Crystal Growth: Physics, Technology and Modeling

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Lecture 3. Growth of semiconductor bulk crystals – an introduction to next lectures

http://www.unipress.waw.pl/~stach/cg-2024-25

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***

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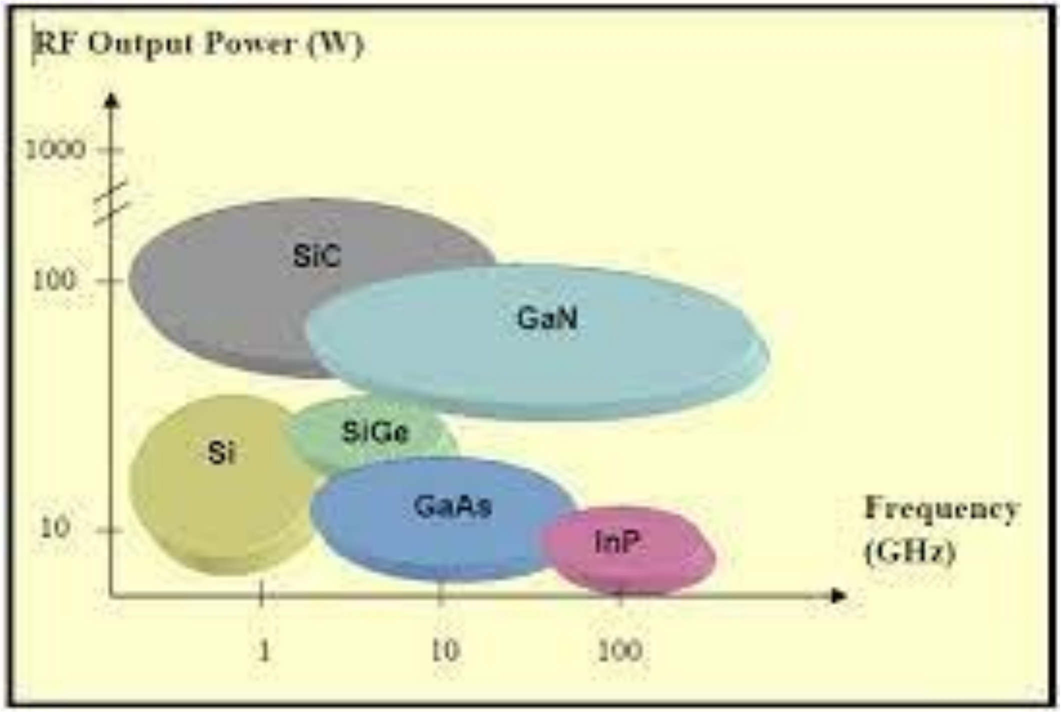
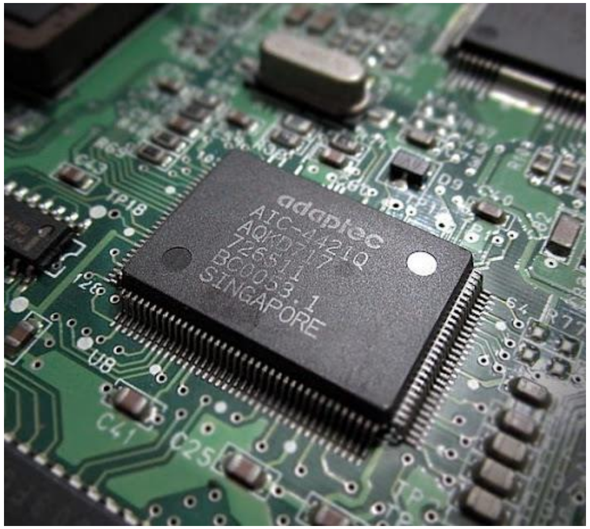
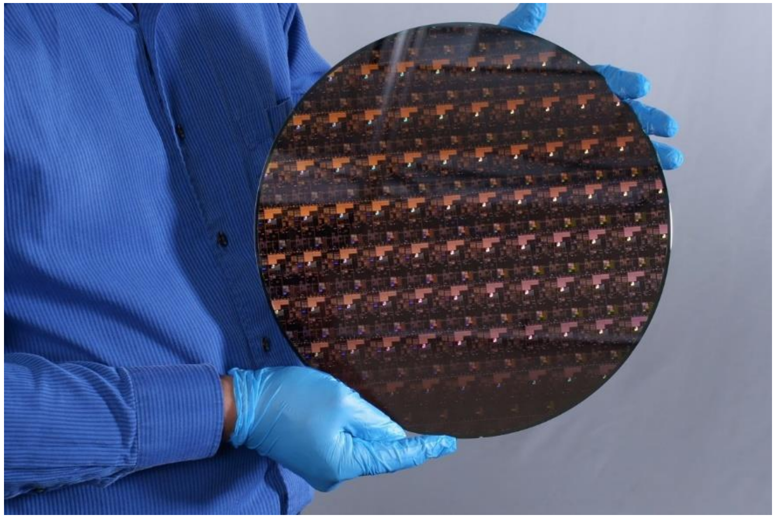
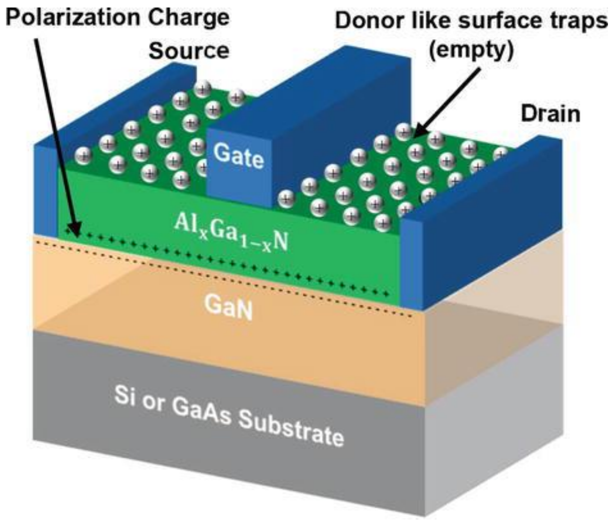
Transistors

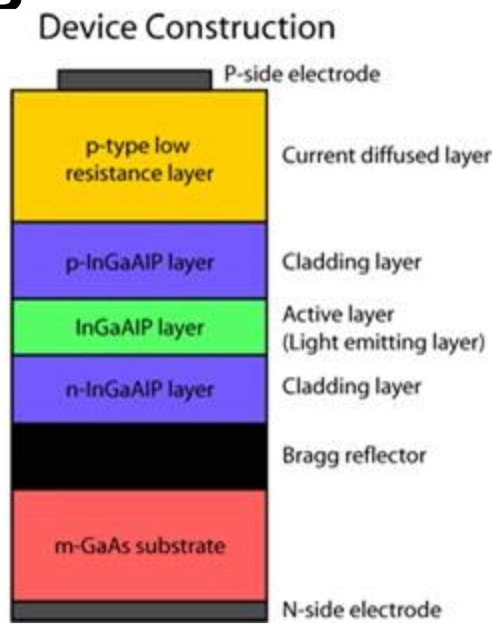


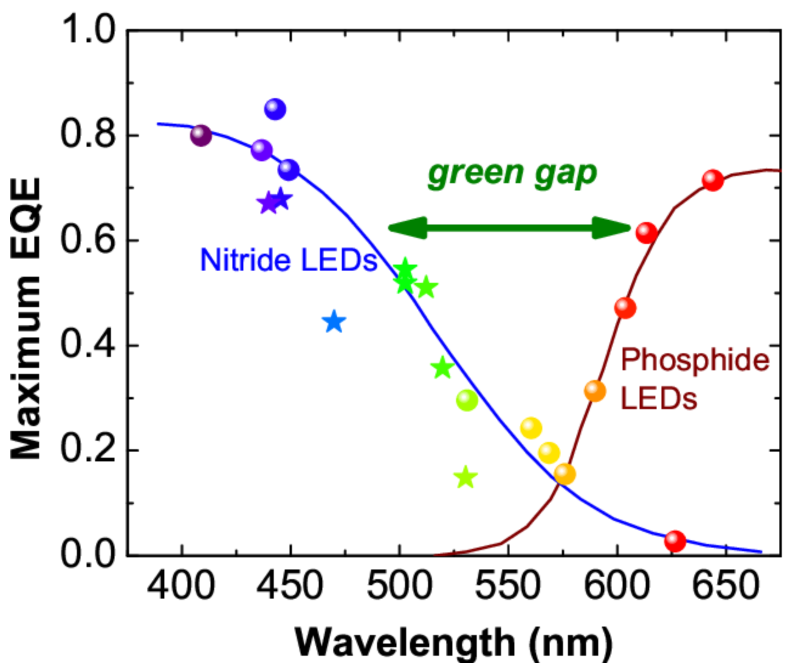


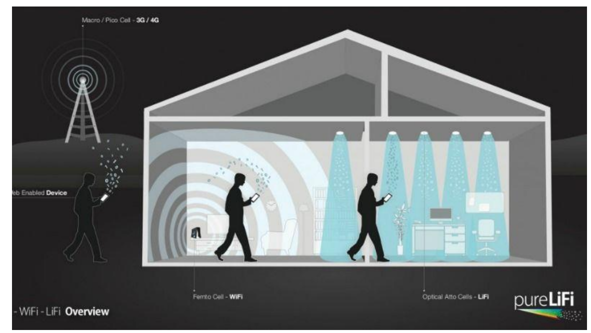




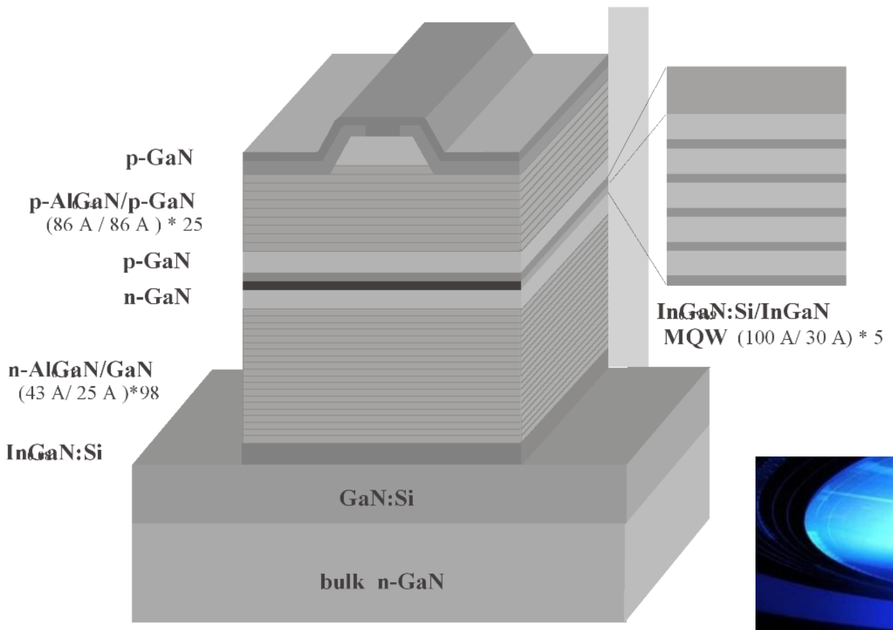
LEDs

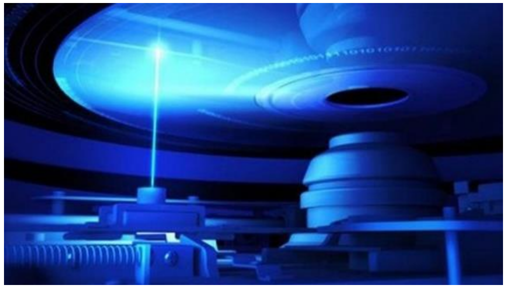

Device Construction
P-side electrode
p-type low resistance layer
Current diffused layer
p-InGaAlP layer
Cladding layer
InGaAlP layer
Active layer (Light emitting layer)
n-InGaAlP layer
Cladding layer
Bragg reflector
m-GaAs substrate
N-side electrode

