

# *Principles of Micro- and Nanofabrication for Electronic and Photonic Devices*

## **Film Deposition** **Part I: Epitaxy 外延生长**

**Xing Sheng 盛兴**



**Department of Electronic Engineering  
Tsinghua University  
[xingsheng@tsinghua.edu.cn](mailto:xingsheng@tsinghua.edu.cn)**

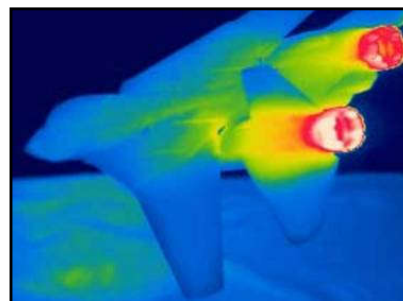
# Optoelectronic Devices



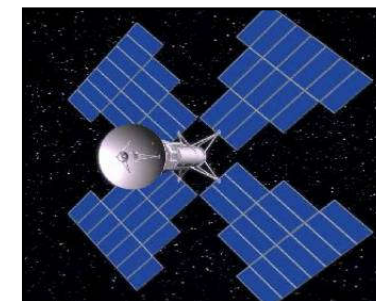
LEDs



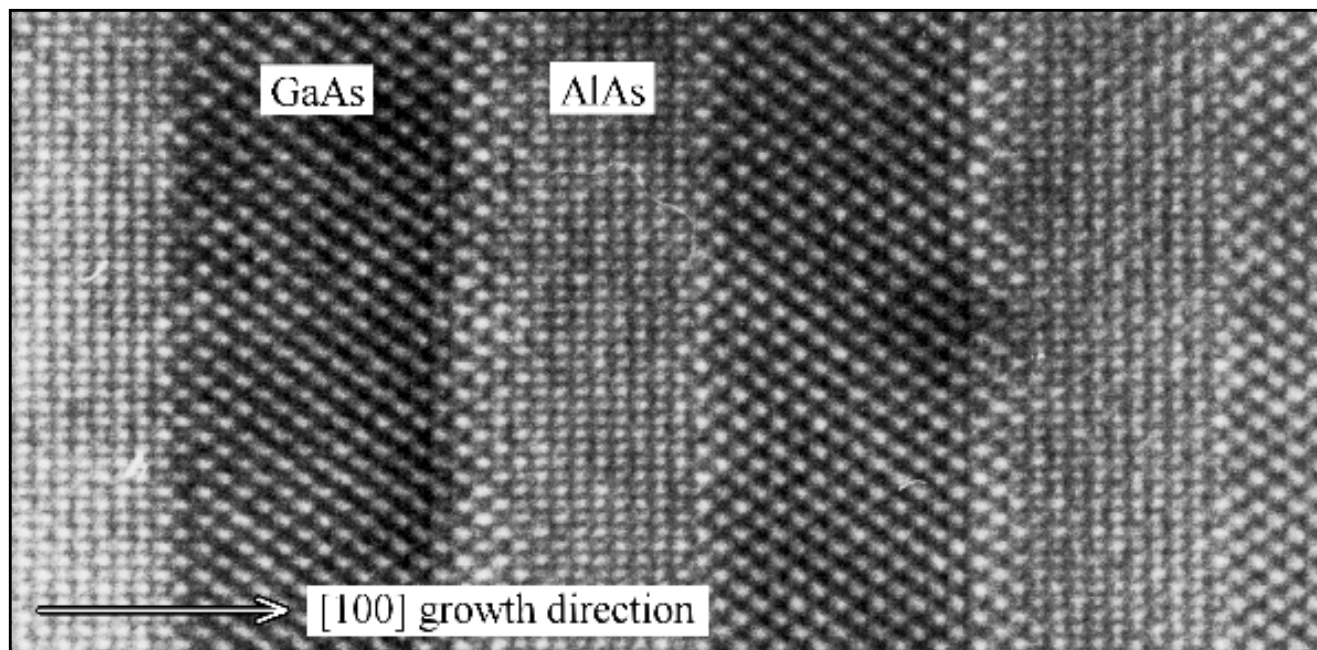
lasers



IR imaging

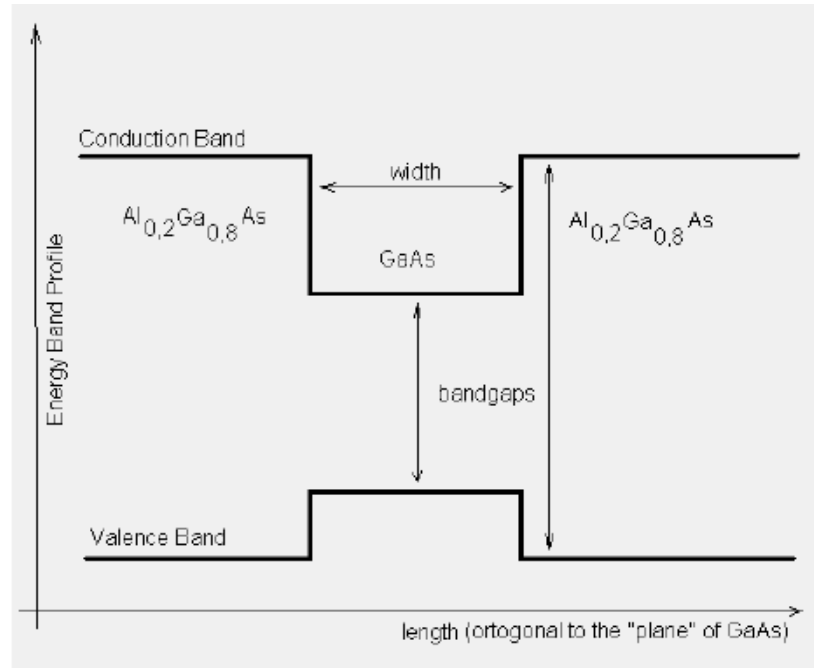


solar cells



grow single crystal films on single crystal substrates

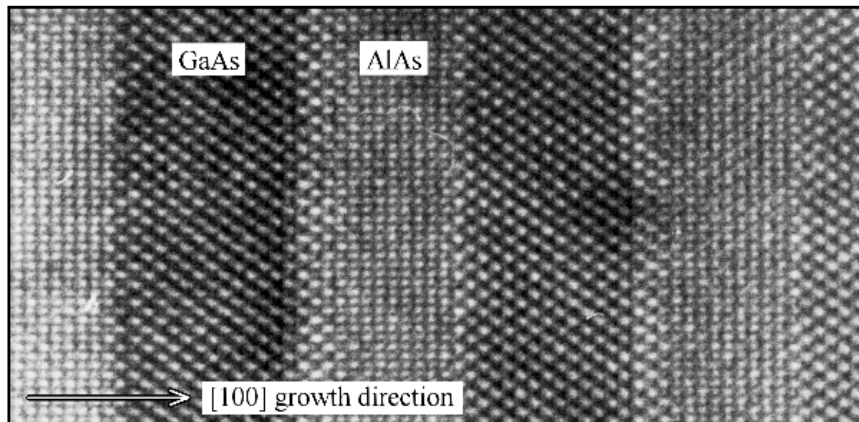
# Semiconductor Heterostructures



**GaAs/AlGaAs heterostructure:  
bandgap engineering**



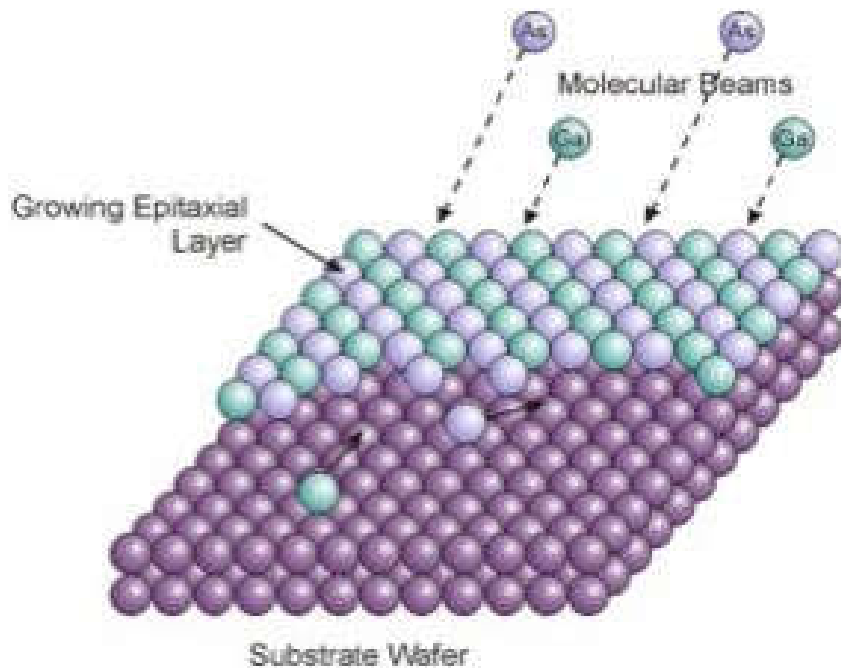
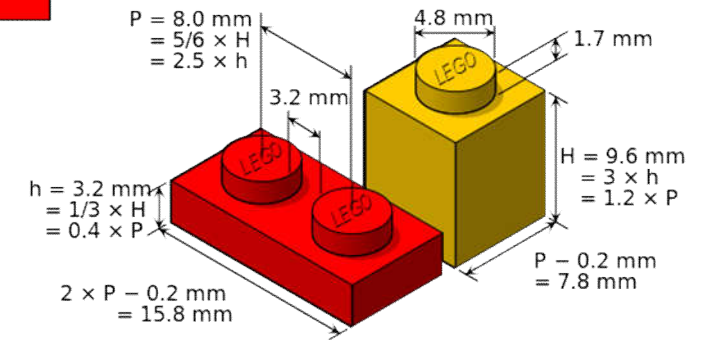
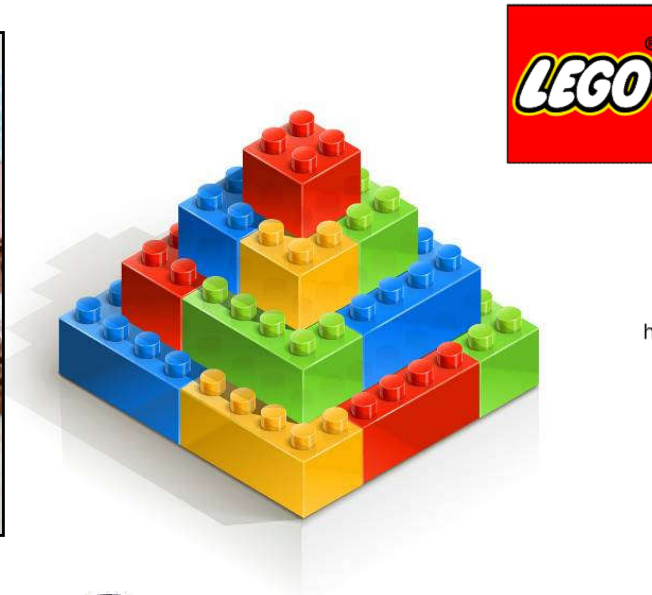
**Z. I. Alferov**



**H. Kroemer**

**2000 Nobel Prize in Physics**

# Epitaxy (外延)

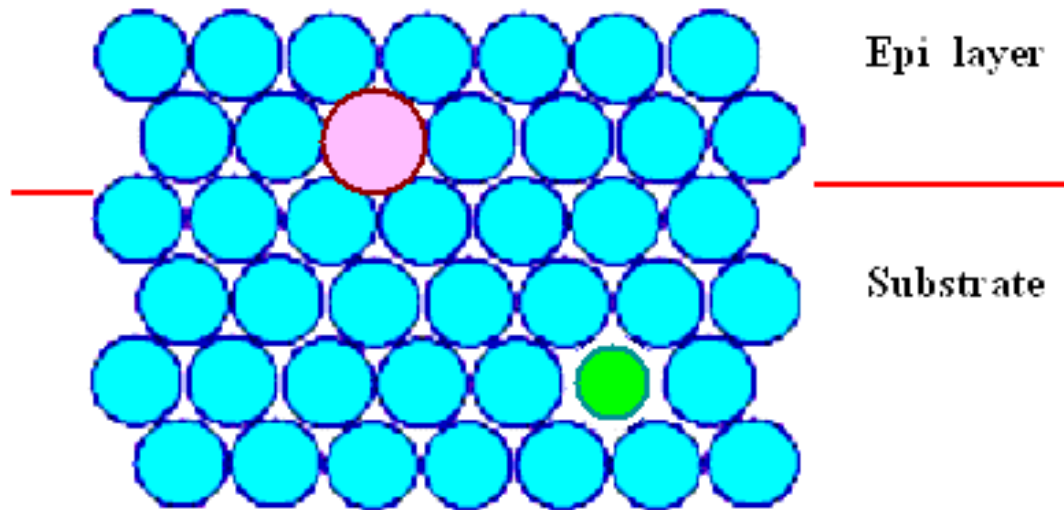


*epi-*  
 surface, 表面  
*-taxy*  
 arrange, 排列



# Epitaxial Growth

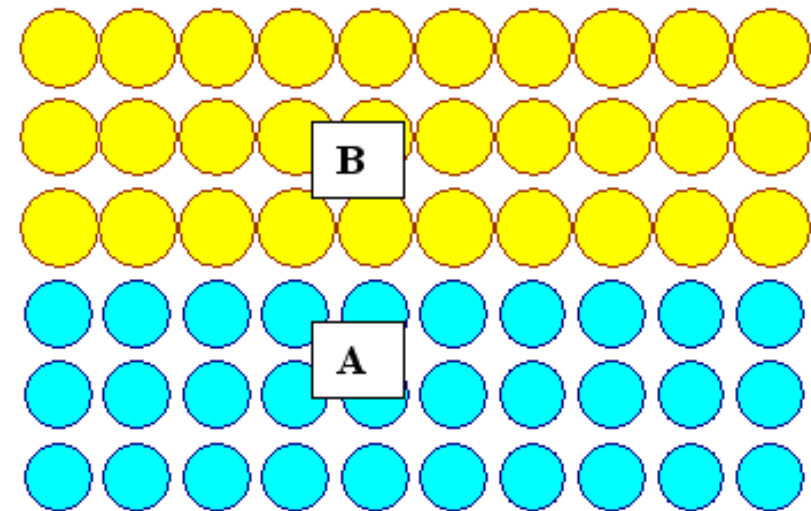
## Homoepitaxy



(doped) Si on Si,  
GaAs on GaAs,

...

## Heteroepitaxy



AlAs on GaAs  
Ge on Si,

...

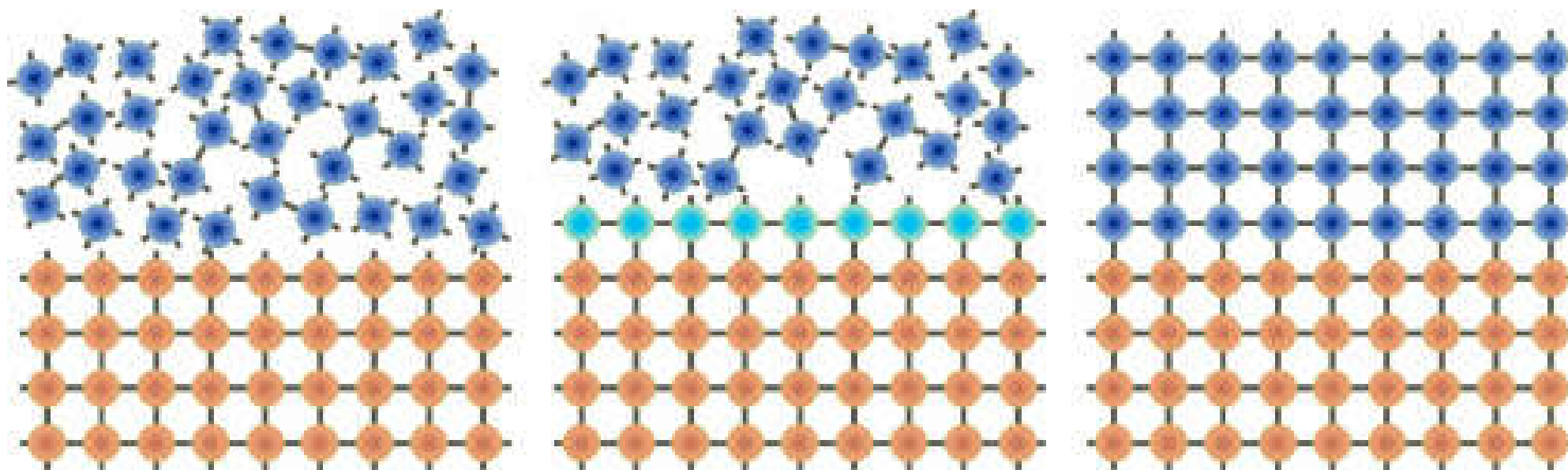
# Methods

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- **Solid Phase Epitaxy (SPE)**
  - **amorphous Si -> crystalline Si**
- **Liquid Phase Epitaxy (LPE)**
  - **$2\text{Ga (l)} + 2\text{AsCl}_3 \text{ (l)} = 2\text{GaAs (s)} + 3\text{Cl}_2 \text{ (g)}$**
- **Chemical Vapor Deposition (CVD)**
  - **$\text{Ga(CH}_3)_3 \text{ (g)} + \text{AsH}_3 \text{ (g)} = \text{GaAs (s)} + 3\text{CH}_4 \text{ (g)}$**
- **Molecular Beam Epitaxy (MBE)**
  - **$2\text{Ga (g)} + \text{As}_2 \text{ (g)} = 2\text{GaAs (s)}$**

# Methods

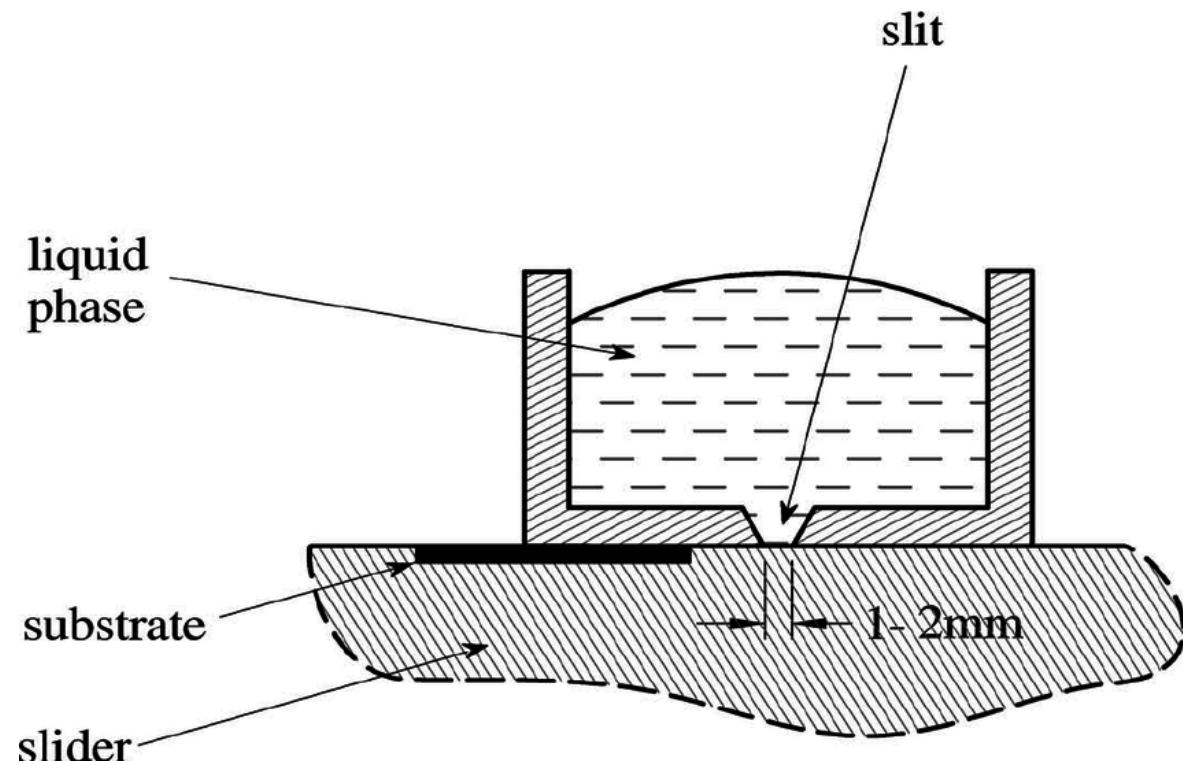
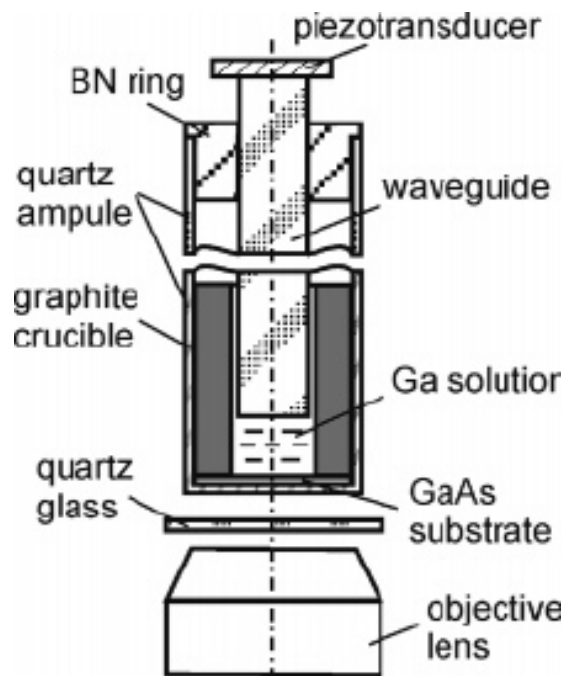
- **Solid Phase Epitaxy (SPE)**
  - **amorphous Si -> crystalline Si**



annealing at high temperature

# Methods

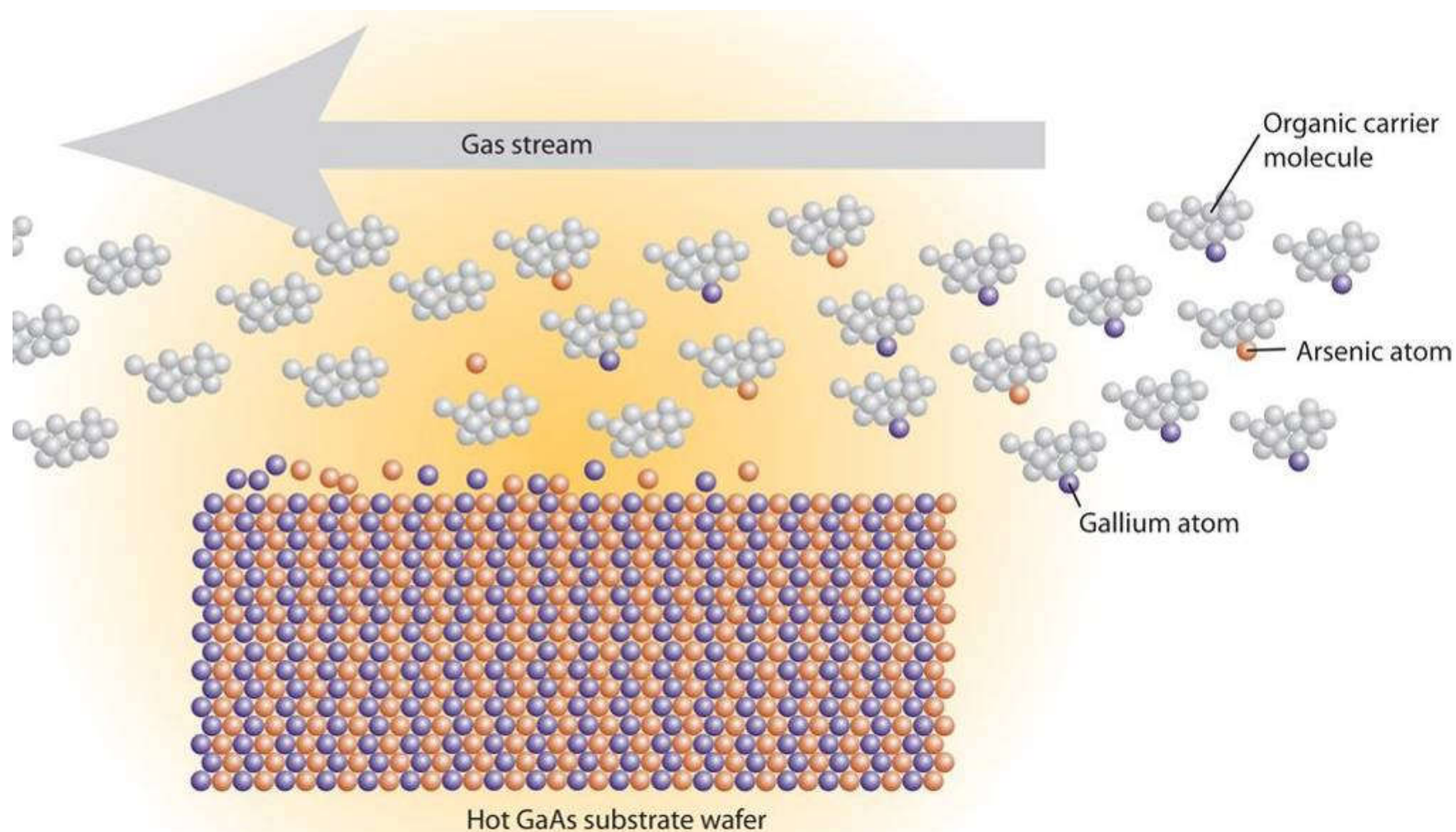
- **Liquid Phase Epitaxy (LPE)**
  - $2\text{Ga (l)} + 2\text{AsCl}_3 \text{ (l)} = 2\text{GaAs (s)} + 3\text{Cl}_2 \text{ (g)}$





