

# Crystal Growth: Physics, Technology and Modeling

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## Lecture 1. Growth of semiconductor bulk crystals – an introduction to next lectures

<http://www.unipress.waw.pl/~stach/cg-2022-23>

# **Growth of semiconductor bulk crystals- an introduction to next lectures**

*Mike Leszczynski*

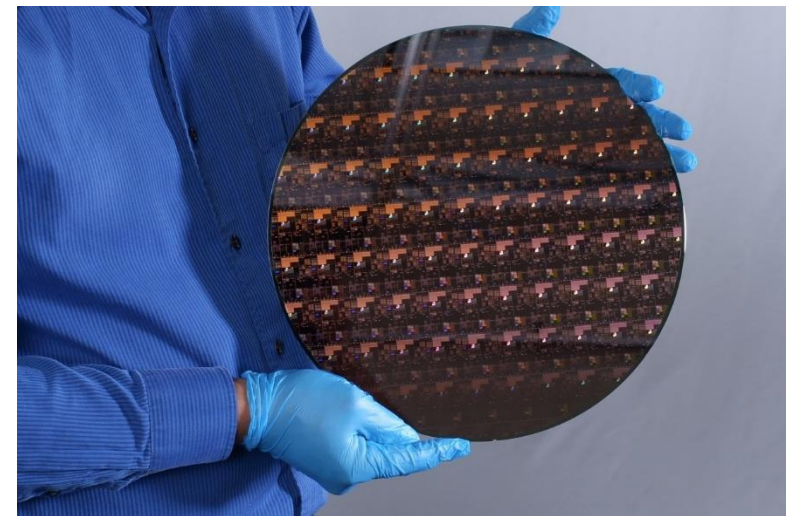
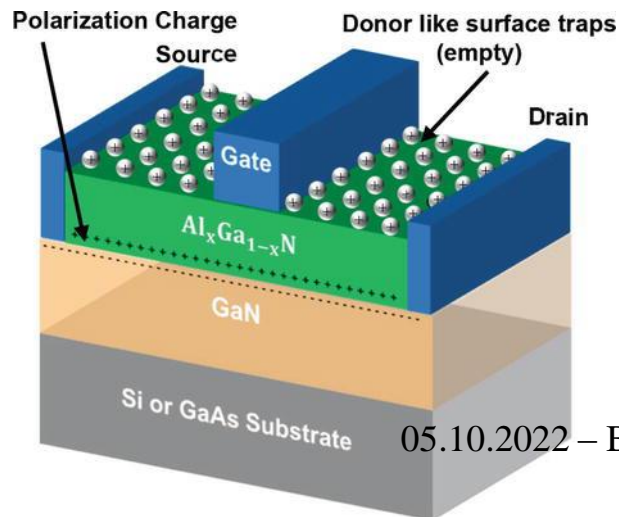
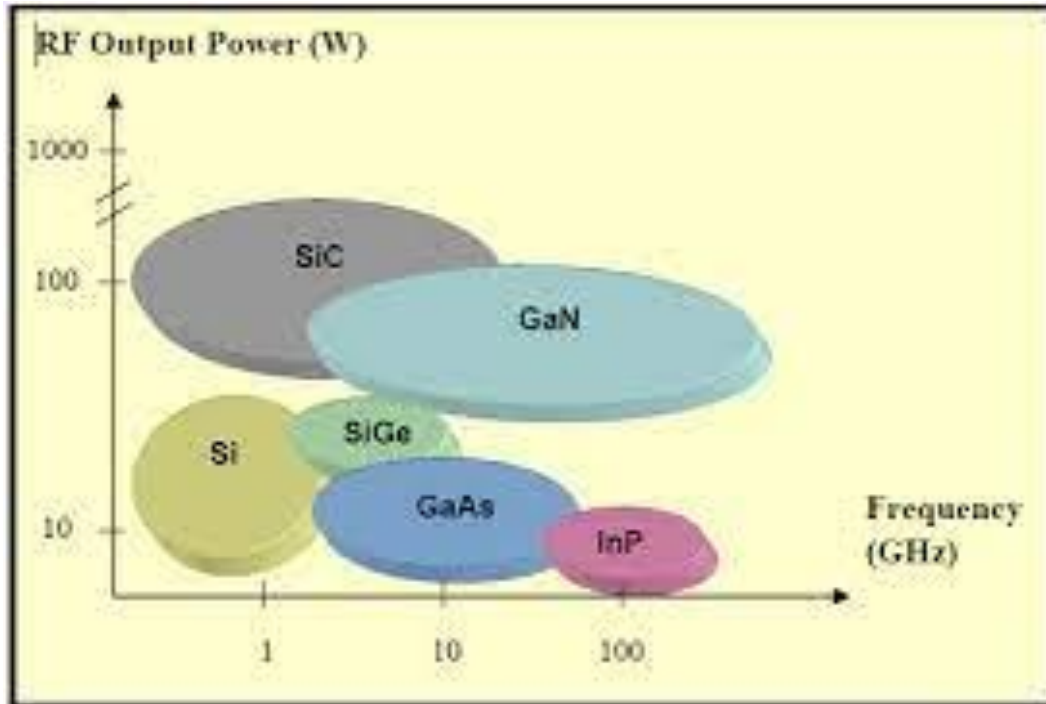
## ***Outline***

- 1. Main semiconductor devices and their applications***
- 2. Why crystal structure is important?***
- 3. Growth of crystals from the melt***
- 4. Growth from the gas phase***
- 5. Growth from the solution***
- 6. Characterization of bulk crystals***

# Outline

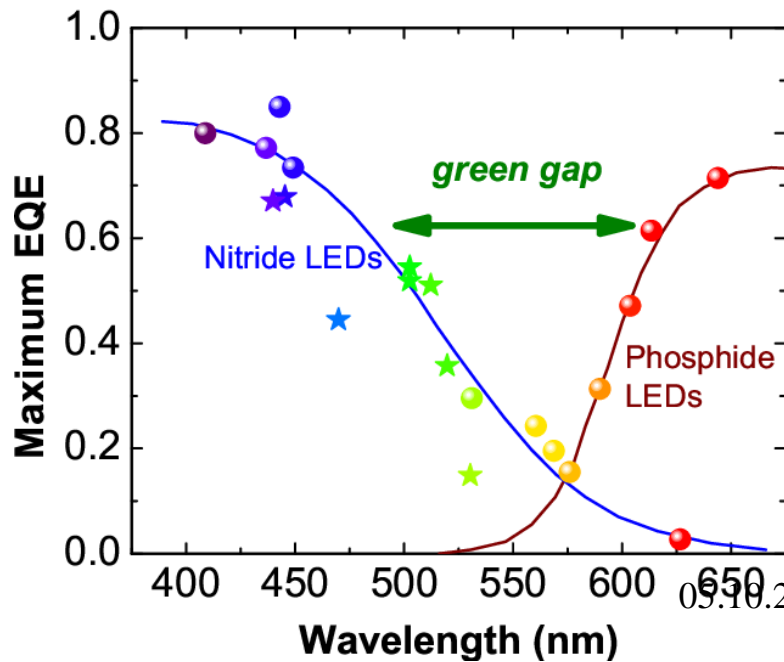
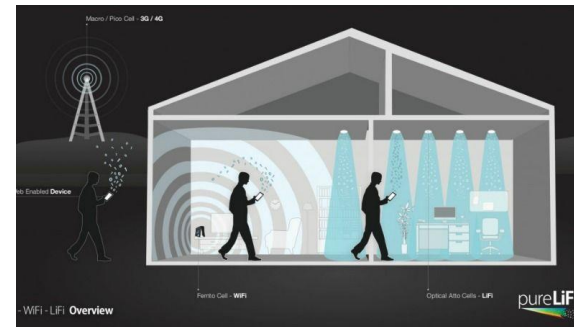
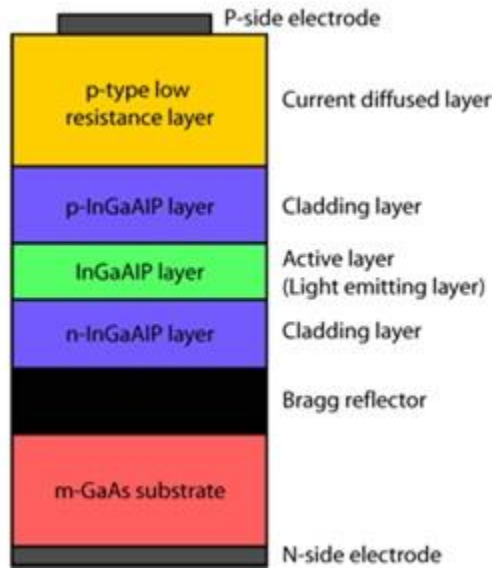
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# Transistors



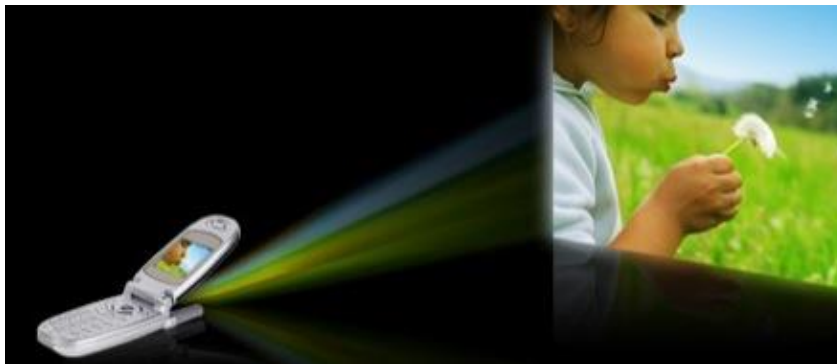
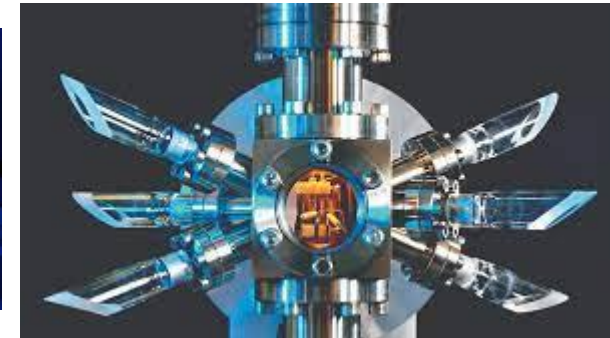
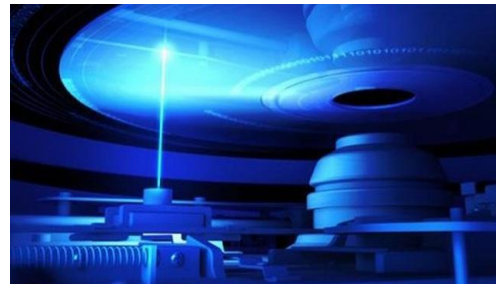
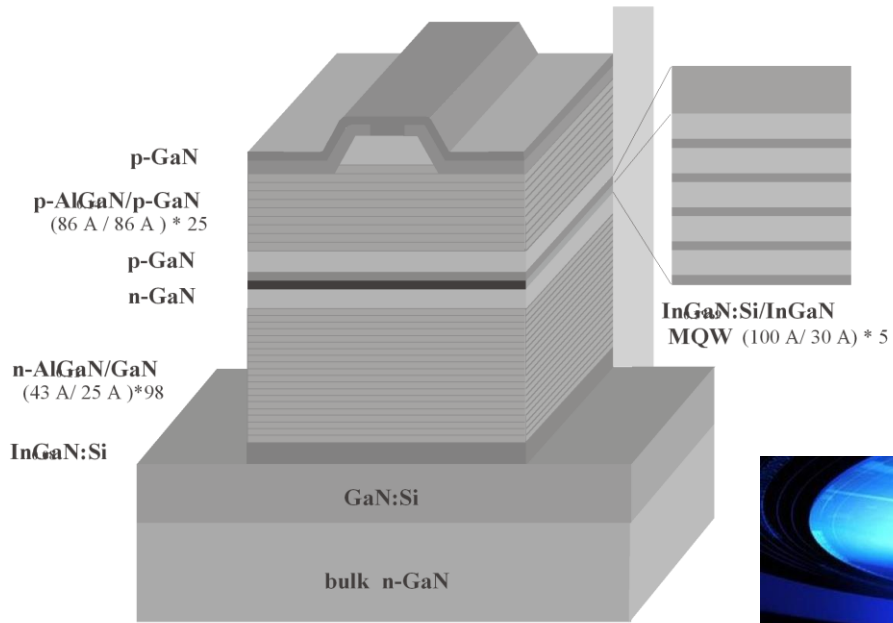
# LEDs