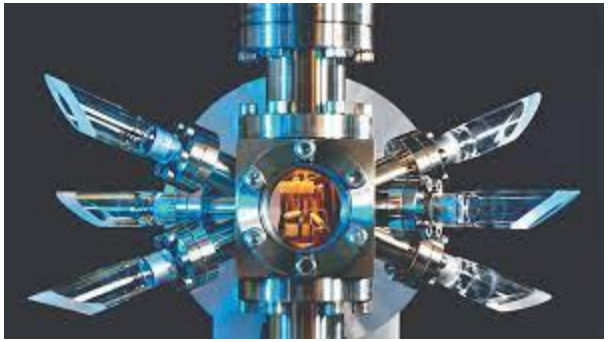

Maximum EQE
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
400
450
500
550
600
650
green gap
Nitride LEDs
Phosphide LEDs


pureLiFi

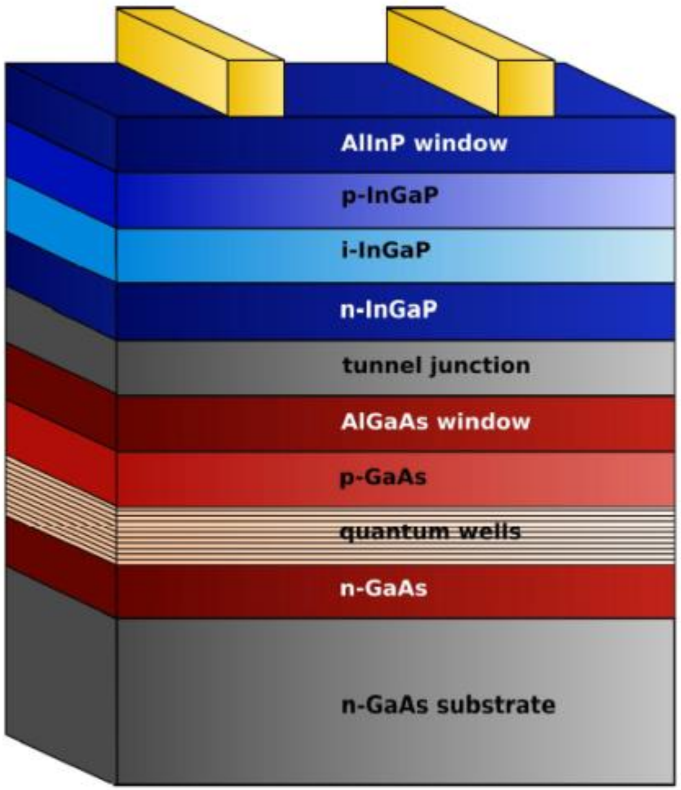
Laser Diodes (LDs)







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

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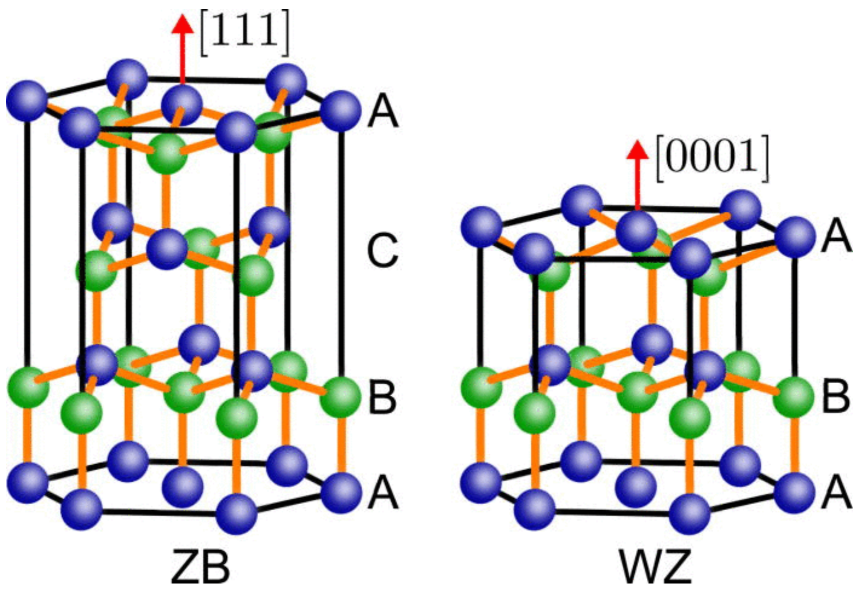
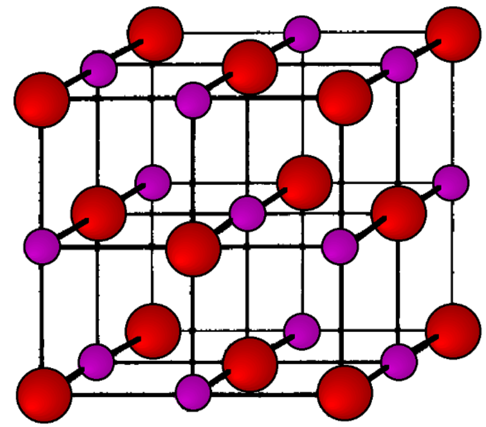
Crystallographic structures

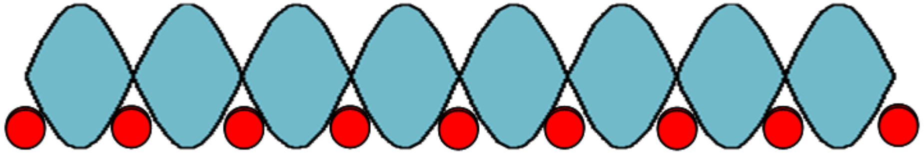




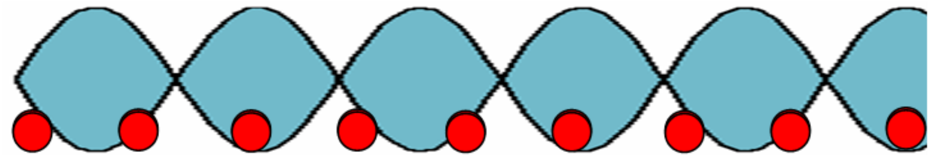
Rock salt (NaCl)

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 …



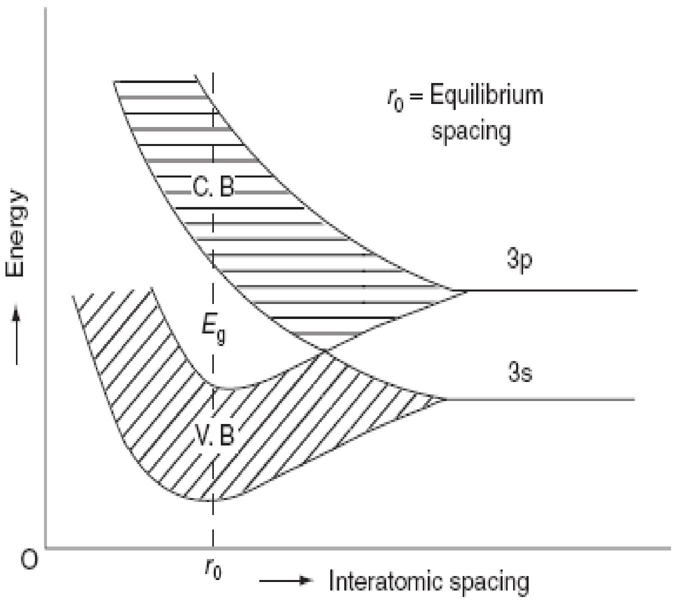
… than this one does.



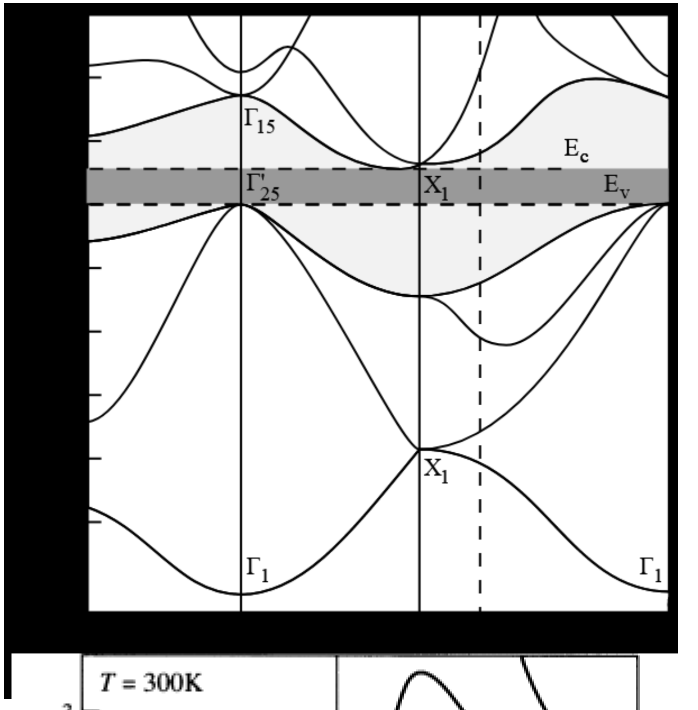
High electron mobility important for transistors.

