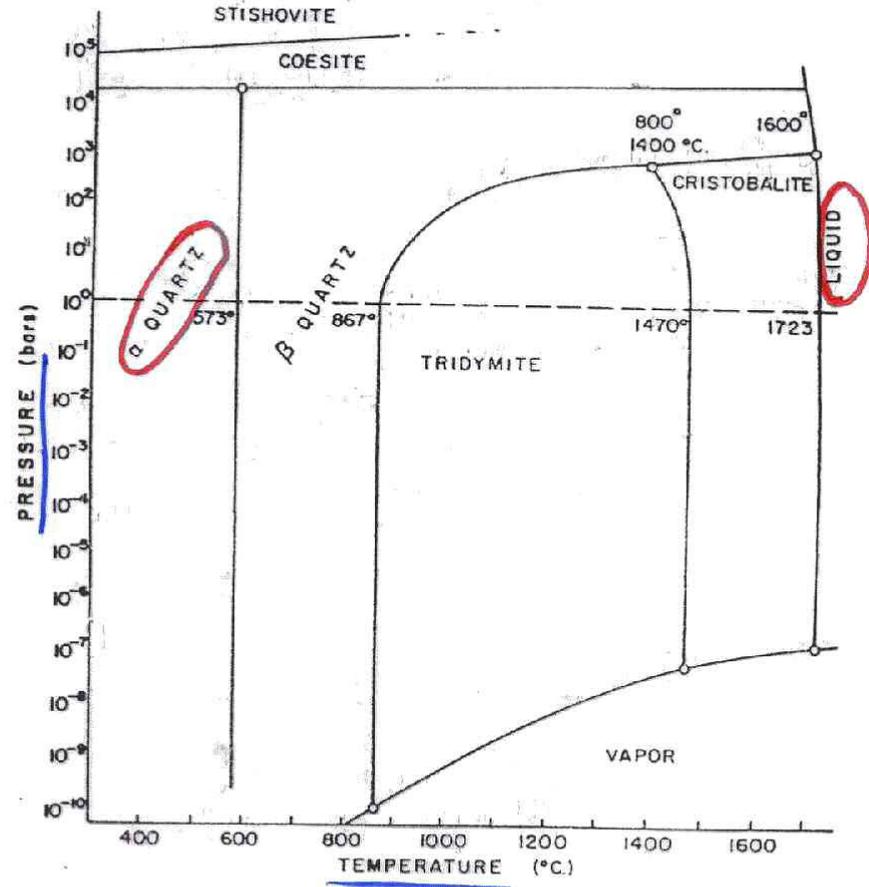
Figure 27. P-T diagram for system SiO_2 drawn to scale. From Roy and White (1975).

# Hydrothermal method (e.g. growth of α-SiO$_2$ from H$_2$O solution (high pressure, high temperature)
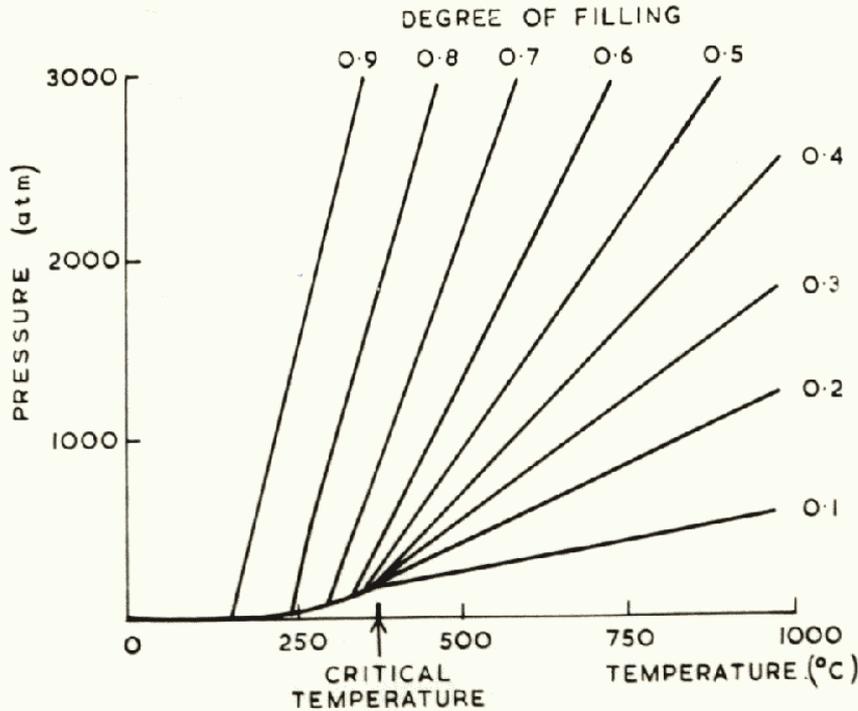
FIG. 14.10. P–T curves for water for various initial degrees of filling, after Kennedy (1950a).

FIG. 14.6. Typical arrangement of furnace and autoclave for hydrothermal growth of crystals.

Solvent: H$_2$O above or near the critical point

Autoclave: p(max) =~ 5 kbar
T(max) = 500-750 °C
Strong materials requirements !