Device Construction

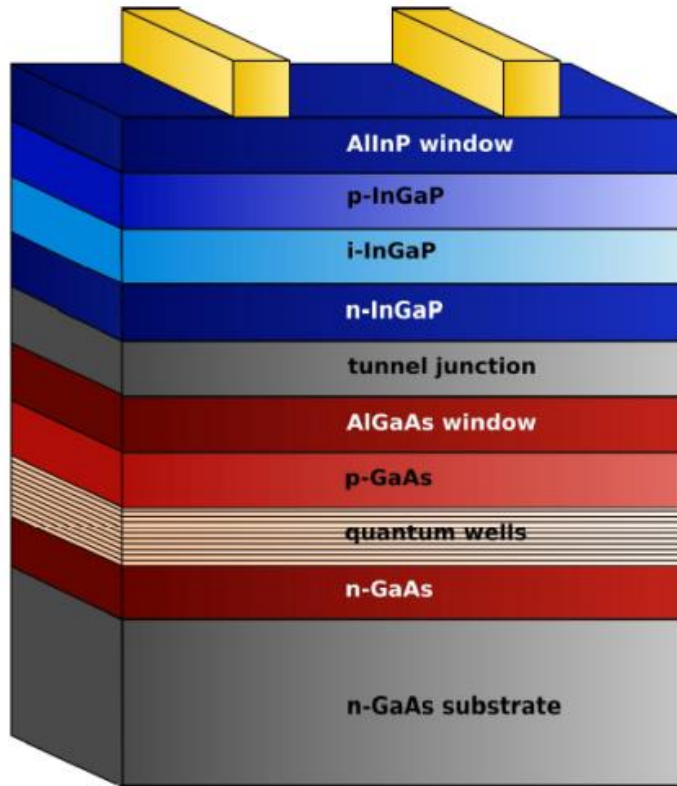




# Laser Diodes (LDs)



# Photovoltaics and sensors



# **SUBSTRATES (Bulk crystals)**

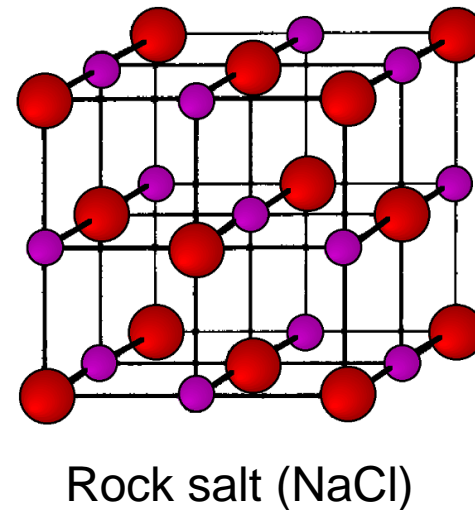
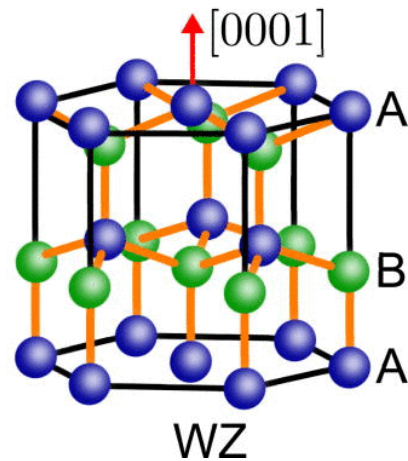
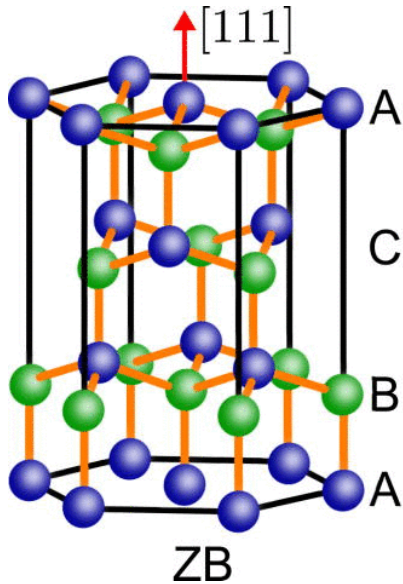
- 1. Dislocation density small**
- 2. Point defects density small**
- 3. Size large**
  
- 4. Off-cut**
- 5. Surface epi-ready**



# Outline

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# Crystallographic structures

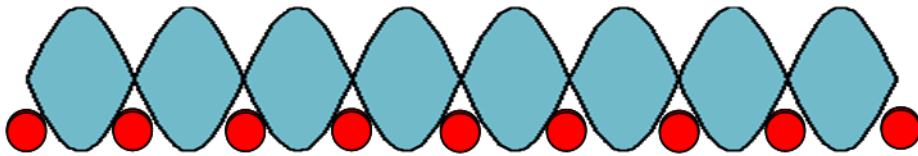


In semiconductors, at 0 K, all electrons take part in the chemical bonds. IV-IV, III-V, II-VI.

At higher temperatures, some electrons may move (in the conduction band).

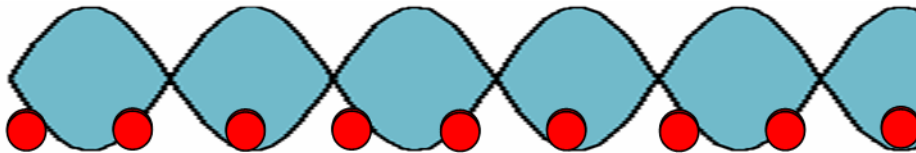
However, there are always some dopants (impurities) and defects, which give electrons to the conduction band.

This electron wave interactions with the lattice less strongly ...



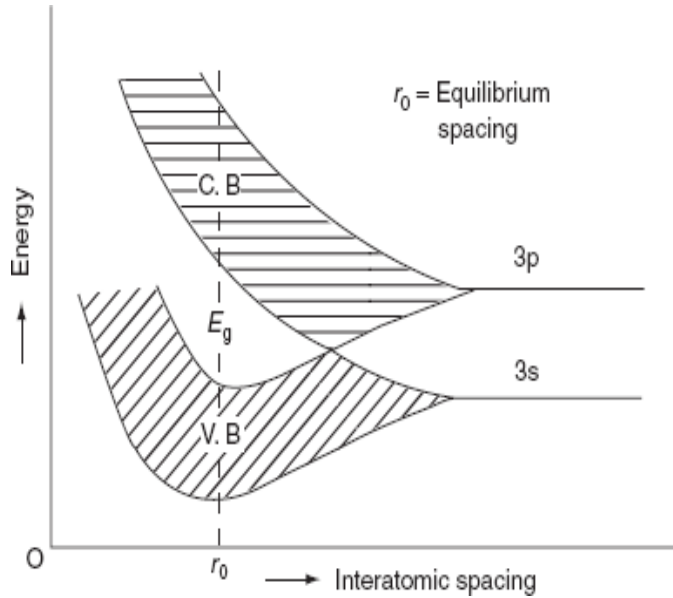
High electron mobility important for transistors.

... than this one does.

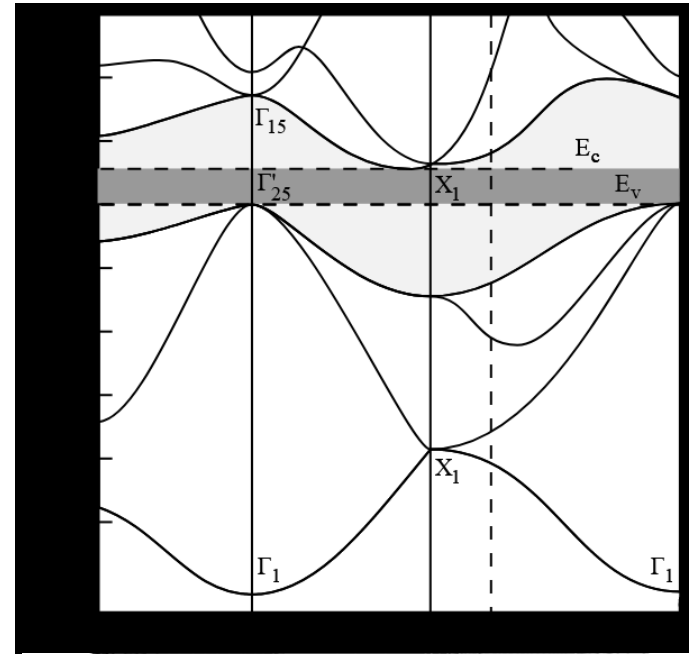


Lack of scattering important for every device- no heat is given off during electron flow

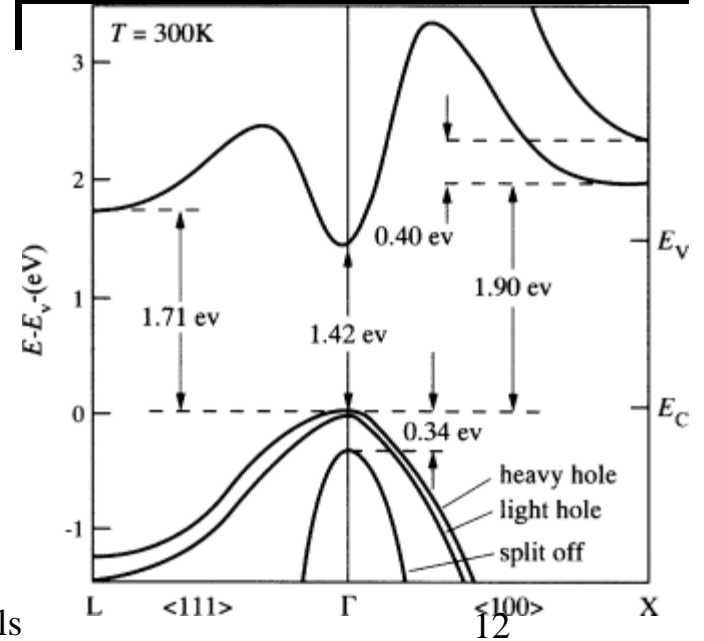
# Energy gaps



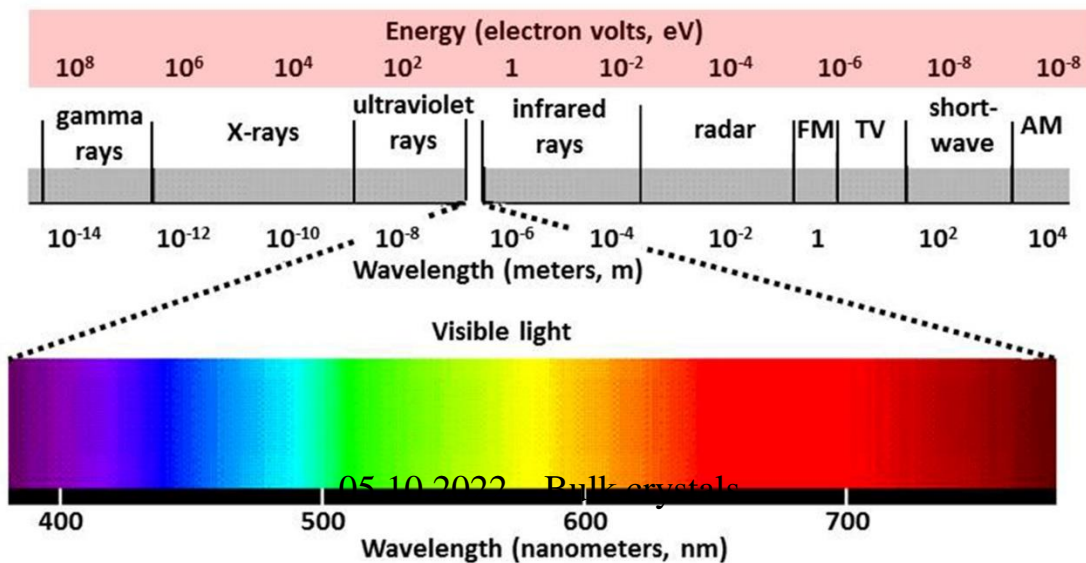
Si indirect band gap



GaAs direct band gap



Semiconductor	Band gap (eV)	Direct/indirect
Si	1.1 (IR)	Indirect
Ge	0.7 (IR)	Indirect
GaAs	1.4 (IR)	Direct
InP	1.3 (IR)	Direct
GaP	2.4 (Y)	Indirect
GaN	3.4 (UVA)	Direct
InN	0.6 (IR)	Direct
AlN	6.2 (UVC)	Direct
SiC	3.2 (B)	Indirect