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

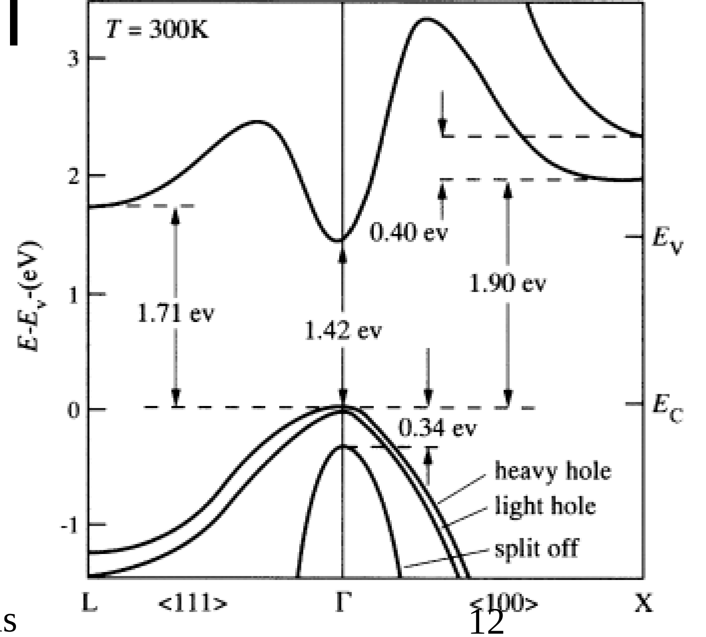
Energy gaps



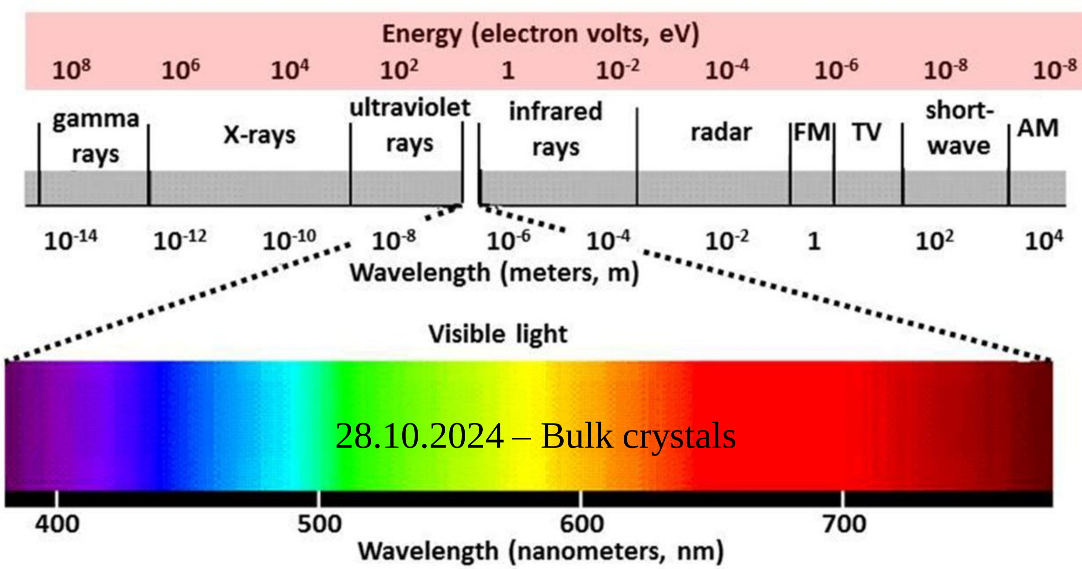
Si indirect band gap



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



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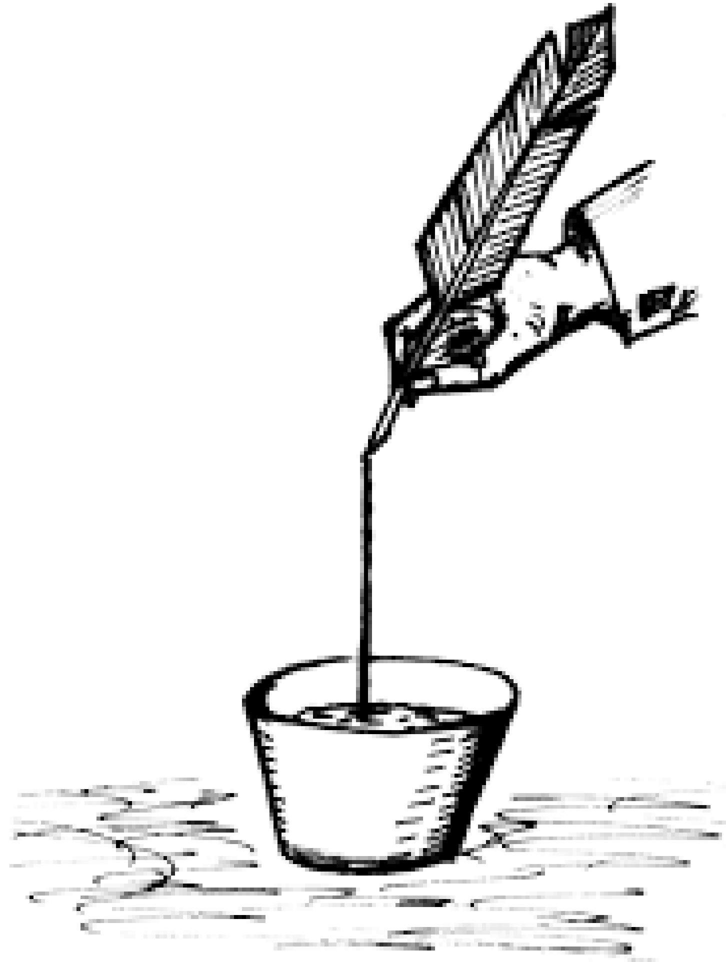
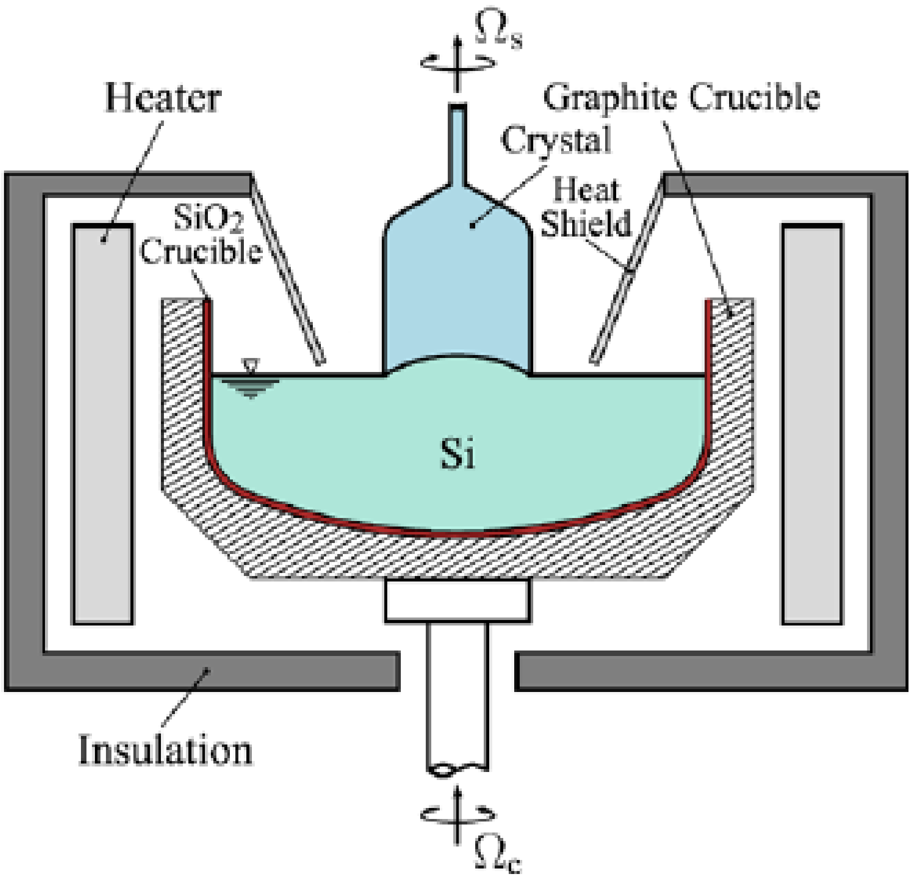
Jan Czochralski



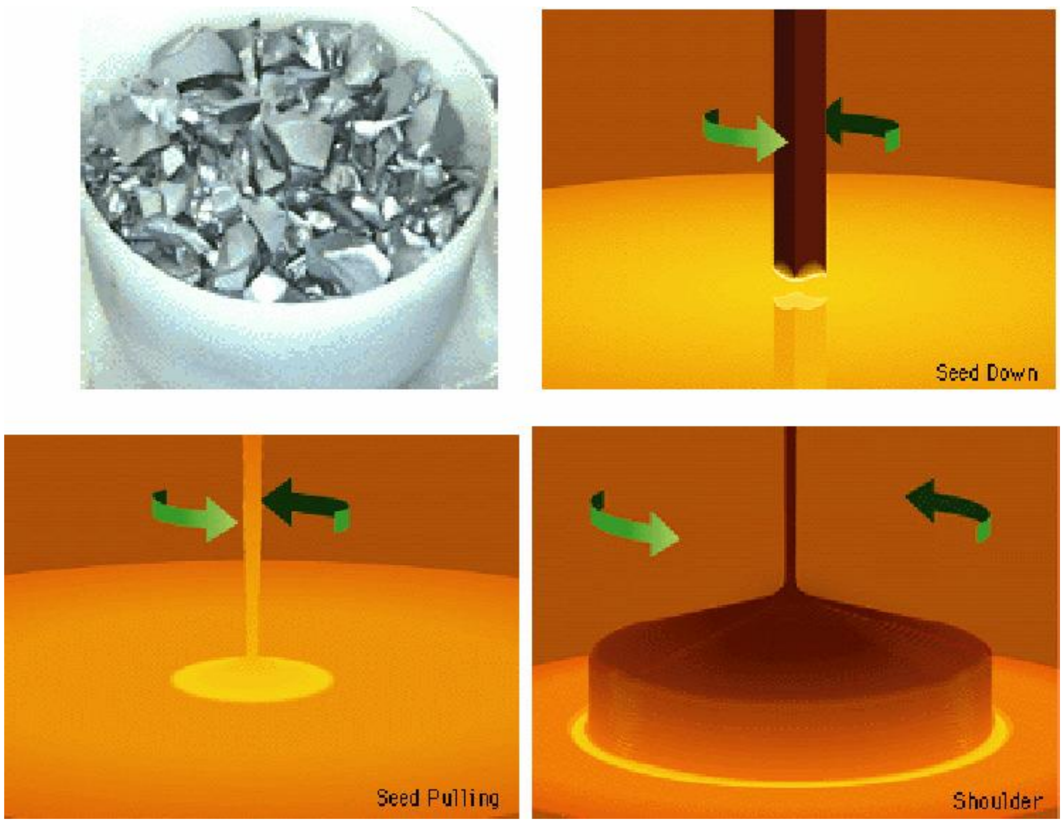
Czochralski method



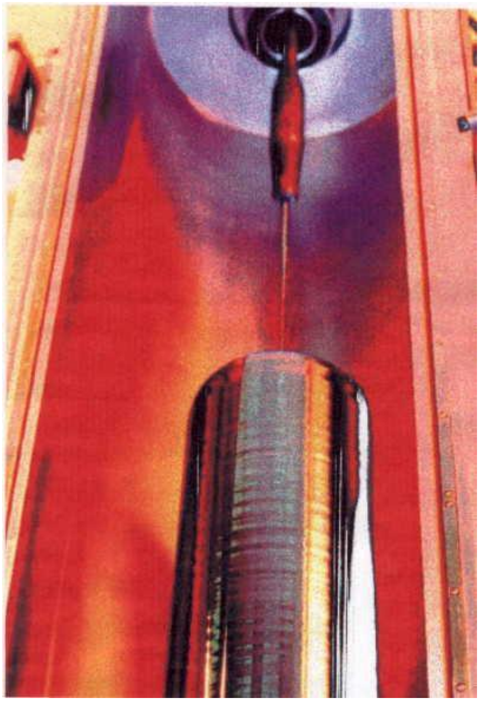
Compound	Melting point (oC)	Pressure (atm)
Si	1400	<1
Ge	938	1
GaAs	1250	1.5
InP	1062	27
GaN	>2220	>60000
InN	>1100	>100000
AlN	>2800	>1000
SiC	>2700	>20000

SILICON

$SiO_2 + 2C \rightarrow Si + 2\,CO$ (1500-2000^{o}C) 98% purity (MG Si)
$Si + 3HCl \rightarrow SiHCl_3 + H_2$ (BCl_3, $FeCl_3$, etc removed by distillation)
$SiHCl_3 + H2 \rightarrow Si + 3HCl$ Si polycrystalline11N



