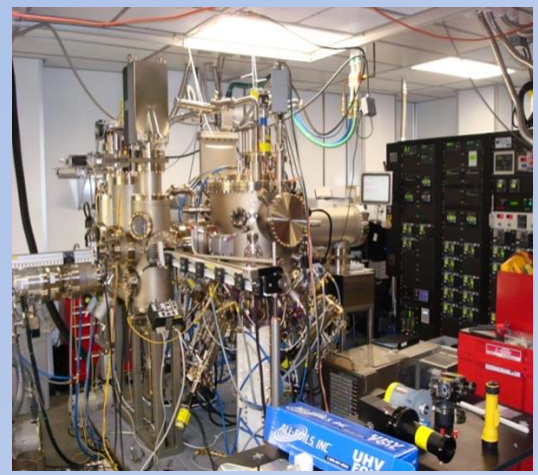
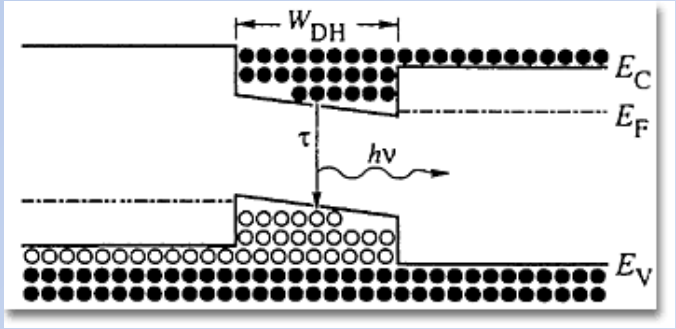
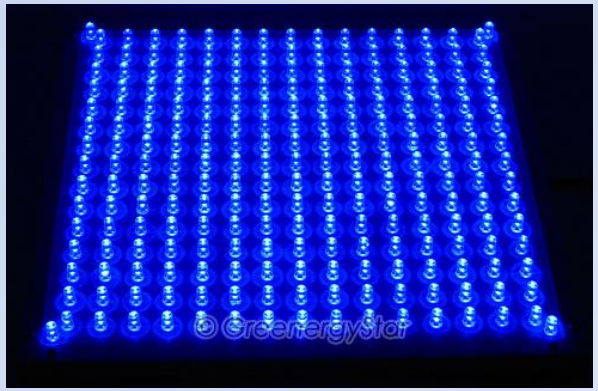
The Art and Science of Molecular Beam Epitaxy and the Nobel Prize for Blue LEDs

John Prineas
Department of Physics and Astronomy, University of Iowa
Oct 20, 2014

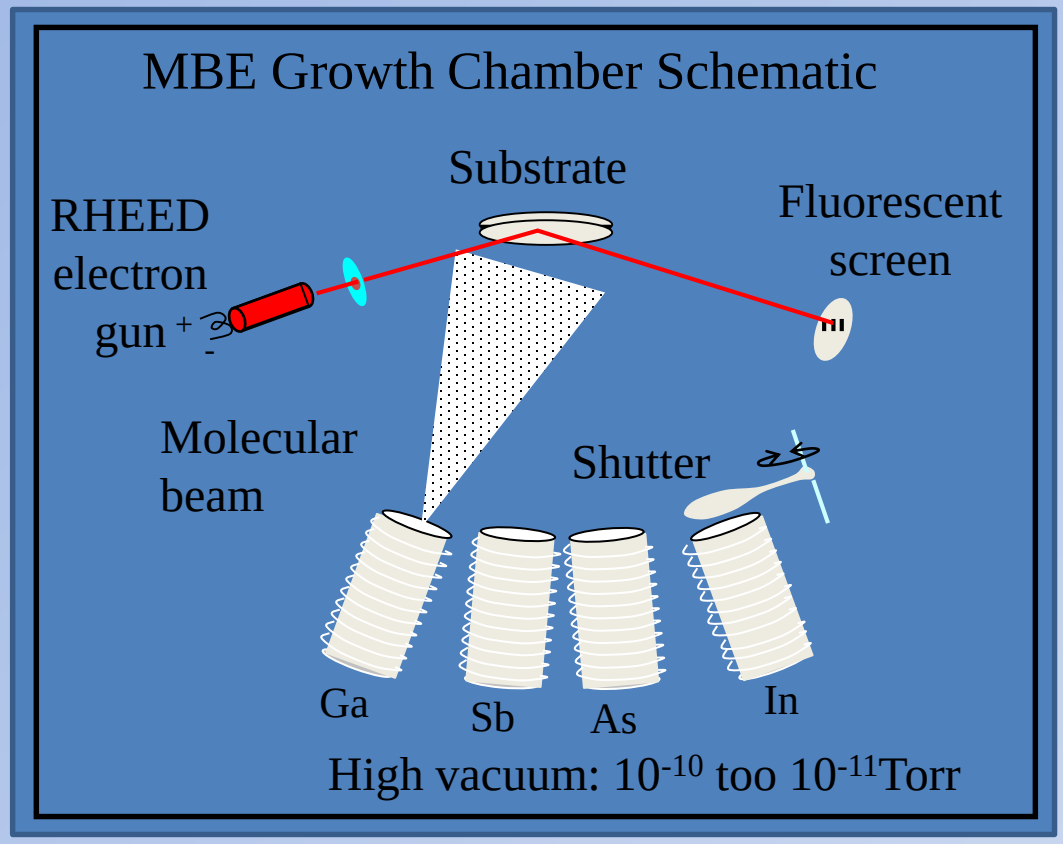




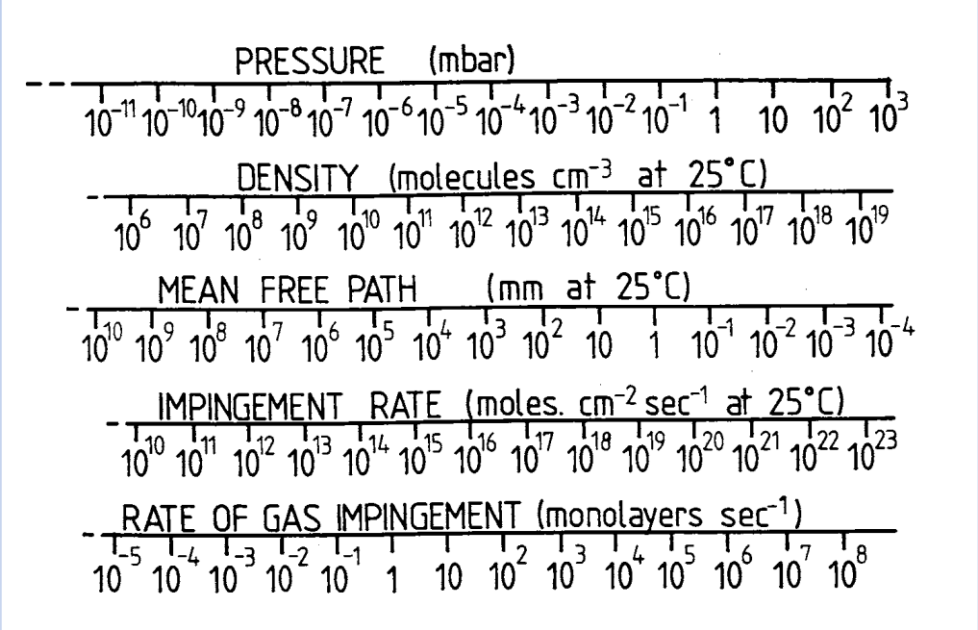


The University of Iowa

What is molecular beam epitaxy? An ultrahigh vacuum technique for deposition of atoms on a crystalline substrate to form crystalline layers or structures



Why ultrahigh vacuum?



From Kublack, Newstead, Sullivan Ch 1 in MBE Applications to Key Materials, ed. Farrow (1995)

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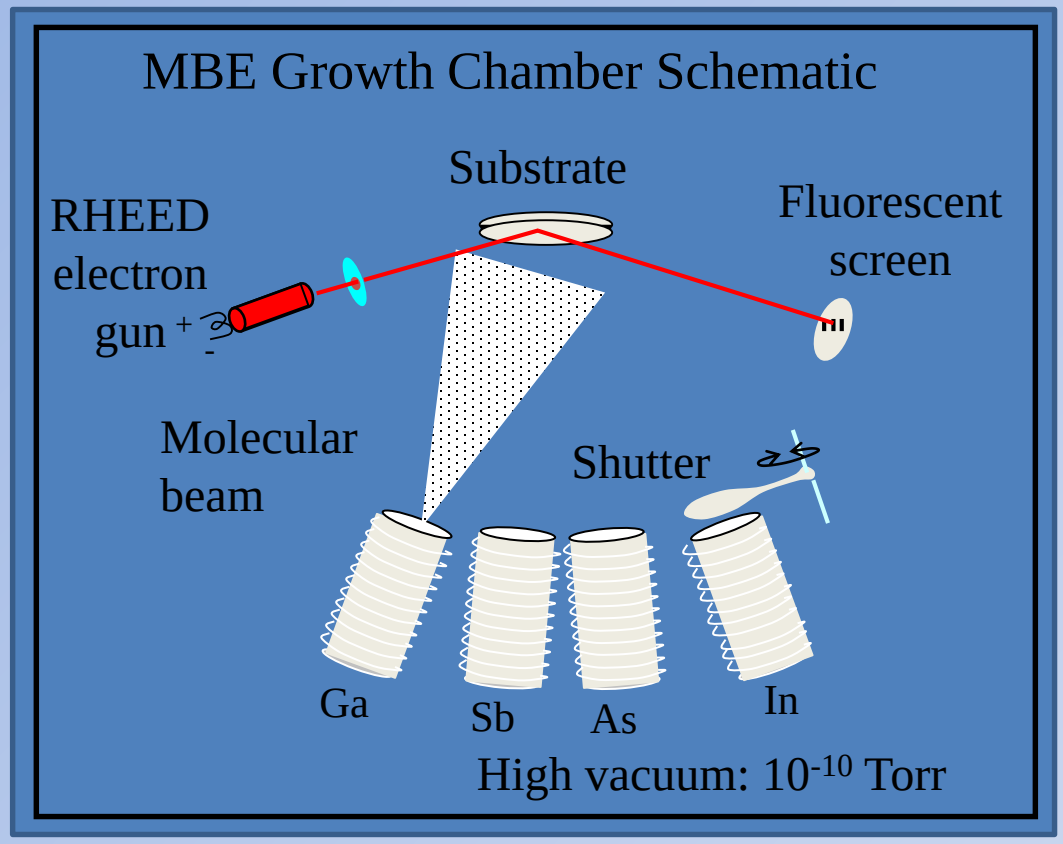
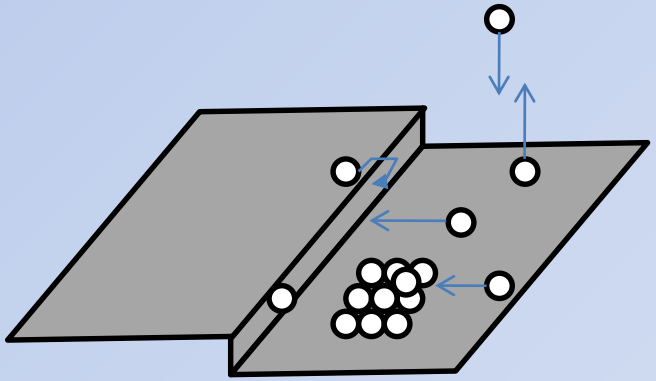
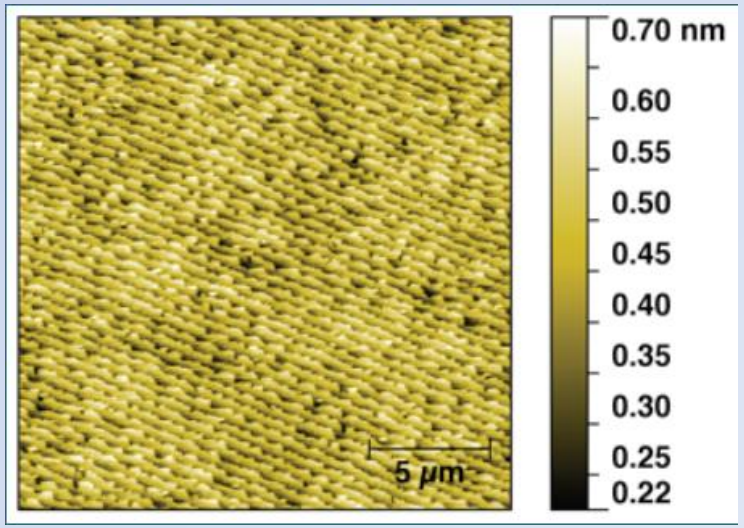


Deposition of compound semiconductor layers with single atomic layer precision





Step flow across a GaSb MBE layer

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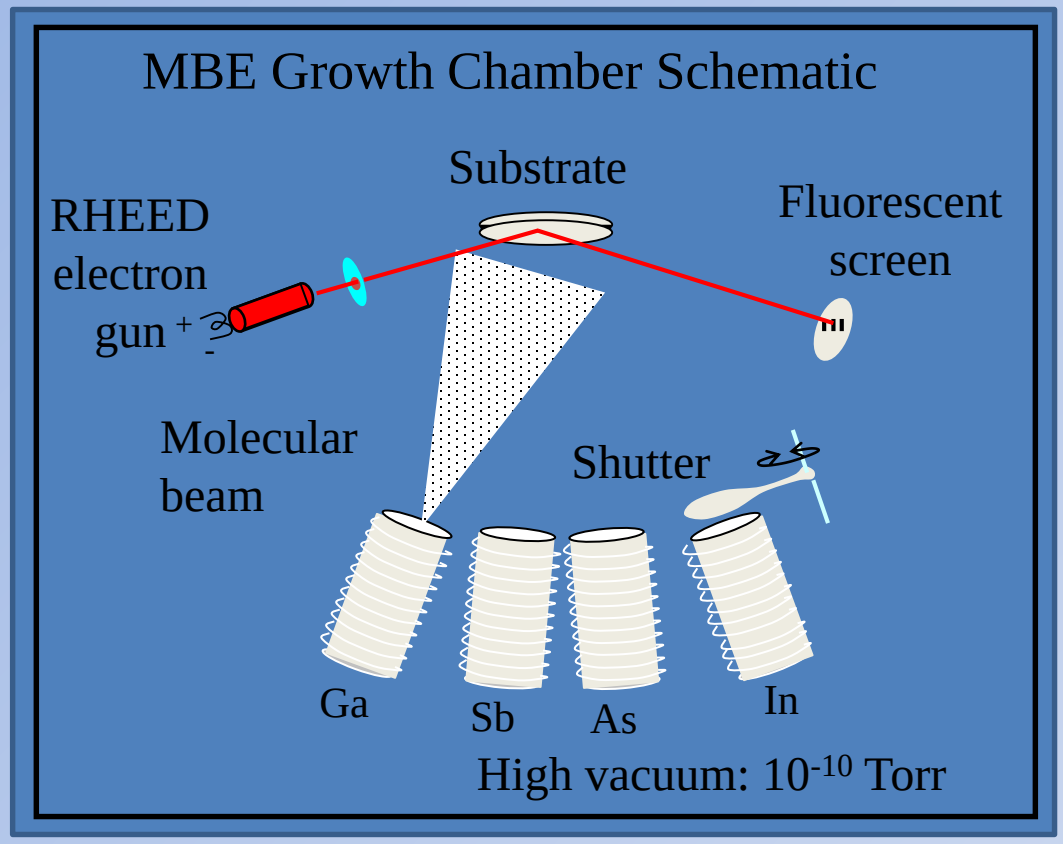
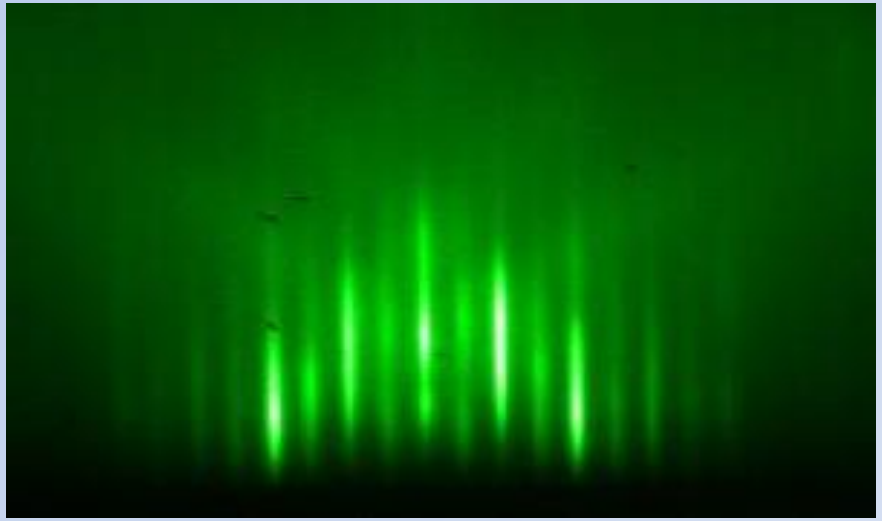


Reflection high energy electron diffraction



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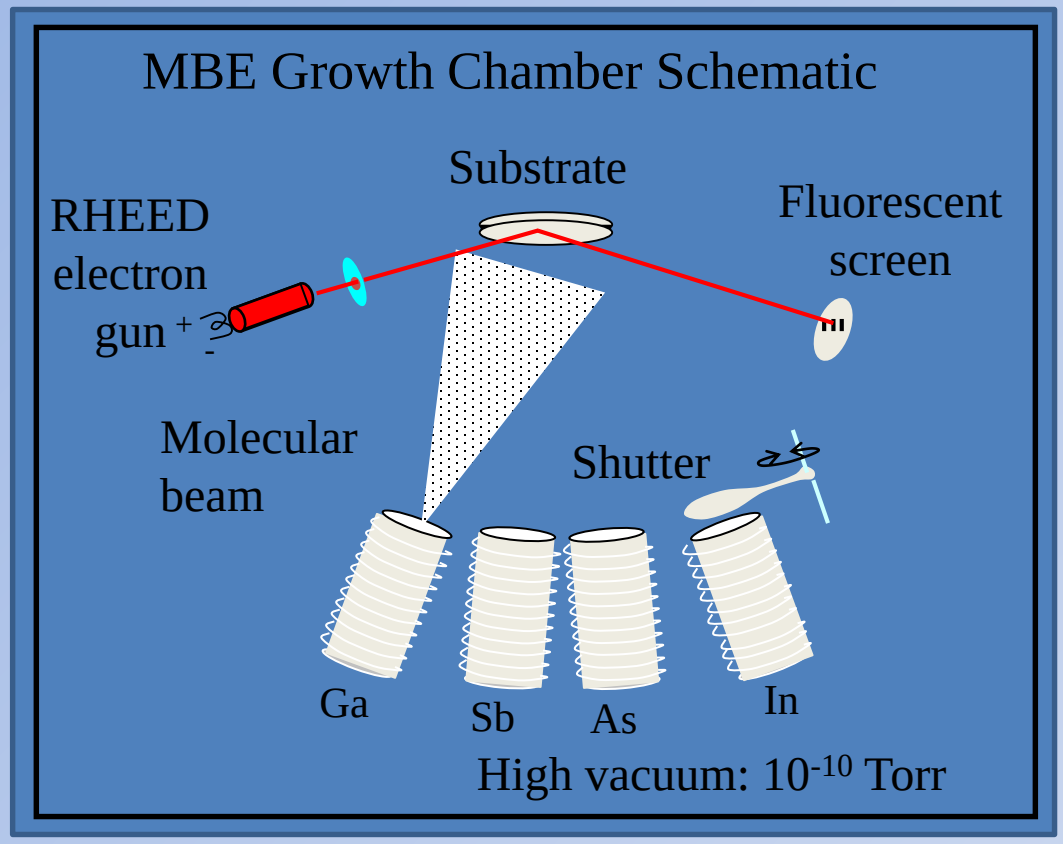

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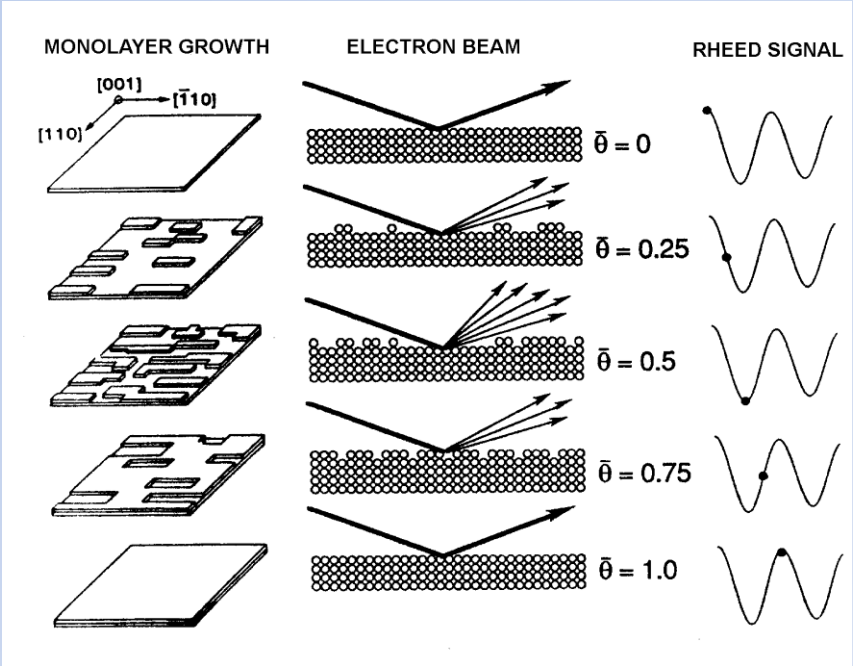