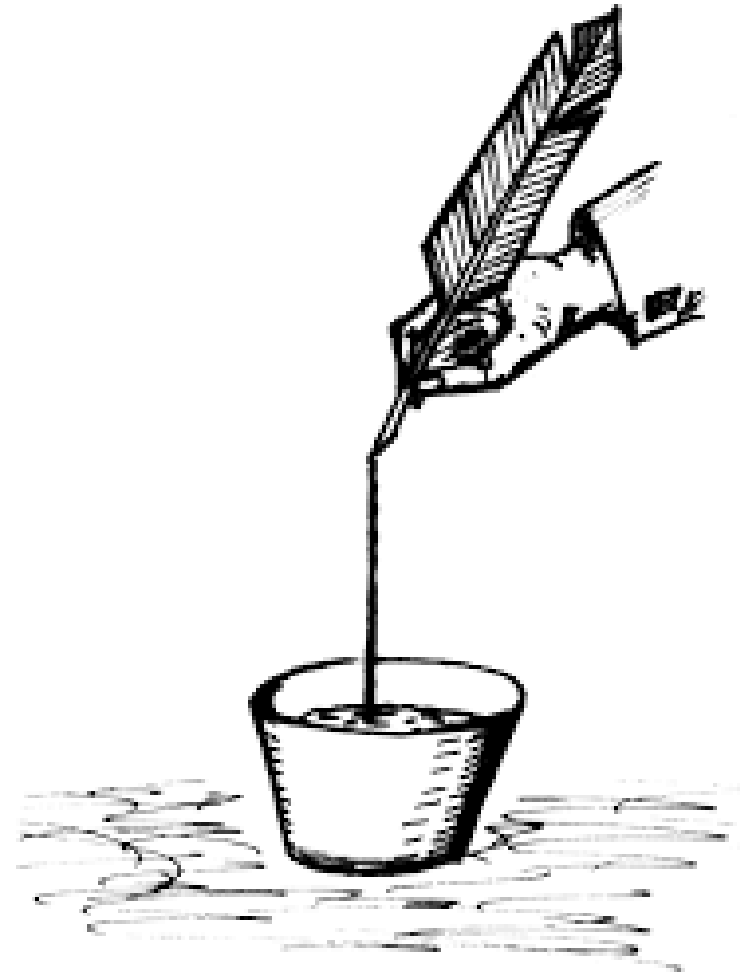


# ***Outline***

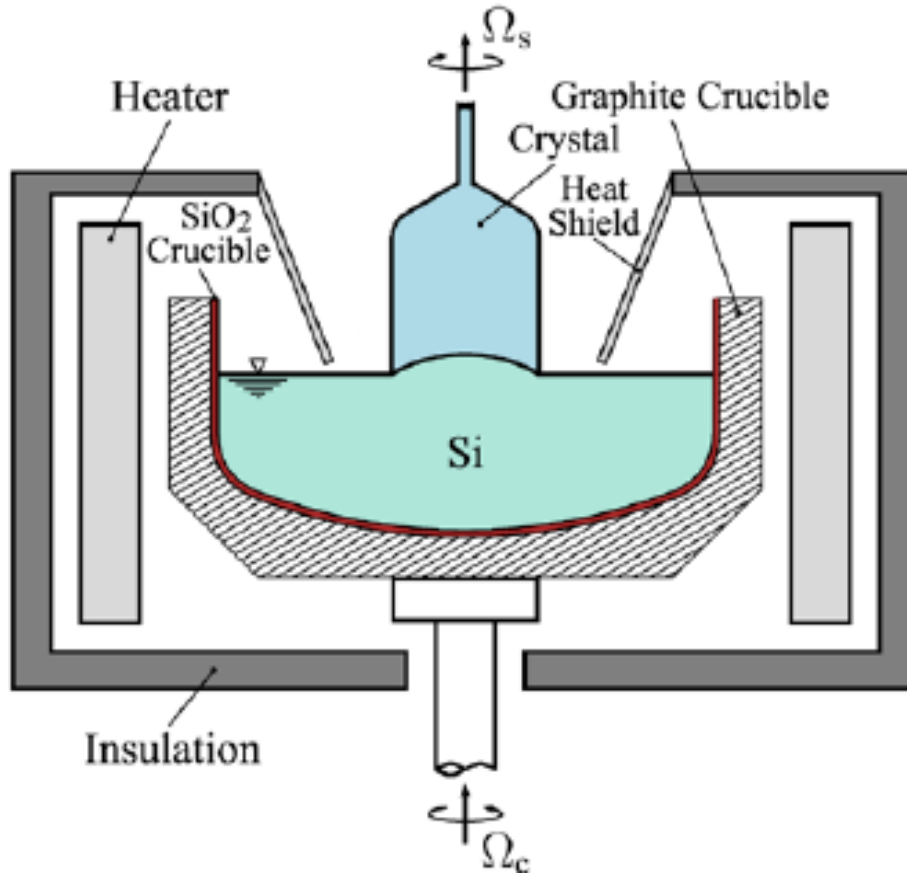
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# Jan Czochralski



# Czochralski method



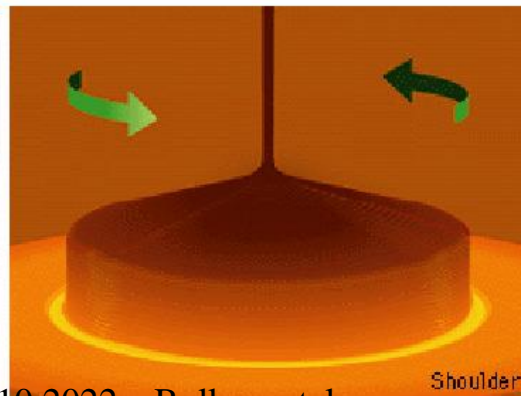
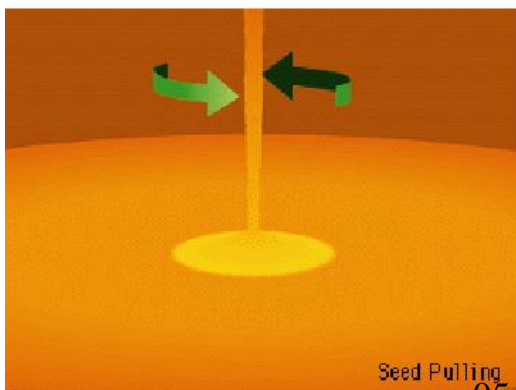
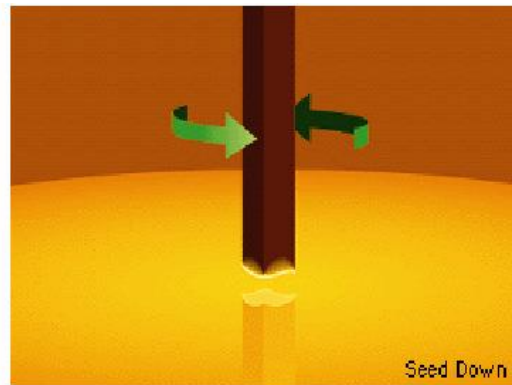
Compound	Melting point (oC)	Pressure (atm)
Si	1400	<1
Ge	938	1
GaAs	1250	1.5
InP	1062	27
GaN	>2220	>60000
InN	>1100	>100000
AlN	>2800	>1000
SiC	>2700	>20000

# SILICON

$\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO}$  (1500-2000°C) 98% purity (MG Si)

$\text{Si} + 3\text{HCl} \rightarrow \text{SiHCl}_3 + \text{H}_2$  ( $\text{BCl}_3$ ,  $\text{FeCl}_3$ , etc removed by distillation)

$\text{SiHCl}_3 + \text{H}_2 \rightarrow \text{Si} + 3\text{HCl}$  Si polycrystalline 11N