Solubility of SiO_2 in H_2O
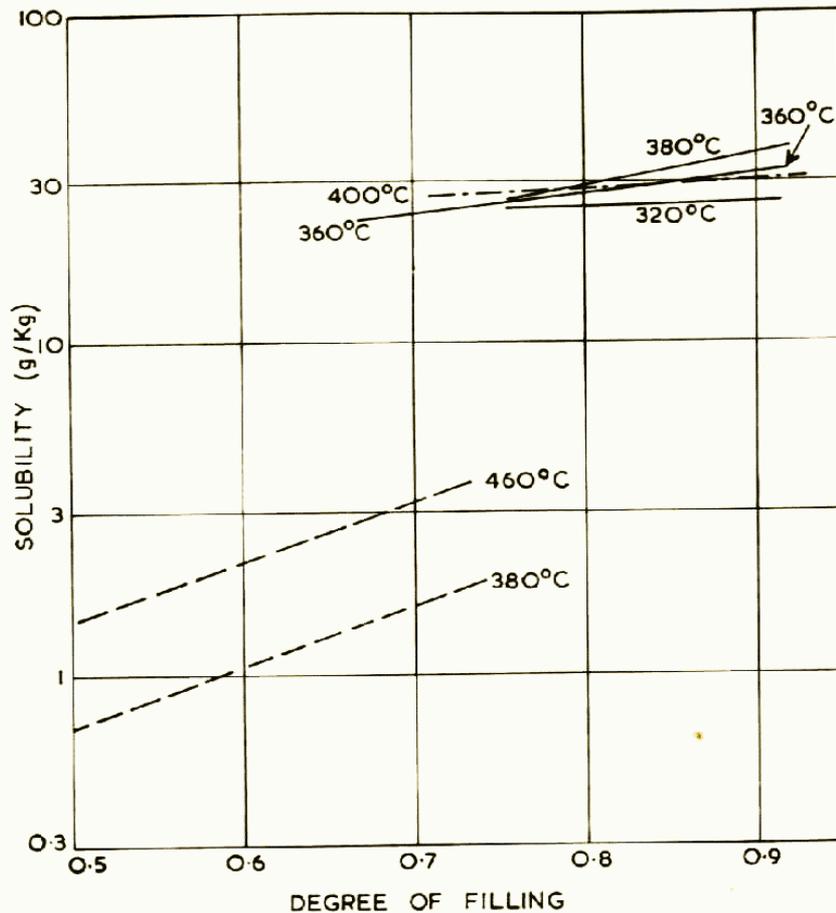
FIG. 14.9. Solubility of quartz in various solutions.
——— 0·5 N NaOH solution, after Laudise and Ballman (1961).
–·–·– 5 per cent Na_2CO_3 solution, after Butuzov and Briatov (1957).
– – – – Pure water, after Kennedy (1950b).

For an increase of solubility, properly selected **mineralizers** are used.

- compounds which favours a formation of complexes with solute material which can be transported in solute phase (e.g. NaOH for SiO_2 growth from H_2O solvent).

Usually few % molar solubility is enough for crystal growth.

Low solubility of SiO_2 in H_2O (no mineralizer)

*J.C. Brice, Phase diagrams of electronic materials*
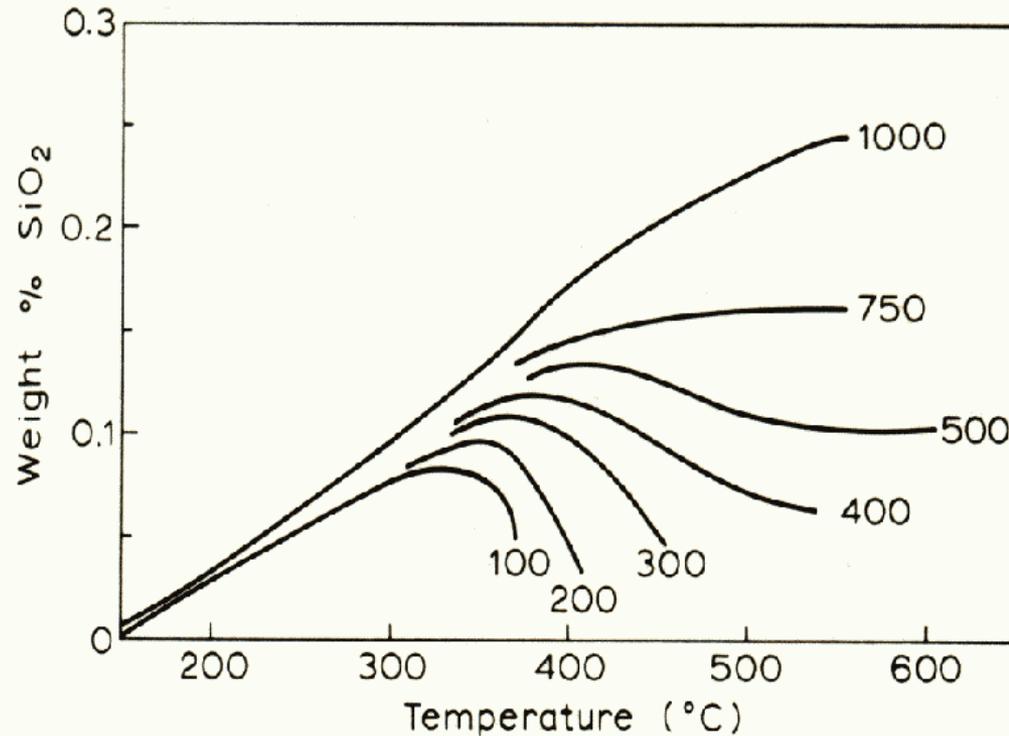
Fig. 2. The solubility of quartz in water at various pressures (in bars).