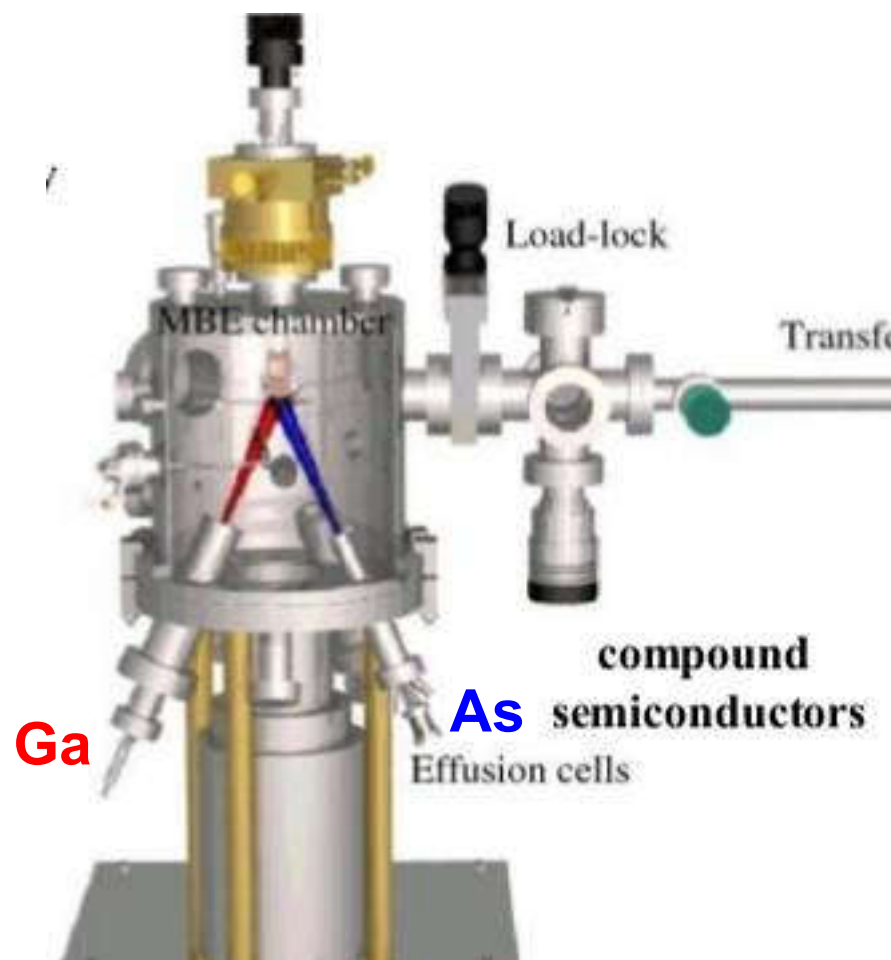
# Methods

## ■ Chemical Vapor Deposition (CVD)

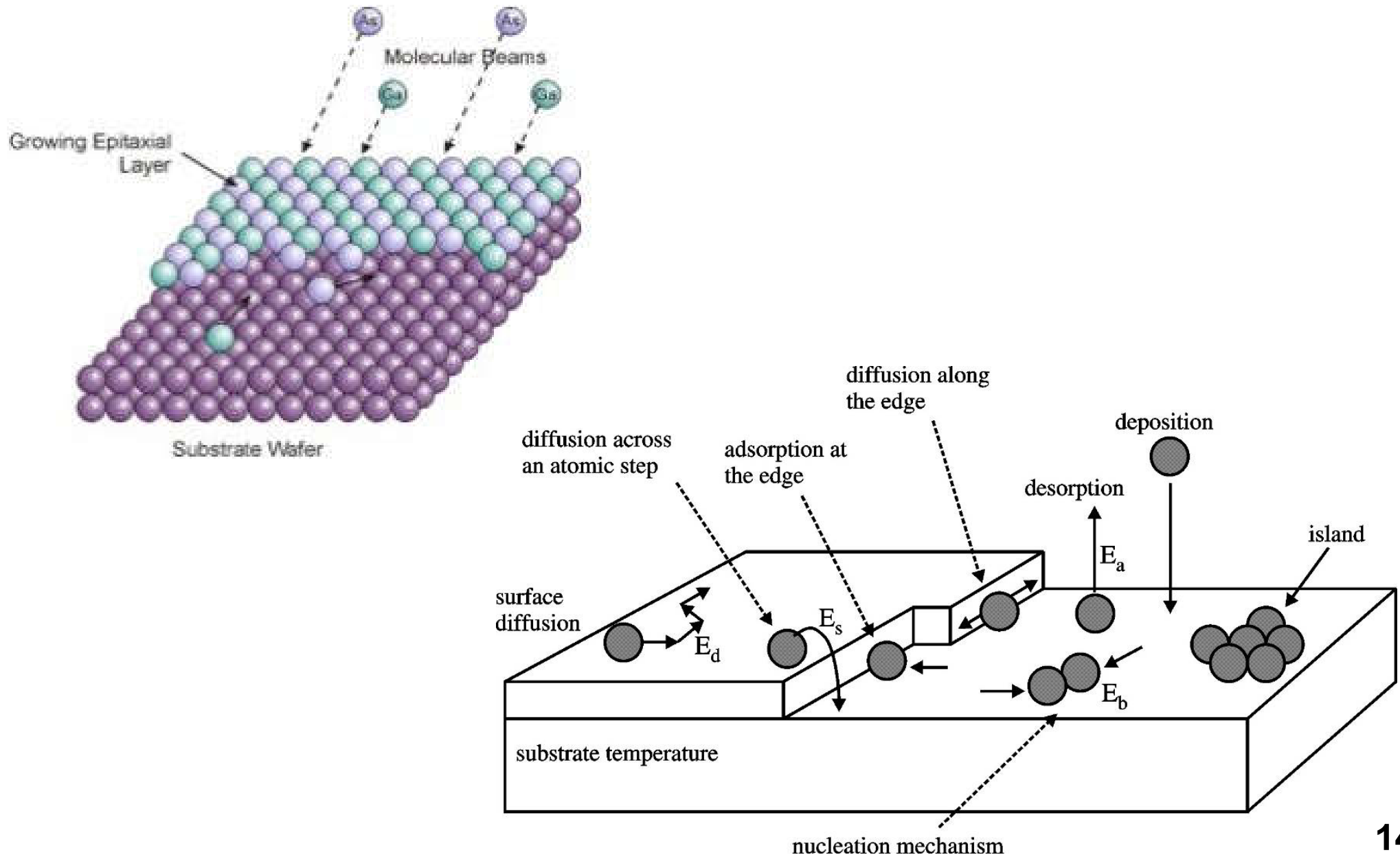


# Methods

- Molecular Beam Epitaxy (MBE)
  - $2\text{Ga (g)} + \text{As}_2 \text{(g)} = 2\text{GaAs (s)}$

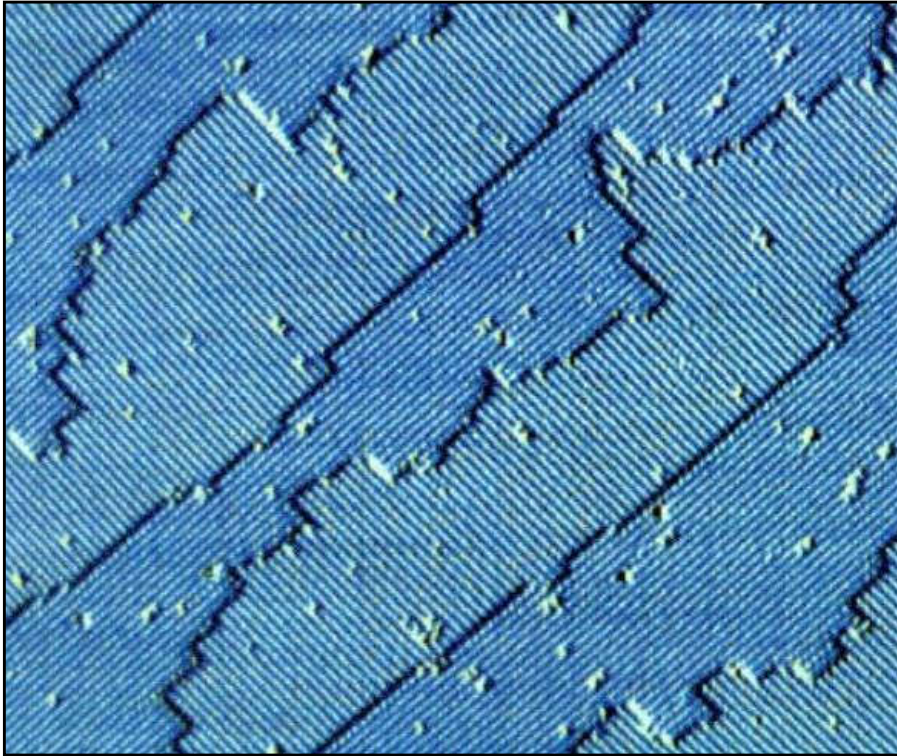


# Deposition at Surfaces





# Deposition at Surfaces



**Si (100) surface**

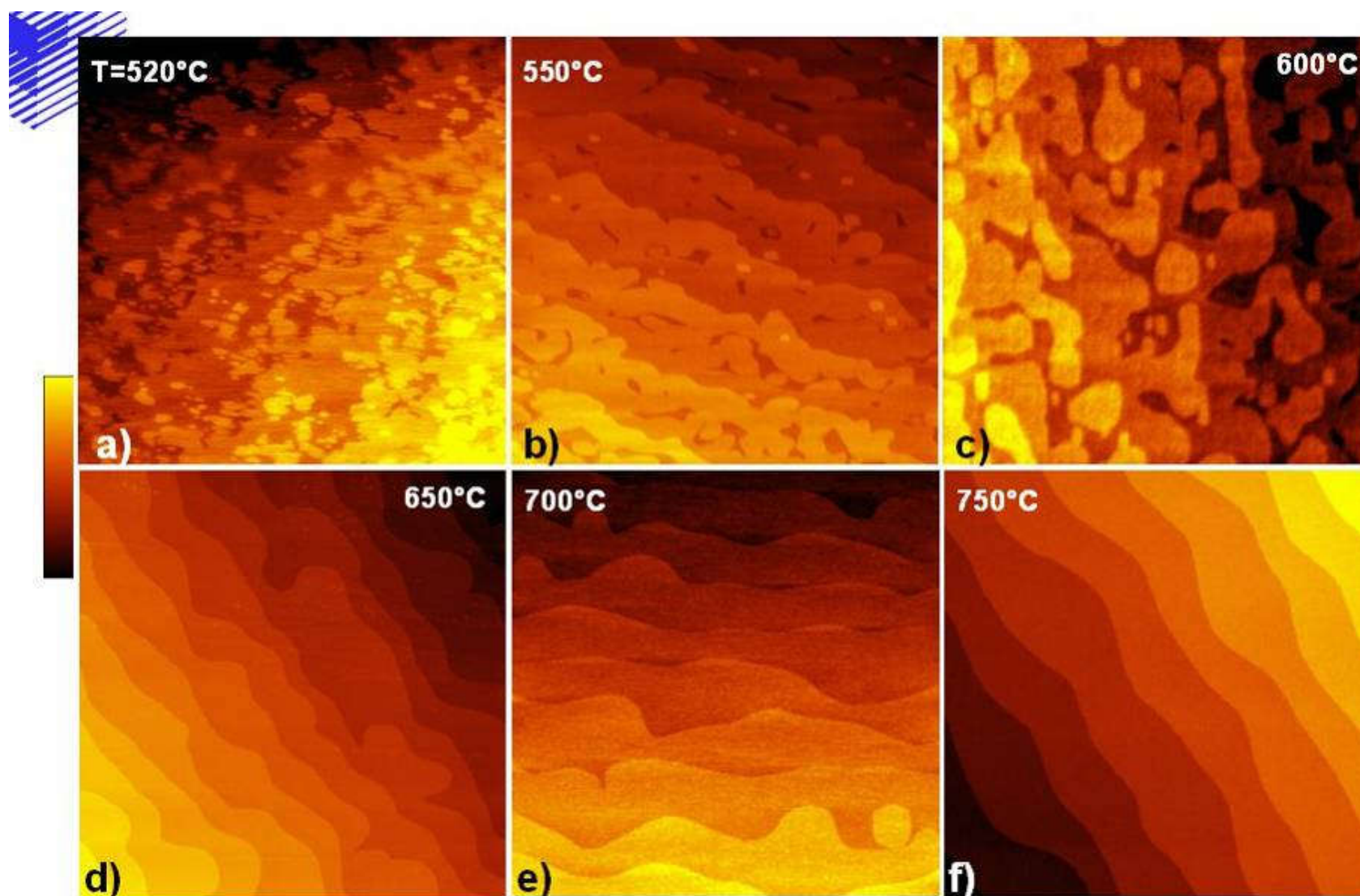
**terrace (梯田)**





# Deposition at Surfaces

GaAs  
growth

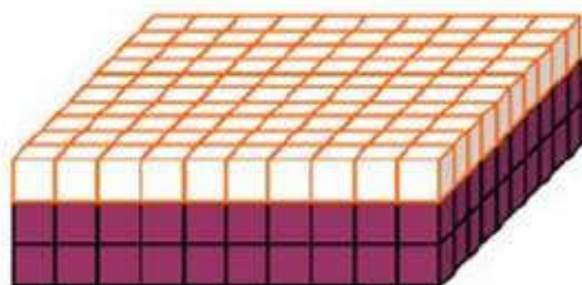


Transition from 2D island nucleation to step flow growth (MOCVD).  
5X5 $\mu\text{m}^2$  post-growth AFM scans, height scale 2-5nm

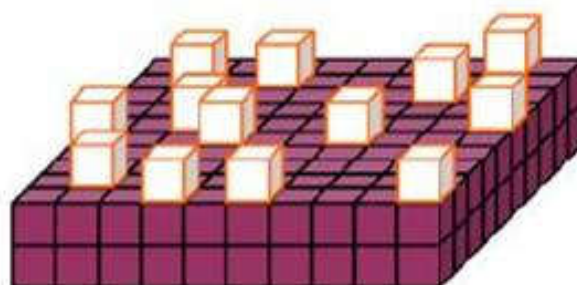


# Growth Mechanisms

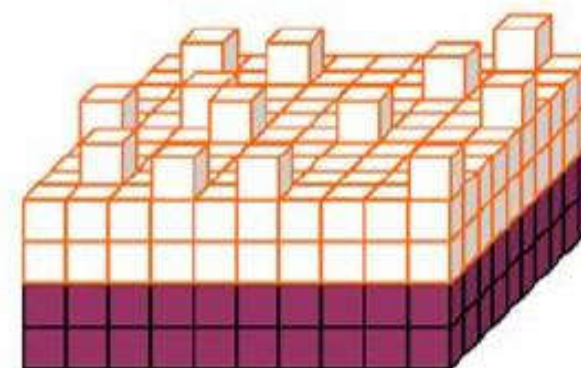
competition between surface and interface energies



Frank-van der Merwe mode  
(2 dimensional growth mode)



Volmer-Weber mode  
(Island growth mode)



Stranski-Krastanov mode  
(Layer & island growth mode)