# SILICON

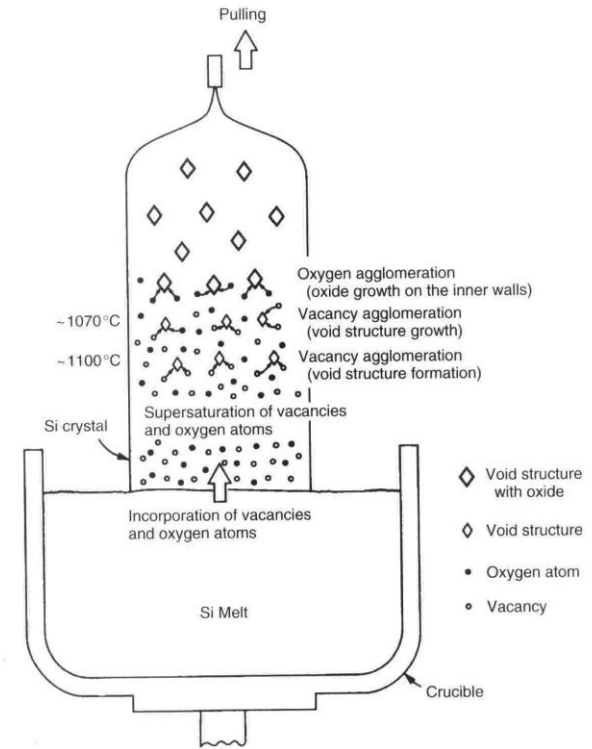
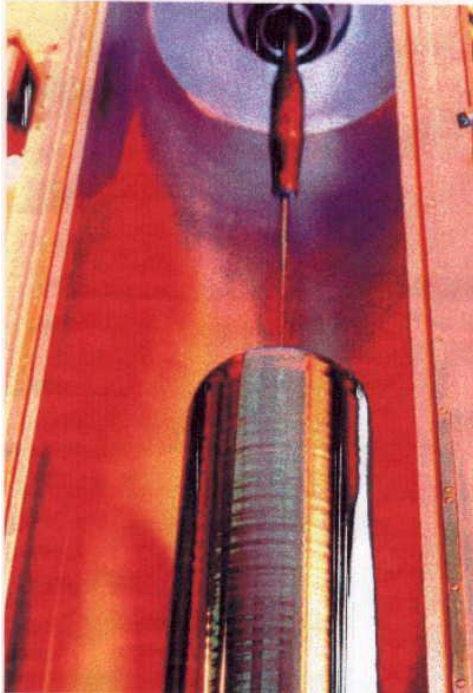
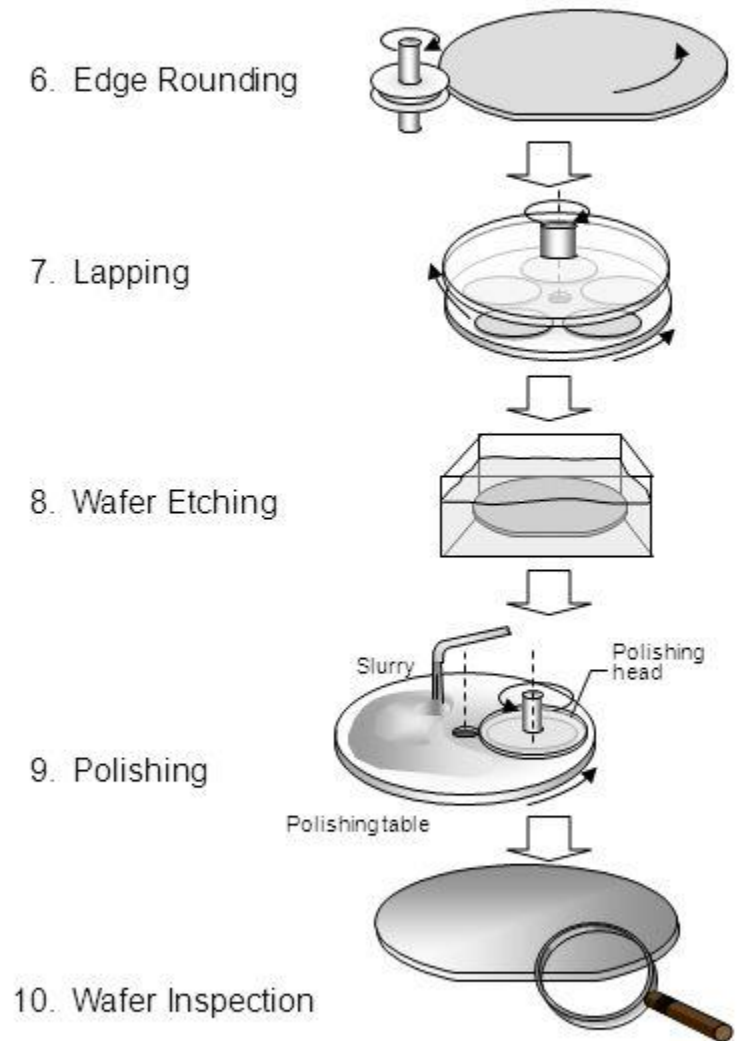
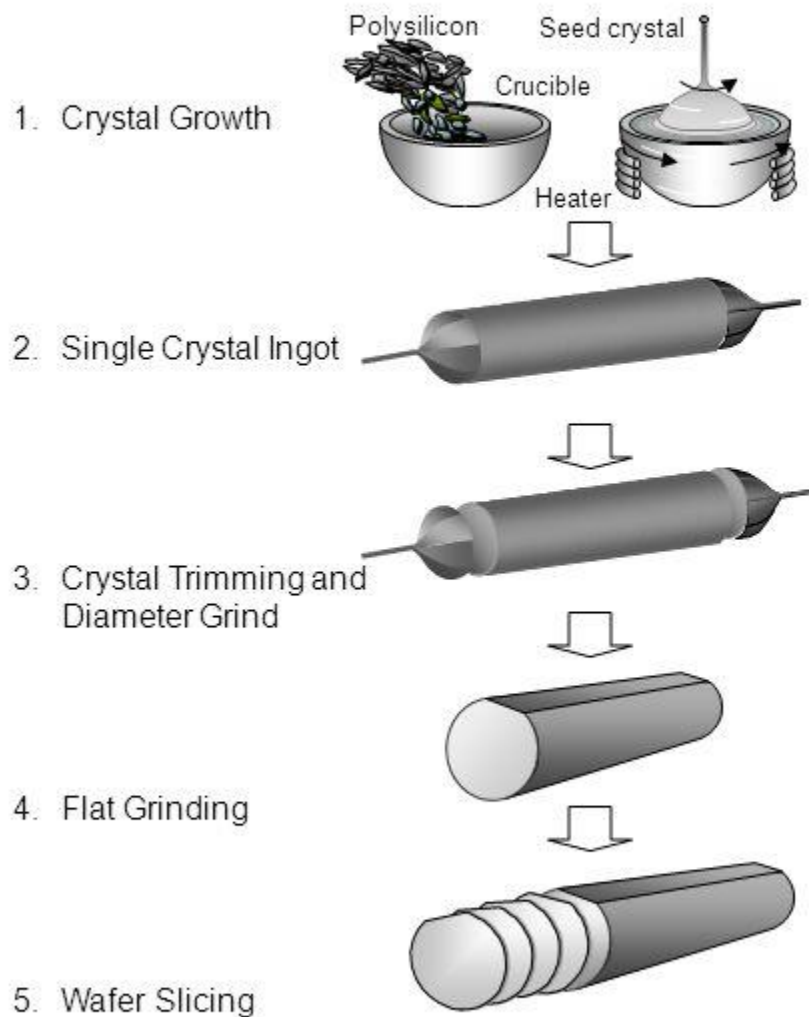


Figure 1.38 Formation of void defects as a result of interaction of vacancies and oxygen (Reprinted from Itsumi in *Crystal Growth Technology*, eds. H. Scheel and T. Fukuda (2003), copyright (2003) with permission from Wiley)

Growth rate 50 mm/h, no dislocations, oxygen precipitates, impurities

# CRYSTAL GROWTH



Diameter (mm)	Thickness (mm)	Area (cm <sup>2</sup> )	Price (Eur/cm <sup>2</sup> )
150	6.75	176	1.2
200	7.25	314	1.0
300	7.75	706	0.8
400	8.25	1256	0.6

## Polished Surface

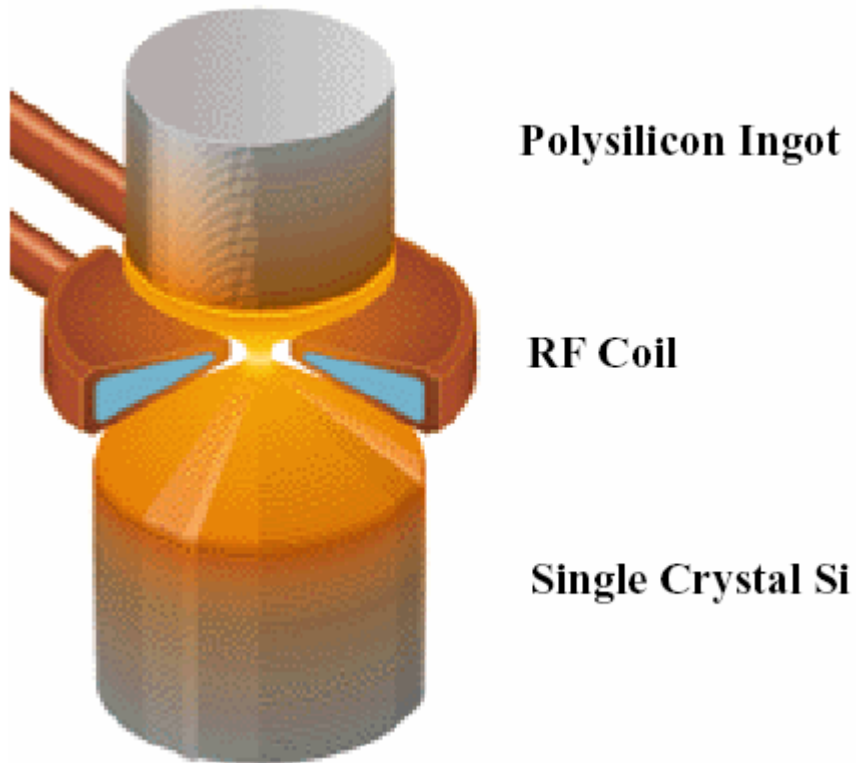


Backside Implant: Ar (50 keV,  $10^{15}/\text{cm}^2$ )

**Argon amorphize back side of the Si wafer. Then annealing at 550°C, makes recrystallization, formation of microbubbles of argon which attract the impurities (mainly metals). At the same time, SiO<sub>x</sub> precipitates are formed lowering the amount of oxygen close to the surface.**