Current Topics in Mat. Sci., vol. 4

Institute of Electronic Materials Technology

α-quartz crystals from
hydrothermal method
ITME, Warszawa, ~1980-2000
(at present facility is not operating)
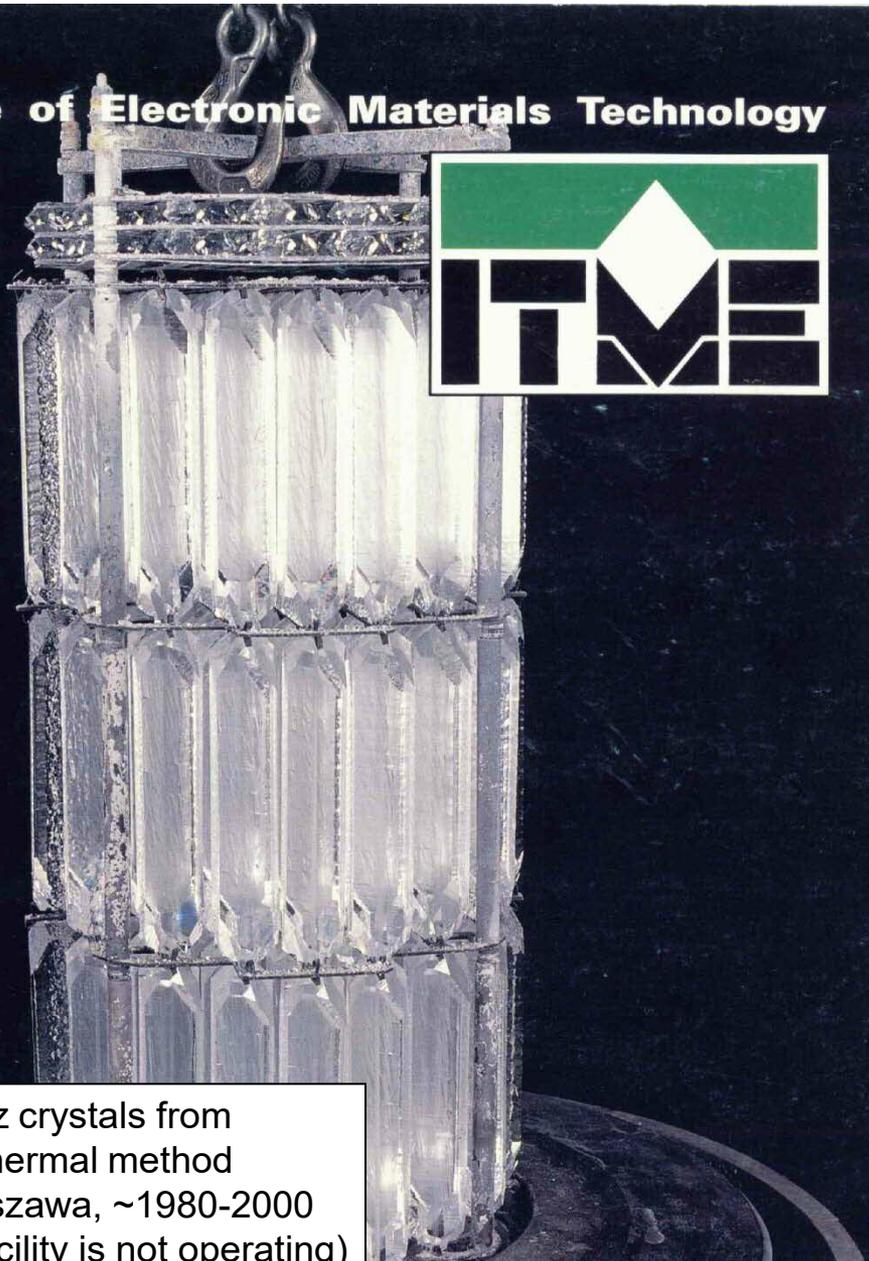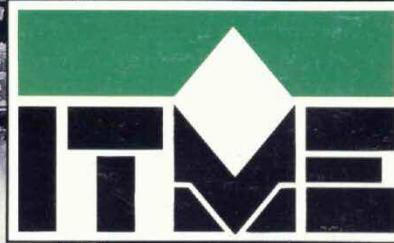
Approx. Growth conditions:

- temp. of dissolution zone = 400 ^{o}C

- temp. of growth zone = 360 ^{o}C
  (T measured at the outher surface of
   pressurized autoclave,
  inside the difference may be lower)

- pressure = 1.5 kbar

- degree of autoclave filling at ambient
  conditions = 0.80

- growth rate = ~ 1 mm / 24 godz (!!!)

     (wg. Laudise, Sullivan (1959)

Many various type of crystals can be grown, e.g.

Table 8.1 Some typical hydrothermal growth conditions

Crystal	Mineralizer	Growth temperature °C	Temperature difference °C	Fill, % (pressure, atm)	Growth rate mm day^{-1}
Al_2O_3	1 m K_2CO_3	490	50	80	0.25
As	10 m HI	430	20	65	0.4
Au	10 m HI	500	-20^*	?	1
$CaCO_3$	2 m $CaCl_2$	200	25	(200)	1
CdS	9 m HBr	430	20	65	0.1
CuS	9 m HBr	420	30	65	0.5
Cu_9S_5	9 m HBr	430	20	65	0.3
Fe_3O_4	2 m NaOH	400	30	80	0.1
HgS	2 m HCl	320	10	58	0.2
$LiGaO_3$	3.5 m NaOH	385	35	70	2
$NiFe_2O_4$	0.5 m NH_4Cl	470	12	70	0.03
PbS	12 m HCl	430	20	55	0.2
$PbTiO_3$	1 m KF	600	35	(1000)	0.05
Se	0.4 m Na_2S	175	25	95	<1
SiO_2	1 m NaOH	375	40	80	1
TiO_2	1.5 m KF	550	50	(800)	0.5
$Y_3Fe_5O_{12}$	20 m KOH	350	10	88	0.1
ZnO	5 m KOH	350	10	85	0.25
ZnS	5 m NaOH	350	10	85	0.05

*The growth zone is hotter than the solution zone.

J.C. Brice (1986)

Ammonothermal method (solution in supercrittical ammonium NH_3) on the example of GaN, AlN

First reports:

1)   D. Peters (@Hoechst), J. Cryst. Growth **104** (1990) 411
       „Ammonothermal Synthesis of AlN"

$$KAl(NH_2)_4 \leftrightarrow KNH_2 + AlN + 2\ NH_3$$

- reversible reaction, controlled by the temperature,
- low, but enough high solubility in NH_3

Fig. 3. SEM photograph of single monocrystalline AlN columns, direction of growth [001]; isothermal chemical transport, $T = 600\,^{\circ}C$, $P = 2$ kbar, $x(K)Al = 9\%$ and $x(NH_3)S = 89\%$.