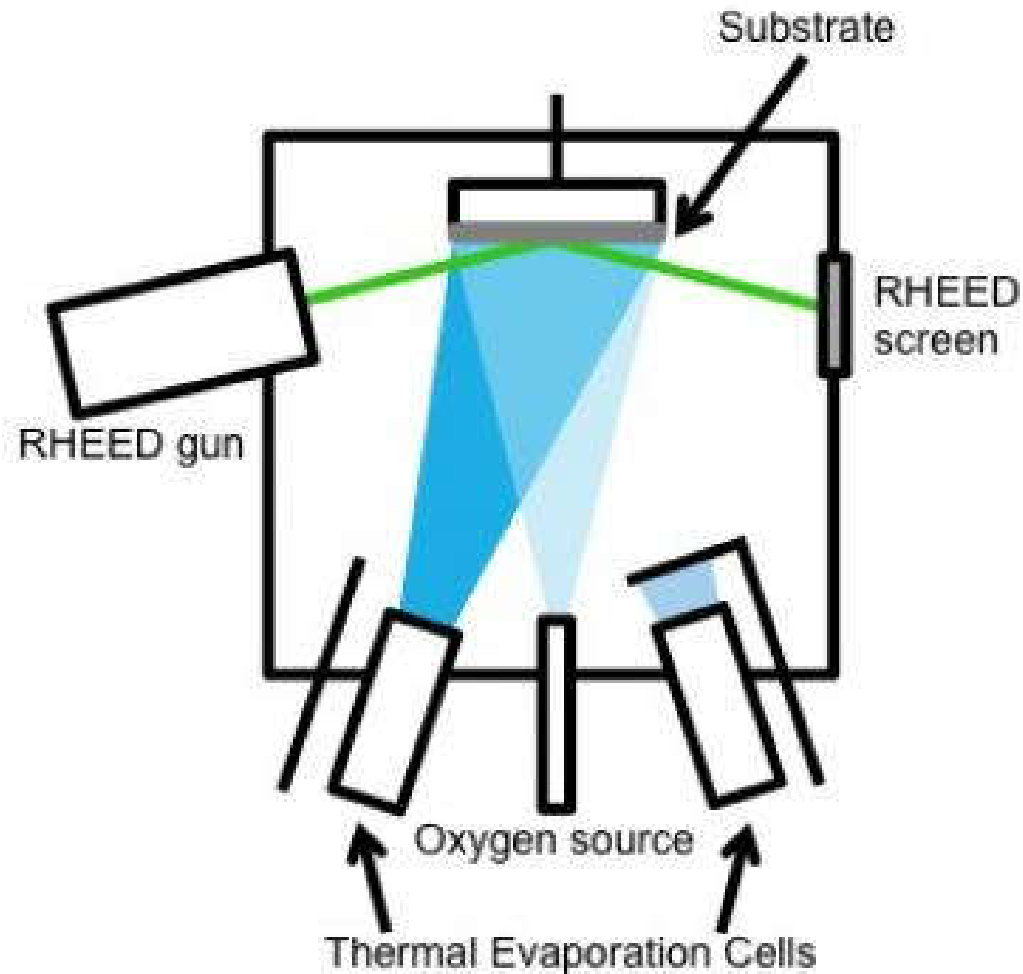
interface energy ↓

interface energy ↑

interface energy ↓ ↑



# Online Surface Monitoring

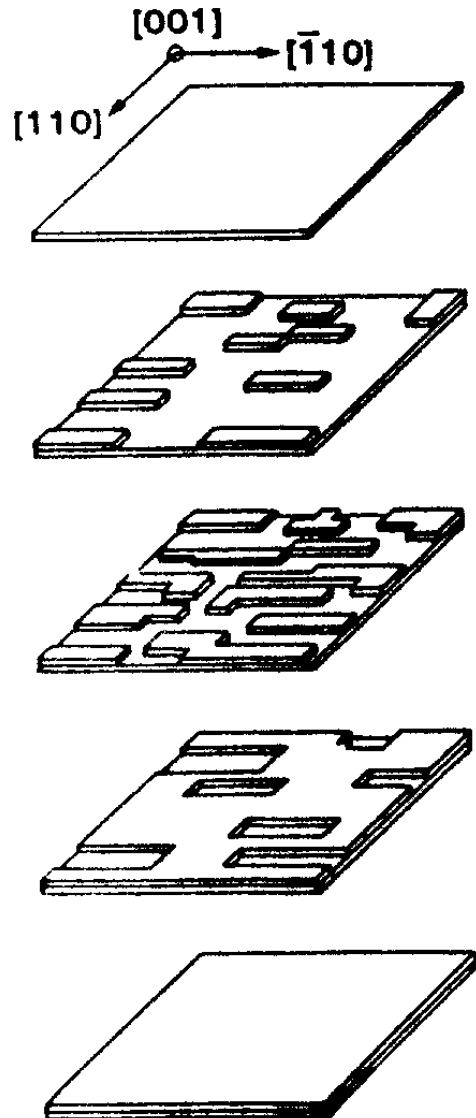


**Reflection high-energy  
electron diffraction  
(RHEED)**

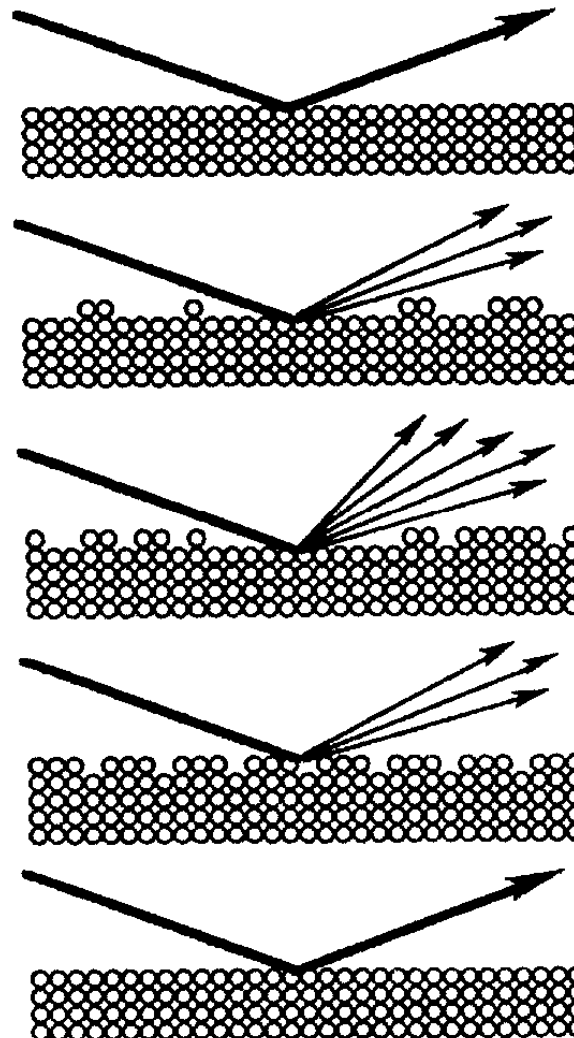
**MBE system**

# Online Surface Monitoring

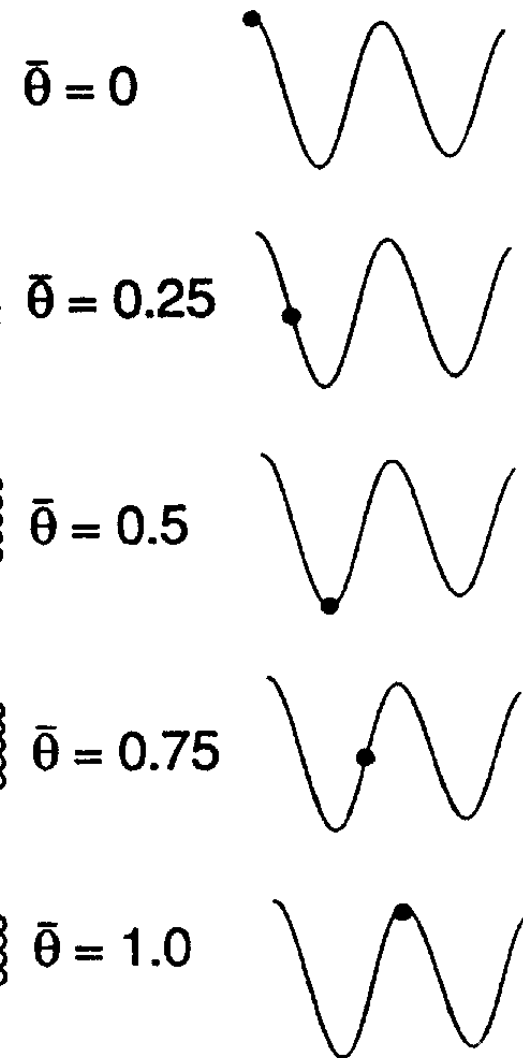
MONOLAYER GROWTH



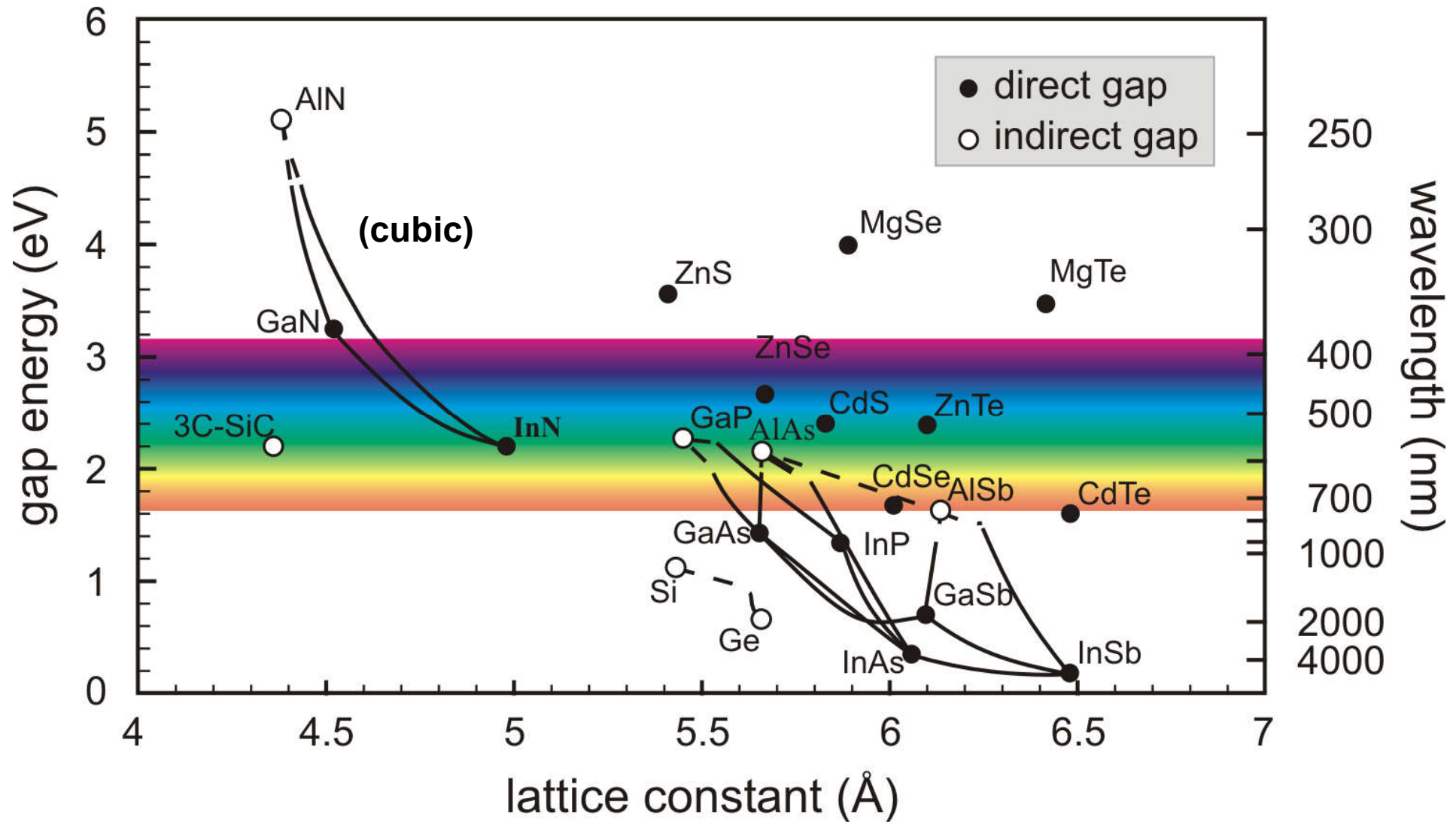
ELECTRON BEAM



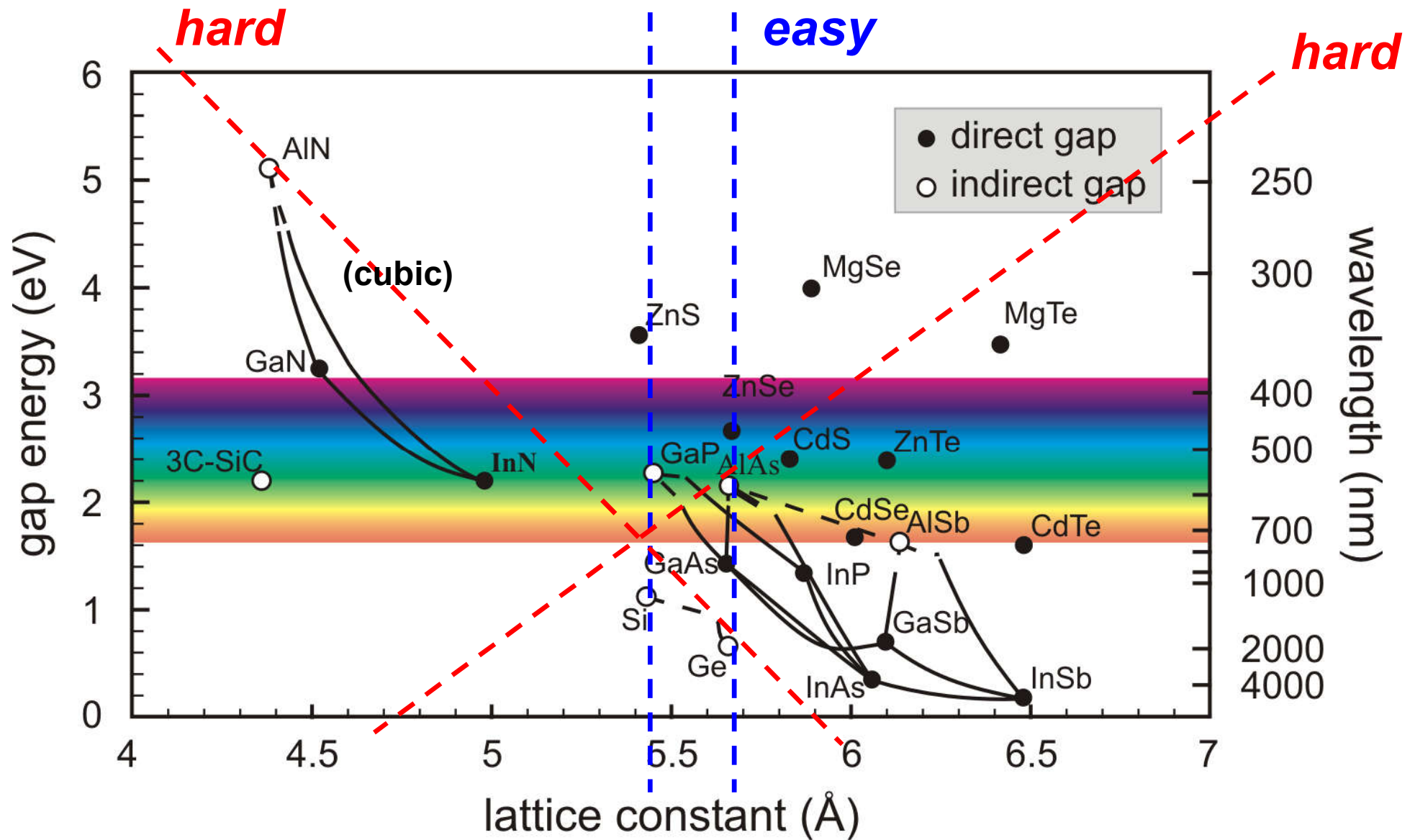
RHEED SIGNAL



# Lattice Constants vs. Bandgap



# Lattice Constants vs. Bandgap





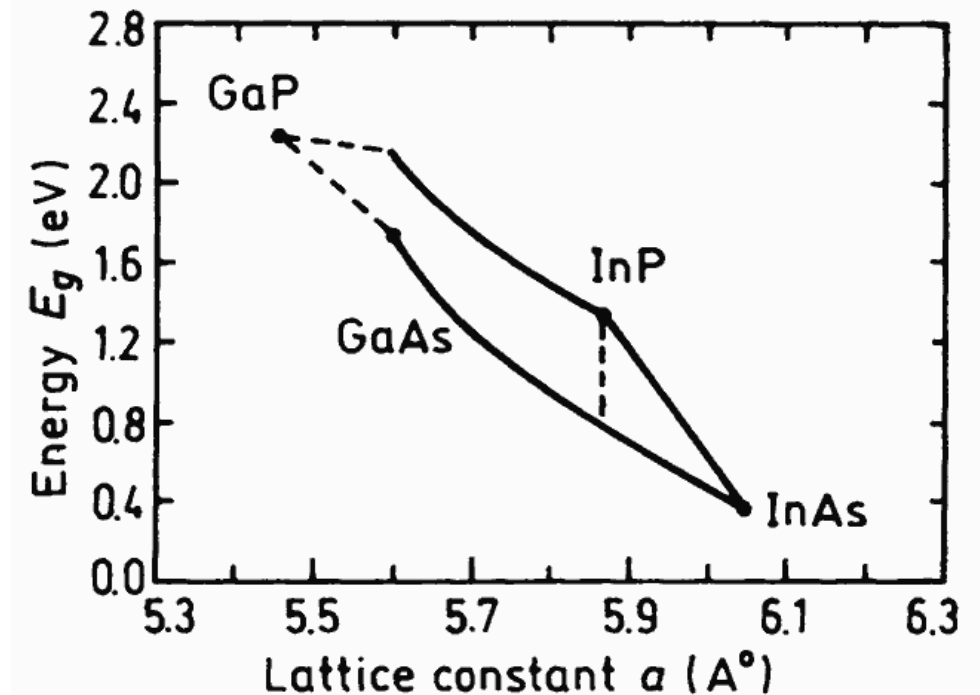
# Lattice Constants vs. Bandgap

Vegard's law: assume linear mixing

For  $A_x B_{1-x}$

$$a = x \cdot a_A + (1 - x) \cdot a_B$$

$$E_g = x \cdot E_{gA} + (1 - x) \cdot E_{gB}$$



**Q:  $In_x Ga_{1-x} As$  on InP?**

**Q: How to design a 1.55  $\mu m$  laser?**

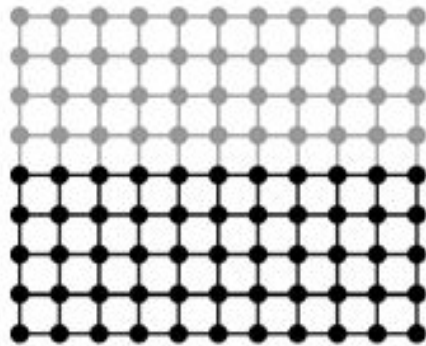
# Lattice Matched/Mismatched Growth

'metamorphic' growth

thin film

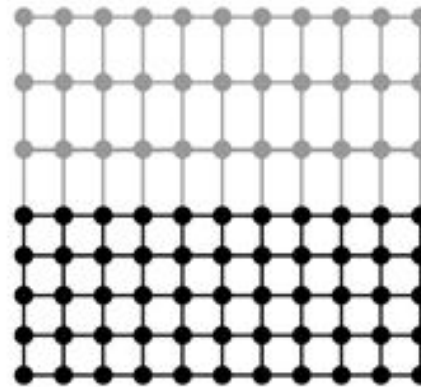
thick film

Lattice matched



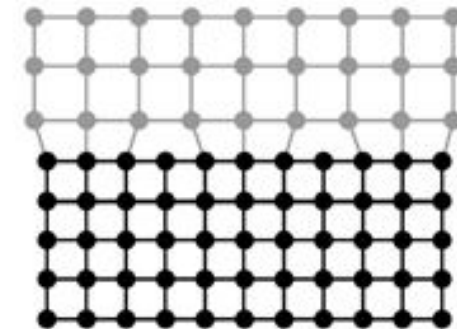
substrate

Strained



substrate

Unstrained



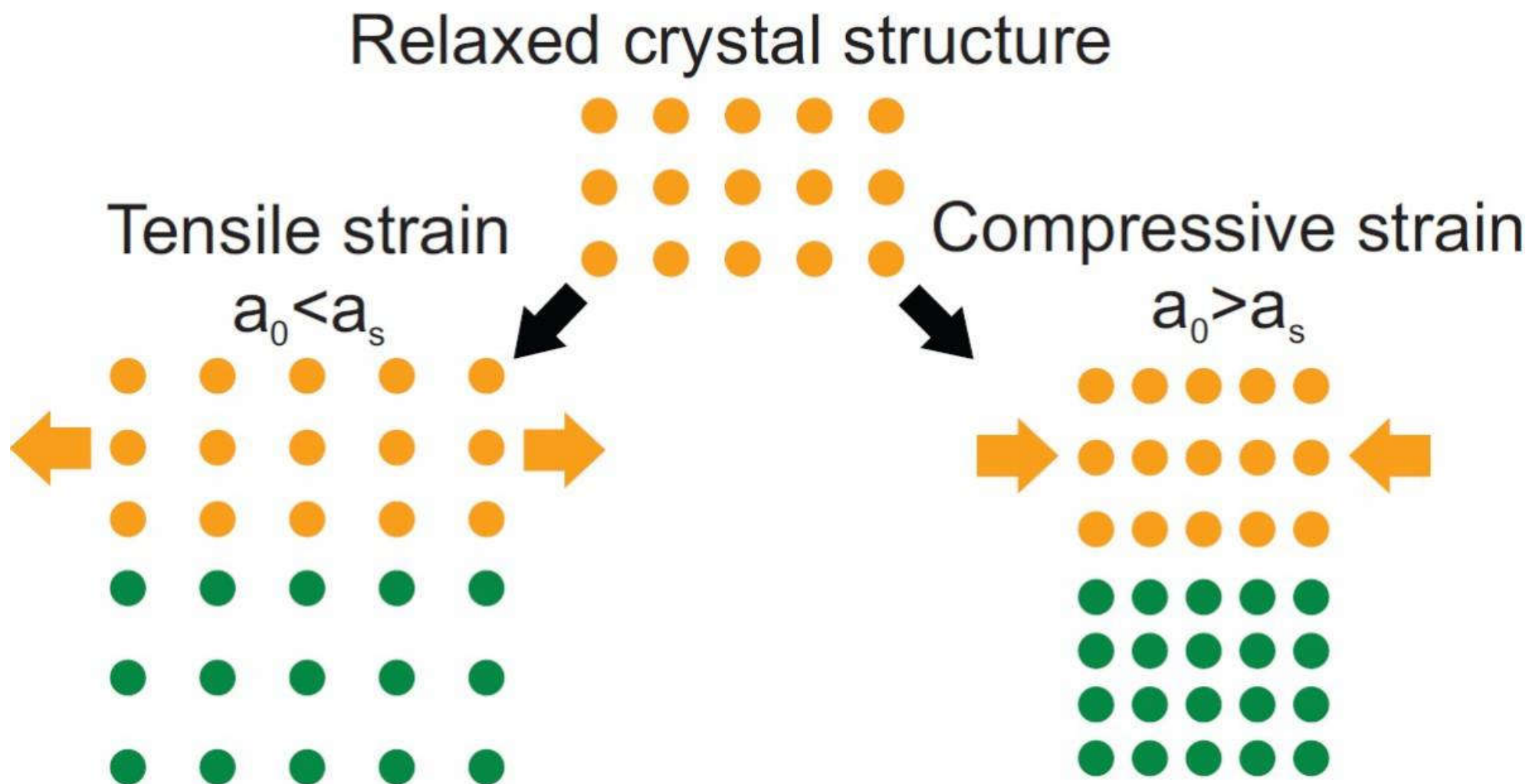
substrate

Si on Si  
GaAs on GaAs  
AlAs on GaAs  
GaAs on Ge

...

GaAs on Si, Ge on Si, GaN on Si, ...

# Strain in the Film



# Growth Energy

## strain energy

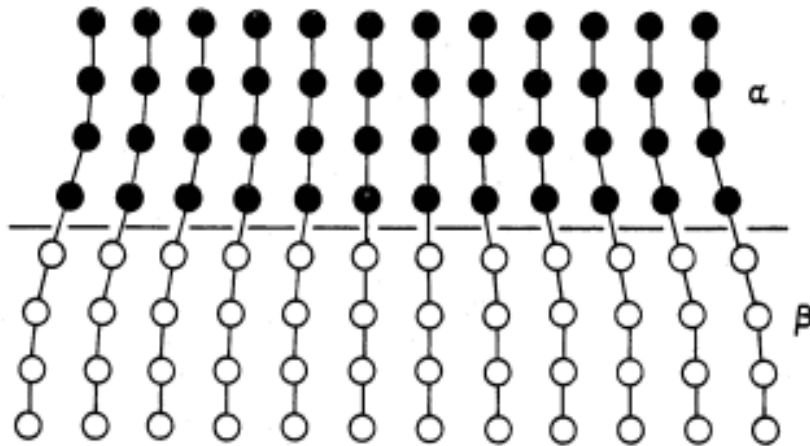


Fig. 3.34 A coherent interface with slight mismatch leads to coherency strains in the adjoining lattices.

## misfit dislocation energy

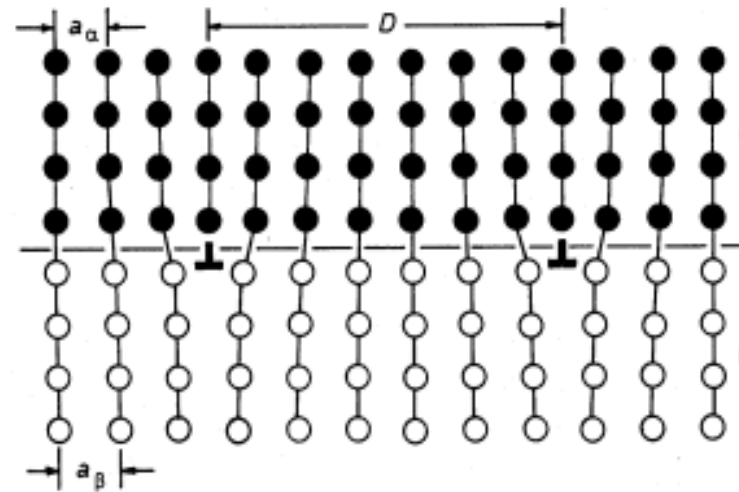


Fig. 3.35 A semicoherent interface. The misfit parallel to the interface is accommodated by a series of edge dislocations.

$$E_{\varepsilon} = \frac{\varepsilon^2 Y}{1 - \nu} d$$

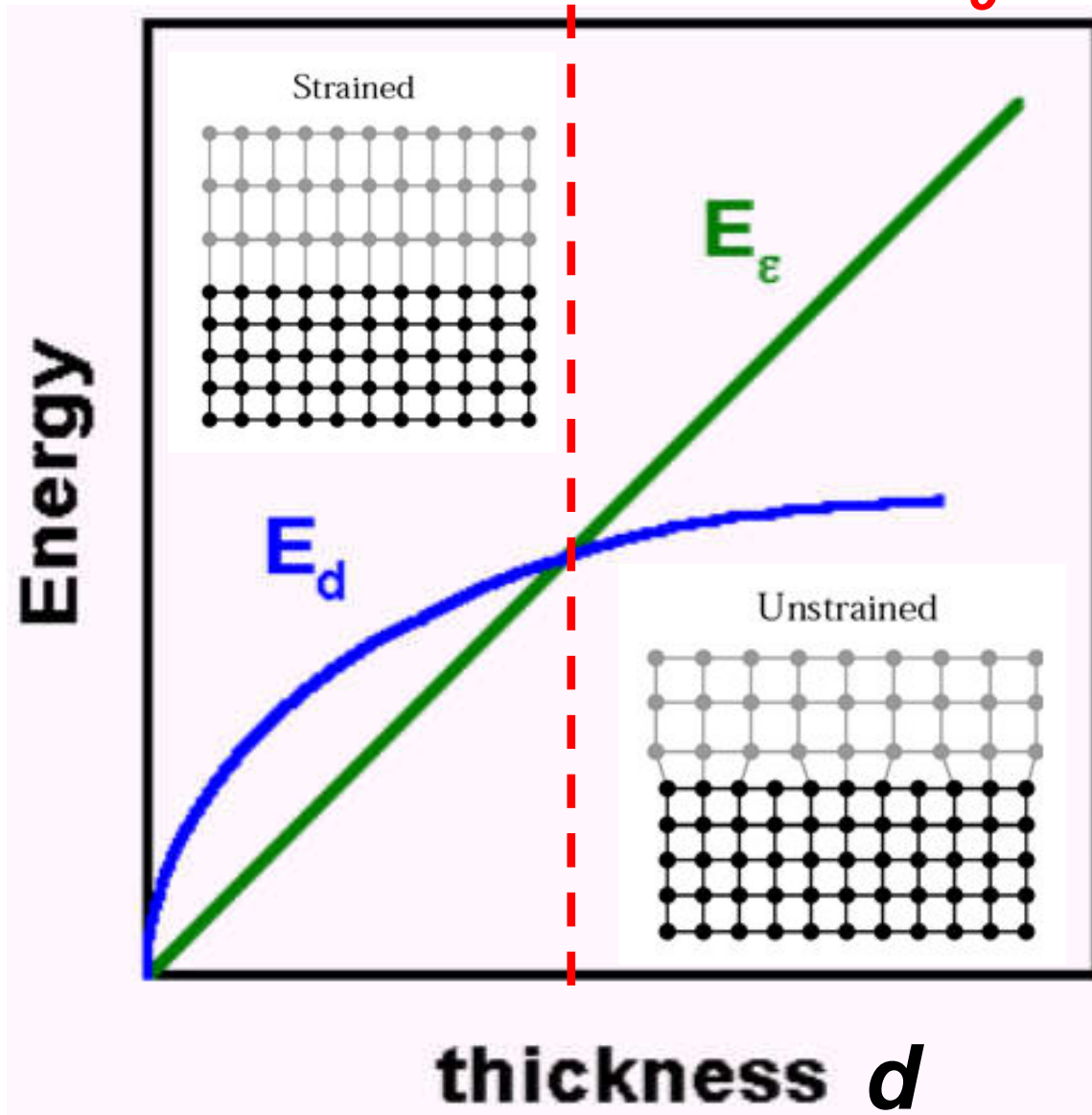
$$E_{\varepsilon} \propto d$$

$$E_d = \frac{\mu b^2}{2\pi(1 - \nu)S} \ln\left(\frac{\beta d}{b}\right)$$

$$E_d \propto \ln(d)$$

# Growth Energy

*critical thickness  $d_c$*

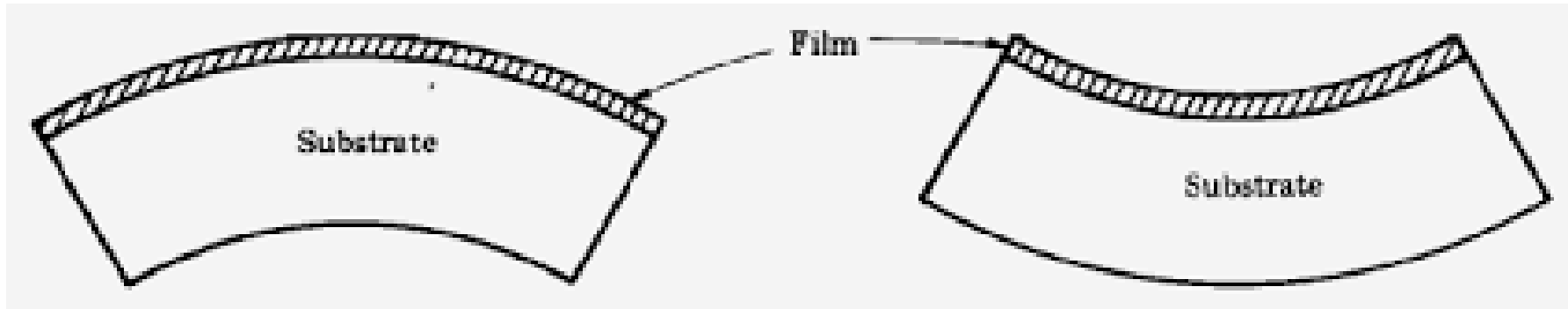


$$E_\varepsilon \propto d$$

$$E_d \propto \ln(d)$$

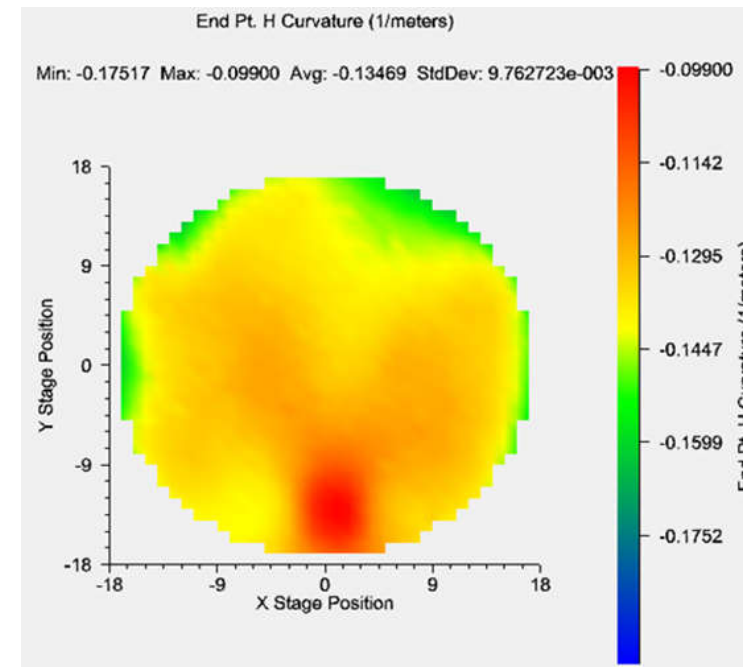
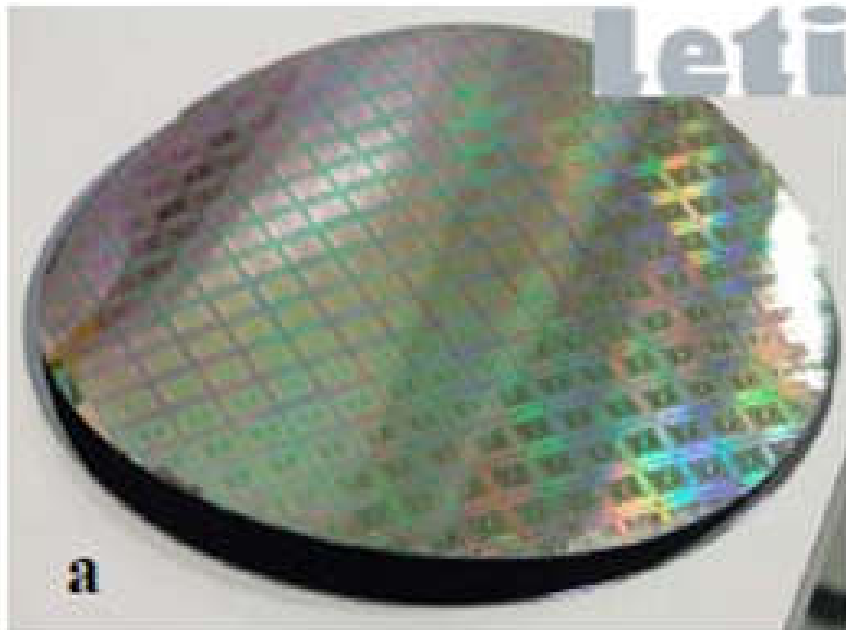