Neave, J. H., Joyce, B. A., Dobson, P. J., and Norton, N., *Appl. Phys.,* A31 :1-8 (1983)

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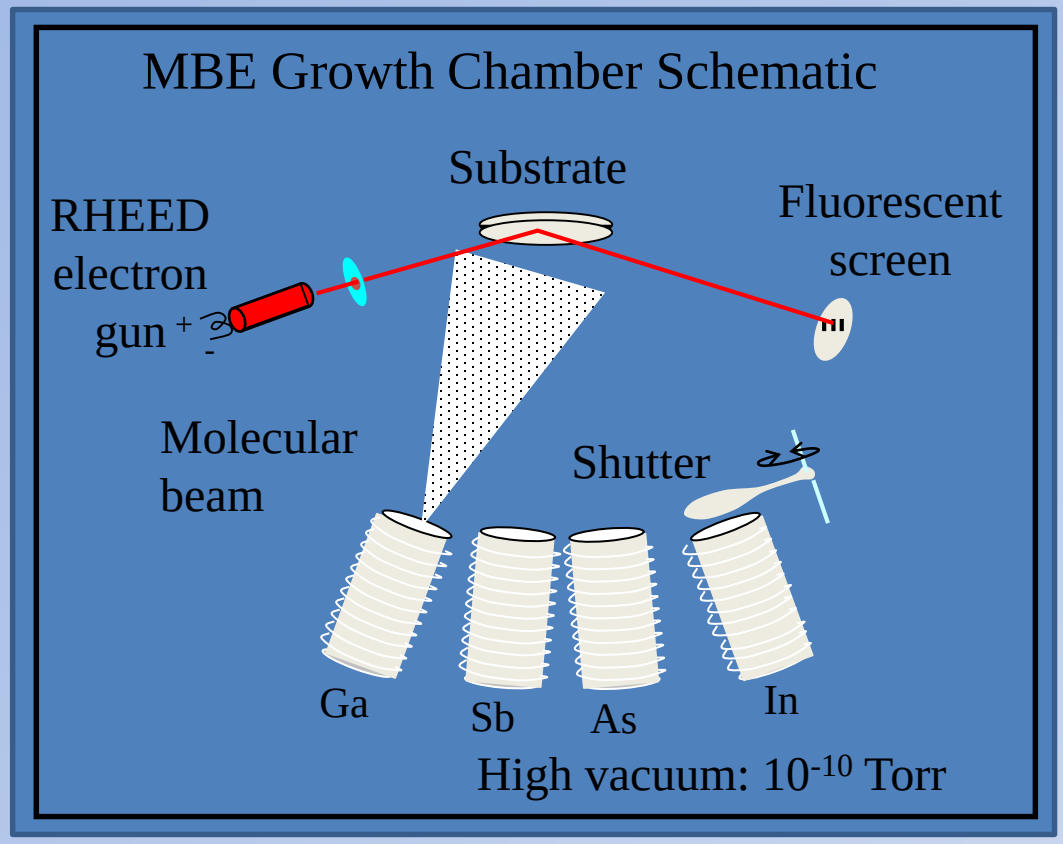

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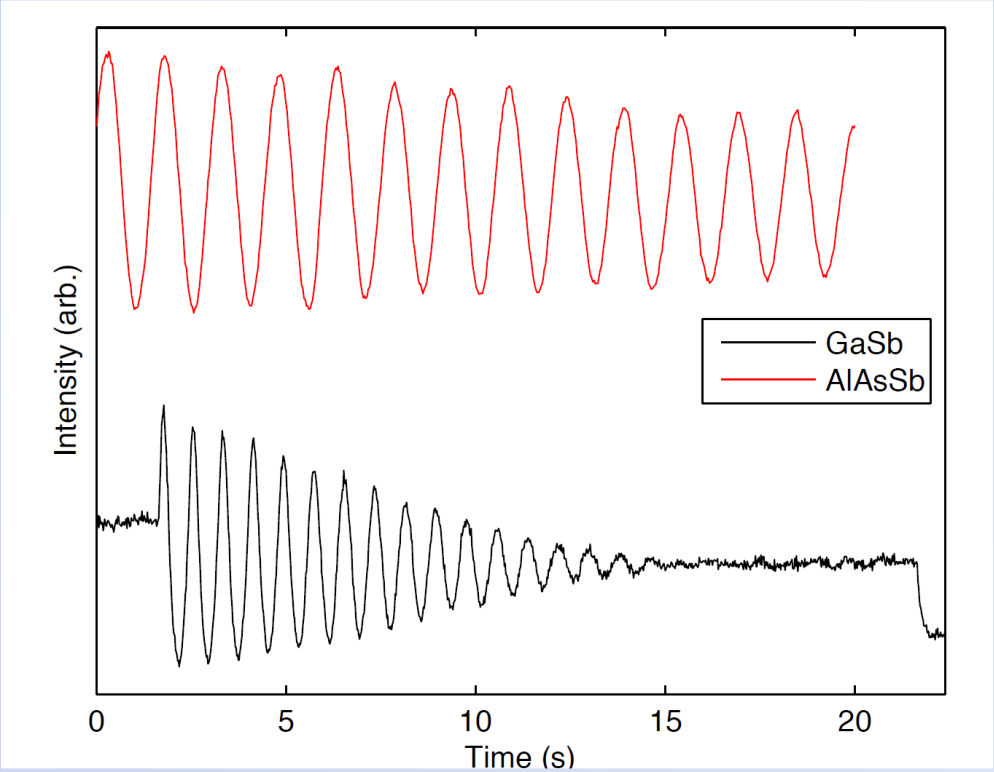
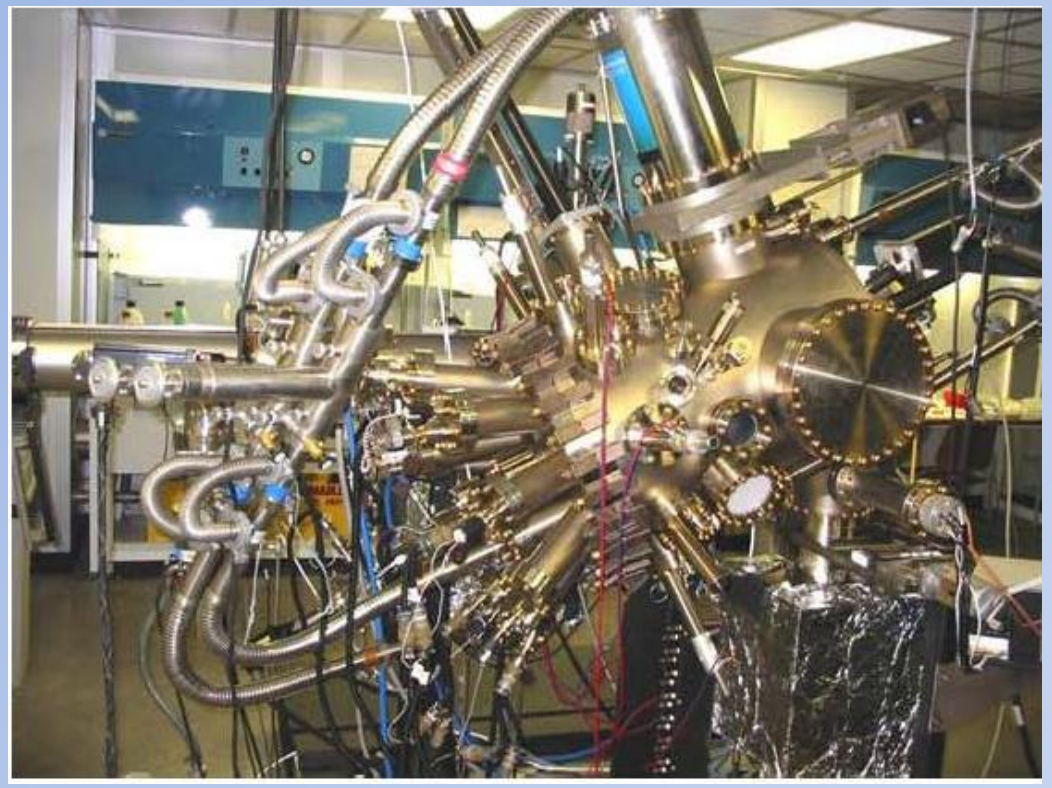
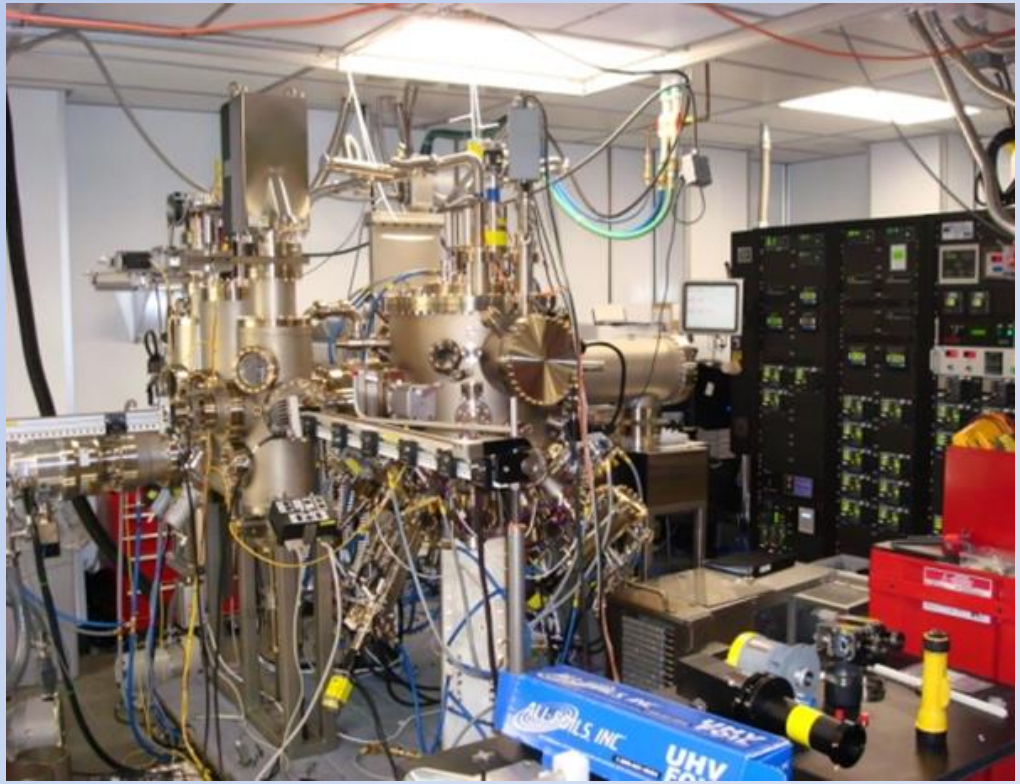


A quick tour of the MBE facilities at the University of Iowa:

EPI930



GEN20



Commercial VEECO machines from headquarters in Minneapolis, MN; one of two principle worldwide suppliers, along with Riber

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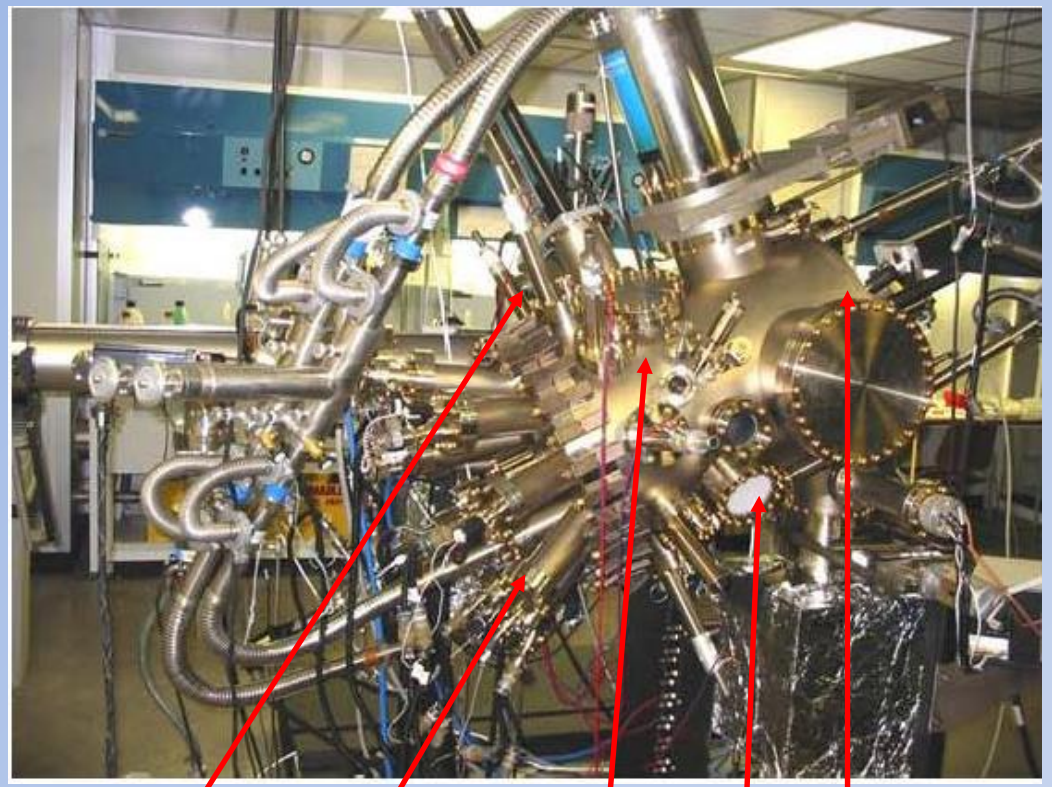


Shutter control

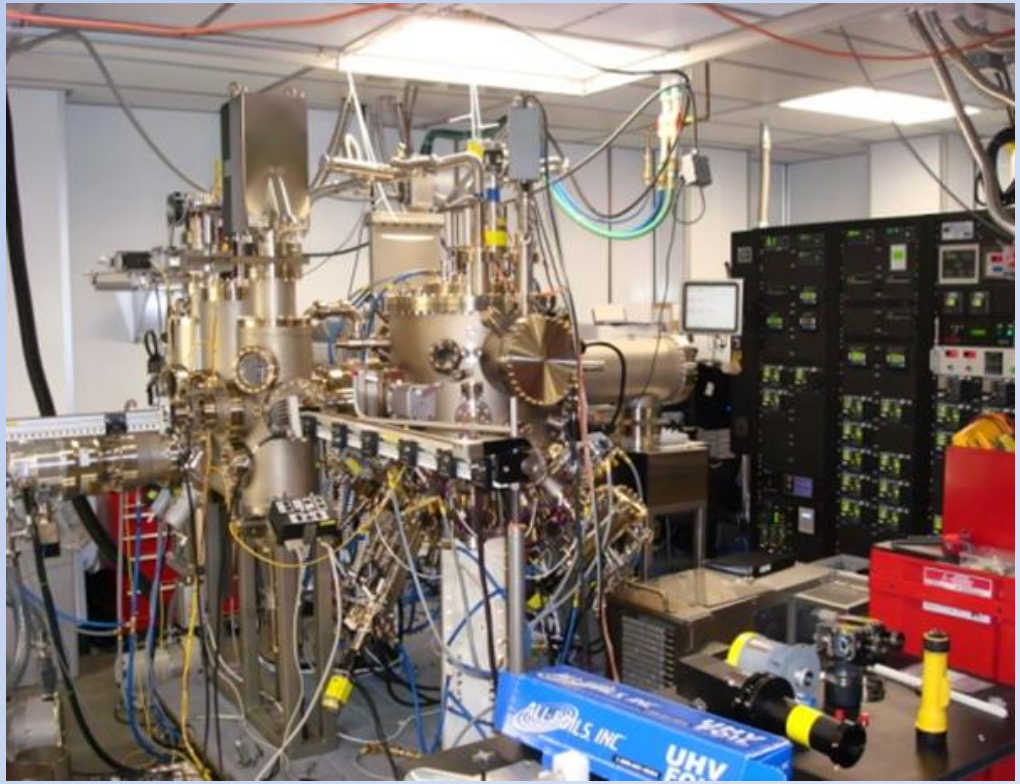
High purity sources

Vacuum chamber

RHEED screen

Substrate manipulator

GEN20



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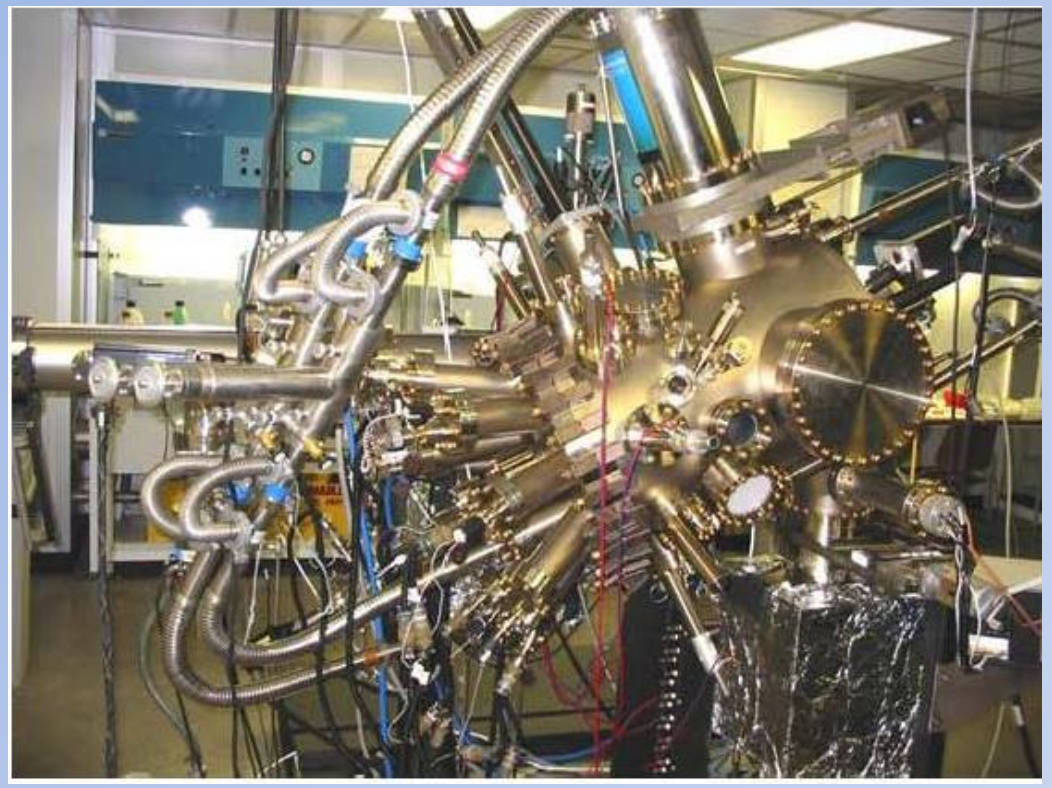

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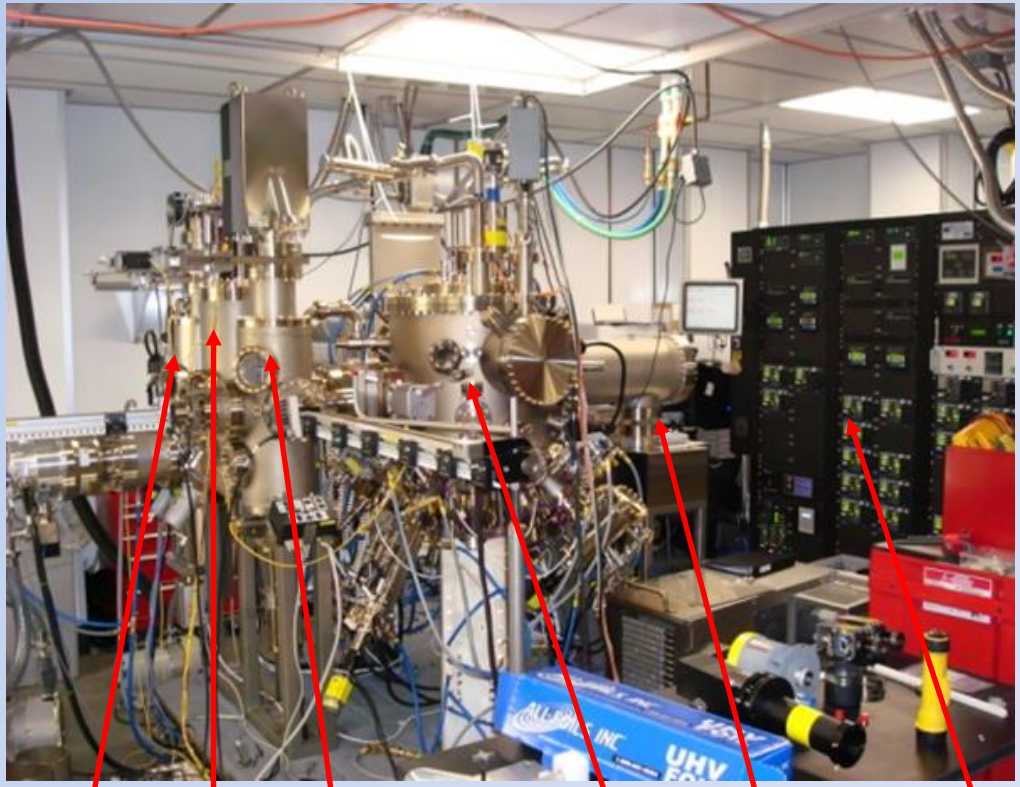

