# 微纳光电子材料与器件工艺原理

# Film Deposition
# Part I: Epitaxy 外延生长

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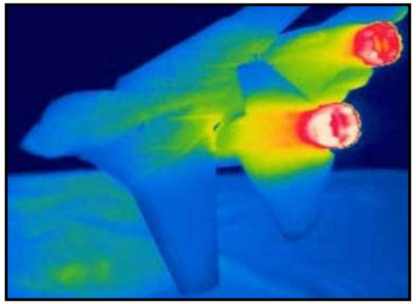
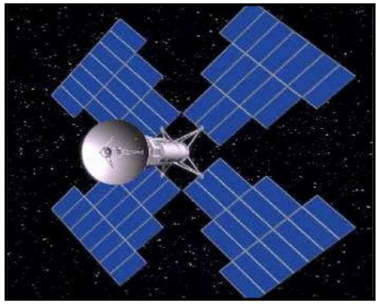
# Optoelectronic Devices

LEDs

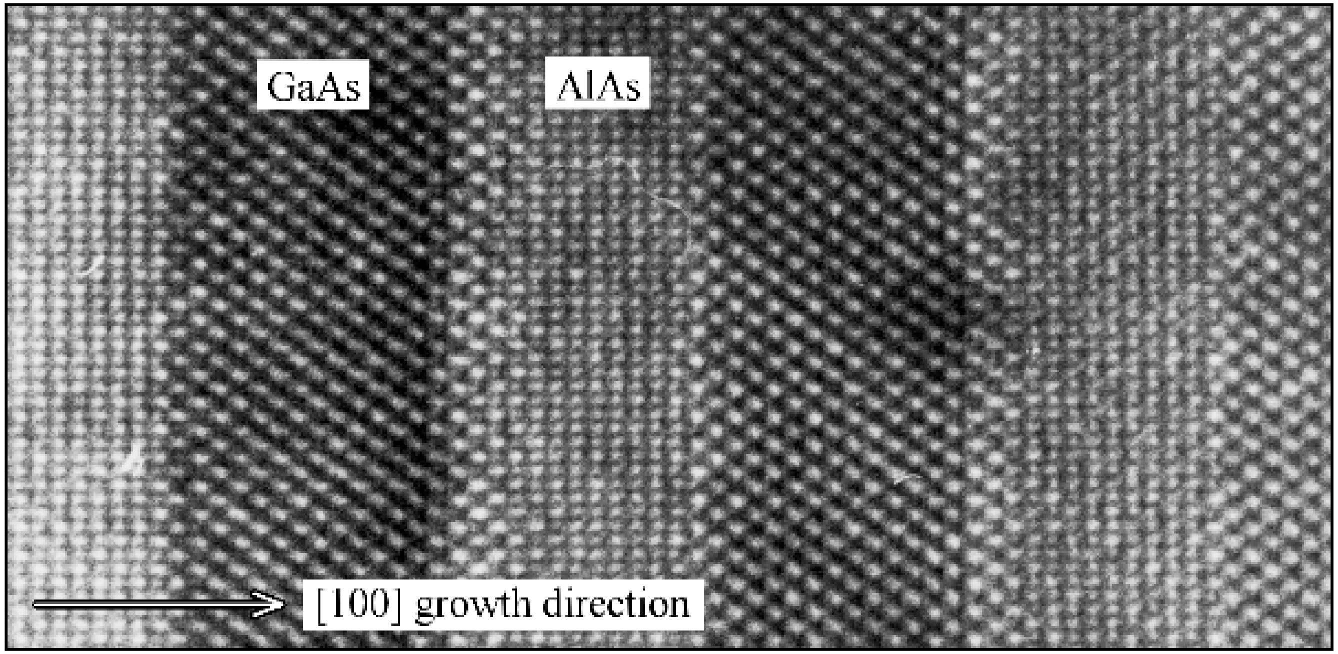
lasers



IR imaging

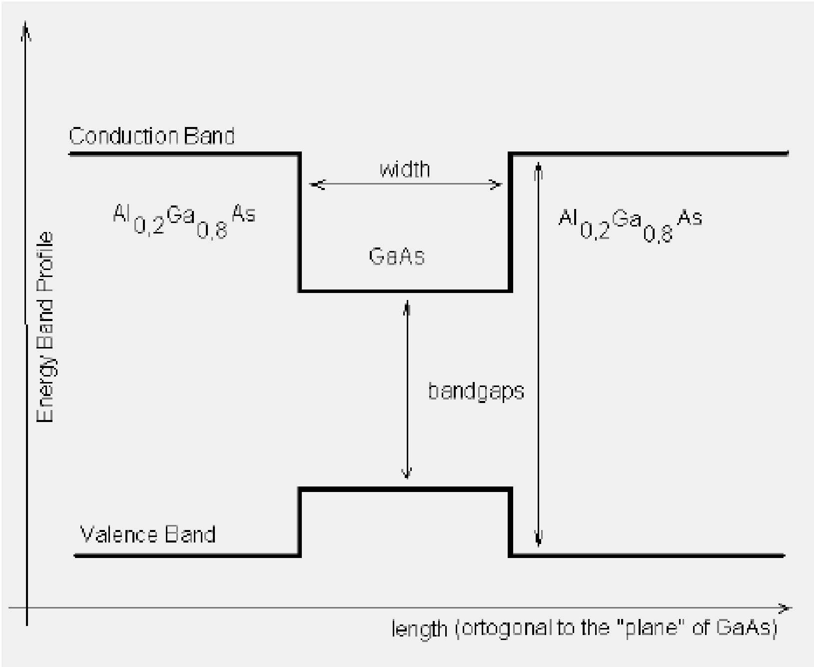


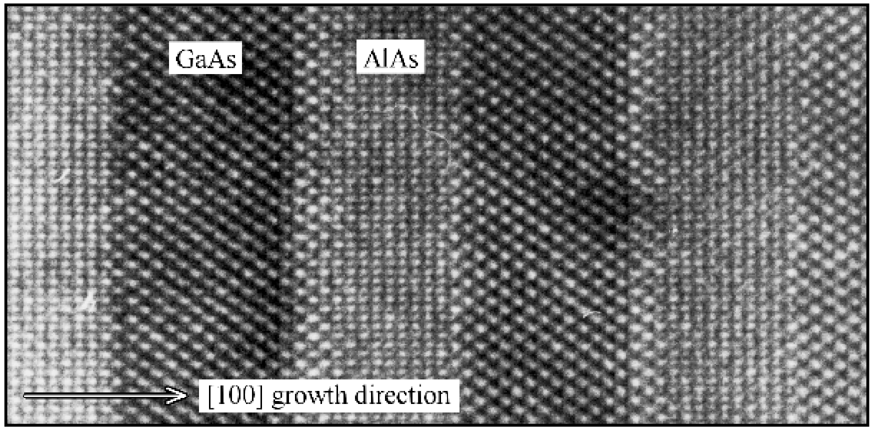
solar cells




**epitaxially grown single crystal materials**

# Semiconductor Heterostructures



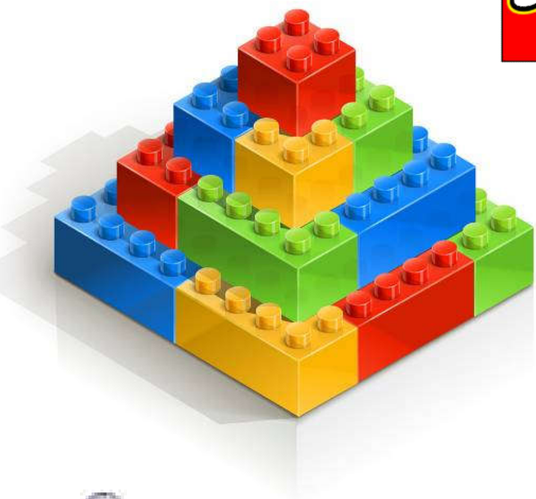

**GaAs/AlGaAs heterostructure: bandgap engineering**

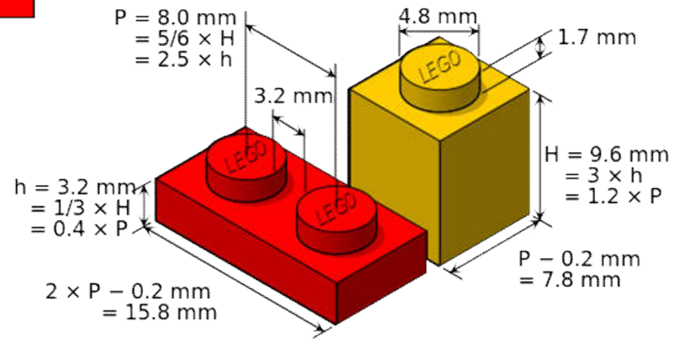
**Z. I. Alferov**

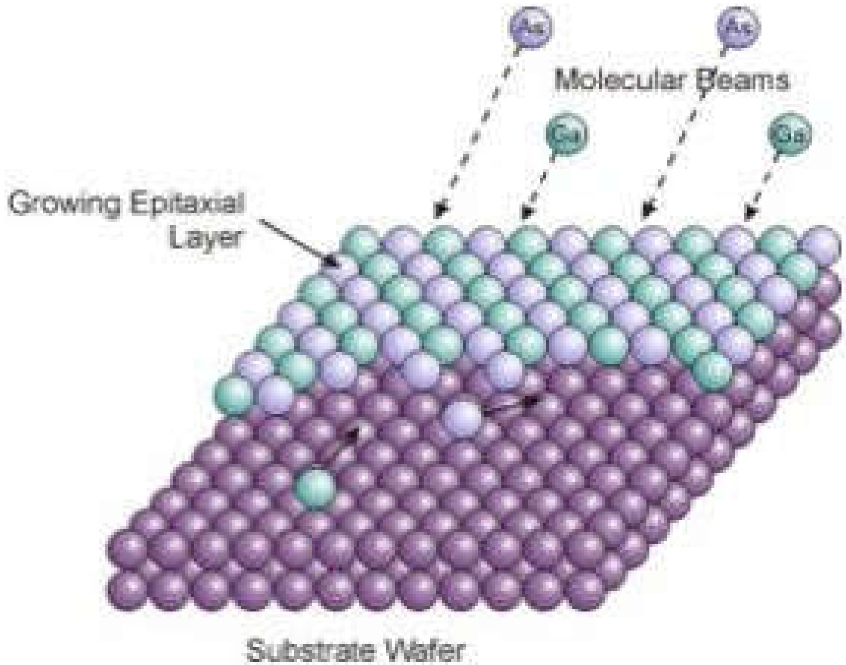
**H. Kroemer**

**2000 Nobel Prize in Physics**

# Epitaxy (外延)






***epi-***

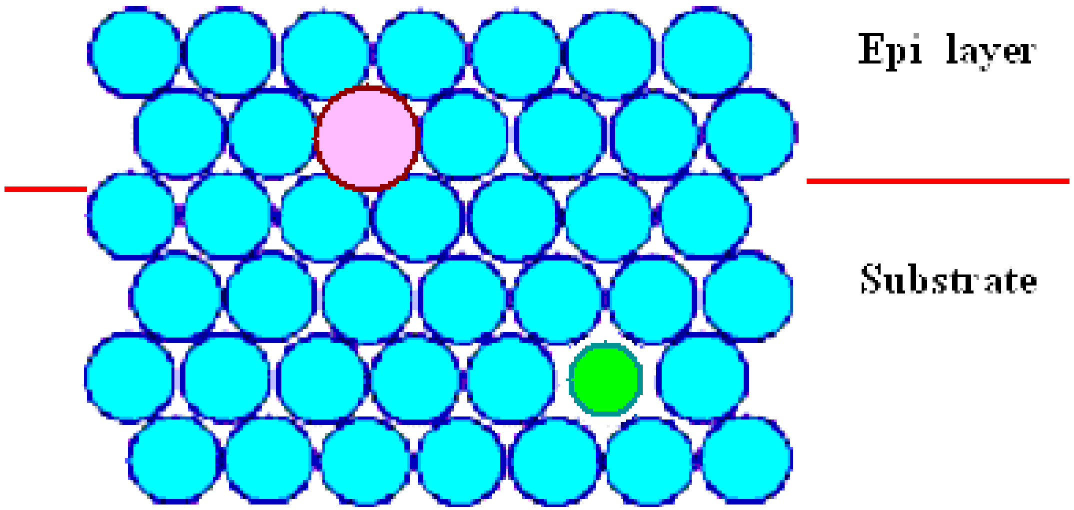