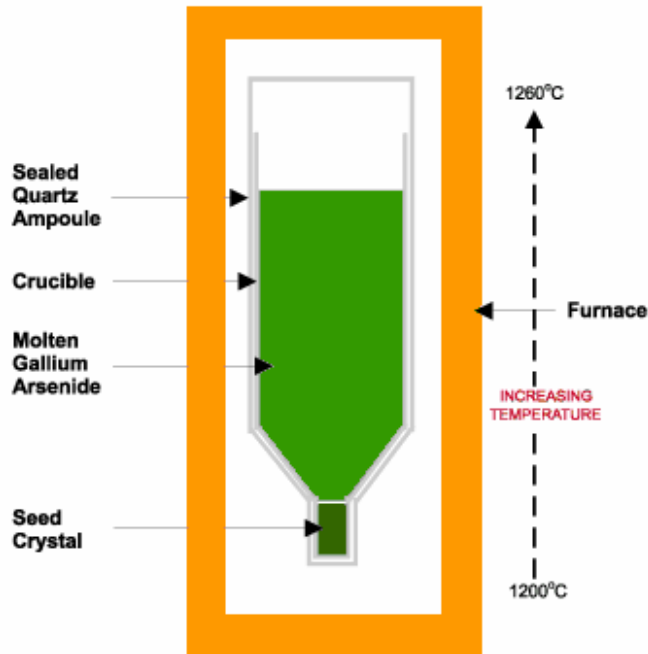


# Floating zone: crystallization and cleaning

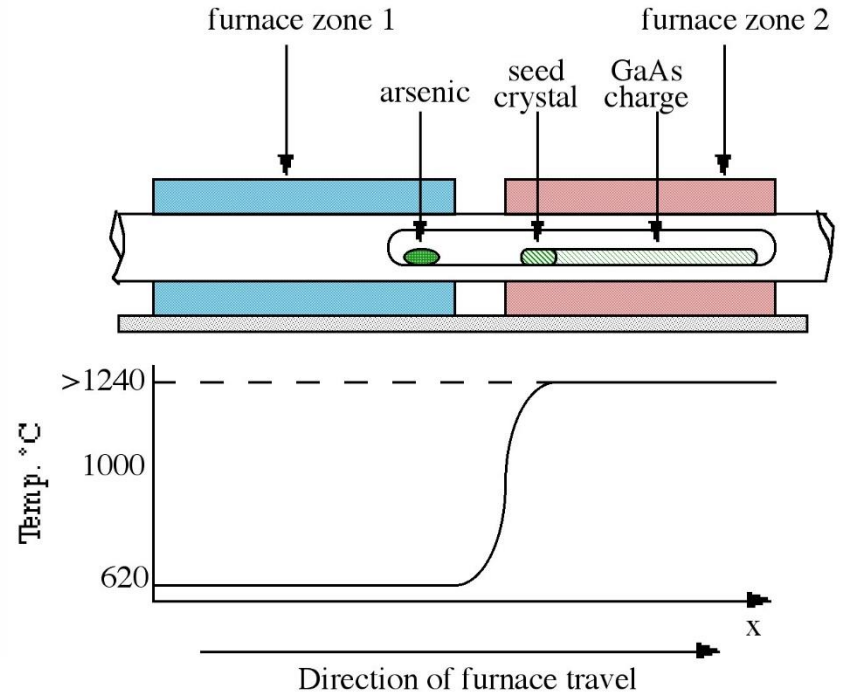


# Other methods of crystal growth from melt

## Gallium Arsenide Crystal Growth by Vertical Gradient Freeze



## Bridgeman method

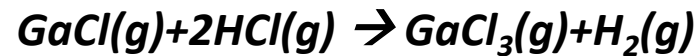
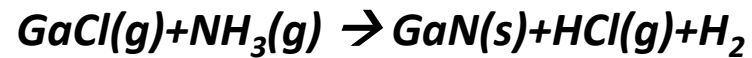
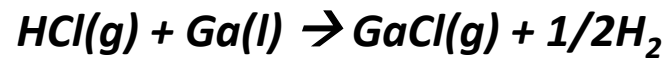
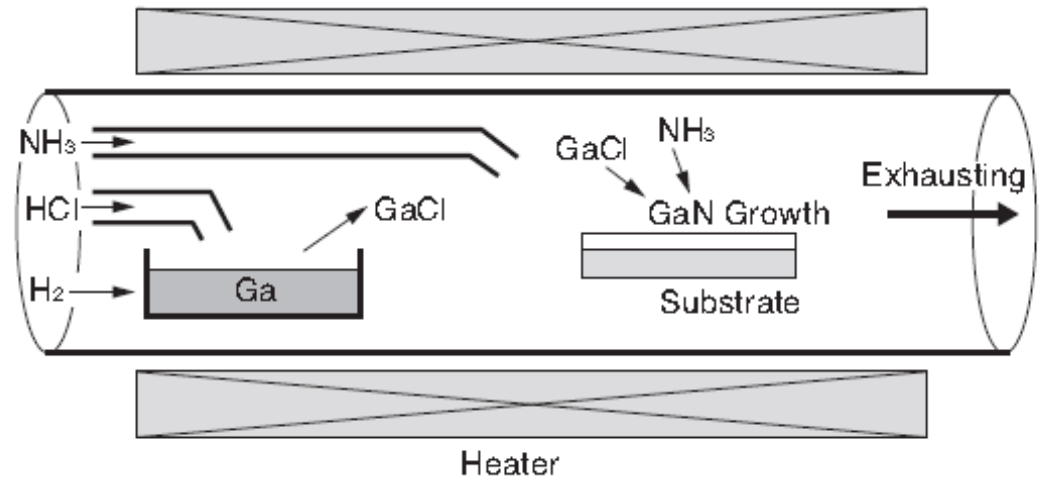
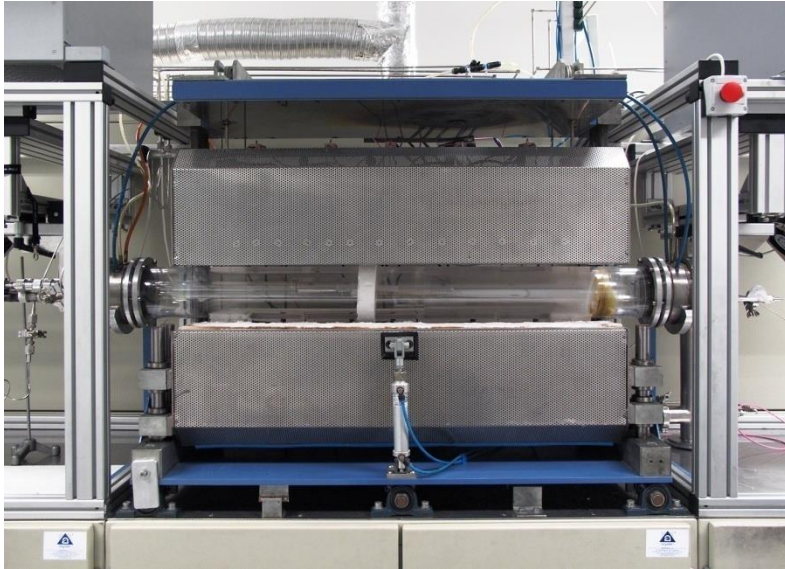


# Outline

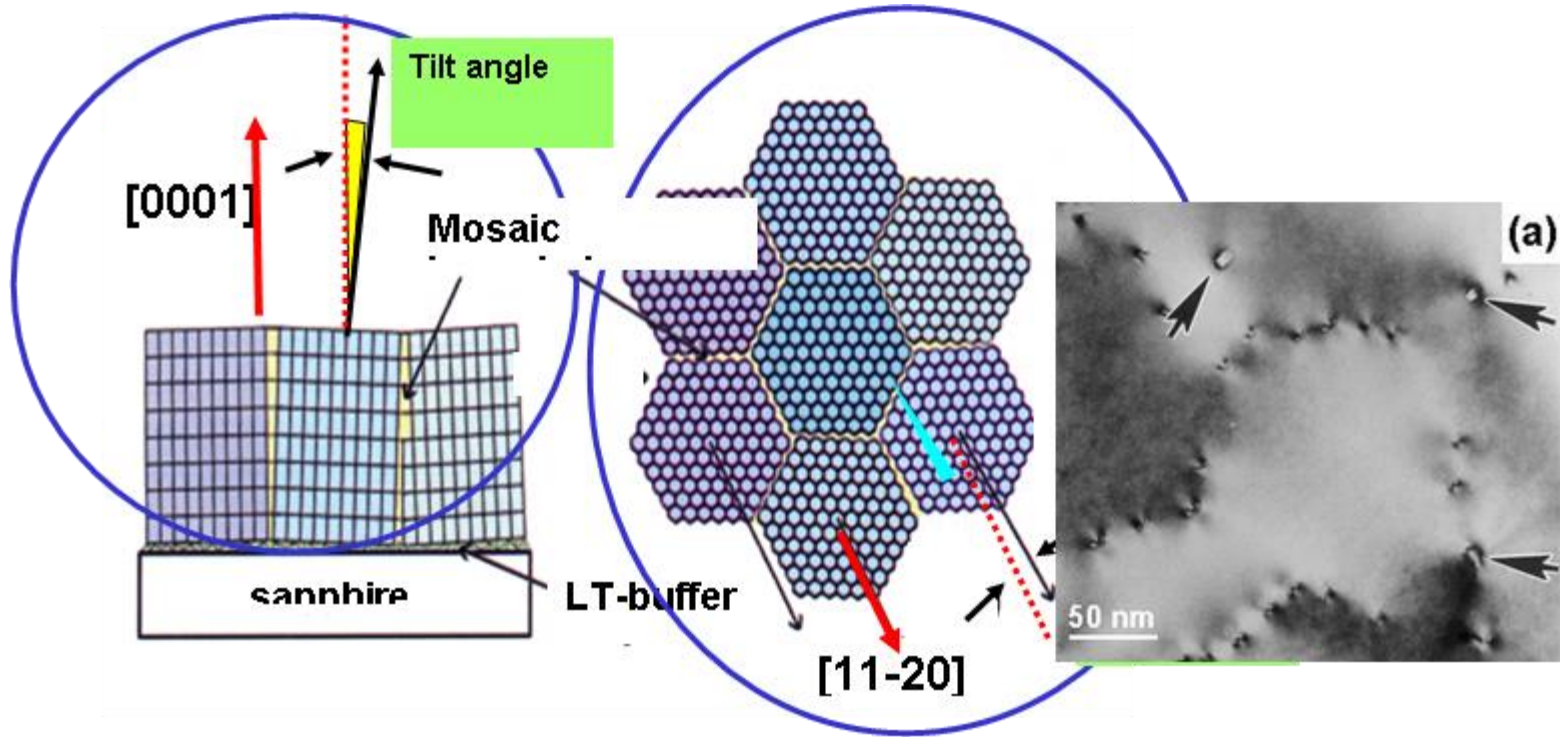
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# ***HVPE growth method***

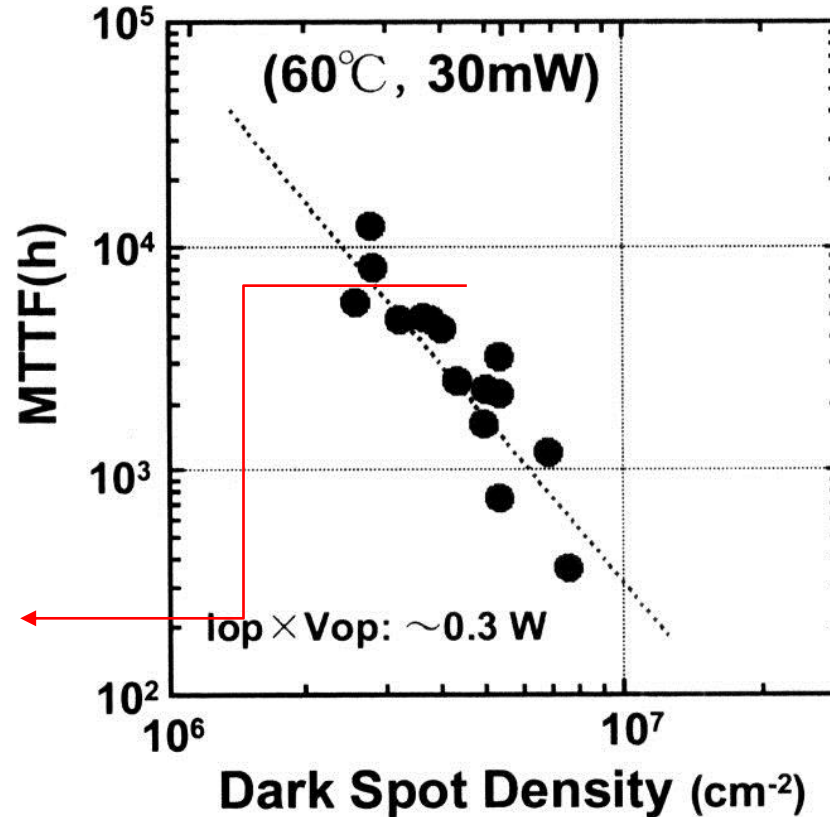
## ***Basic***



# Growth of GaN on sapphire



# Life time of laser diodes vs dislocation density



S. Uchida et al. Sony Shiroishi Semicond. Inc

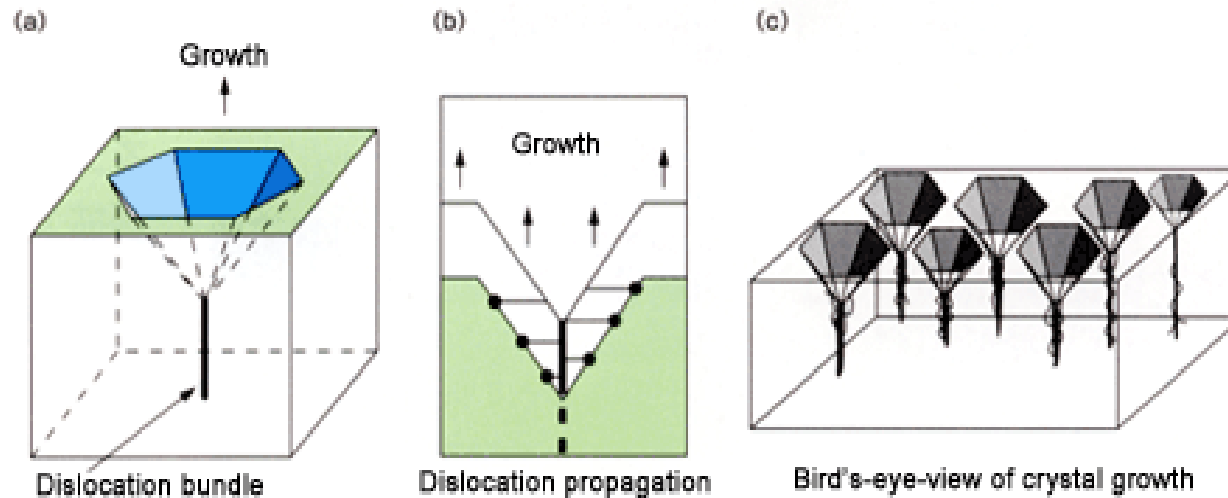
*IEEE J. of Selected Topics in Quantum Electronics* 9, no 5,  
(2003)1252.