Intro chamber

Prep chamber

Storage chamber

Growth chamber

Computer control

Electronics rack

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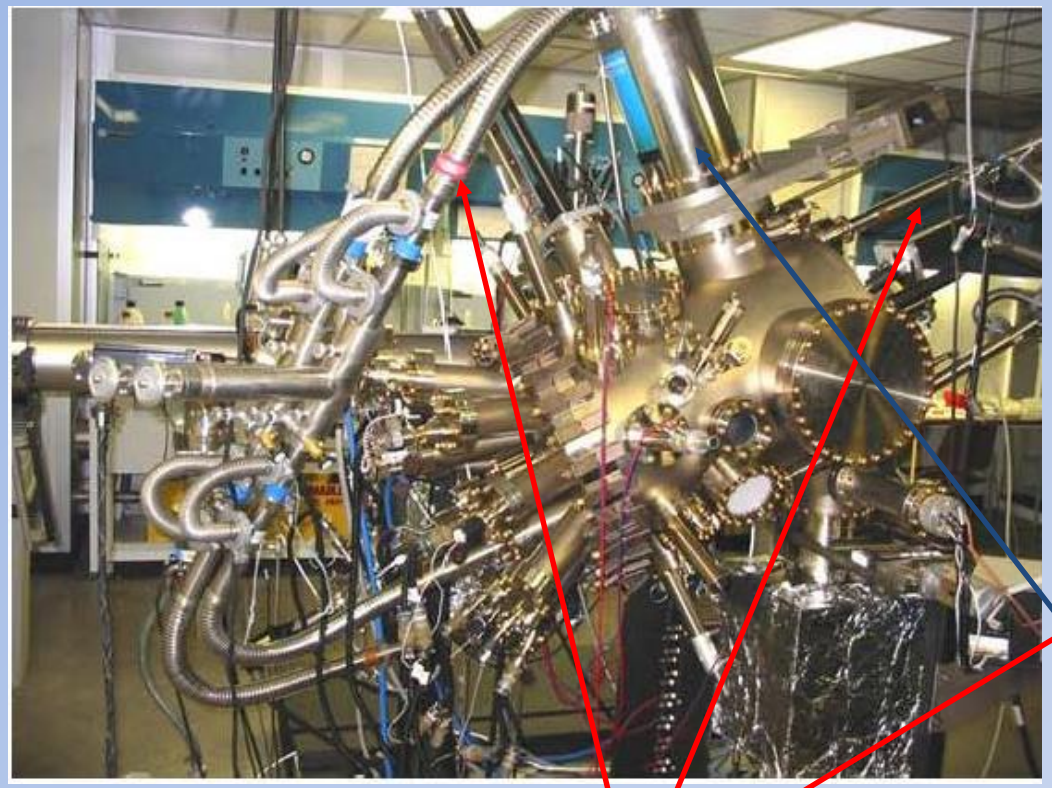

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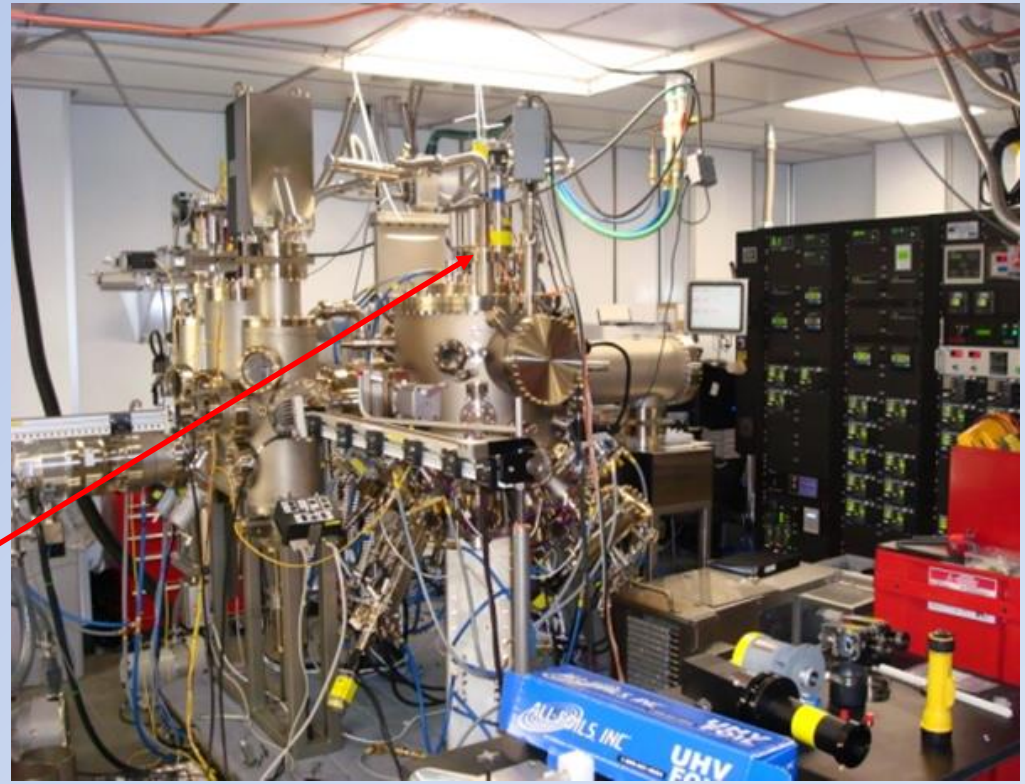


Liquid nitrogen lines

Closed cycle He cryopump

Group III Knudsen cell and group V cracker cell

Group III K-cell

PBN crucible

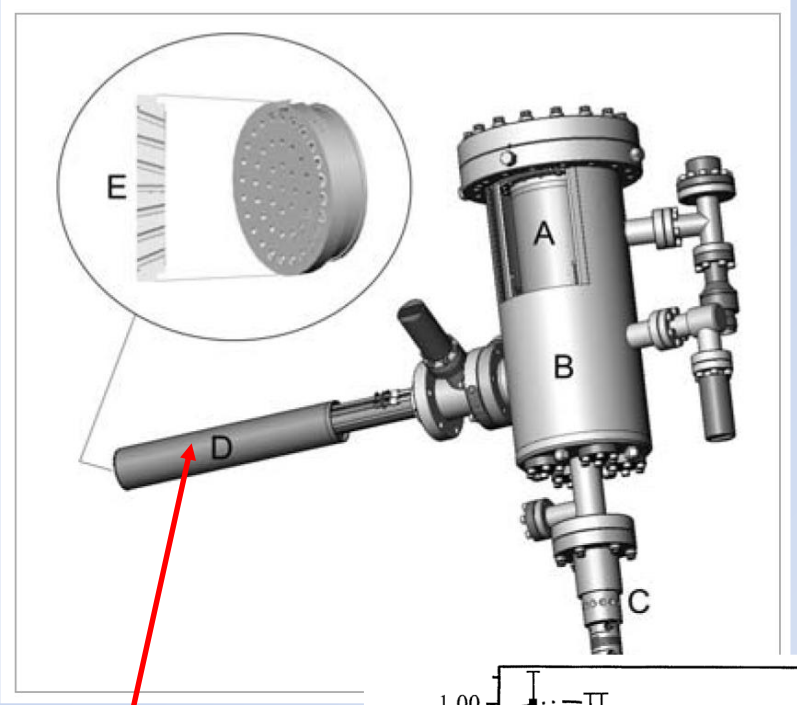
Power feedthrough

Thermocouple feedthroughs

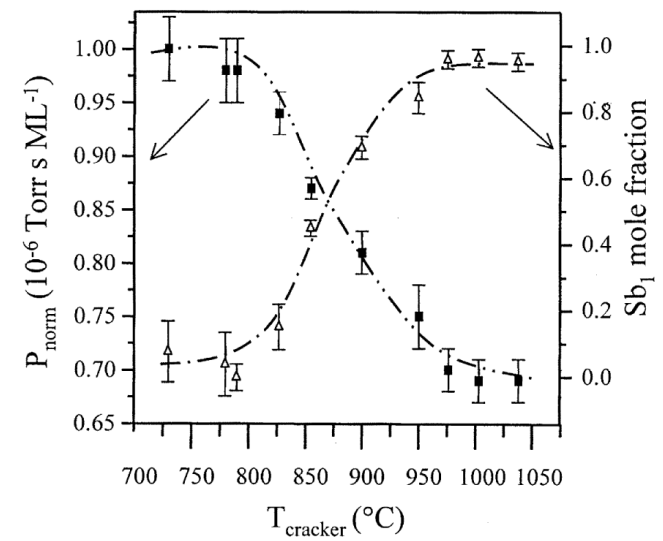
$$Flux \propto p_0 \exp(-L_0/RT)$$

L_0: latent heat of vaporization
R: gas constant
T: temperature

Group V cracker cell



Cracking zone



Where did MBE come from?

- Invented in 1968 by John Arthur (from Iowa State University) and Alfred Cho at Bell Laboratories
  - Arthur: UHV technique for surface science
  - Cho: RHEED and growth of device quality materials
- Built upon principles from materials thermodynamics, metallurgy

- The Delhi iron pillar was forged in 500 CE from wrought iron, but has never rusted.

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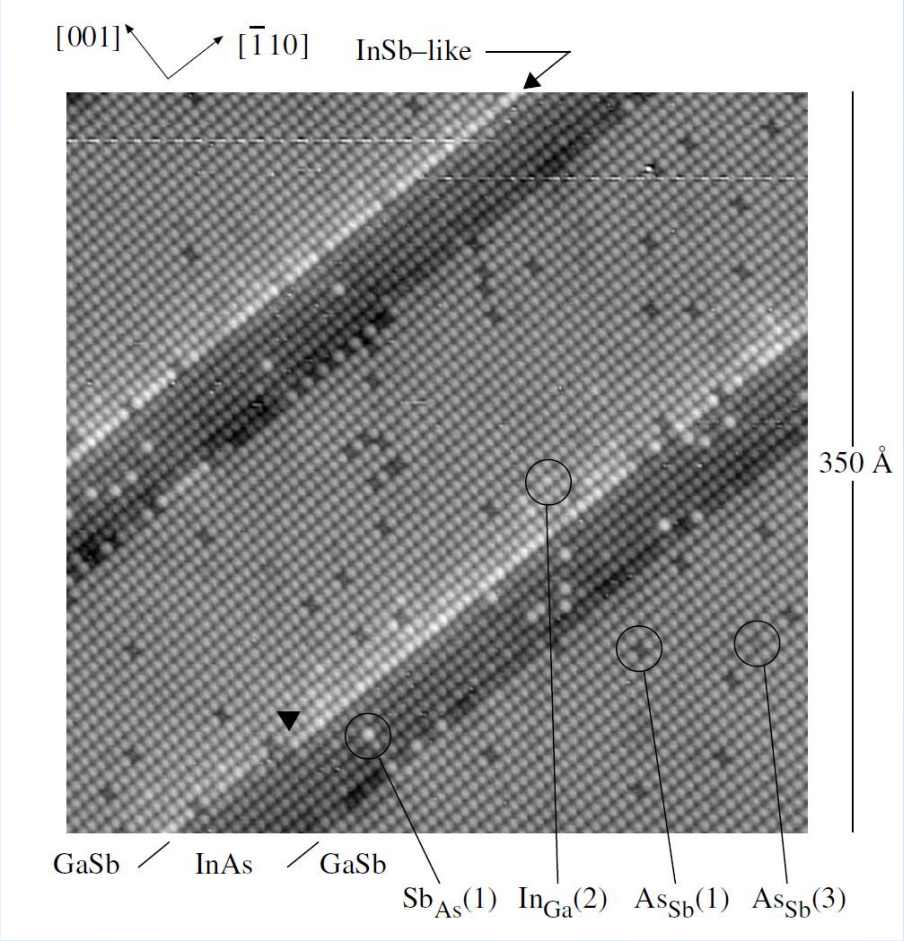
- Technique has evolved with the invention of powerful vacuum and surface analysis technologies: mass spectrometry (1950's and 60's), RHEED, scanning tunneling microscopy (early 1980's), atomic force microscopy (late 1980's)

- Scanning tunneling microscope cross section of InAs/GaSb superlattice (Steinshnider etal, PRL 85, 2953 (2000))



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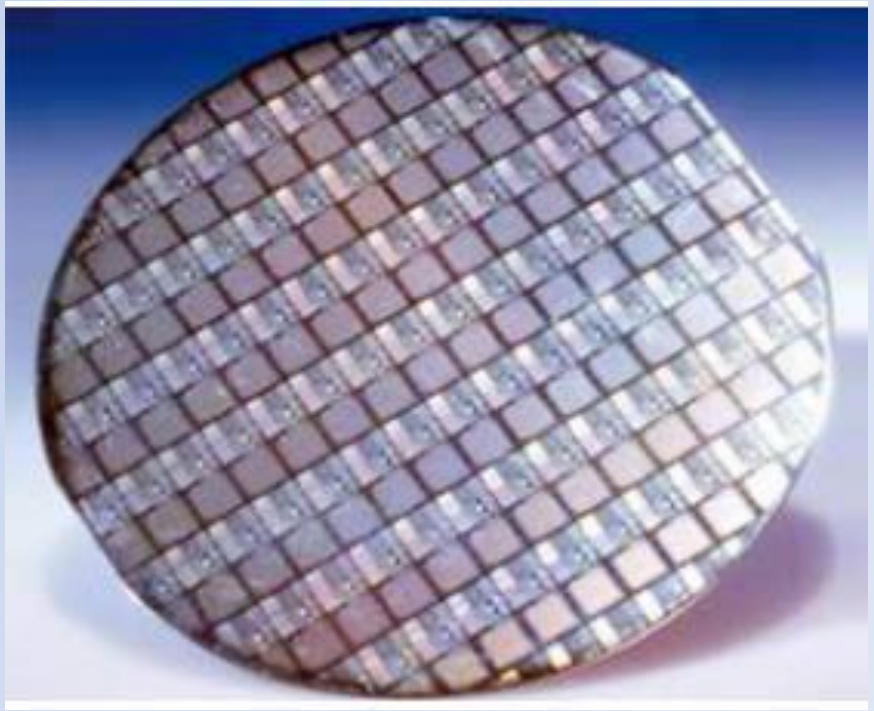
- Key technology for research, development, and industrial production of compound semiconductor materials for solid state devices such as laser diodes, light emitting diodes, detectors, solar cells, and transistors



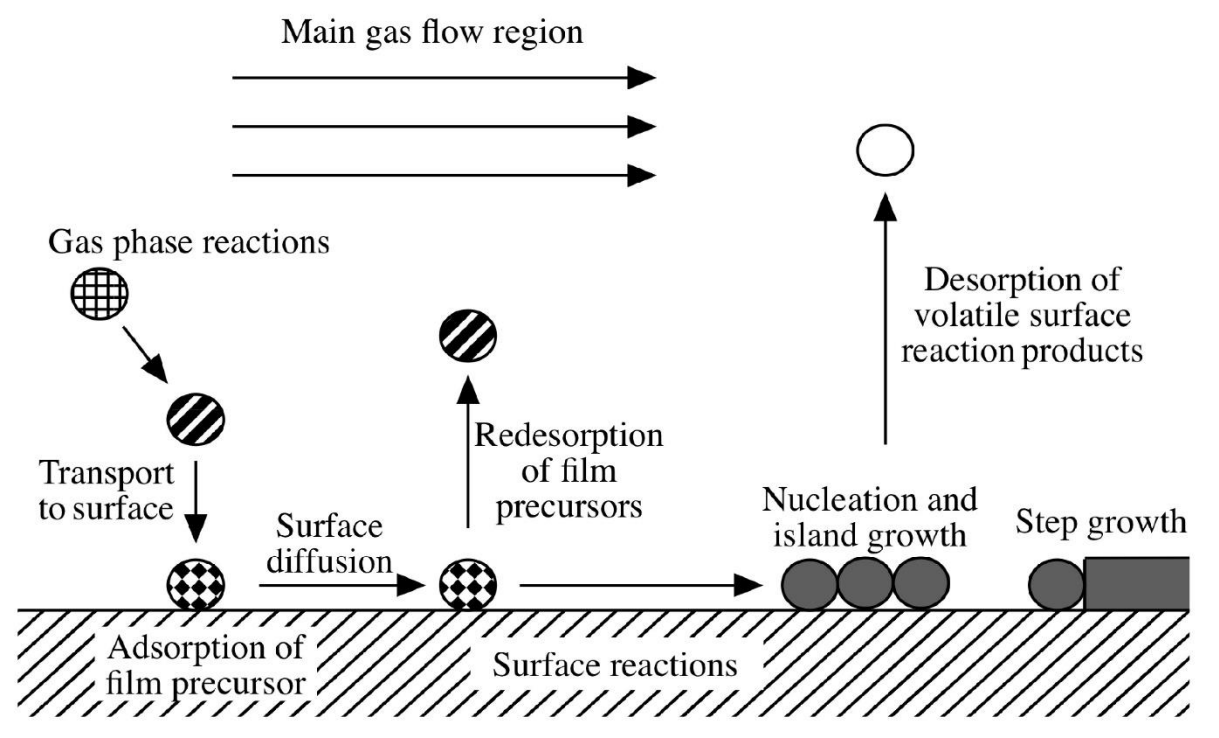
- GaAs pHEMT wafer

Metal organic vapor phase epitaxy: flexible, high throughput technique

Source gases:

$Ga(CH_3)_3$
$In(CH_3)_3$
$Al(CH_3)_3$

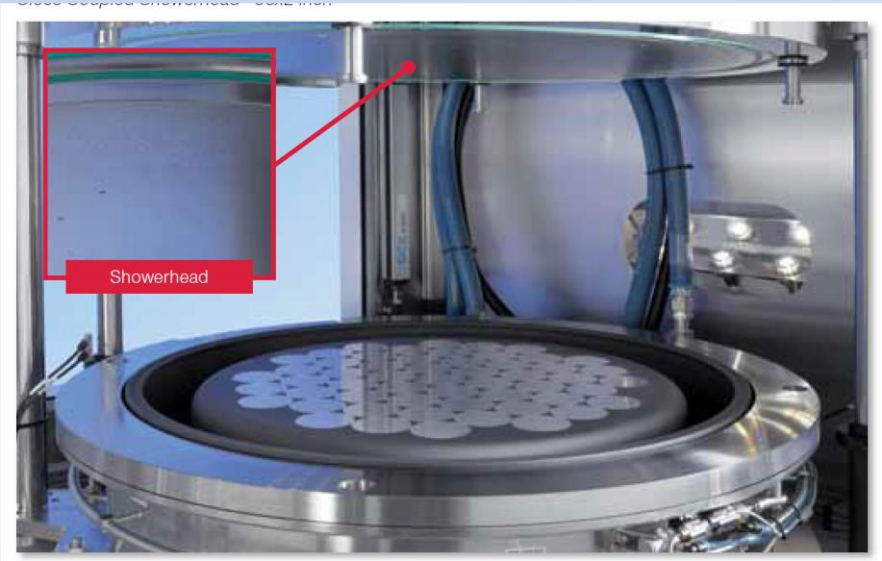
SiH_3
AsH_3
PH_3
NH_3



- Metal + precursor gas carried to substrate
- Moderate growth rates (1-10 um/hr)
- Good uniformity, high throughput

- Thin layers, but less abrupt interfaces
- In-situ monitoring harder (high pressure)
- Toxic gases
- Higher growth temperatures