**surface, 表面**

***-taxy***

**arrange, 排列**

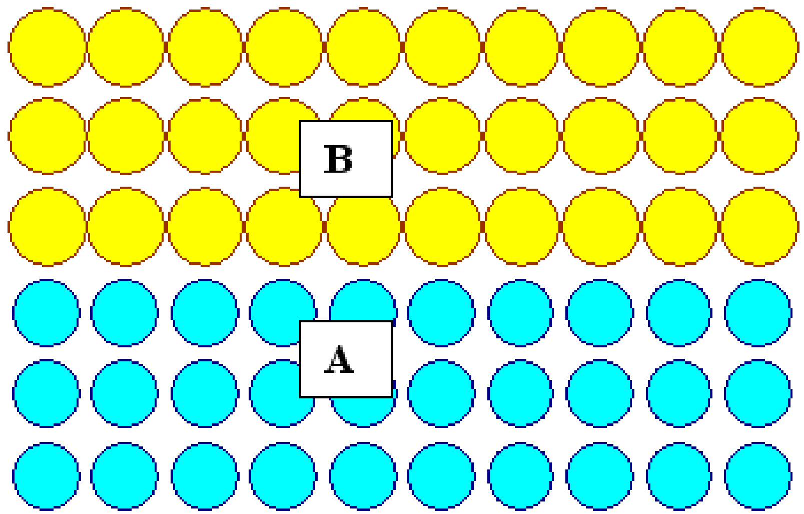
# Epitaxial Growth

## Homoepitaxy




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

## Heteroepitaxy



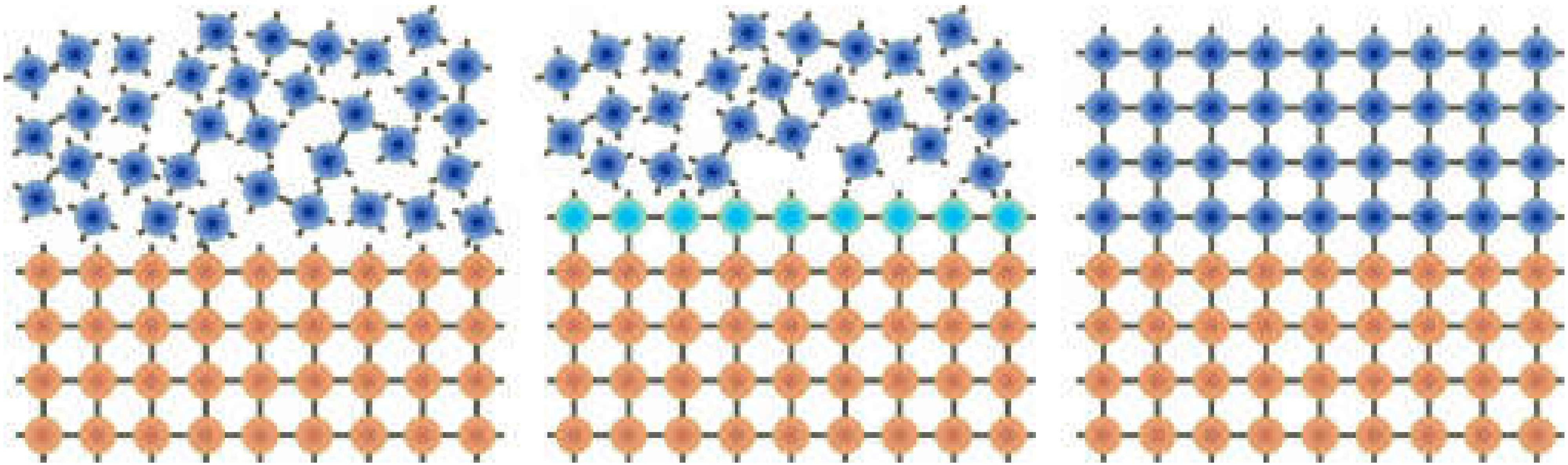

AlAs on GaAs
Ge on Si,
...

# Methods

- Solid Phase Epitaxy (SPE)
  - amorphous Si -> crystalline Si
- Liquid Phase Epitaxy (LPE)
  - $2Ga\ (l) + 2AsCl_3\ (l) = 2GaAs\ (s) + 3Cl_2\ (g)$
- Chemical Vapor Deposition (CVD)
  - $Ga(CH_3)_3\ (g) + AsH_3\ (g) = GaAs\ (s) + 3CH_4\ (g)$
- Molecular Beam Epitaxy (MBE)
  - $2Ga\ (g) + As_2\ (g) = 2GaAs\ (s)$

# Methods

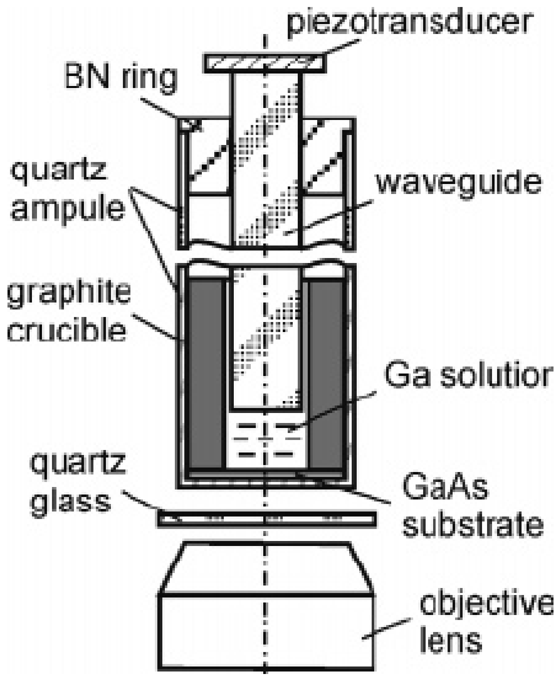
- Solid Phase Epitaxy (SPE)
  - amorphous Si -> crystalline Si