2) R. Dwiliński et al. (@ Faculty of Physics, U. of Warsaw),
    Acta Physica Pol., A 90 (1996) 763
    „On GaN crystallization by ammonothermal method"

    MRS Internet J. Nitride Semicond. Res. 3 (1998) 25
    „Ammono method of BN, AlN and GaN synthesis and crystal growth"

- pioneers of GaN ammonothermal growth
   (yes, you guess well, it was in Warsaw)
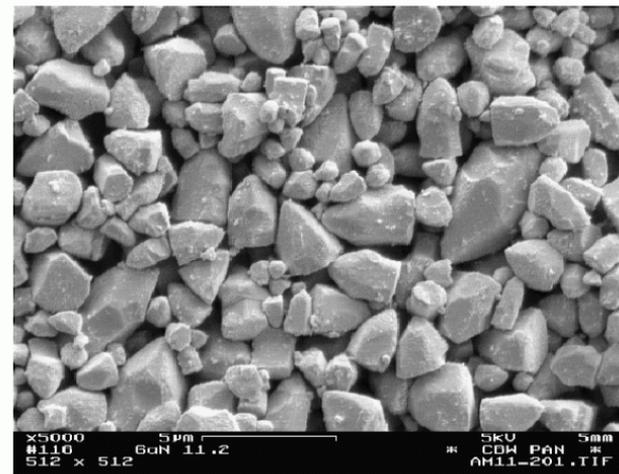

Figure 1. GaN crystals obtained in a synthesis process under the following conditions: $T=550\,^{\circ}C$, $p=5$ kbar, Ga:LiNH$_2$:NH$_3$=1:2:20.

Solubility of GaN in NH$_3$ + KNH$_2$ mineralizer
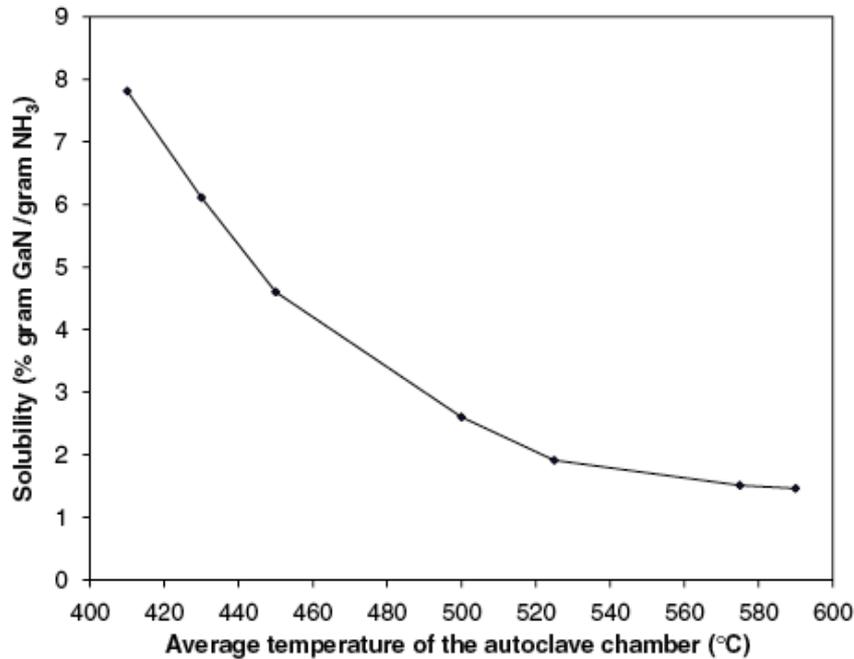
Fig. 1. Retrograde solubility of GaN measured in KNH$_2$–NH$_3$ solutions. Potassium amide concentration is about 3.5 ± 0.5 M, the temperature difference $\sim 10\,°C/cm$, pressure $1.2-2.4$ kbar.

Wang et al., J.Cryst. Growth **287** (2006) 376
- GaN 10 x 10 x 1 mm^3
- growth rate ~ 50 µm/24 hours
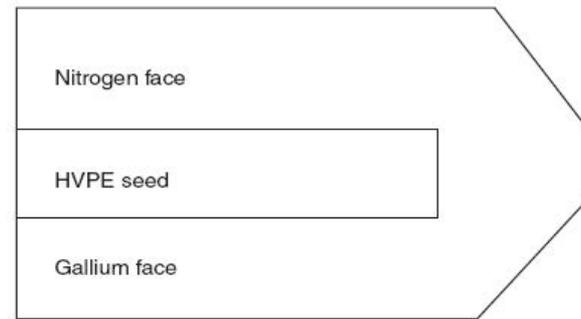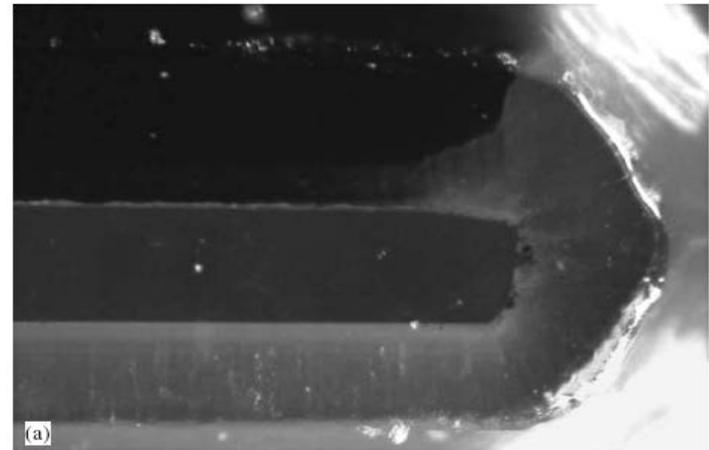
Fig. 3. (a) Optical transmission (Xenon lamp) image of the cross-section of an as-grown ammonothermal GaN crystal and (b) schematic drawing of the crystal in (a) with 200 µm thick HVPE GaN seed.