- Dominant technology for solid state lighting



55x2” showerhead growth chamber

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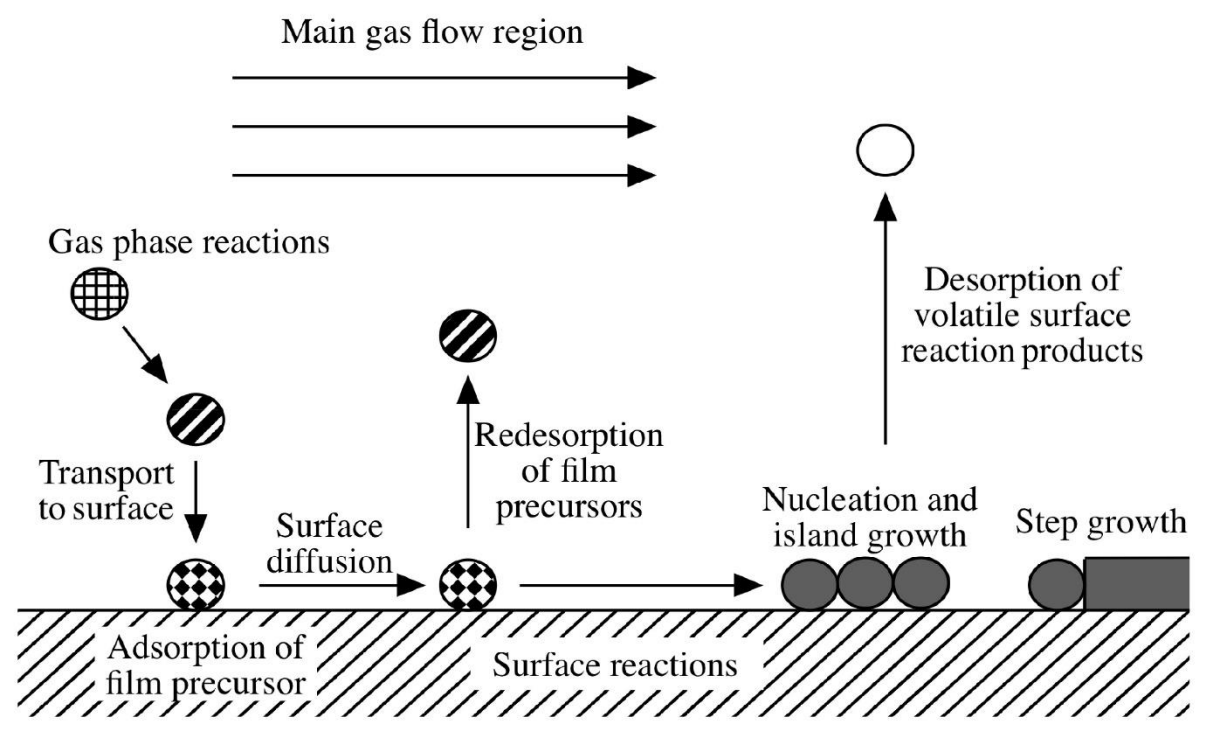

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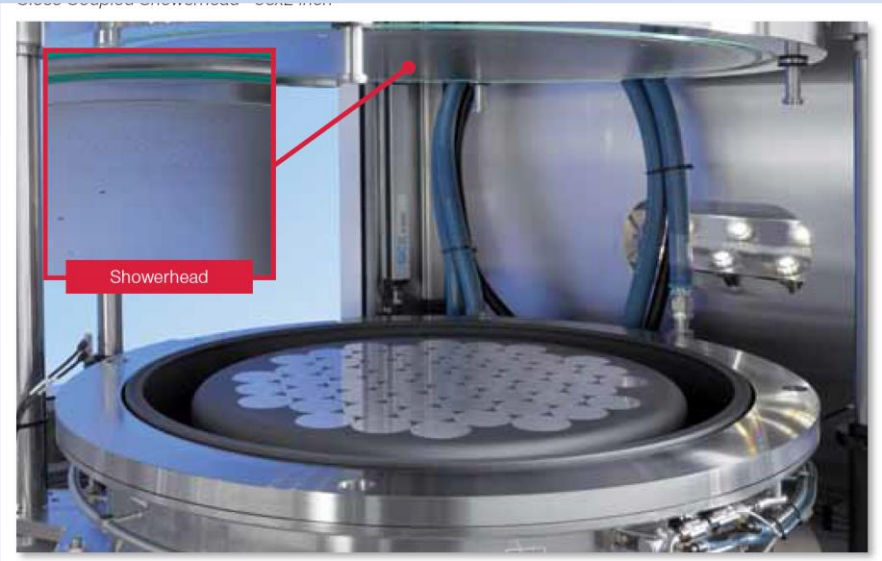


55x2” showerhead growth chamber

- MBE is a more flexible technique used prominently in research, for growth of materials with very thin layers with abrupt interfaces, and for better per wafer layer uniformity.

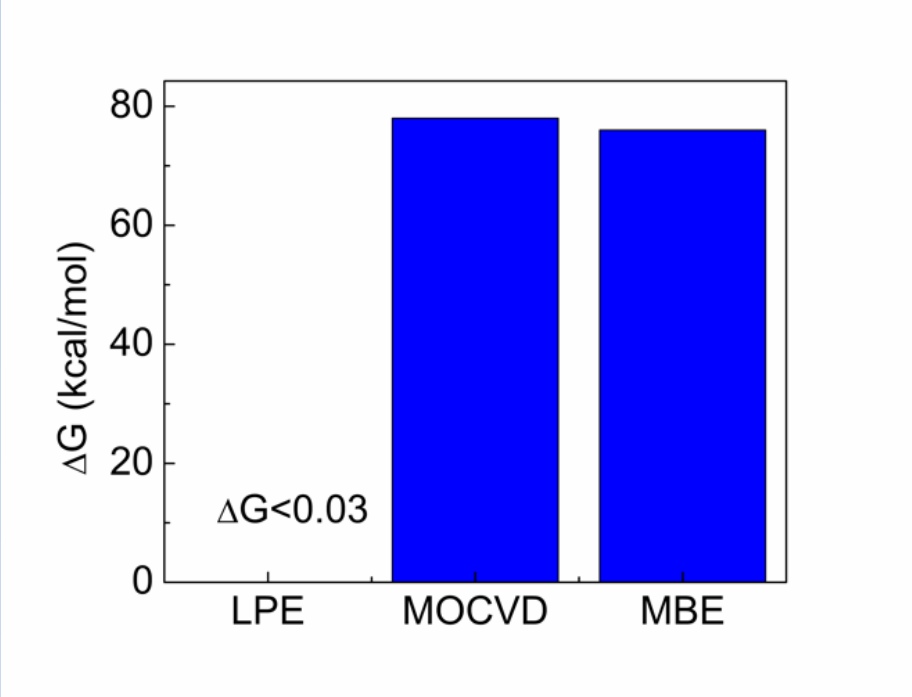
MBE is considered to be a nonequilibrium growth technique, similar to metal organic vapor phase epitaxy (MOVPE) but unlike liquid phase epitaxy due to large driving force for crystal growth

Driving force for epitaxy:

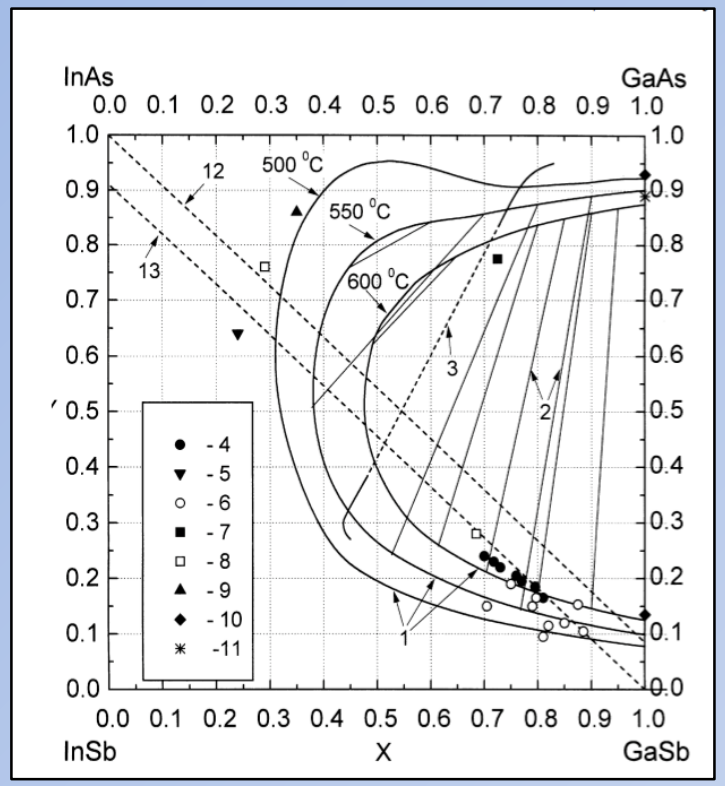
$$\Delta\mu_{driving} = \mu_{products} - \mu_{sources}$$

- μ is the chemical potential
- Sources are molecular beams from the K-cells
- Products are the crystal layers that form on the substrate

Growth phase determined by surface thermodynamics rather than by bulk thermodynamics



MBE can be used to grow thermodynamically unstable alloys



- Binodal isotherms (1) for GaInAsSb.

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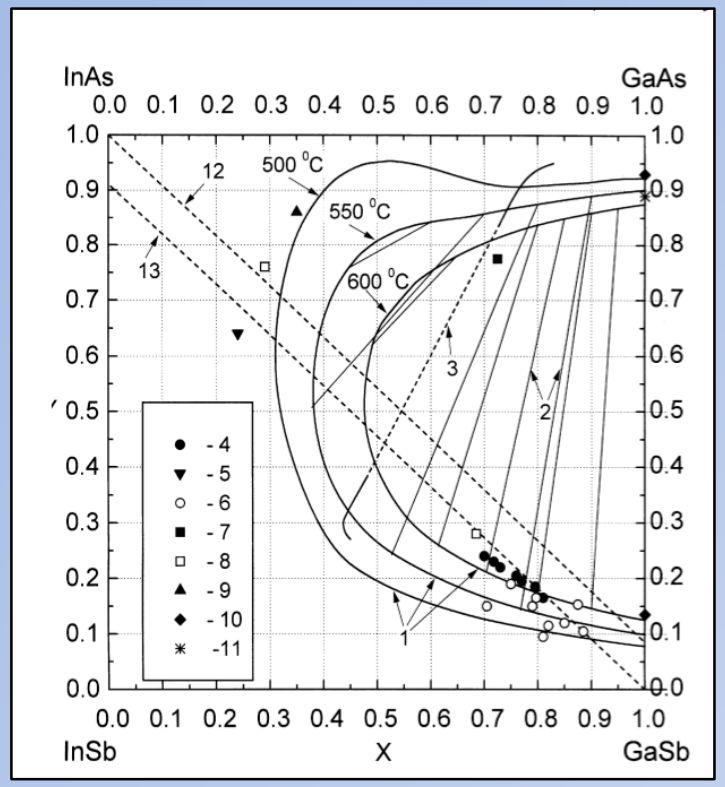

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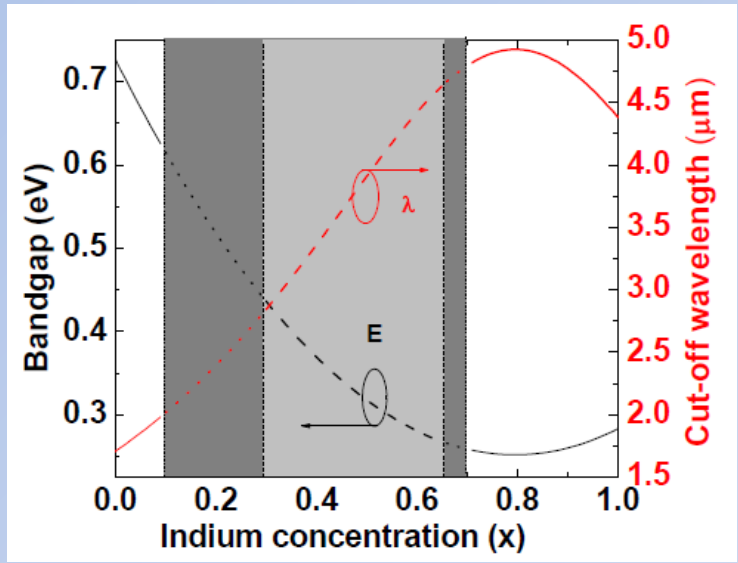

- Ga(1-x)In(x)As(y)Sb(1-y) lattice-matched to GaSb for growth at 500 C
- Stable alloy (white), metastable (dark grey), stable (light grey)

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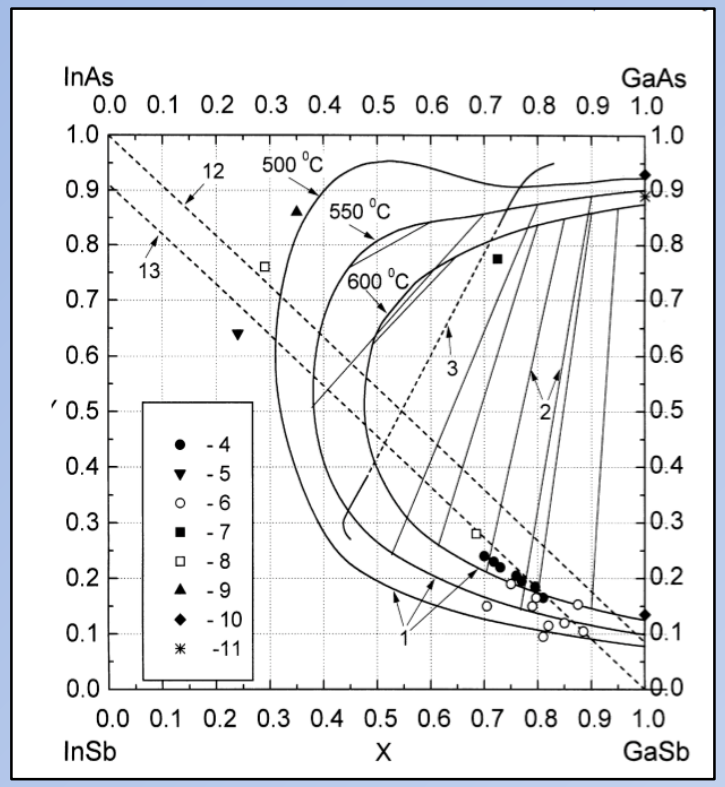

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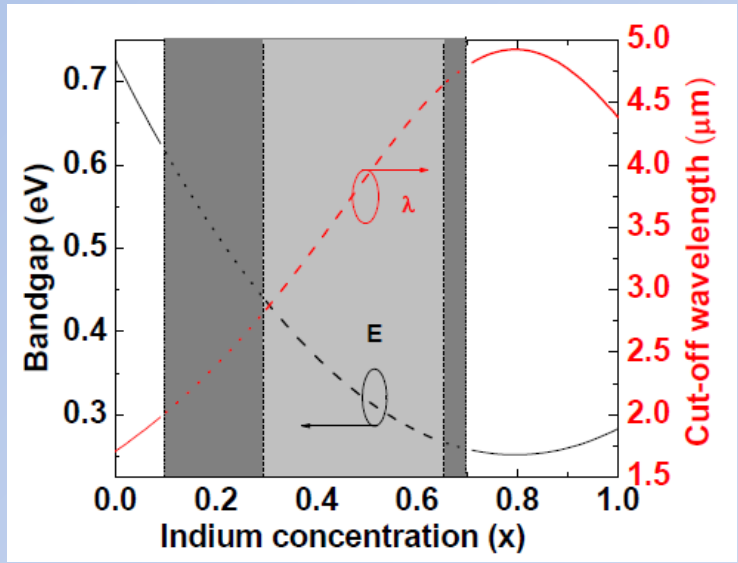

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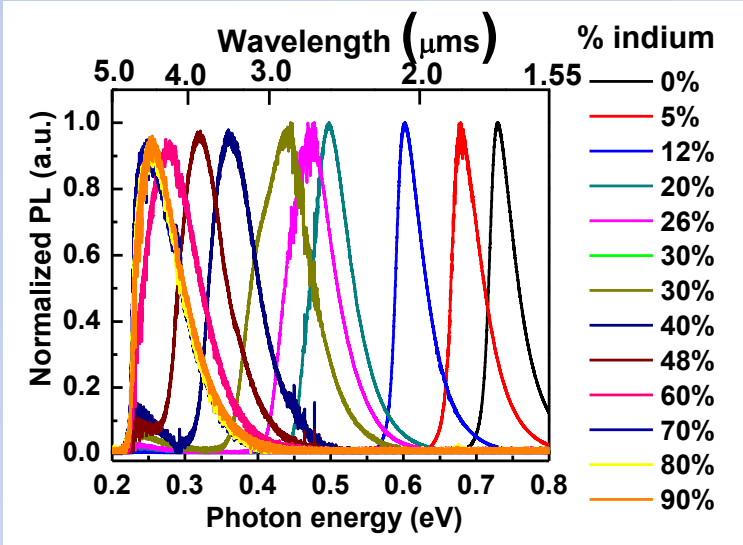
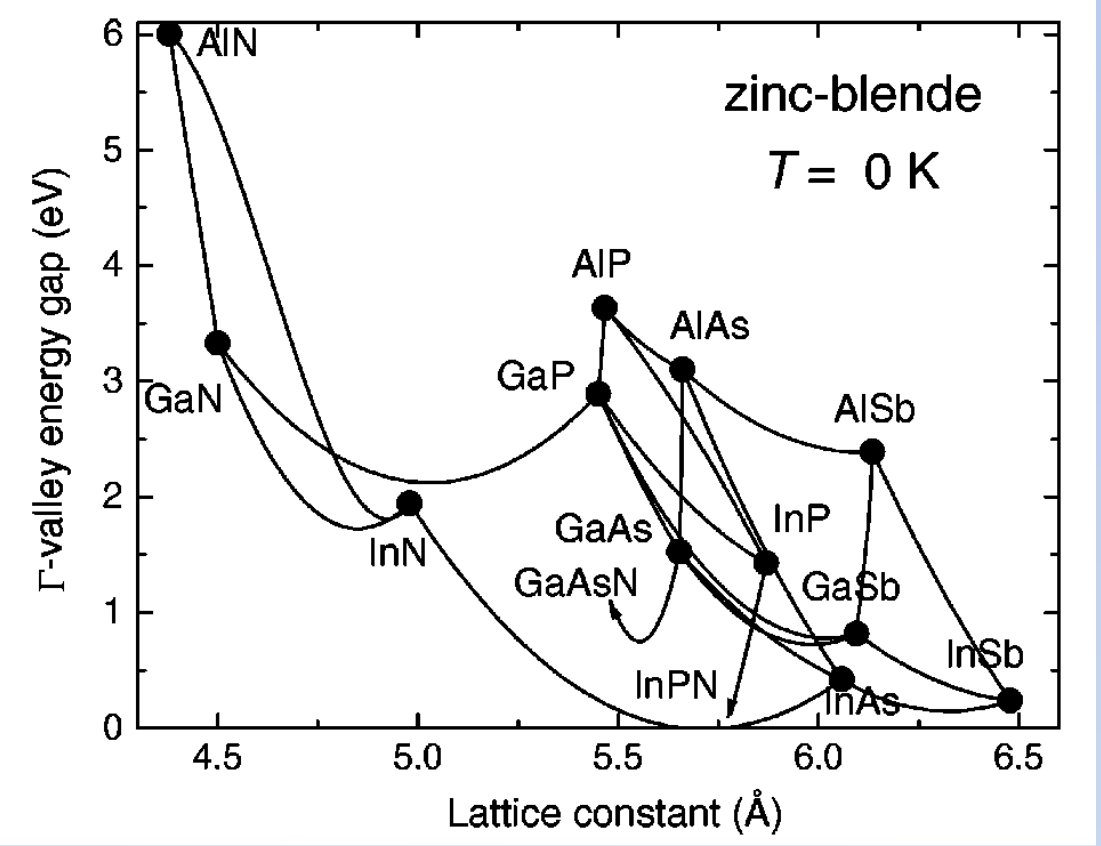
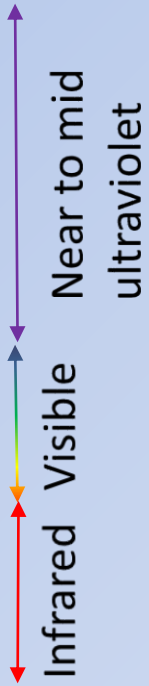


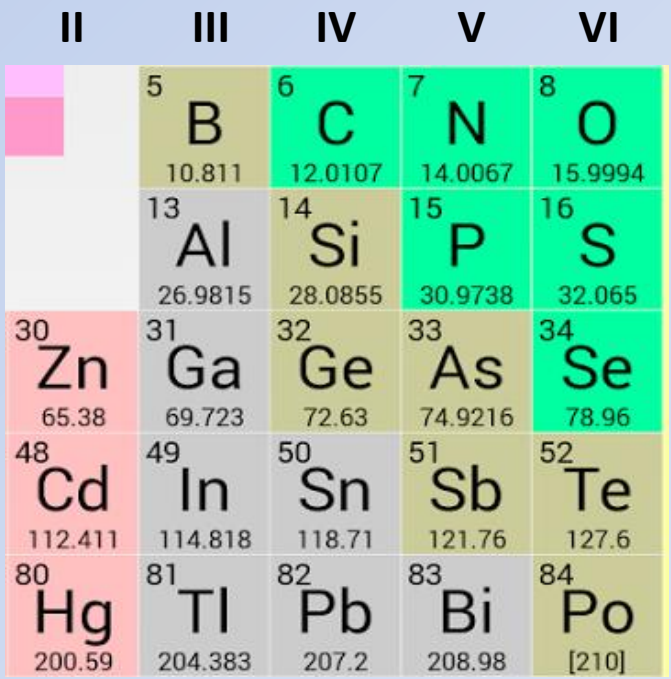
- We used MBE to grow high quality alloys across the compositional range at 400-450 C
- Room temperature photoluminescence across compositional range

Epitaxial growth unleashed an explosion of materials research and engineering that vigorously continues to this day

Group III-V compound semiconductors have very good optical properties compared to e.g. group IV







Vurgaftman etal, *Appl Phys Lett* **89**, 5815 (2001)