SILICON



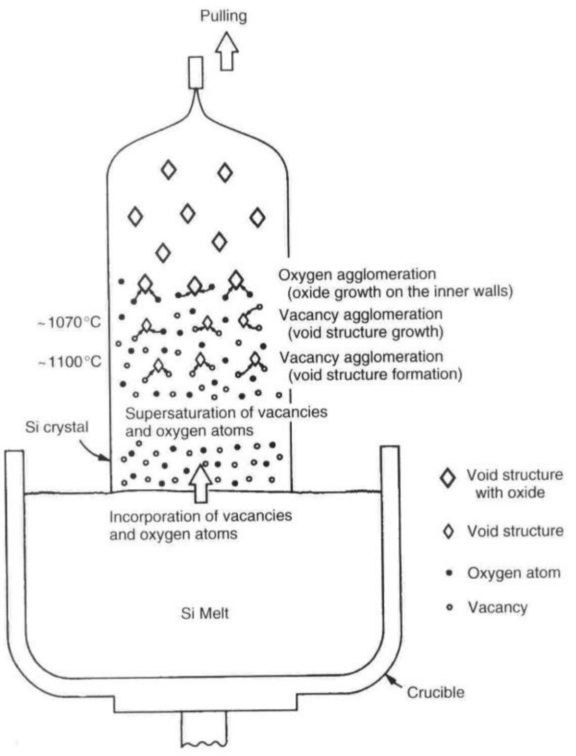
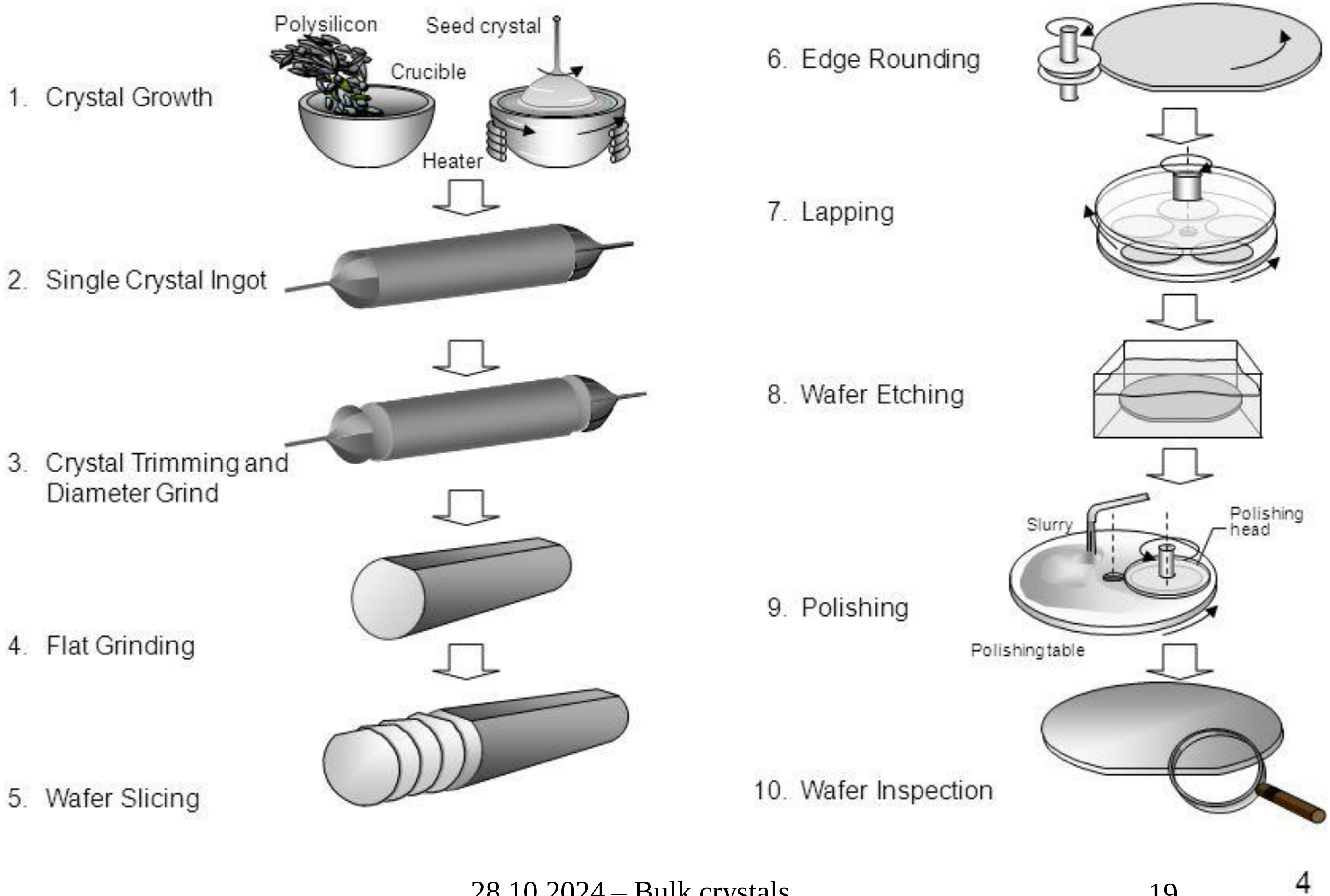


Figure 1.38 Formation of void defects as a result of interaction of vacancies and oxygen (Reprinted from Itsumi in *Crystal Growth Technology*, eds. H. Scheel and T. Fukuda (2003), copyright (2003) with permission from Wiley)

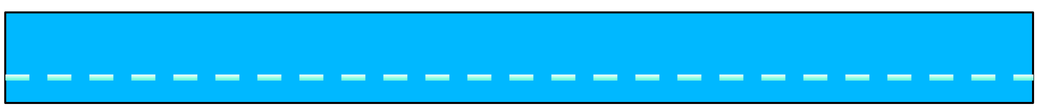
Growth rate 50 mm/h, no dislocations, oxygen precipitates, impurities

CRYSTAL GROWTH



Diameter (mm)	Thickness (mm)	Area (cm2)	Price (Eur/cm2)
150	6.75	176	1.2
200	7.25	314	1.0
300	7.75	706	0.8
400	8.25	1256	0.6

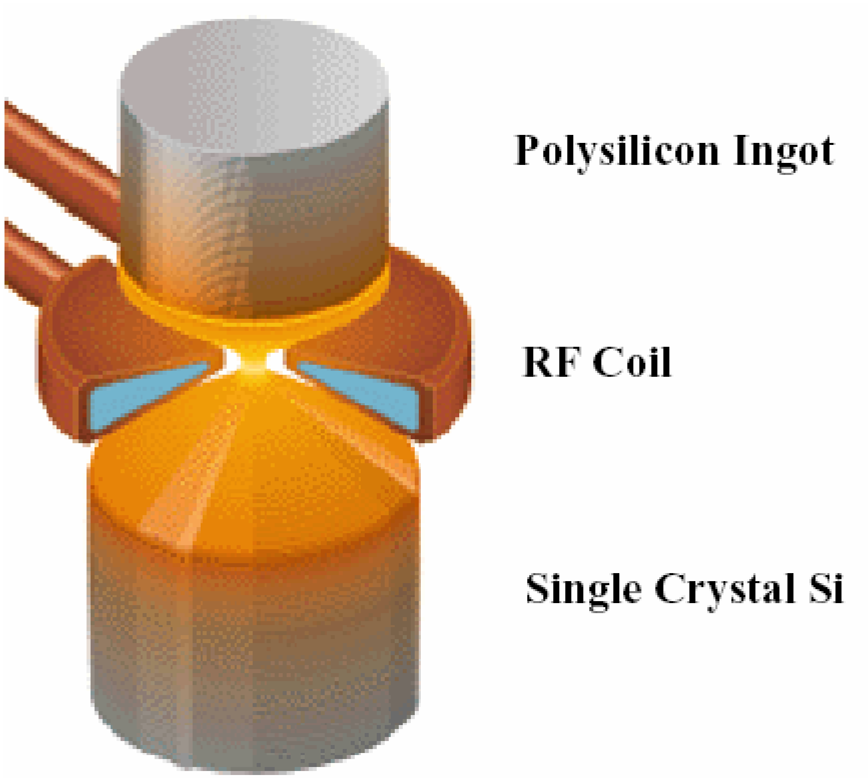
Polished Surface



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

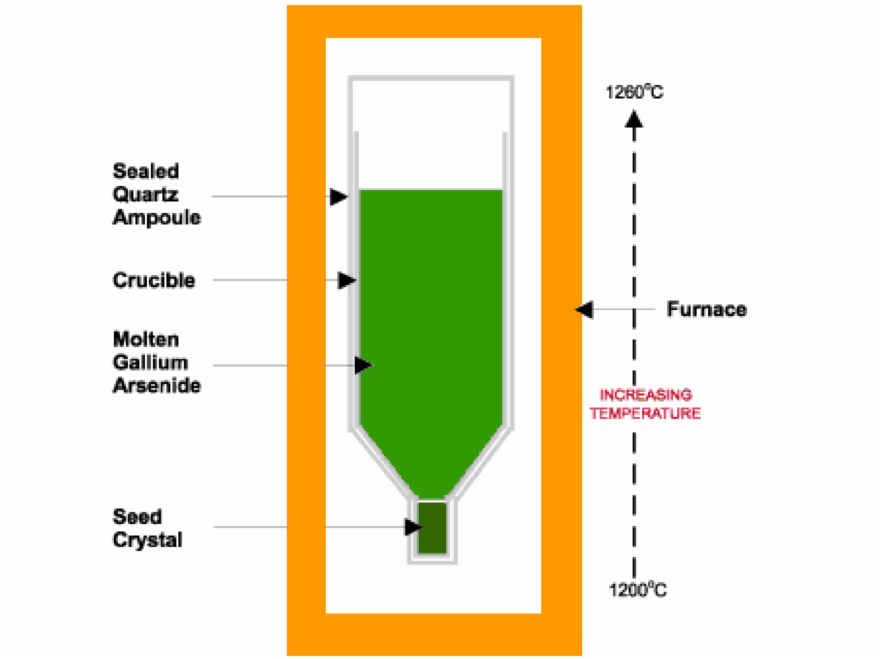
Argon amorphize back side of the Si wafer. Then annealing at 550 °C, makes recrystallization, formation of microbubbles of argon which attract the impurities (mainly metals). At the same time, SiO_x precipates are formed lowering the amount of oxygen close to the surface.