Growth of gallium nitride via fluid transport in supercritical ammonia

Tadao Hashimoto*, Kenji Fujito, Benjamin A. Haskell, Paul T. Fini, James S. Speck, Shuji Nakamura

Materials Department, University of California, ERATO/JST UCSB Group, Santa Barbara, CA 93106-5050, USA

Available online 8 December 2004
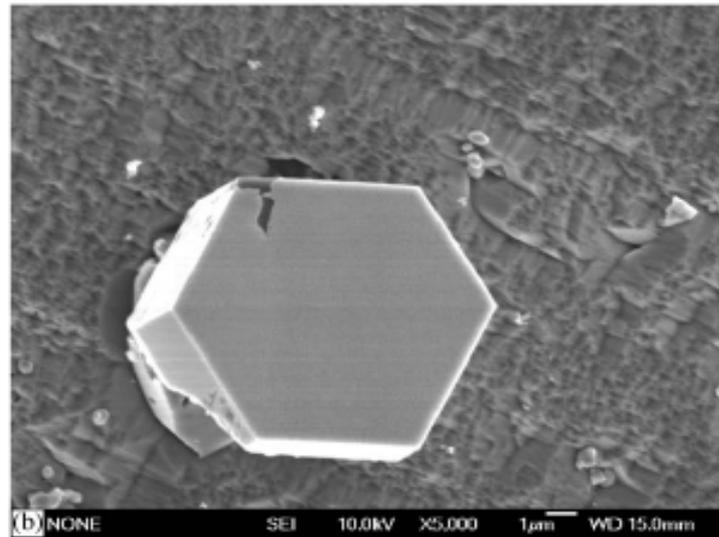
Fig. 4. SEM micrographs of GaN precipitates: (a) typical size, (b) largest size so far. The scale bar represents 1 μm.

(54) **BULK MONOCRYSTALLINE GALLIUM NITRIDE**

(75) Inventors: **Robert Tomasz Dwiliński**, Warszawa (PL); **Roman Marek Doradziński**, Warszawa (PL); **Jerzy Garczyński**, Lomianki (PL); **Leszek Piotr Sierzputowski**, Union, NJ (US); **Yasuo Kanbara**, Anan (JP)

(73) Assignees: **Nichia Corporation**, Anan (JP); **Ammono Sp. z o.o.**, Warsaw (PL)

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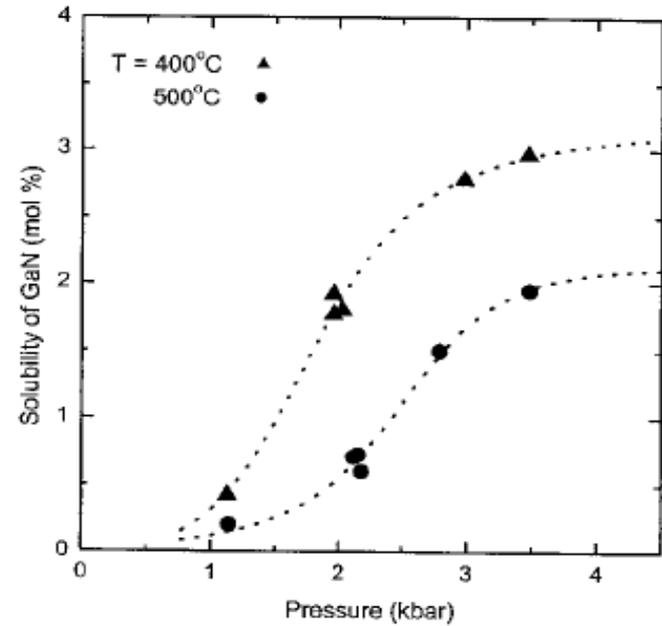
(19) **United States**
(12) **Patent Application Publication**
D'Evelyn et al.

(10) Pub. No.: **US 2005/0098095 A1**
(43) **Pub. Date:** **May 12, 2005**

(54) **GALLIUM NITRIDE CRYSTALS AND WAFERS AND METHOD OF MAKING**

(75) Inventors: **Mark Philip D'Evelyn**, Niskayuna, NY (US); **Dong-Sil Park**, Niskayuna, NY (US); **Steven Francis LeBoeuf**, Schenectady, NY (US); **Larry Burton Rowland**, Scotia, NY (US); **Kristi Jean Narang**, Voorheesville, NY (US); **Huicong Hong**, Niskayuna, NY (US); **Stephen Daley Arthur**, Glenville, NY (US); **Peter Micah Sandvik**, Clifton Park, NY (US)

Correspondence Address:
**GENERAL ELECTRIC COMPANY
GLOBAL RESEARCH
PATENT DOCKET RM. BLDG. K1-4A59
NISKAYUNA, NY 12309 (US)**

(73) Assignee: **General Electric Company**

(21) Appl. No.: **11/010,507**

(22) Filed: **Dec. 13, 2004**

Related U.S. Application Data

(63) Continuation-in-part of application No. 10/329,981, filed on Dec. 27, 2002.

Publication Classification

(51) Int. Cl.[7] **C30B 23/00**; C30B 25/00; C30B 28/12; C30B 28/14
(52) U.S. Cl. **117/105**

(57) **ABSTRACT**

A GaN crystal having up to about 5 mole percent of at least one of aluminum, indium, and combinations thereof. The GaN crystal has at least one grain having a diameter greater than 2 mm, a dislocation density less than about 10^4 cm^{-2}, and is substantially free of tilt boundaries.