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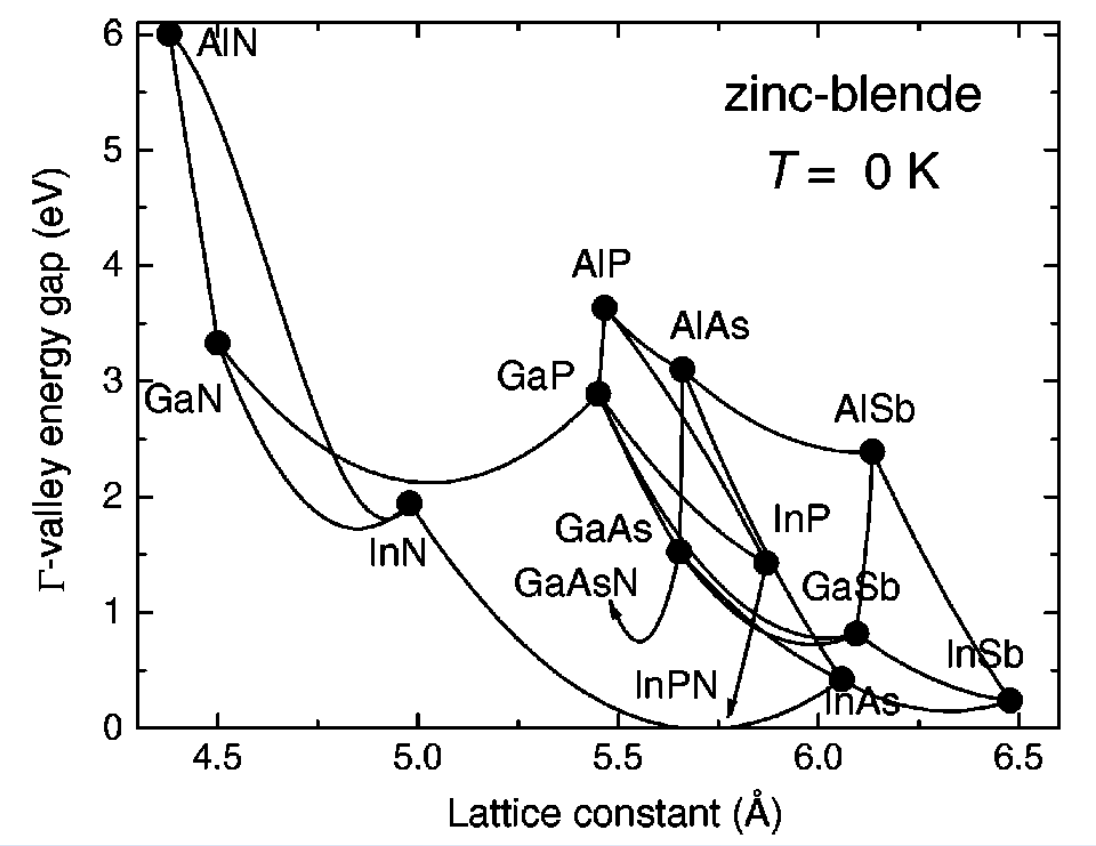

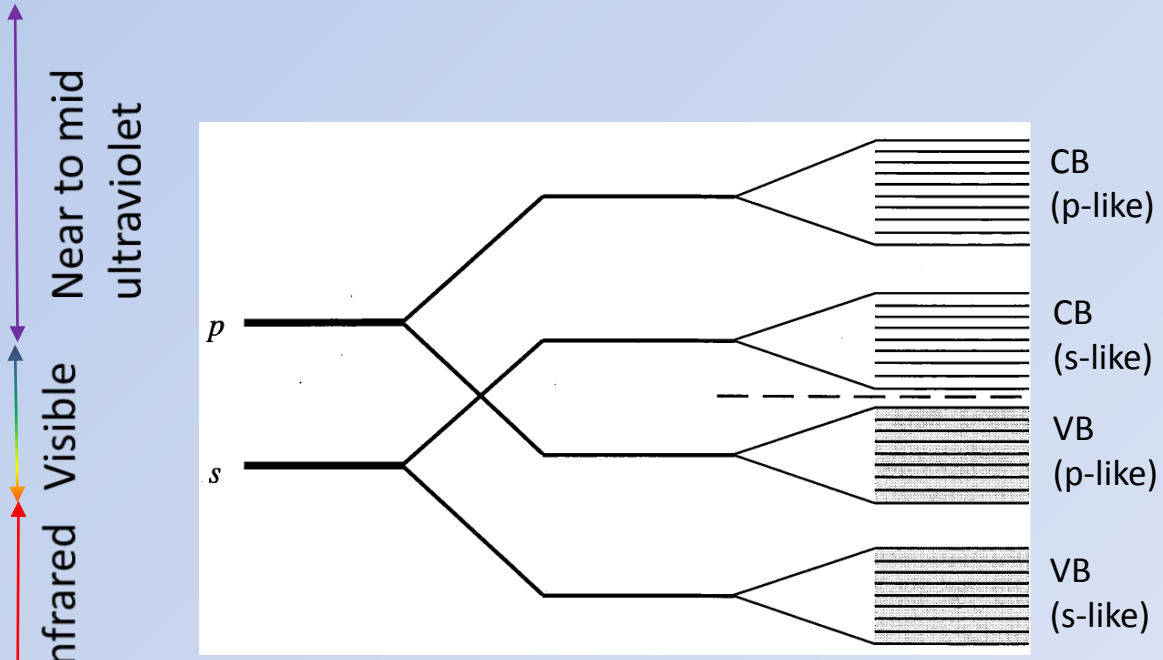

Discrete molecular energy levels broaden into energy bands in crystalline solid

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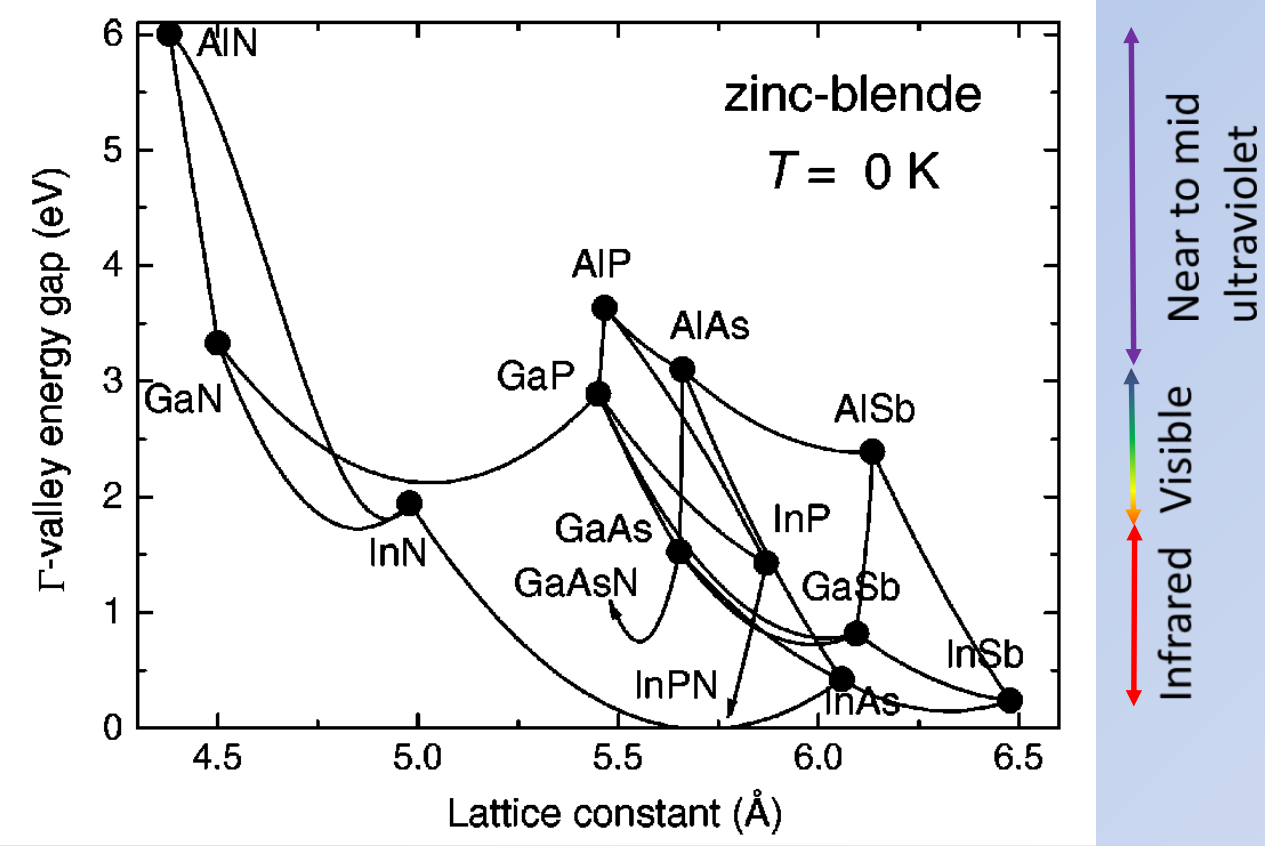
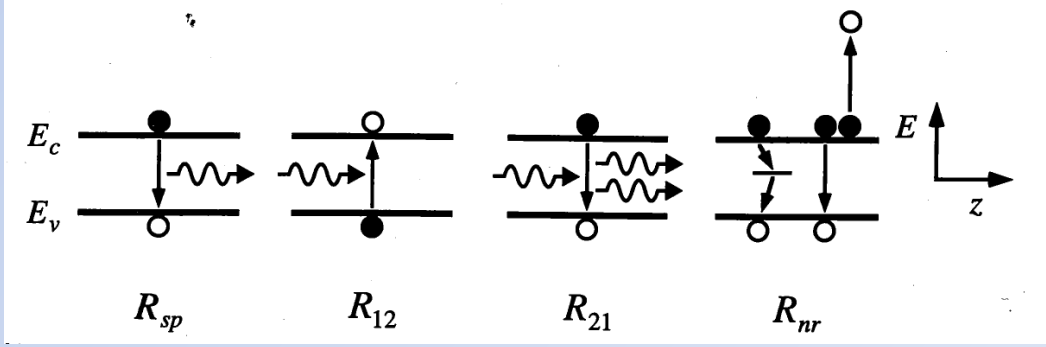


- Transitions of electronic carriers between bands can generate light (radiative) or heat (nonradiative)
- Energy gaps in binary semiconductors span the infrared through the mid-ultraviolet.



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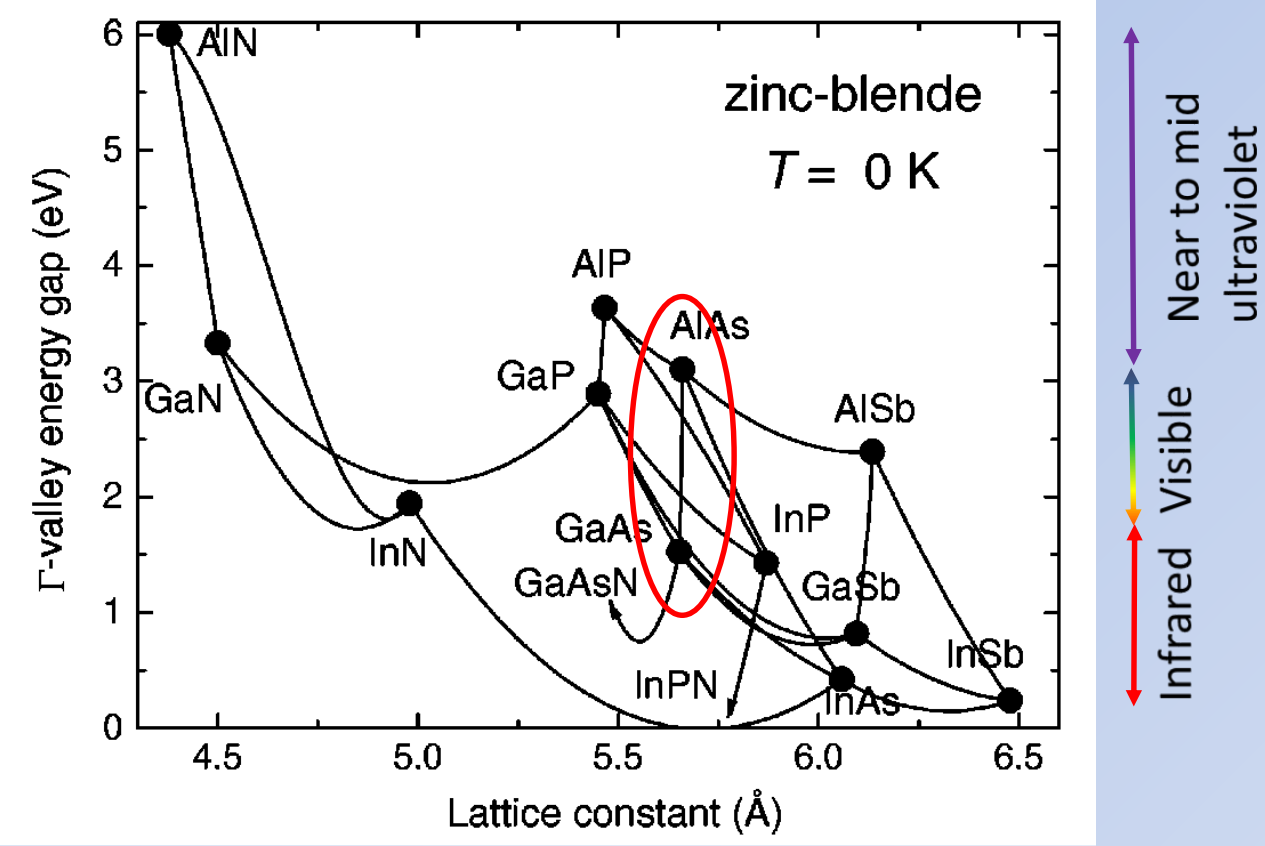

5.65 Å materials (GaAs substrate)

Initially, materials with nearly the same lattice constant such as GaAs/Al(Ga)As stacked together in a layered heterostructure.

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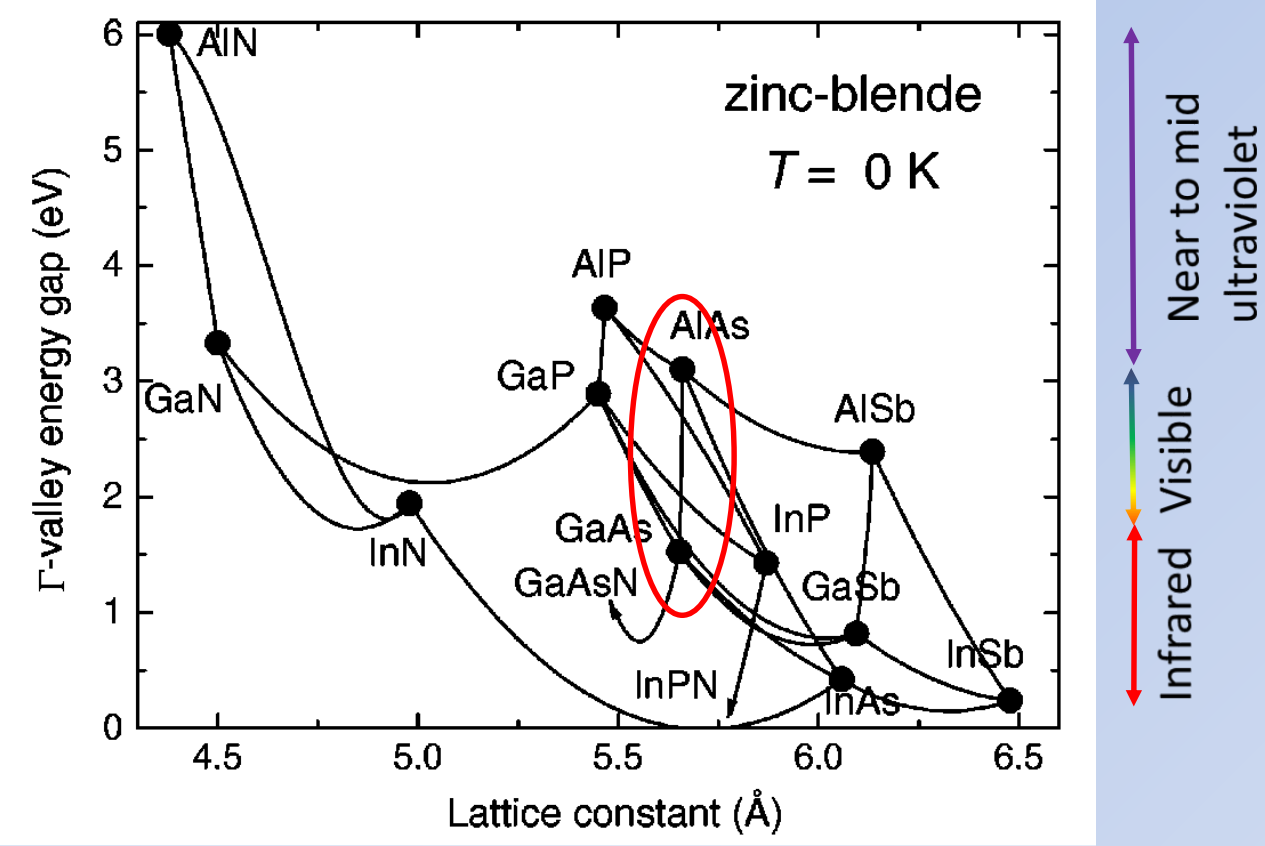
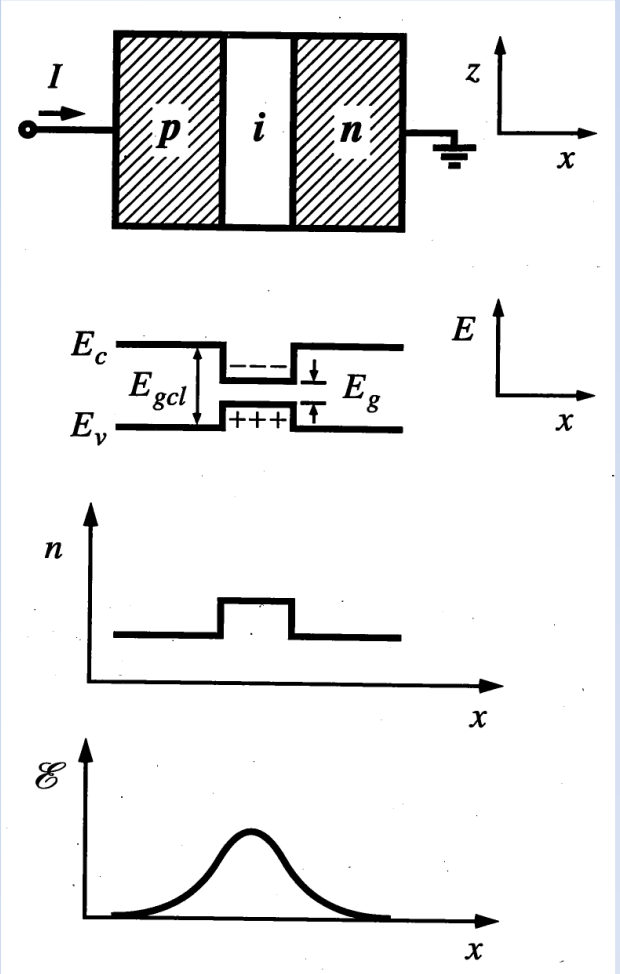
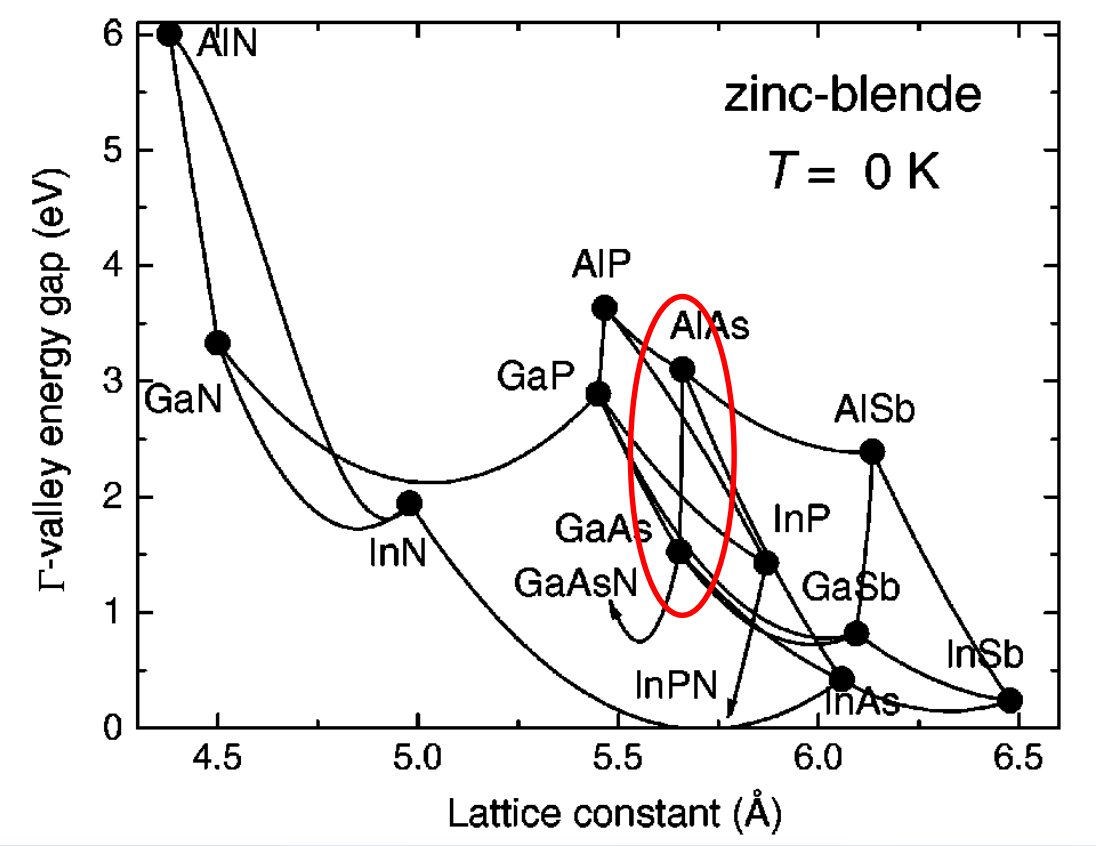