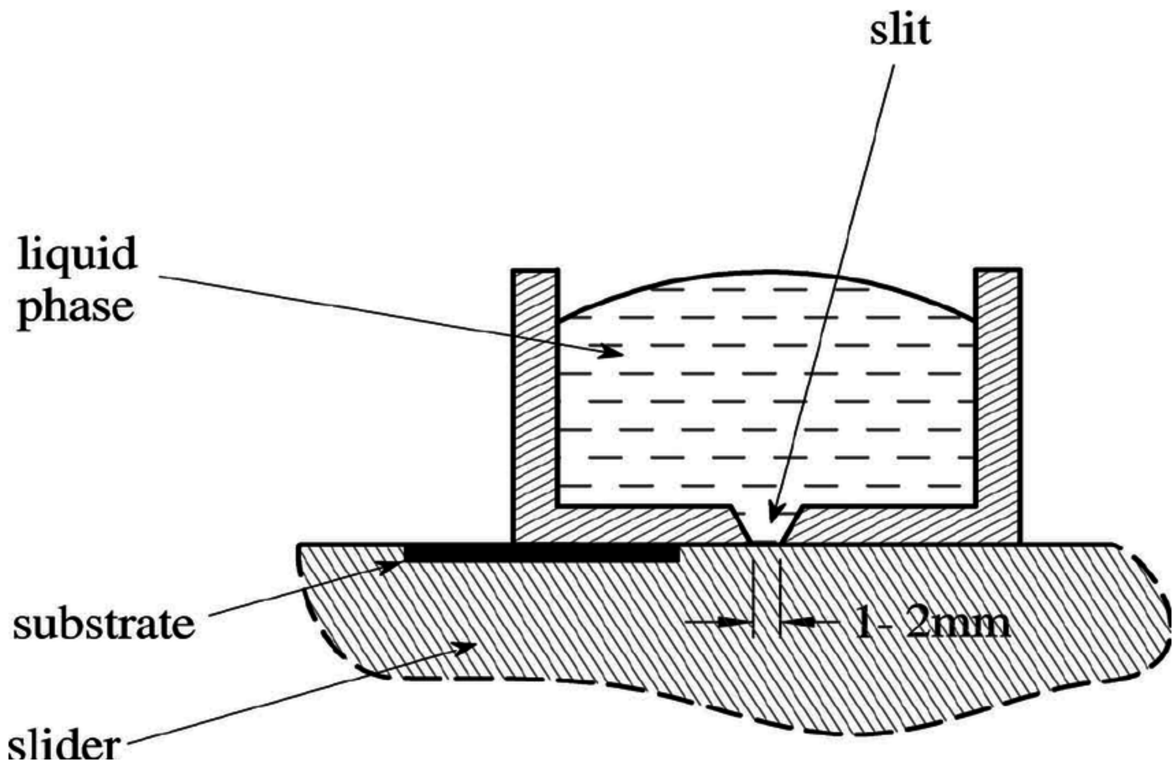


annealing at high temperature

# Methods

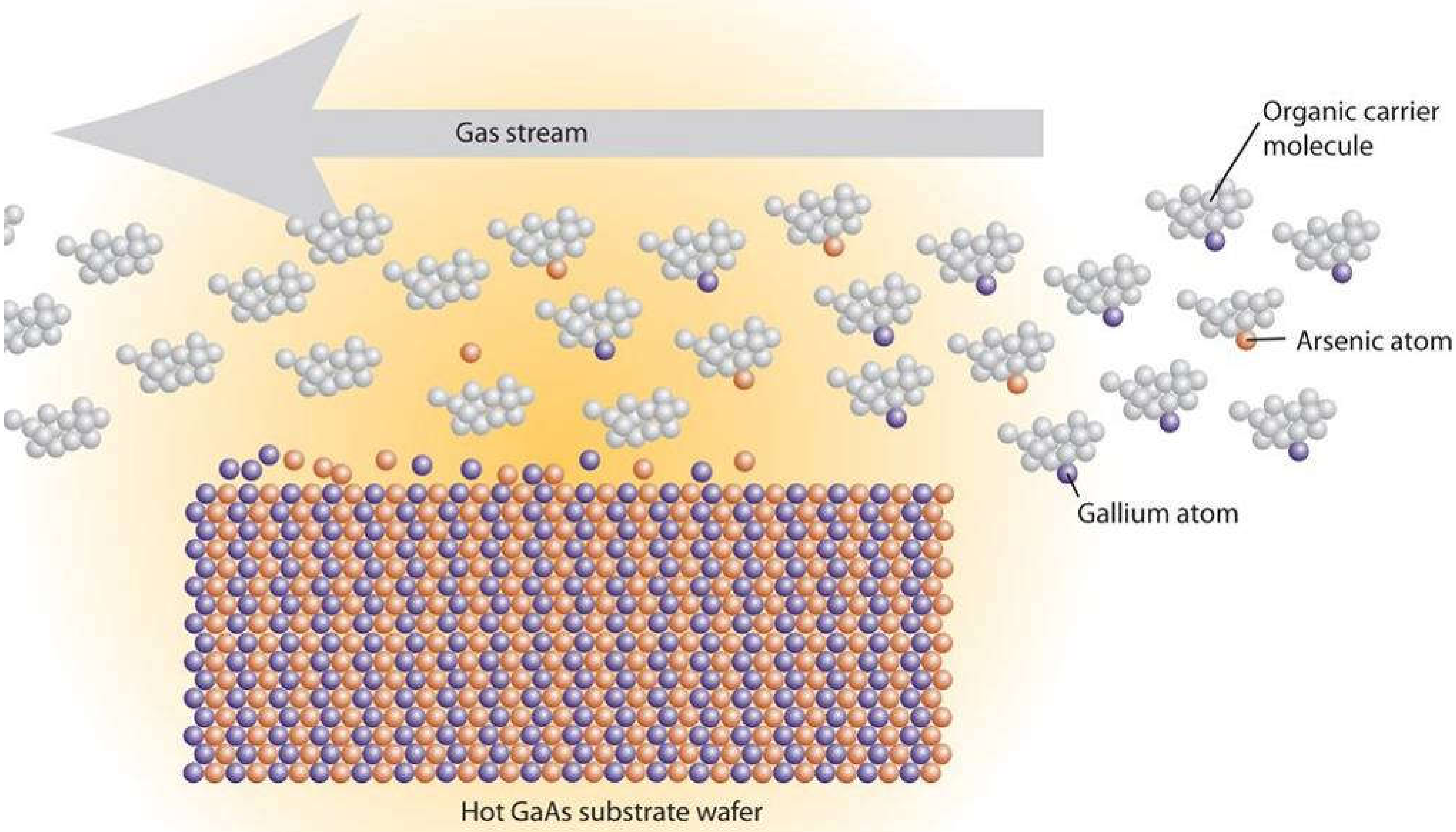
- **Liquid Phase Epitaxy (LPE)**
  - $2Ga\ (l) + 2AsCl_3\ (l) = 2GaAs\ (s) + 3Cl_2\ (g)$



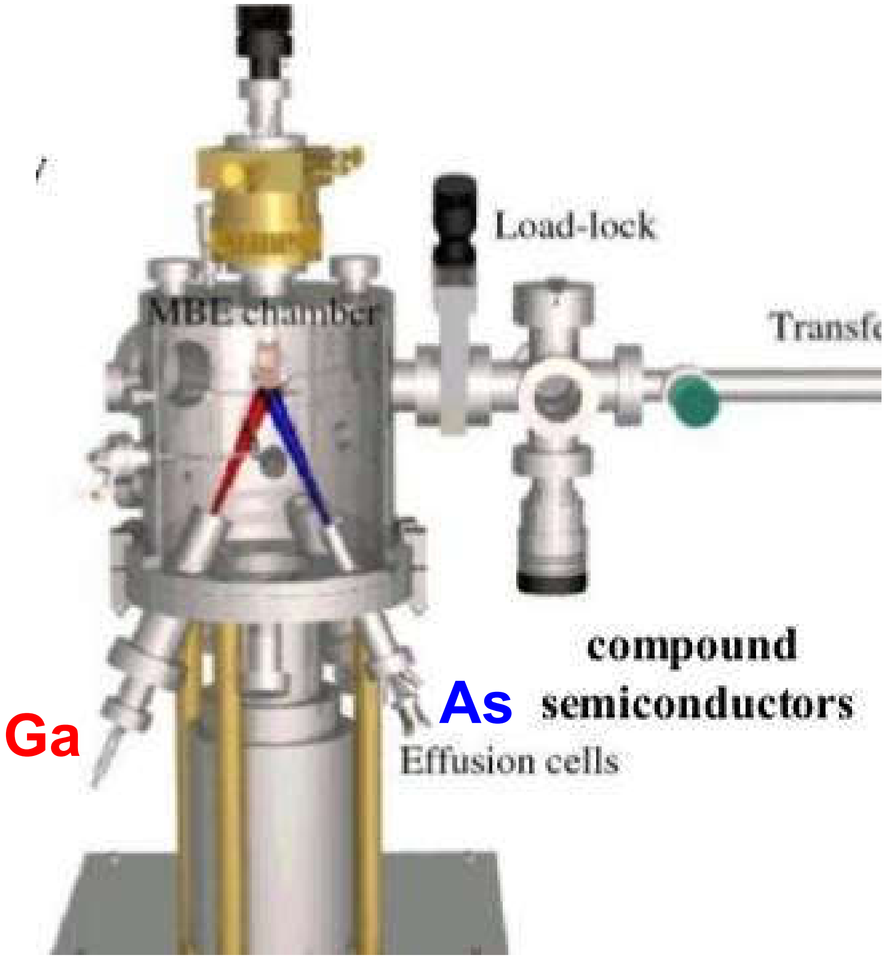
# Methods

- **Chemical Vapor Deposition (CVD)**
  - $Ga(CH_3)_3$ (g) + $AsH_3$ (g) = $GaAs$ (s) + $3CH_4$ (g)