# Wafer 'Bowling' by Stress



**compressive**

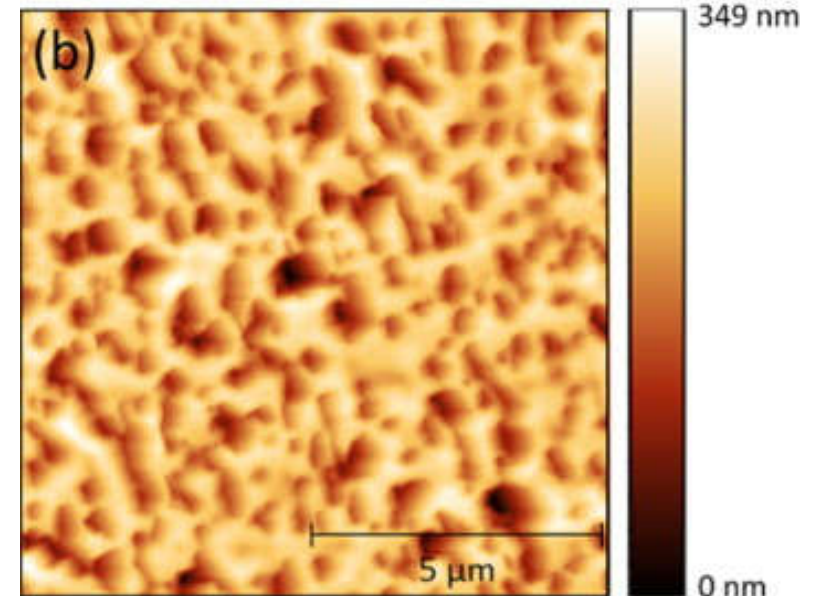
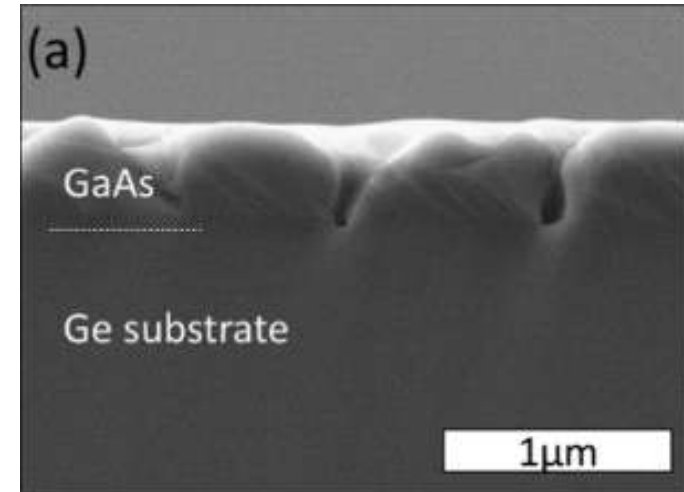
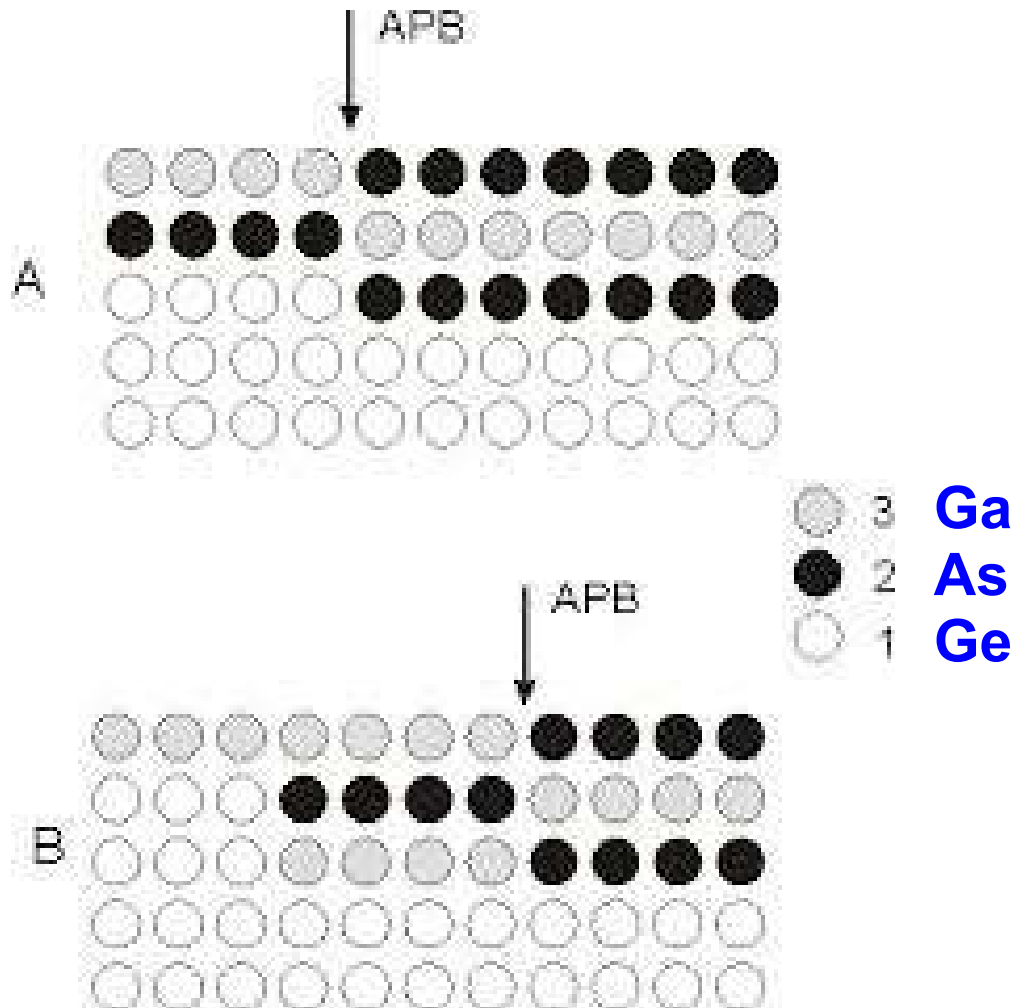
**tensile**



**stress measured by curvature**

# Anti-Phase Boundary (APB)

GaAs is lattice matched to Ge,  
but ...



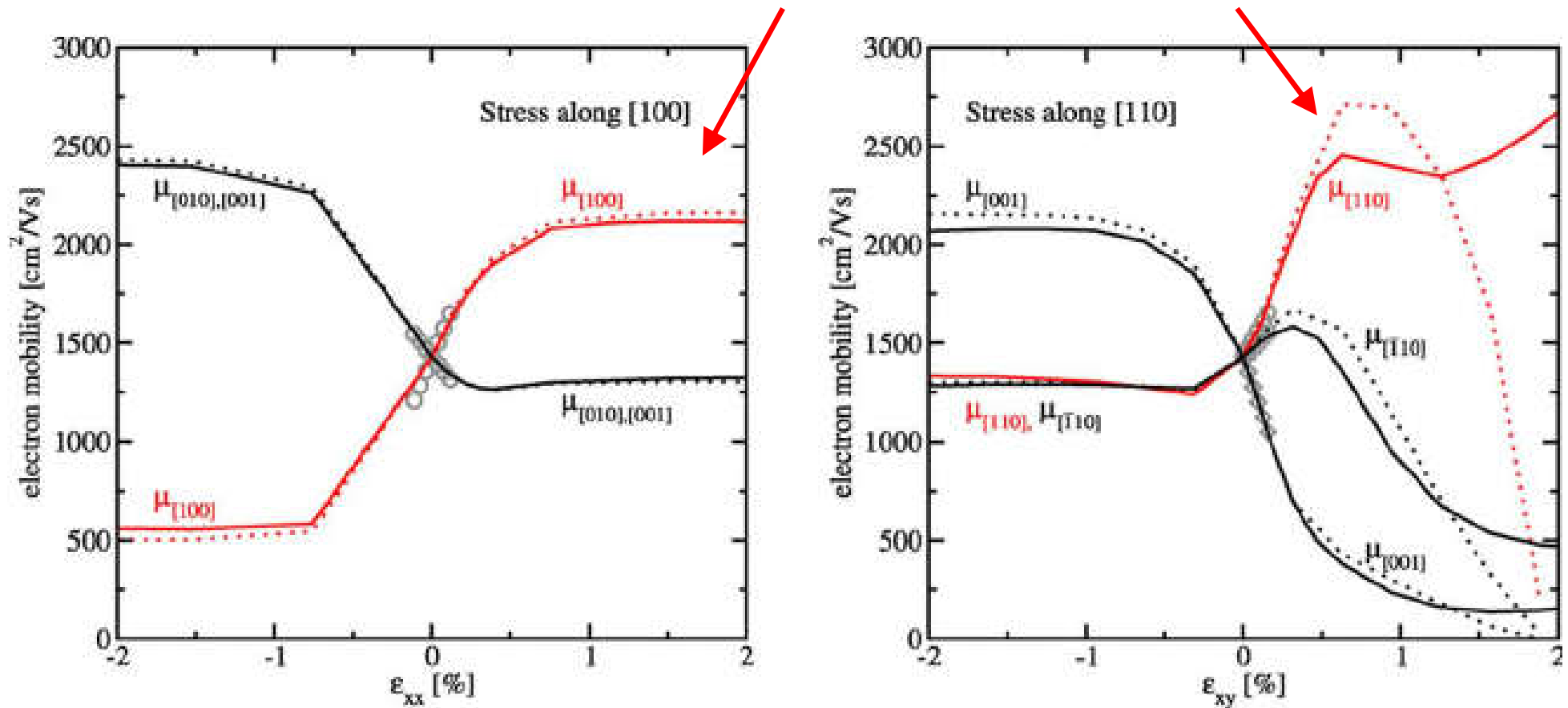
# Applications

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- **Strained Si for CMOS**
- **Quantum Wells**
- **III-V Quantum Dots**
- **Colloidal Quantum Dots**
- **Superlattice**
- **Selective Area Growth**
- **GaN Growth**
- **Nanowires**
- **2D Materials Growth**
- **Multijunction Solar Cells**
- **Epitaxial Liftoff**

# Strained Silicon

*tensile strain increases electron mobility*



*compressive strain increases hole mobility*

# Strained Silicon

NMOS: uniaxial tensile stress  
from stressed SiN film

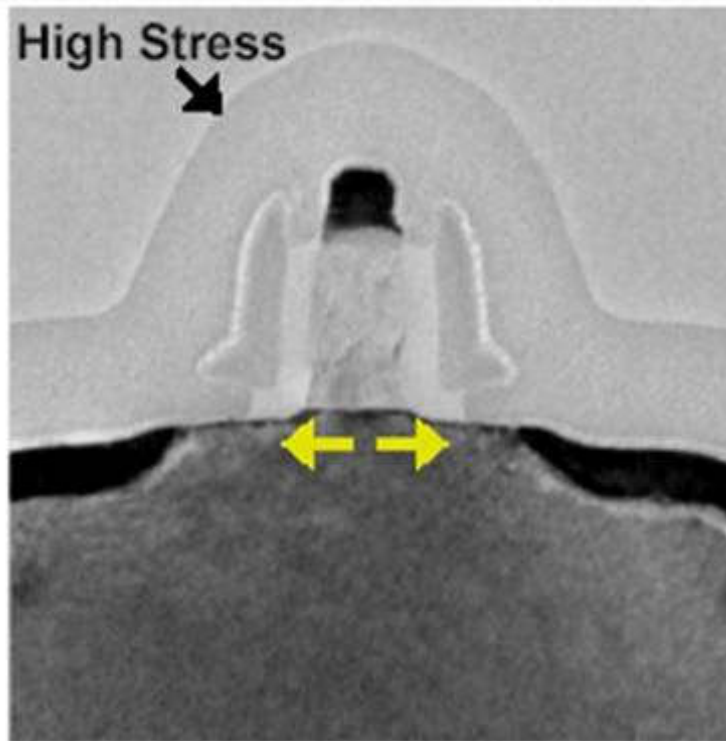


Fig. 3 TEM of NMOS transistor showing high tensile stress nitride overlayer.

PMOS: uniaxial compressive  
stress from sel. SiGe in S/D

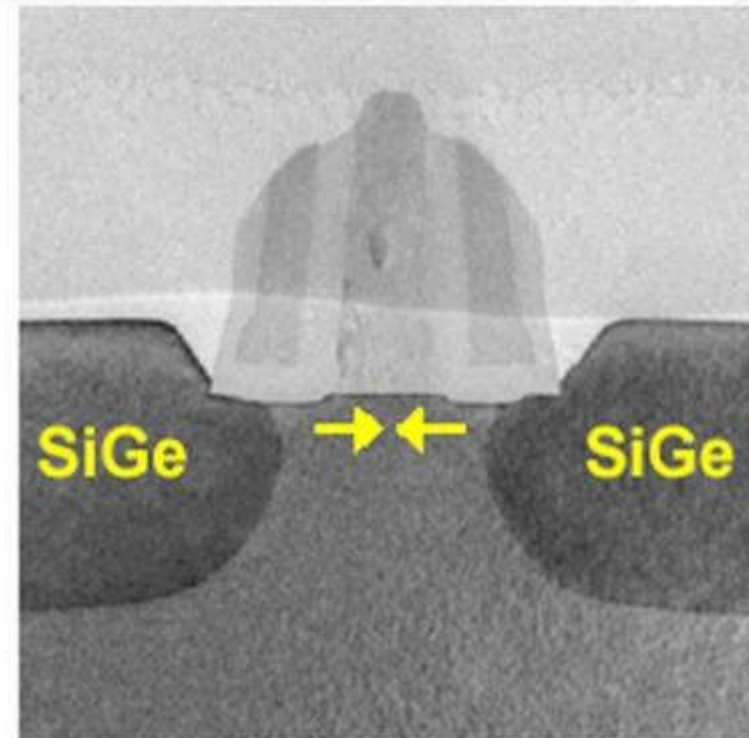


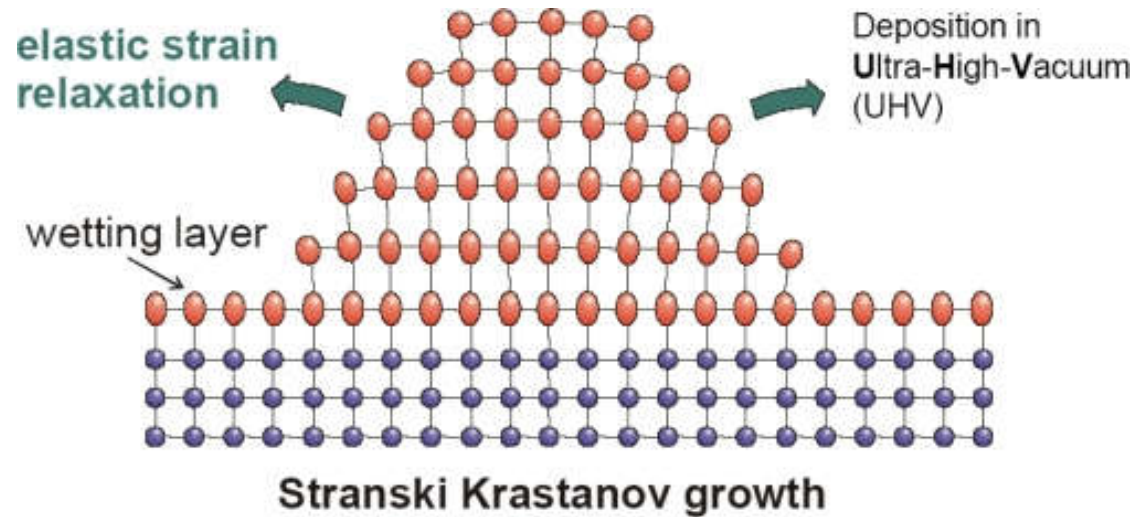
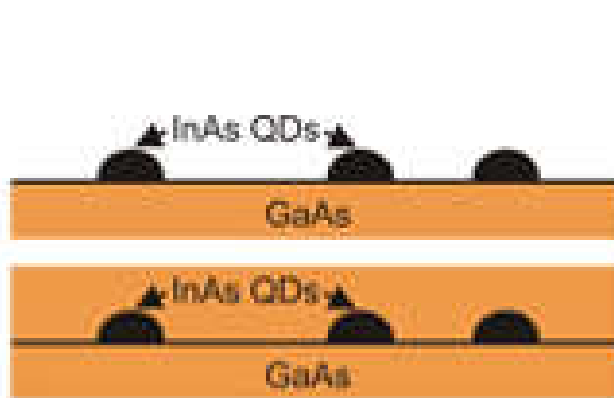
Fig. 4 TEM of PMOS showing SiGe heteroepitaxial S/D inducing uniaxial strain.


From K. Mistry et al., "Delaying Forever: Uniaxial Strained Silicon Transistors in a 90nm CMOS Technology," *2004 VLSI Technology Symposium*, pp. 50-51.




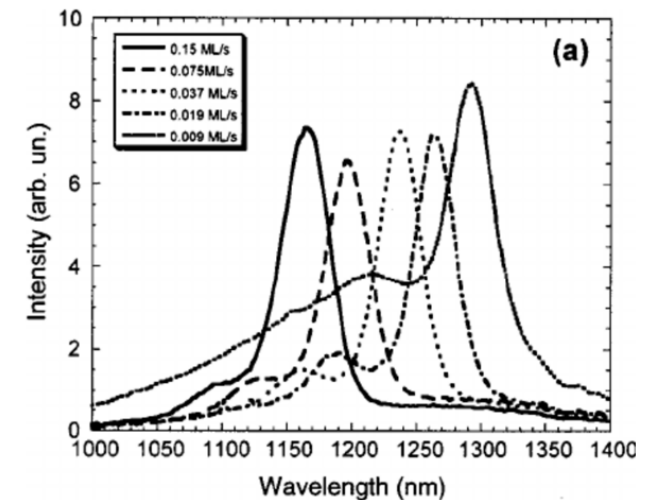
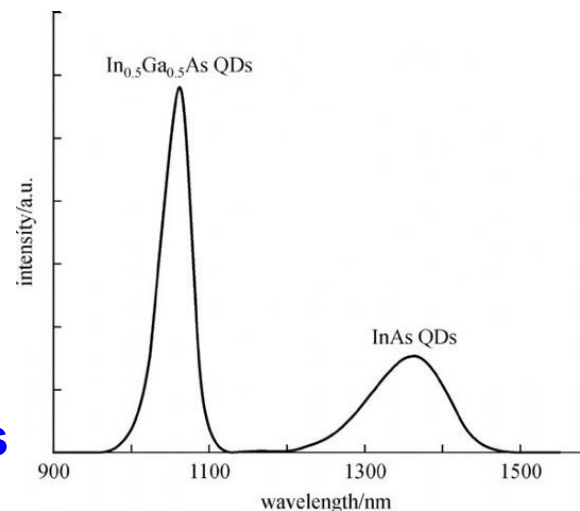
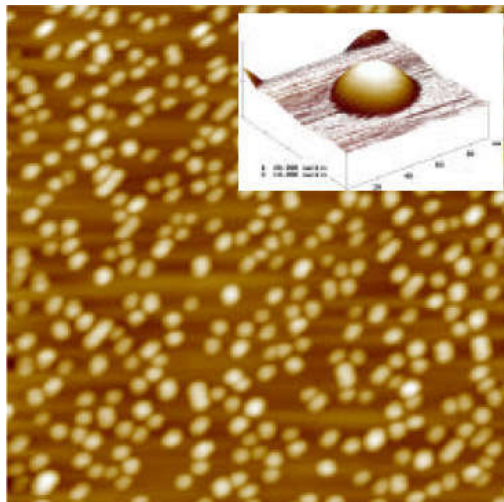
# III-V Quantum Dots

