

# *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)

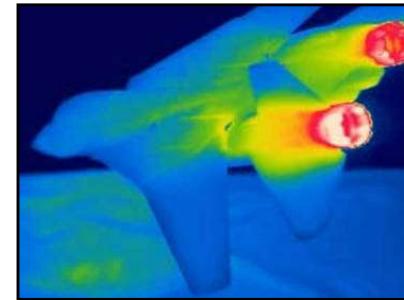
# Optoelectronic Devices



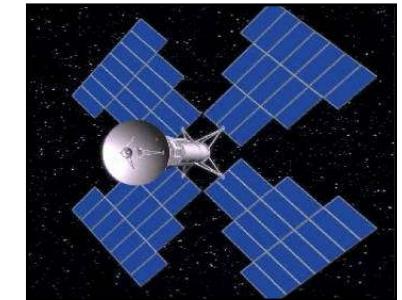
LEDs



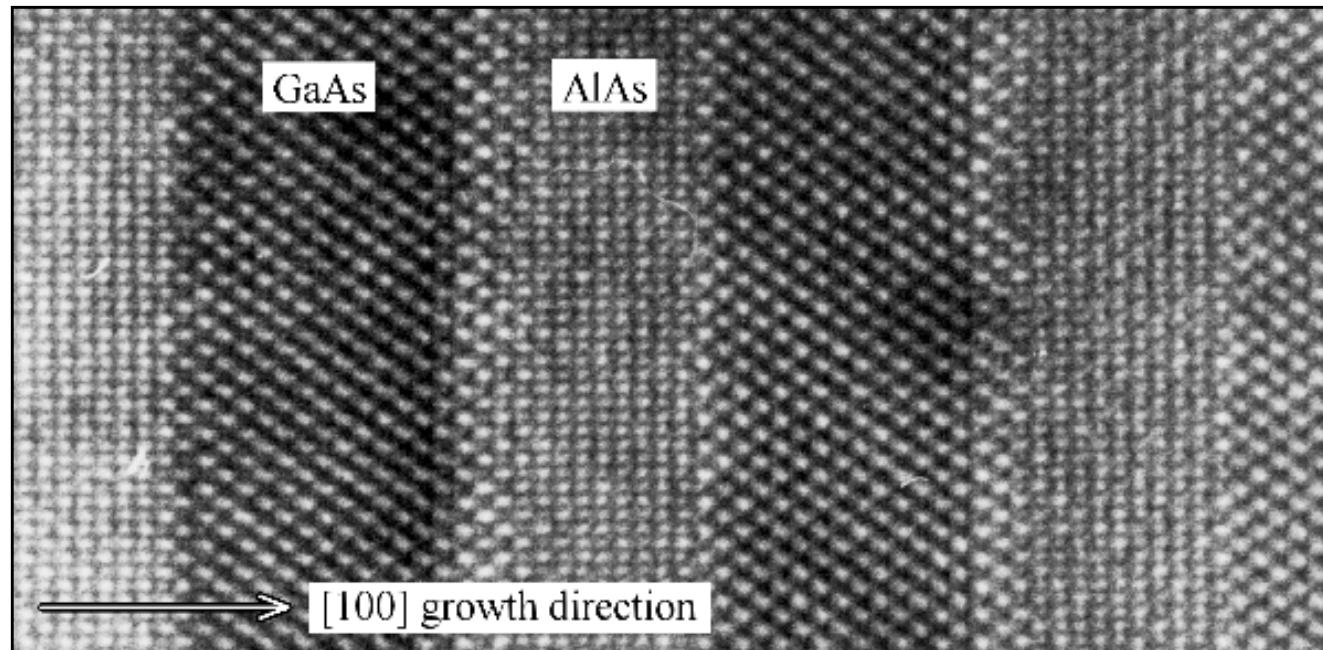
lasers



IR imaging

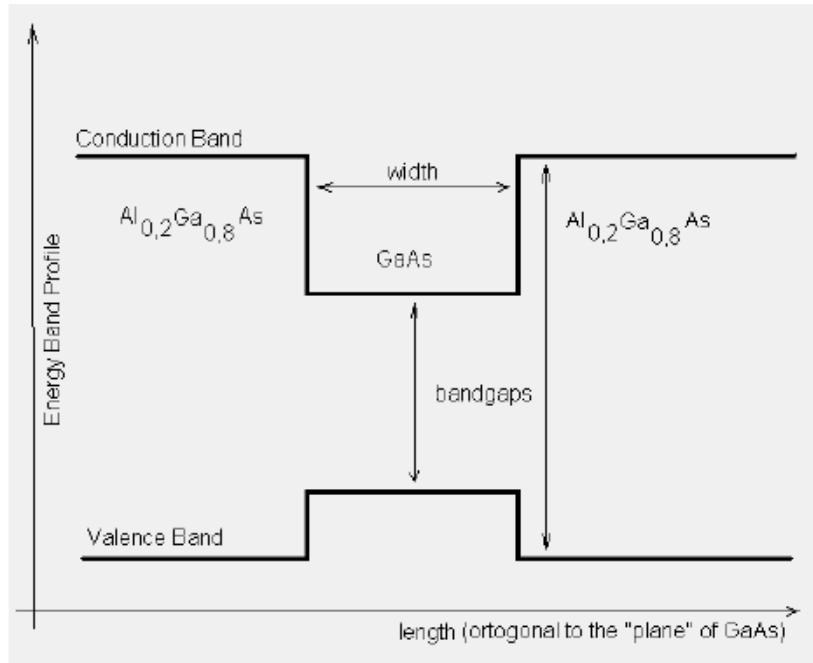


solar cells



grow single crystal films on single crystal substrates

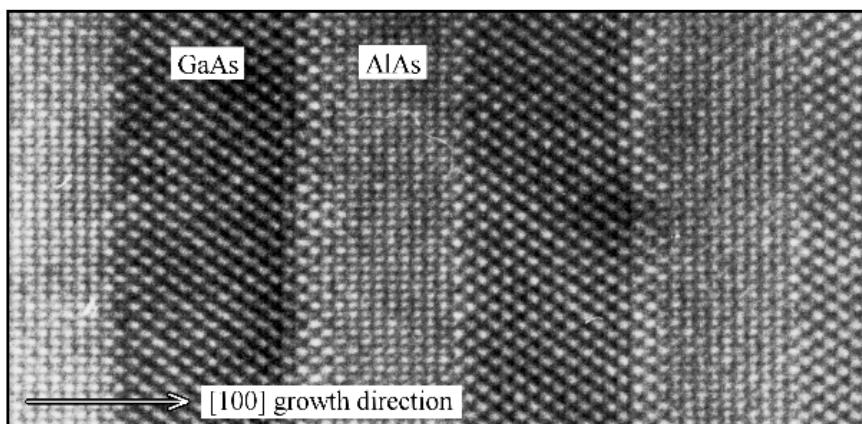
# Semiconductor Heterostructures



**GaAs/AlGaAs heterostructure:  
bandgap engineering**



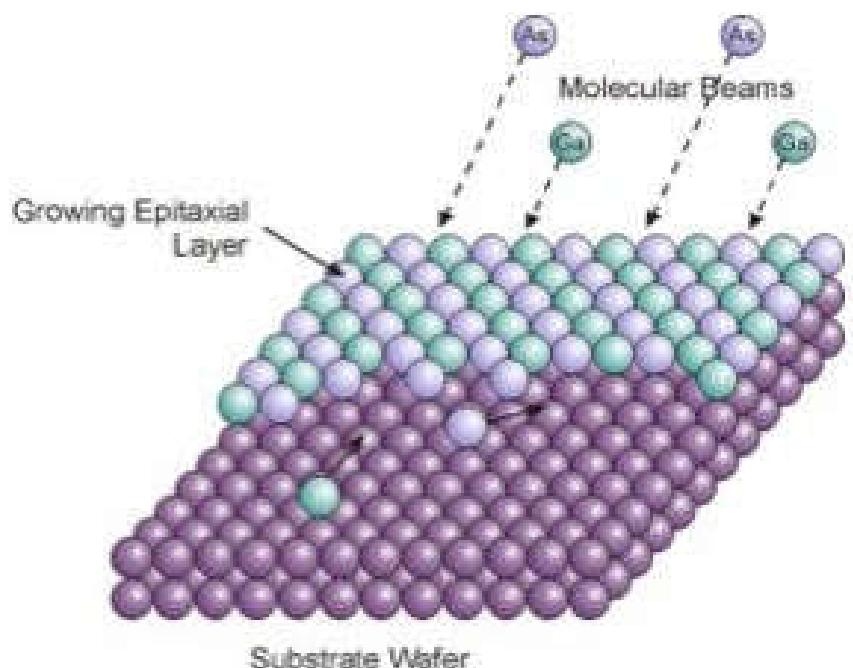
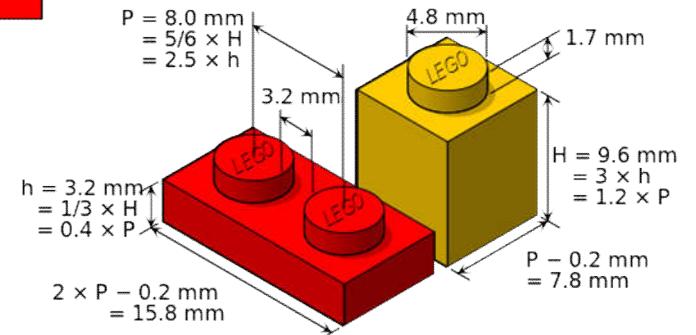
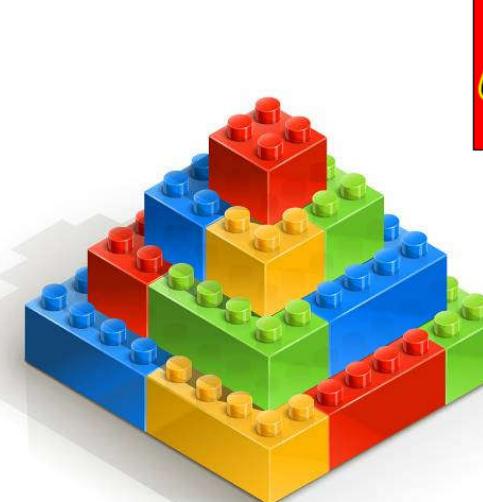
**Z. I. Alferov**



**H. Kroemer**

**2000 Nobel Prize in Physics**

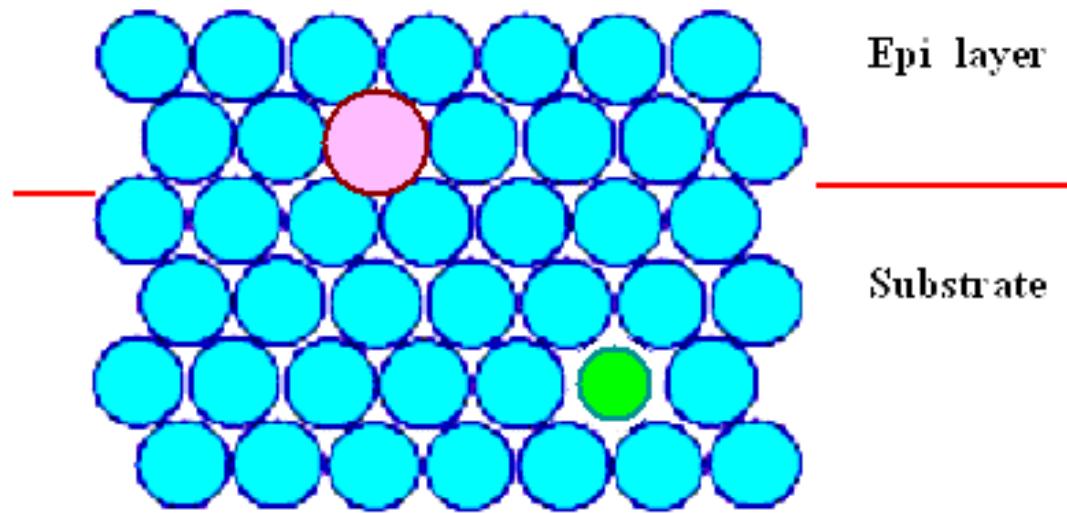
# Epitaxy (外延)



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

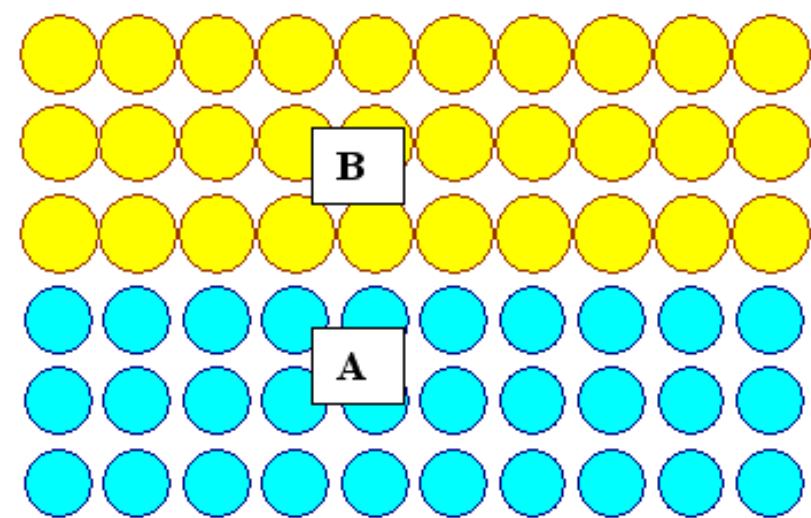
# Epitaxial Growth

## Homoepitaxy



(doped) Si on Si,  
GaAs on GaAs,  
...

## Heteroepitaxy



AlAs on GaAs  
Ge on Si,  
...

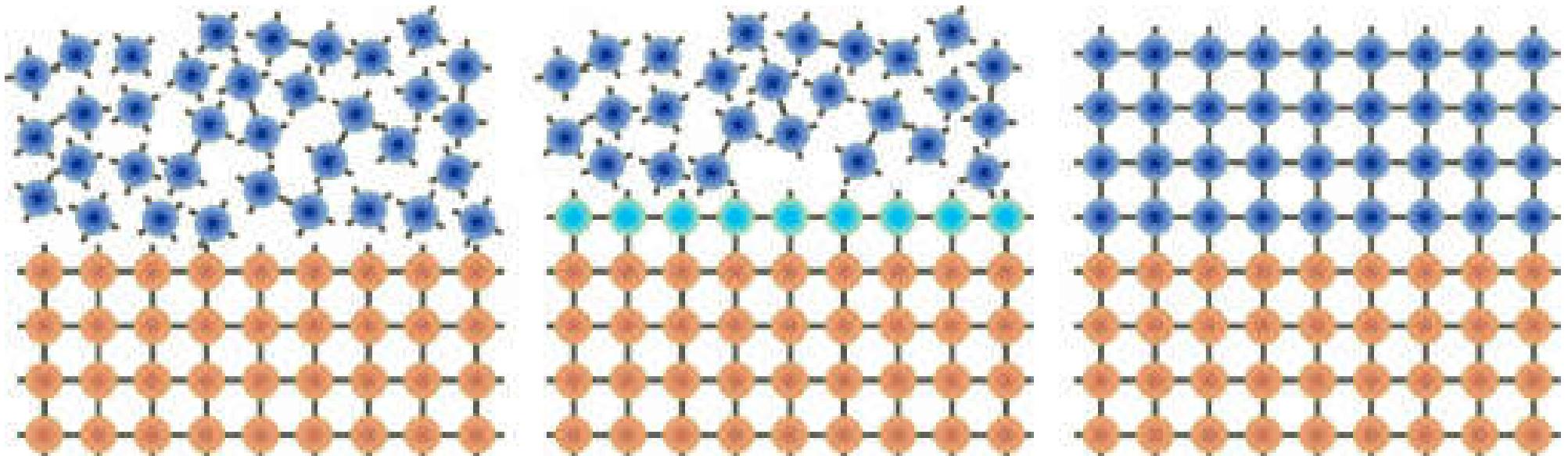
# Methods

---

- Solid Phase Epitaxy (SPE)
  - amorphous Si  $\rightarrow$  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

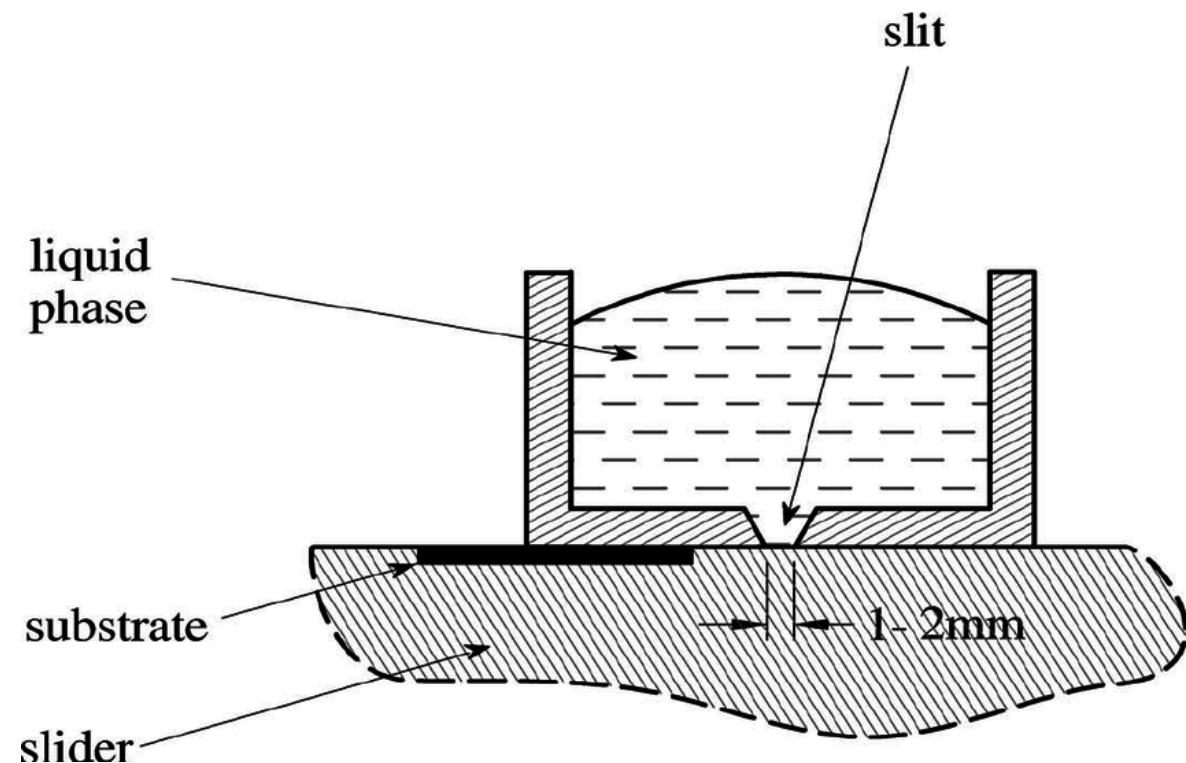
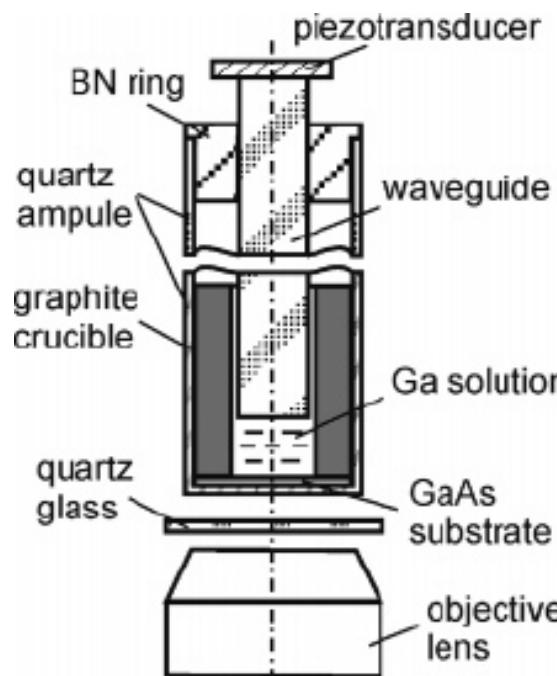
- Solid Phase Epitaxy (SPE)
  - amorphous Si  $\rightarrow$  crystalline Si



annealing at high temperature

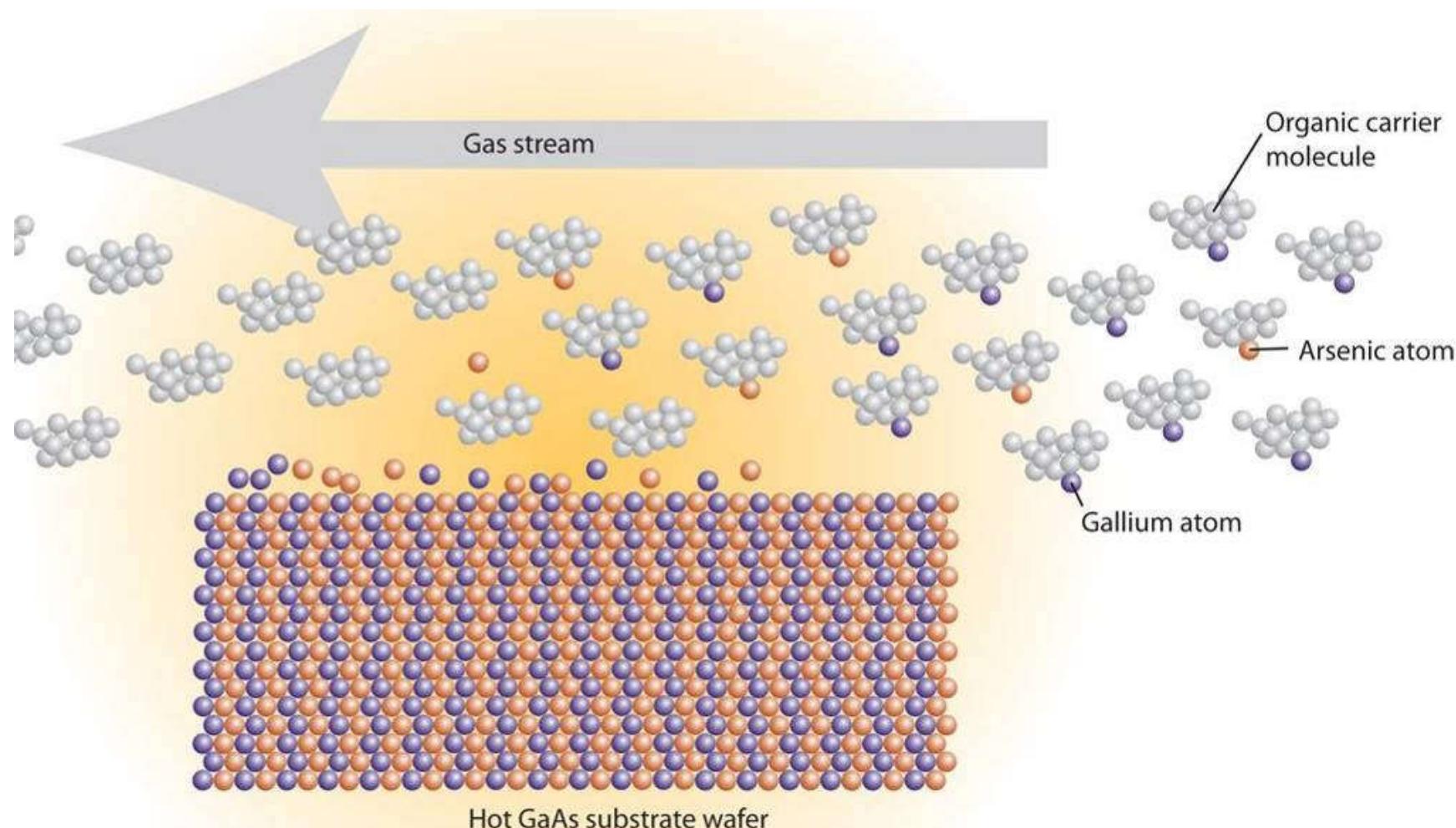
# Methods

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



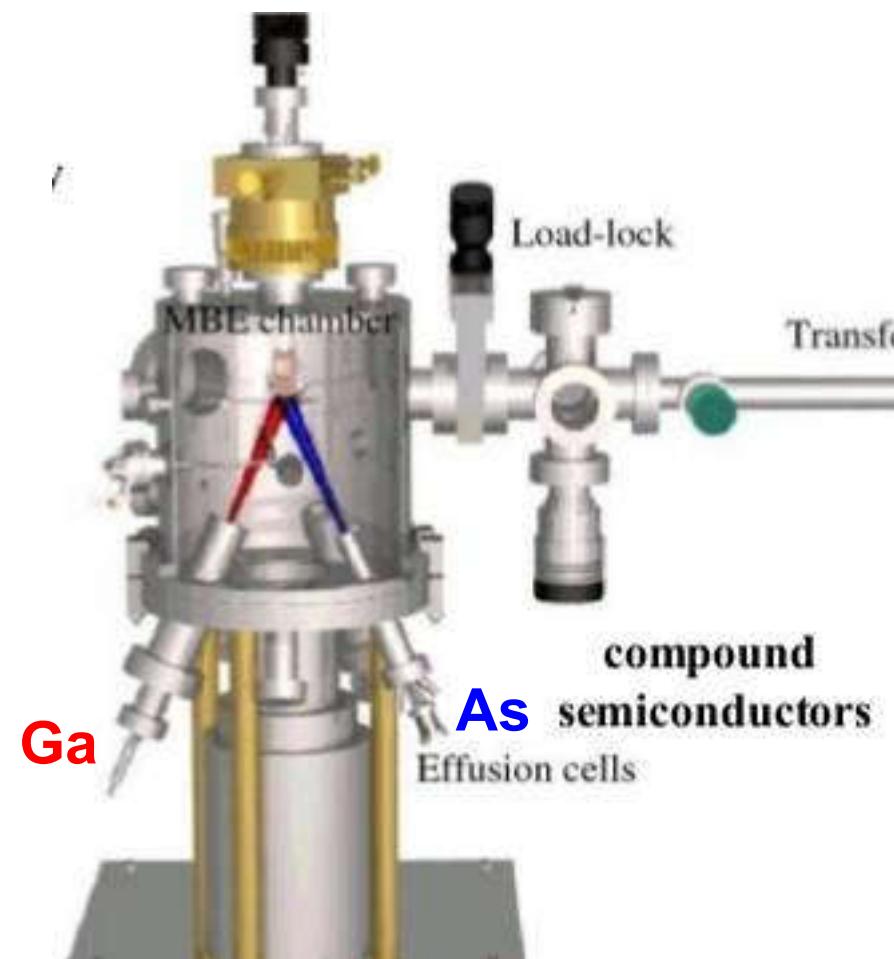
# Methods

- Chemical Vapor Deposition (CVD)
  - $\text{Ga}(\text{CH}_3)_3 \text{ (g)} + \text{AsH}_3 \text{ (g)} = \text{GaAs (s)} + 3\text{CH}_4 \text{ (g)}$