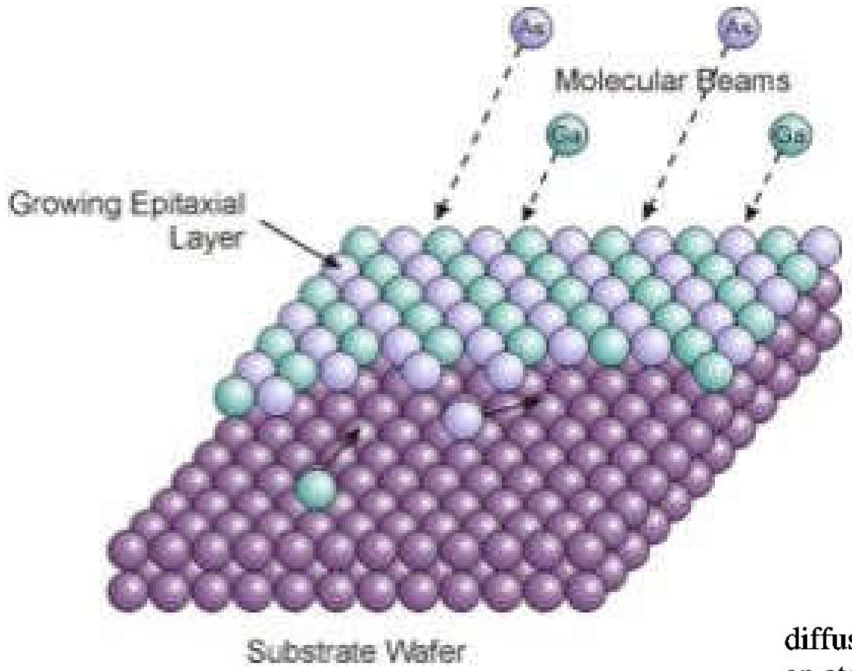


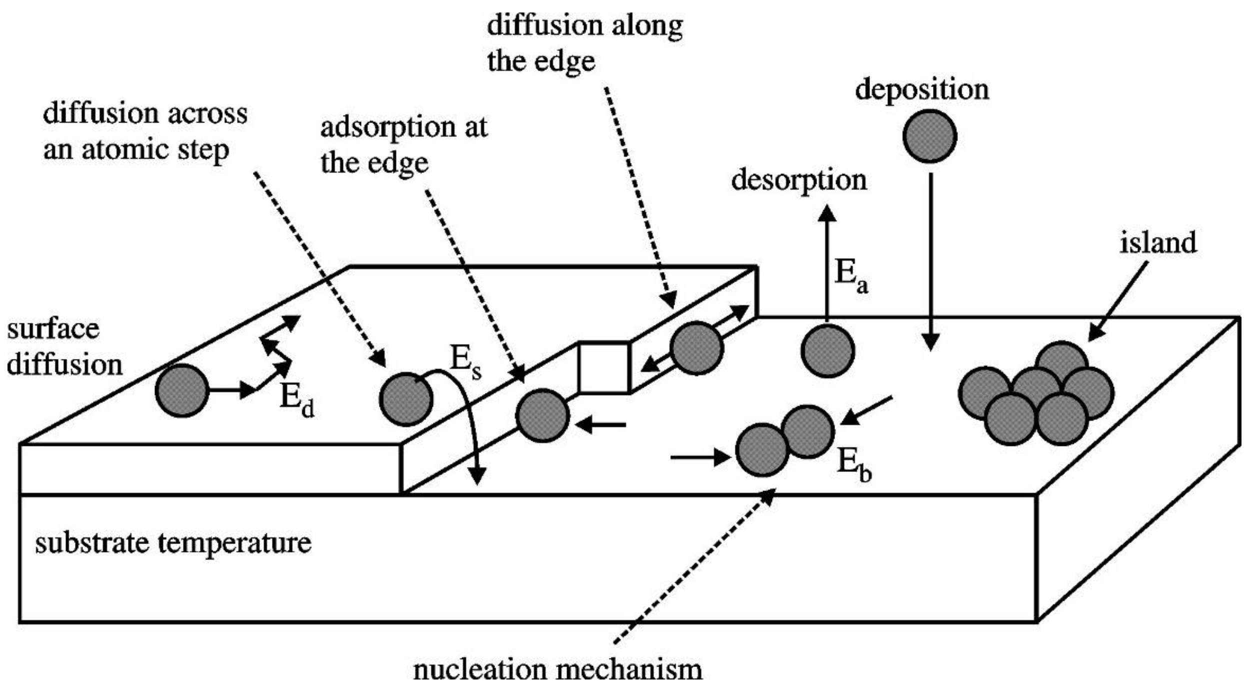
# Methods

- **Molecular Beam Epitaxy (MBE)**
  - **$2Ga\ (g) + As_2\ (g) = 2GaAs\ (s)$**

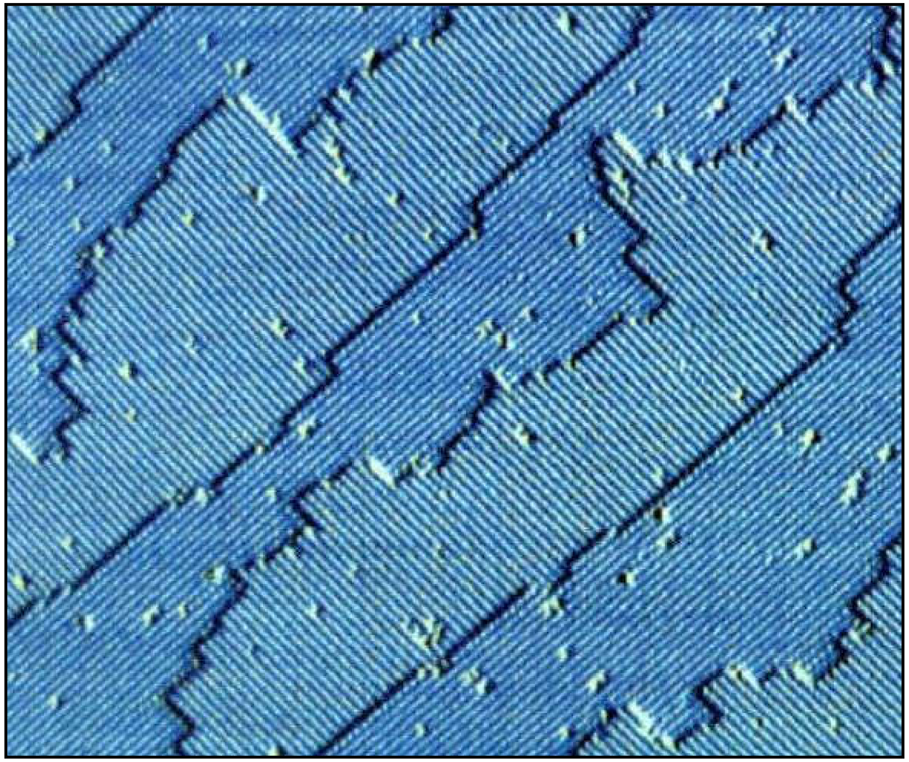


# Deposition at Surfaces



# Deposition at Surfaces

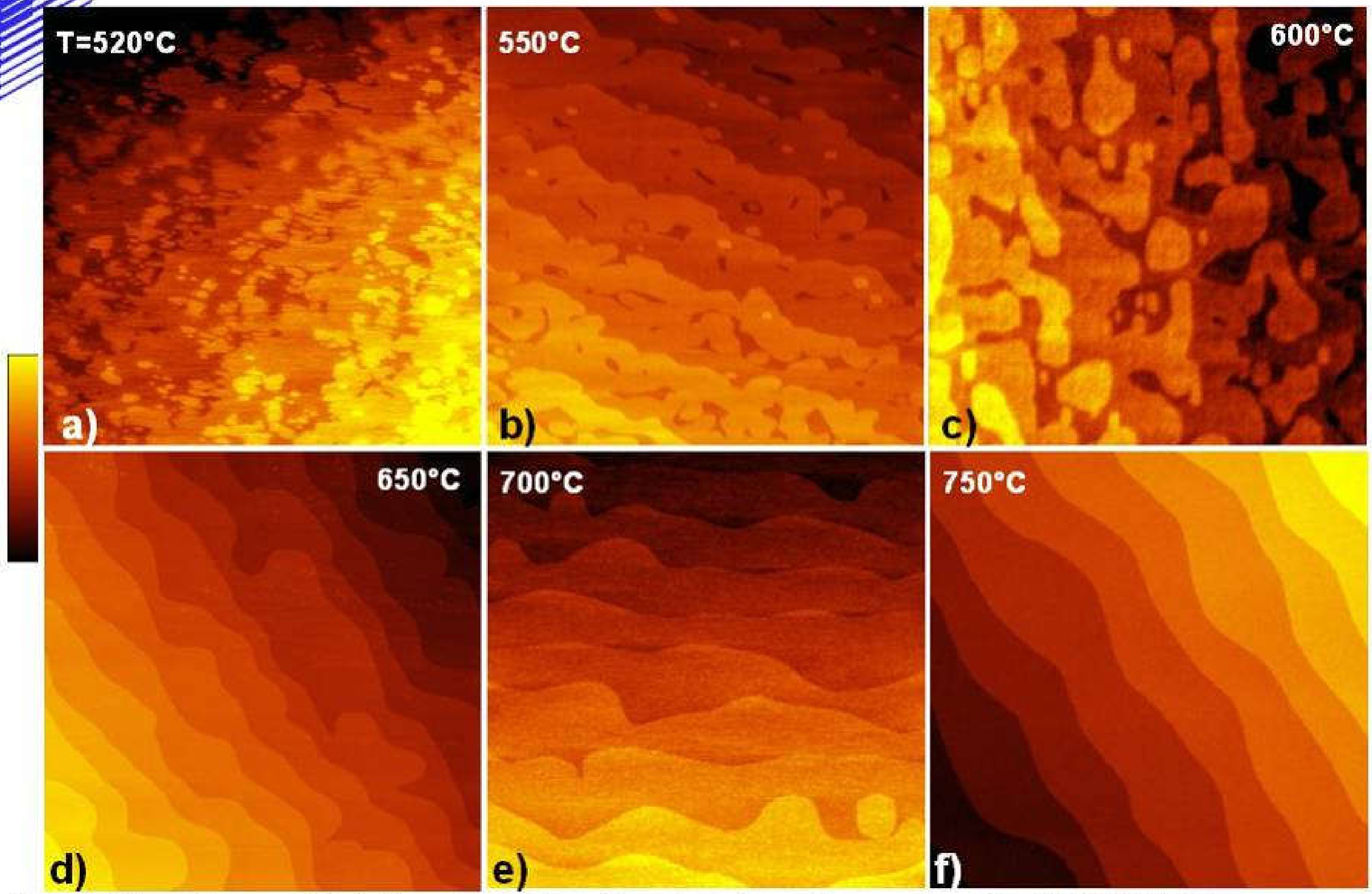


Si (100) surface

terrace (梯田)

# Deposition at Surfaces

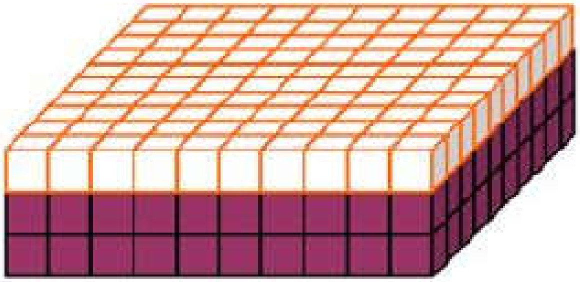
**GaAs growth**




Transition from 2D island nucleation to step flow growth (MOCVD).
5X5μm² post-growth AFM scans, heigth scale 2-5nm