InGaAs is not lattice matched to GaAs



 smaller lattice constant,  
large band gap  
e.g.: Si, GaAs, GaInP

 larger lattice constant,  
smaller band gap  
e.g.: Ge, InAs, InP



Quantum Dot based lasers

# III-V Quantum Dots

## InGaN quantum dot LEDs

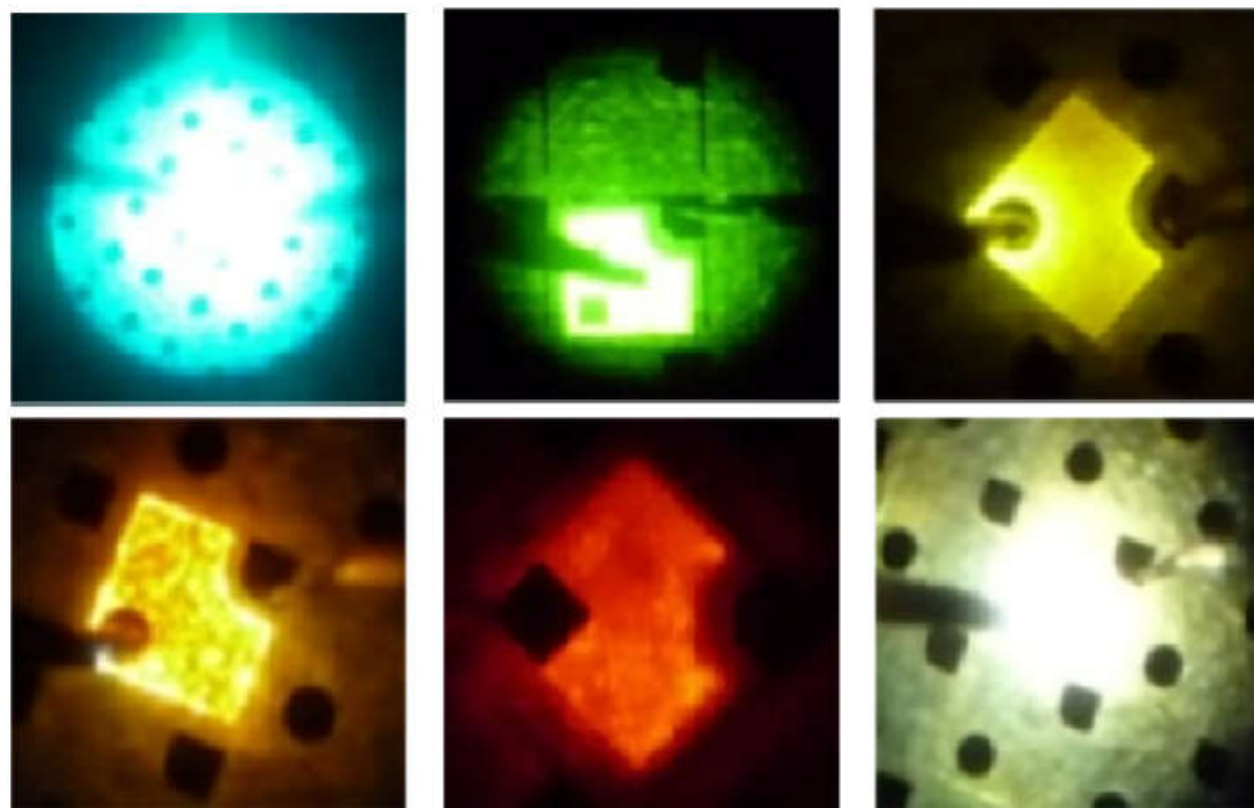
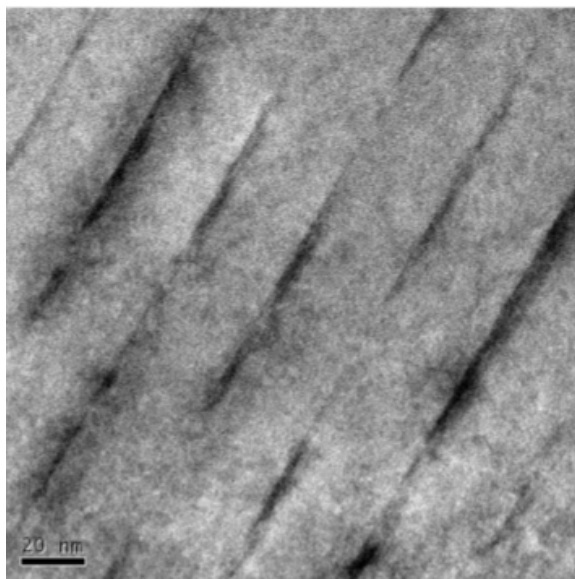
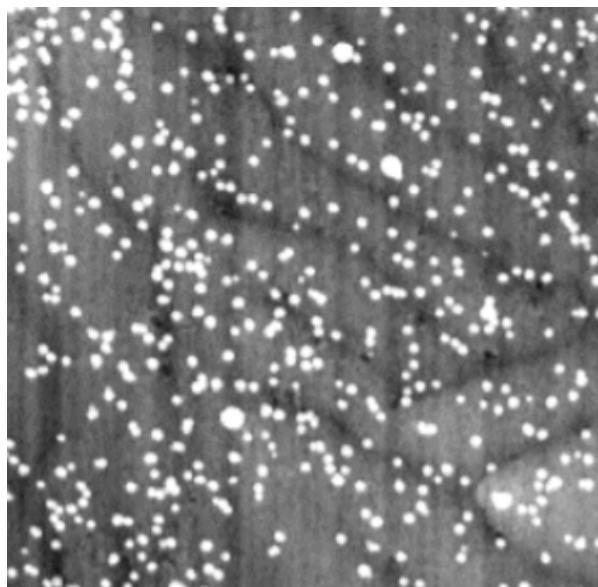
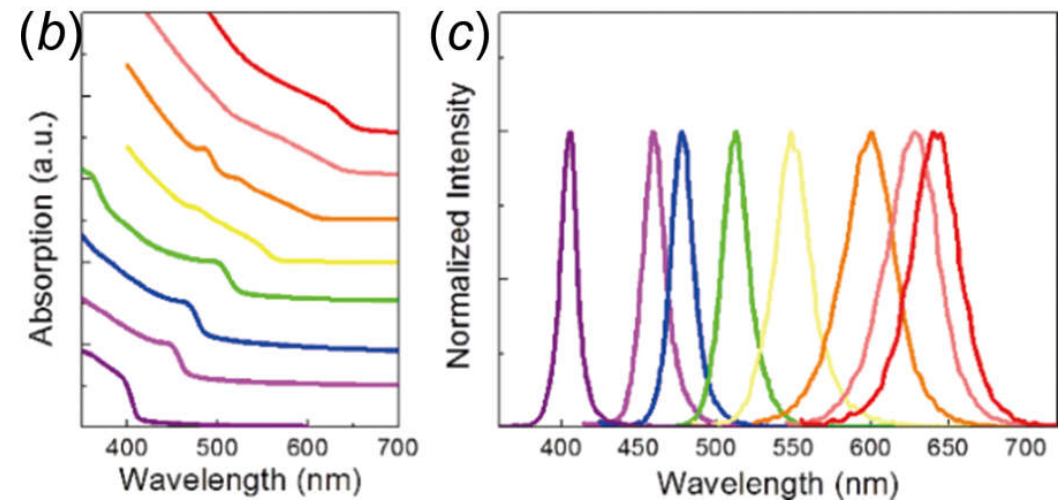
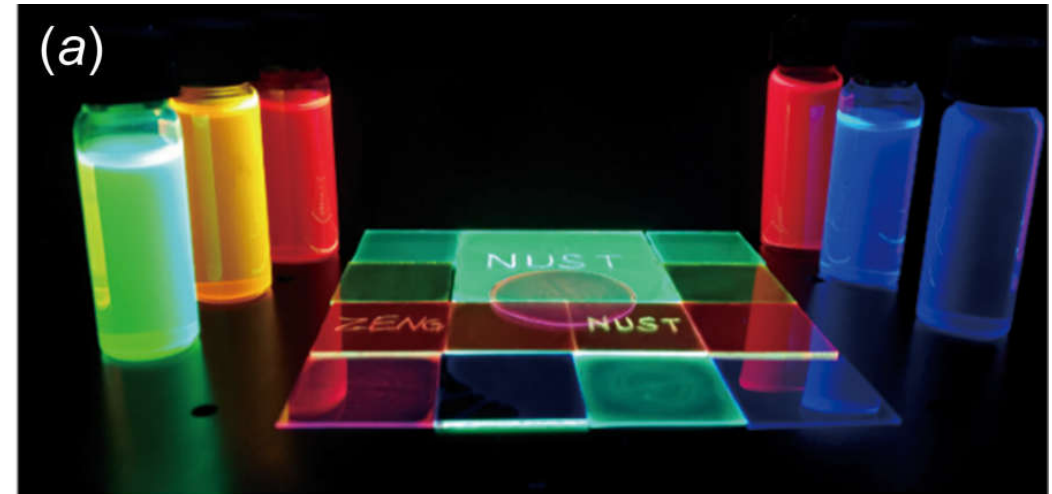
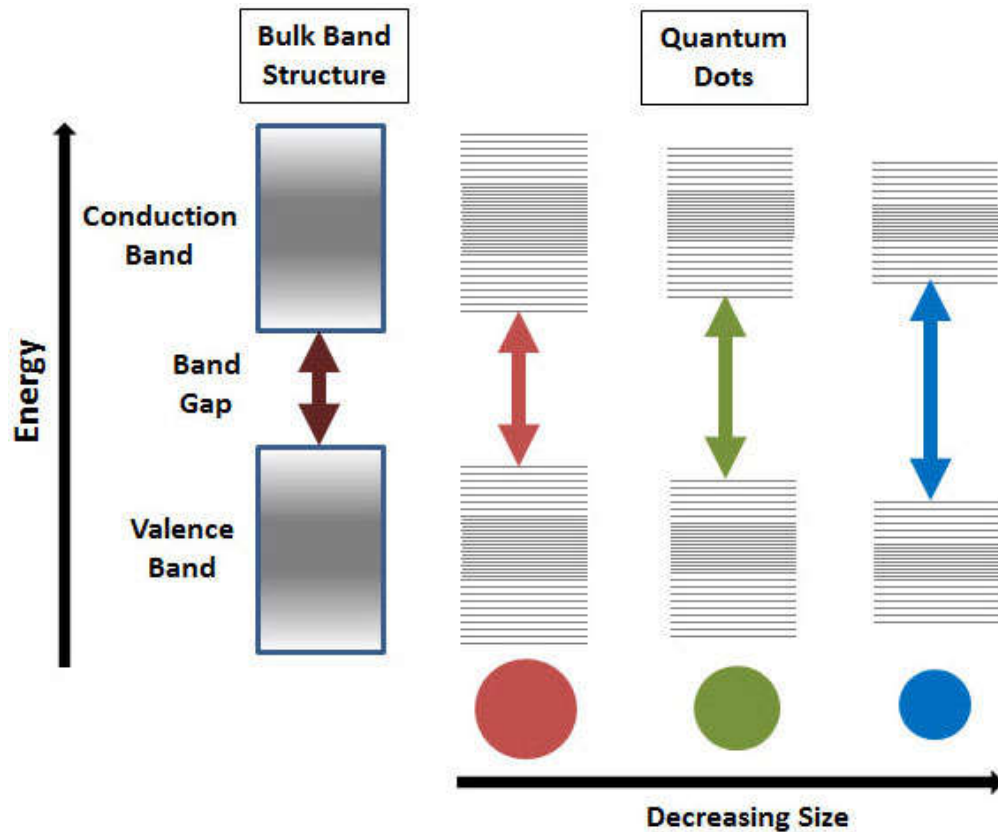


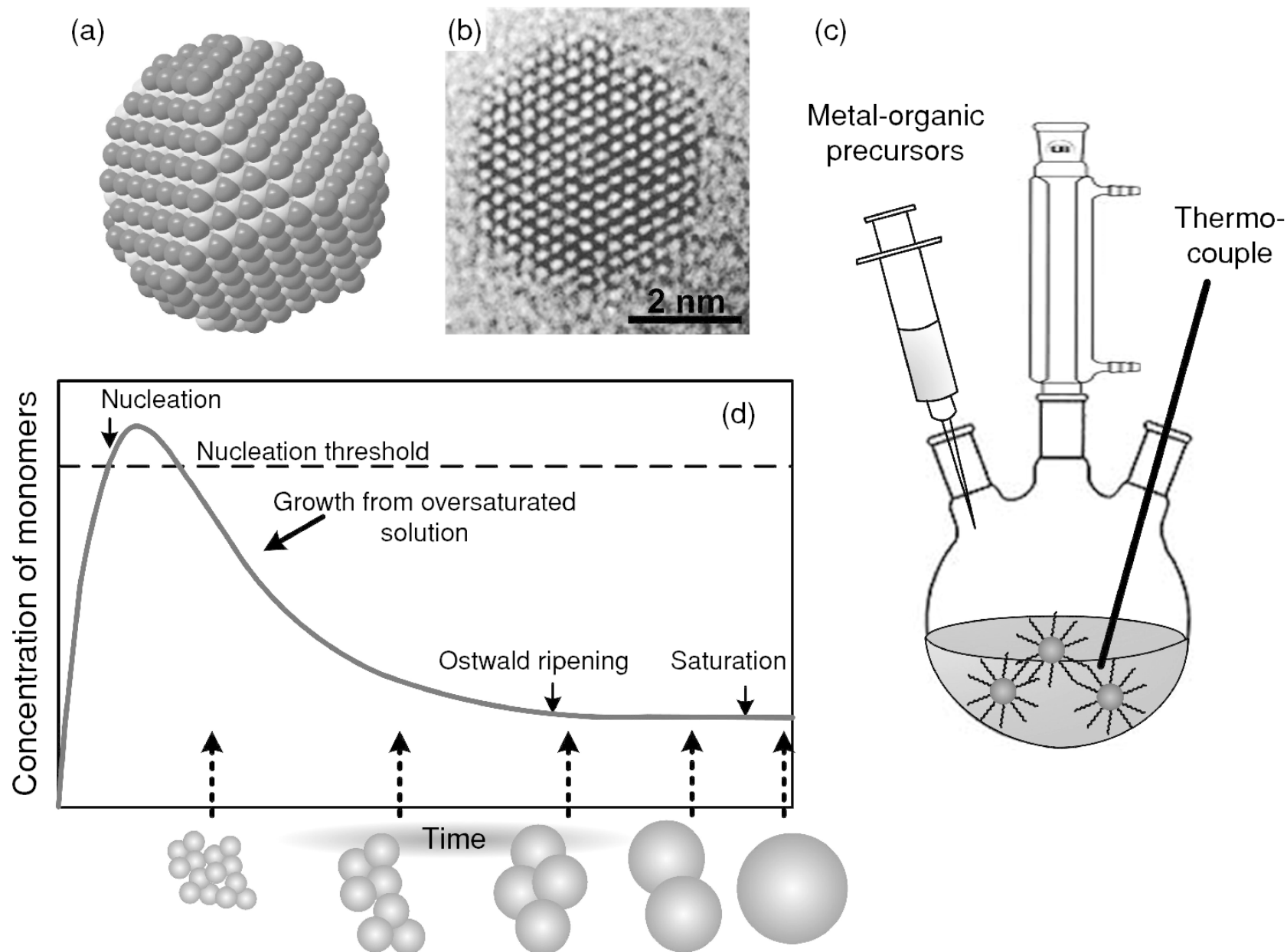
Fig. 2. Luminescence photos of InGaN QDs LEDs.

# Colloidal Quantum Dots



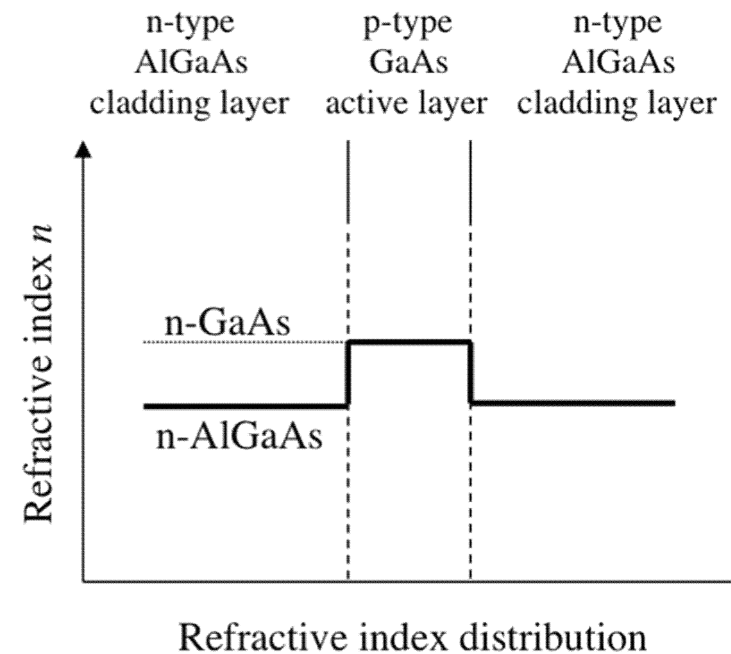
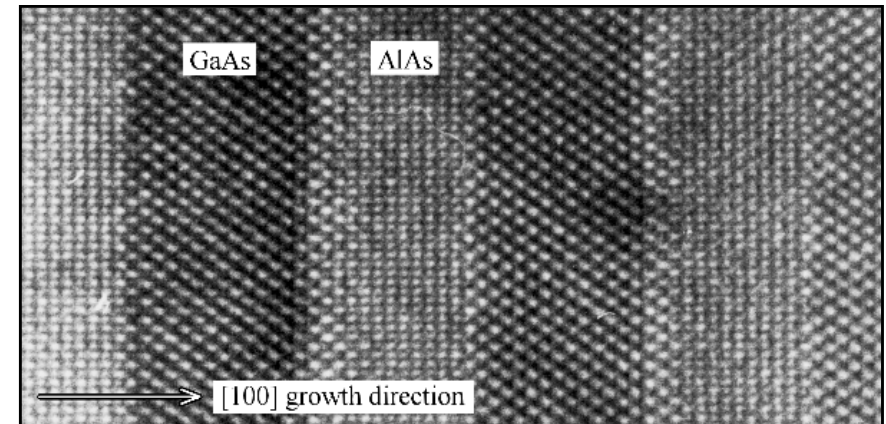
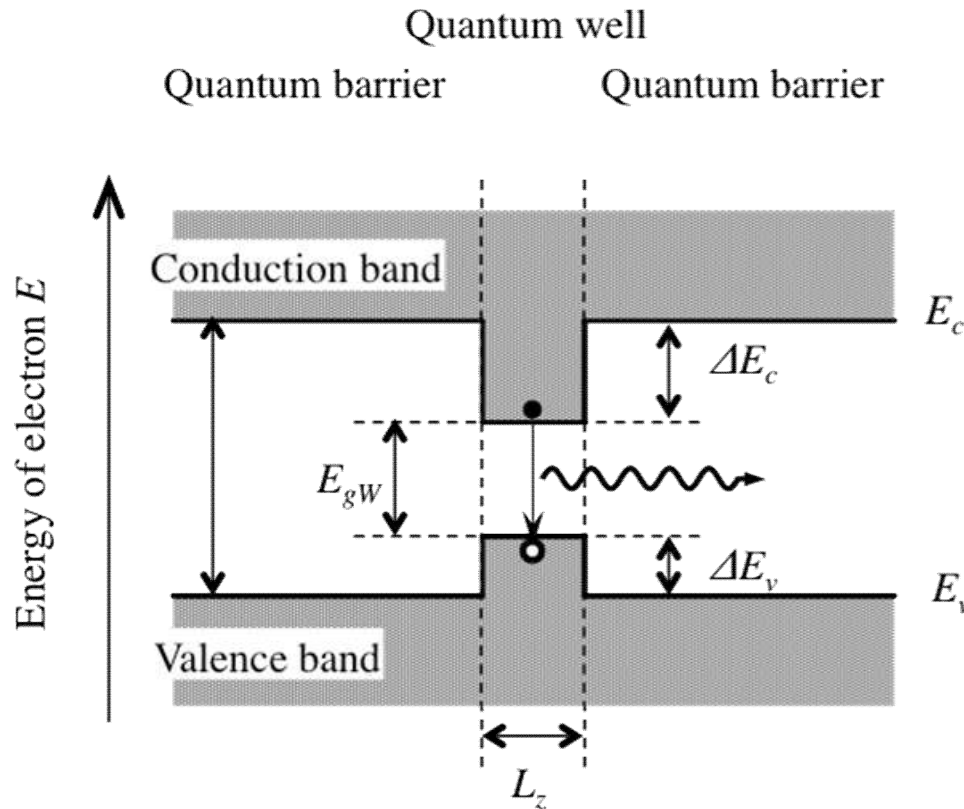


# Colloidal Quantum Dots



# Quantum Wells

## AlGaAs / GaAs quantum wells

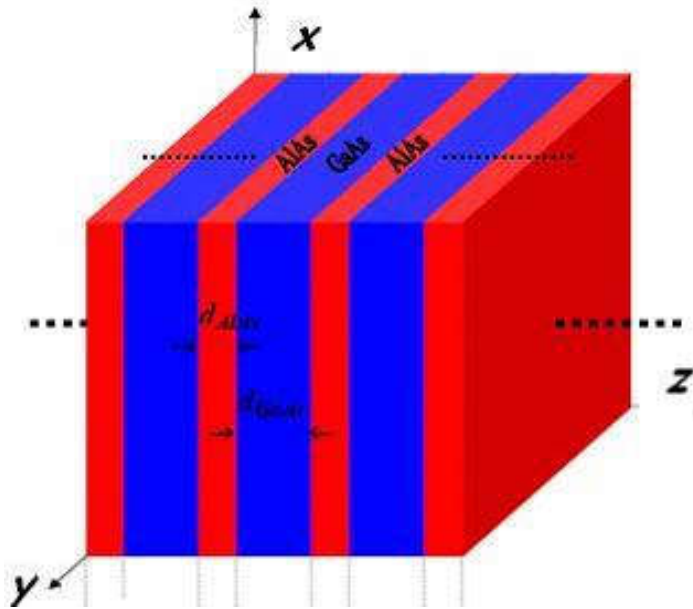


1. electronic confinement
2. optical confinement

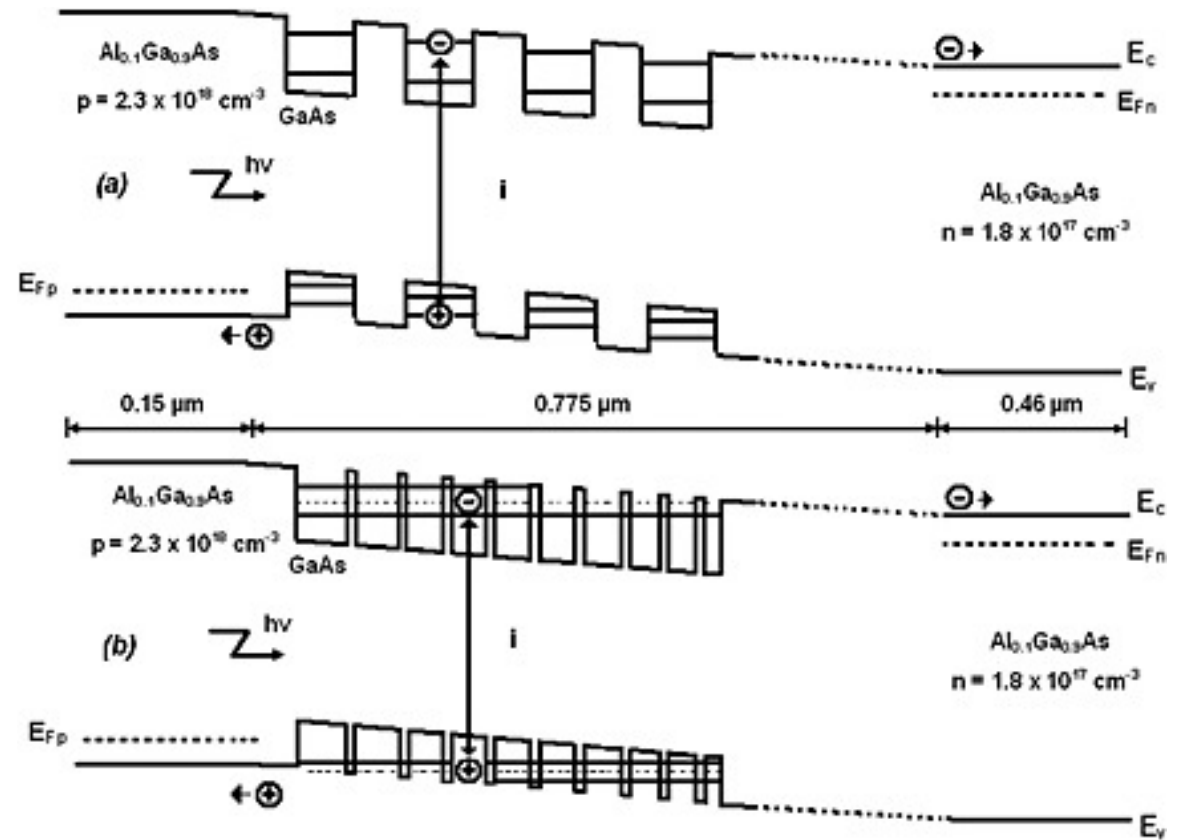
2000 Nobel Prize in Physics



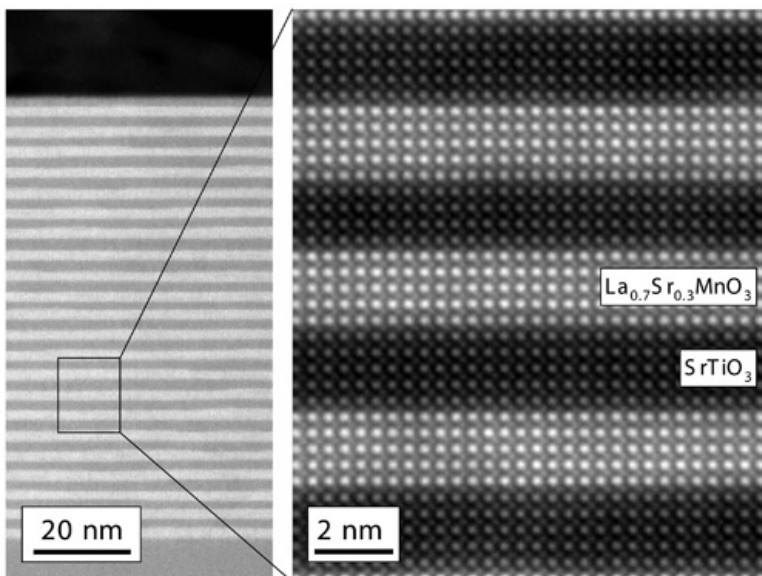
# Superlattice 超晶格



## conventional quantum wells

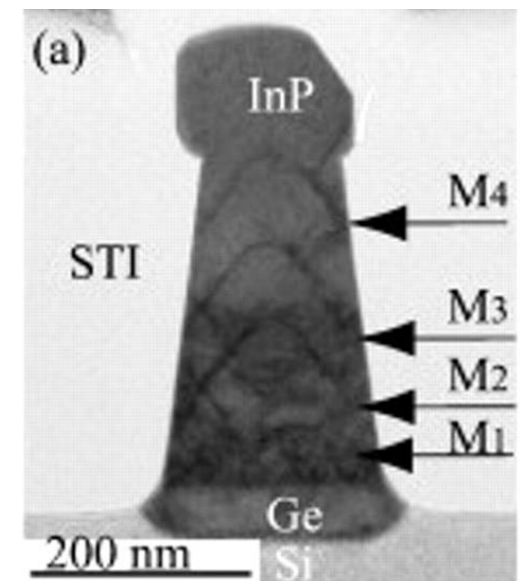
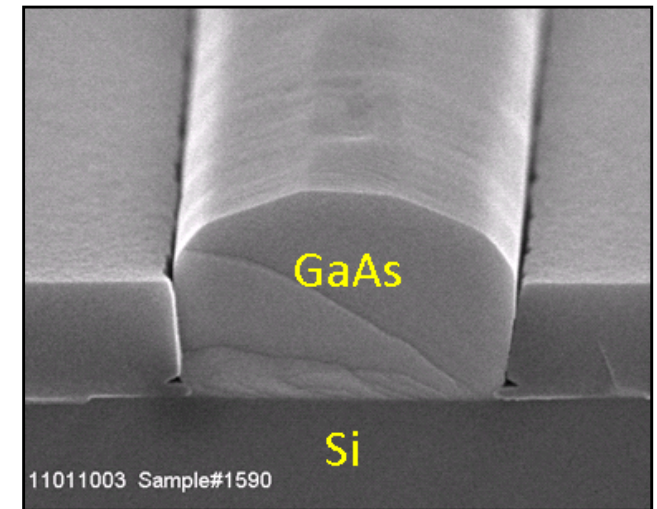
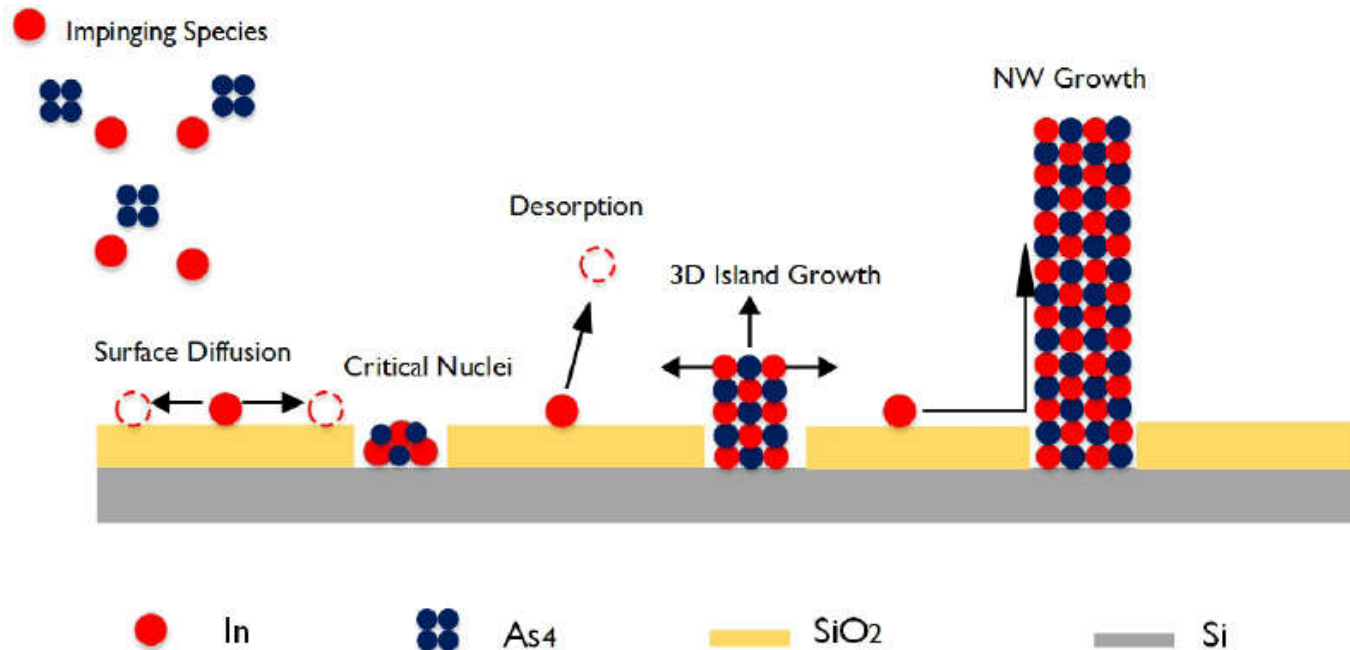