5.65 Å materials (GaAs substrate)

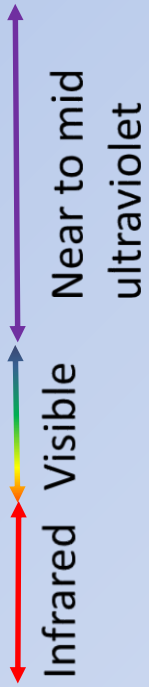
First room temperature laser (1970) a GaAs/AlGaAs double heterostructure grown by liquid phase epitaxy



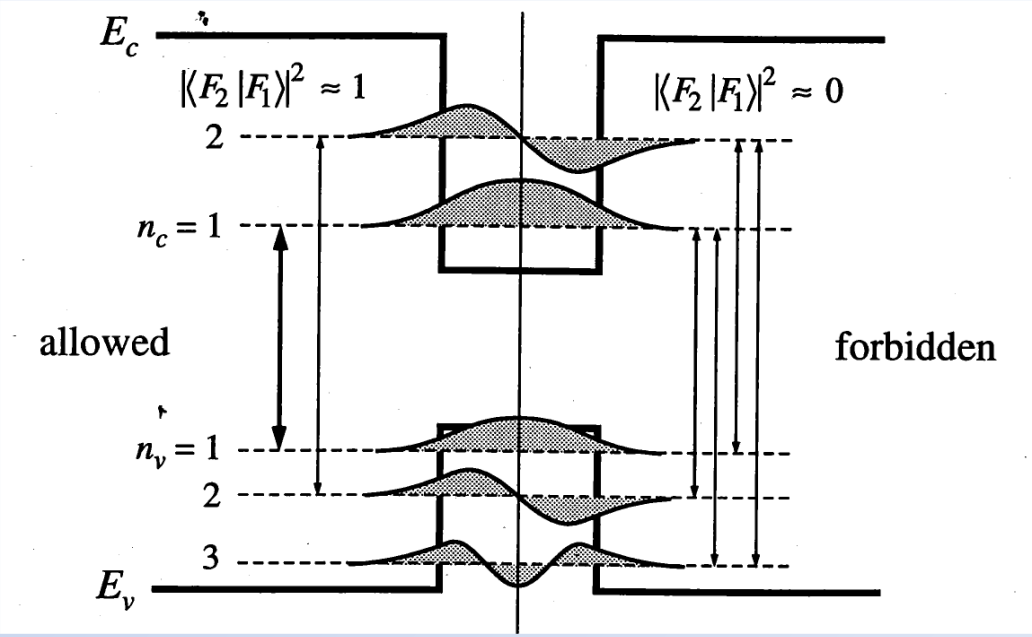
Epitaxial growth unleashed an explosion of materials research and engineering that vigorously continues to this day



5.65 Å materials (GaAs substrate)



By making layers thin compared to the electron de Broglie wavelength (~30-40 nm GaAs), quantum wells can be created



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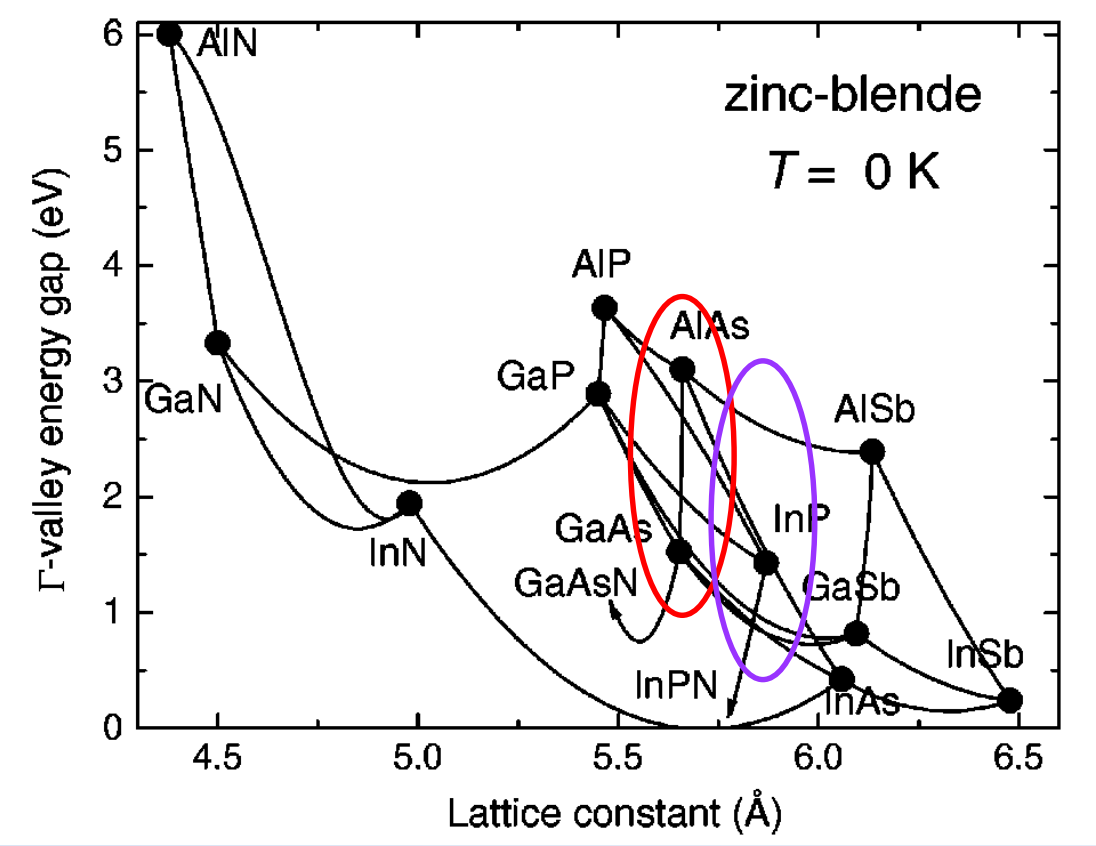
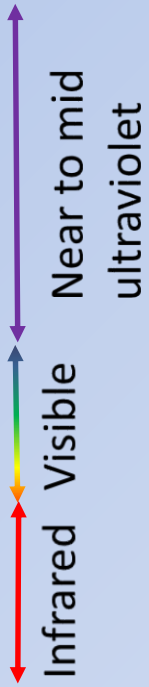
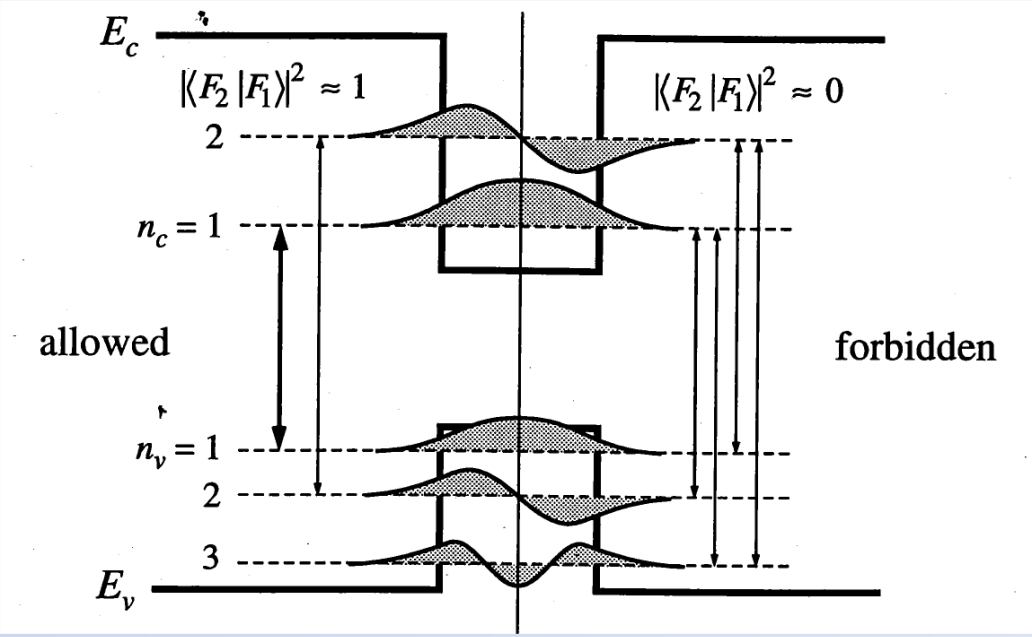




5.65 Å materials (GaAs substrate)
5.87 Å materials (InP substrate)

GaInAsSb/InP QWs on InP substrates as well as GaAs/AlAs QWs on GaAs important for infrared laser diodes and light emitting diodes for telecom at 0.8, 1.3 and 1.55 ums



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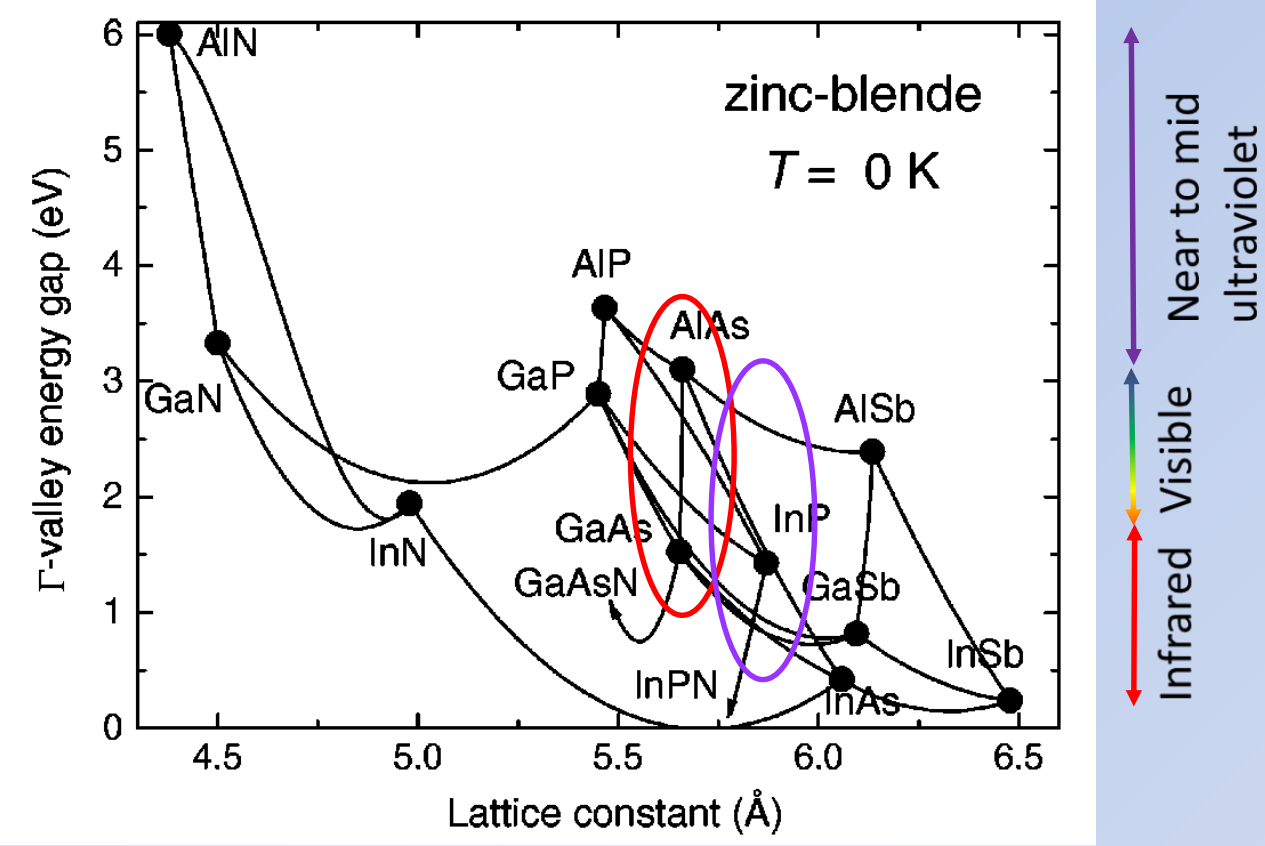
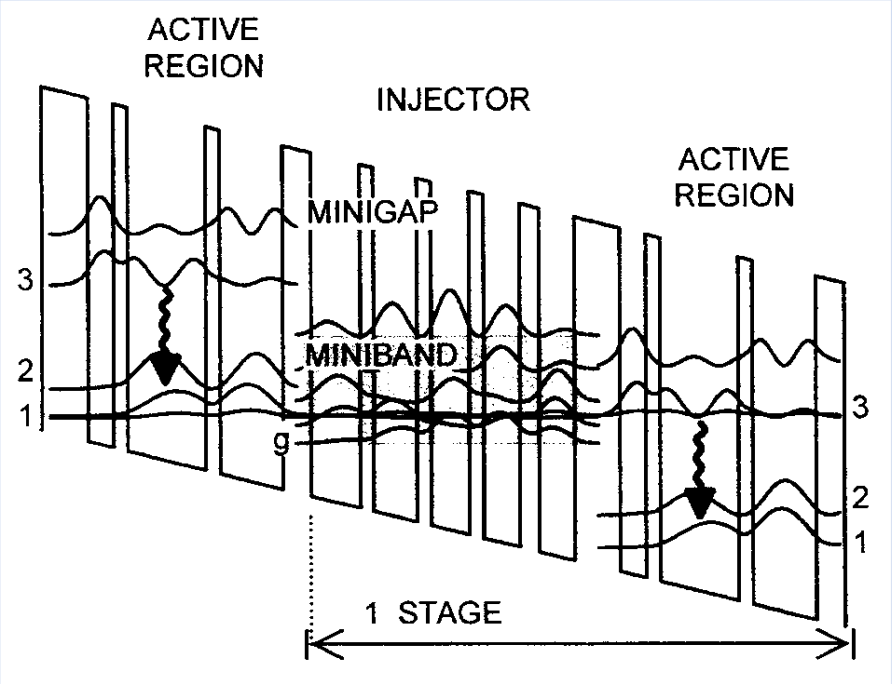
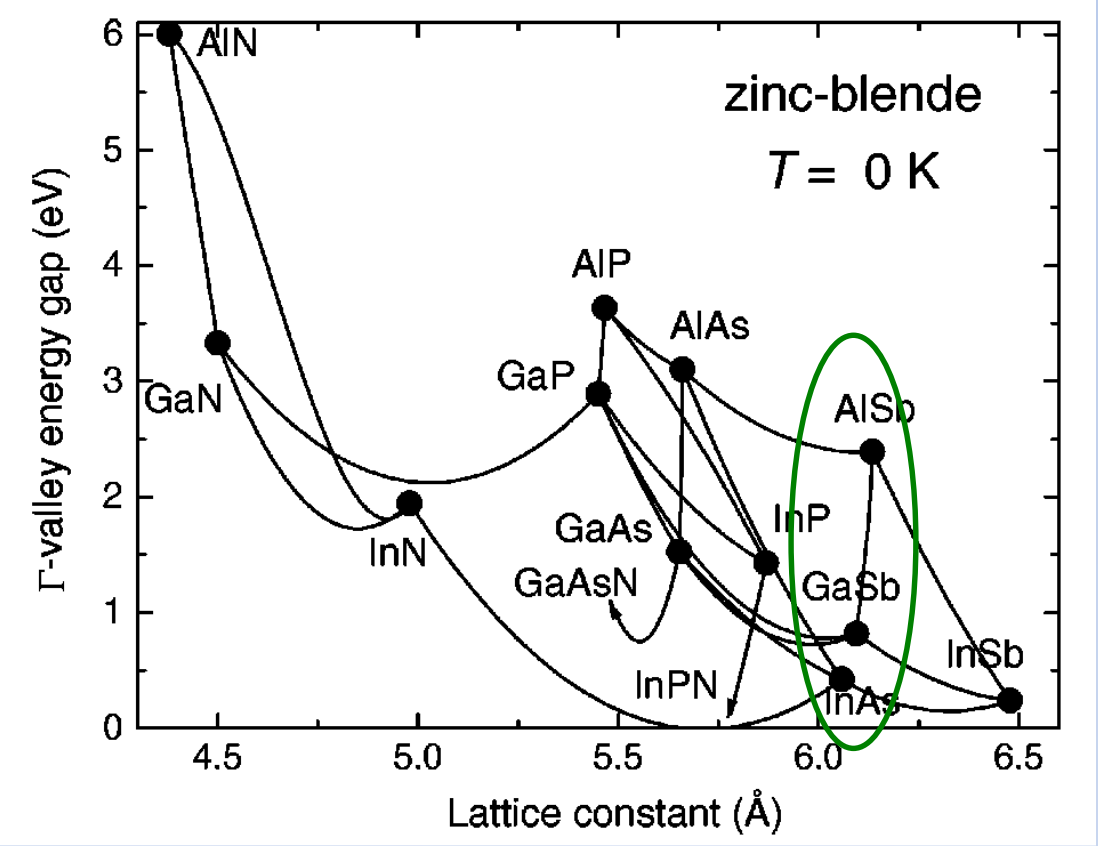


5.65 Å materials (GaAs substrate)
5.87 Å materials (InP substrate)

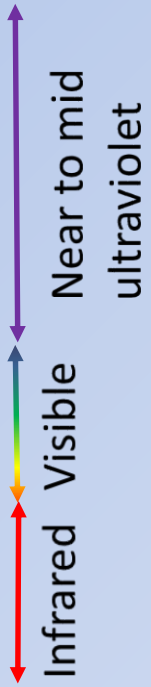
Electronic coupling of quantum wells from the same materials, and using intersubband transisions led to quantum cascade lasers emitting from the mid to far infrared, 4 ums to >100 ums (0.3 eV to 0.012 eV)



Epitaxial growth unleashed an explosion of materials research and engineering that vigorously continues to this day

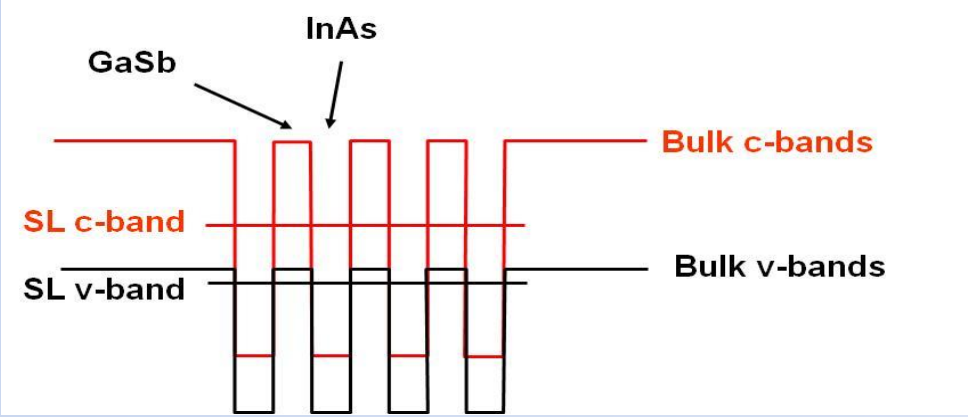


6.1 Å materials (GaSb substrate)



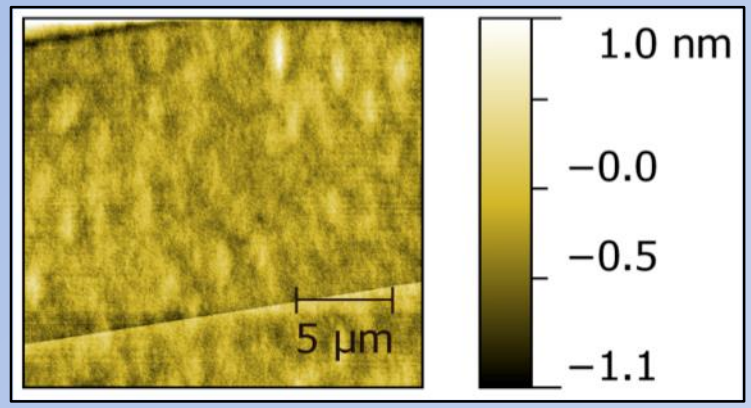
The 6.1 Å materials are a flexible system of narrow gap semiconductors for producing mid- and long-wave optoelectronics.