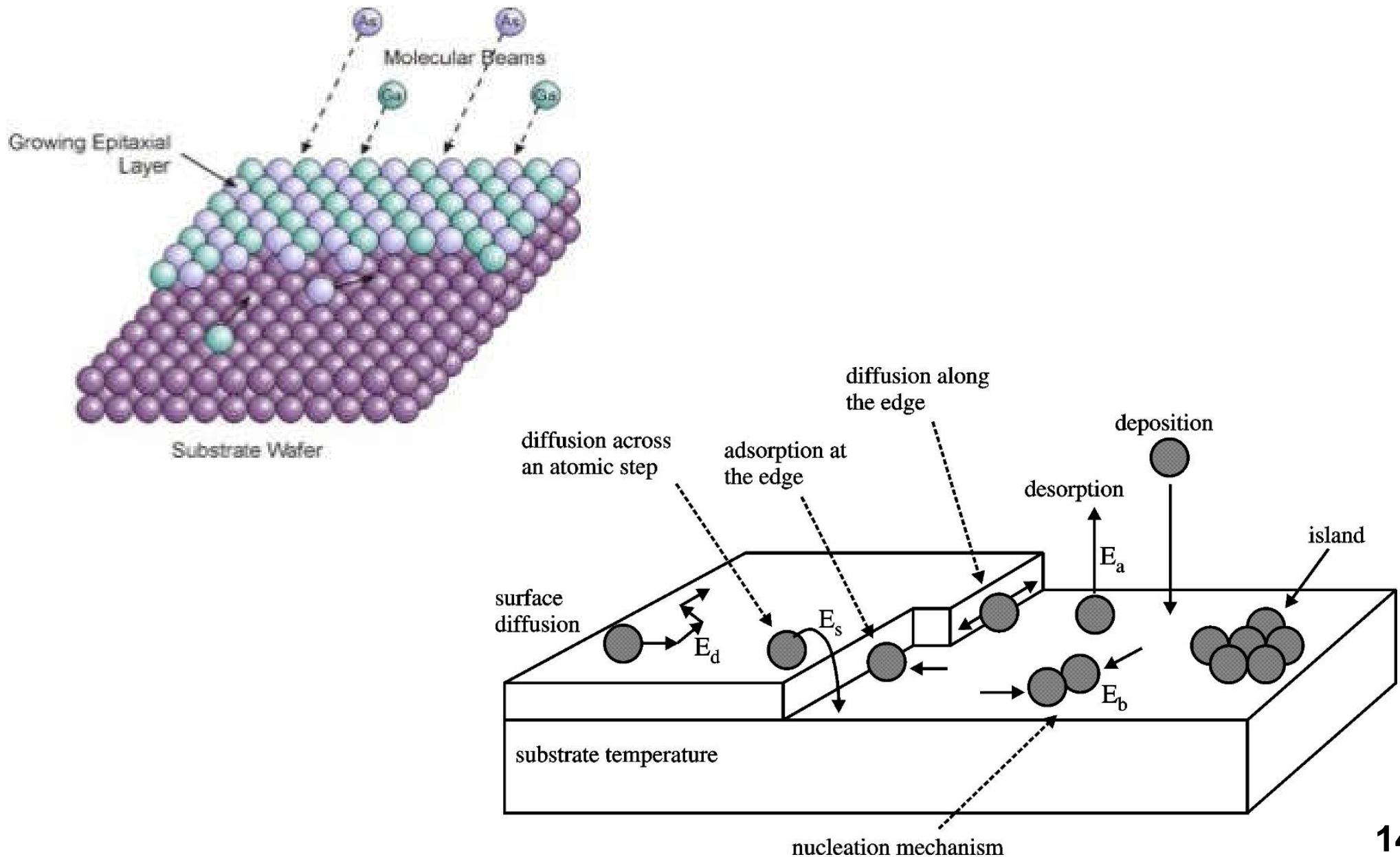


# Methods

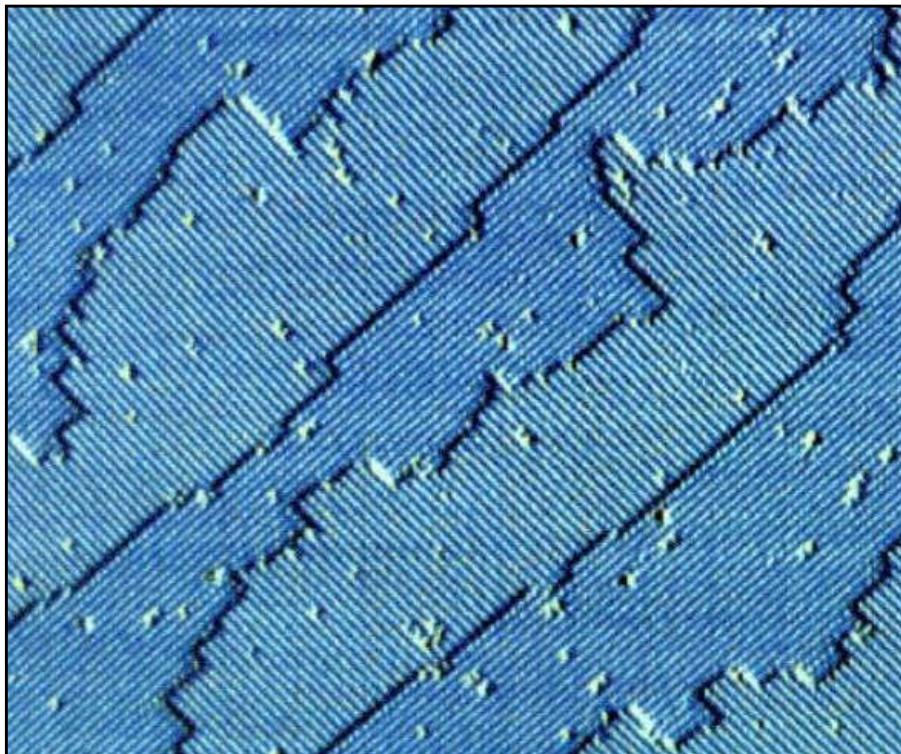
- Molecular Beam Epitaxy (MBE)
  - $2\text{Ga (g)} + \text{As}_2\text{ (g)} = 2\text{GaAs (s)}$



# Deposition at Surfaces



# Deposition at Surfaces



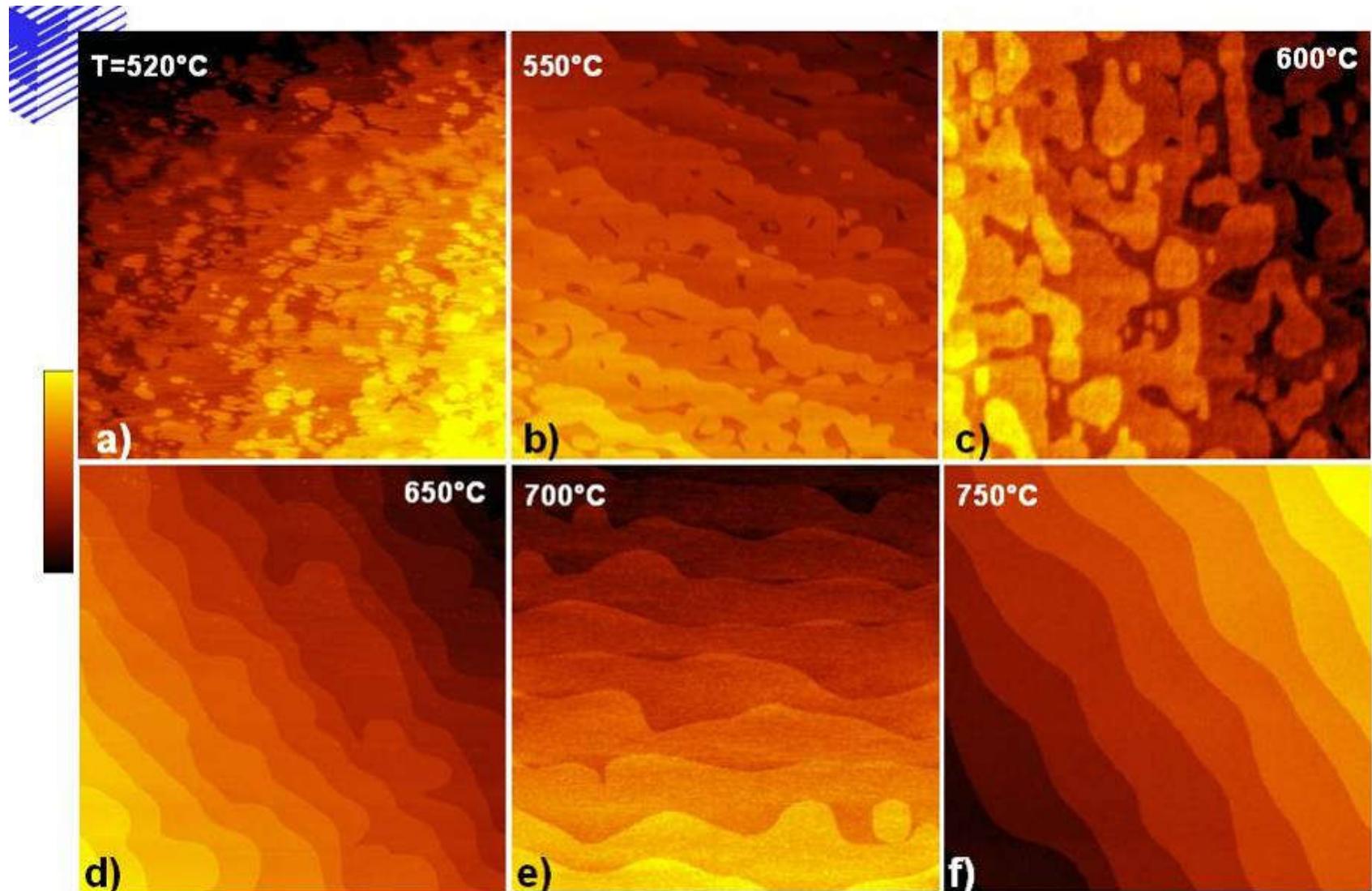
**Si (100) surface**

**terrace (梯田)**



# Deposition at Surfaces

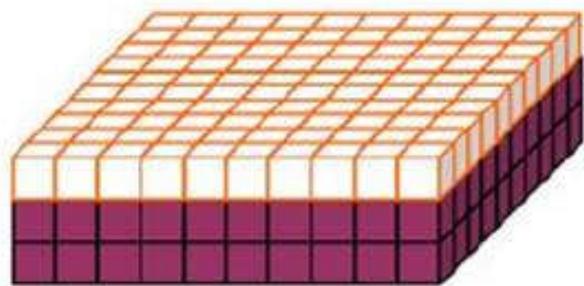
GaAs  
growth



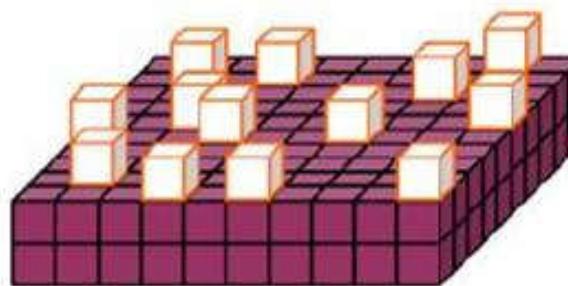
Transition from 2D island nucleation to step flow growth (MOCVD).  
5X5 $\mu\text{m}^2$  post-growth AFM scans, height scale 2-5nm

# Growth Mechanisms

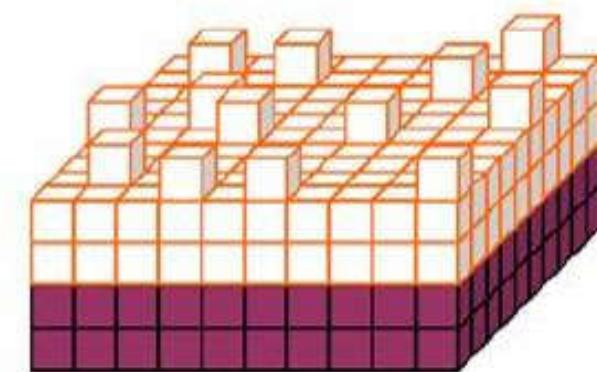
**competition between surface and interface energies**



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



Volmer-Weber mode  
(Island growth mode)



Stranski-Krastanov mode  
(Layer & island growth mode)

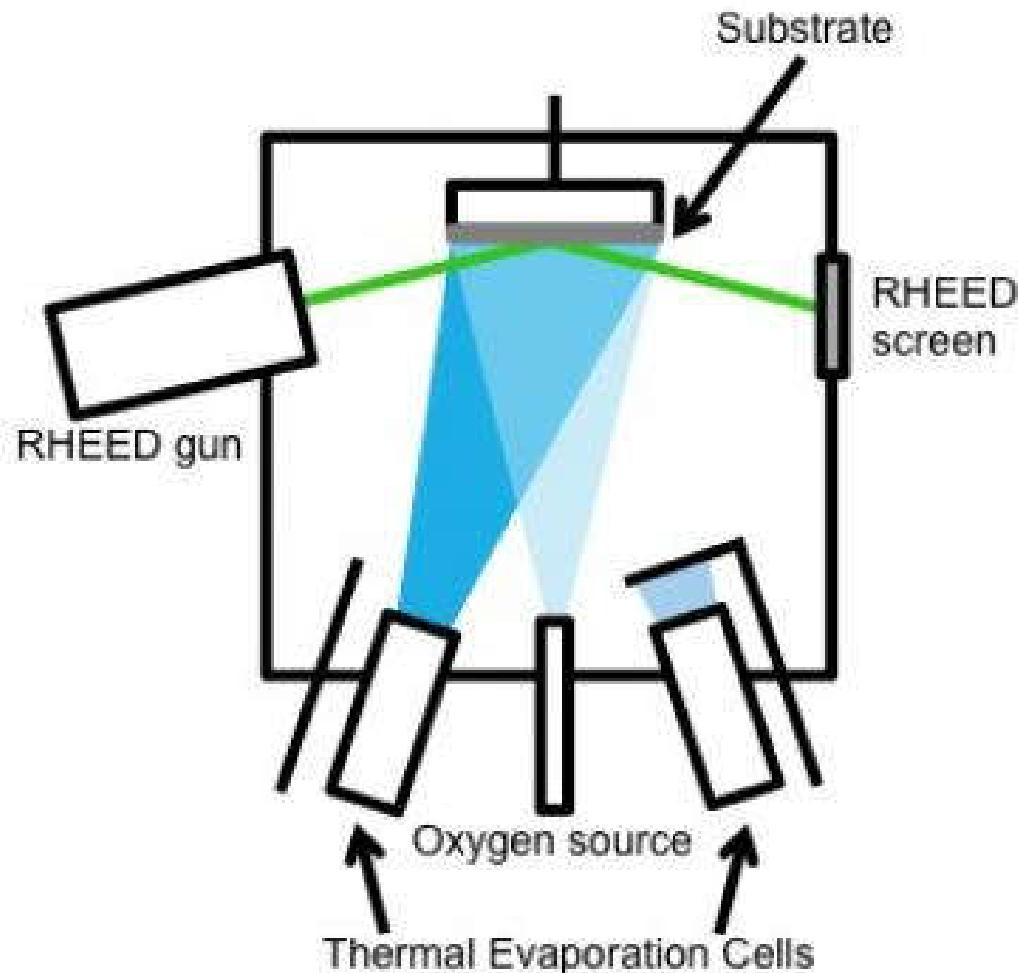
interface energy ↓

interface energy ↑

interface energy ↓ ↑



# Online Surface Monitoring

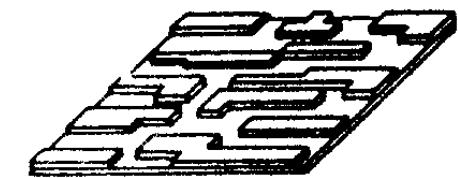
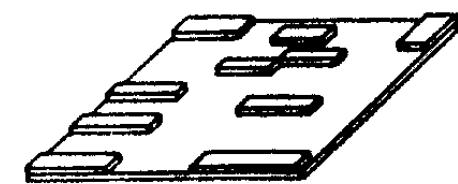
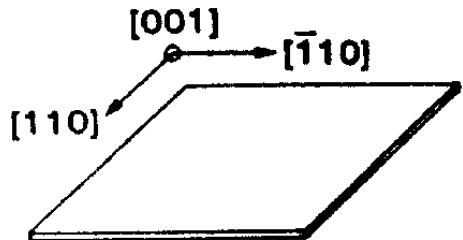


**Reflection high-energy  
electron diffraction  
(RHEED)**

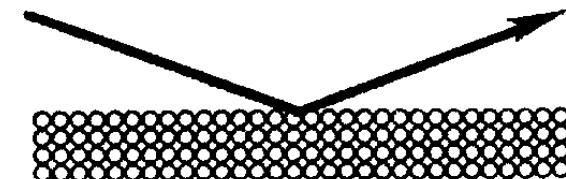
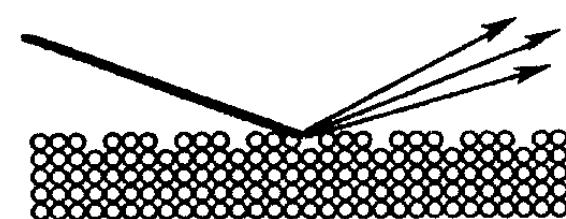
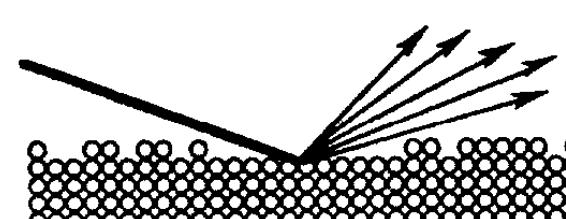
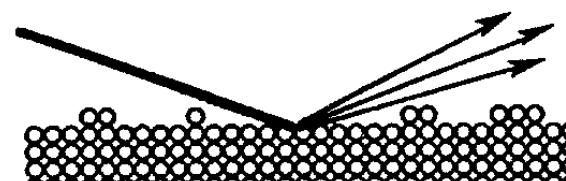
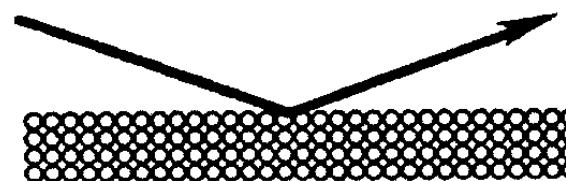
**MBE system**