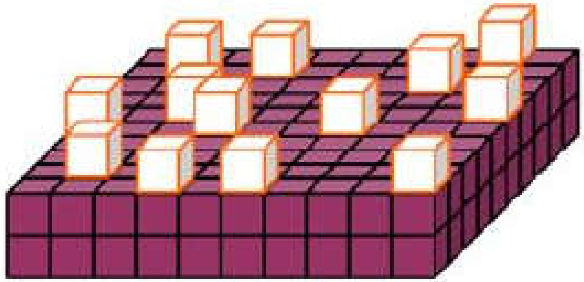
# Growth Mechanisms

## competition between surface and interface energies



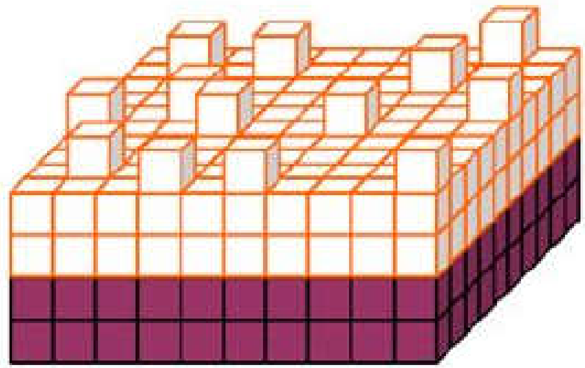
Frank-van der Merwe mode
(2 dimensional growth mode)

interface energy ↓



Volmer-Weber mode
(Island growth mode)

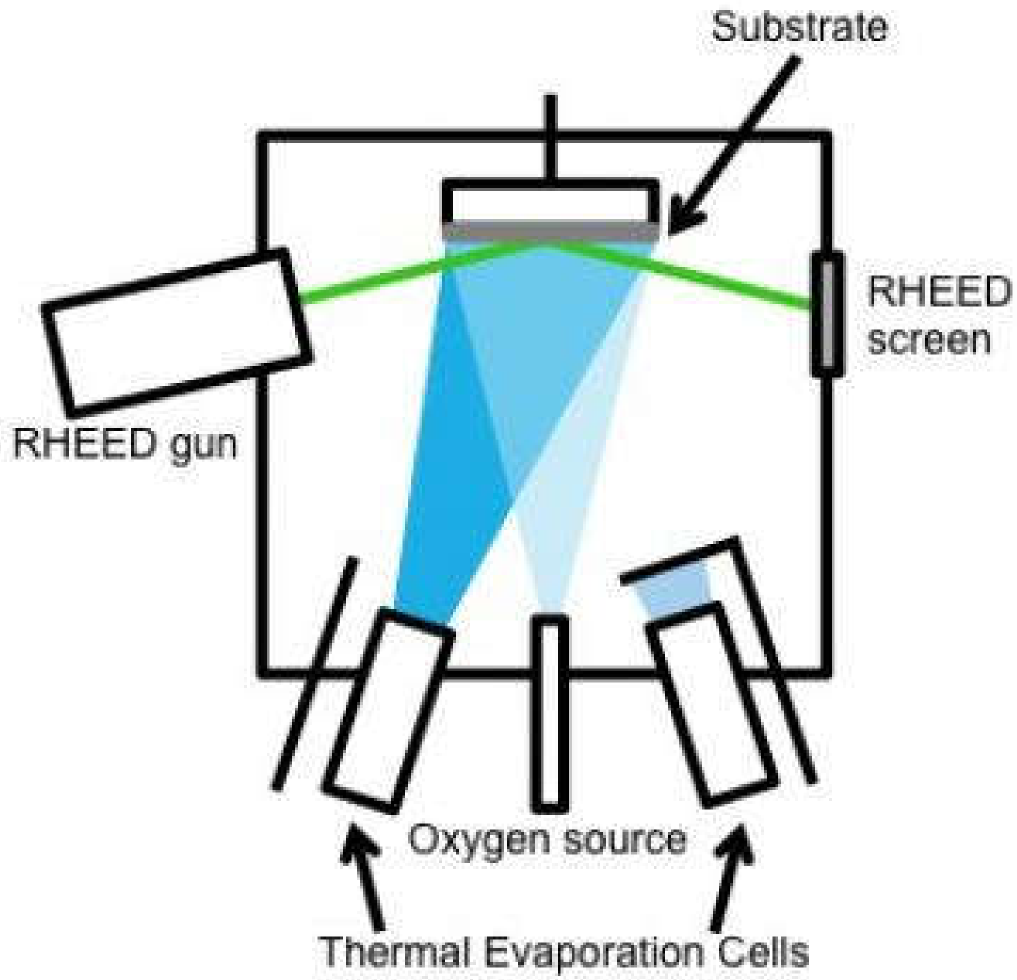
interface energy ↑



Stranski-Krastanov mode
(Layer & island growth mode)