Fig. 10
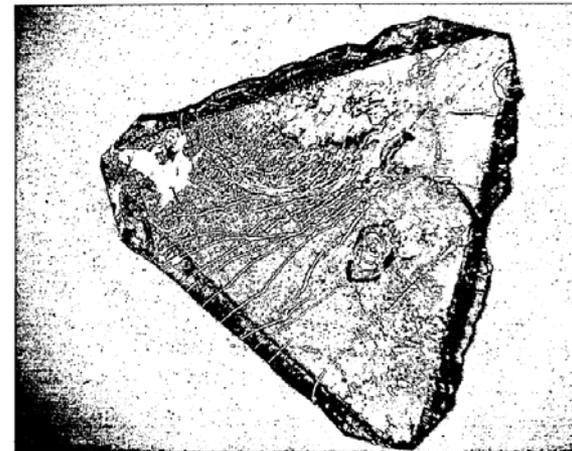
(19) **United States**

(12) **Patent Application Publication**   (10) Pub. No.: **US 2008/0001165 A1**

Hashimoto et al.   (43) **Pub. Date:**   **Jan. 3, 2008**

(54) **OPTO-ELECTRONIC AND ELECTRONIC DEVICES USING N-FACE OR M-PLANE GAN SUBSTRATE PREPARED WITH AMMONOTHERMAL GROWTH**

(76) Inventors: **Tadao Hashimoto**, Santa Barbara, CA (US); **Hitoshi Sato**, Santa Barbara, CA (US); **Shuji Nakamura**, Santa Barbara, CA (US)

Correspondence Address:
GATES & COOPER LLP
HOWARD HUGHES CENTER
6701 CENTER DRIVE WEST, SUITE 1050
LOS ANGELES, CA 90045 (US)

(21) Appl. No.: **11/765,629**

(22) Filed: **Jun. 20, 2007**

Related U.S. Application Data

(60) Provisional application No. 60/815,507, filed on Jun. 21, 2006.

Publication Classification

(51) Int. Cl.
H01L	33/00	(2006.01)
C30B	23/06	(2006.01)
H01L	29/04	(2006.01)

(52) U.S. Cl. **257/103**; 117/109; 257/E33; 257/E33; 257/E29

(57) **ABSTRACT**

A method for growing III-V nitride films having an N-face or M-plane using an ammonothermal growth technique. The method comprises using an autoclave, heating the autoclave, and introducing ammonia into the autoclave to produce smooth N-face or M-plane Gallium Nitride films and bulk GaN.

- mineralizatory zawierajace metale grupy 2, np. Ca, Ba, Mg i/lub niemetale grupy 7: Cl, Br, I.

H. Jacobs and D. Schmidt, *High-pressure ammonolysis* 389

Fig. 3. High-pressure autoclave – closed system. (1) Hexagonal nut; (2) draw plate; (3) allen screw; (4) screwed fitting; (5) sealing rod; (6) sealing ring; (7) sealing ring; (8) thrust collar; (9) autoclave body; (10) high pressure valve; (11) sealing cone; (12) steel diaphragm; (13) nut; (14) sealing ring; (15) screwed fitting; (16) allen screw; (17) pull plate; (18) push plate; (19) countersunk screw; (20) ball joint; (21) allen screw; (22) allen screw and (23) ammonia inlet screw fitting.

Early autoclaves at Faculty of Physics, U. of Warsaw

(grup of prof. M. Kamińska, ~ 1993-2000)

Current Topics in Mat. Sci., vol. 8 (1982)
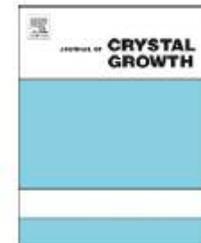
Recent achievements in AMMONO-bulk method

R. Dwiliński [a,*], R. Doradziński [a], J. Garczyński [a], L. Sierzputowski [a], R. Kucharski [a], M. Zając [a], M. Rudziński [b], R. Kudrawiec [c], J. Serafińczuk [d], W. Strupiński [b]

[a] AMMONO sp. z.o.o., Czerwonego Krzyża 2/31, 00-377 Warsaw, Poland
[b] Institute of Electronic Materials Technology, Wólczyńska 133, 01-919 Warsaw, Poland
[c] Institute of Physics, Wroclaw University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
[d] Faculty of Microsystem Electronics and Photonics, Wroclaw University of Technology, Janiszewskiego 11/17, 50-372 Wrocław, Poland

ARTICLE INFO

ABSTRACT

In this paper we present progress made recently in the development of the growth of truly bulk GaN crystals by the ammonothermal method in basic environment. High quality 2-in c-plane GaN seeds are shown. Non-polar wafers can also be cut out from thick GaN crystals grown by ammonothermal method. Perfect crystallinity manifests in very narrow peaks in X-ray rocking curves (the full width at half maximum equals about 15 arcsec). GaN epilayers deposited on these substrates exhibit intrinsic narrow exciton lines, which are very sensitive to the optical selection rules typical for hexagonal symmetry, proving the truly non-polar character of such AMMONO-GaN substrates. Other challenges like homogenous insulating properties or high p-type conductivity have been also accomplished by means of ammonothermal method. Semi-insulating crystals of resistivity up to 10^{11} Ω cm and p-type conductivity within hole concentration up to 10^{18} cm^{-3} are already available in diameters up to 1.5-in.