# Online Surface Monitoring

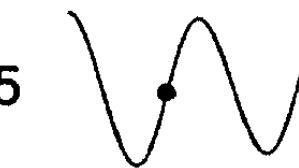
MONOLAYER GROWTH



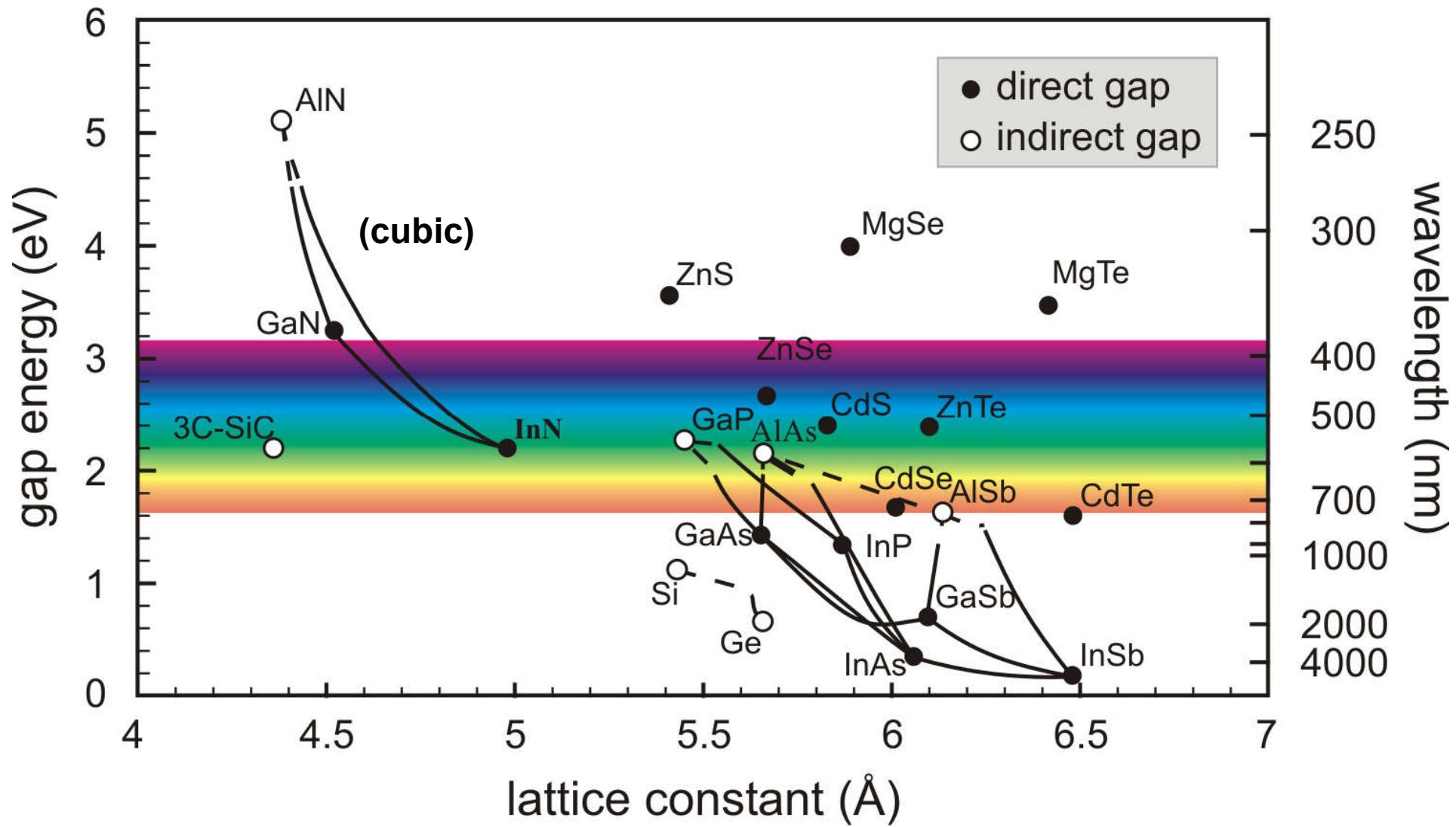
ELECTRON BEAM



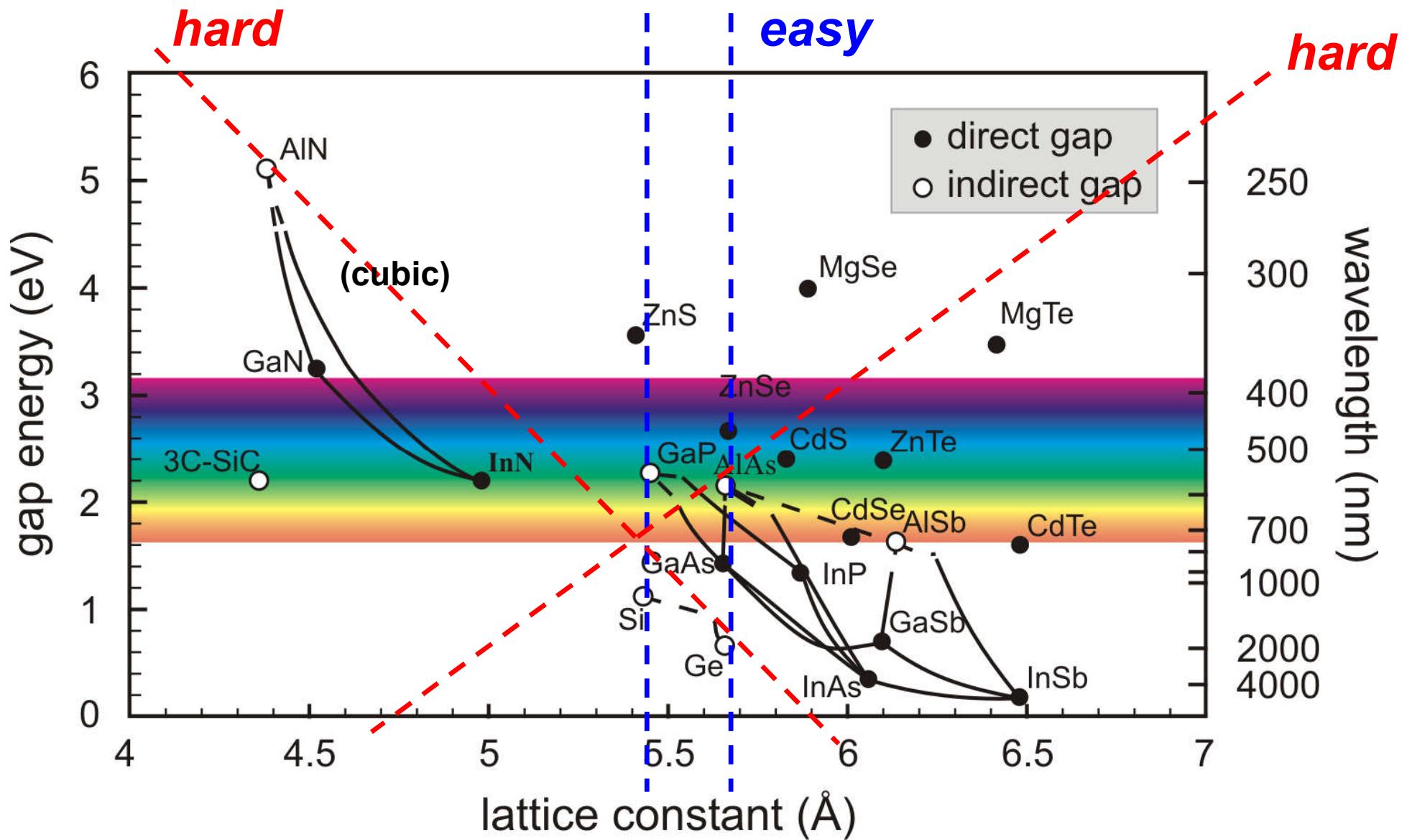
RHEED SIGNAL

 $\bar{\theta} = 0$  $\bar{\theta} = 0.25$  $\bar{\theta} = 0.5$  $\bar{\theta} = 0.75$  $\bar{\theta} = 1.0$ 

# Lattice Constants vs. Bandgap



# Lattice Constants vs. Bandgap



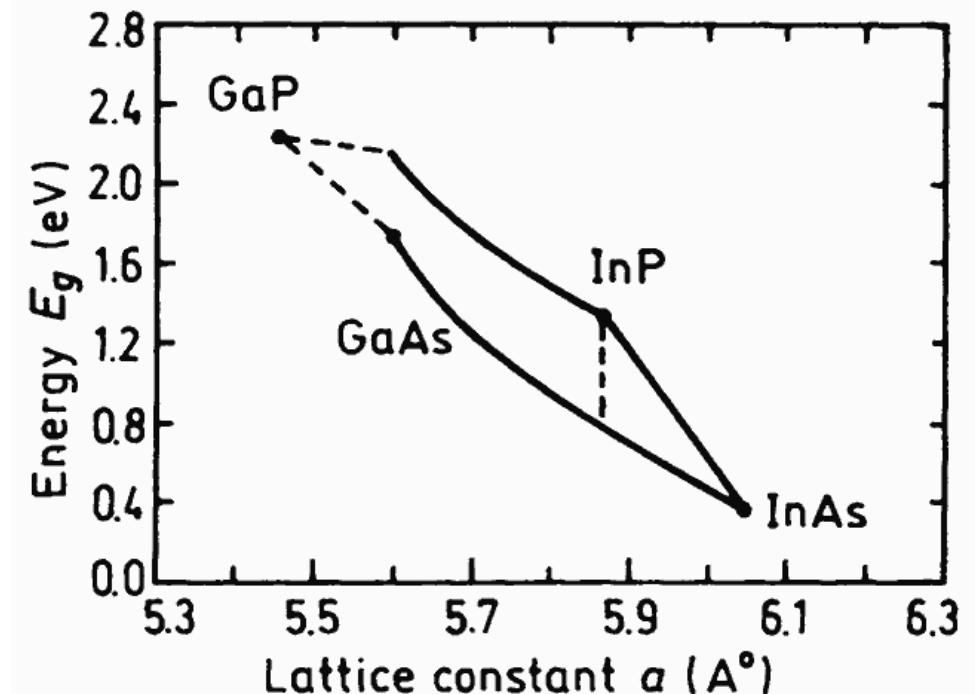
# Lattice Constants vs. Bandgap

Vegard's law: assume linear mixing

For  $A_x B_{1-x}$

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

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

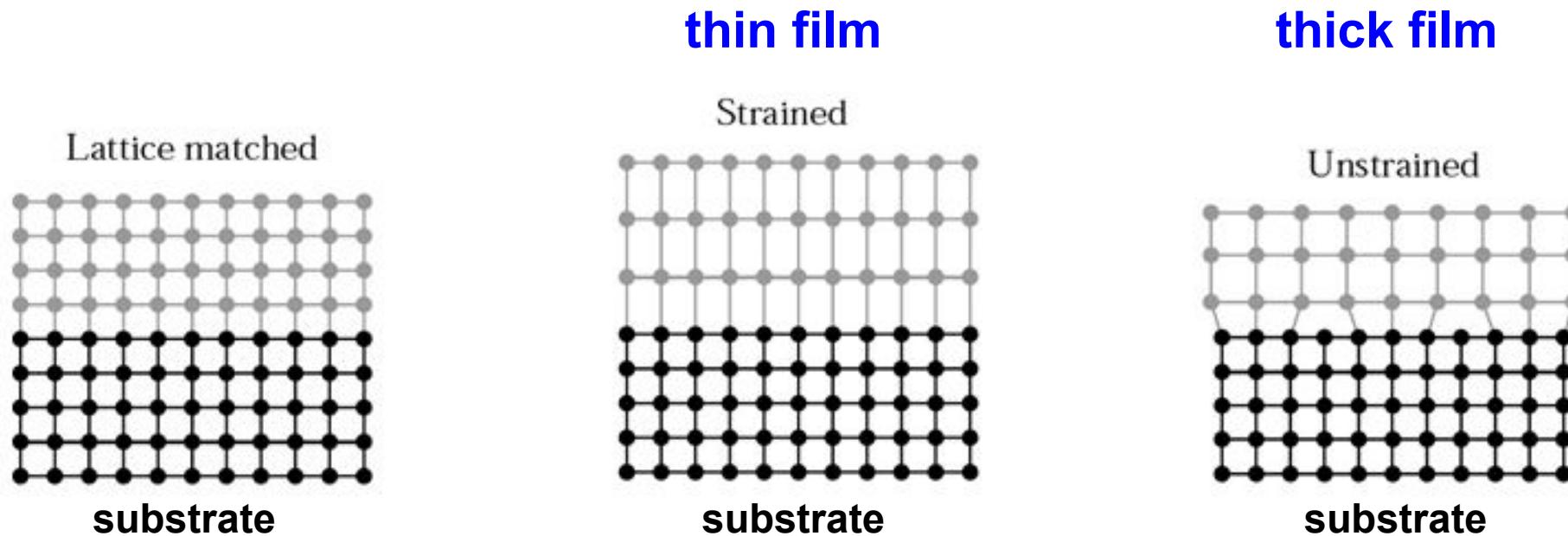


*Q:  $In_x Ga_{1-x} As$  on  $InP$ ?*

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

# Lattice Matched/Mismatched Growth

'metamorphic' growth



**Si on Si**

**GaAs on GaAs**

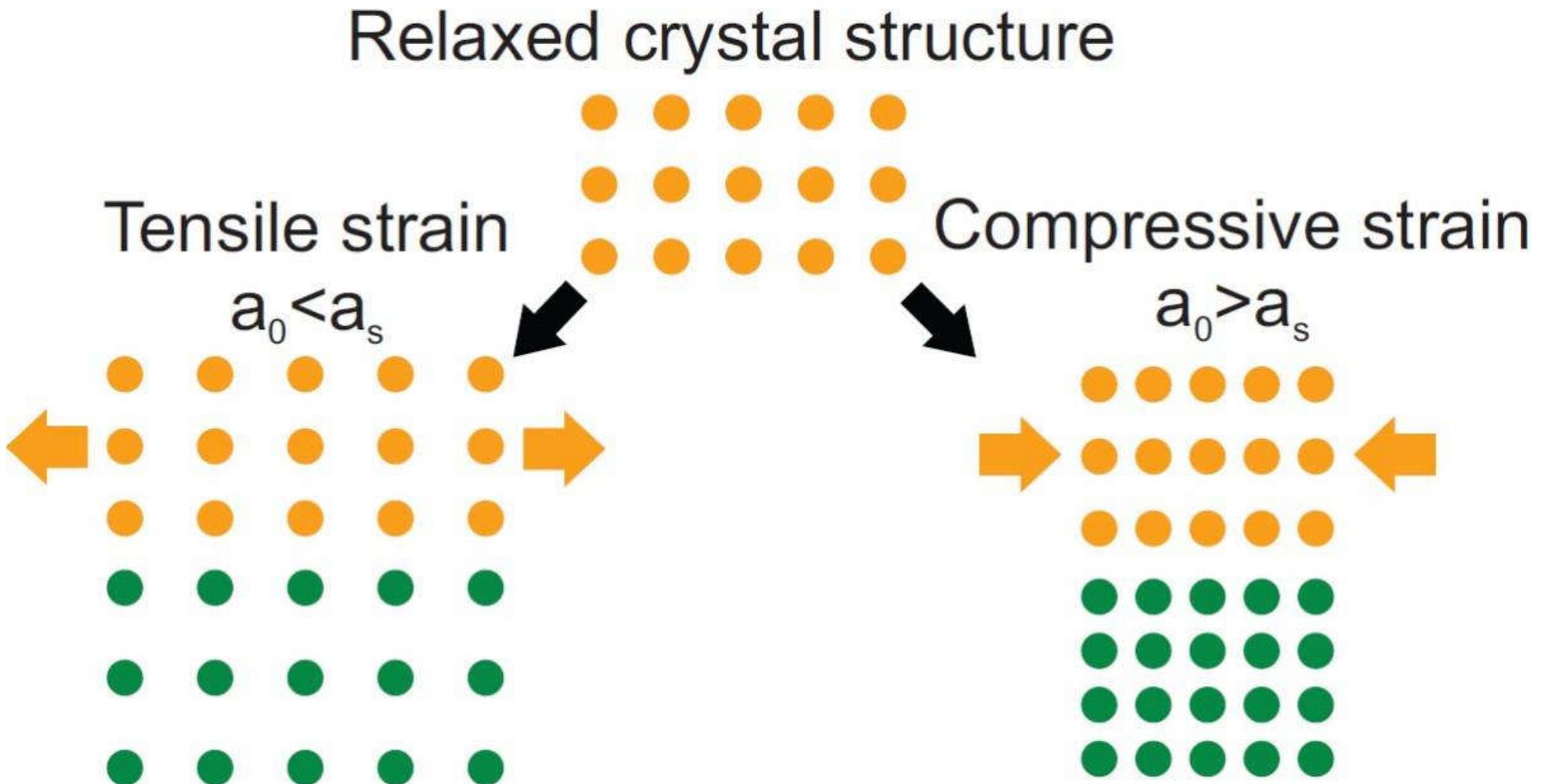
**AlAs on GaAs**

**GaAs on Ge**

...

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

# Strain in the Film



# Growth Energy

## strain energy

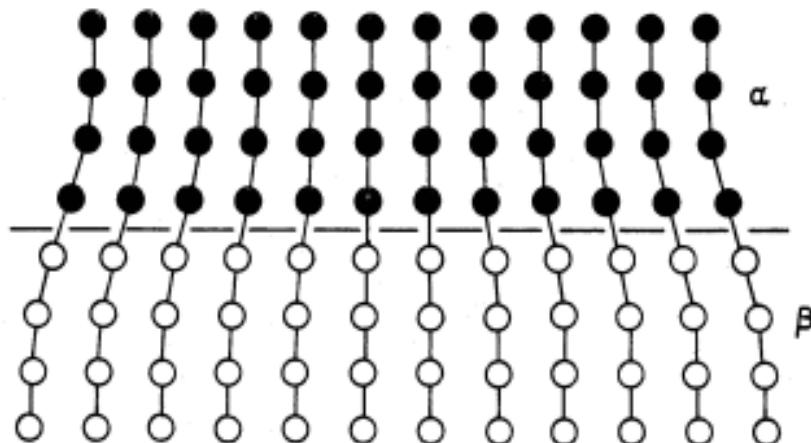


Fig. 3.34 A coherent interface with slight mismatch leads to coherency strains in the adjoining lattices.

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

$$E_\varepsilon \propto d$$

## misfit dislocation energy

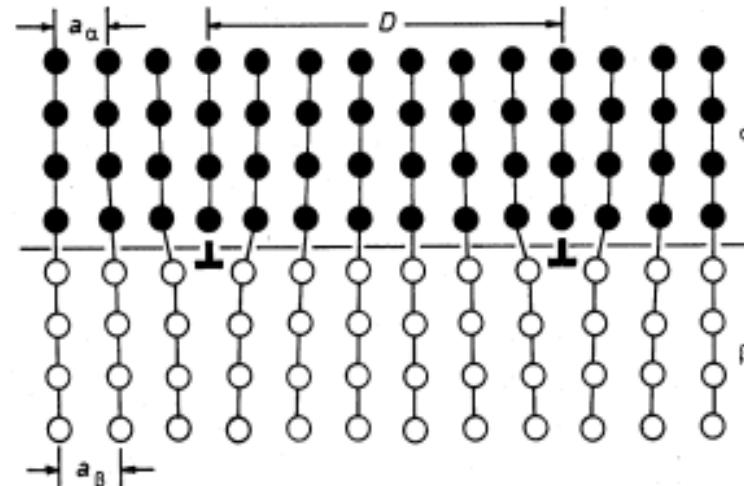
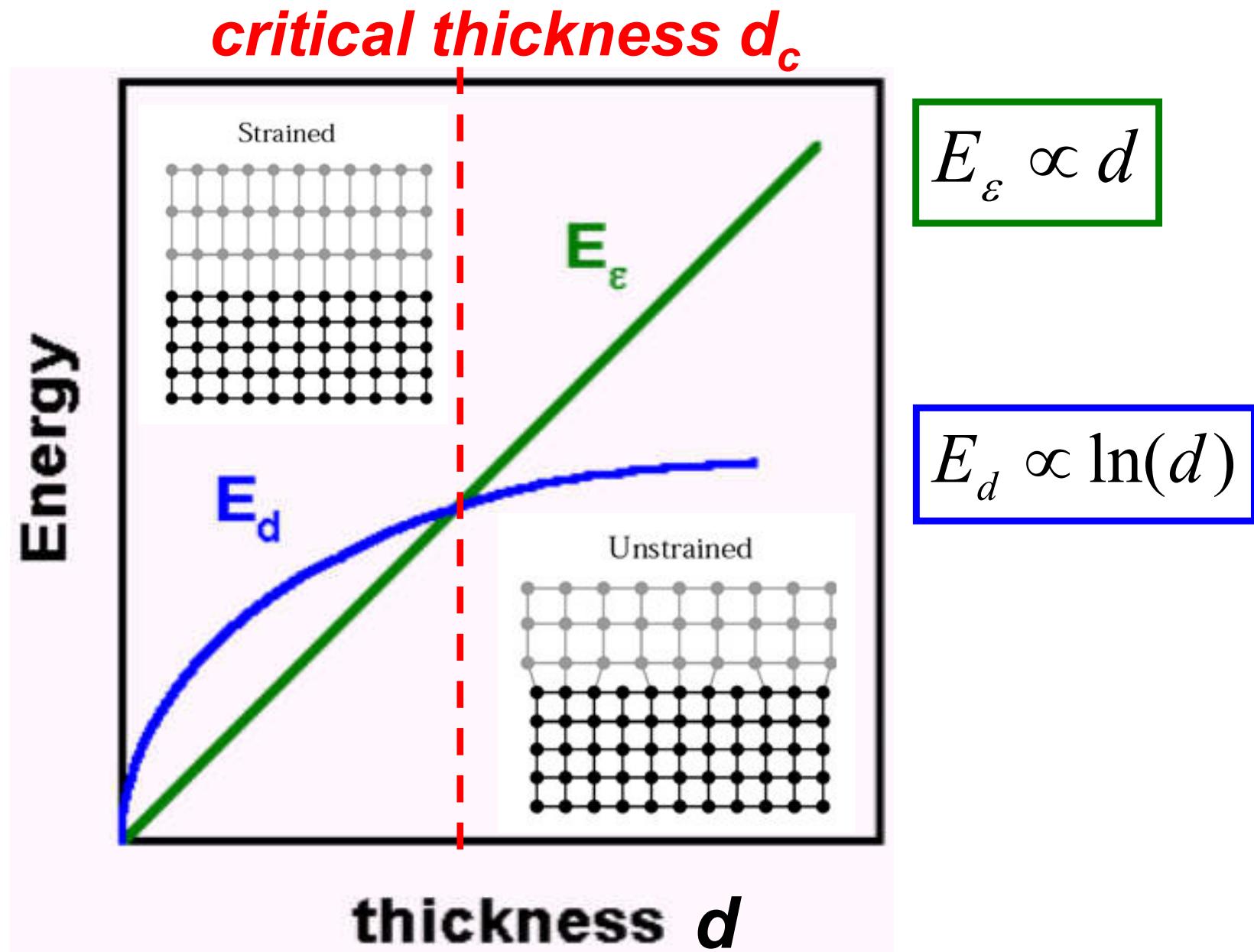


Fig. 3.35 A semicoherent interface. The misfit parallel to the interface is accommodated by a series of edge dislocations.

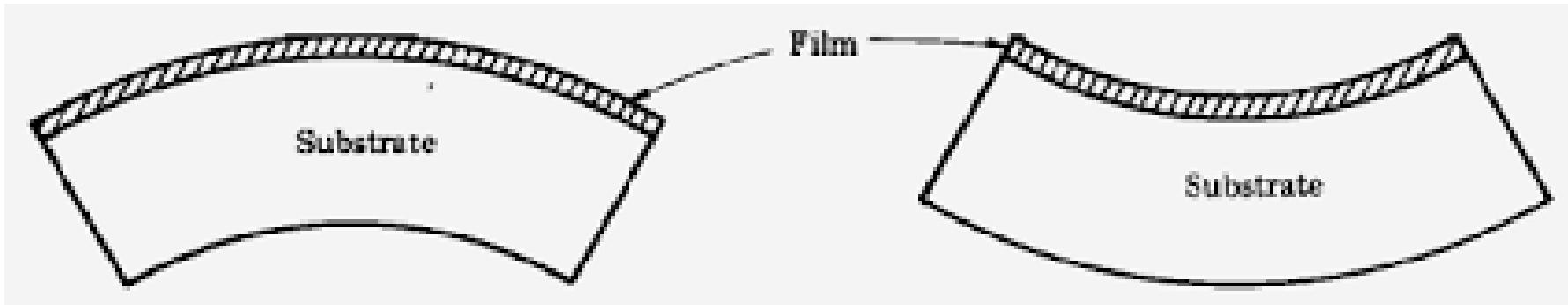
$$E_d = \frac{\mu b^2}{2\pi(1-\nu)S} \ln\left(\frac{\beta d}{b}\right)$$

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

# Growth Energy

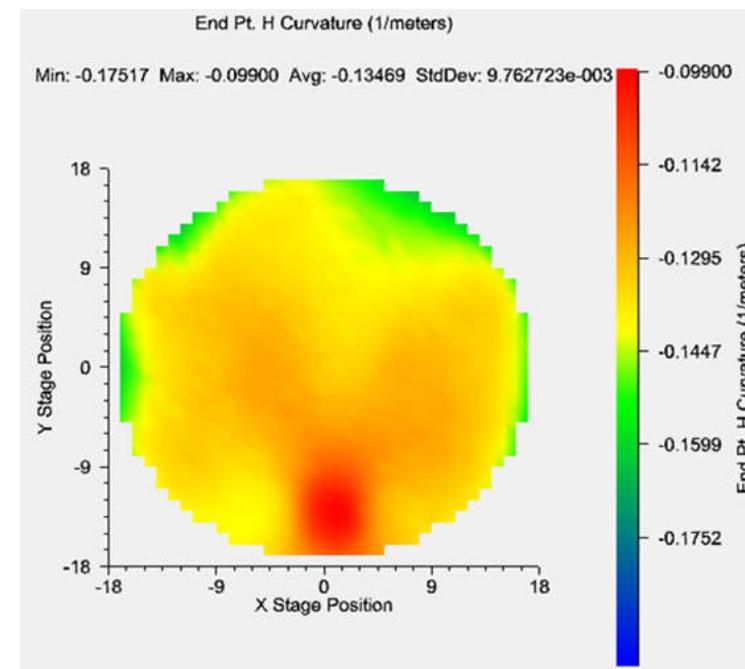
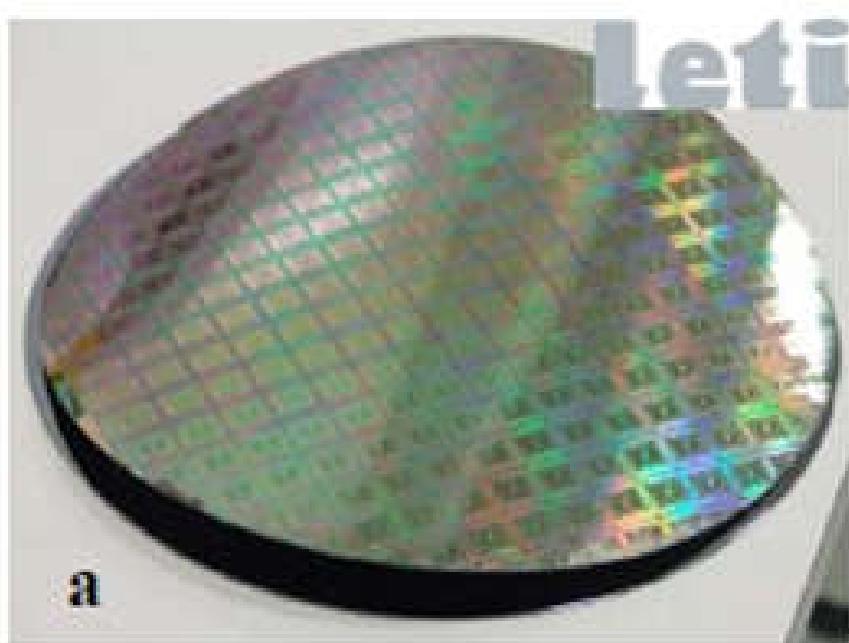