interface energy ↓ ↑

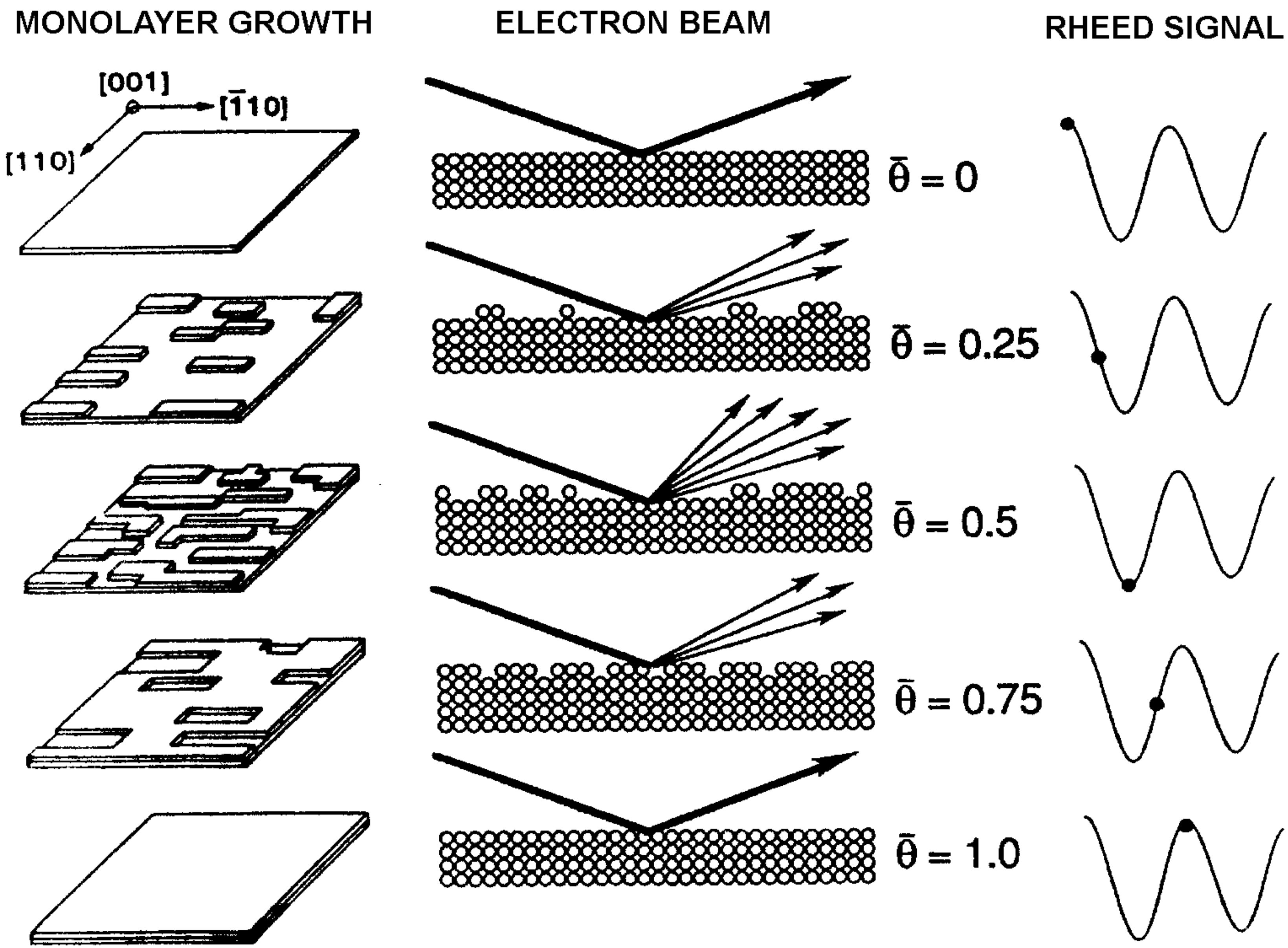
# Online Surface Monitoring



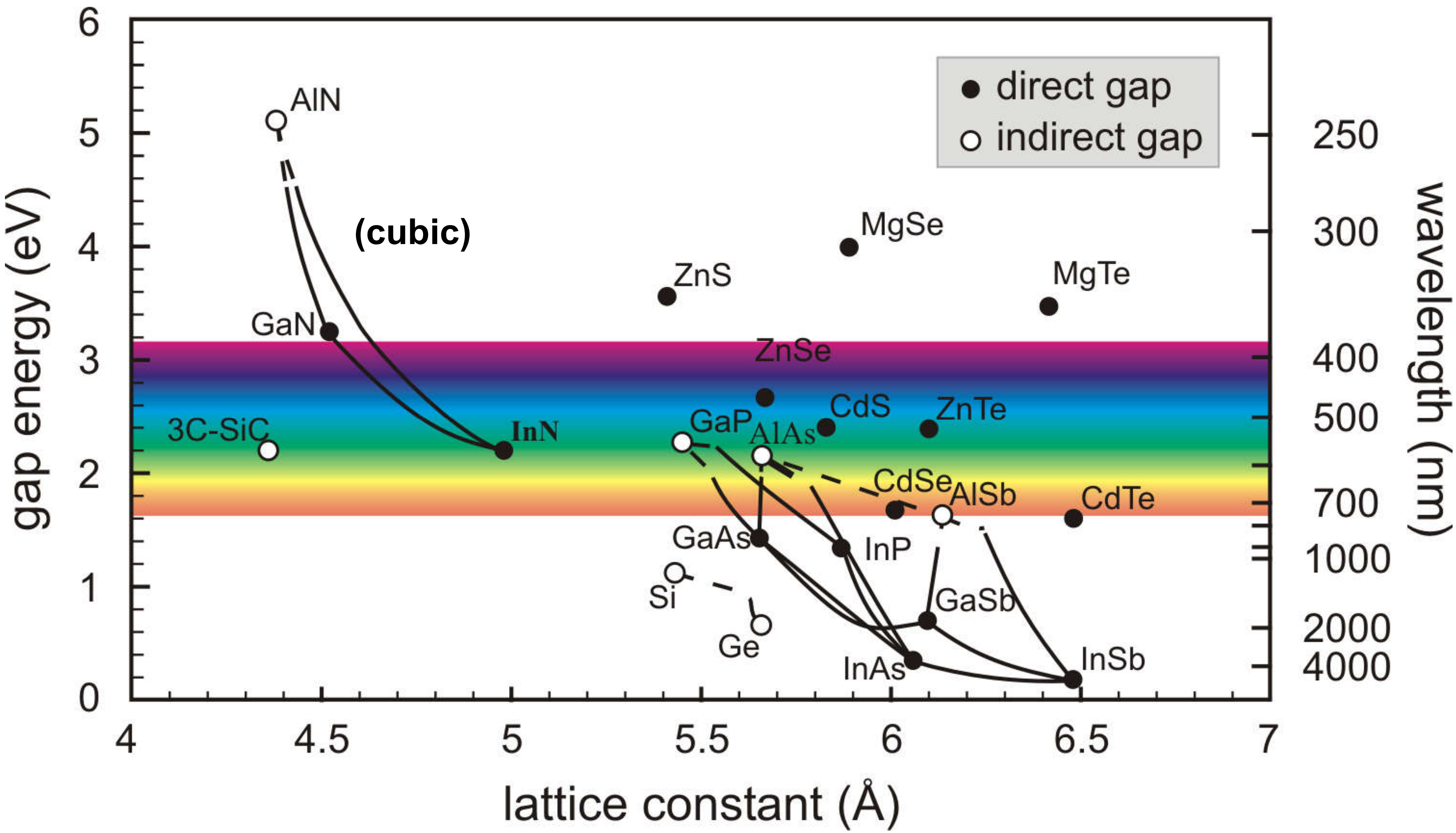

**MBE system**

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

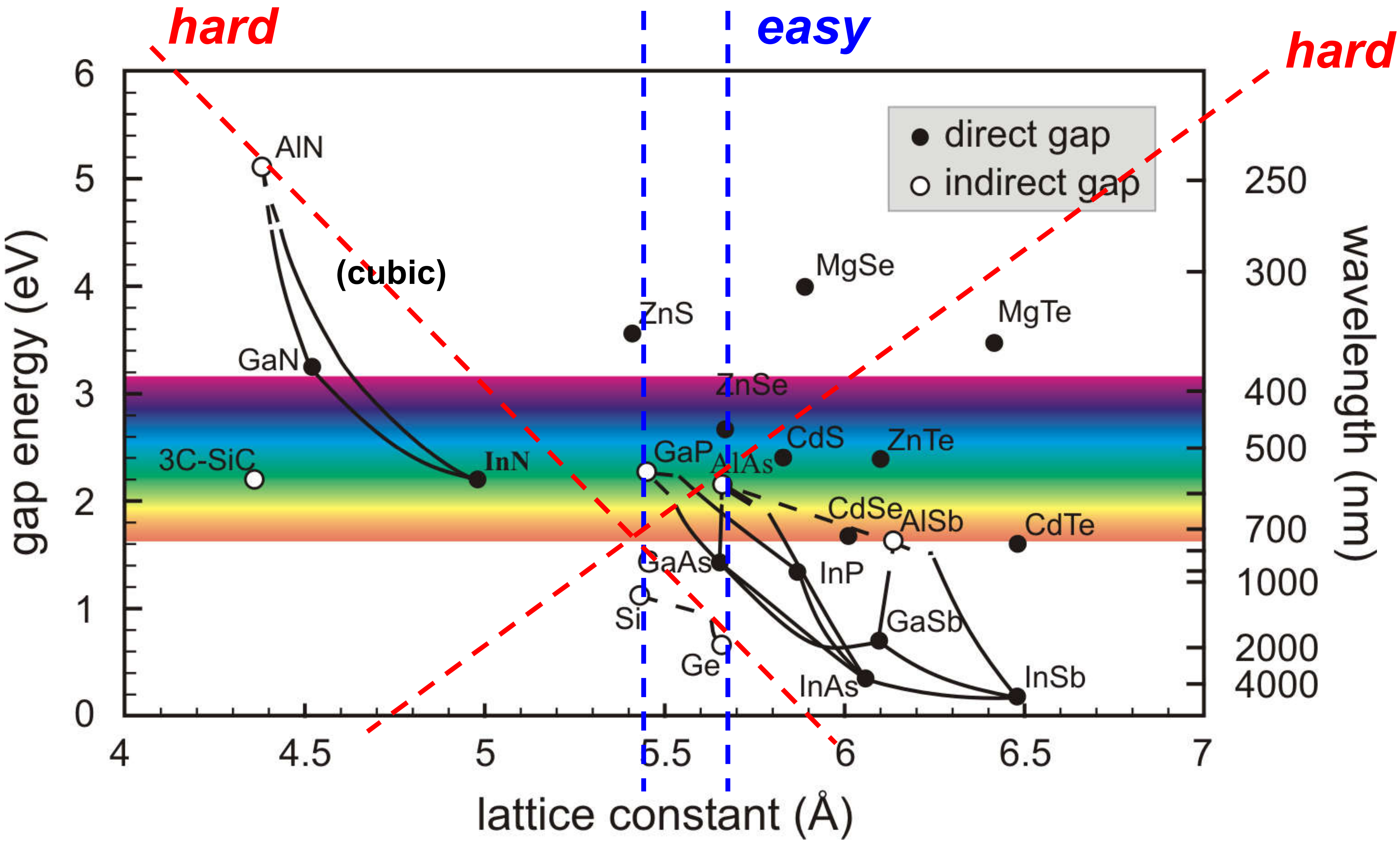
# Online Surface Monitoring



# Lattice Constants vs. Bandgap



# Lattice Constants vs. Bandgap



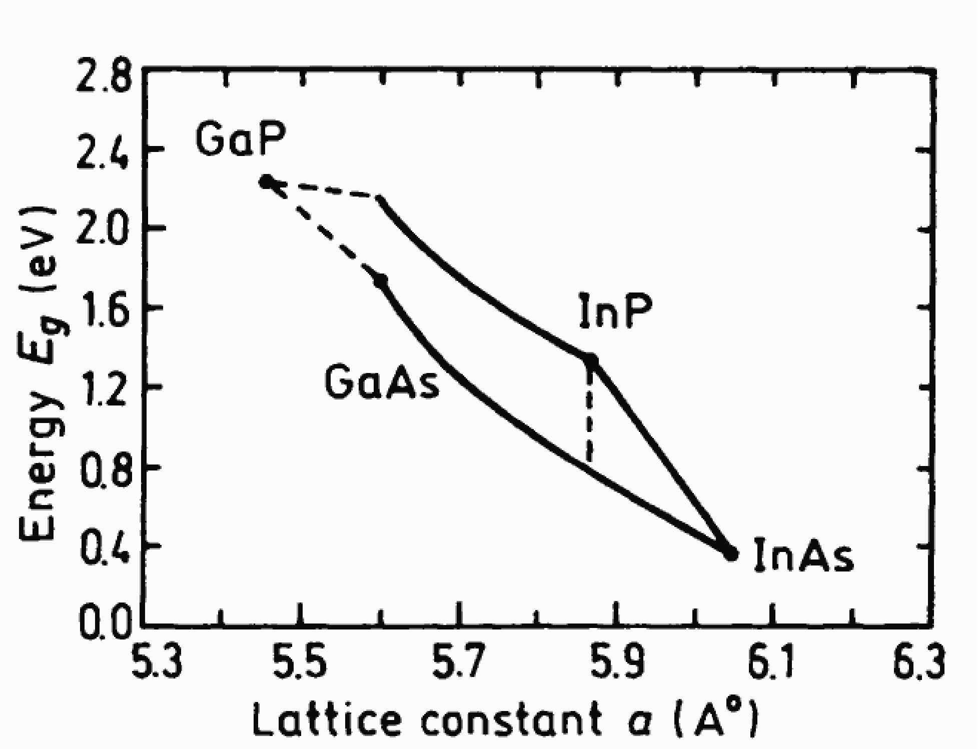
# Lattice Constants vs. Bandgap

## Vegard's law: assume linear mixing

For $A_x B_{1-x}$

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

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



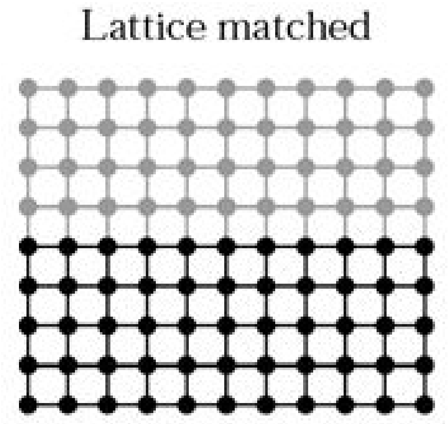

***Q: $In_xGa_{1-x}As$ on InP?***

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

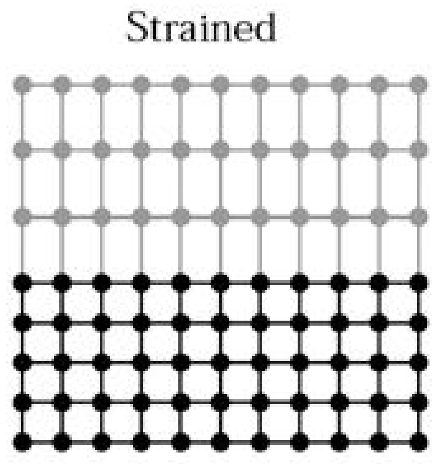