05.10.2022 – Bulk crystals

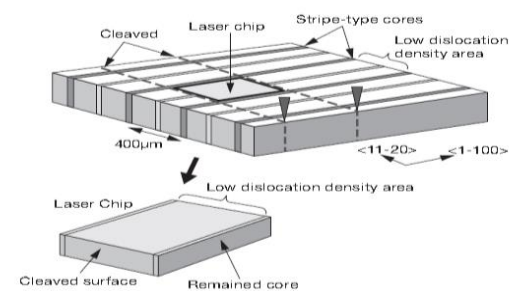
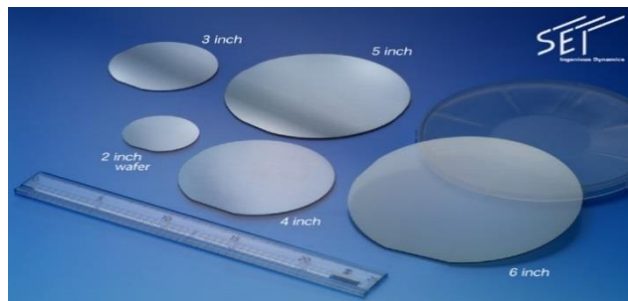


# SUMITOMO- leader of GaN bulk crystal growth

## 'DEEP' Dislocation Elimination Technique



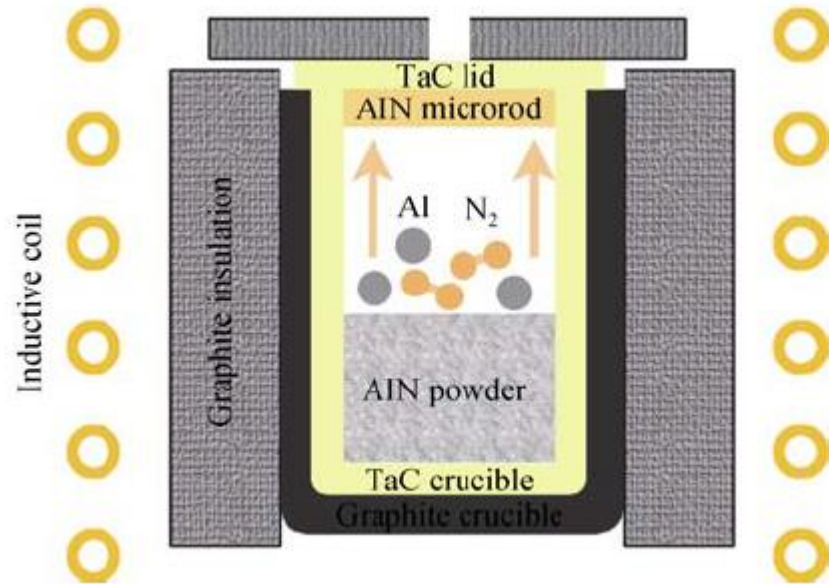
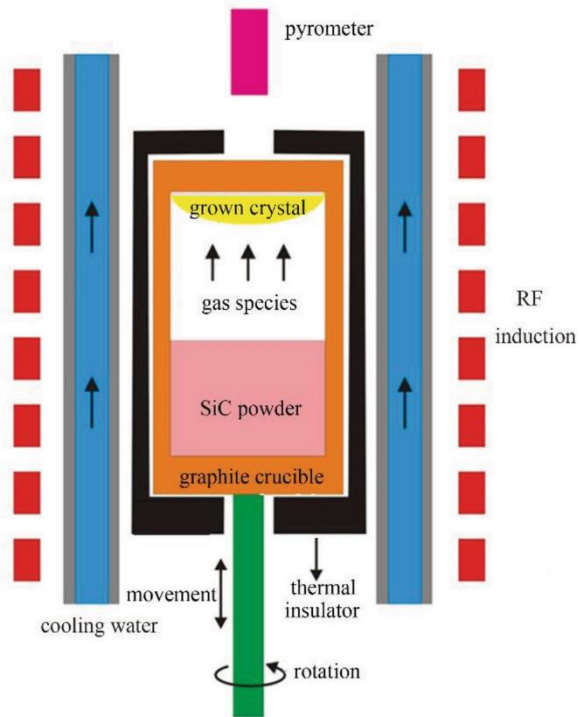
As the facets of huge pit grow, dislocations are concentrated to the bottom of the pit.



[http://global-sei.com/news/press/10/10\\_25.html](http://global-sei.com/news/press/10/10_25.html)

05.10.2022 – Bulk crystals

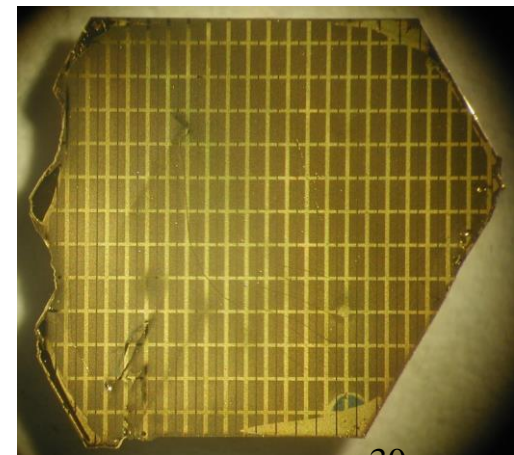
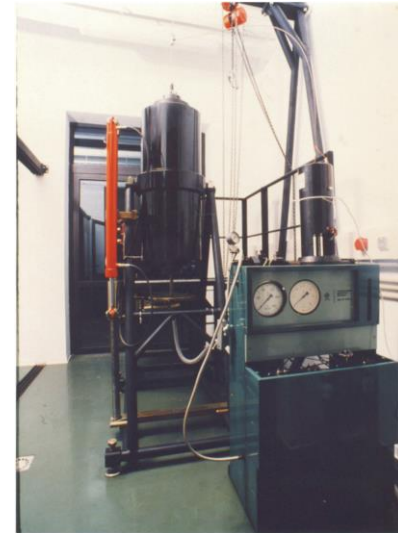
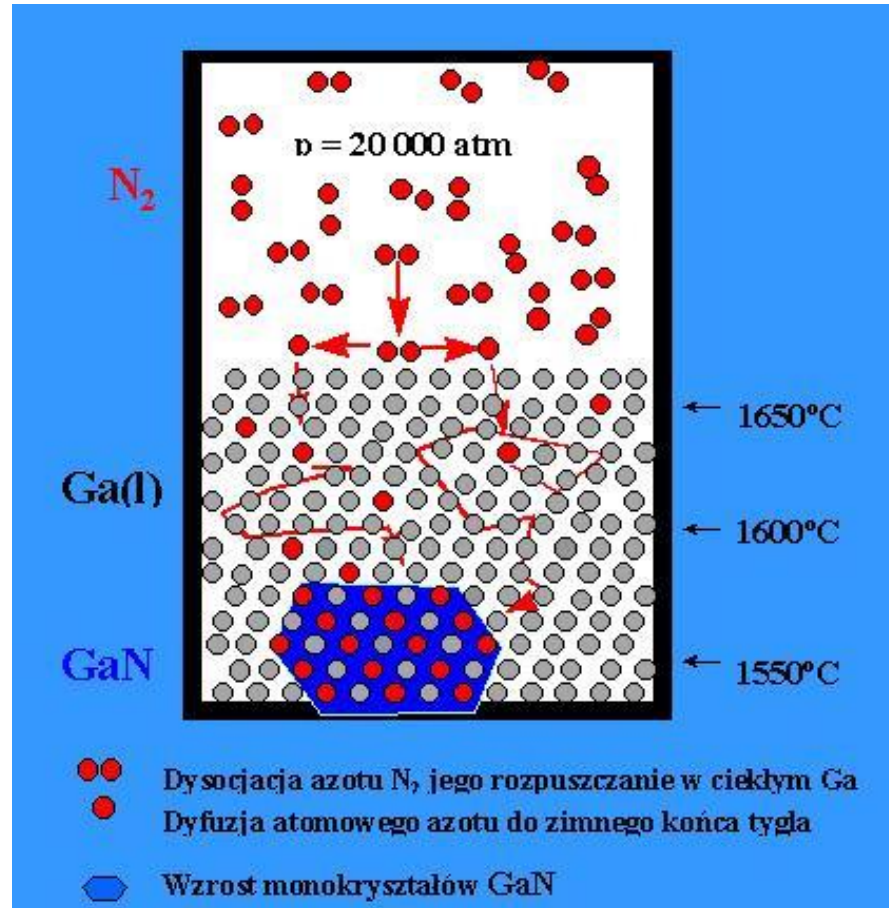
# Sublimation



## Outline

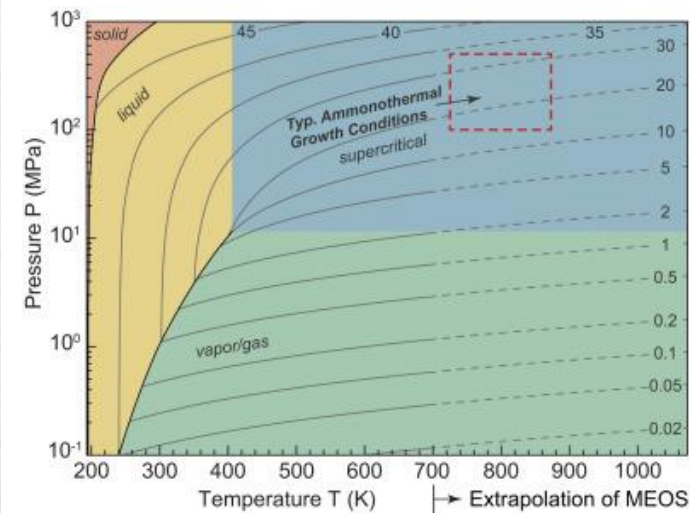
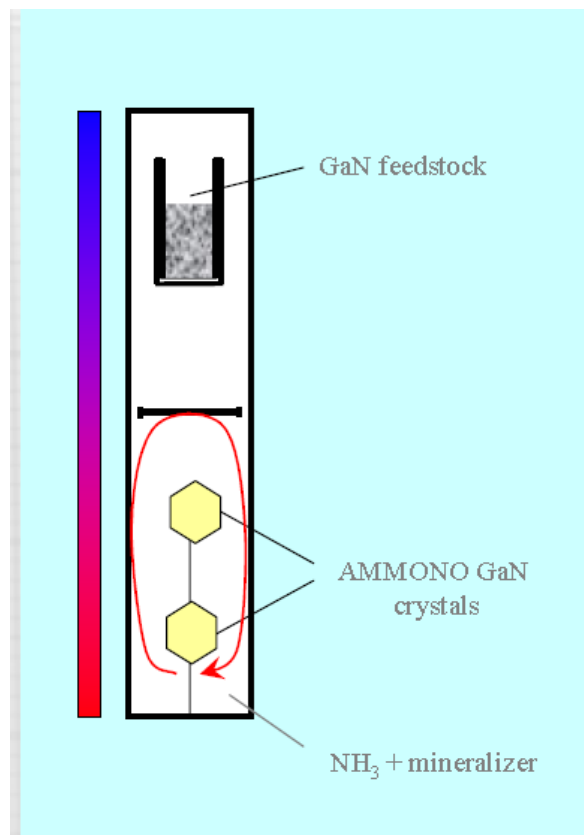
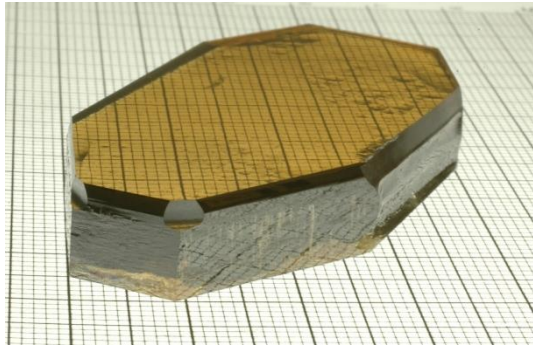
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# Growth of GaN crystals from nitrogen solution in gallium



# Ammono-GaN technology

- analogous to hydrothermal crystallization of quartz or oxide crystals such as ZnO
- ammonia is used instead of water; ammonia is in supercritical state (enhanced reactivity)
- applied pressure and temperatures: 0.1-0.4 GPa i 673–873 K