T. Słupiński, IF PAN
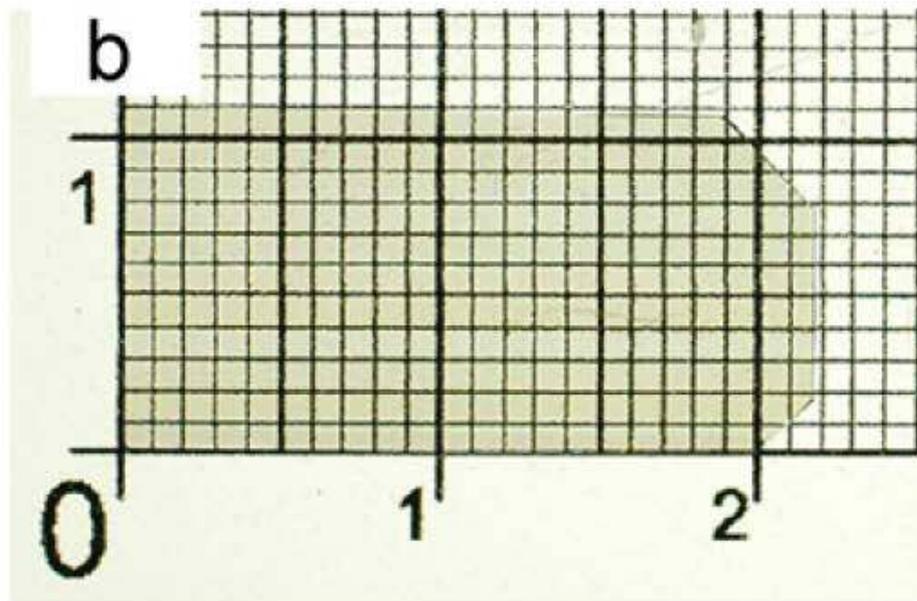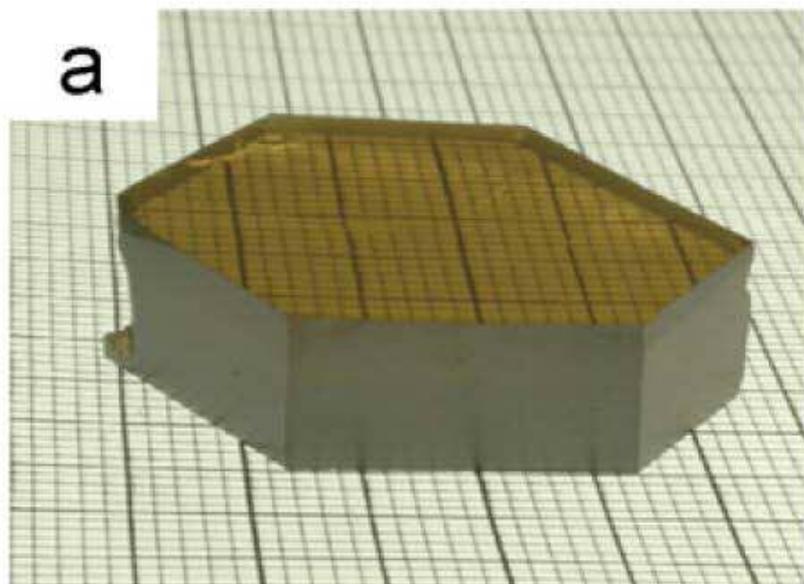
Fig. 2. The thick 1-in AMMONO-GaN crystal (a) and 11 mm × 22 mm non-polar (*m*-plane) substrate cut out of this crystal (b).

SEMICONDUCTORS / MATERIALS

COVER

The World's Best Gallium Nitride

A little Polish company you've never heard of is beating the tech titans in a key technology of the 21st century

By RICHARD STEVENSON / JULY 2010

Photos: Robert Laska

GALLIUM DUST: [Left] Ammono's first gallium nitride crystals were tiny, and metallic impurities gave them a brownish tint.

GALLIUM JEWEL: [Right] After nearly two decades of refinement, Ammono's growth technique now yields wondrously fine hexagonal crystals up to 2 inches across.

Want to revolutionize the electronics industry, become a multimillionaire, and earn your place as an immortal in the tech pantheon? Your job is simple: Figure out a cost-effective way to make really good, reasonably large crystals of pure gallium nitride.

With such crystals as the foundation for the growth of devices made of the same material, manufacturers would have a far richer yield of the violet lasers on which the opto-electronics industry increasingly depends. For example, the short wavelengths of these lasers are needed to read the hyperfine, data-rich

Good ideas may result in an own factory
(but business is sometimes a more difficult play than crystal growth)

Location of Ammono sp. z o.o. in Nieporęt near Warsaw (~2010).

Now, this technology is further developed as part of Institute of High Pressure Physics,
 Polish Academy of Sciences, „Unipress".
Unipress developes both methods from solutions:
 - its own High Temperature High Pressure Ga-solution growth,
 - ammonothermal growth.

If you are interested, you may ask Professor Michał Boćkowski – your next-week lecturer.
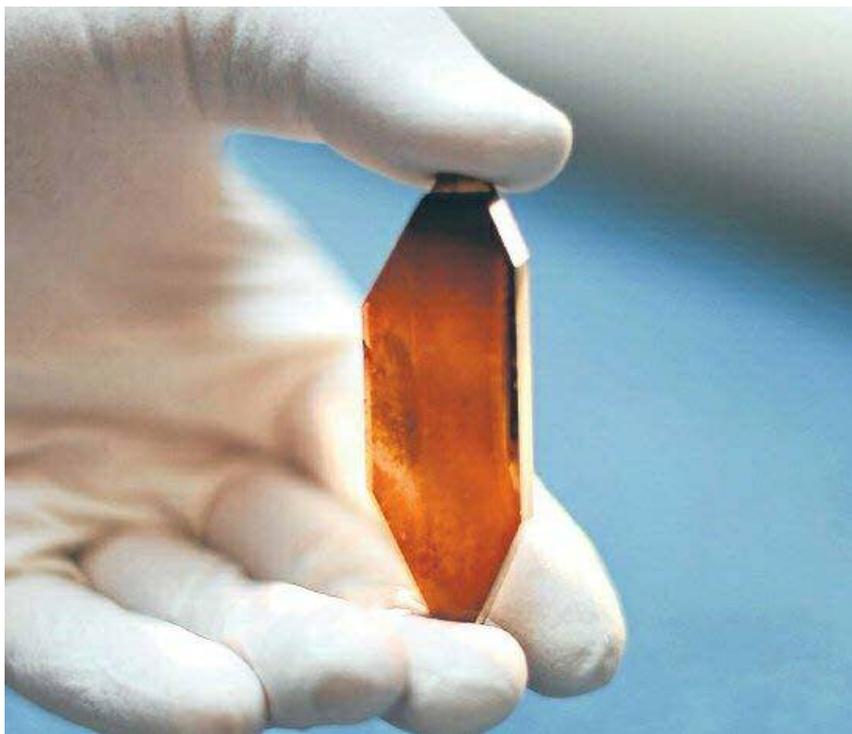
photo from: Gazeta Wyborcza, 2010


Photo: Robert Laska

AMMONO'S AUTOCLAVES: In a single run, they now produce over 70 2-inch crystals of gallium nitride.