Floating zone: crystallization and cleaning

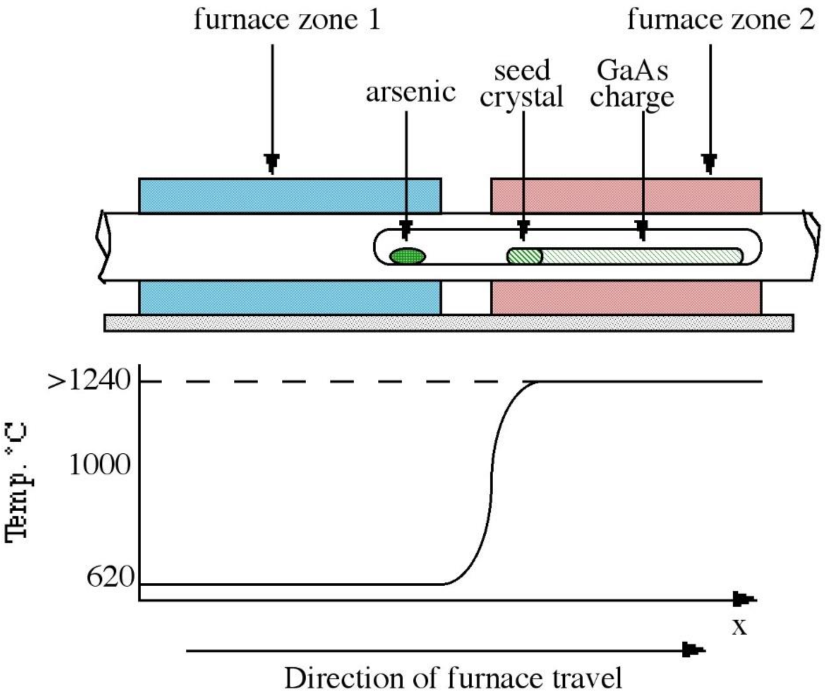


Other methods of crystal growth from melt

Gallium Arsenide Crystal Growth by Vertical Gradient Freeze



Bridgeman method



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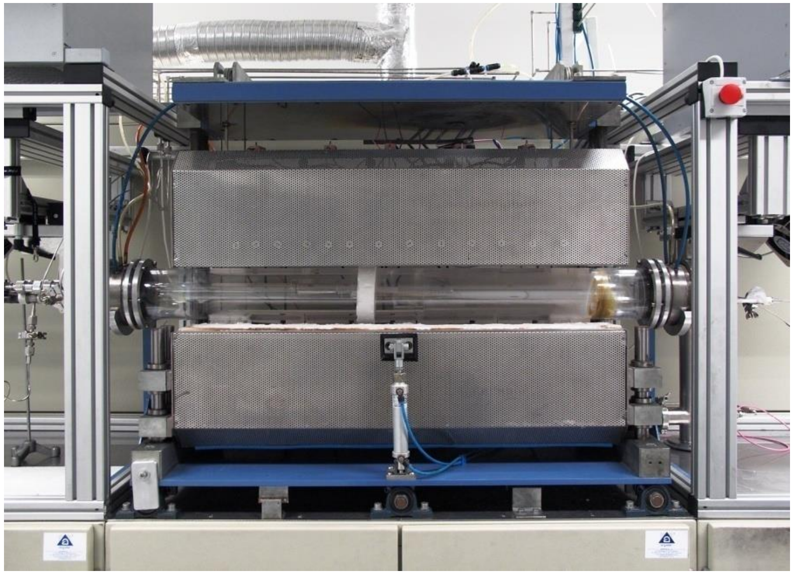
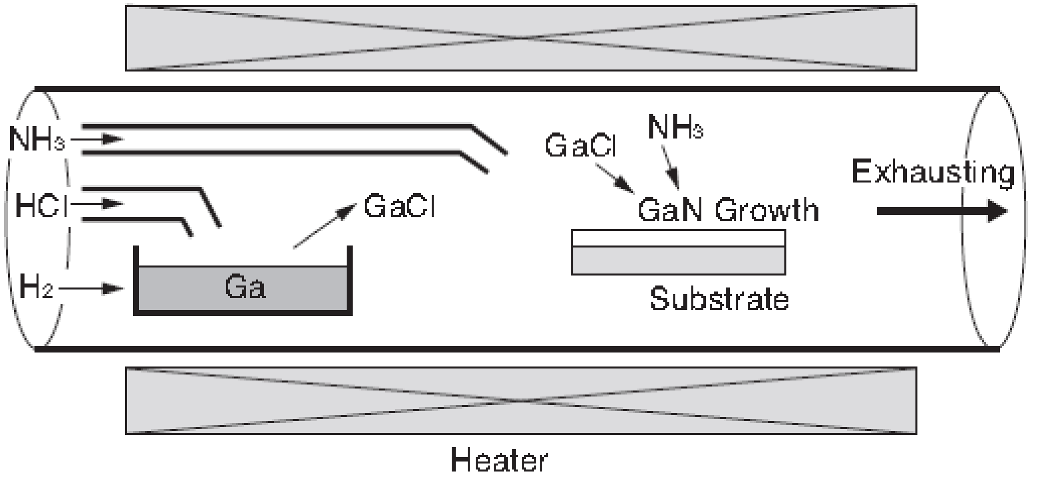
HVPE growth method
Basic



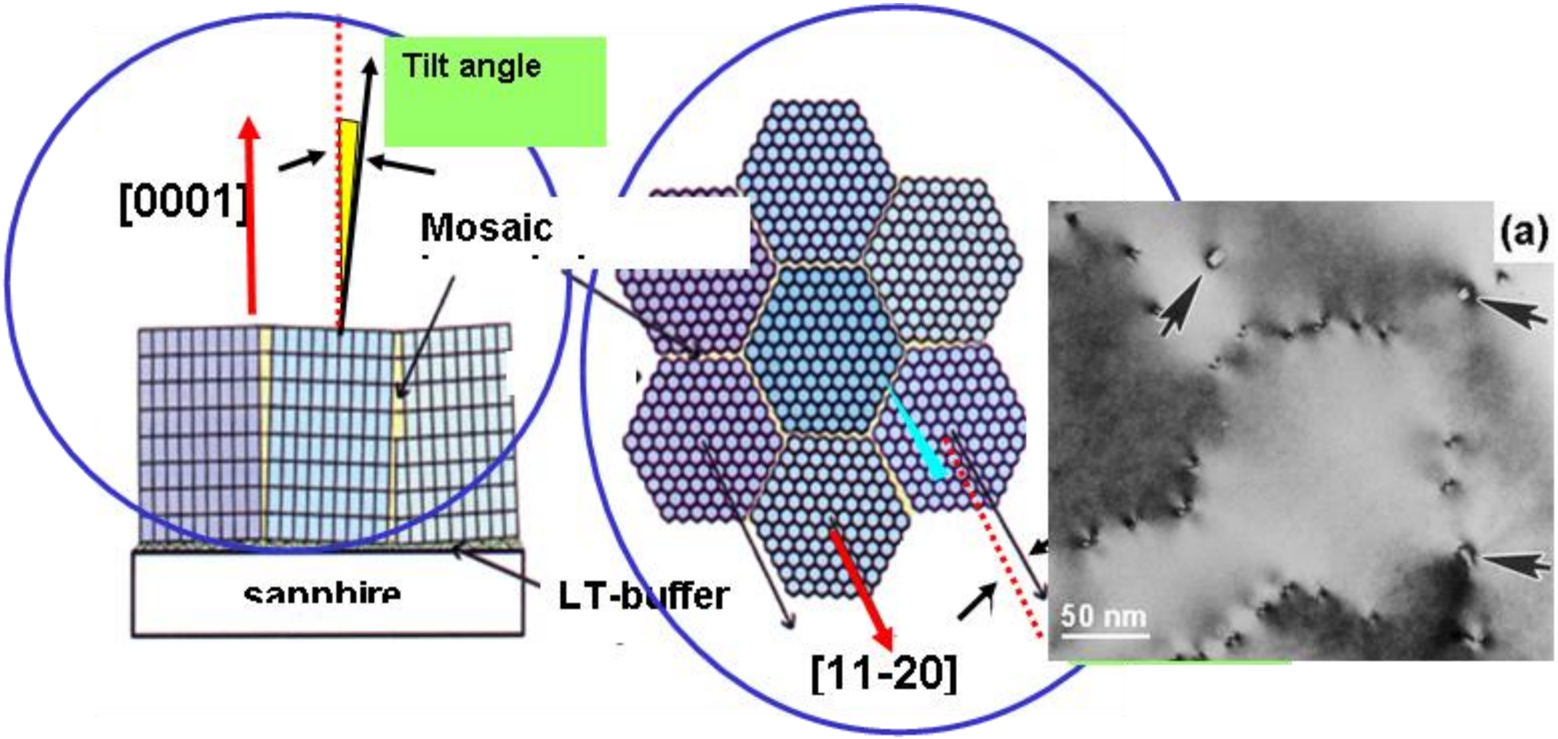


$HCl(g) + Ga(l) \rightarrow GaCl(g) + 1/2H_2$

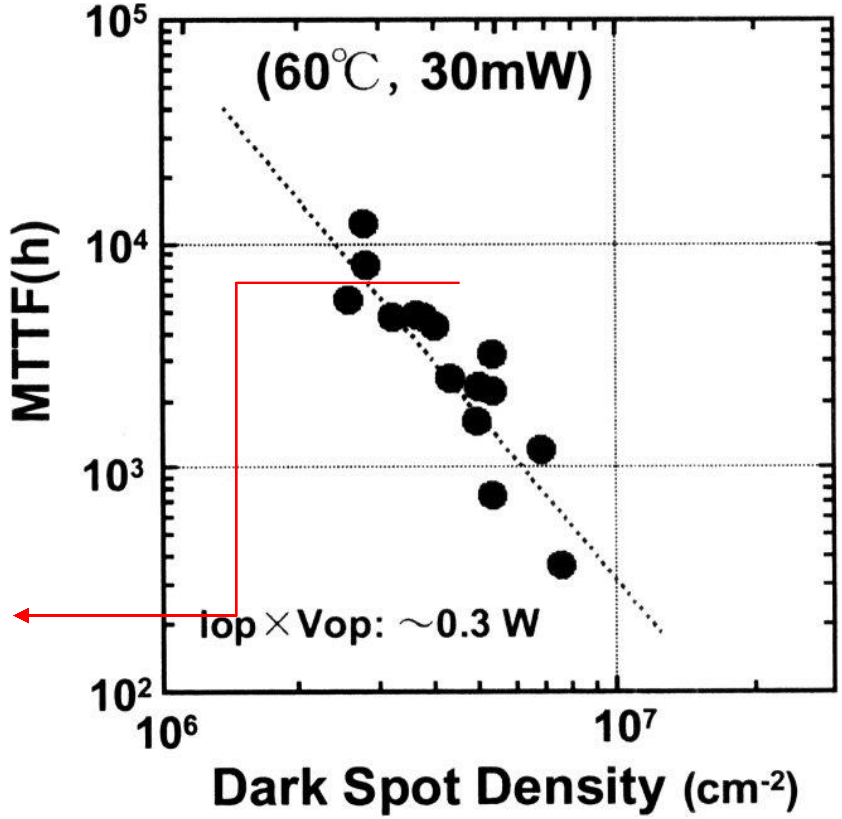
$GaCl(g)+NH_3(g) \rightarrow GaN(s)+HCl(g)+H_2$

$GaCl(g)+2HCl(g) \rightarrow GaCl_3(g)+H_2(g)$

Groth of GaN on sapphire



Life time of laser diodes vs dislocation density

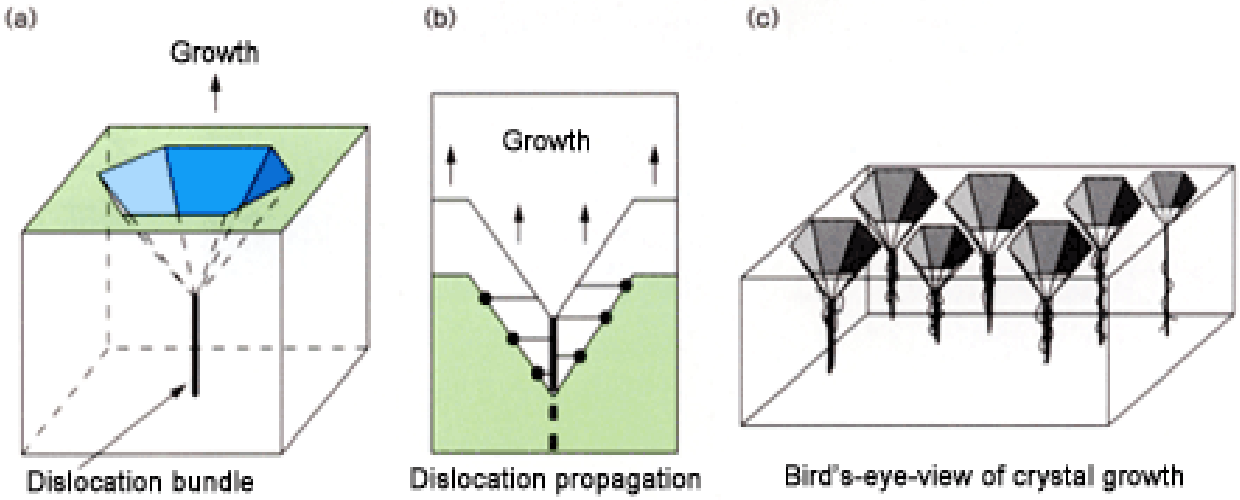


S. Uchida et al. Sony Shiroishi Semicond. Inc

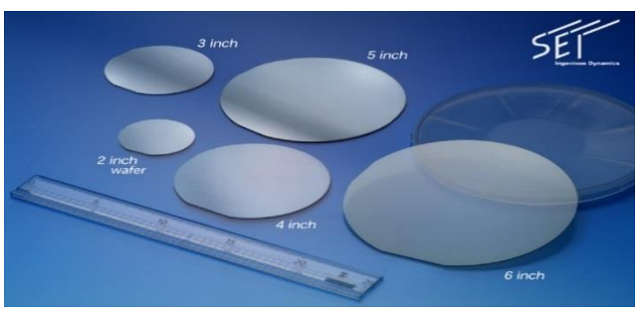
IEEE J. of Selected Topics in Quantum Electronics 9, no 5, (2003)1252.