## superlattice



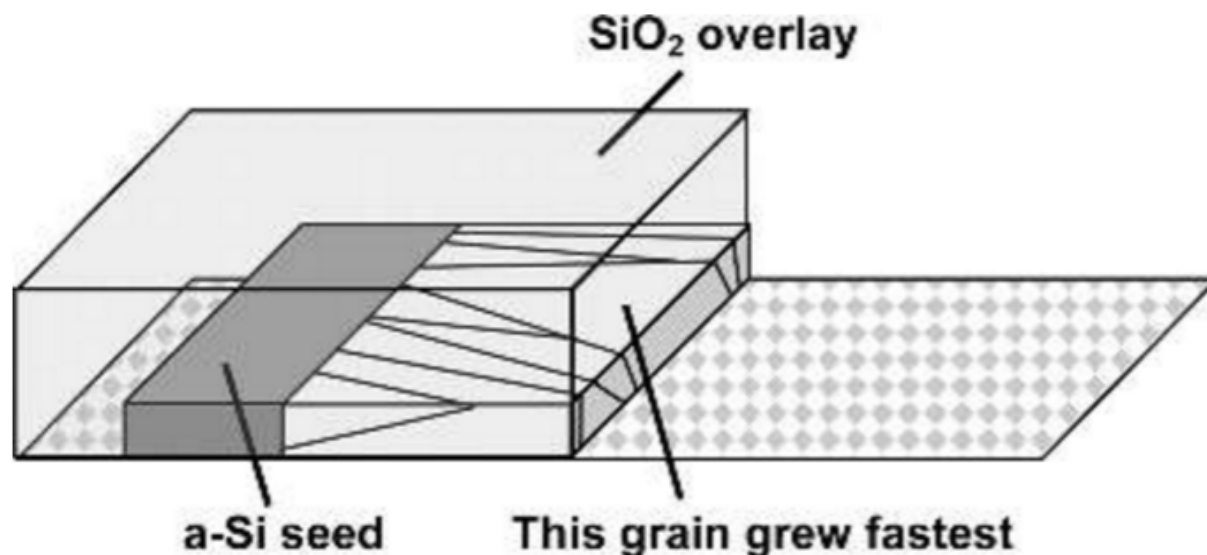
# Selective Area Growth

At high T, Ge, III-Vs grow on Si, but not on SiO<sub>2</sub>



# Selective Area Growth

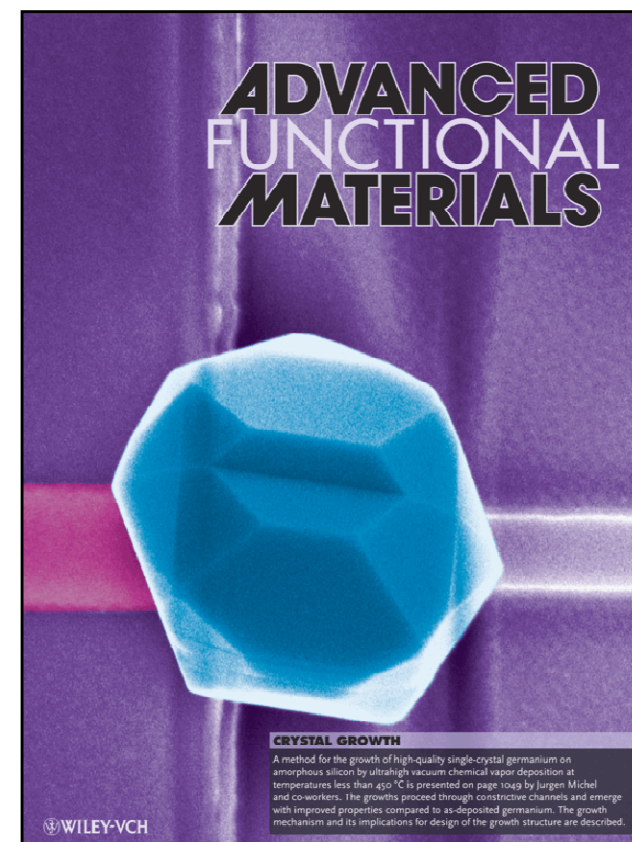
Grow Ge single crystals on amorphous substrate



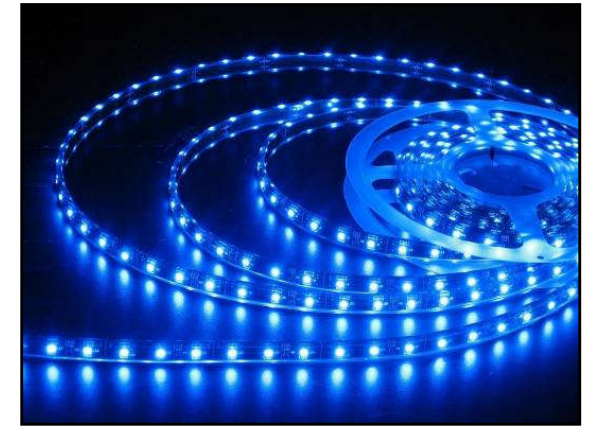
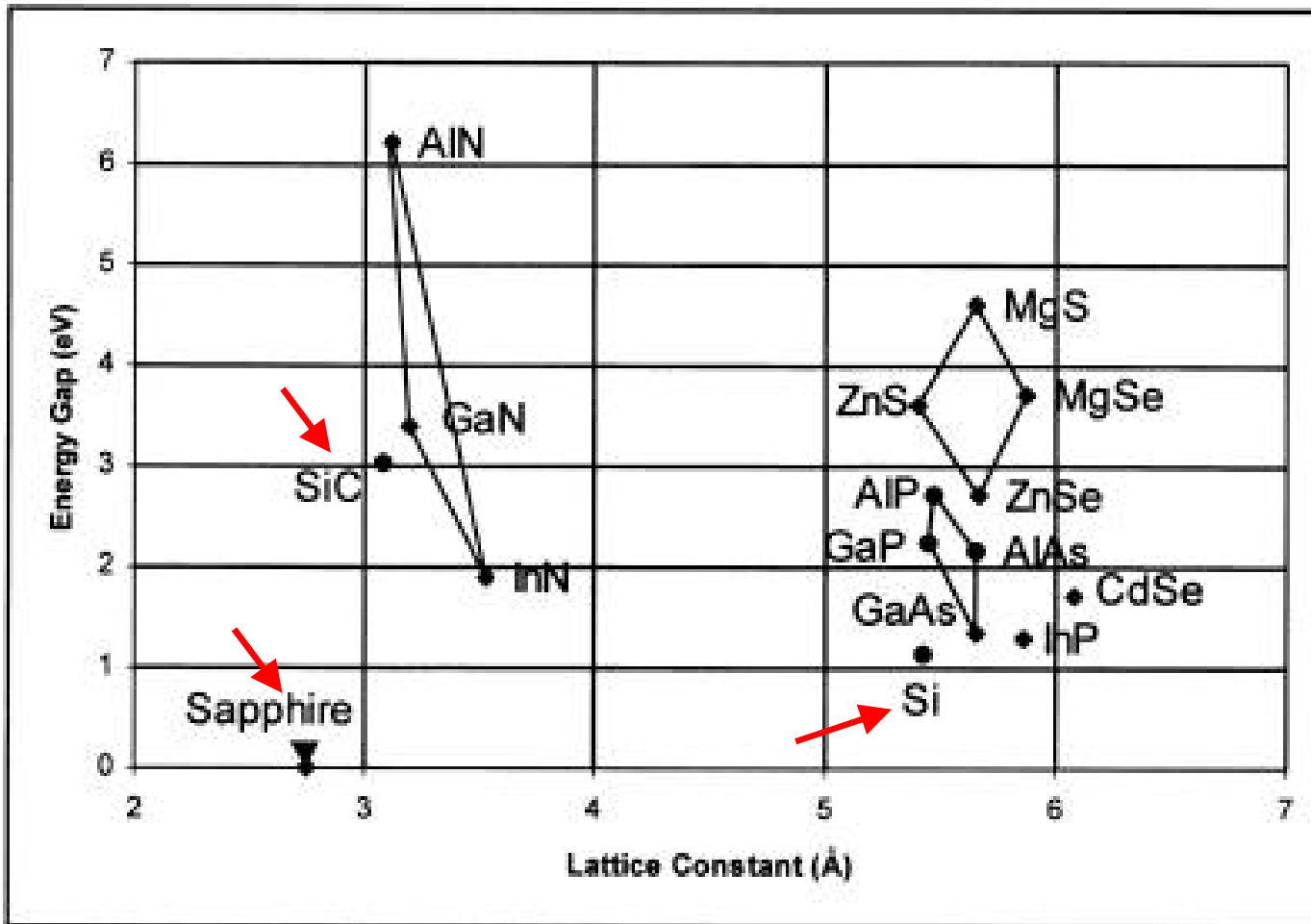
UHVCVD



*selective, only on Si, not SiO<sub>2</sub>*  
*GeO is not stable*



# GaN Growth



InGaN blue LEDs

substrate price

<b>GaN</b>	\$\$\$\$
<b>SiC</b>	\$\$\$
<b>sapphire</b>	\$\$
<b>silicon</b>	\$



# Gallium Nitride (GaN) LED

- **GaN LED on sapphire**
  - 日本, Nichia
  - 2014 Nobel Prize in Physics

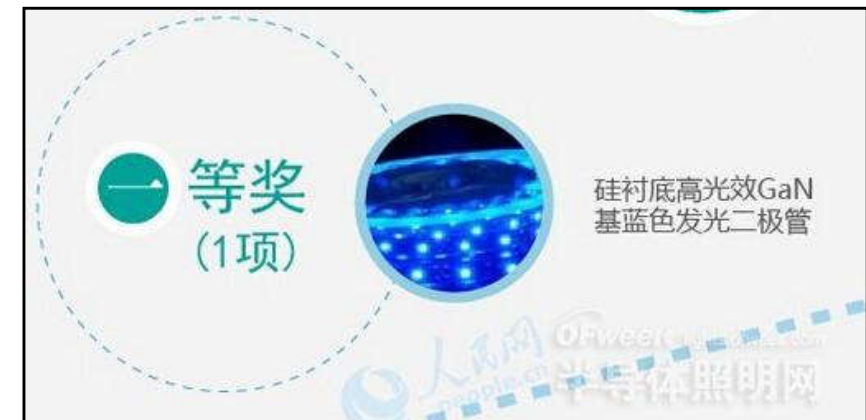


I. Akasaki H. Amano S. Nakamura

- **GaN LED on silicon carbide (SiC)**
  - USA, Cree

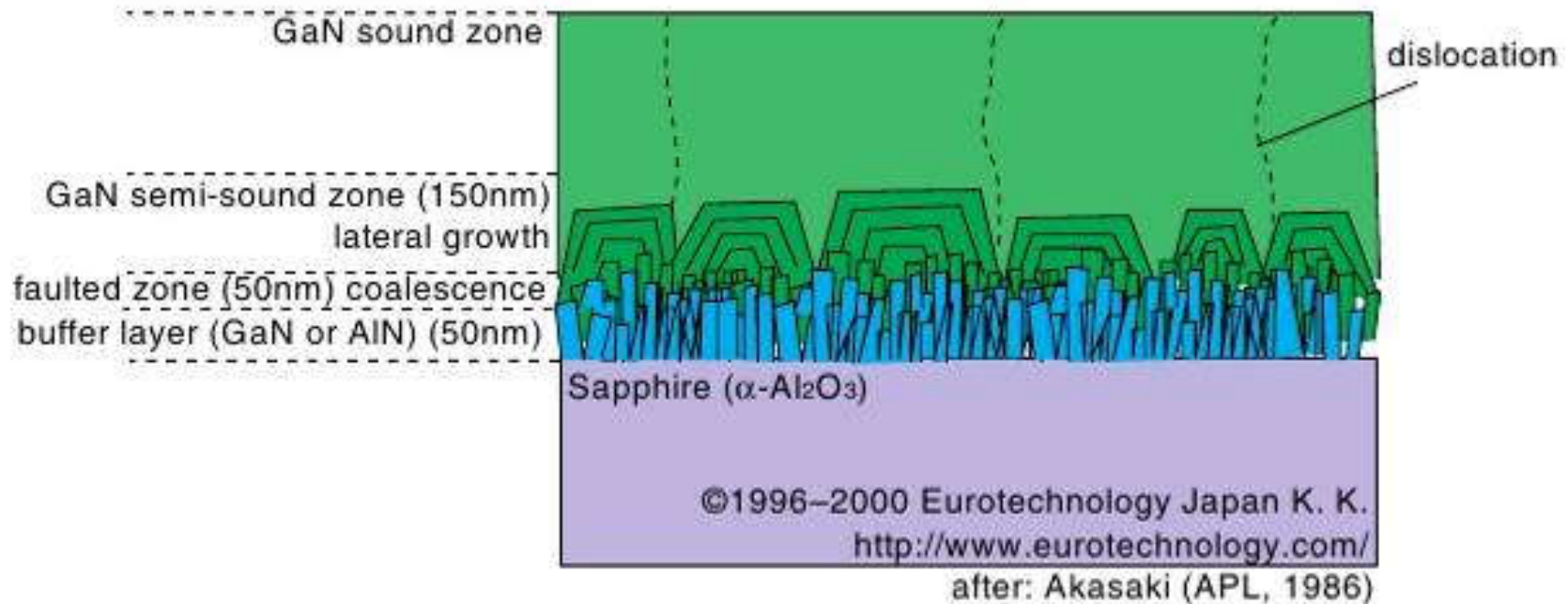


- **GaN LED on silicon**
  - 中国, 南昌大学
  - 2015年中国技术发明一等奖





# GaN Growth on Sapphire



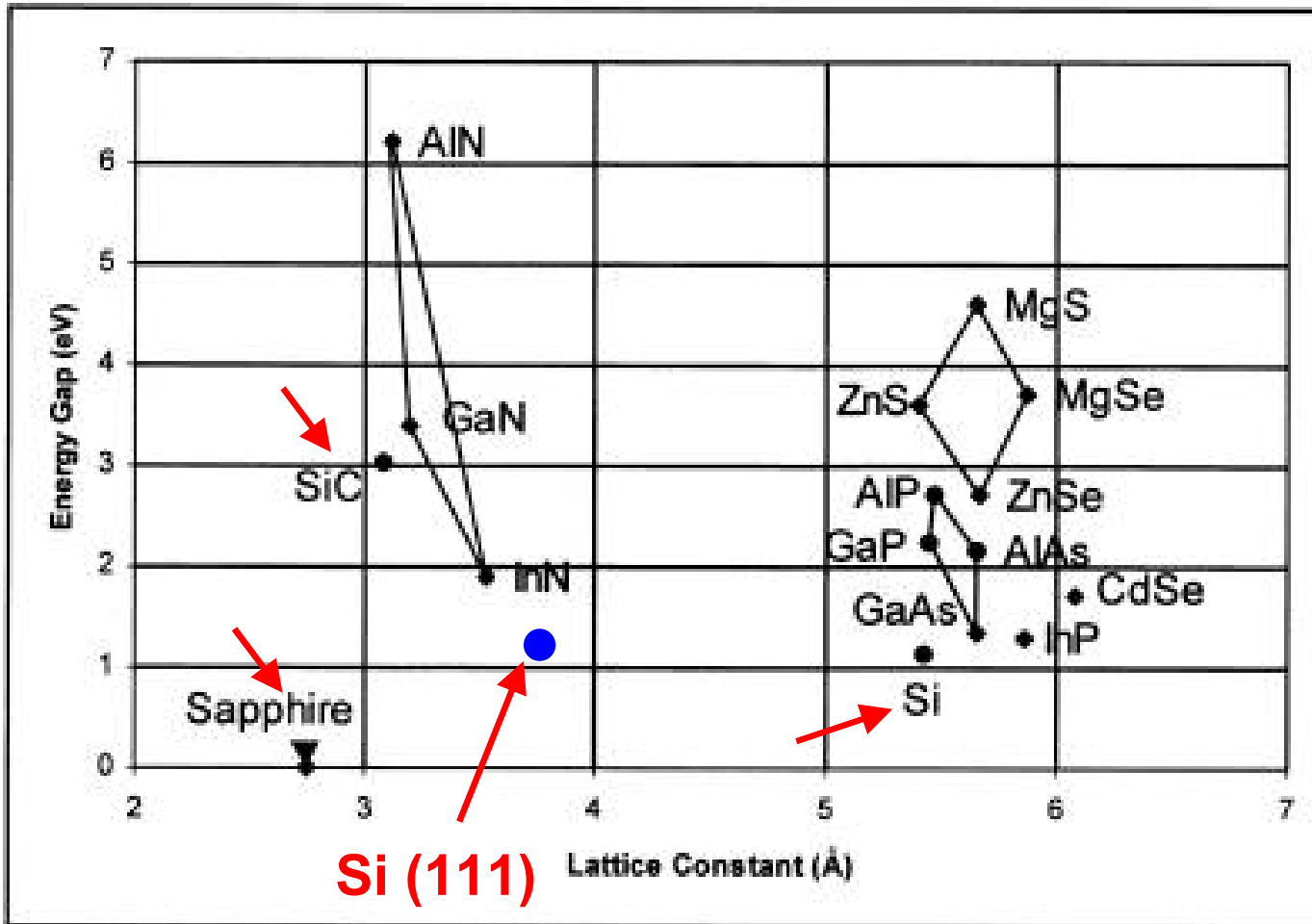
I. Akasaki H. Amano S. Nakamura

**2014 Nobel Prize in Physics**

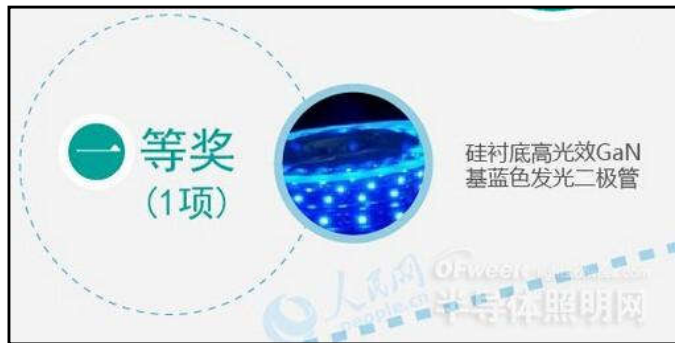
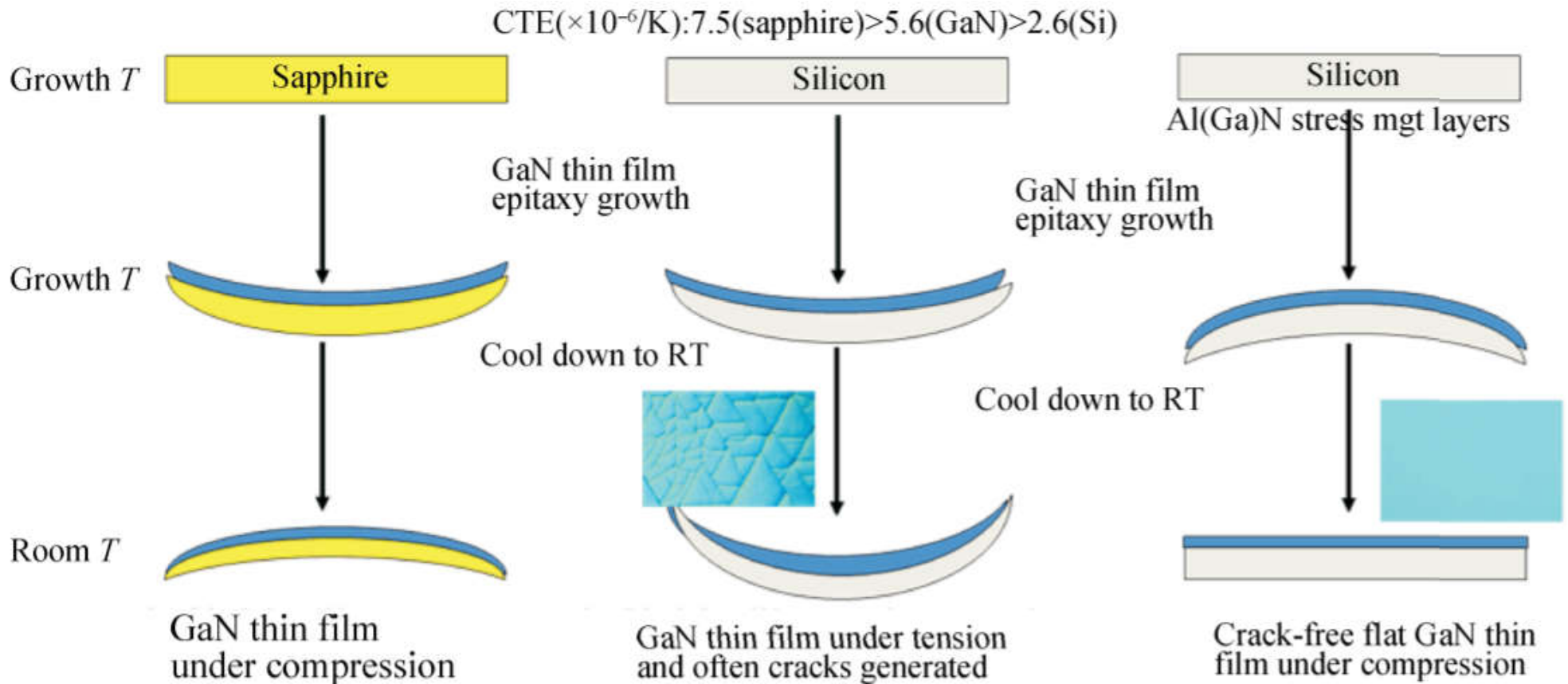
H. Amano, *et al.*, *Appl. Phys. Lett.* **48**, 353 (1986)  
 H. Amano, *et al.*, *Jpn. J. Appl. Phys.* **28**, L2112 (1989)  
 S. Nakamura, *et al.*, *Appl. Phys. Lett.* **64**, 1687 (1994)

1. growth with AlN buffer
2. GaN p-type doping
3. GaN blue LED!