# Wafer 'Bowing' by Stress



compressive

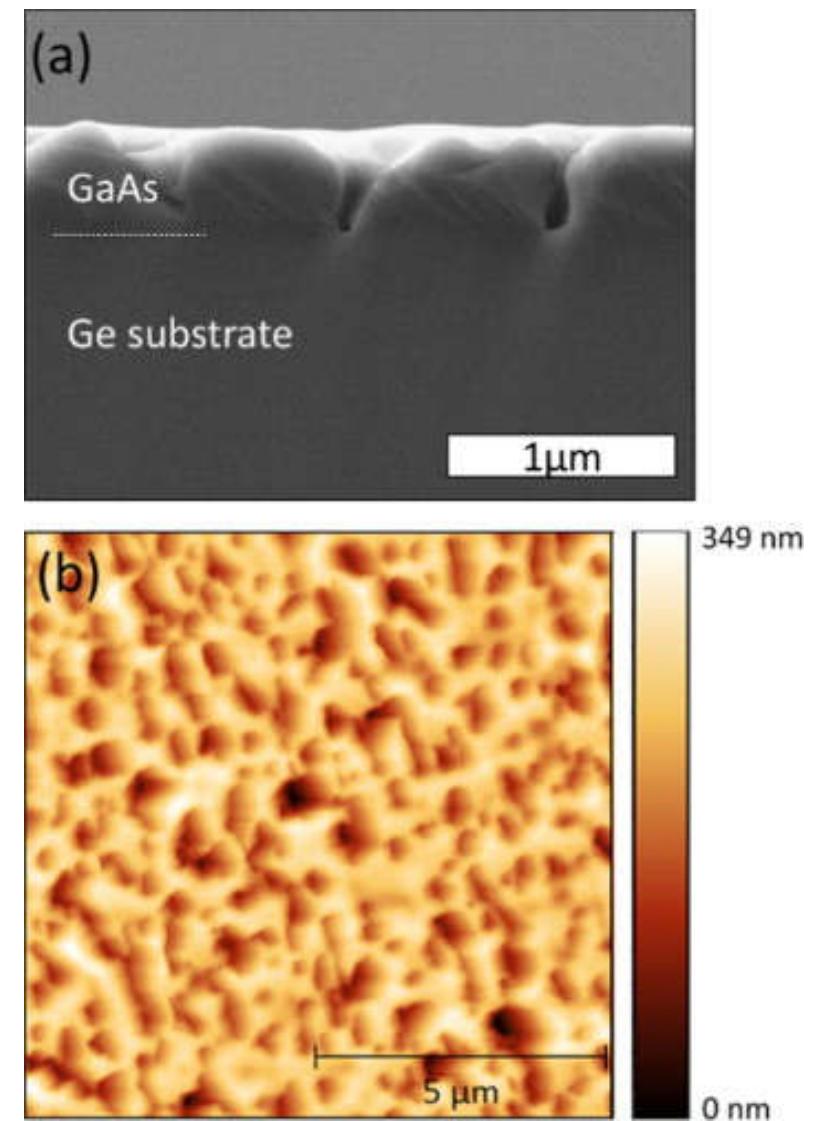
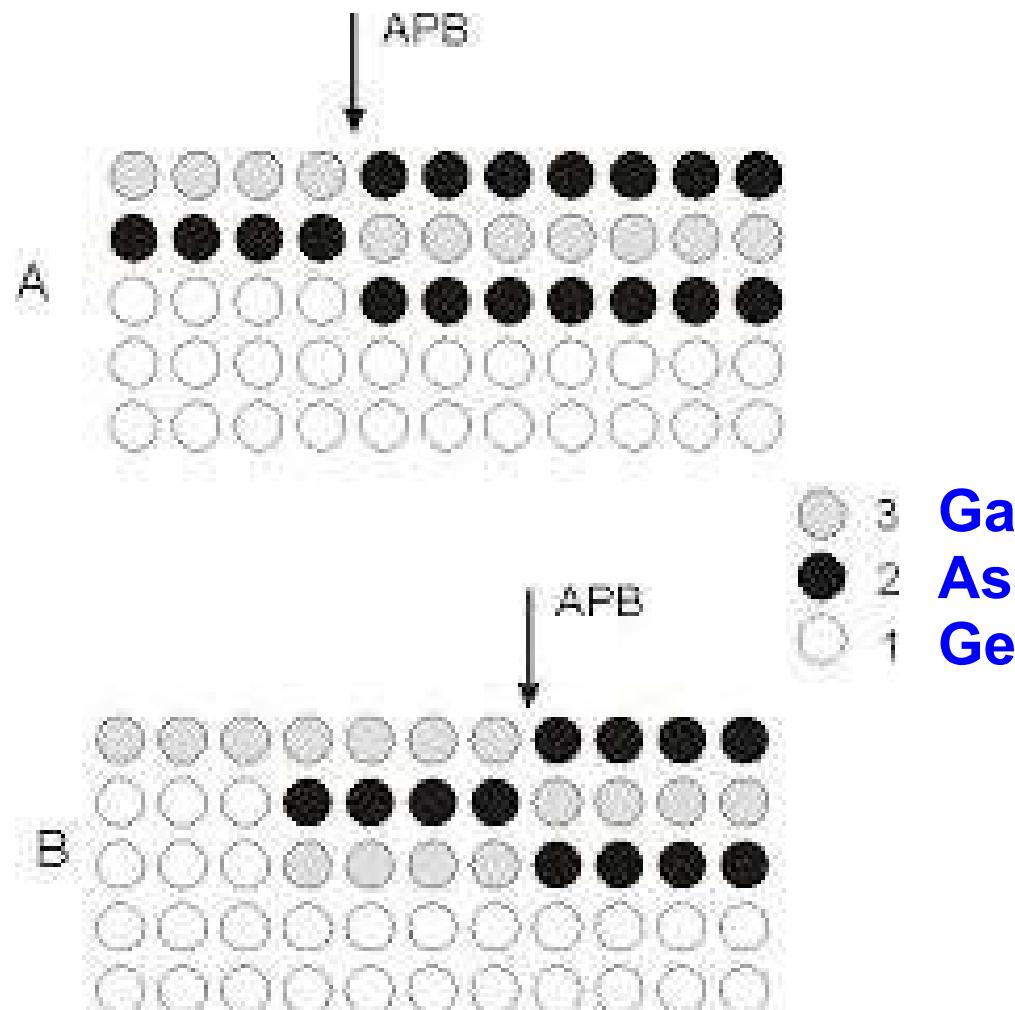
tensile



stress measured by curvature

# Anti-Phase Boundary (APB)

GaAs is lattice matched to Ge,  
but ...



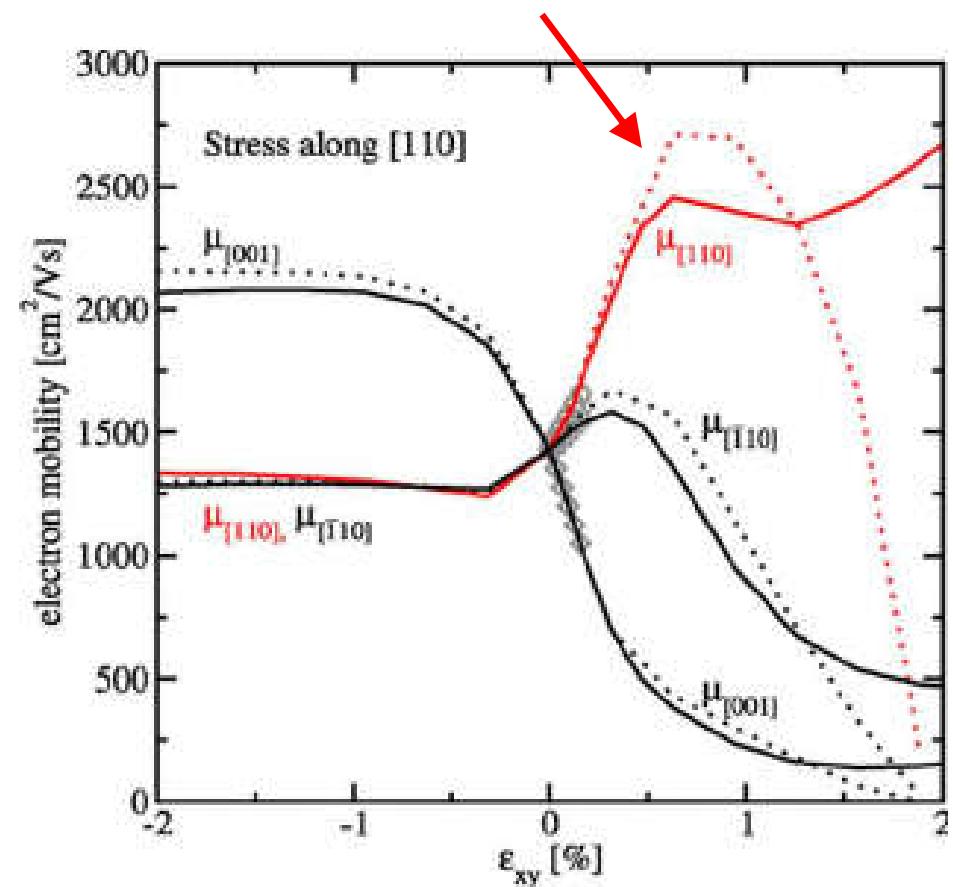
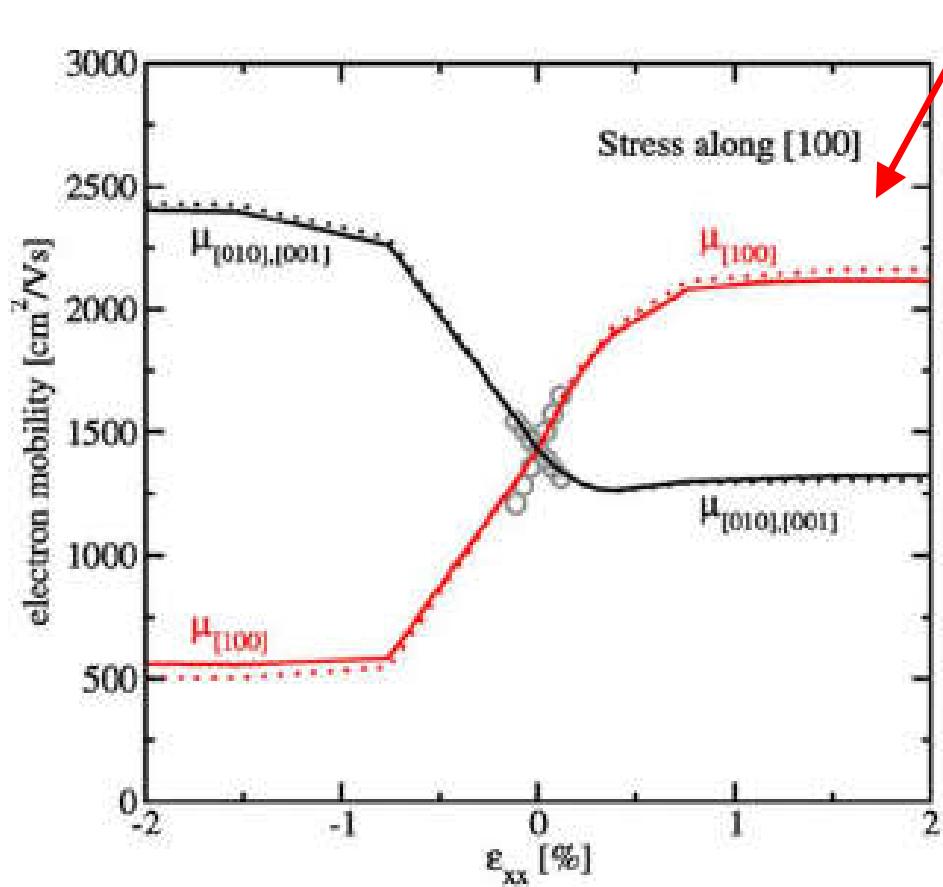
# Applications

---

- 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

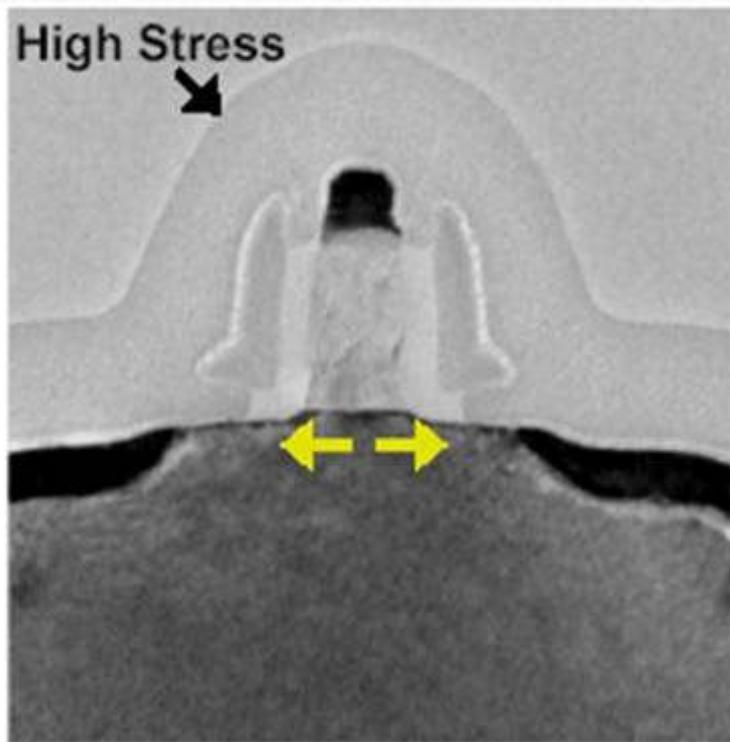


Fig. 3 TEM of NMOS transistor showing high tensile stress nitride overlayer.

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

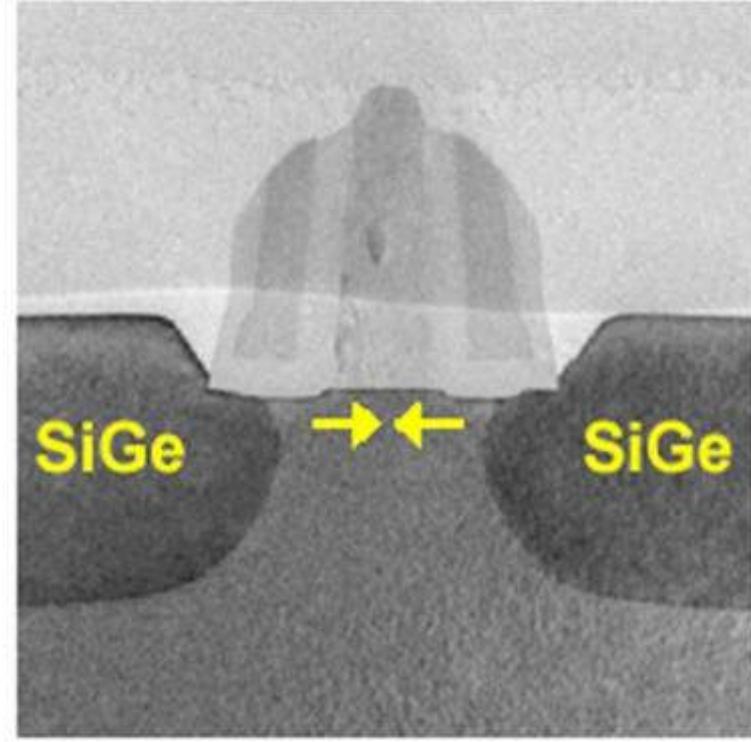
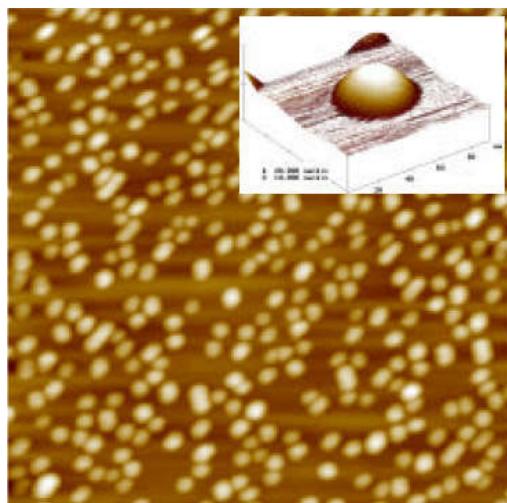
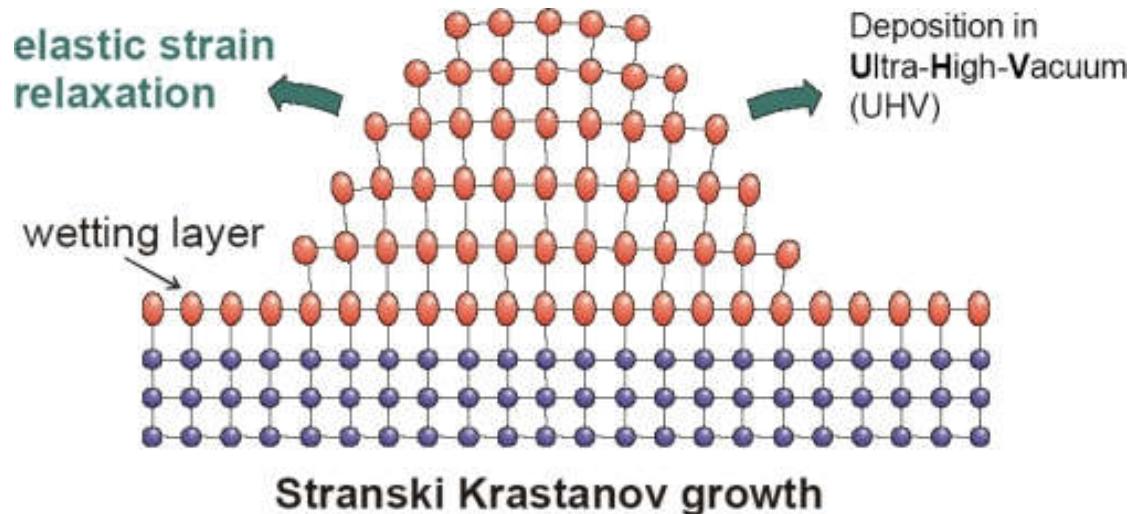
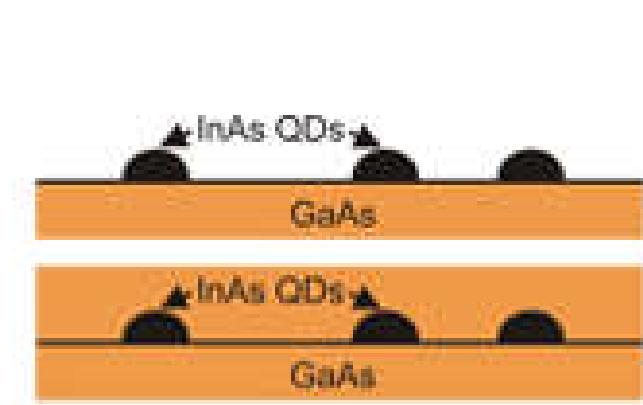


Fig. 4 TEM of PMOS showing SiGe heteroepitaxial S/D inducing uniaxial strain.

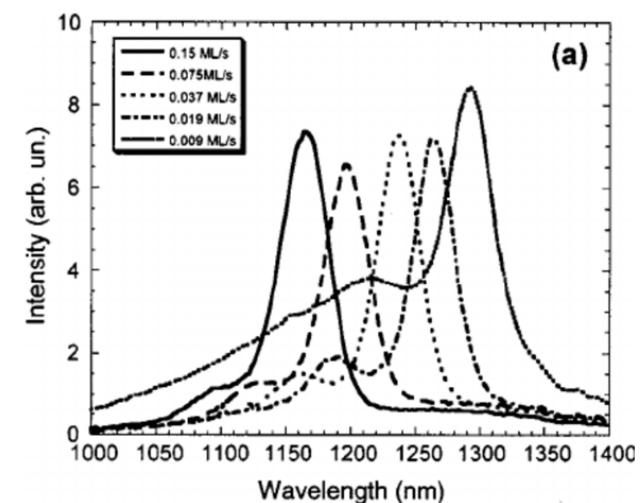
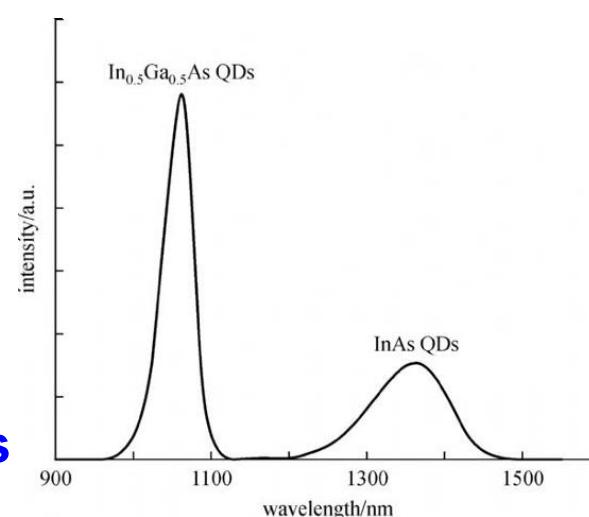
From K. Mistry et al., “Delaying Forever: Uniaxial Strained Silicon Transistors in a 90nm CMOS Technology,” 2004 VLSI Technology Symposium, pp. 50-51.