Photo from: 07-2010: spectrum.ieee.org

T. Słupiński, IF PAN

Growth of GaN from a solution Ga+Na

heater

pylorytic BN crucible

sintered BN crucible

Ni cup

SUS-vessel

thermocouples

N_2 gas
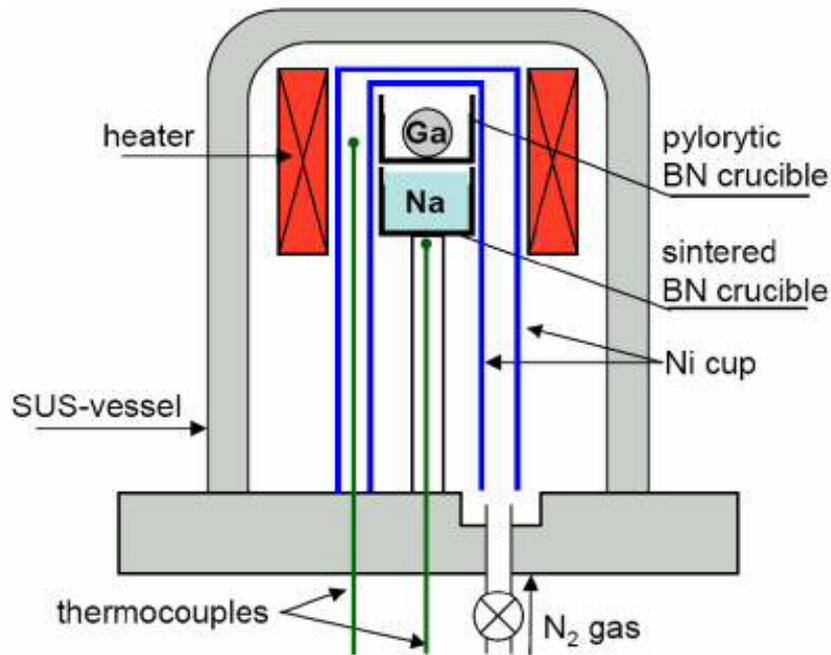
Fig. 1 Schematic drawing of the apparatus used for the crystal growth. A pyrolytic BN (or sintered BN) crucible containing Ga was placed on a sintered BN crucible containing Na. These crucibles were covered with a Ni cap.

(a)   (b)

1mm/div
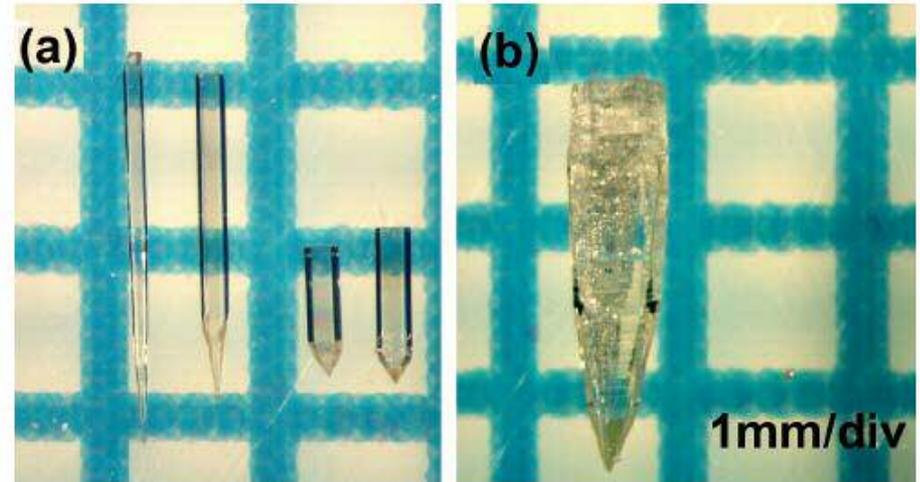
Fig. 2 Optical micrographs of prismatic crystals (a) and a hopper crystal (b) prepared by heating a Ga melt in Na vapor at 800°C and the N_2 pressure of 7.0 MPa.

T. Yamada, H. Yamane i in.,
Tohoku University, Sendai, Japonia
2005-6: J. Cryst. Growth, vol. 281, p. 242
vol. 286, p. 494

T. Słupiński, IF PAN

Comparison of some rules of crystal growth from the melt and from the solution

Growth from melt:

- available only for materials which melts congruently (= the same composition of liquid and solid phase at equilibrium), and nder the conditions that termodynamical parameters are technically accessible.
- high growth rates,
- supercooling is the factor which controls the growth,
- precise control of temperature field in growth zone is required,
- good control of impurities is possible   (impurities < ~0.1 %at.), but may require a proper care.

Growth from solution:

- for many various materials providing the chemically proper solvent can be found,
- dissolution reaction must be reversible and possible to control (p, T)
- small growth rates, but simple control of growth
- supersaturation is the factor which controls the growth
- a precise controll of components transport conditions from dissolution zone to growth zone is required.

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  – kilka tomów z artykułami przeglądowymi nt. wielu metod wzrostu (~1995)

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              np. JCG vol. 264 (2004) - seria interesujacych przegladowych artykulów
                            nt. różnych ważnych technik z punktu widzenia
                            zastosowań,
              a także publikacje z różnych konferencji dot. wzrostu kryształów,

        "Progress in Crystal Growth and Characterization" - often review articles,
         "Crystal Growth and Design"

… and many, many others,

and your own EXPERIENCE !!!