InAs/GaSb superlattice

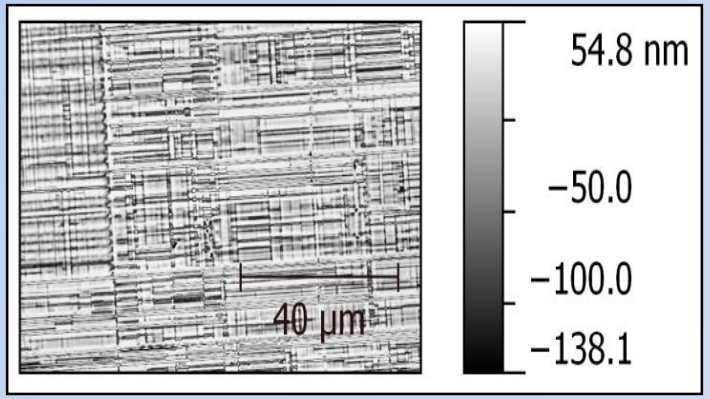


Materials combinations can be vastly increased through pseudomorphic growth

- Pseudomorphic growth: coherently strained mismatched materials
  - Thickness x strain ~ constant



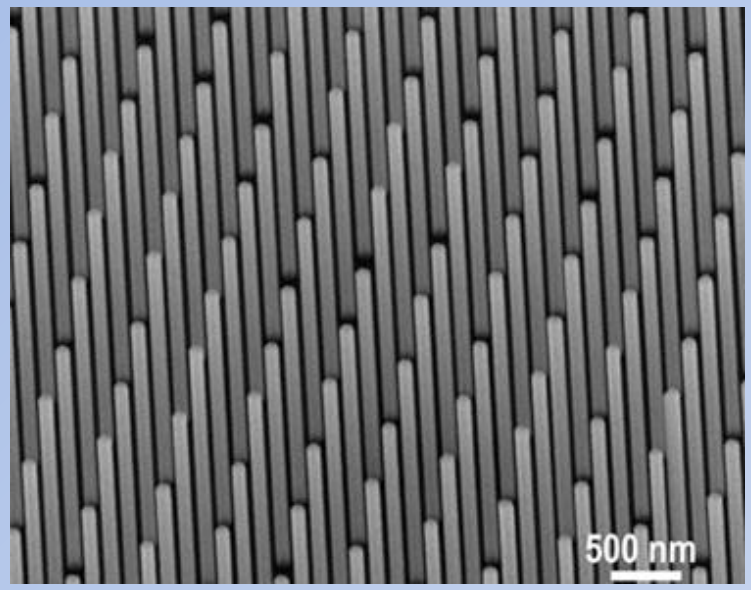
Weakly relaxed



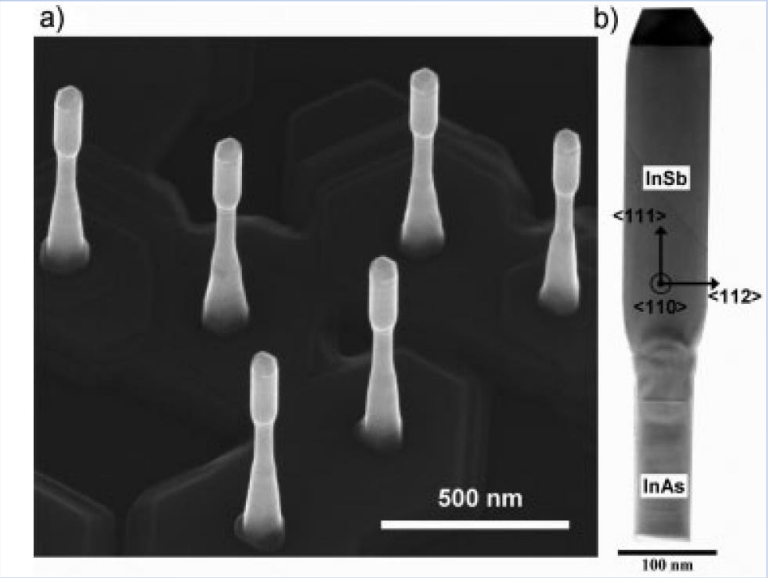
Strongly relaxed

Materials combinations can be greatly increased through pseudomorphic growth

GaAs nanowires on Si[1]



InSb / InAs segmented nanowires[2]

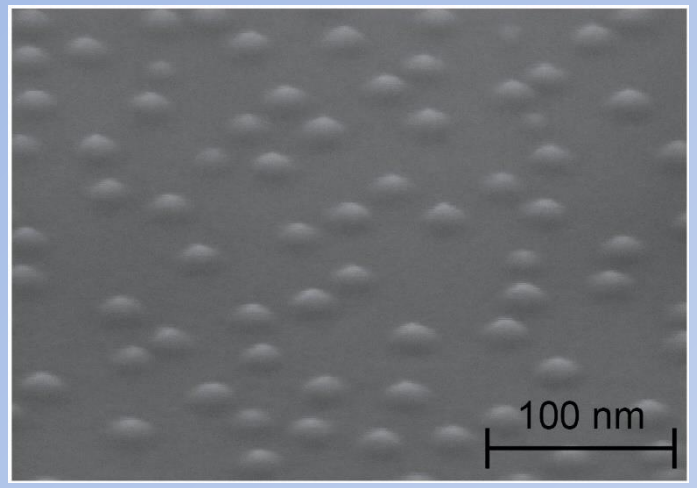


[1]Tomioka etal, *Nanotechnology* **20**, 145302 (2009)

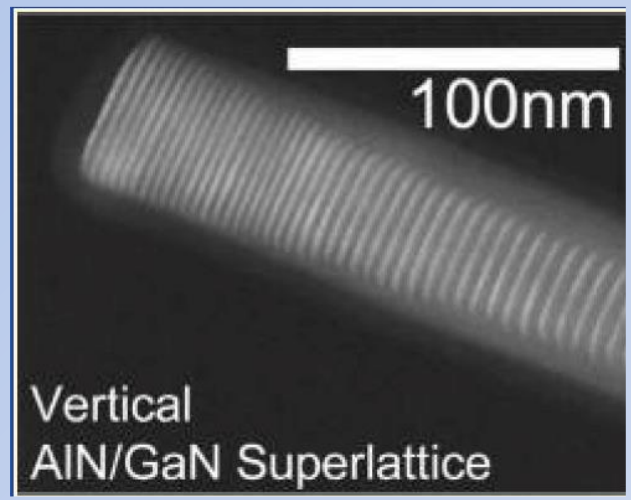
[2]Caroff etal, *Small* **4**(7), 878–882 (2008)

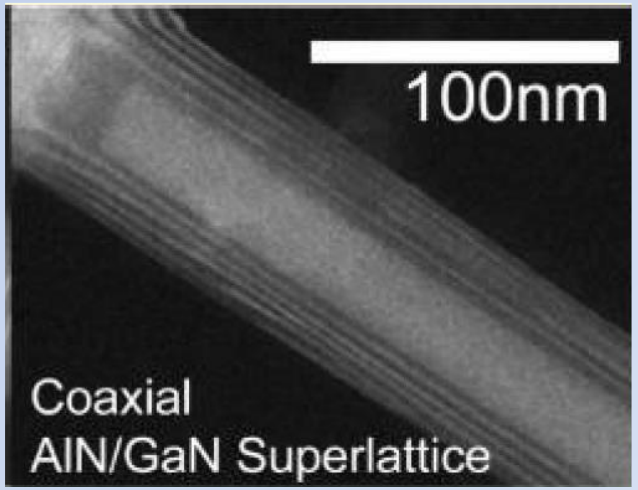
Materials combinations can be greatly increased through pseudomorphic growth

InAs quantum dots on GaAs[2]



Axial layering and core shell nanowires[2]

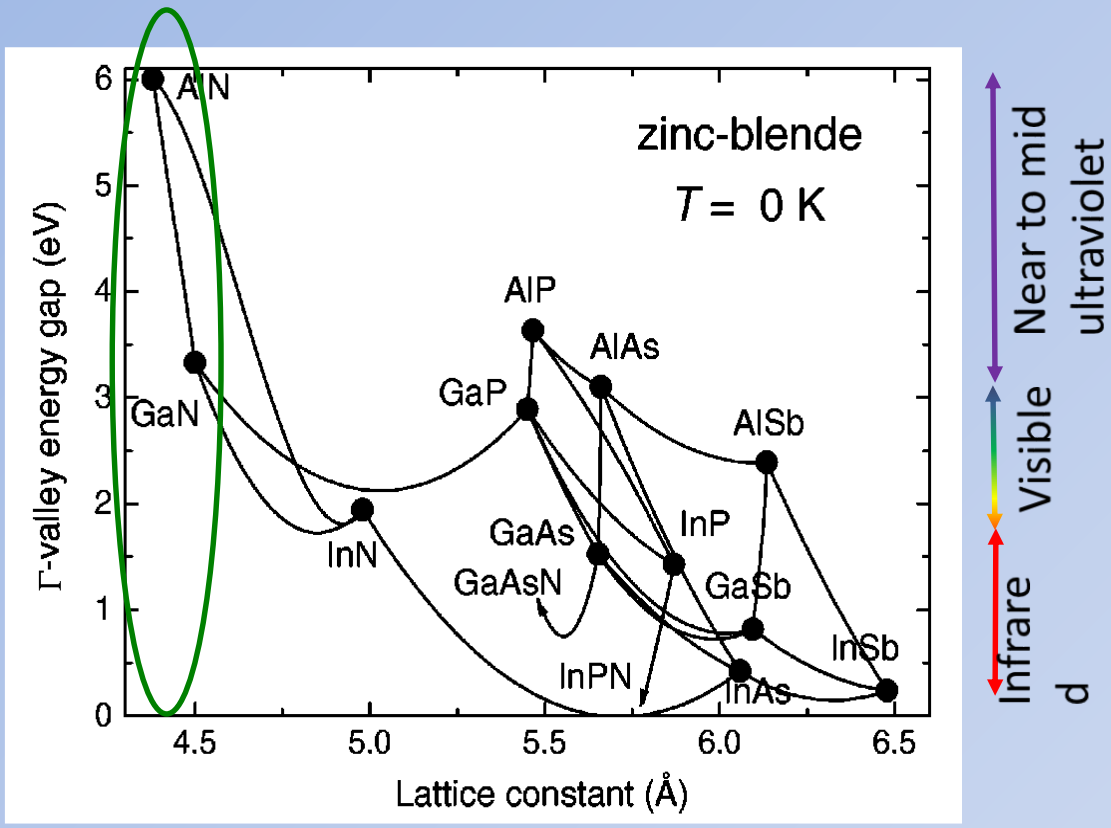




[2] W. Stumpf, http://www.mbe.ethz.ch/index.php?id=mbe

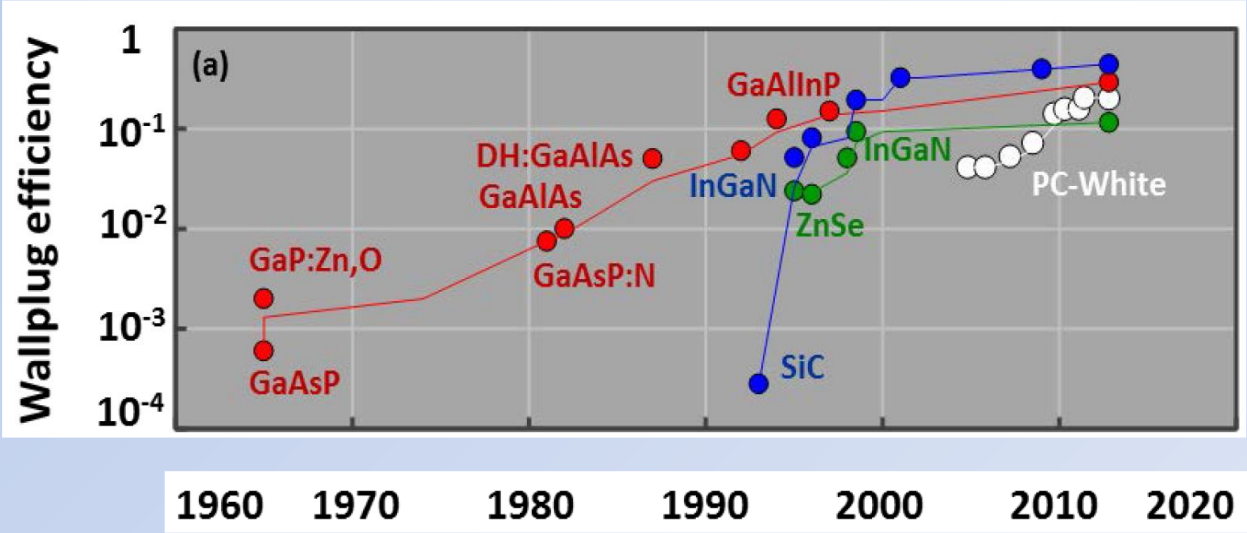
[2]Carnevale etal., *Nano Lett.* **211**, 866–871 (2011)

GaN was grown very early on (1960's) along with other binary semiconductors.
Why did it take 30-40 years to see bright commercial blue leds and laser diodes?



6.1 Å materials (GaSb substrate)

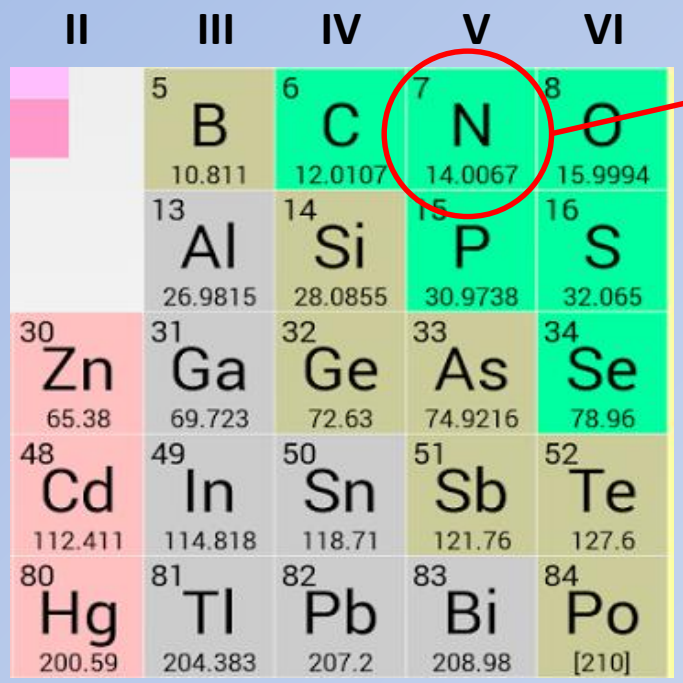
History of red/green/blue LEDs



Crawford etal in D.L. Andrews, Ed., "Photonics Volume 3: Photonics Technology and Instrumentation" (Wiley, 2013).

GaN was grown very early on (1960's) along with other binary semiconductors. Why did it take 30-40 years to see bright commercial blue leds and laser diodes?

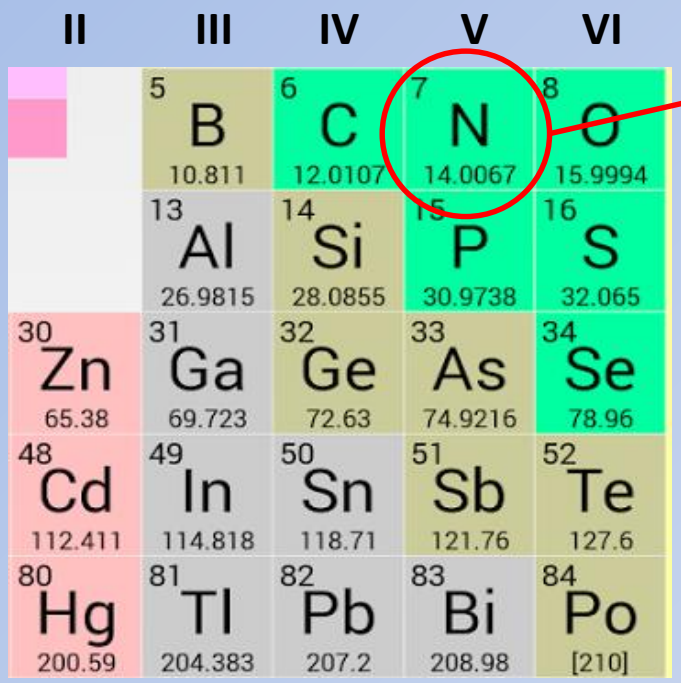
- Nitrogen is typically gaseous N_2, so liquid phase epitaxy could not be used.
- Initially grown by HVPE, but had to await development of MOVPE and MBE for higher quality films



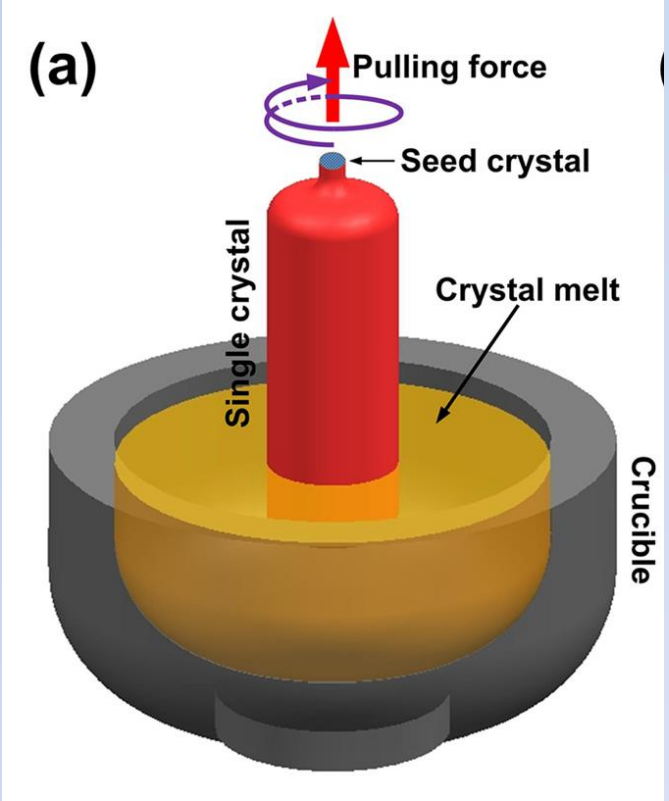
Gaseous N_2 under typical conditions

GaN was grown very early on (1960's) along with other binary semiconductors. Why did it take 30-40 years to see bright commercial blue leds and laser diodes?

- **Metamorphic growth is** required on foreign substrates, typically sapphire (~15% lattice mismatch)
- Substrates like GaAs, GaP, GaSb cut from boules grown from melts; nitrogen is typically a gas



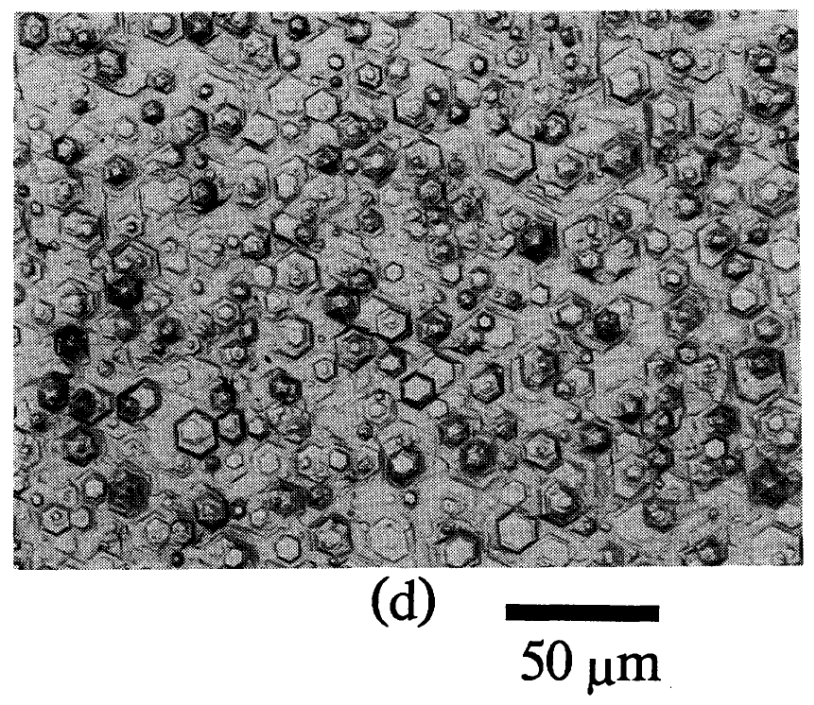
Gaseous N_2 under typical conditions



Czochralski schematic

GaN was grown very early on (1960's) along with other binary semiconductors. Why did it take 30-40 years to see bright commercial blue leds and laser diodes?