# Lattice Matched/Mismatched Growth

'metamorphic' growth

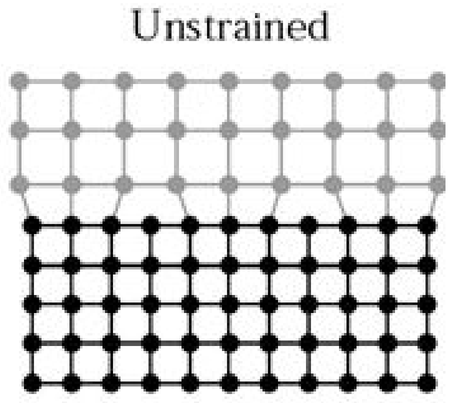
thin film | thick film




substrate




substrate

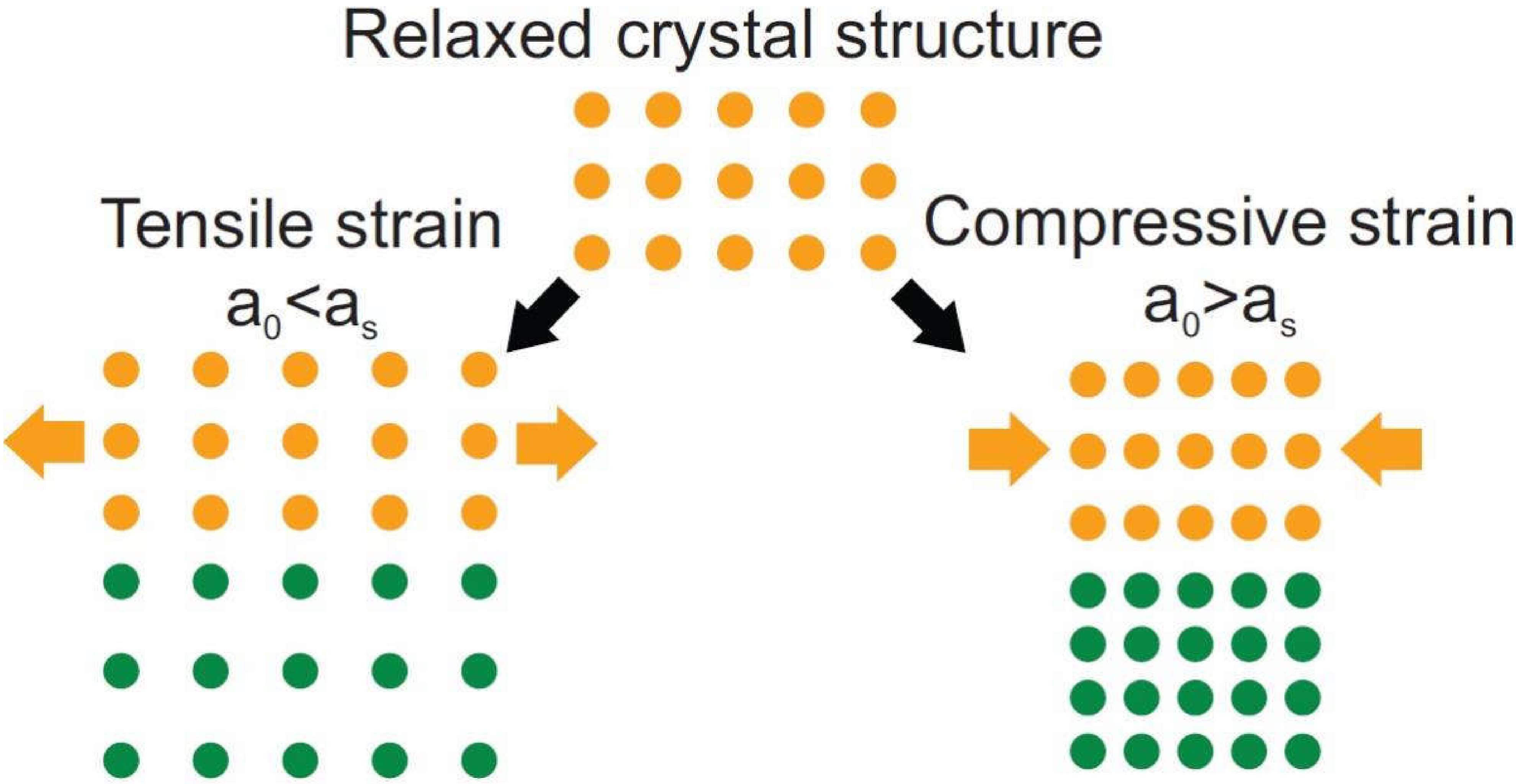



substrate

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

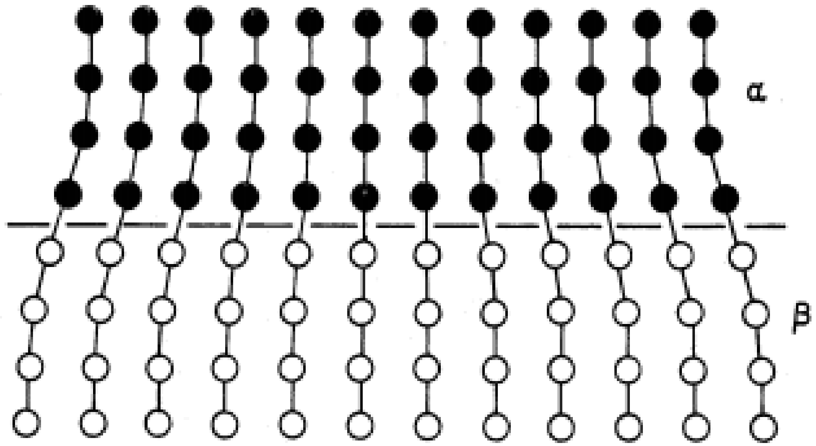



Fig. 3.34 A coherent interface with slight mismatch leads to coherency strains in the adjoining lattices.

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

$$E_\varepsilon \propto d$$

## misfit dislocation energy

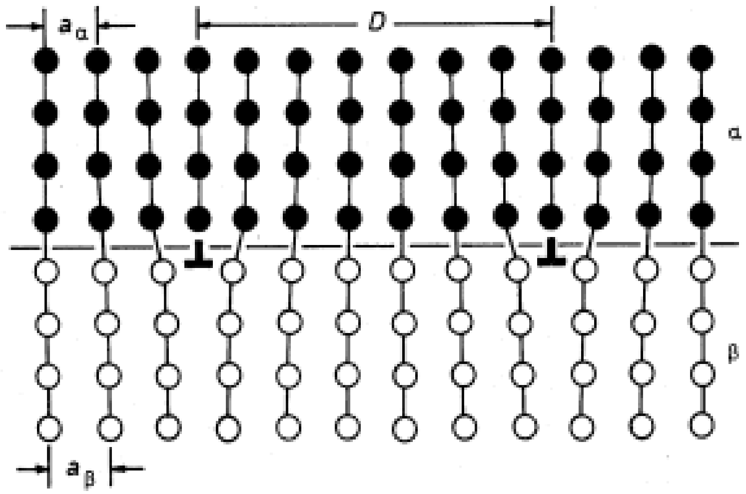
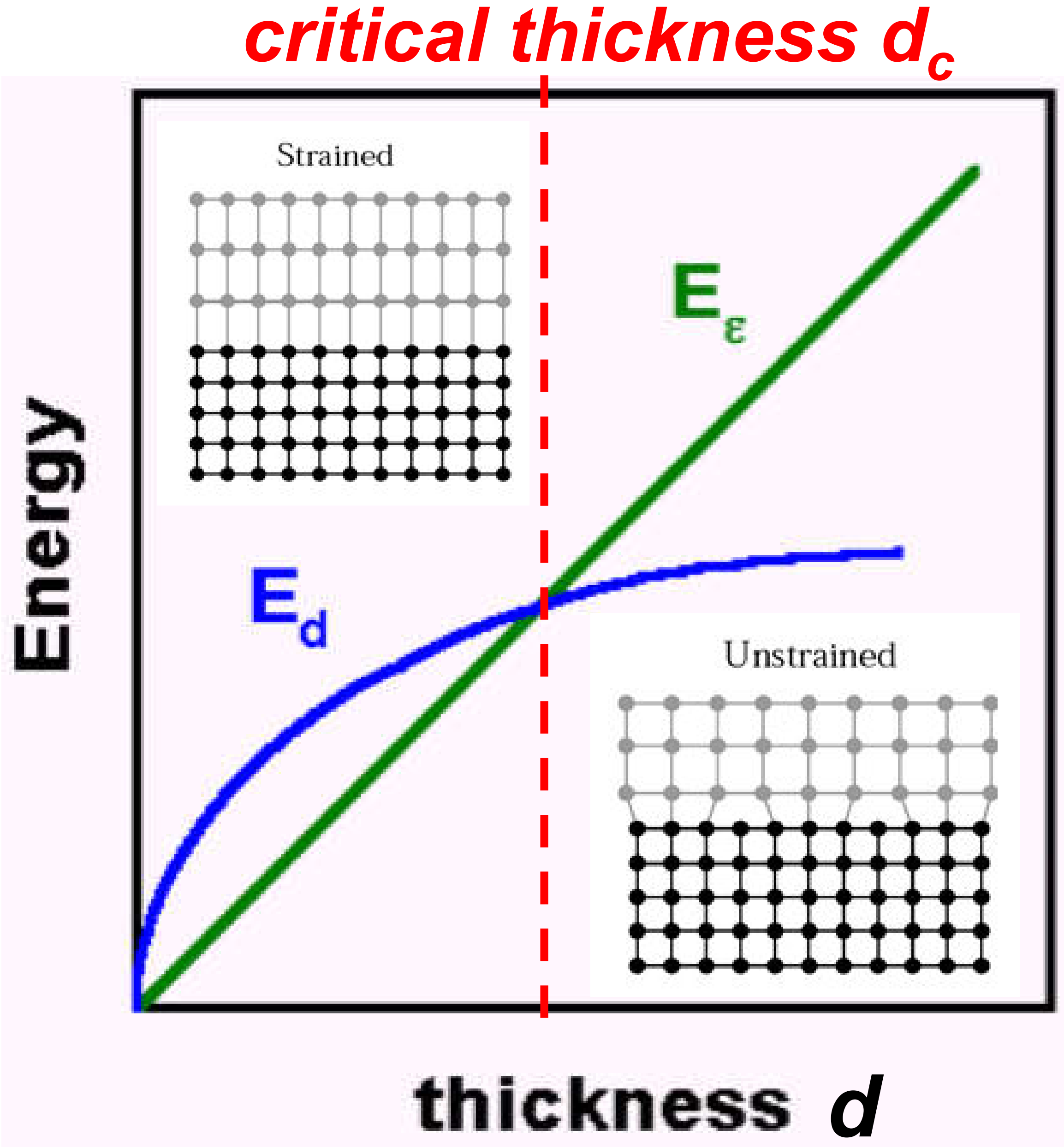



Fig. 3.35 A semicoherent interface. The misfit parallel to the interface is accommodated by a series of edge dislocations.