# III-V Quantum Dots

InGaAs is not lattice matched to GaAs



Quantum Dot based lasers



# III-V Quantum Dots

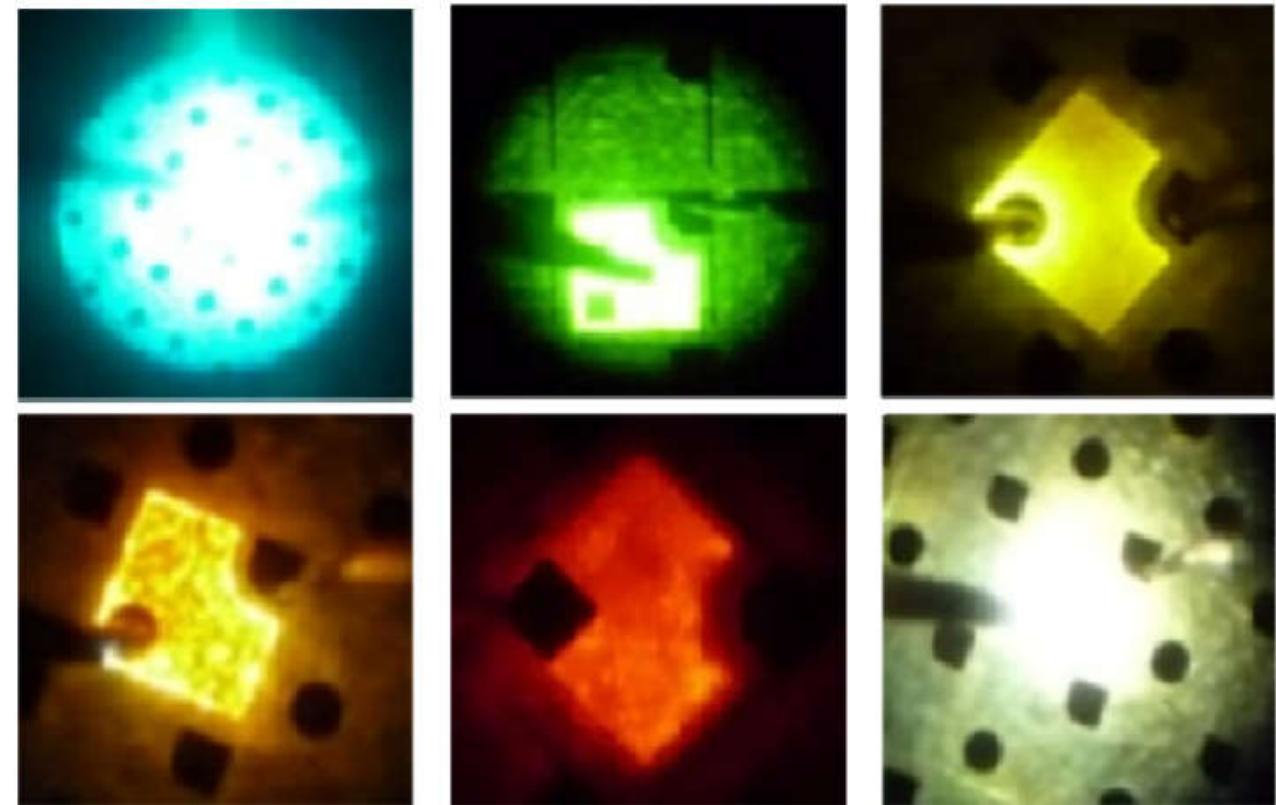
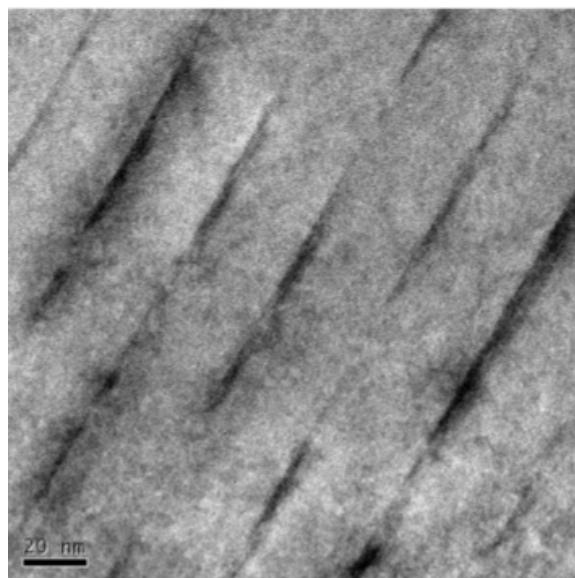
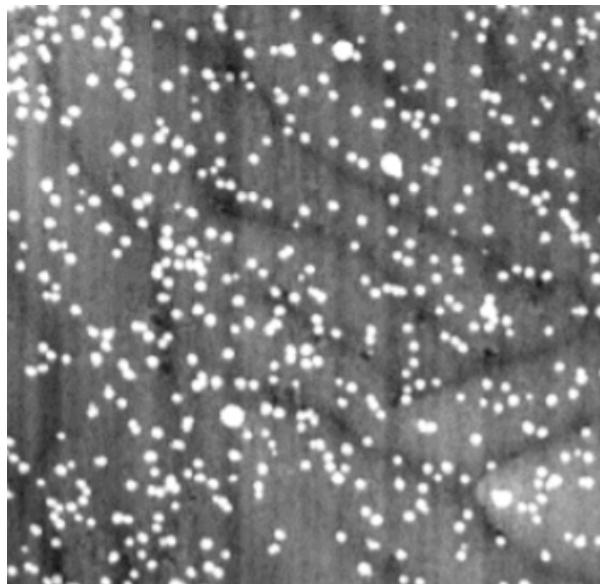
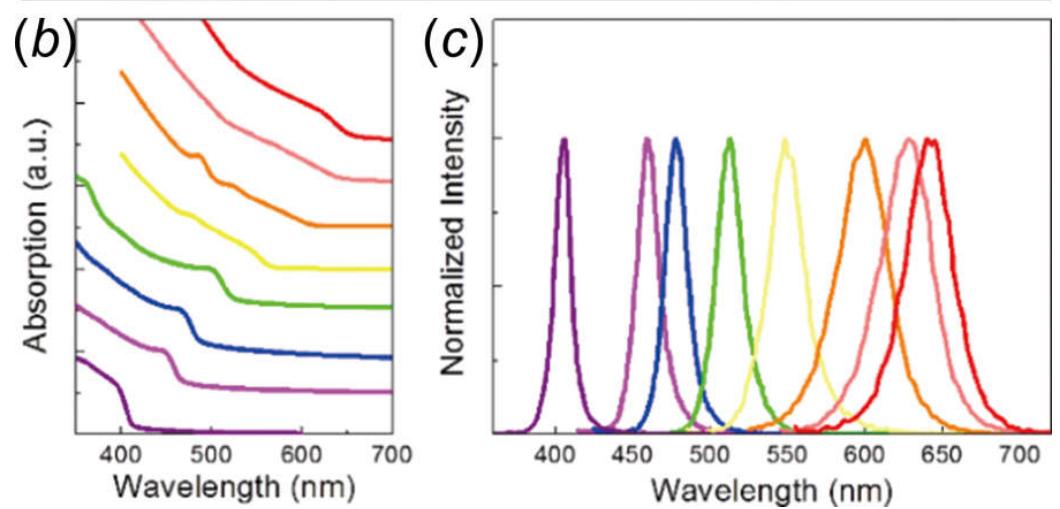
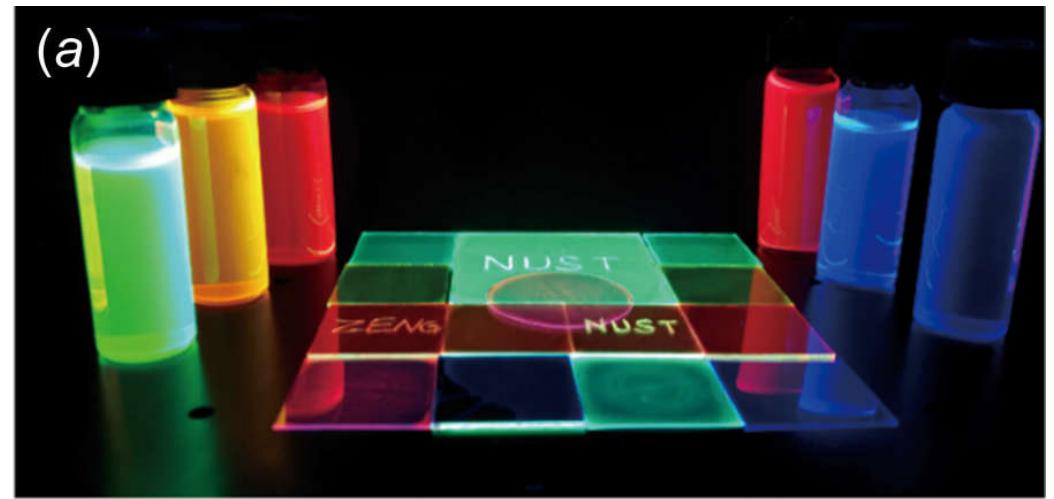
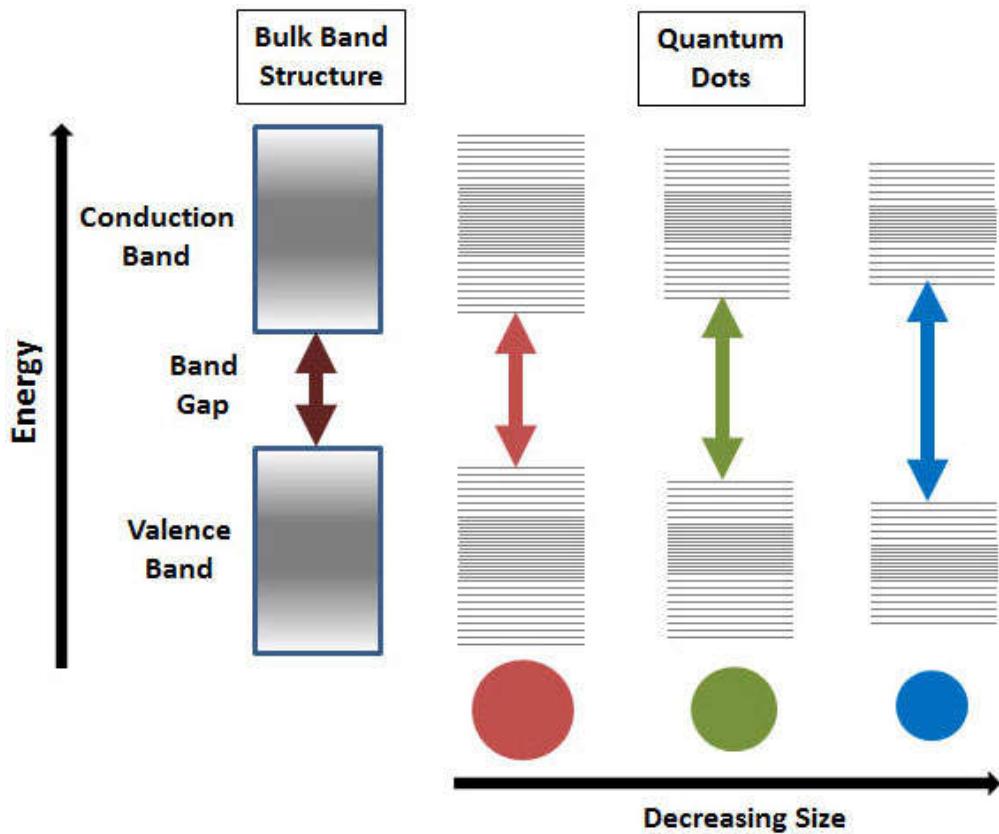
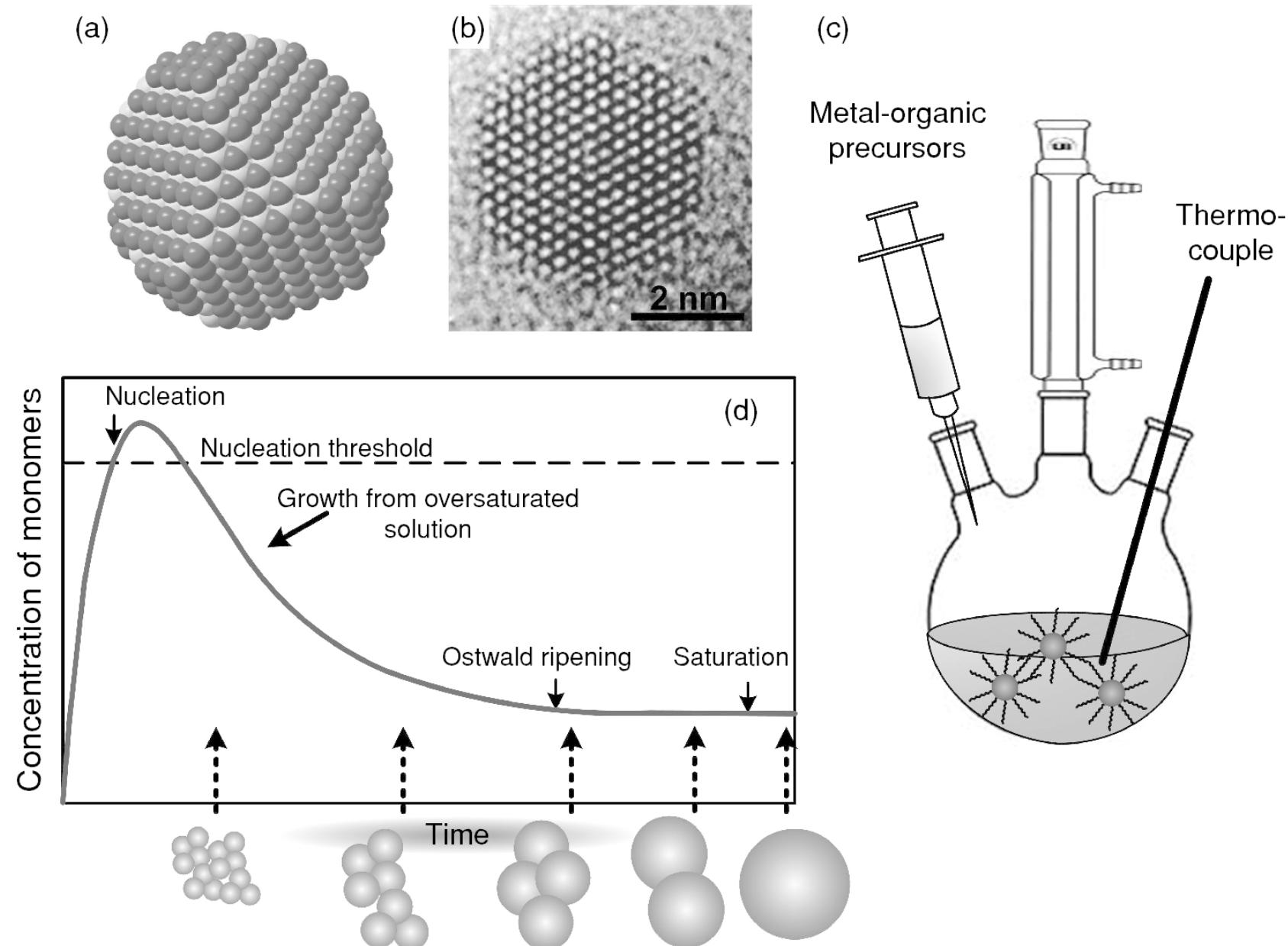


Fig. 2. Luminescence photos of InGaN QDs LEDs.

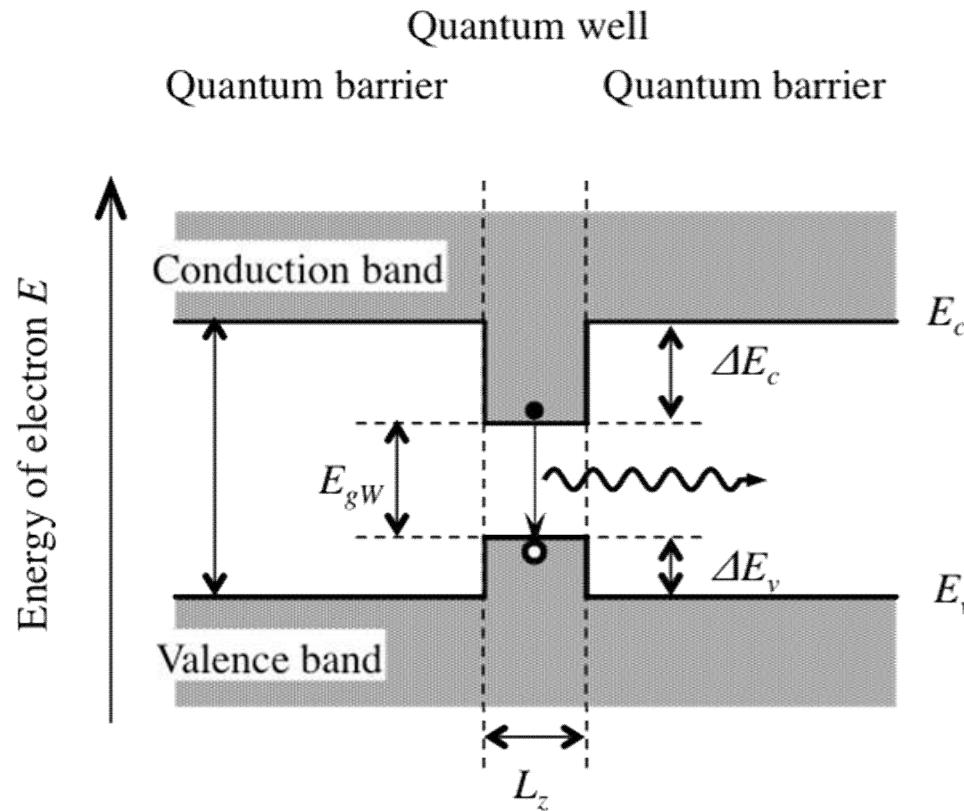
# Colloidal Quantum Dots



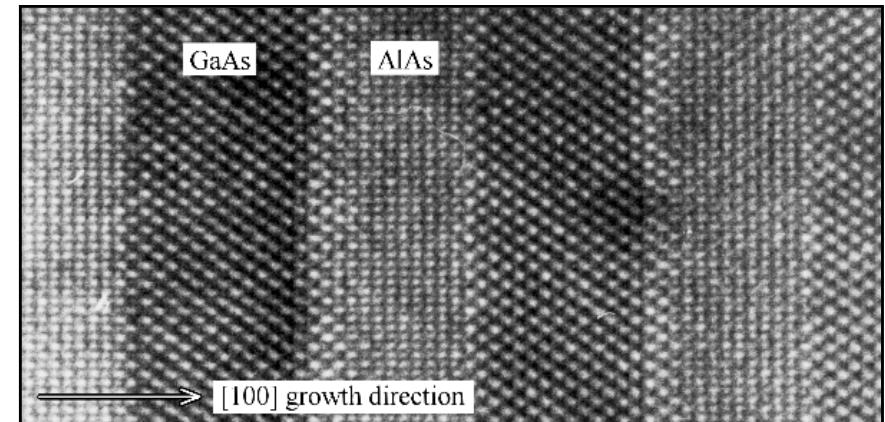
# Colloidal Quantum Dots



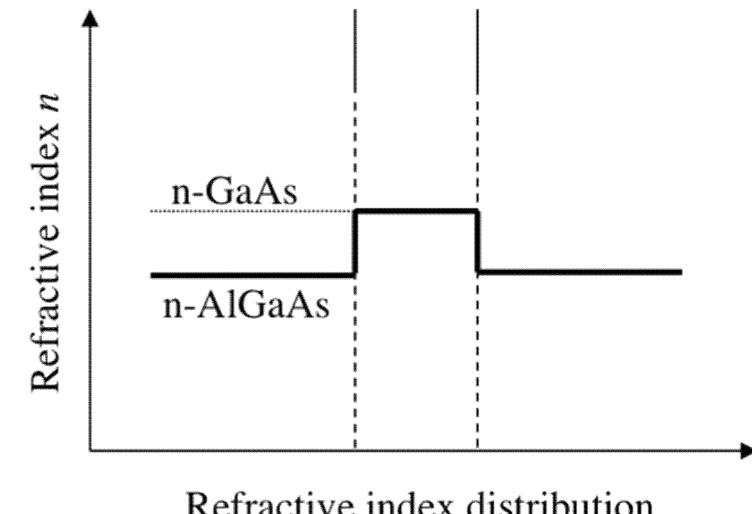
# Quantum Wells



## AlGaAs / GaAs quantum wells



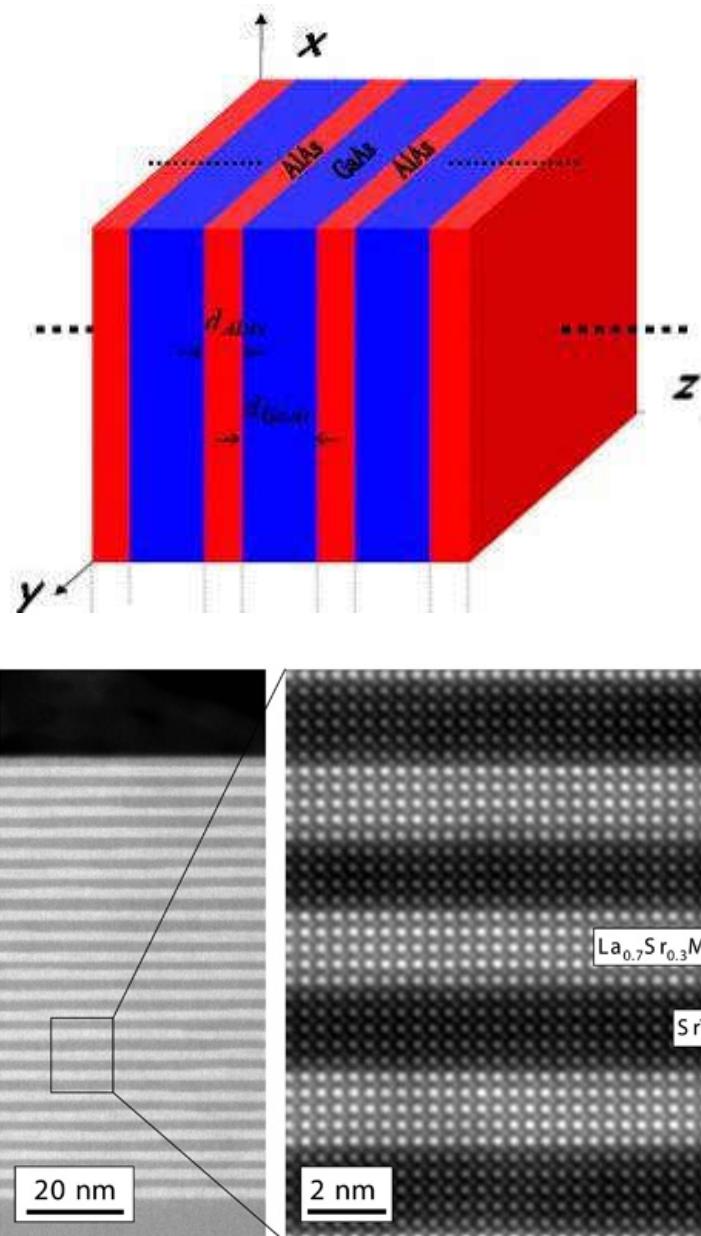
n-type AlGaAs  
cladding layer      p-type GaAs  
active layer      n-type AlGaAs  
cladding layer



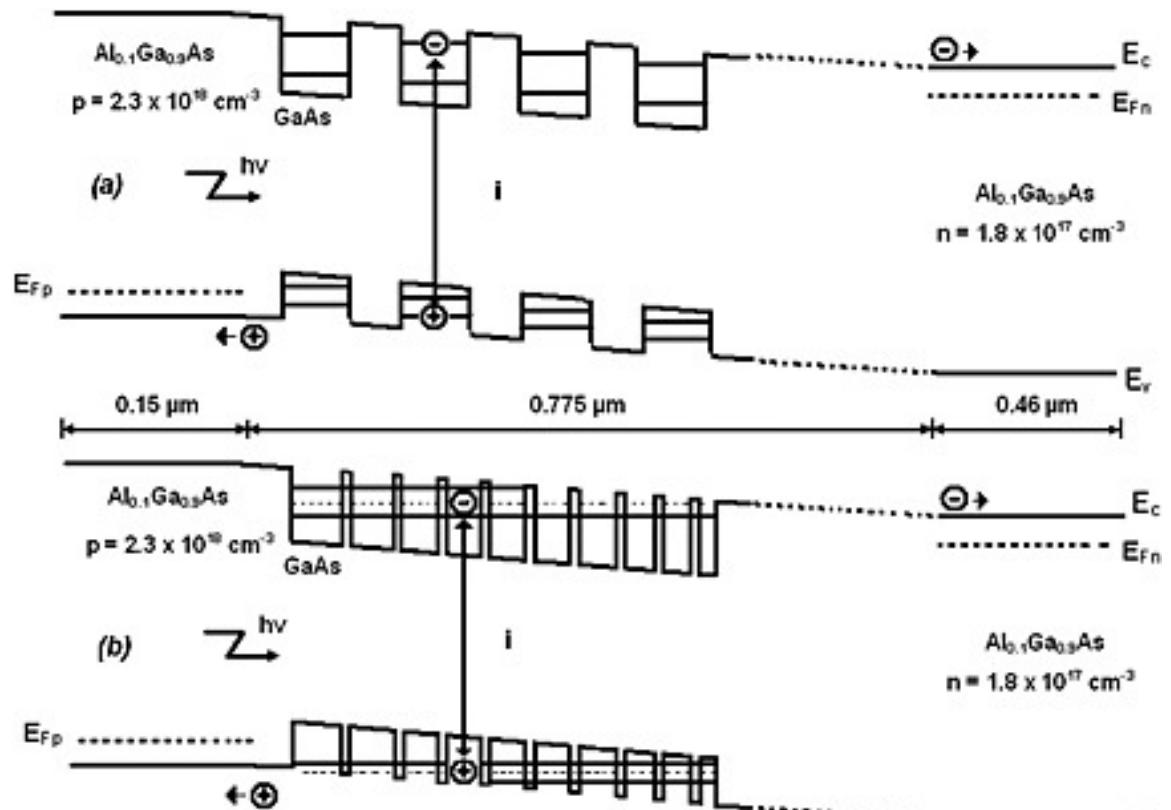
- 1. electronic confinement**
- 2. optical confinement**