# GaN Growth on Silicon



# GaN Growth on Silicon

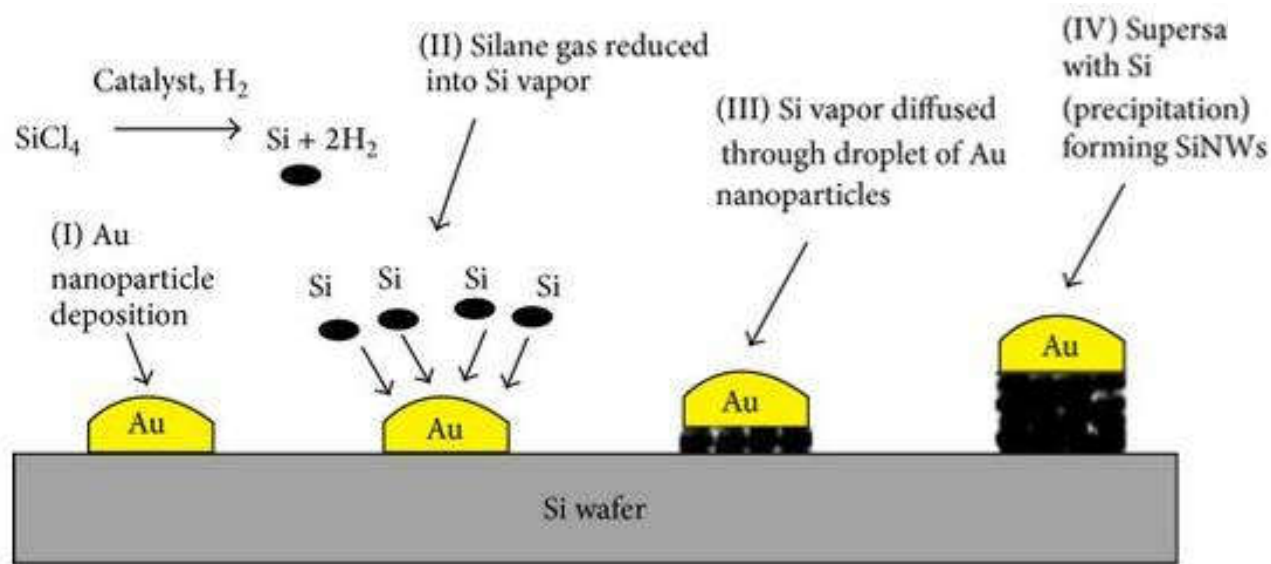


Q. Sun, *et al.*, *J. Semicon.* **37**, 044006 (2016)

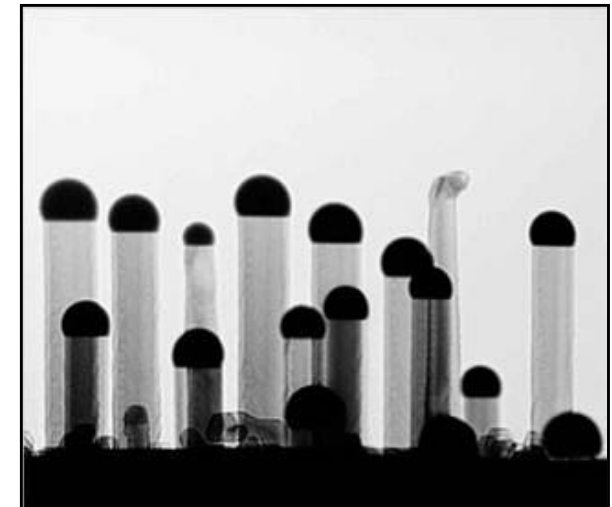
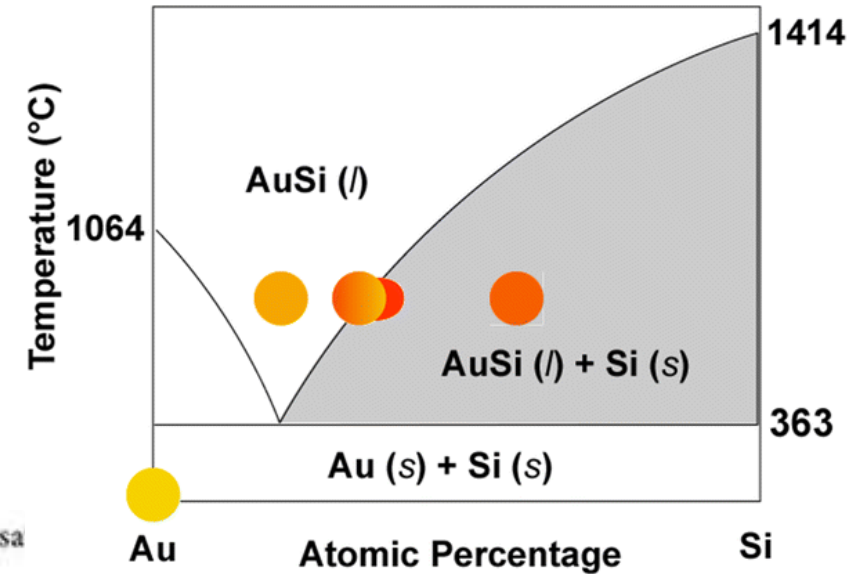
2015年中国技术发明一等奖

# Si Nanowire Growth

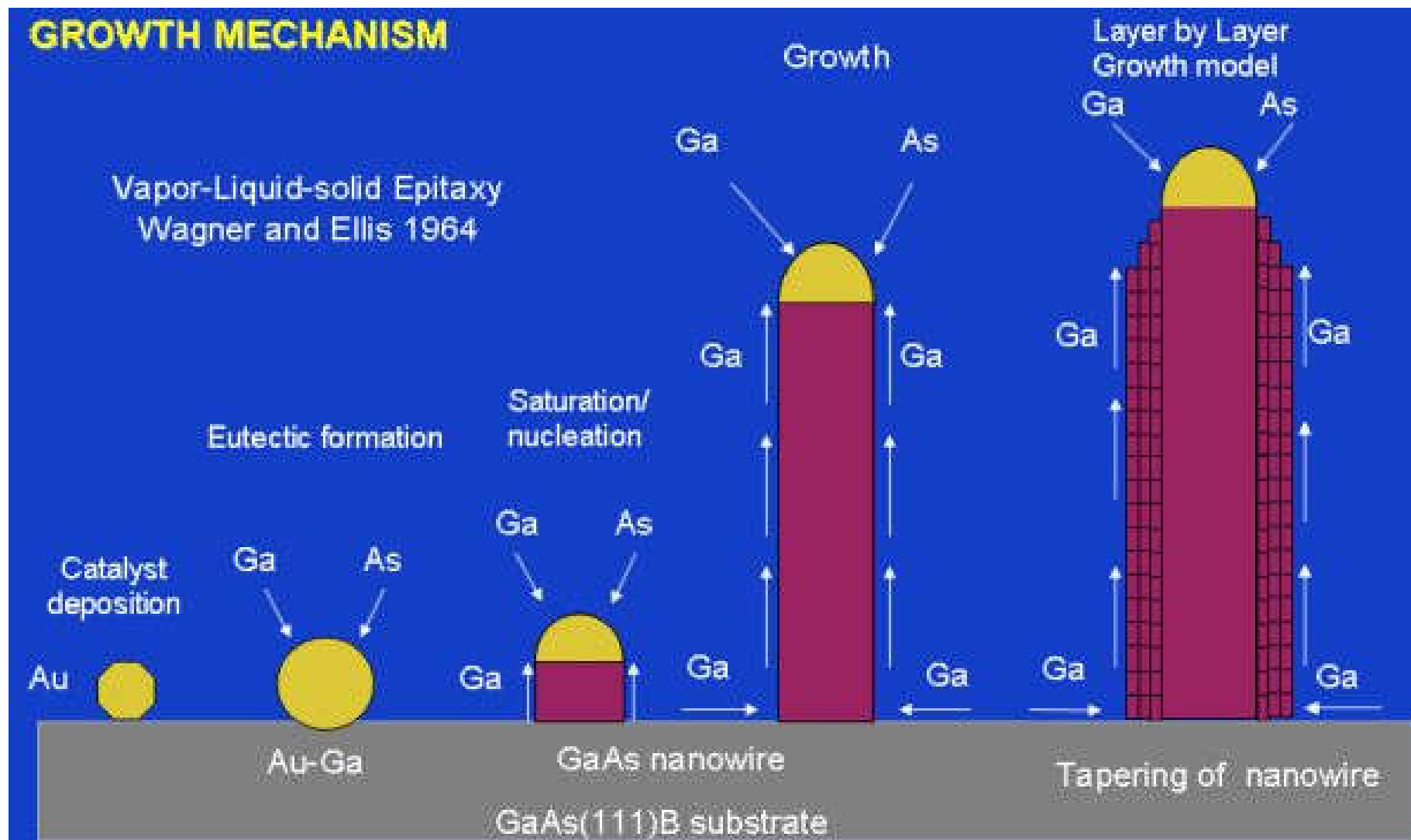
**VLS: Vapor-Liquid-Solid**



**Au-Si eutectic alloy**



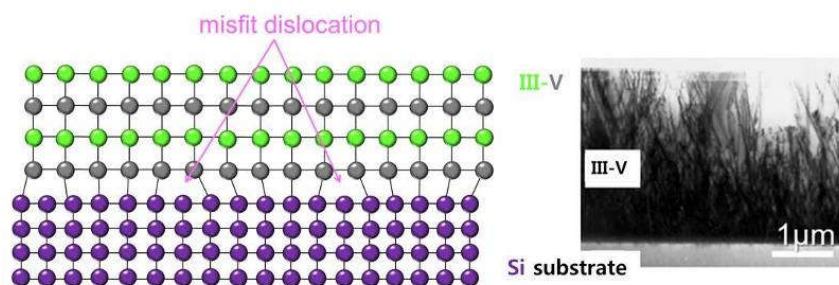
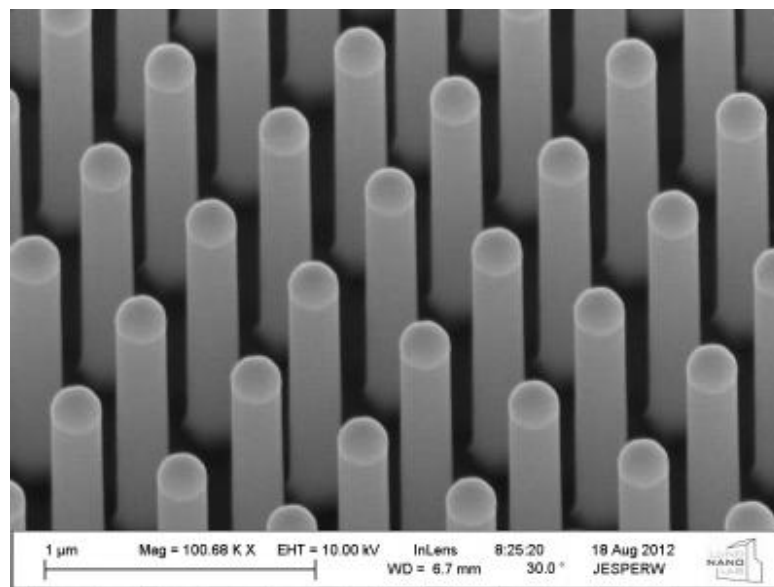
# III-V Nanowire Growth



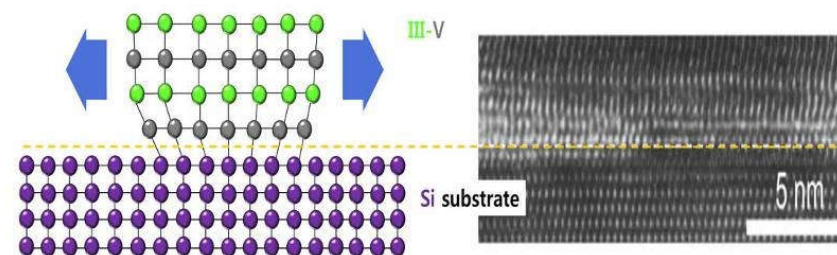
***metal catalysts reduce growth temperature***



# III-V Nanowire Growth

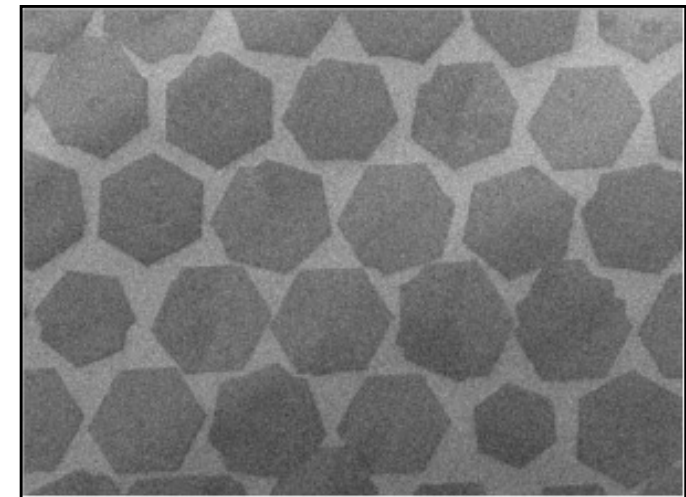
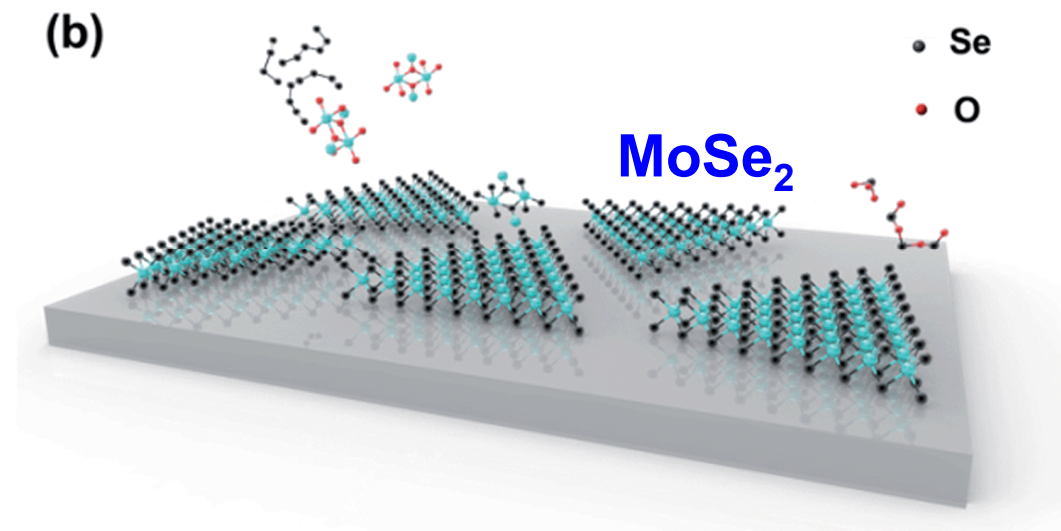
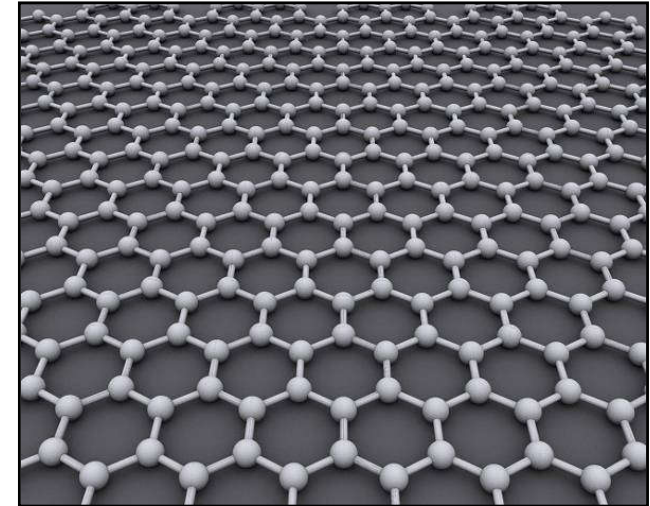
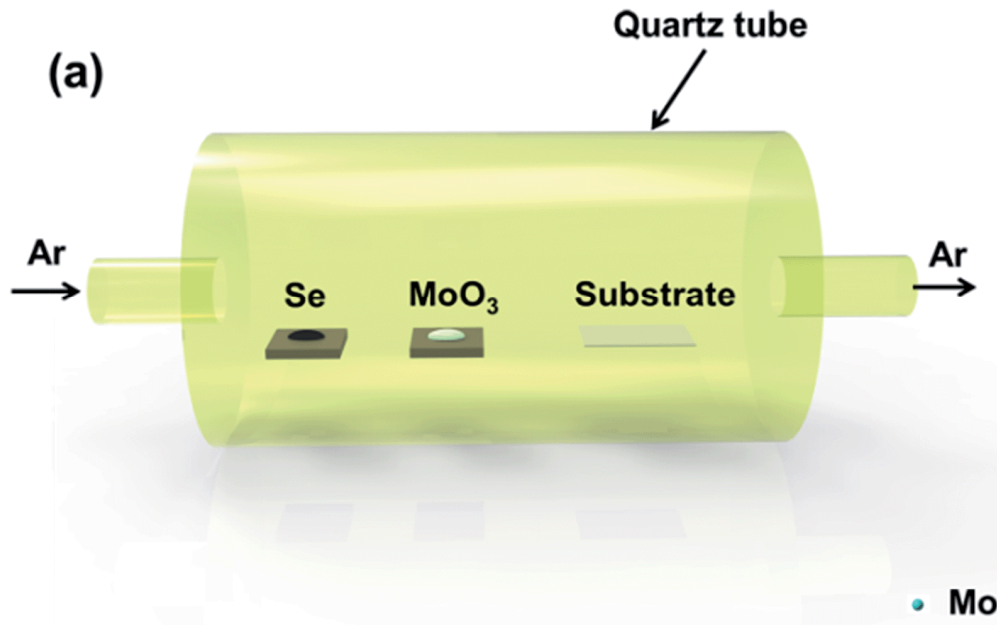


- **Direct growth of III-V film on Si:**  
Creation of massive threading dislocation due to the large lattice mismatch strain between III-V and Si



- **Direct growth of III-V film on Si:**  
Defect-free III-V can be grown on Si because lattice mismatch strain can be relieved via the nanowire sidewall

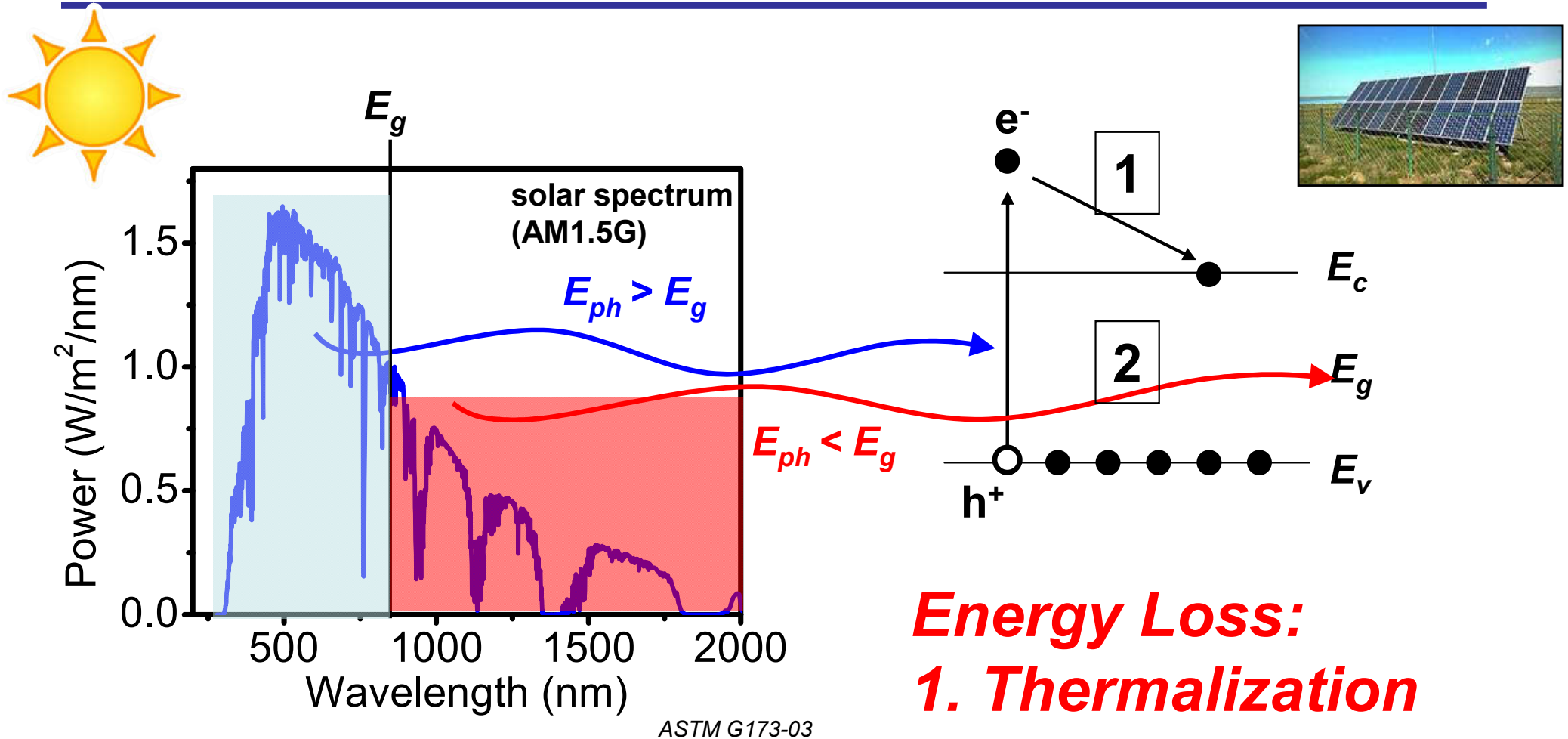
# 2D Materials Growth



grain boundaries exist

*lattice match is not restrict for monolayers*

# Solar Cells



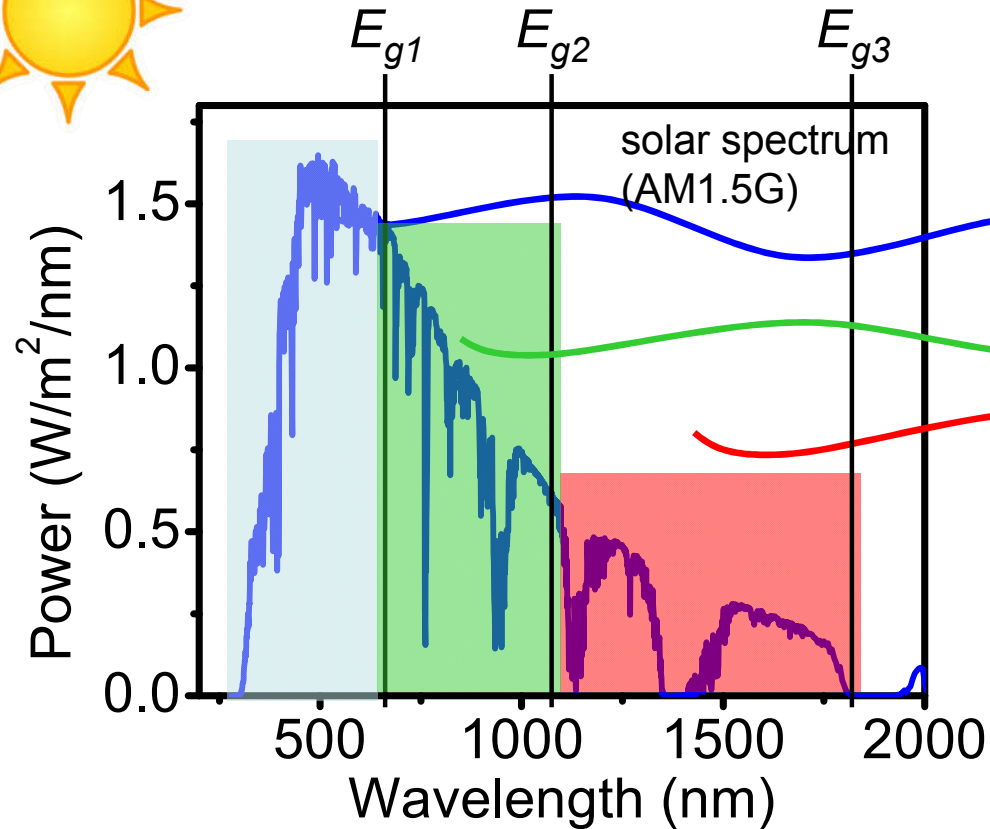
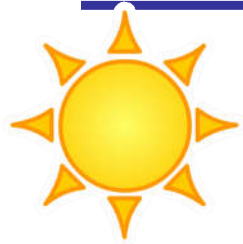
**Energy Loss:**

- 1. Thermalization**
- 2. Sub-bandgap pass**

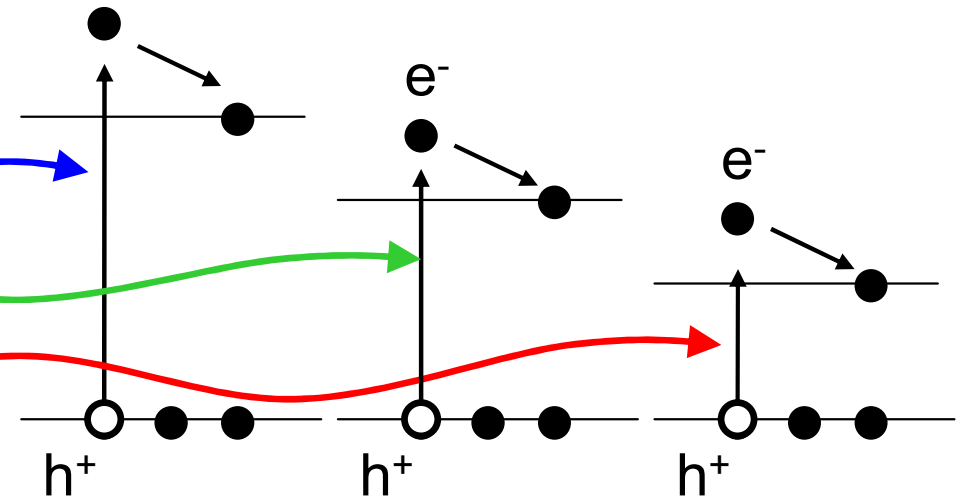
**A single junction cell  
cannot get >37% efficiency**

W. Shockley and H. A. Queisser, *J. Appl. Phys.* **32**, 510 (1961)  
C. H. Henry, *J. Appl. Phys.* **51**, 4494 (1980)

# Multijunction Solar Cells



ASTM G173-03

1J:  $\eta = 37\%$ 2J:  $\eta = 50\%$ 3J:  $\eta = 56\%$ infinite J:  $\eta = 72\%$ 