# Summary

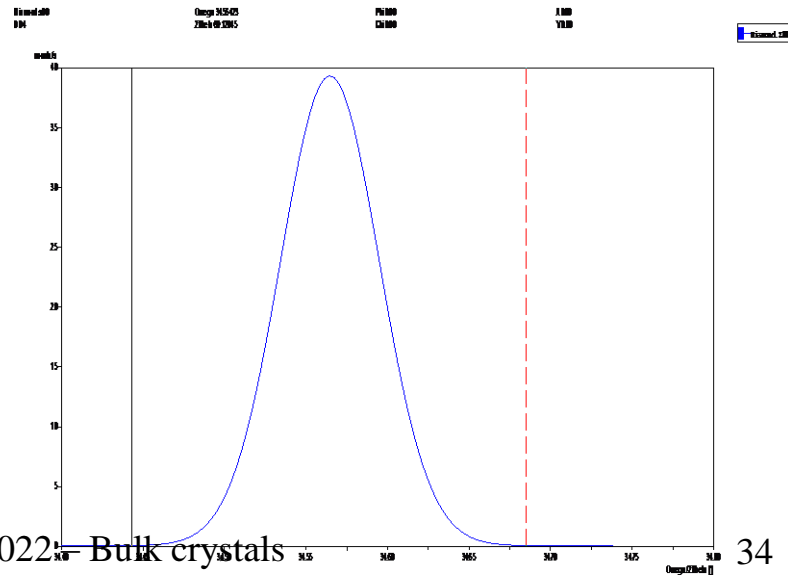
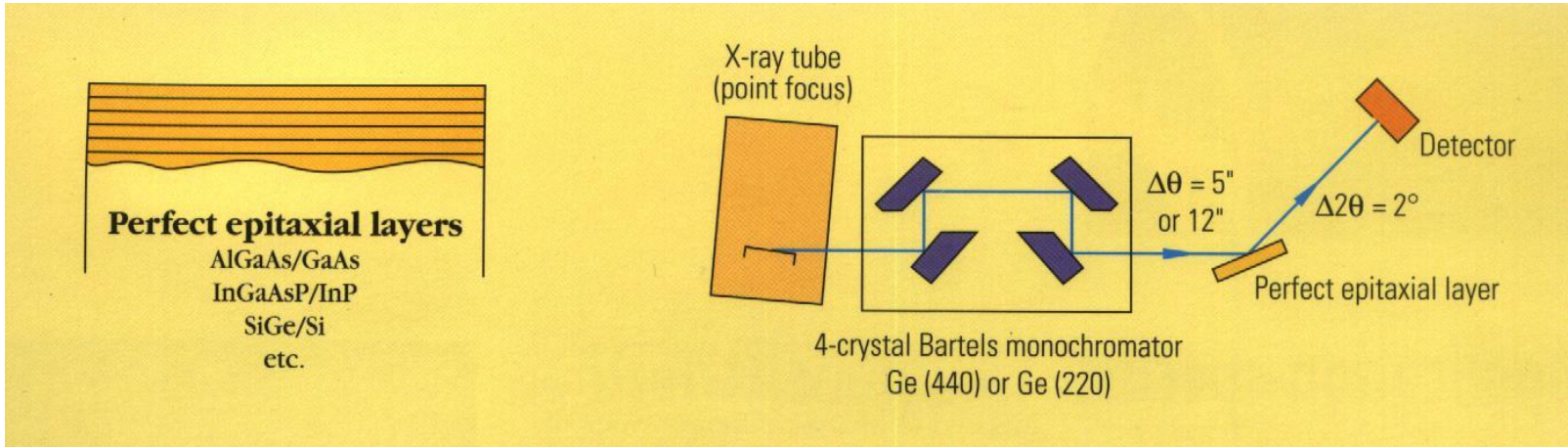
Compound	Max diameter (cm)	Dislocation density	Approx. price (Eur/cm <sup>2</sup> )
Si (Cz)	40	0	1
Ge (Cz)	15	0	20
GaAs (Cz)	20	100	20
InP (Cz)	10	100	40
GaN (HVPE)	15	1000000	50
GaN (Ammono)	5	1000	200
AlN (subl)	5	1000	300
SiC (subl)	15	100	50



# Outline

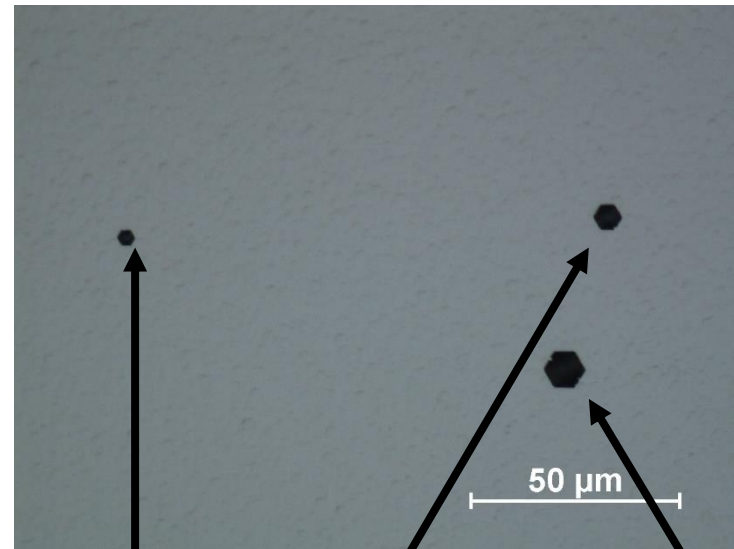
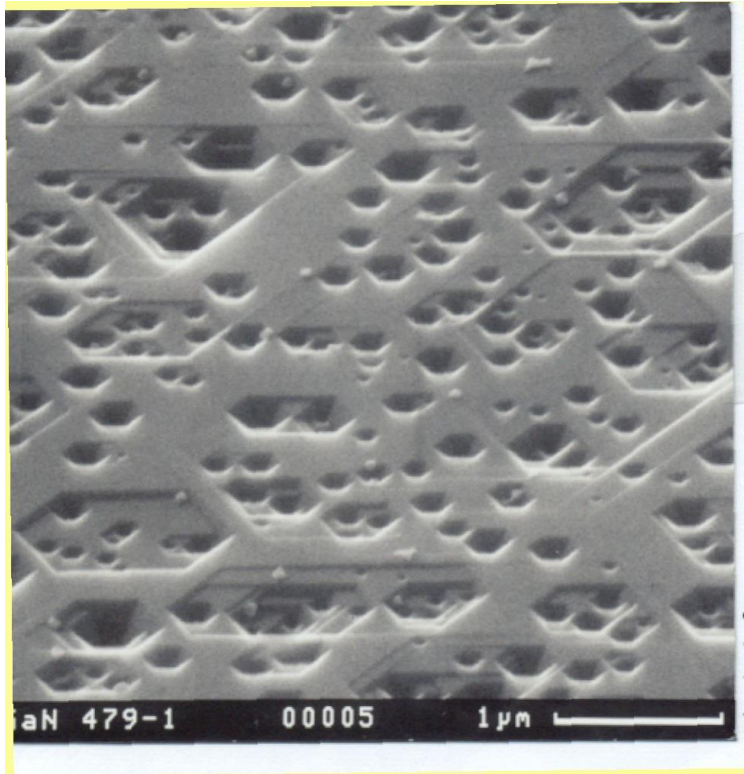
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# X-ray Diffraction XRD



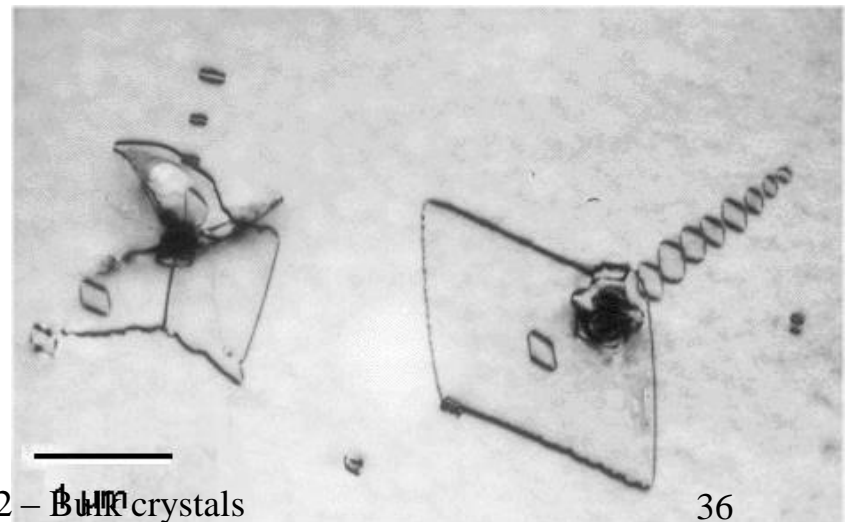
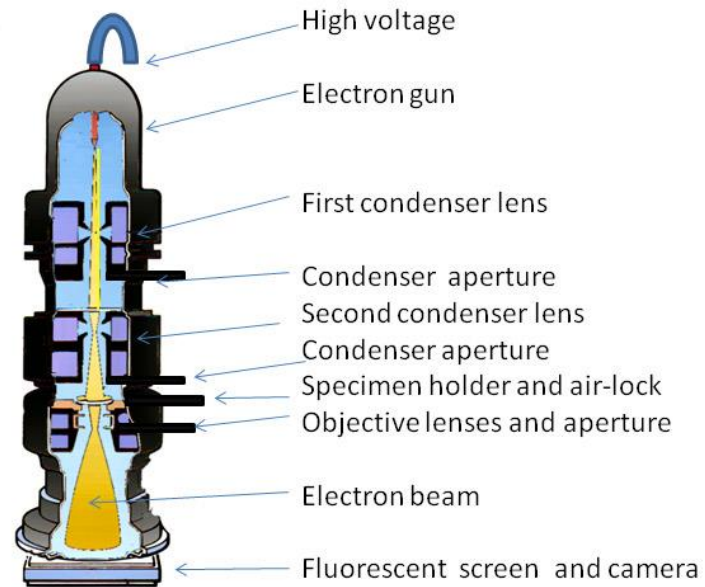
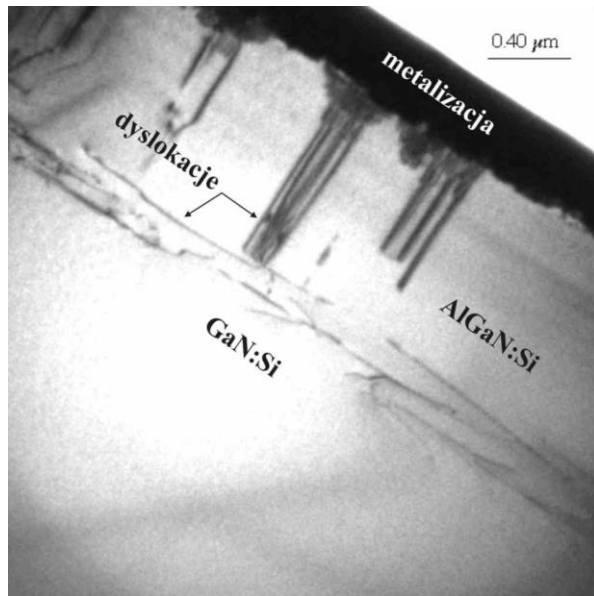
# Selective Etching (Etch Pit Density EPD)

Visualization of:  
Dislocations  
Carrier density  
Polarity

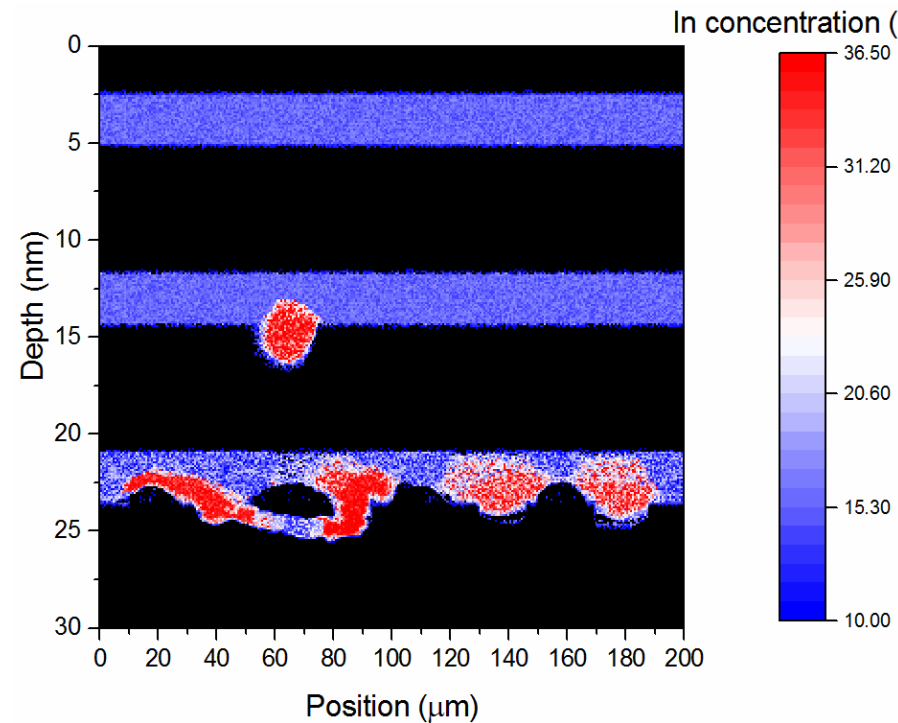
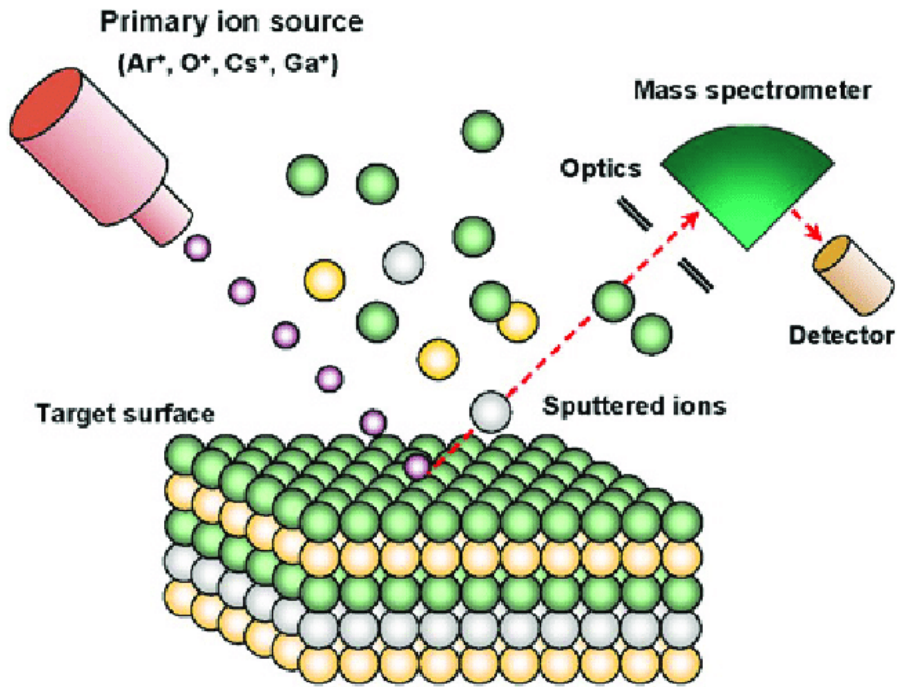