2000 Nobel Prize in Physics

# Superlattice 超晶格



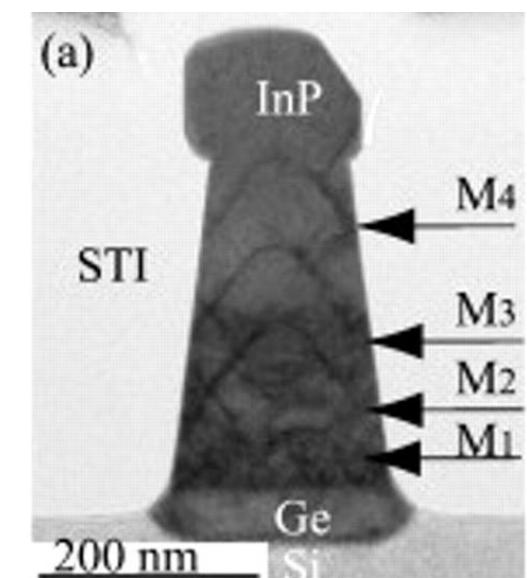
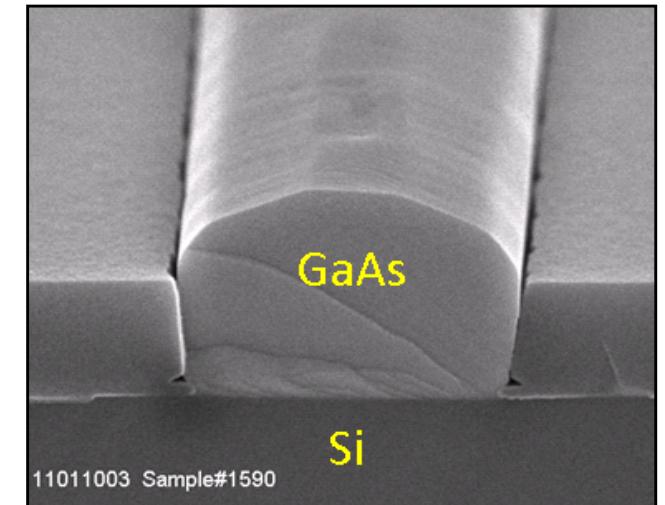
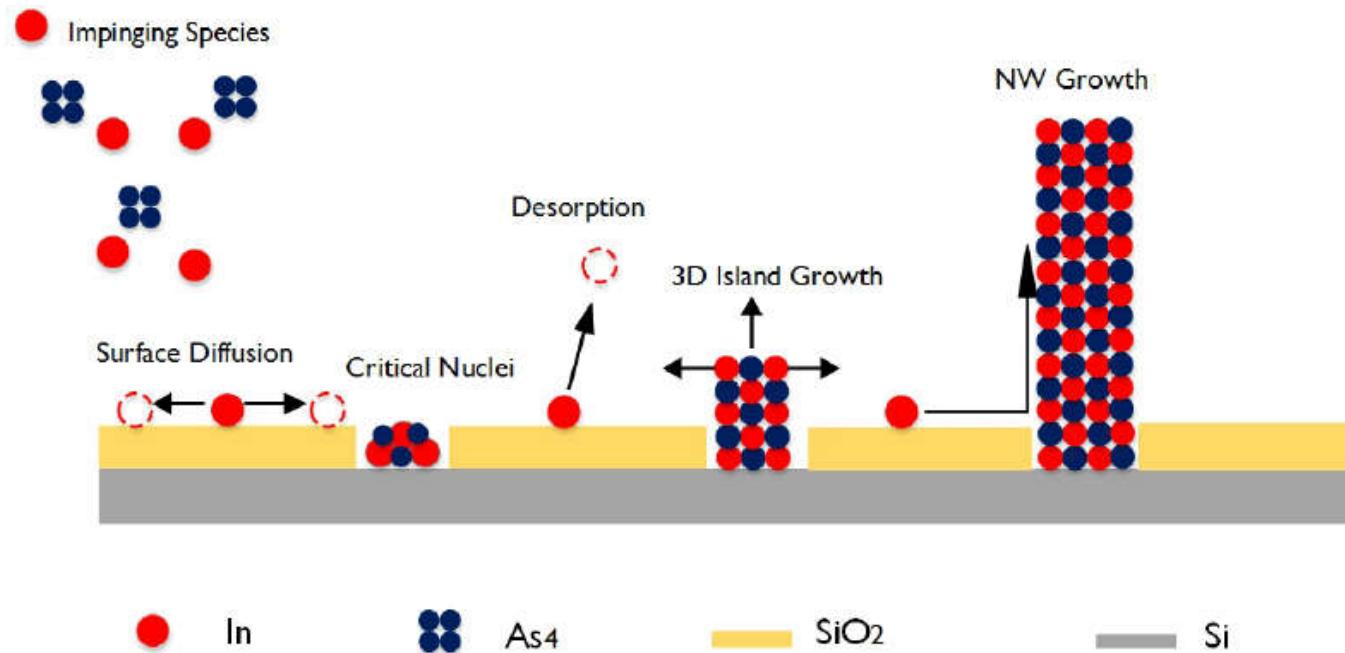
**conventional quantum wells**



**superlattice**

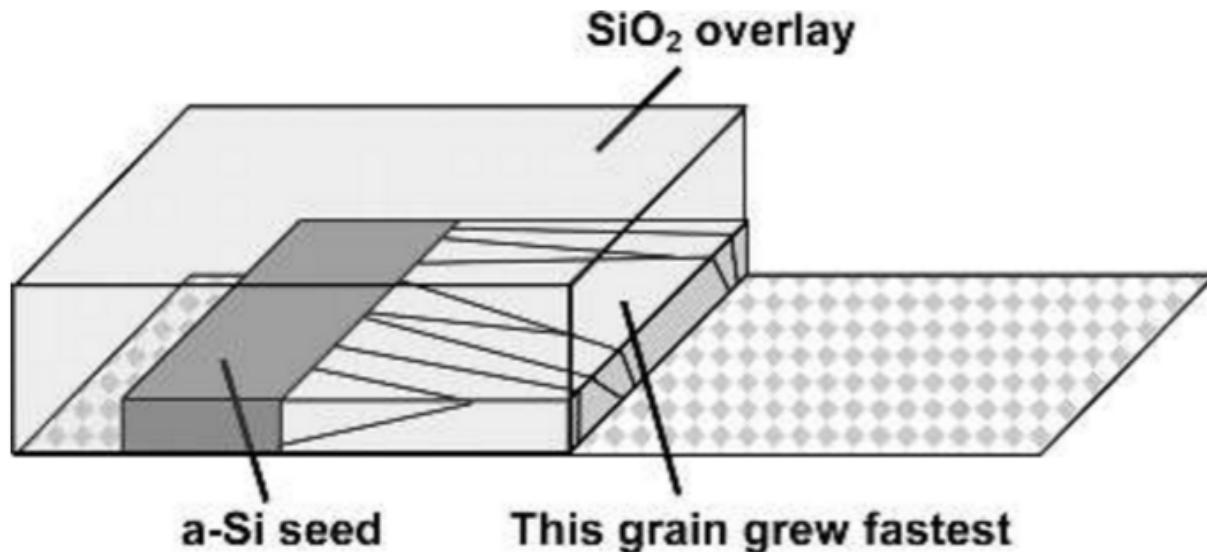
# Selective Area Growth

At high T, Ge, III-Vs grow on Si, but not on  $\text{SiO}_2$

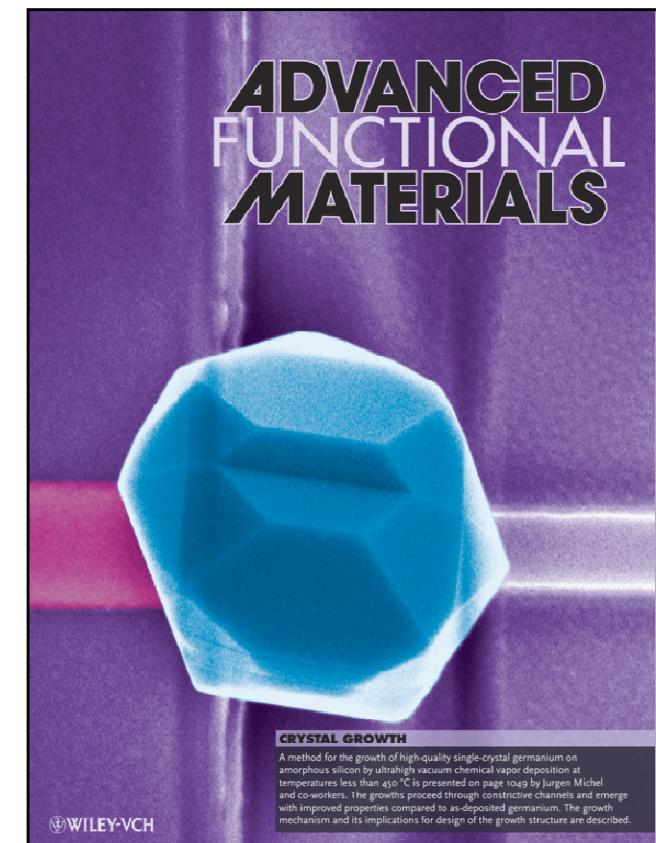


# Selective Area Growth

**Grow Ge single crystals on amorphous substrate**



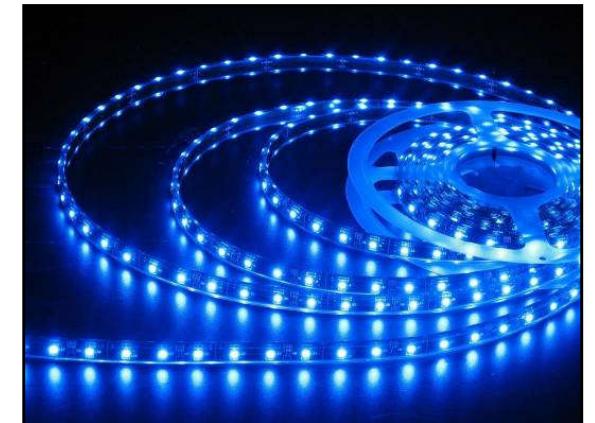
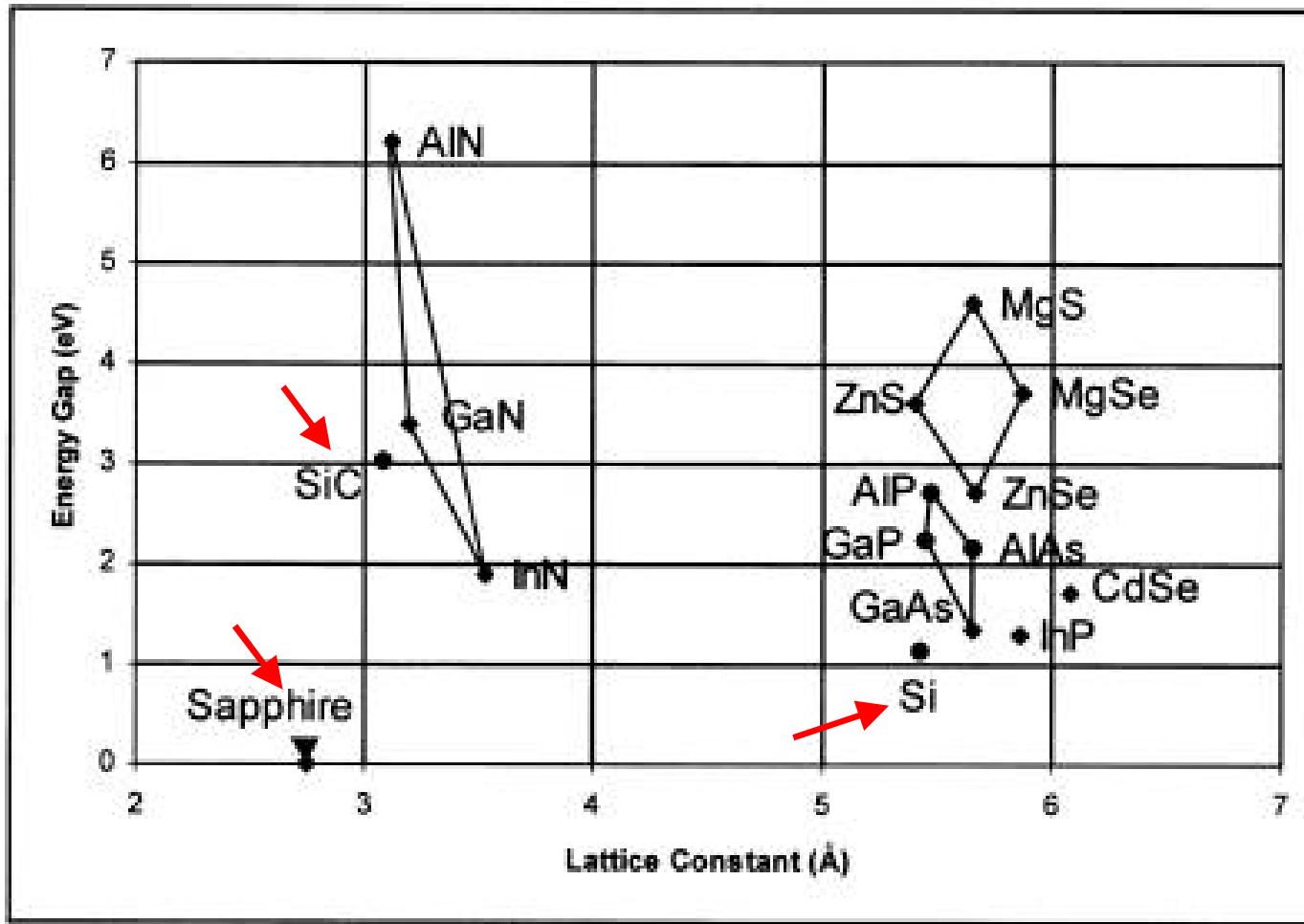
**UHVCVD**



*selective, only on Si, not  $\text{SiO}_2$*

*GeO is not stable*

# GaN Growth



InGaN blue LEDs

substrate price

GaN	\$\$\$\$
SiC	\$\$\$
sapphire	\$\$
silicon	\$

# Gallium Nitride (GaN) LED

## ■ GaN LED on sapphire

- 日本, Nichia
- 2014 Nobel Prize in Physics



I. Akasaki



H. Amano



S. Nakamura

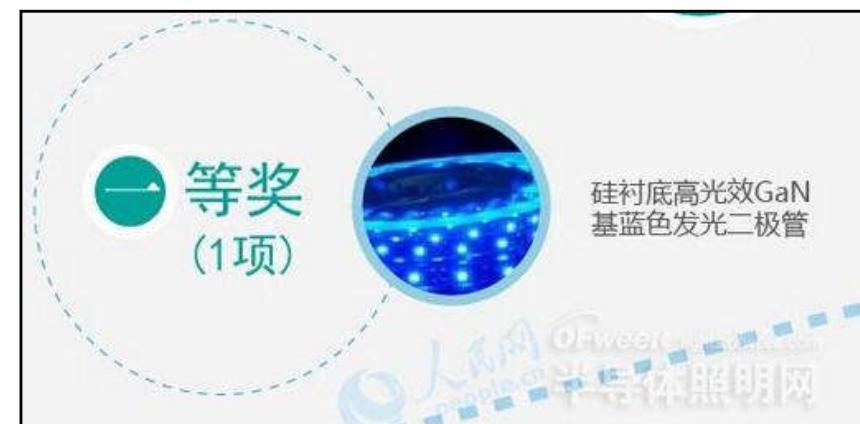
## ■ GaN LED on silicon carbide (SiC)

- USA, Cree

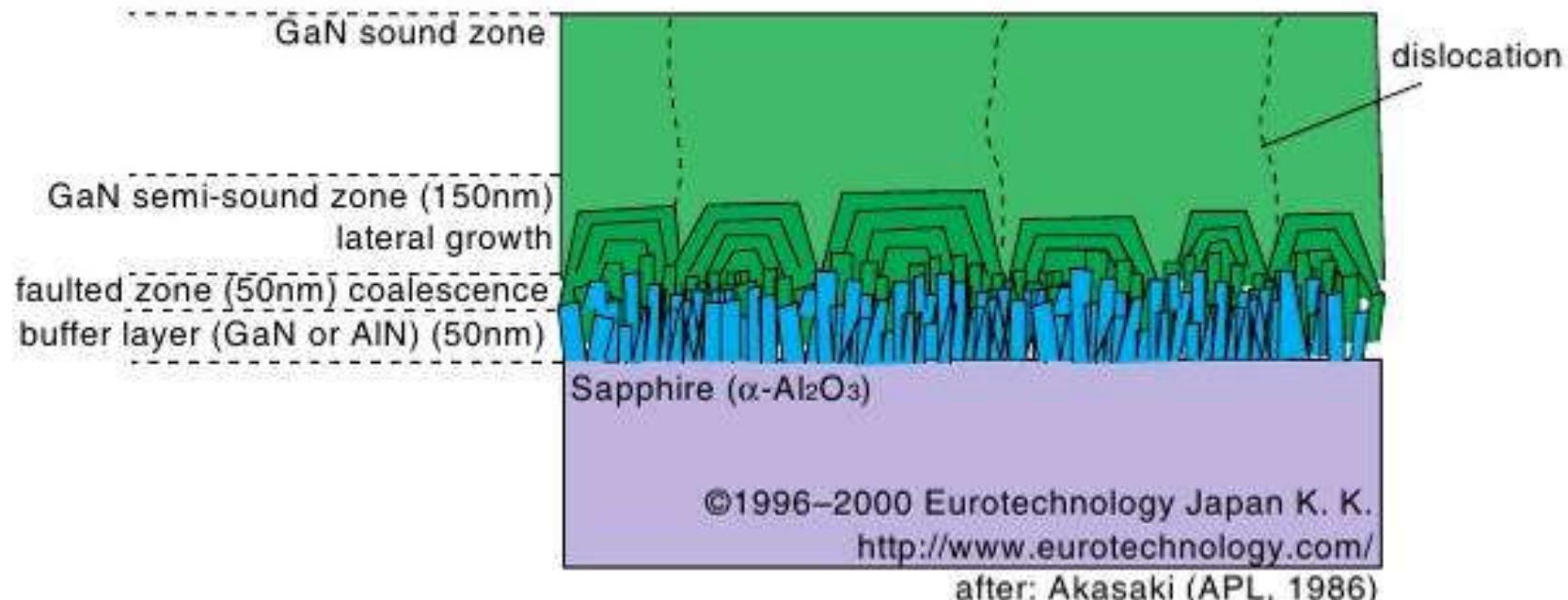


## ■ GaN LED on silicon

- 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



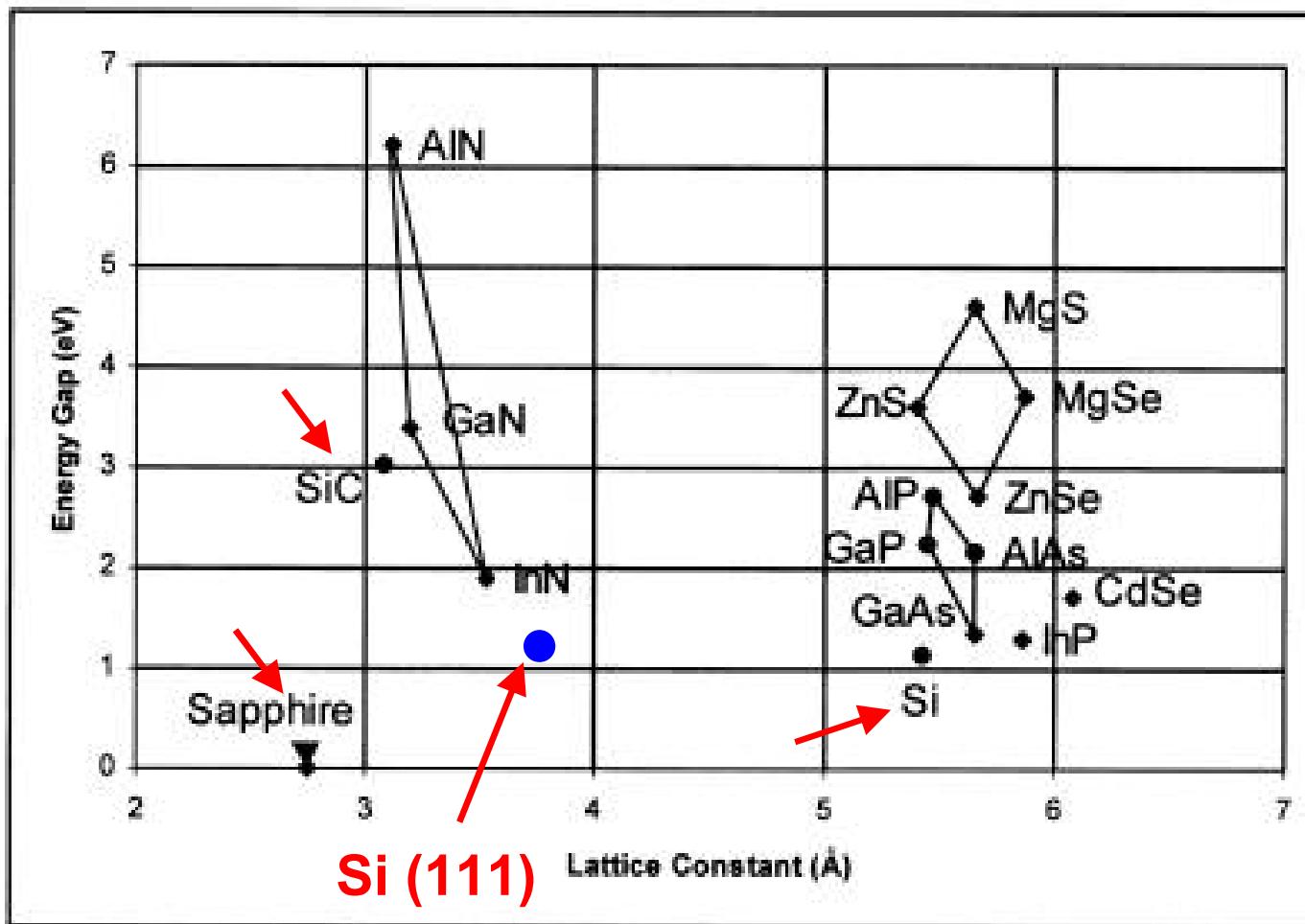
S. Nakamura

**2014 Nobel Prize in Physics**

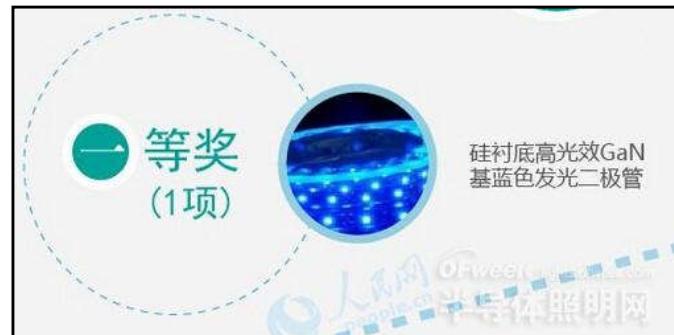
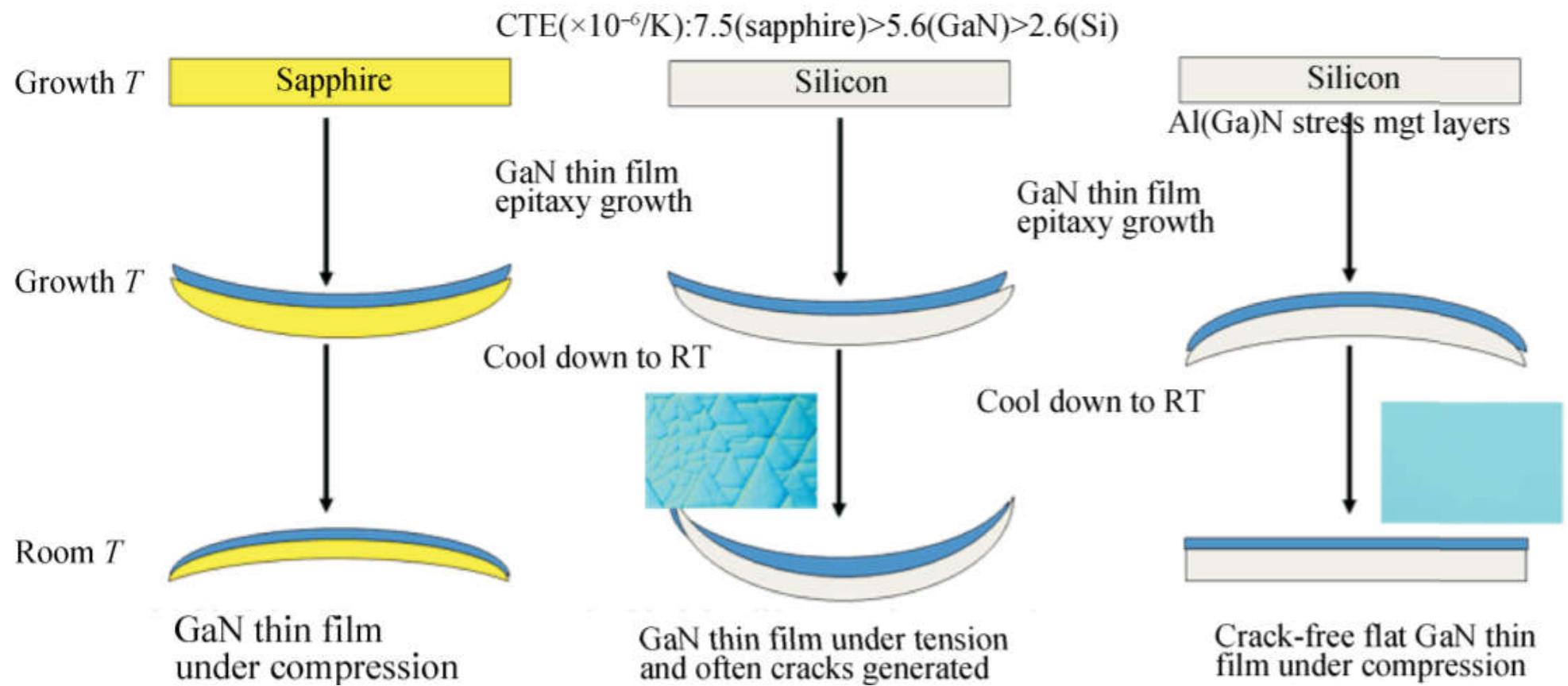
H. Amano, *et al.*, *Appl. Phys. Lett.* **48**, 353 (1986)  
 H. Amano, *et al.*, *Jpn. J. Appl. Phys.* **28**, L2112 (1989)  
 S. Nakamura, *et al.*, *Appl. Phys. Lett.* **64**, 1687 (1994)