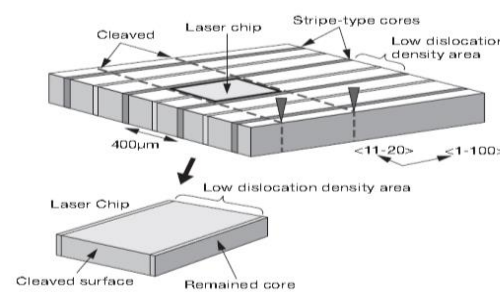
SUMITOMO- leader of GaN bulk crystal growth

'DEEP' Dislocation Elimination Technique



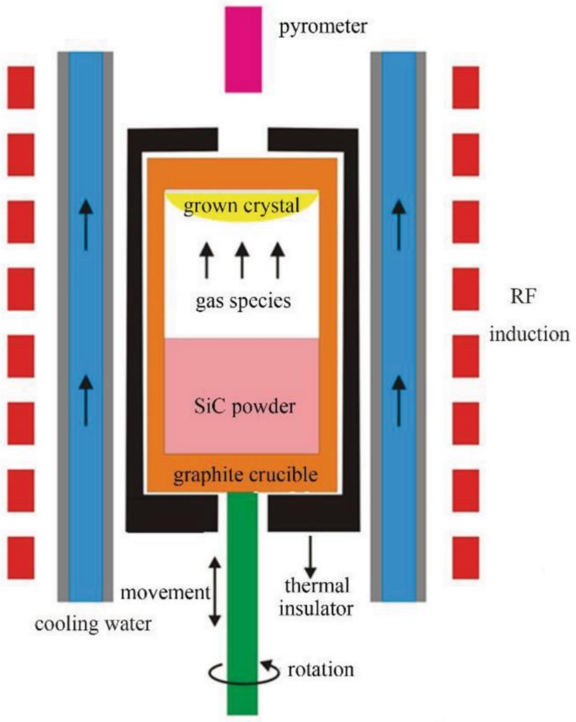
As the facets of huge pit grow, dislocations are concentrated to the bottom of the pit.

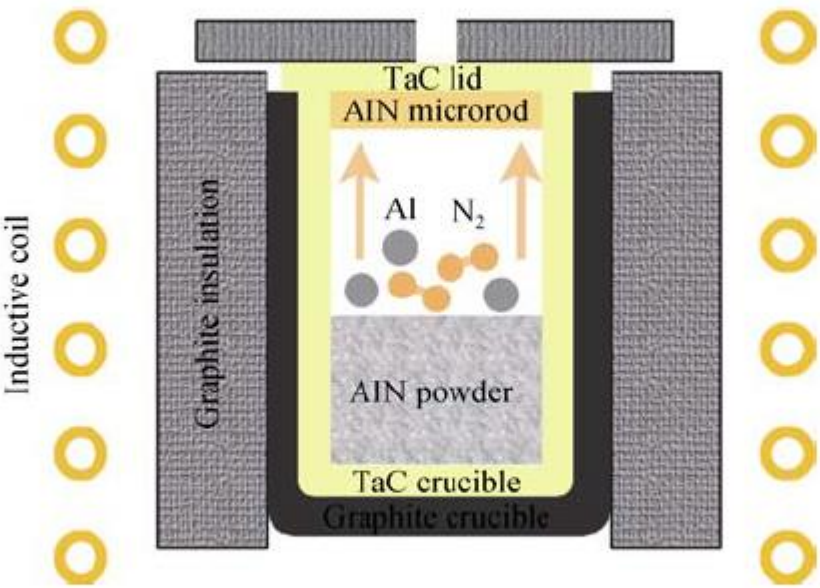




http://global-sei.com/news/press/10/10_25.html

Sublimation





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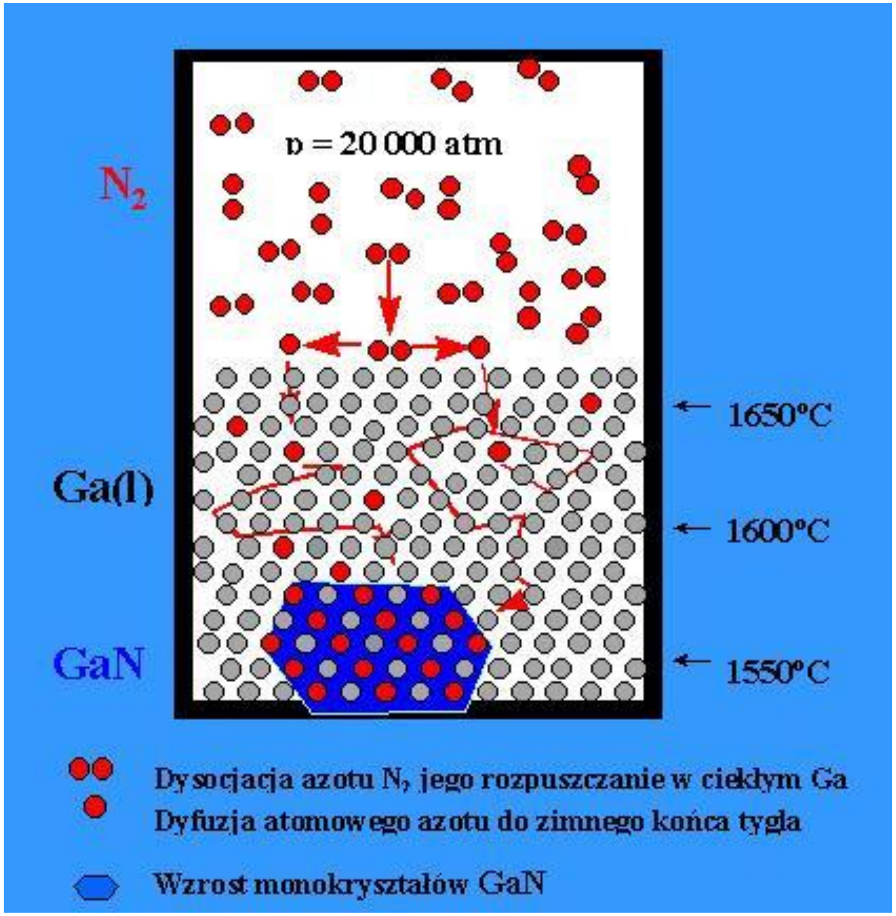
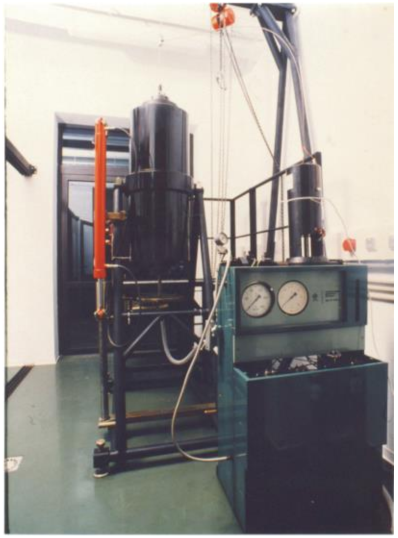
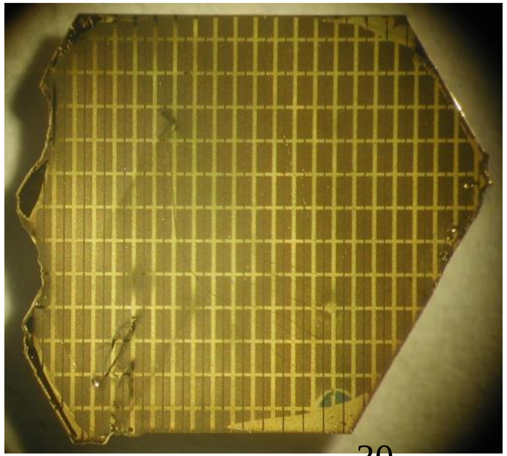
Growth of GaN crystals from nitrogen solution in gallium

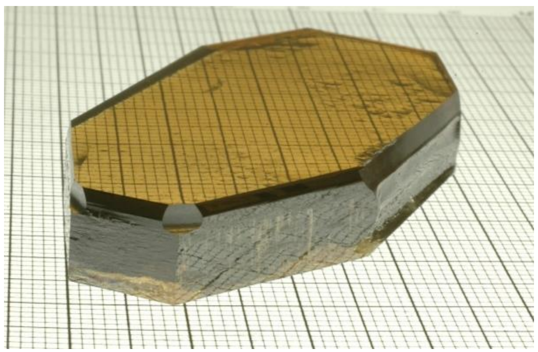


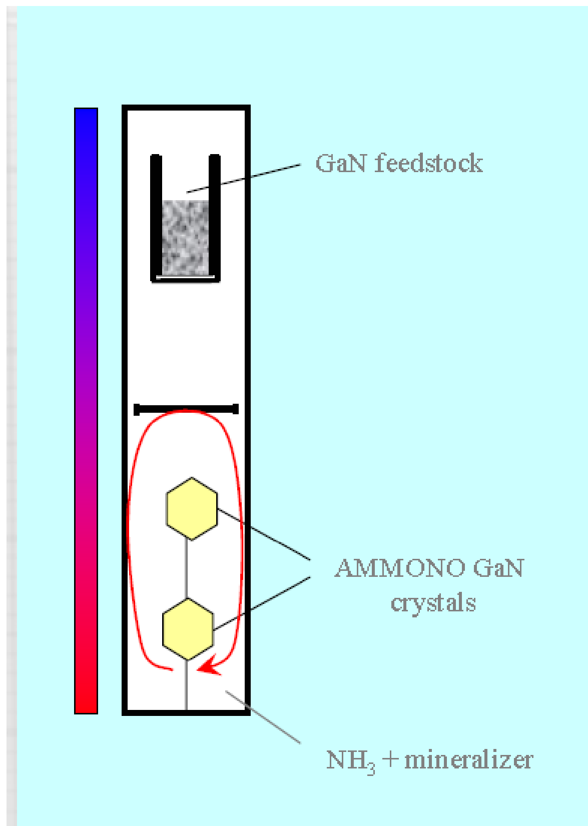


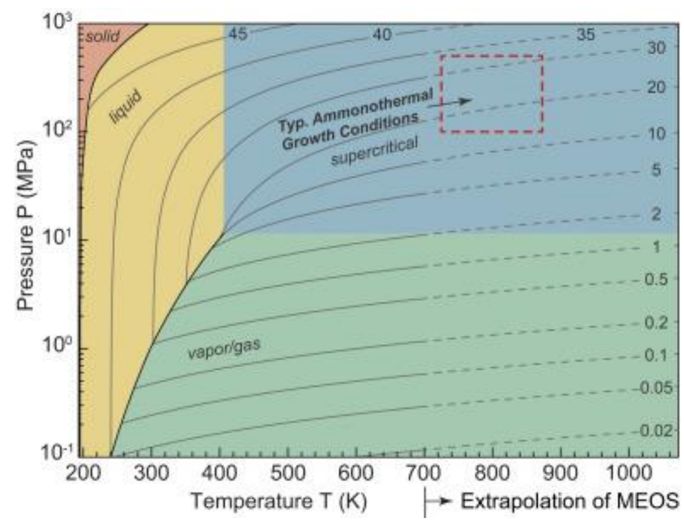


Ammono-GaN technology

- ***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/cm2)
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