**Dislocations:**      **Edge**      **Mixed**      **Screw**

# Transmission Electron Microscopy TEM

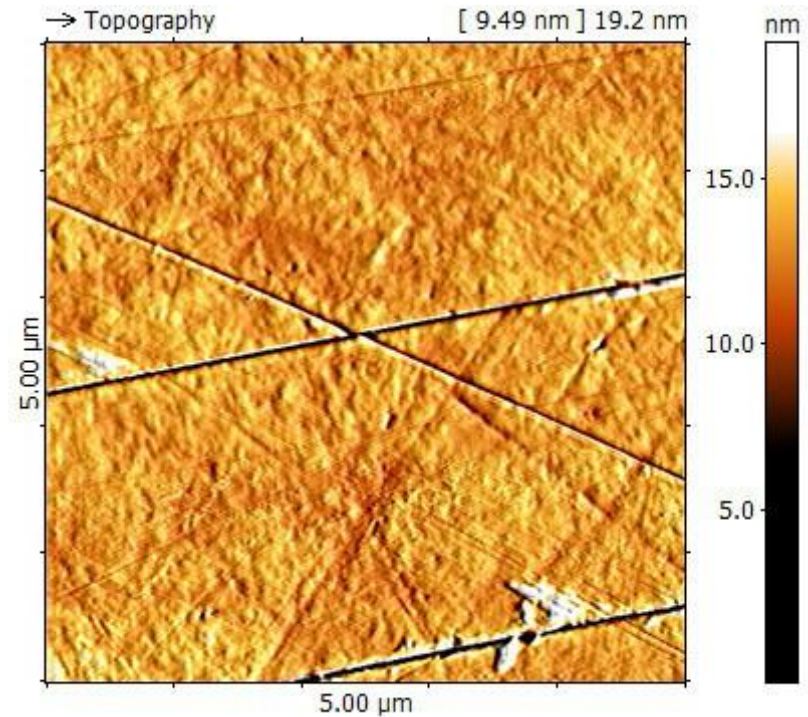
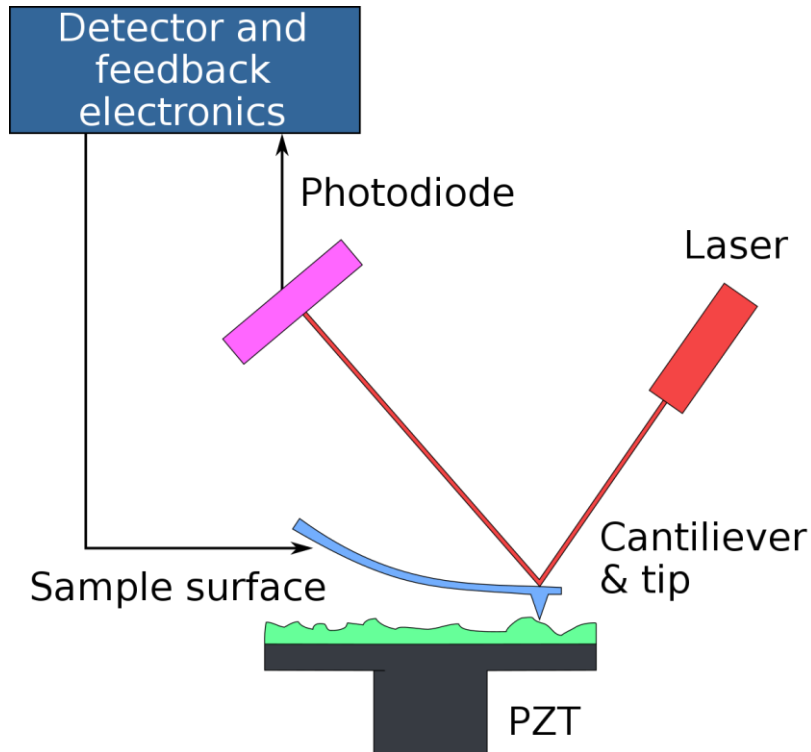


# Secondary Ion Mass Spectrometry SIMS

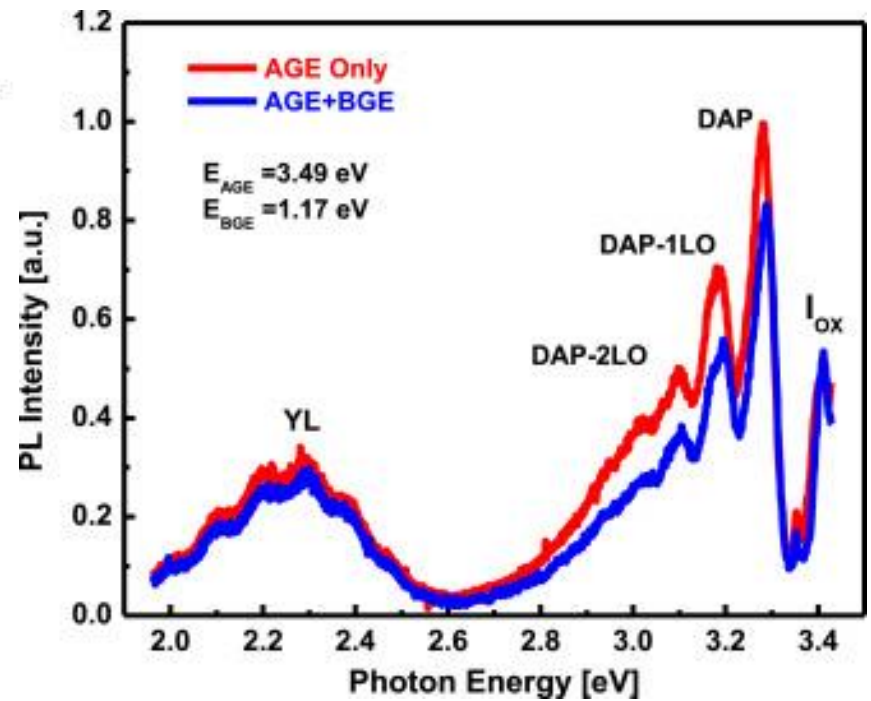
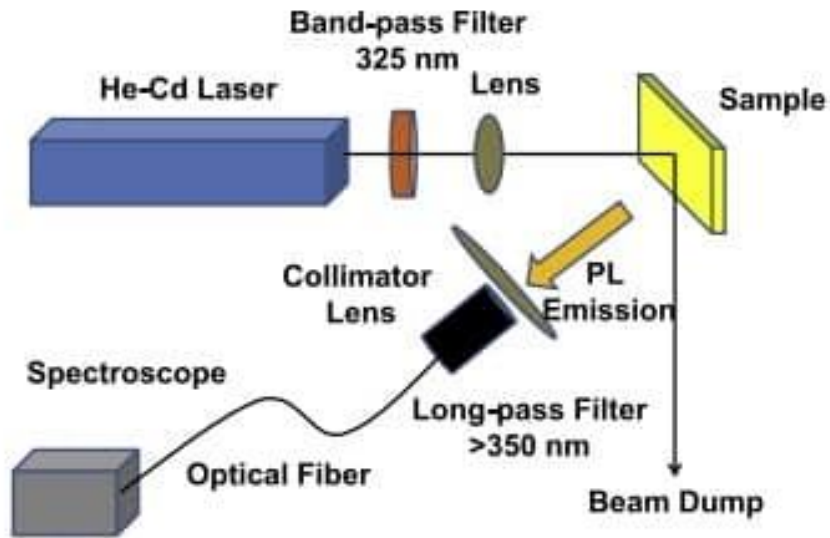




# Atomic Force Microscopy AFM

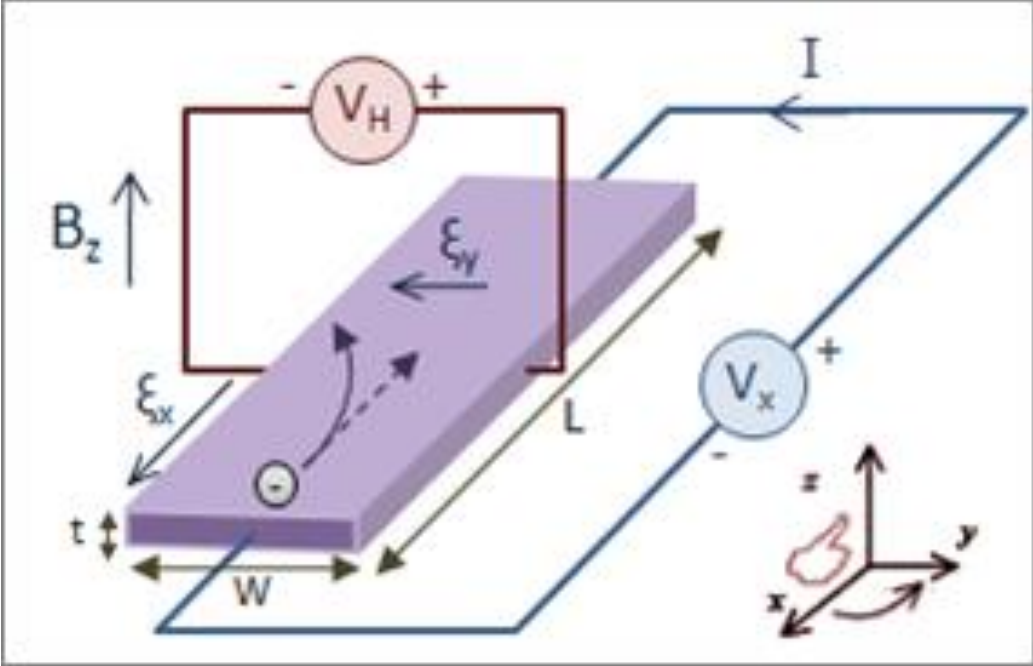


# Optical characterization





# Electrical characterization



Free carrier concentration  
Mobility

## ***Final remarks***

- 1. Semiconductor bulk crystals belong to „enabling technologies“.***
- 2. In every technology, a large number of growth parameters must be taken into account.***
- 3. The final test of every substrate is epitaxy (next lecture)***
- 4. It is desirable to understand not only mechanisms of crystal growth, but also what is really measured in analytical characterization methods.***