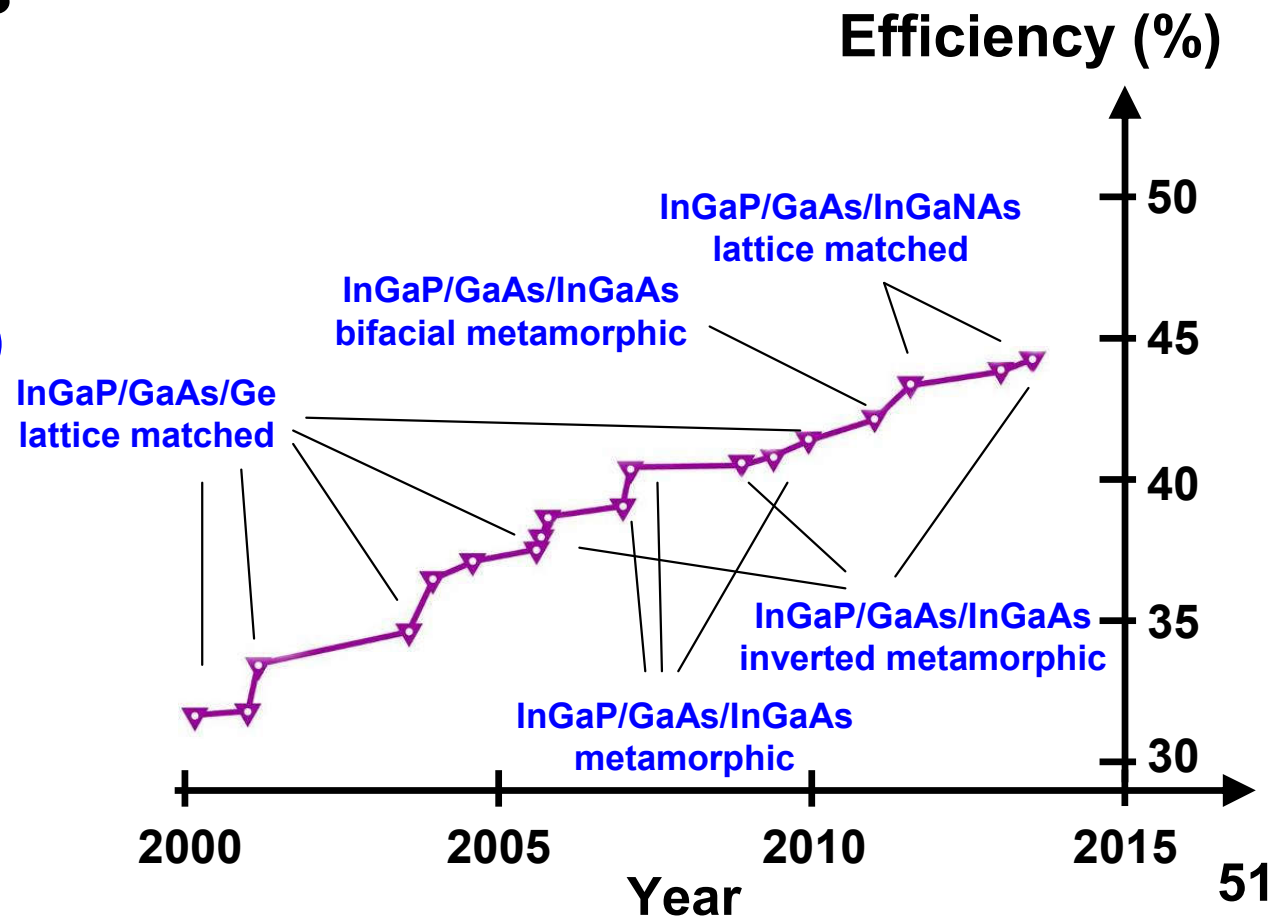
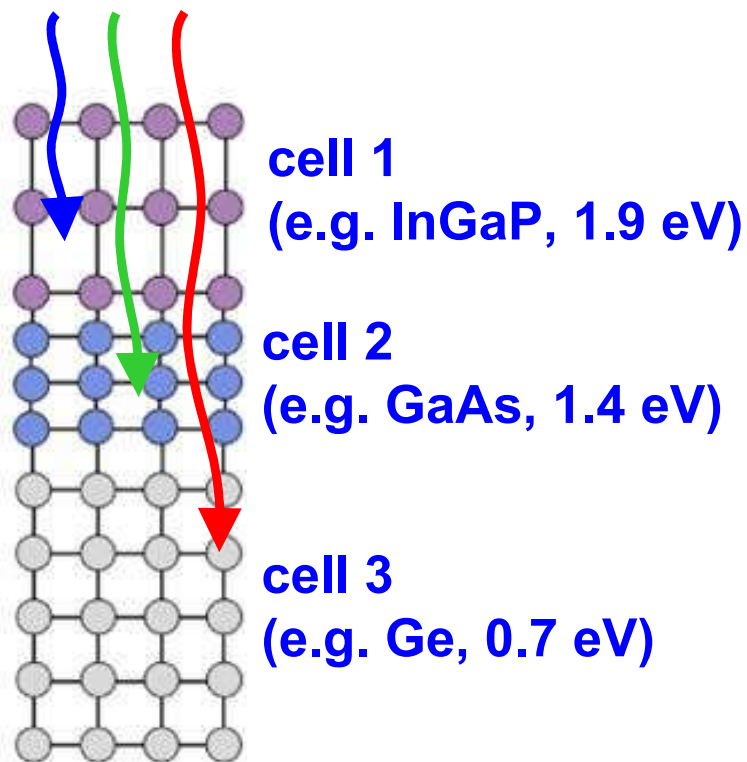
**Use the entire solar spectrum**

W. Shockley and H. A. Queisser, *J. Appl. Phys.* **32**, 510 (1961)C. H. Henry, *J. Appl. Phys.* **51**, 4494 (1980)



# Multijunction Solar Cells

- Lattice matched epi-growth (MOCVD or MBE)
- Current matching
- Suitable bandgaps



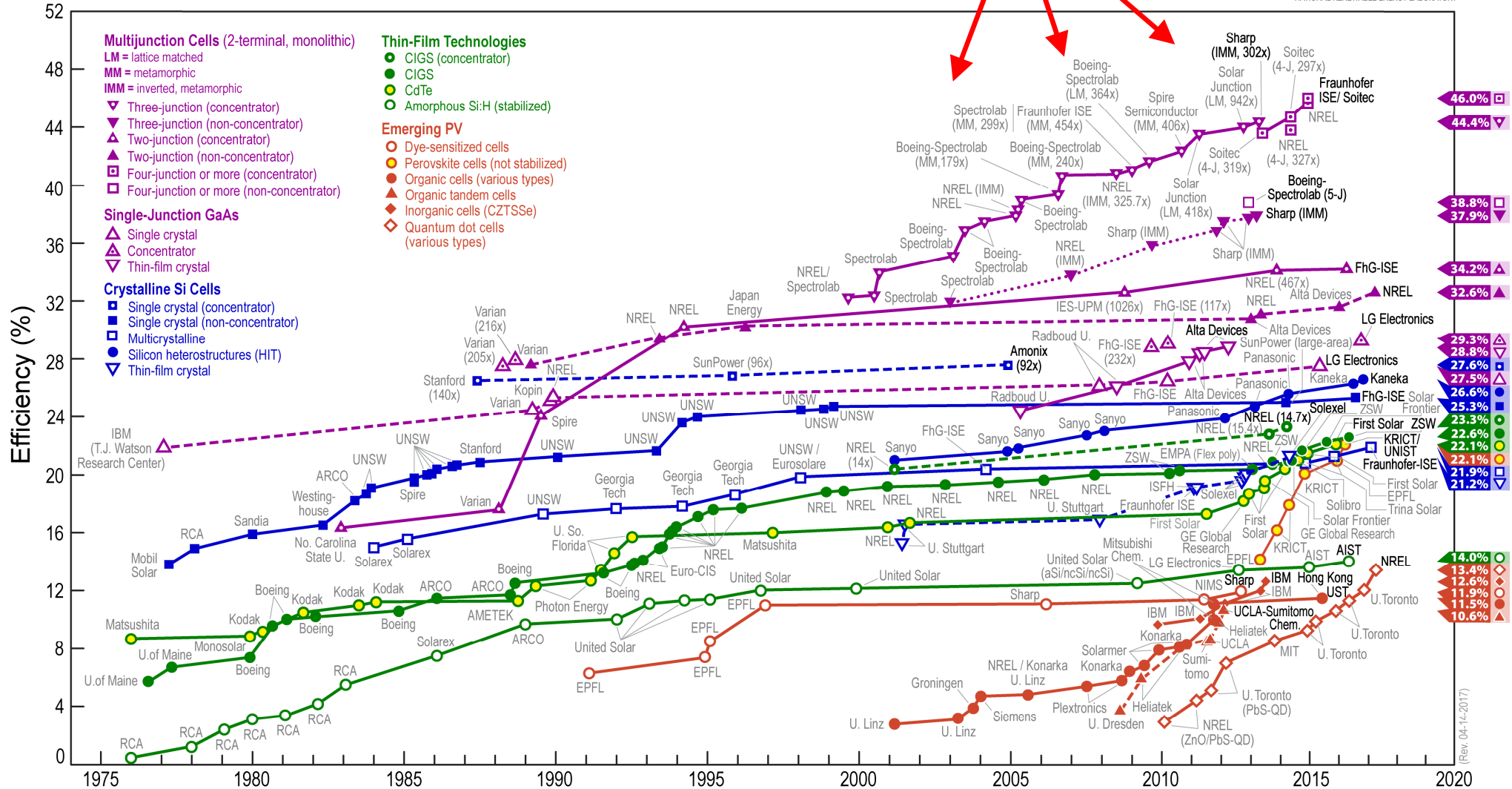


# Multijunction Solar Cells

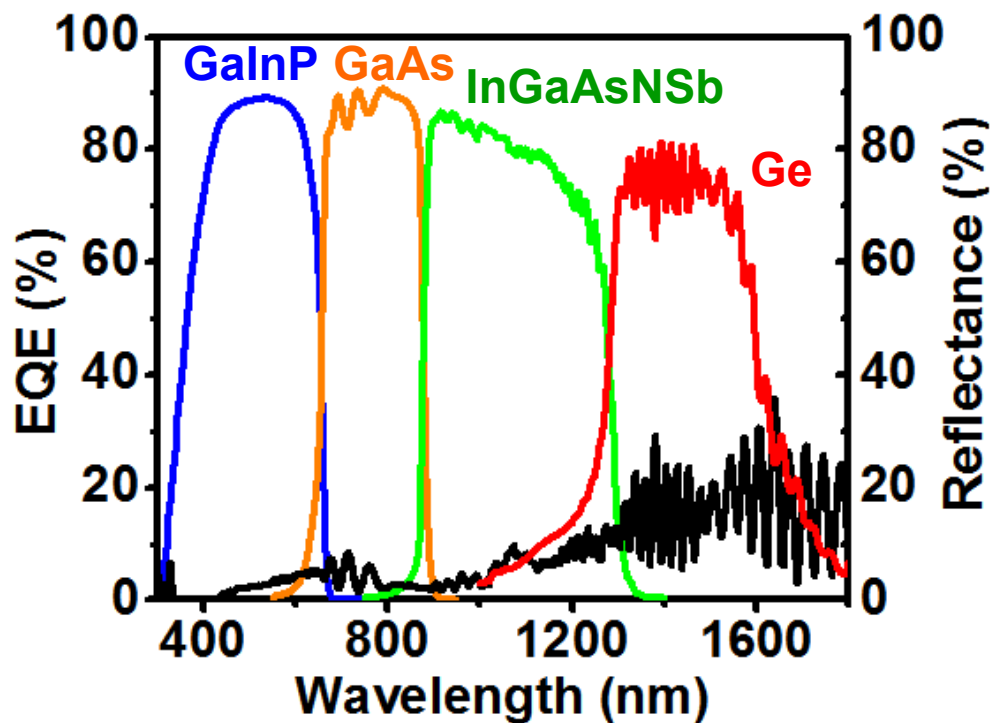
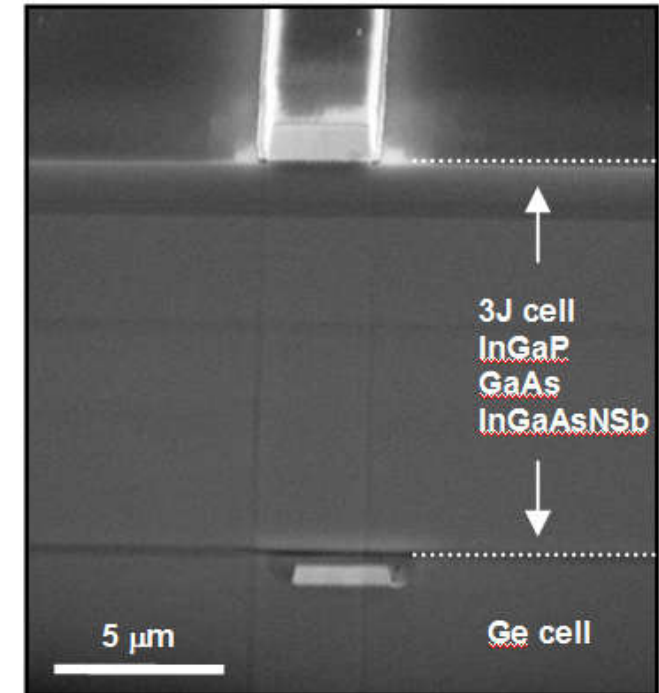
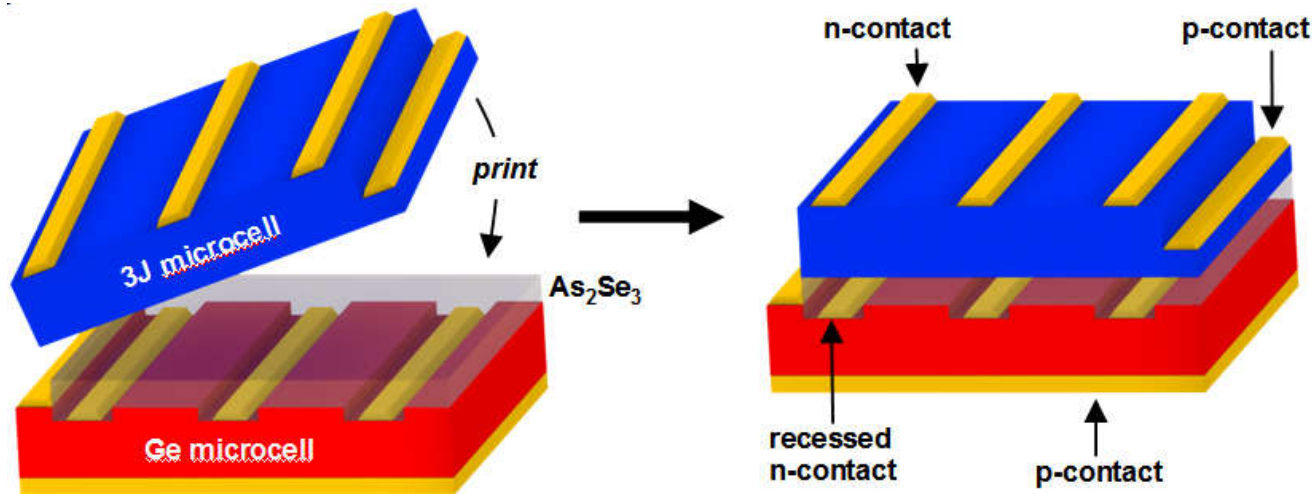
*most efficient solar cells*



## Best Research-Cell Efficiencies



# Stacked MJ Solar Cells

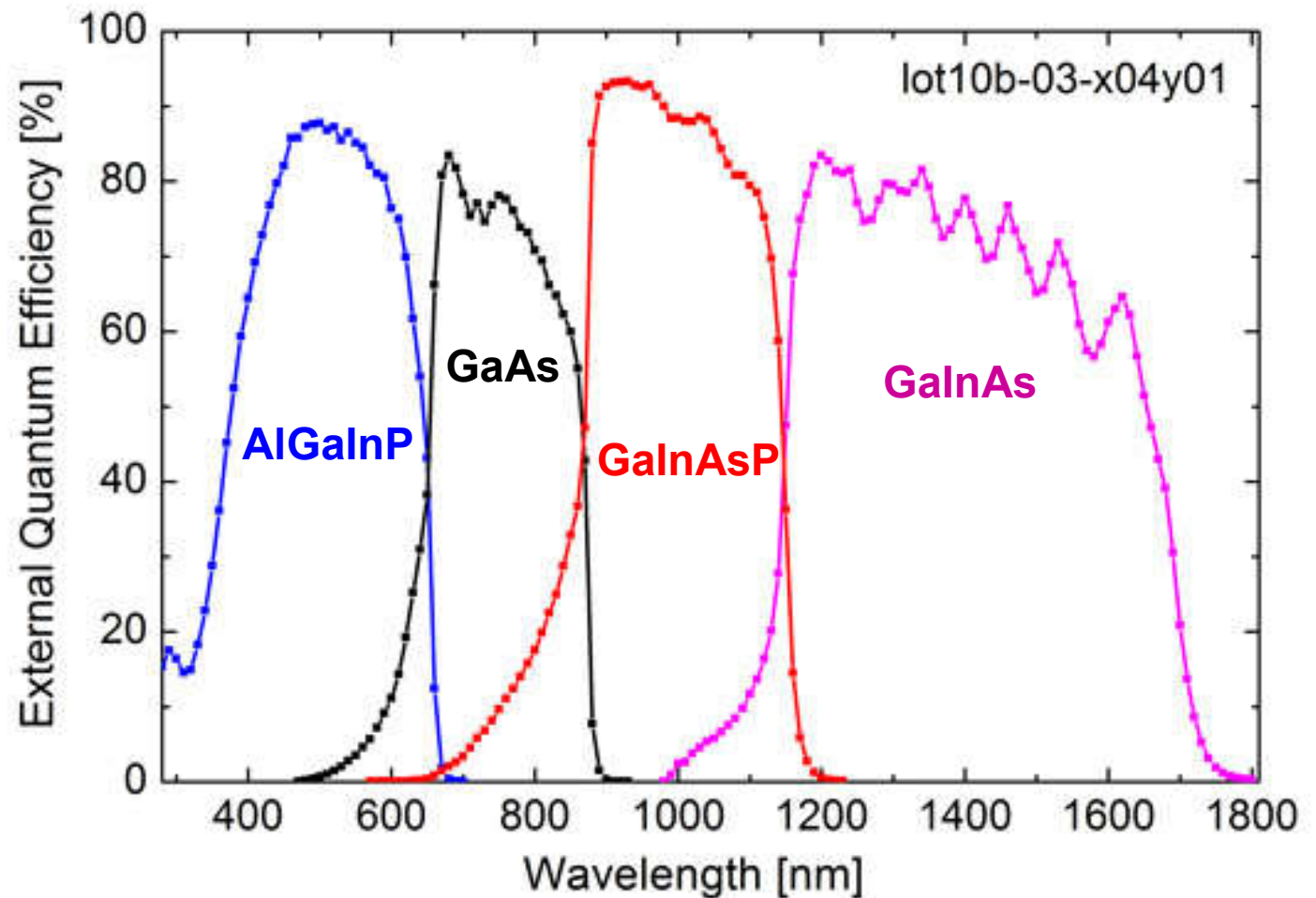
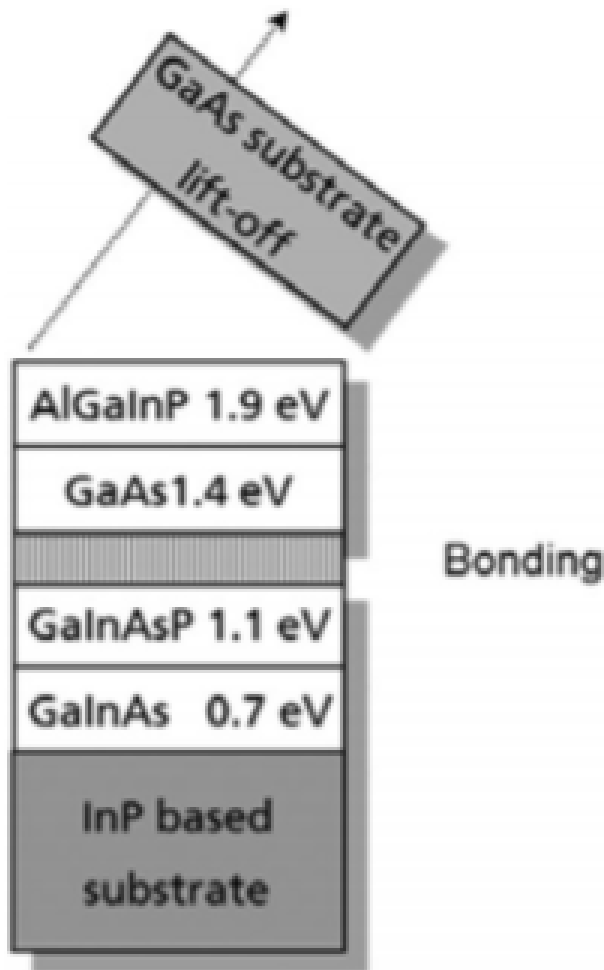


stacked  
GaInP/GaAs/InGaAsNSb // Ge  
solar cells

**Efficiency: 44%**

# Stacked MJ Solar Cells

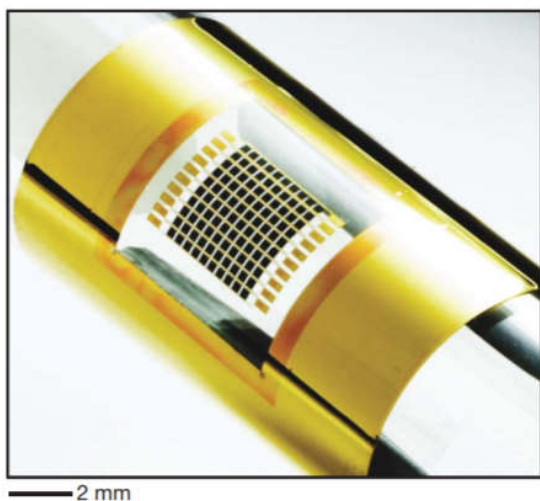
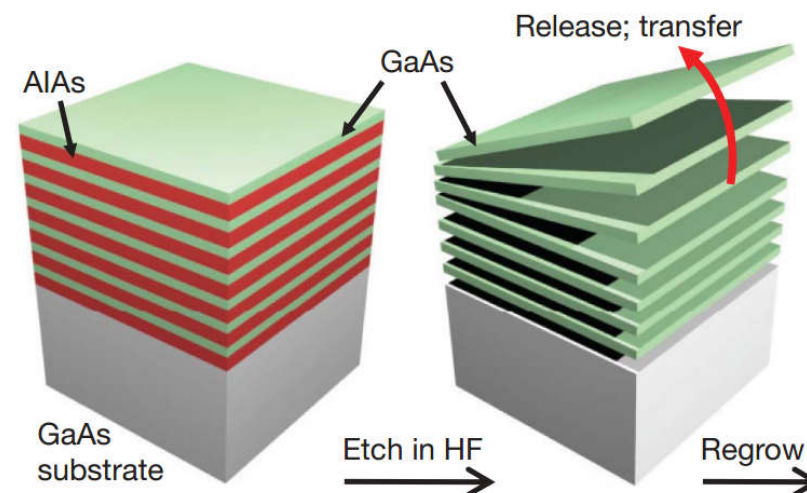
bonded AlGaInP/GaAs // GaInAsP/GaInAs solar cells



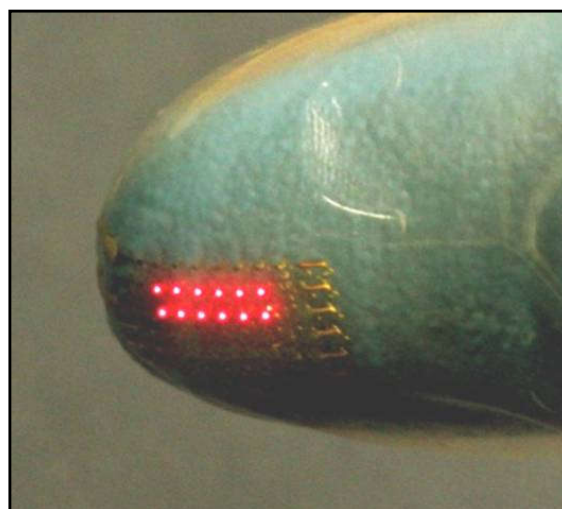
**World record efficiency: 46%**

# Epitaxy Liftoff

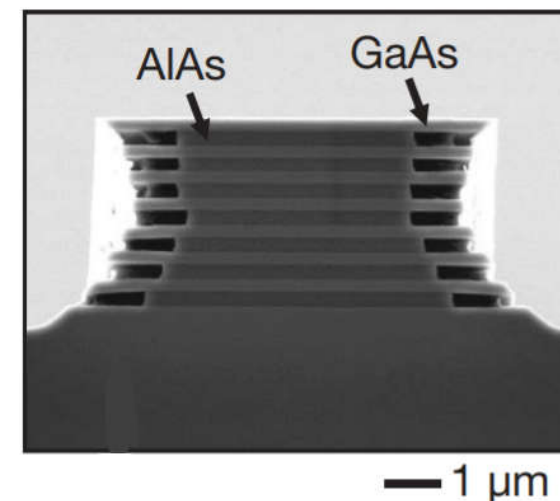
- **GaAs and AIAs**
  - lattice matched growth
  - AIAs is selectively etched by HF
  
- **flexible III-V devices**



**solar cells**



**LED**





# 'Remote' Epitaxy

## Remote epitaxy through graphene enables two-dimensional material-based layer transfer

Yunjo Kim<sup>1\*</sup>, Samuel S. Cruz<sup>1\*</sup>, Kyusang Lee<sup>1\*</sup>, Babatunde O. Alawode<sup>1</sup>, Chanyeol Choi<sup>1</sup>, Yi Song<sup>2</sup>, Jared M. Johnson<sup>3</sup>, Christopher Heidelberg<sup>4</sup>, Wei Kong<sup>1</sup>, Shinhyun Choi<sup>1</sup>, Kuan Qiao<sup>1</sup>, Ibraheem Almansouri<sup>1,5</sup>, Eugene A. Fitzgerald<sup>4</sup>, Jing Kong<sup>2,6</sup>, Alexie M. Kolpak<sup>1</sup>, Jinwoo Hwang<sup>3</sup> & Jeehwan Kim<sup>1,4,6</sup>