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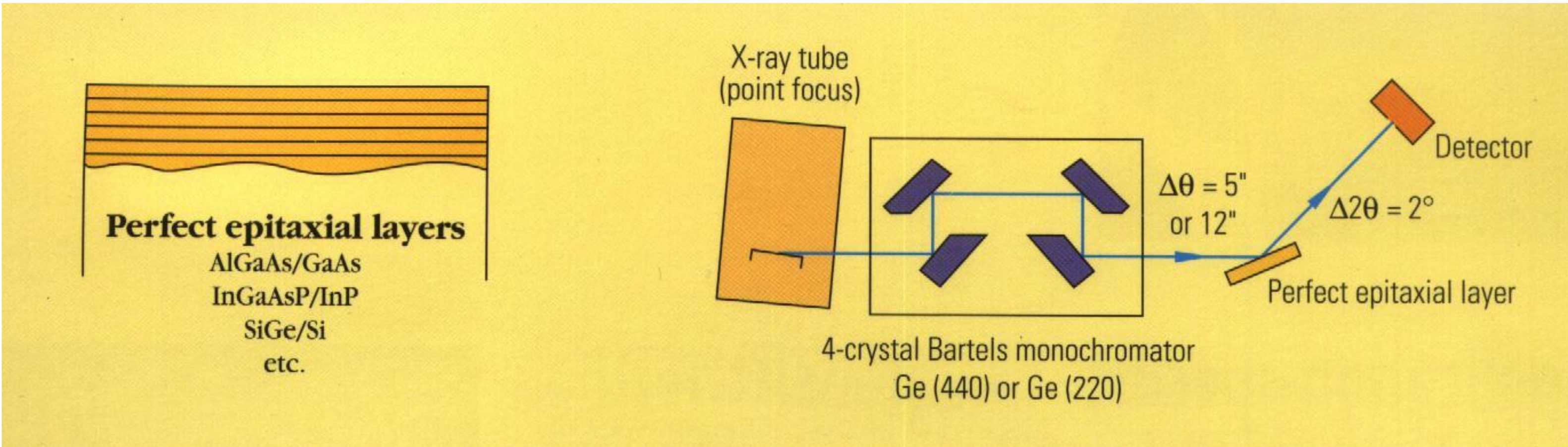
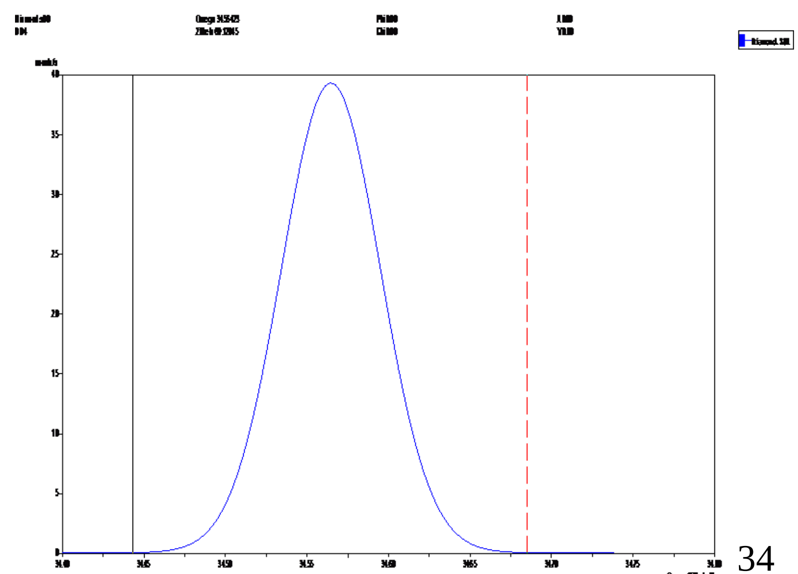
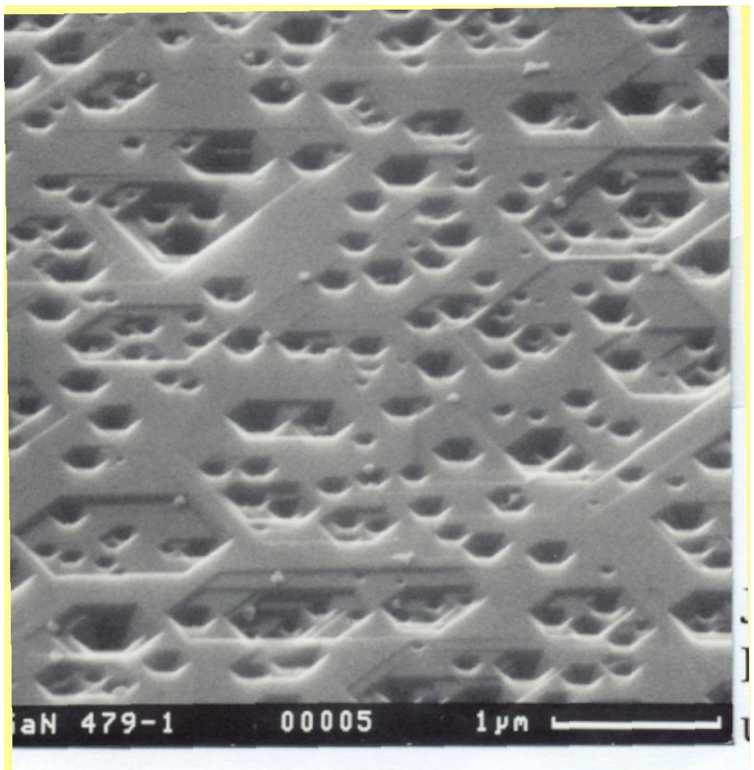
X-ray Diffraction XRD

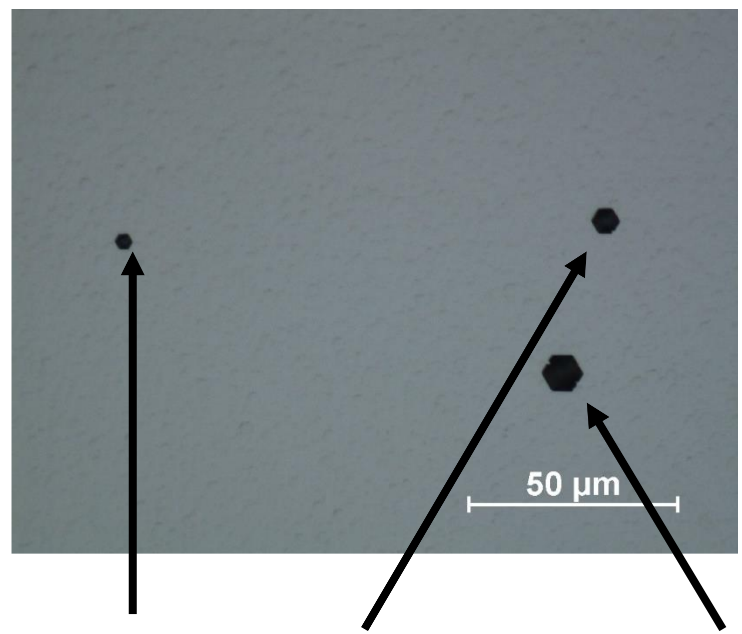




Selective Etching (Etch Pit Density EPD)

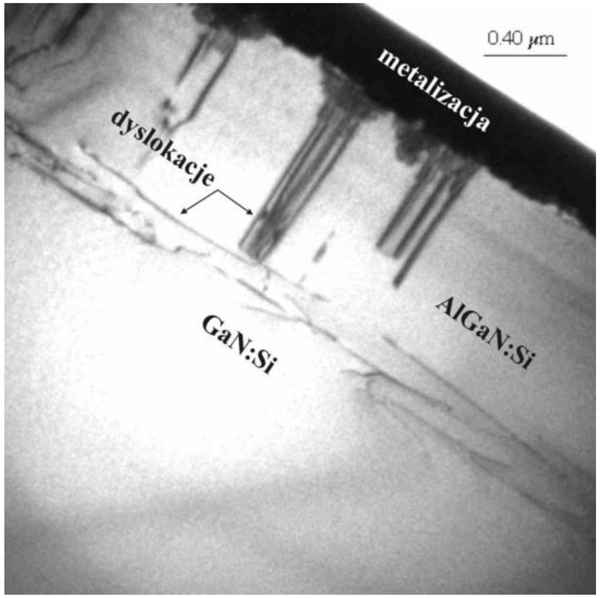
Visualization of:
Dislocations
Carrier density
Polarity