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

# GaN Growth on Silicon



# GaN Growth on Silicon

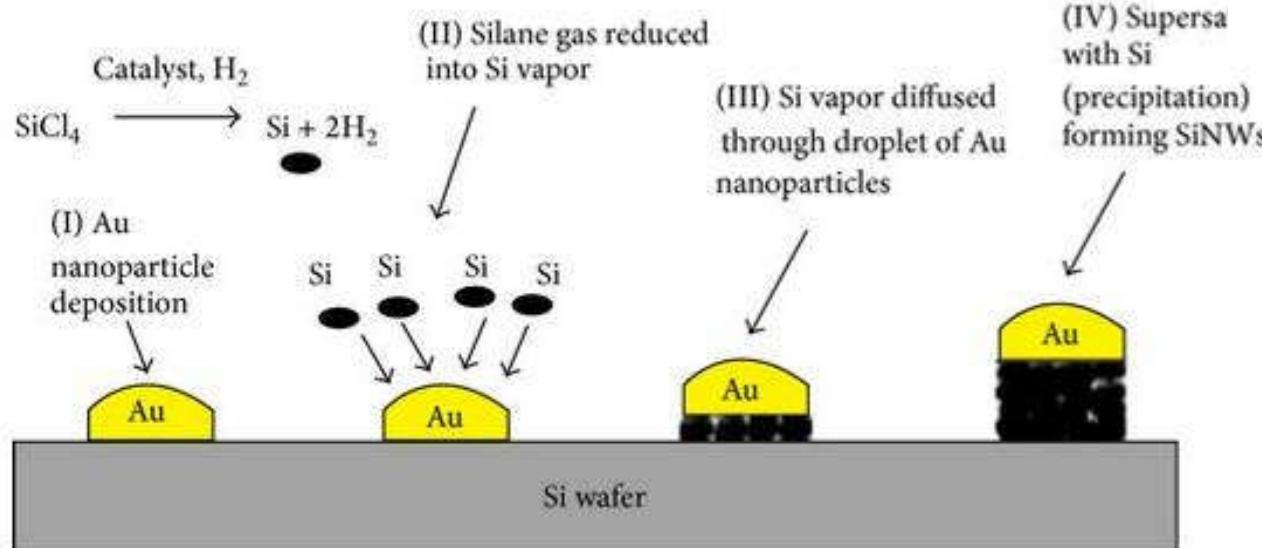


Q. Sun, et al., J. Semicon. 37, 044006 (2016)

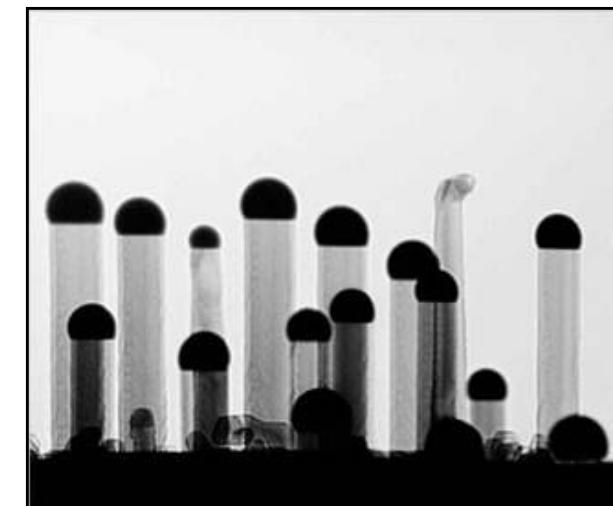
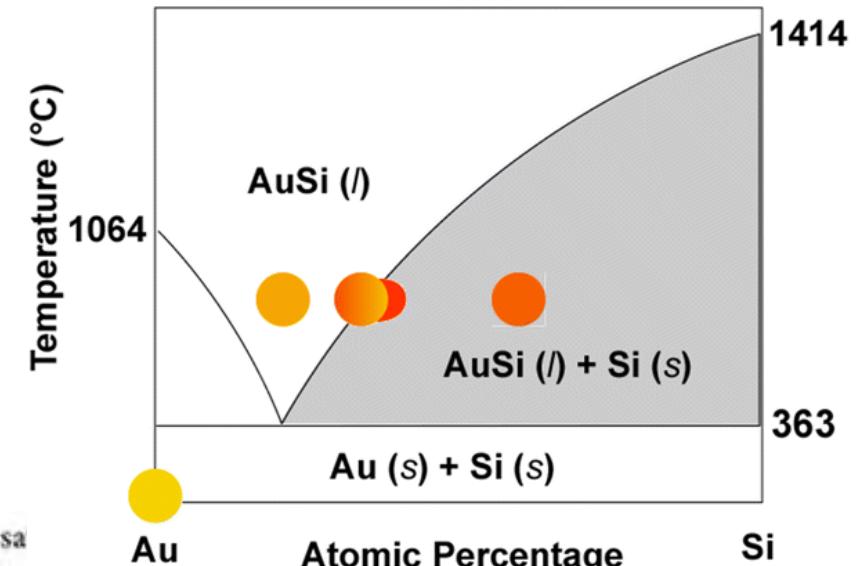
2015年中国技术发明一等奖

# Si Nanowire Growth

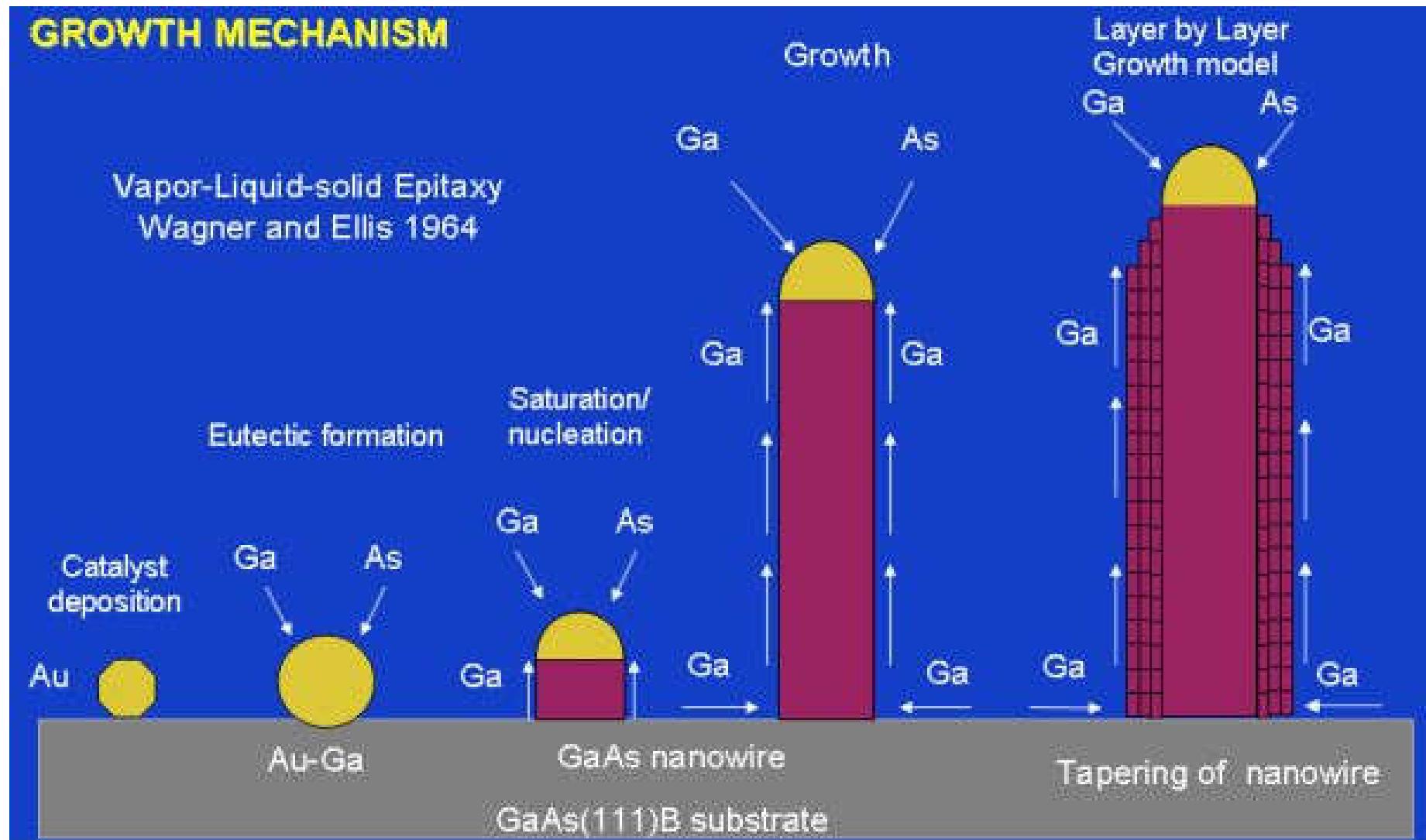
**VLS: Vapor-Liquid-Solid**



**Au-Si eutectic alloy**

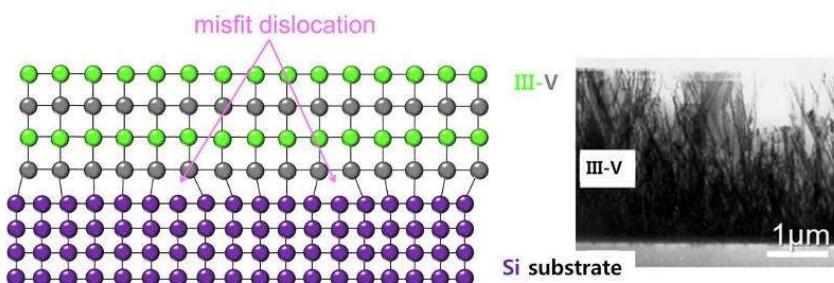
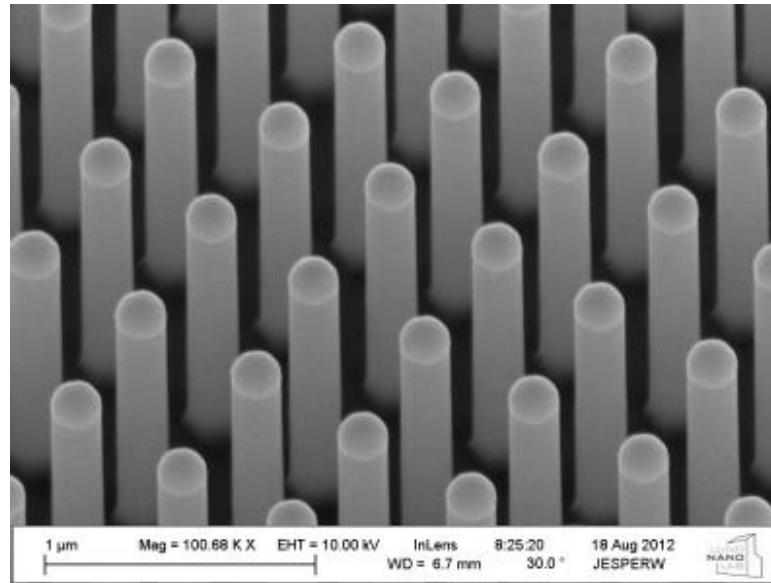


# III-V Nanowire Growth



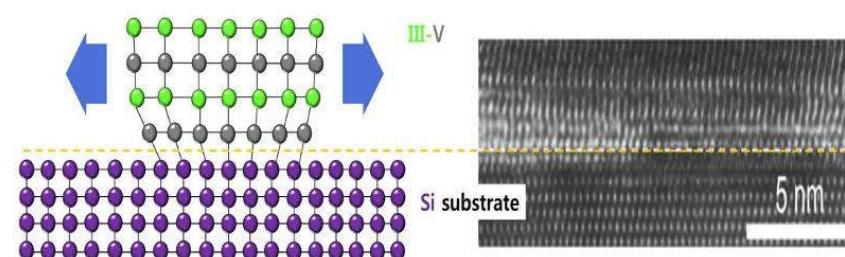
*metal catalysts reduce growth temperature*

# III-V Nanowire Growth



- **Direct growth of III-V film on Si:**

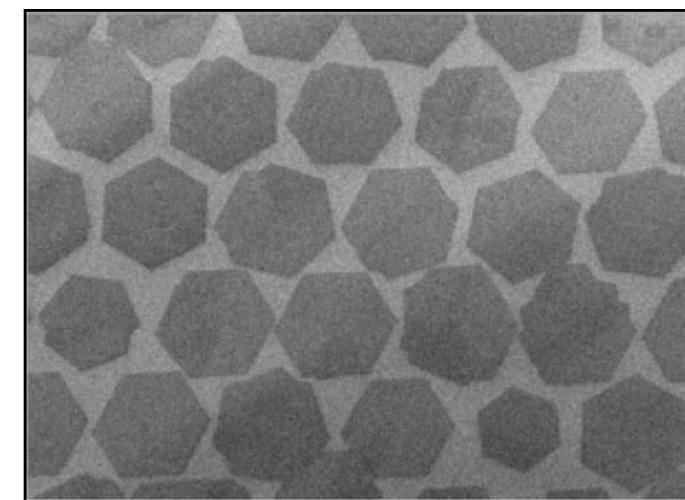
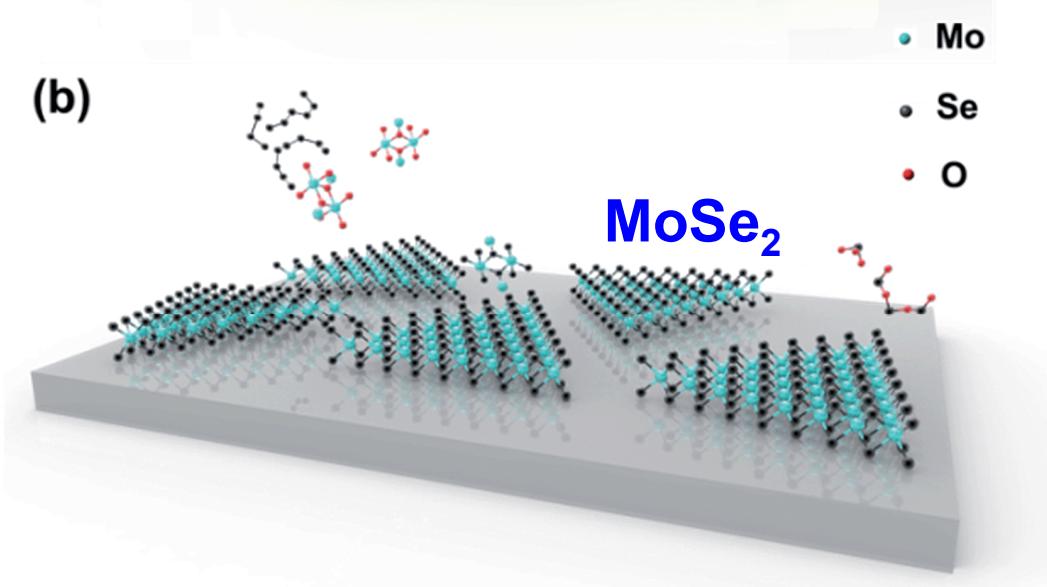
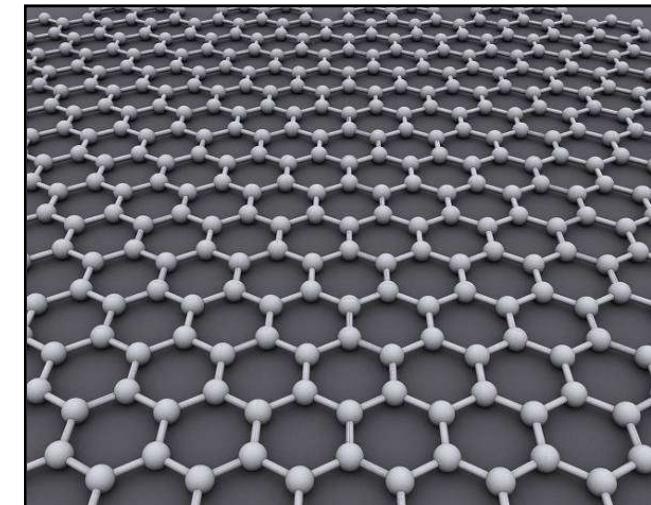
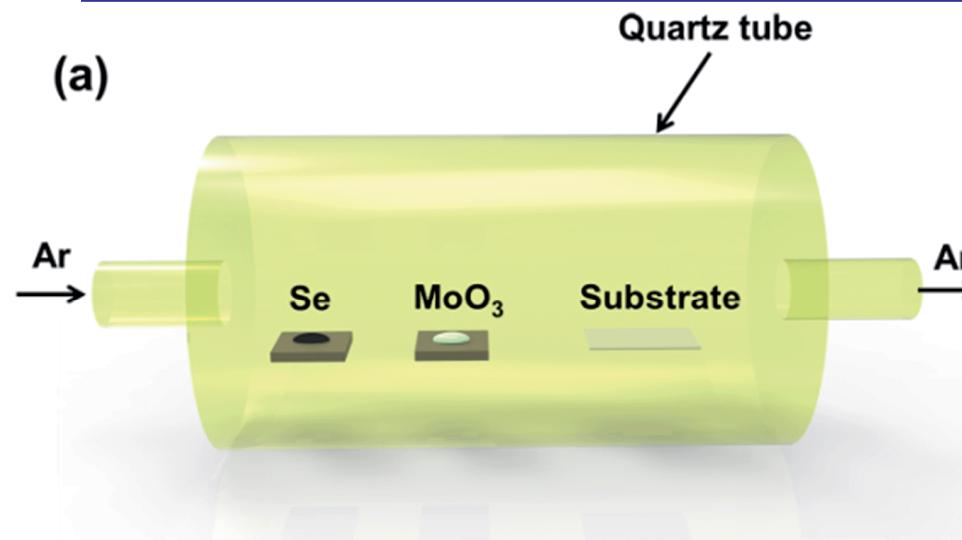
Creation of massive threading dislocation due to the large lattice mismatch strain between III-V and Si



- **Direct growth of III-V film on Si:**

Defect-free III-V can be grown on Si because lattice mismatch strain can relieved via the nanowire sidewall