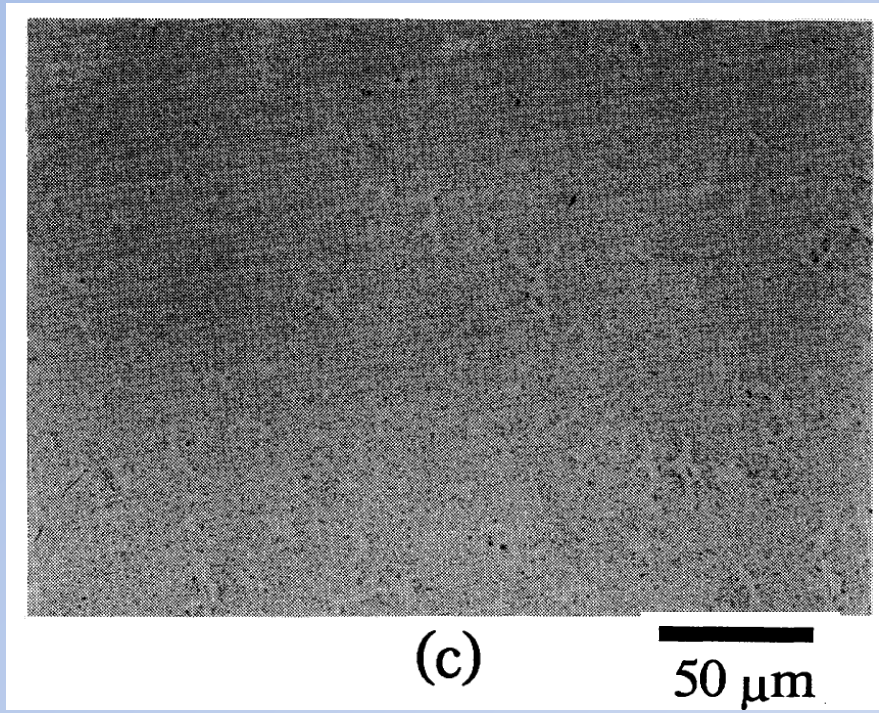
- MOVPE and MBE metamorphic layers on sapphire had high dislocation density and poor quality early on



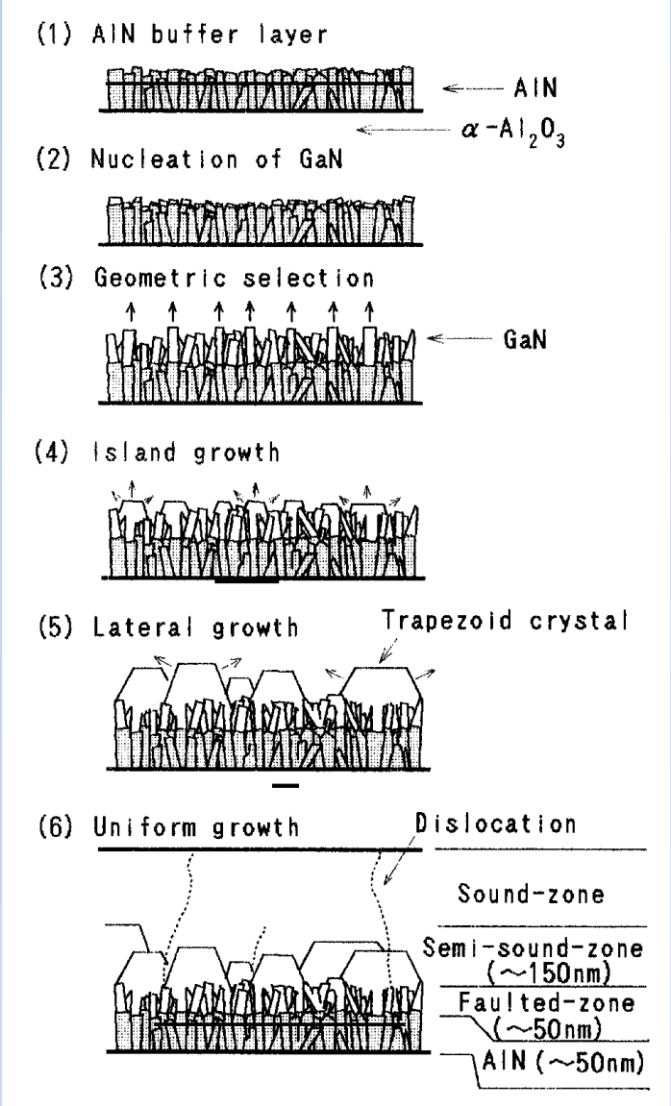
Nakamura, Jap. J. of Appl. Phys **30**, L1705 (1991)

GaN was grown very early on (1960's) along with other binary semiconductors. Why did it take 30-40 years to see bright commercial blue leds and laser diodes?

- Key advance (1983-91) was development of low-temperature-grown GaN and AlN buffer layers between sapphire and GaN



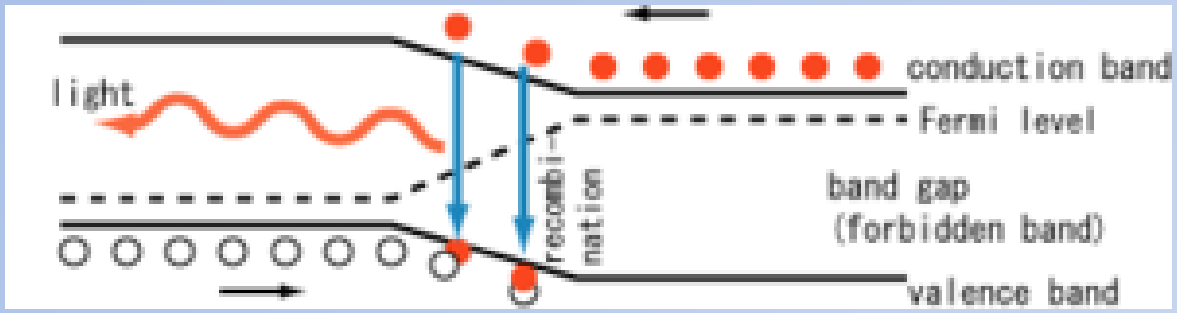
Nakamura, Jap. J. of Appl. Phys **30**, L1705 (1991)



K. Hiramatsu *et al.*, *J. Crystal Growth* **115**, 628 (1991)

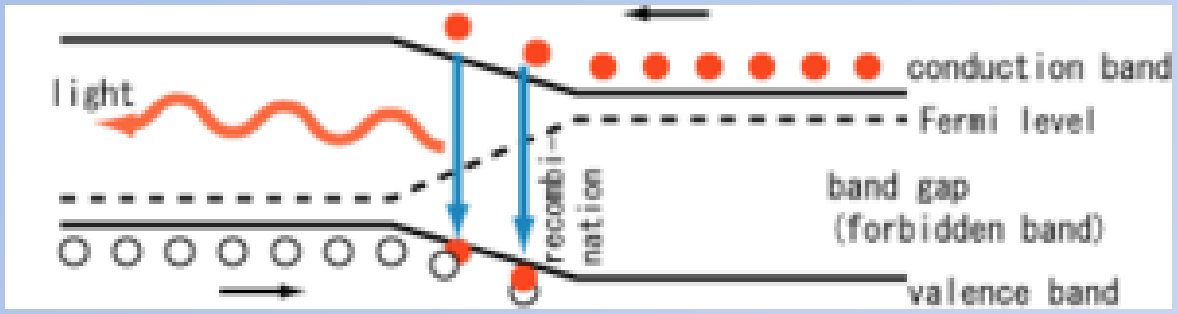
GaN was grown very early on (1960's) along with other binary semiconductors. Why did it take 30-40 years to see bright commercial blue leds and laser diodes?

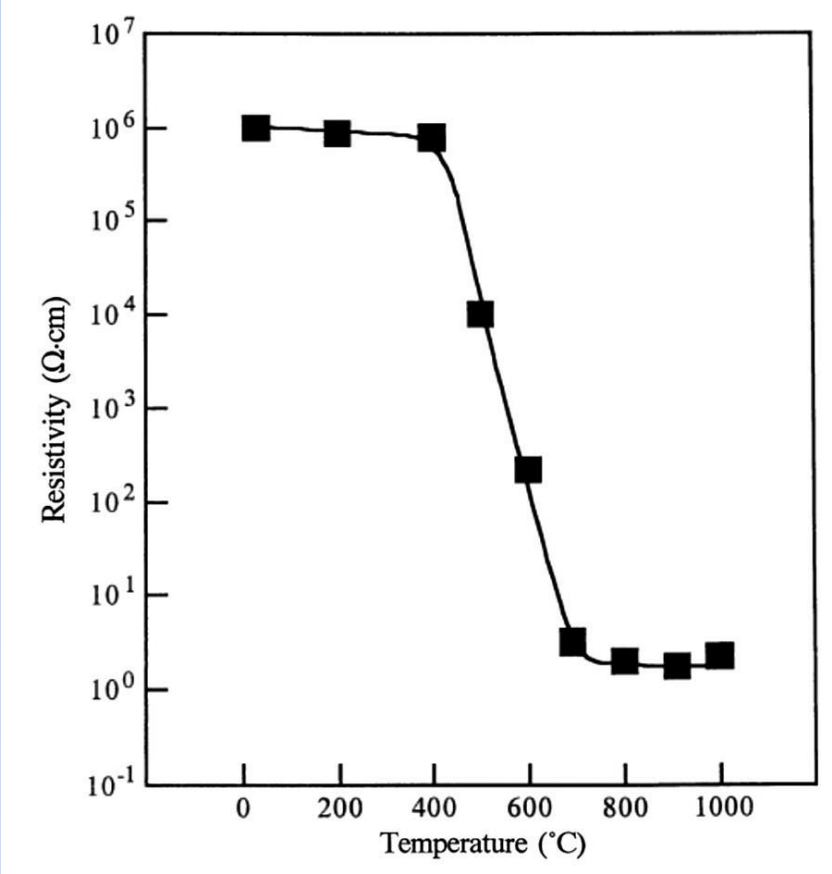
- LEDs need pn junction
- **Doping problem**: GaN films were consistently n-type and could not be p-doped



GaN was grown very early on (1960's) along with other binary semiconductors. Why did it take 30-40 years to see bright commercial blue leds and laser diodes?

- Key development: p-dopants (Mg) were being passivated by hydrogen present in the precursor, but could be liberated by a simple post growth anneal in a non-hydrogen atmosphere

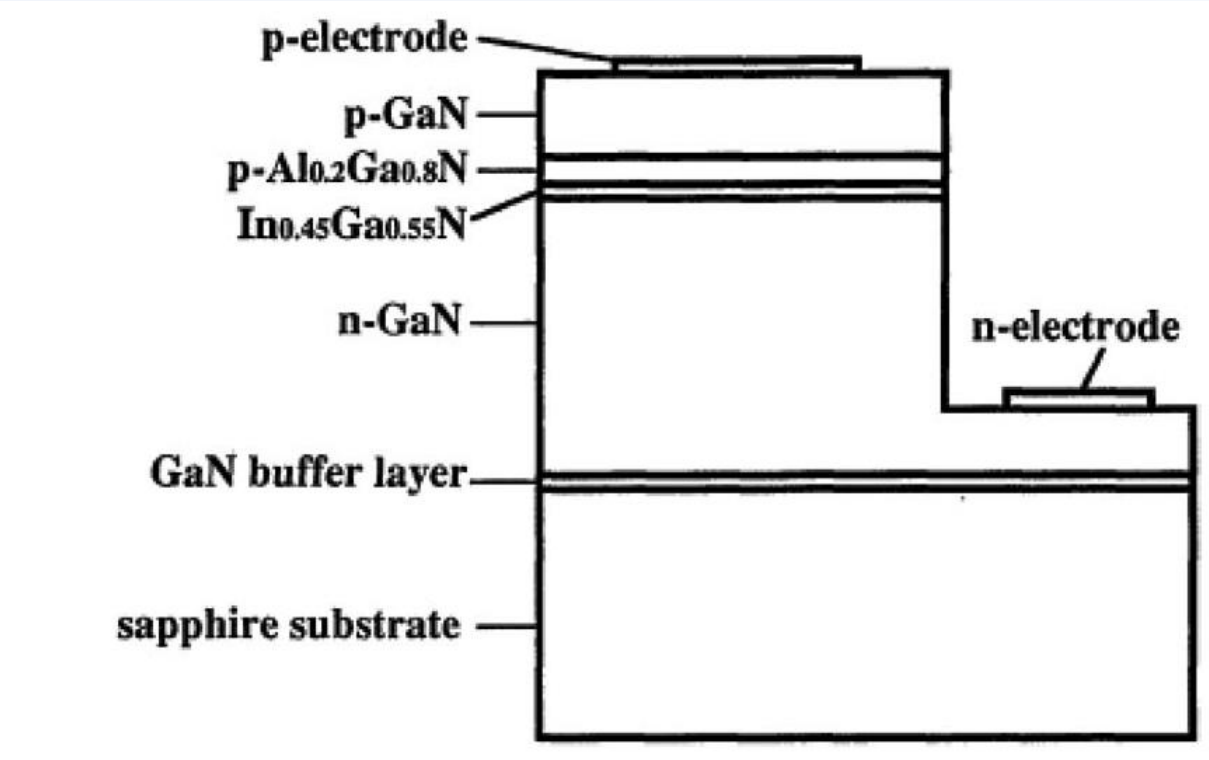


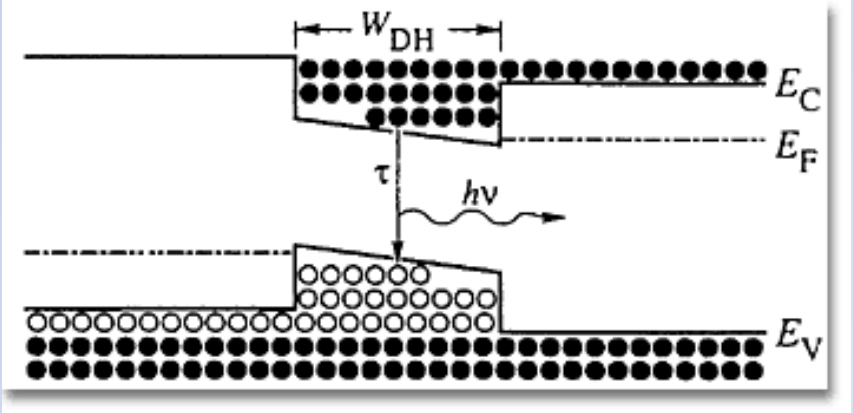


S. Nakamura etal, Jpn. J. Appl. Phys., 31, L139 (1992)

GaN was grown very early on (1960's) along with other binary semiconductors. Why did it take 30-40 years to see bright commercial blue leds and laser diodes?

- Finally, the development of Al(Ga)N and In(Ga)N growth allowed the growth of heterostructures, key for high performance LEDs





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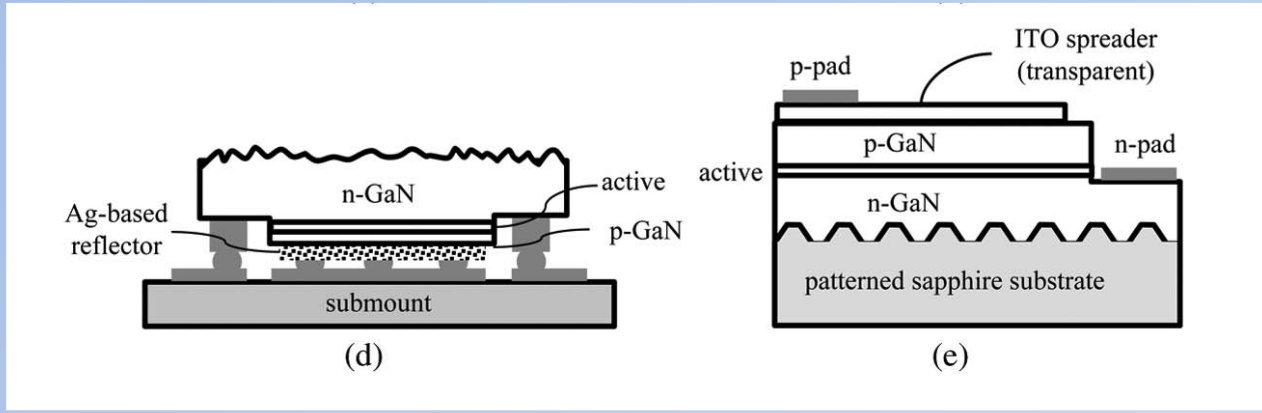
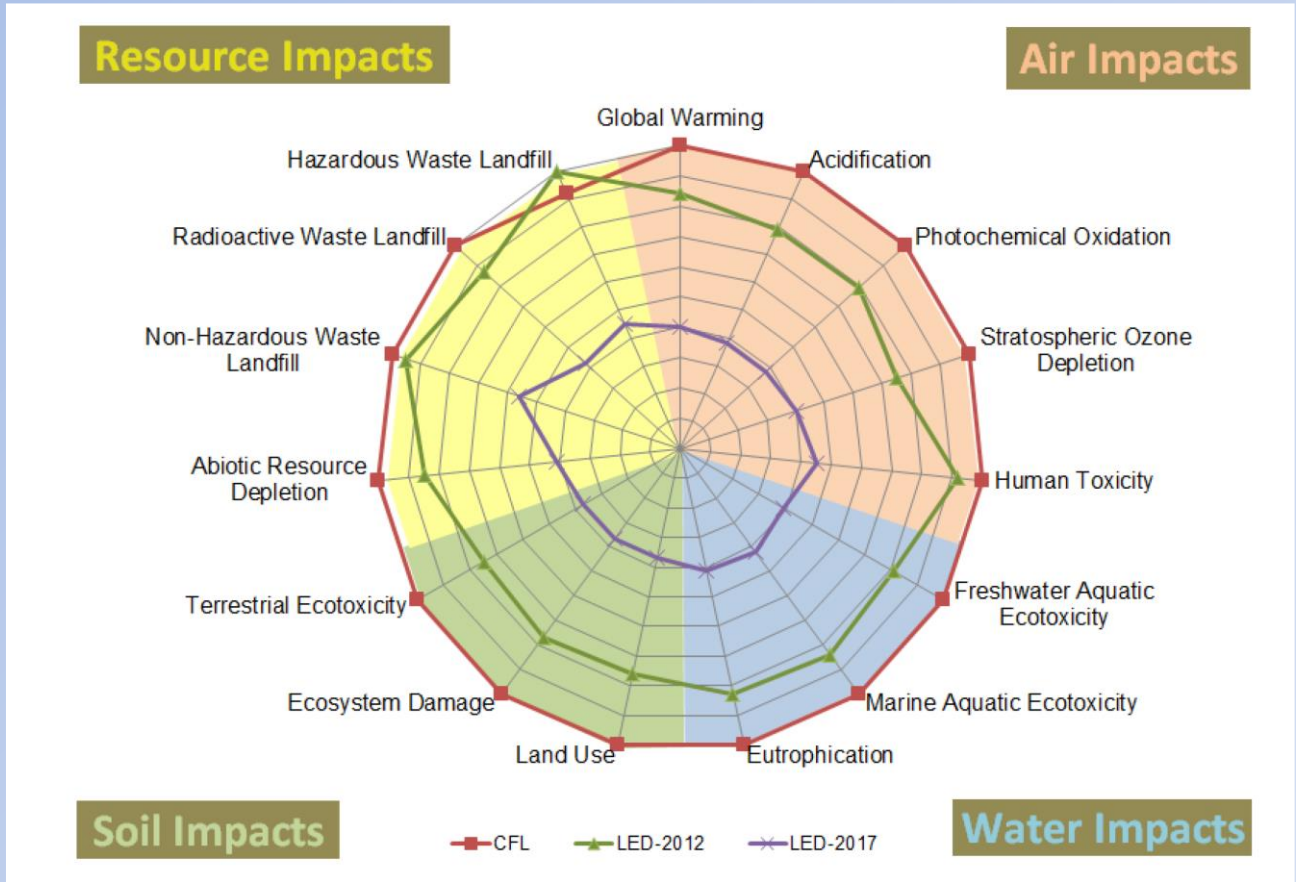


- Light extraction efficiency limited to $1/(4n^2)$ normally due to total internal reflection.
- Extraction efficiencies as high as 80-90% achieved
- State-of-the art wallplug efficiencies (power out/power in) exceed 50%

Nakamura etal, *Proceedings of the IEEE* **101**, 0018-9219 (2013)

Characteristics	Incandescent	CFL	LED lamp – 2012	LED lamp – 2017
Power Consumption	60 watts	15 watts	12.5 watts	6.1 watts
Lumen Output	900 lumens	825 lumens	812 lumens	824 lumens
Efficacy	15 lm/W	55 lm/W	65 lm/W	134 lm/W
Lamp Lifetime	1500 hours	8000 hours	25,000 hours	40,000 hours
Total Lifetime Light Output	1.35 Mlm-hr	6.6 Mlm-hr	20.3 Mlm-hr*	33.0 Mlm-hr
Impacts Scalar	15.04	3.08	1.00	0.61


Resource Impacts
Air Impacts
Global Warming
Acidification
Photochemical Oxidation
Stratospheric Ozone Depletion
Human Toxicity
Freshwater Aquatic Ecotoxicity
Marine Aquatic Ecotoxicity
Eutrophication
Land Use
Ecosystem Damage
Terrestrial Ecotoxicity
Abiotic Resource Depletion
Non-Hazardous Waste Landfill
Radioactive Waste Landfill
Hazardous Waste Landfill
Soil Impacts
Water Impacts
CFL
LED-2012
LED-2017

Conclusions

- Molecular beam epitaxy:
  - Is an ultrahigh vacuum technique for deposition of high purity epitaxial layers with high uniformity, thin layers with atomic layer precision, and abrupt interfaces
  - Invented in the 1970's, and is a flexible and continually evolving technology for an increasing array of materials
  - Is a complementary technique to MOVPE for basic research, development, and commercial growth of semiconductor heterostructures.

- GaN was a challenging material to develop for epitaxial growth:
  - Gaseous group V atom
  - No lattice matched substrates (were) available
  - Difficulty p-doping the material

  but GaN solid state lighting is rapidly becoming the highest efficiency, most economical, and cleanest source of lighting for the future