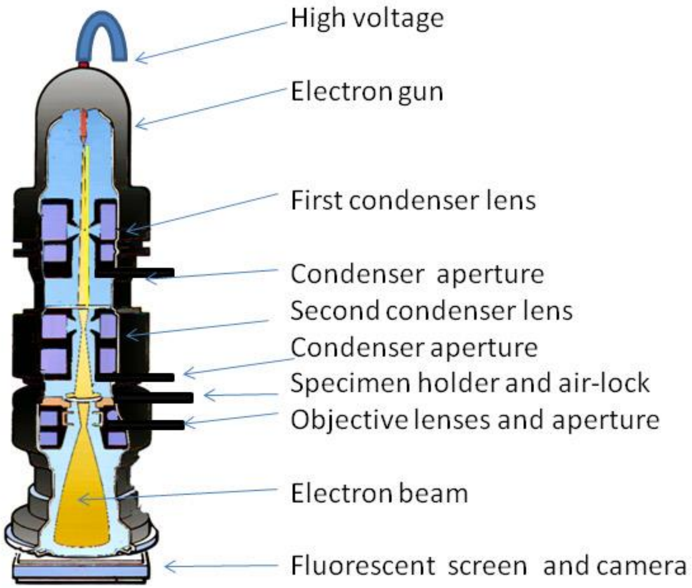


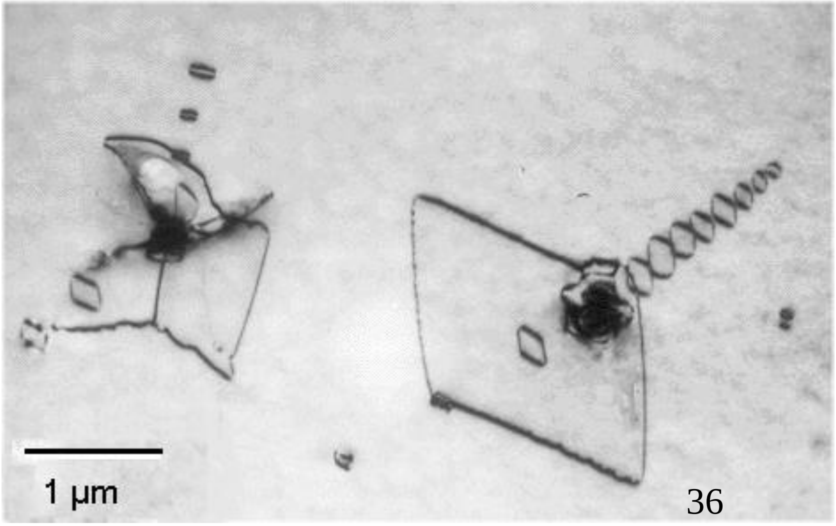


Dislocations: Edge Mixed Screw

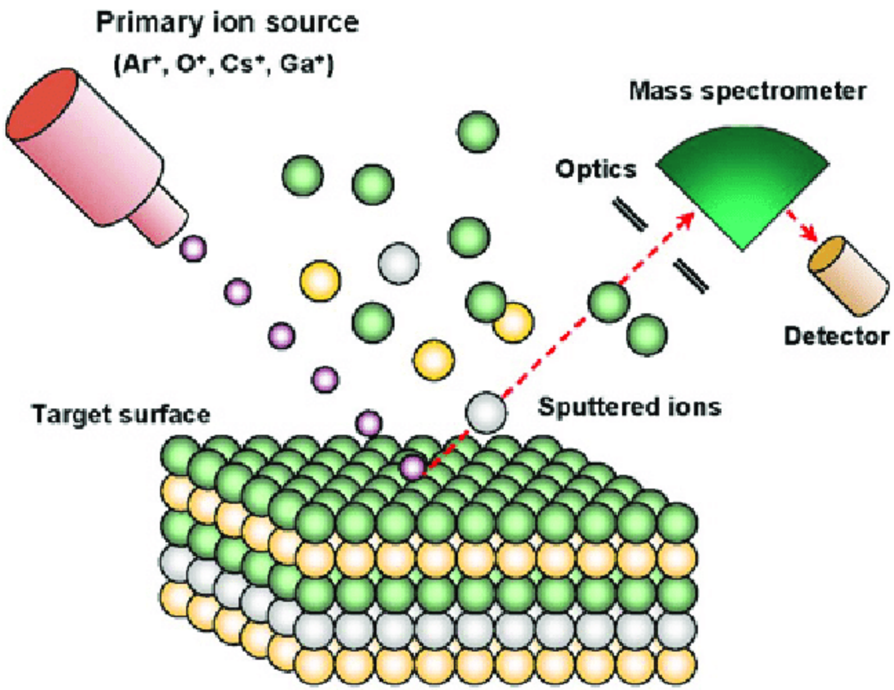
Transmission Electron Microscopy TEM

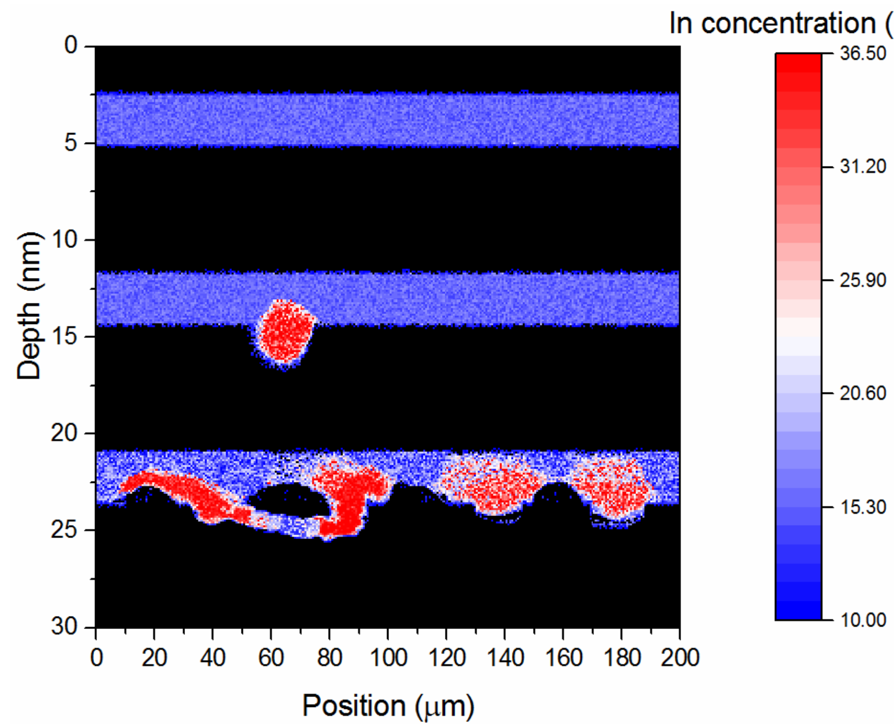




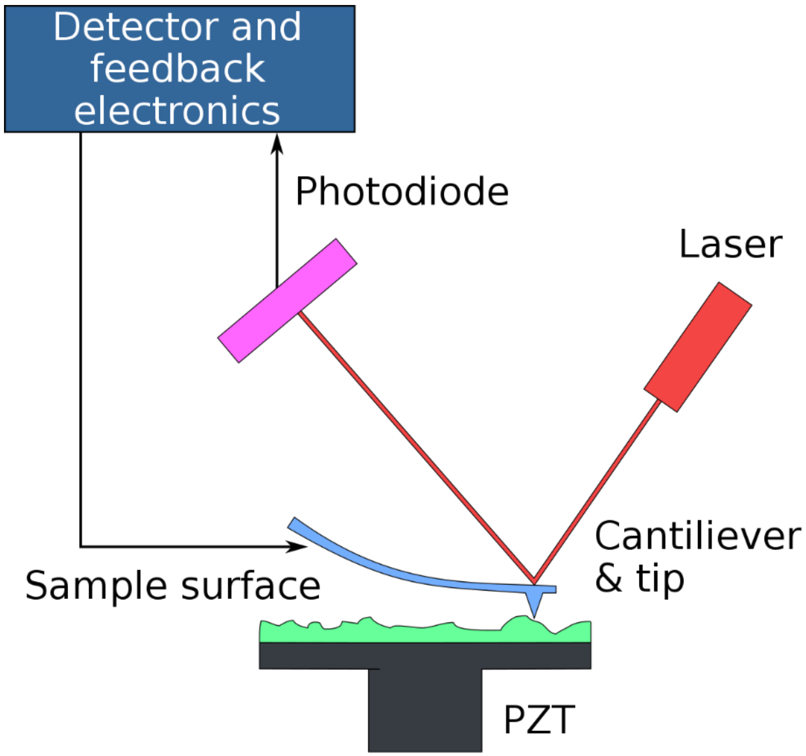


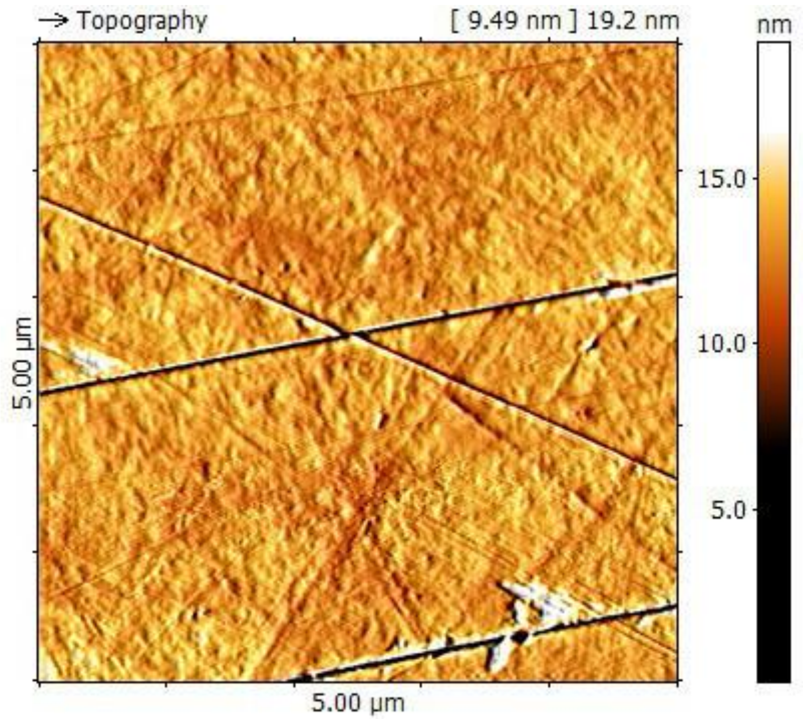
Secondary Ion Mass Spectrometry SIMS



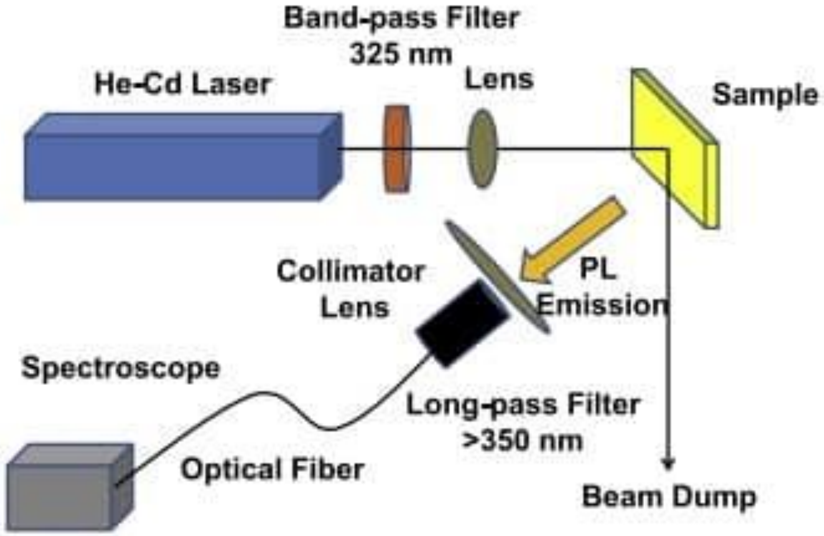


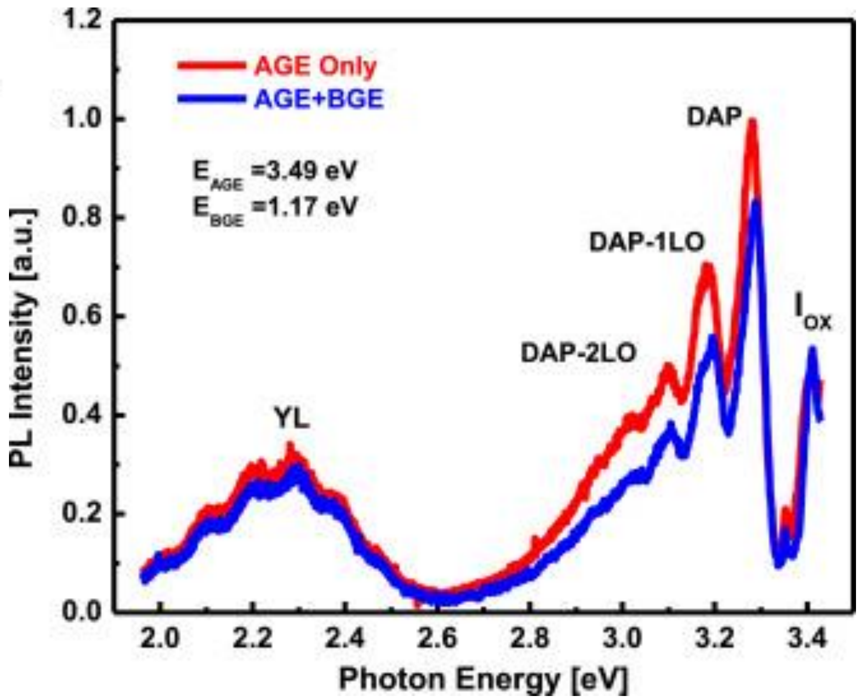
Atomic Force Microscopy AFM



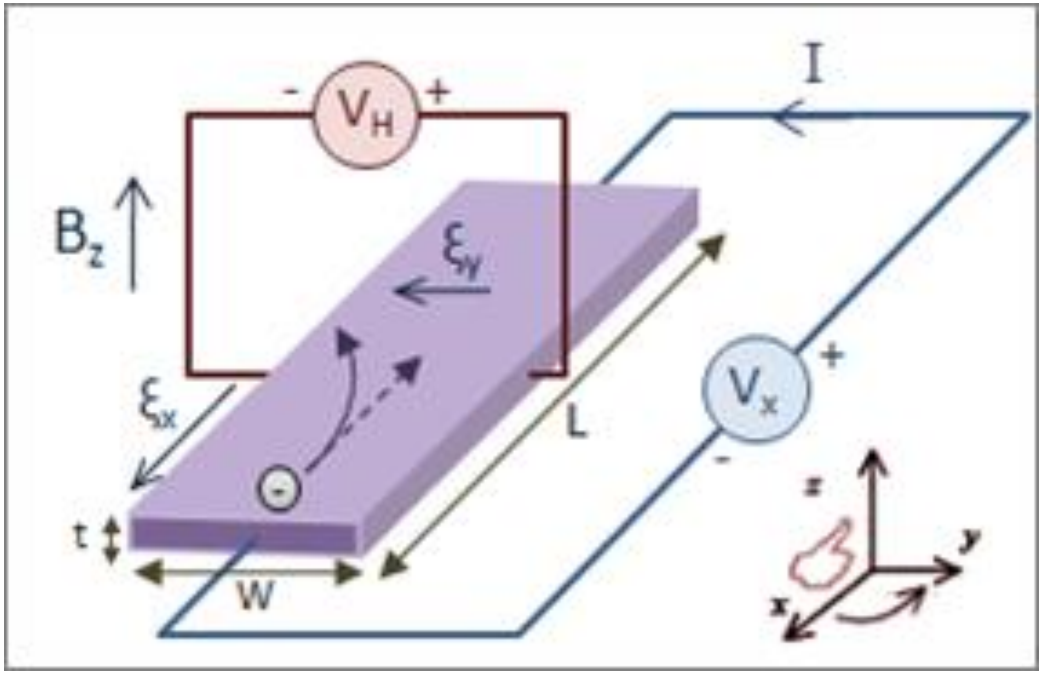


Optical characterization





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.***