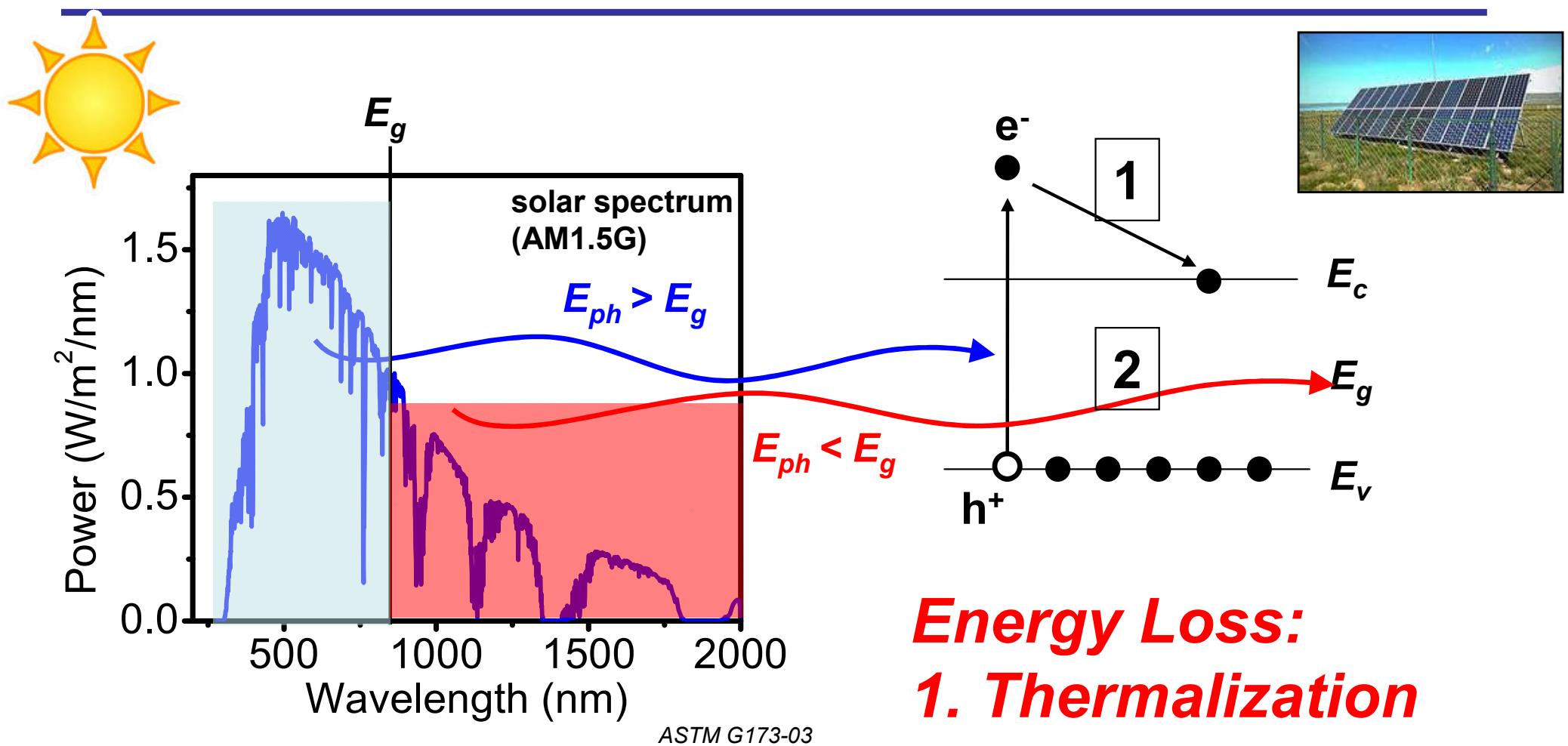
# 2D Materials Growth



grain boundaries exist

*lattice match is not restrict for monolayers*

# Solar Cells

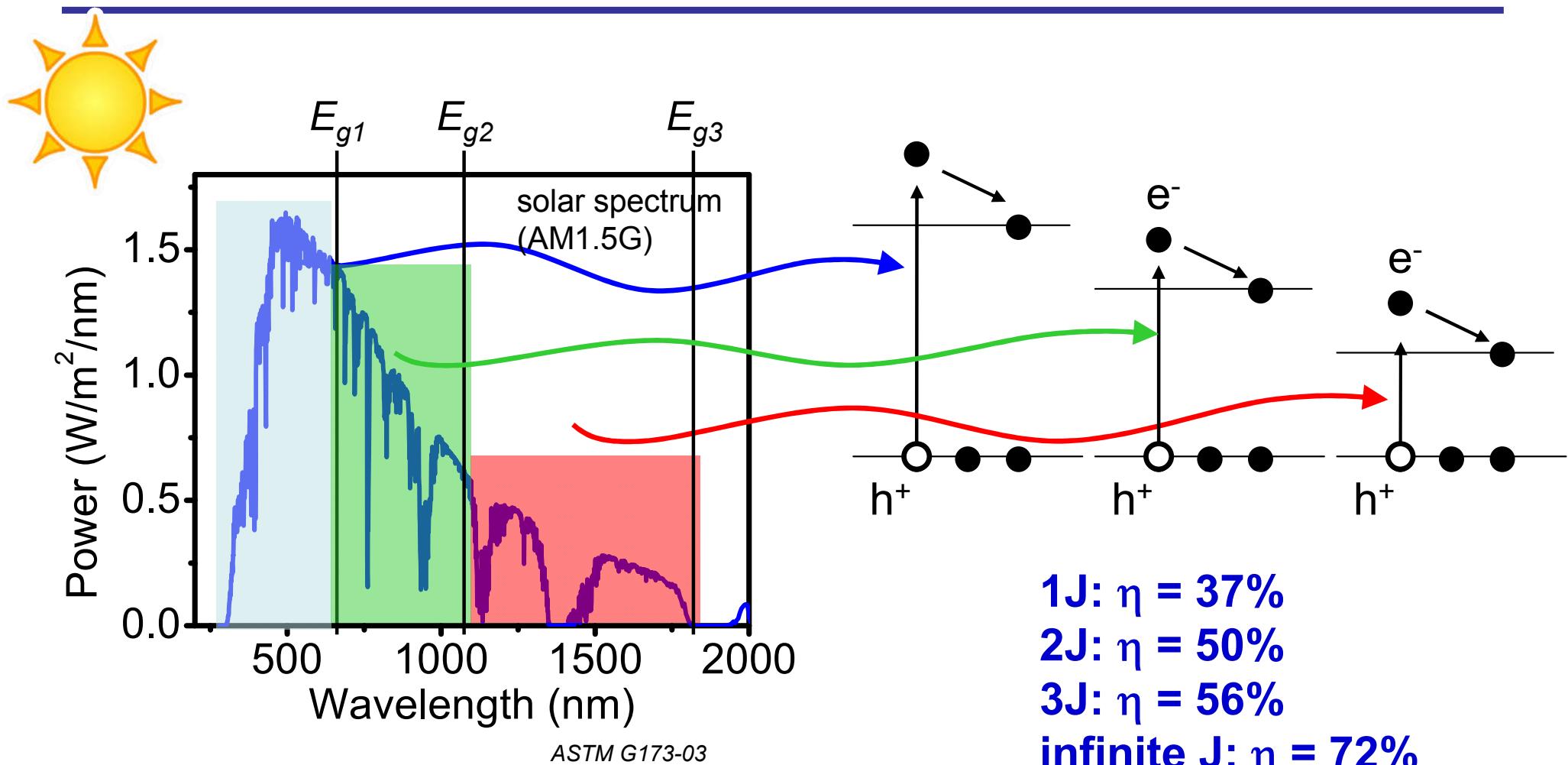


*A single junction cell  
cannot get >37% efficiency*

**Energy Loss:**  
**1. Thermalization**  
**2. Sub-bandgap pass**

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

# Multijunction Solar Cells

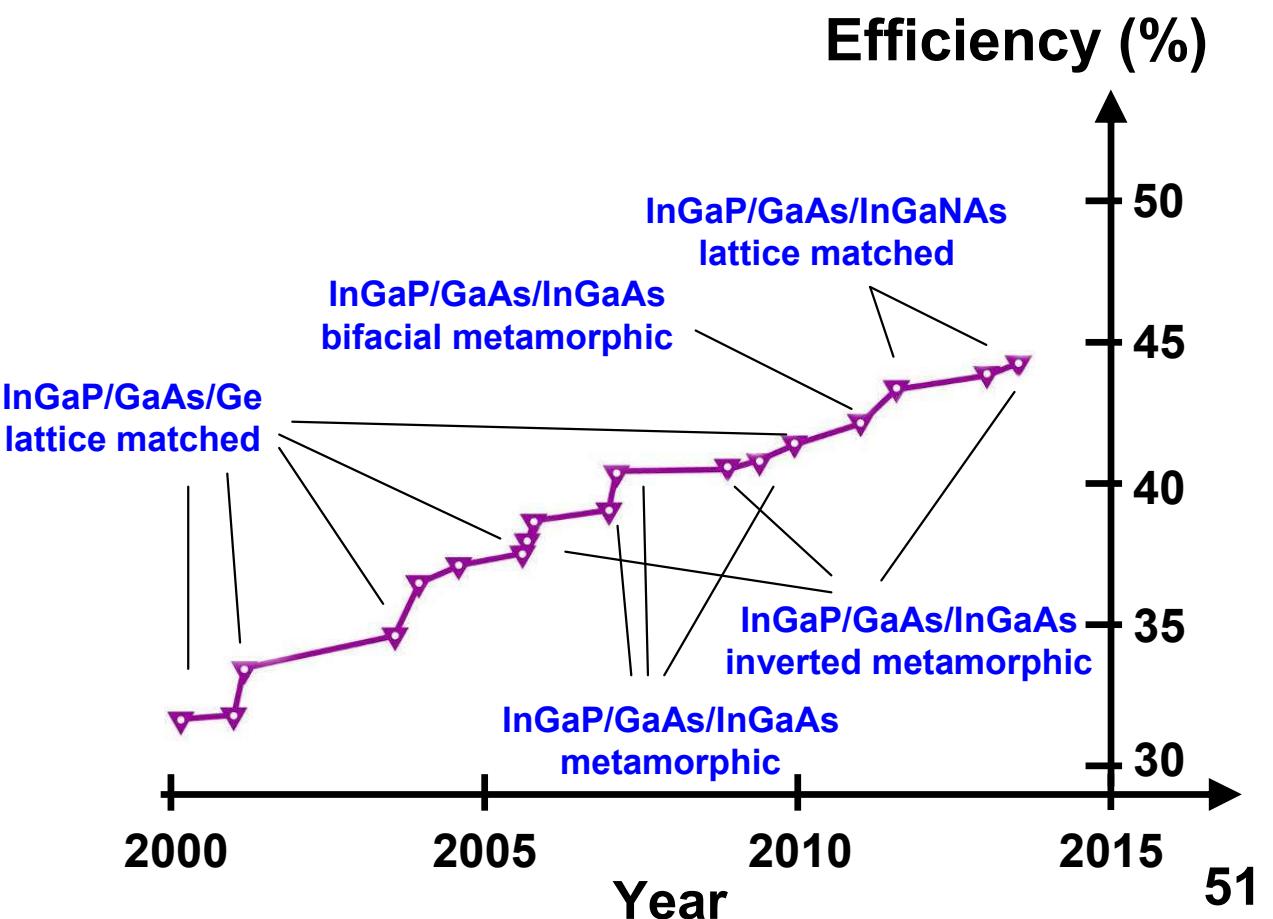
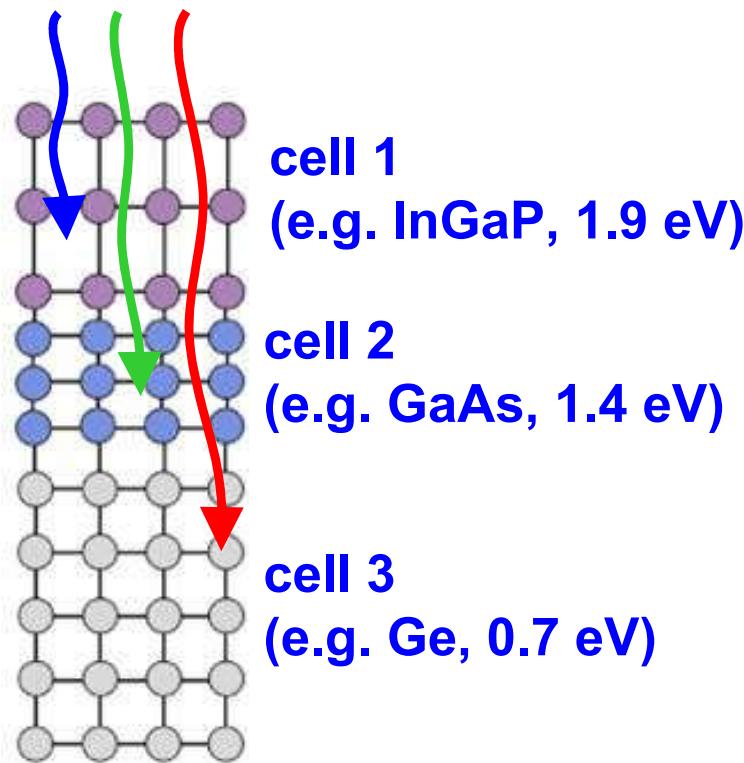


***Use the entire solar spectrum***

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

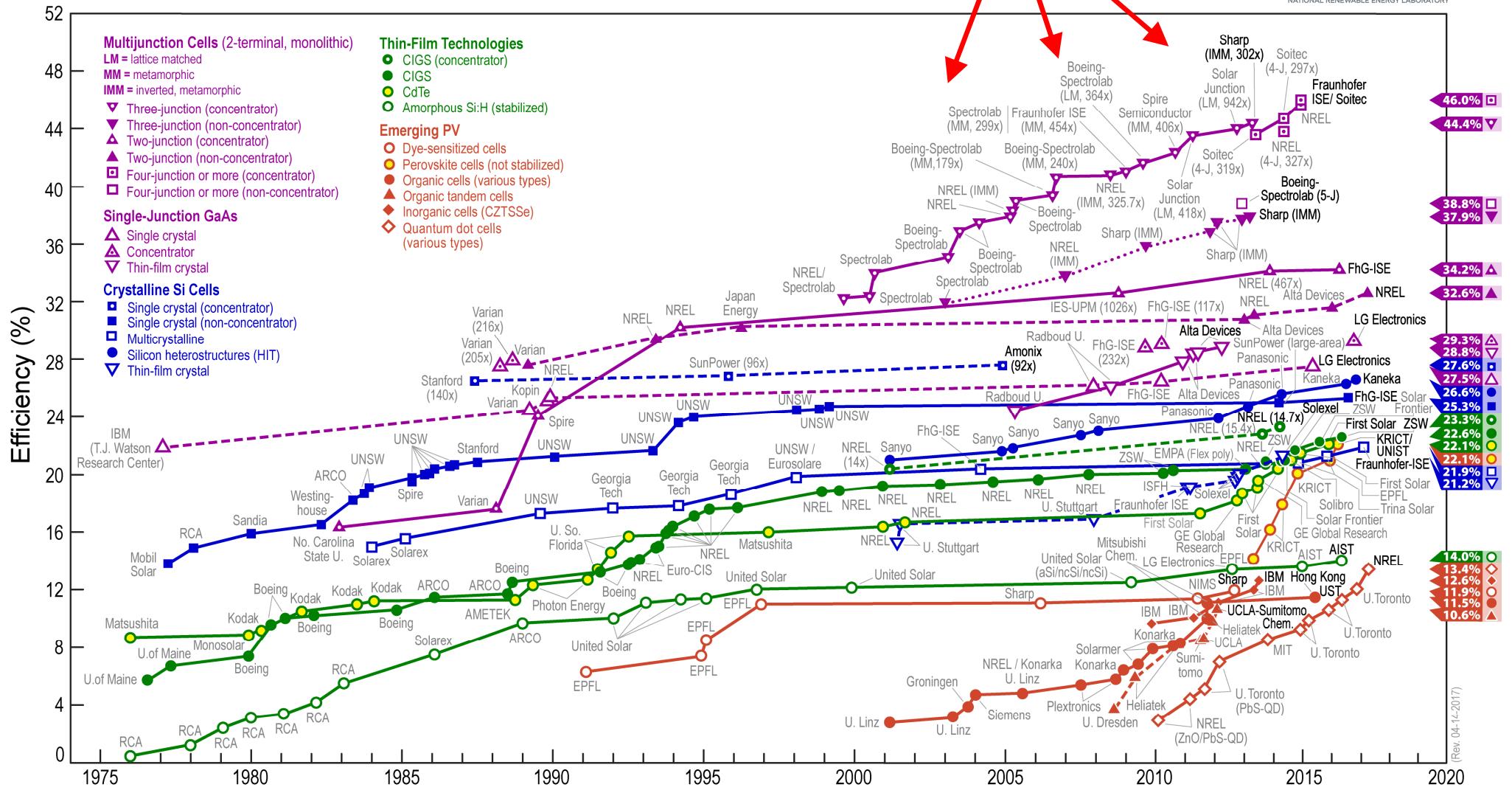


# Multijunction Solar Cells

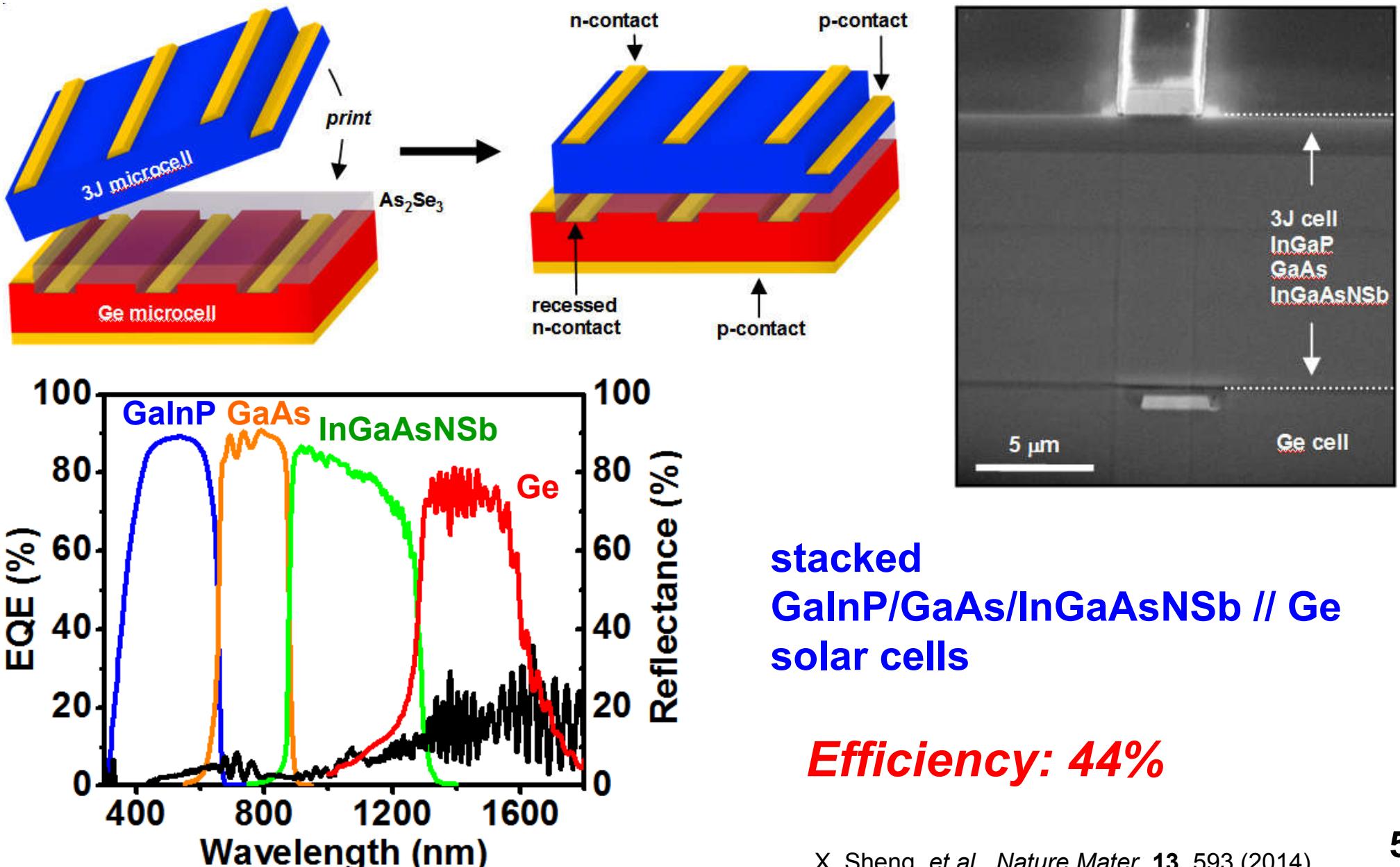
*most efficient solar cells*



## Best Research-Cell Efficiencies

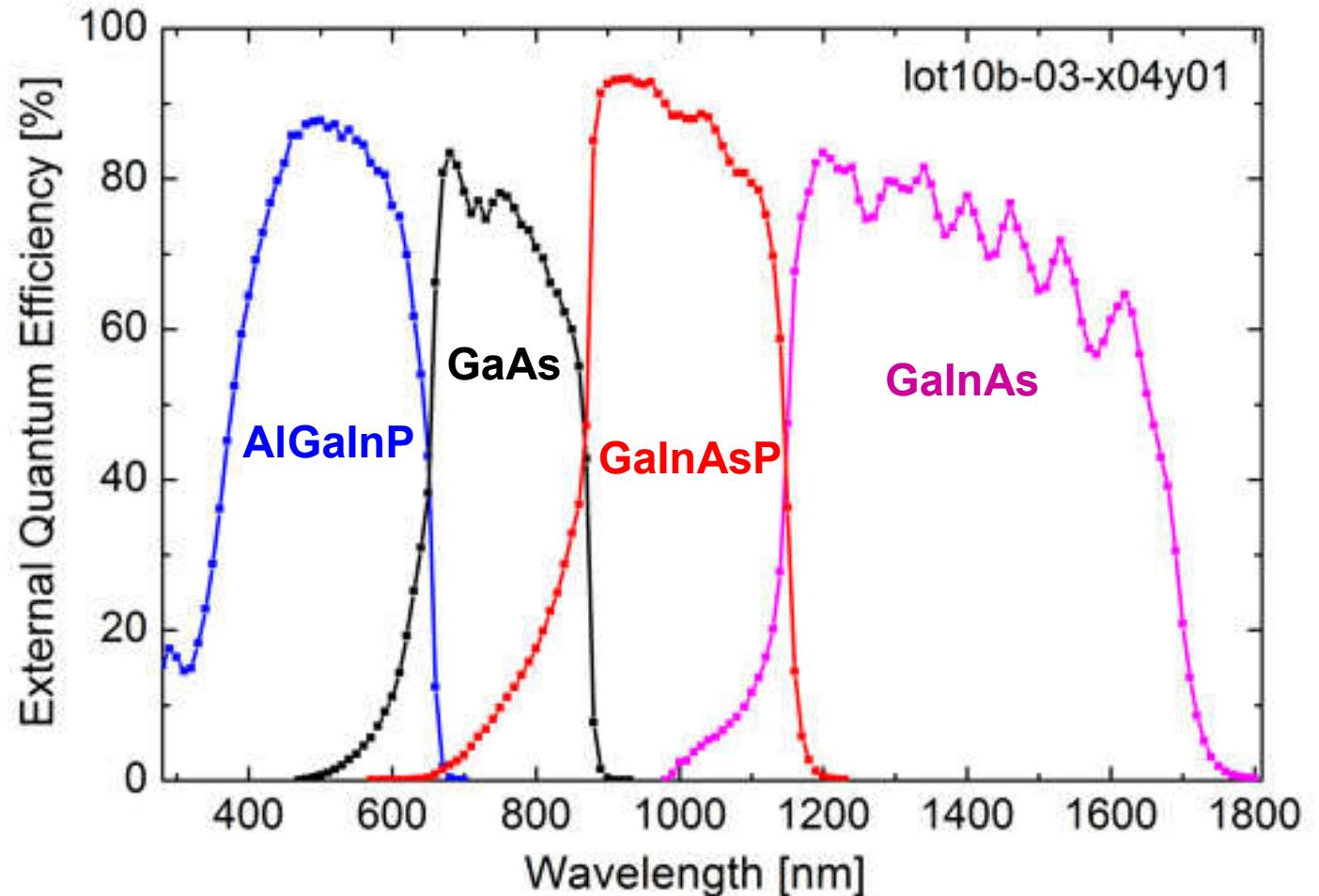
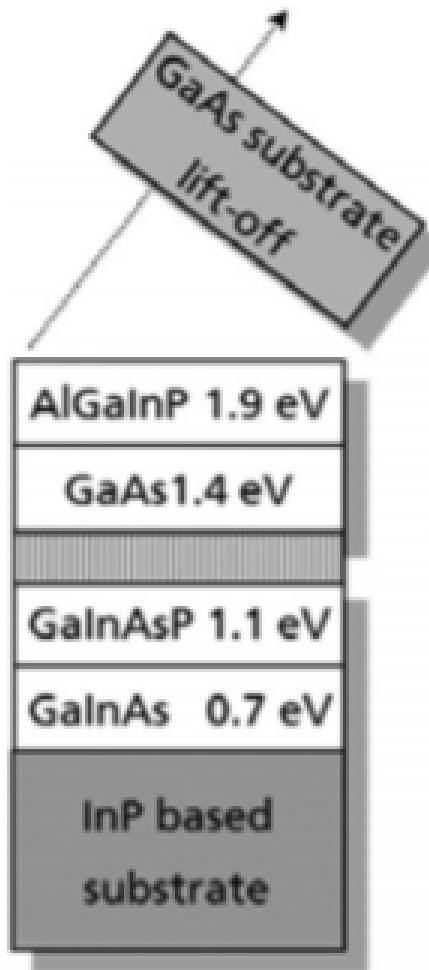


# Stacked MJ Solar Cells



# Stacked MJ Solar Cells

bonded AlGaNp/GaAs // GaInAsP/GaInAs solar cells



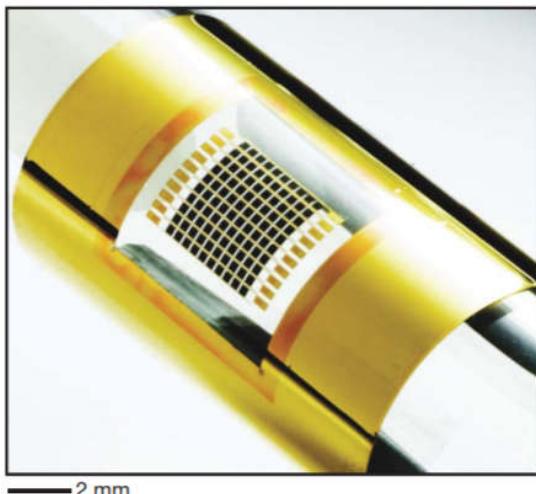
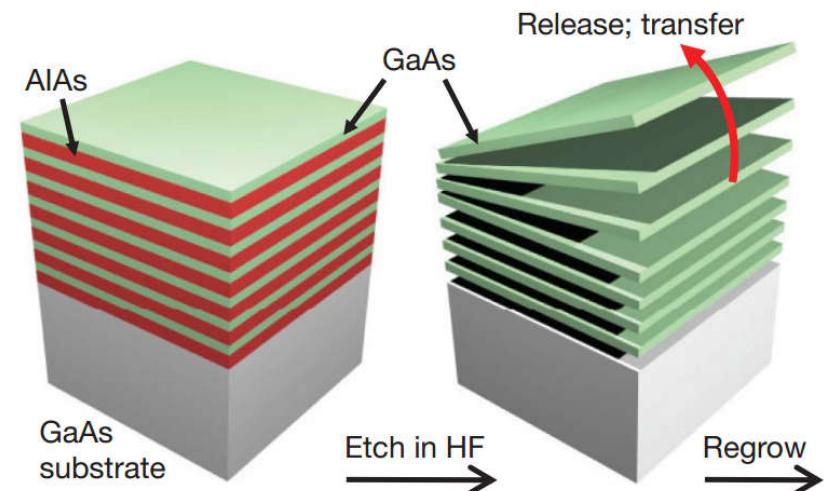
**World record efficiency: 46%**

# Epitaxy Lift-off

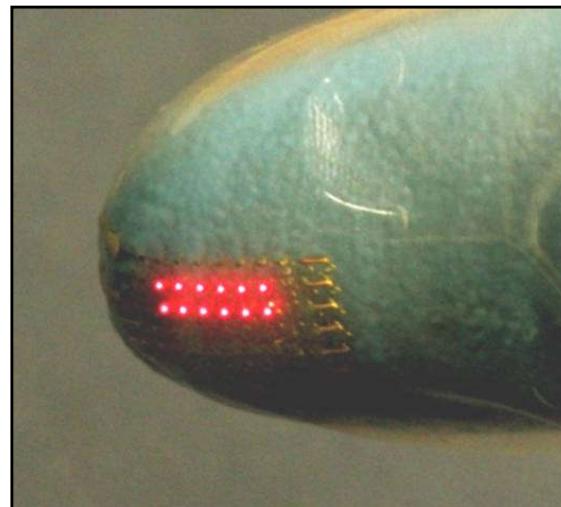
- **GaAs and AlAs**

- lattice matched growth
- AlAs is selectively etched by HF

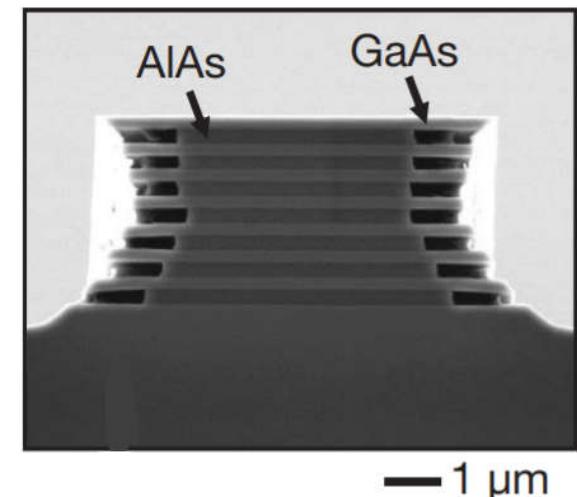
- **flexible III-V devices**



**solar cells**



**LED**



S. I. Park, et al., *Science* **325**, 977 (2009)  
J. Yoon, et al., *Nature* **465**, 329 (2010)

# '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 Heidelberger<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>