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

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

# Growth Energy

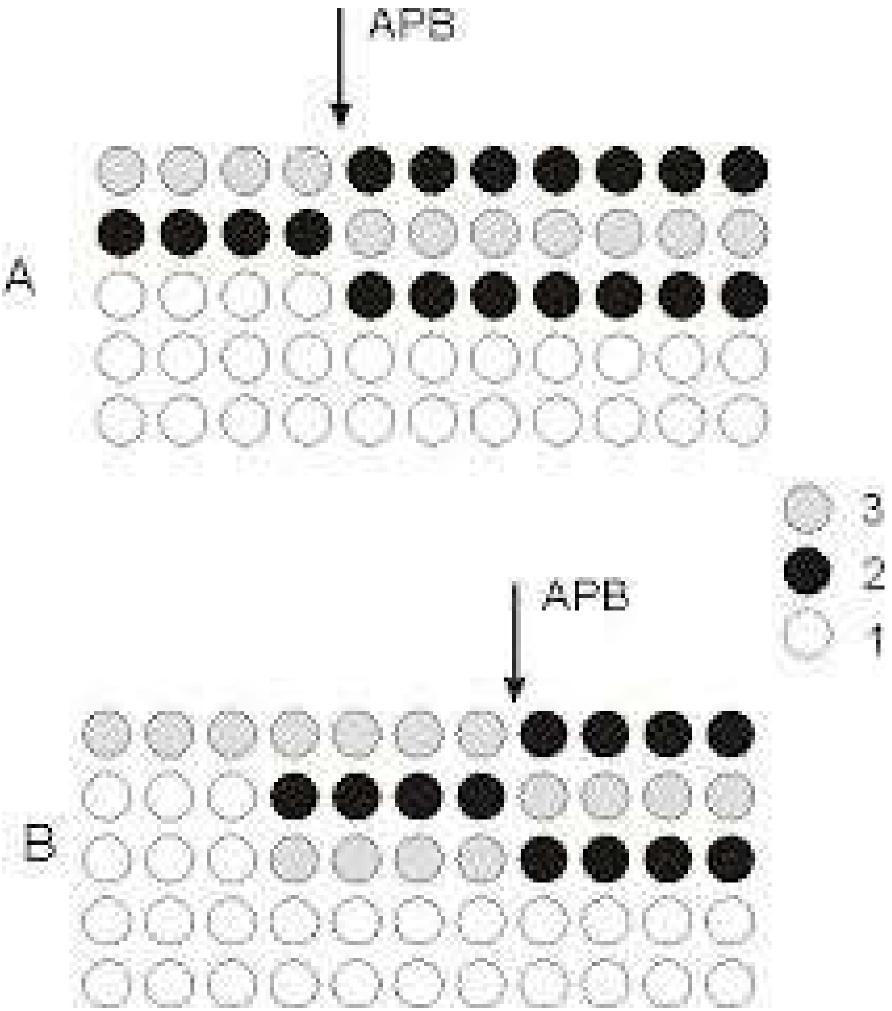



$$E_{\varepsilon} \propto d$$

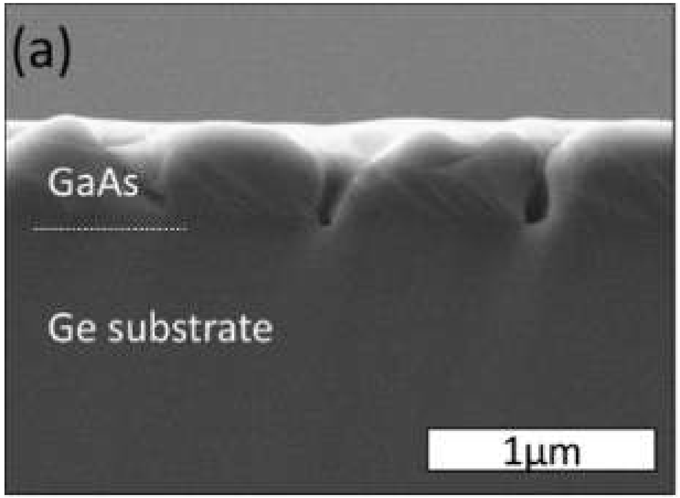
$$E_{d} \propto \ln(d)$$

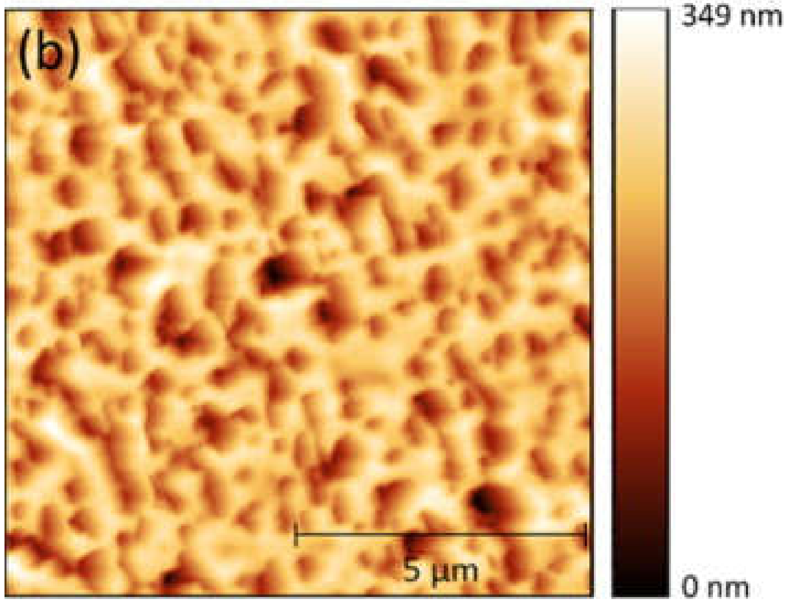
# Anti-Phase Boundary (APB)

**GaAs is lattice matched to Ge, but ...**




**Ga**
**As**
**Ge**



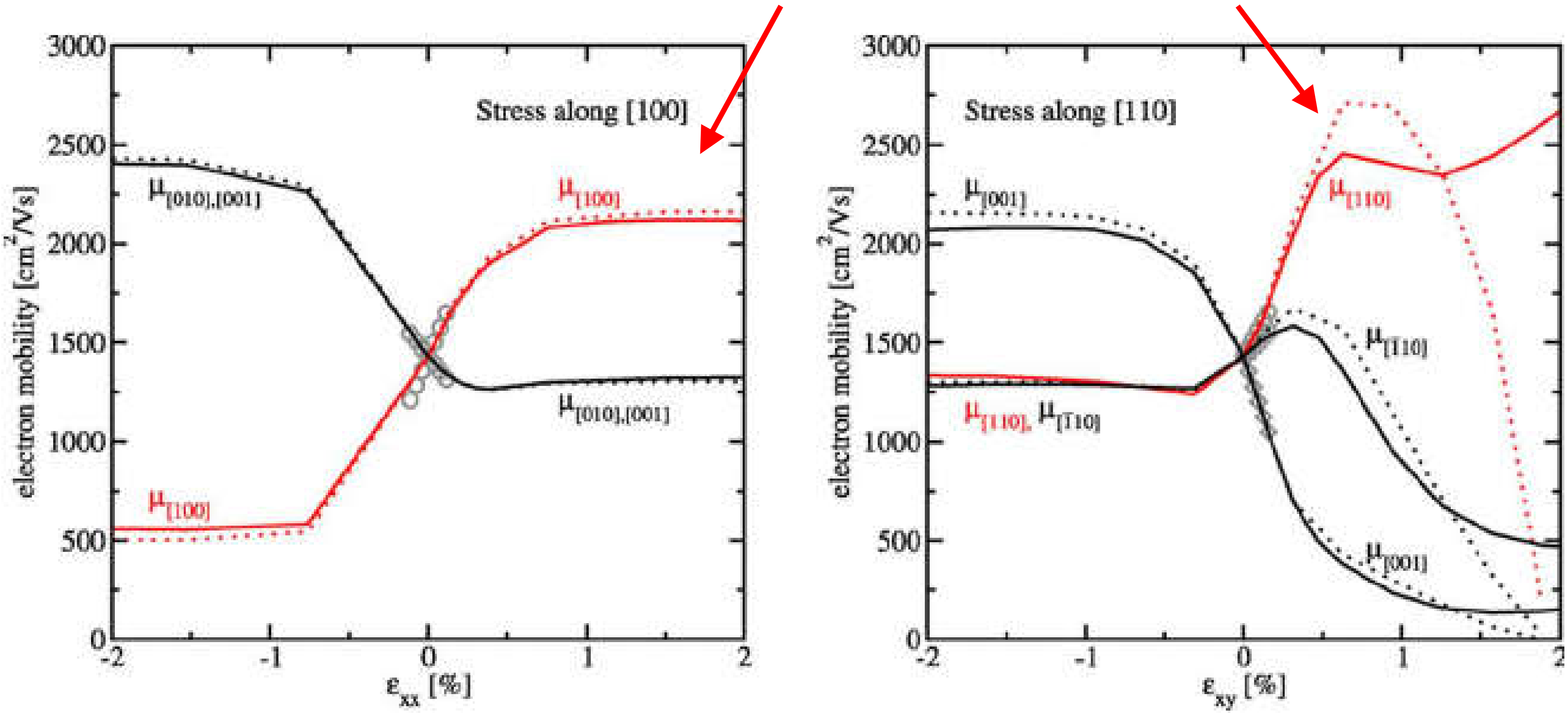



# Applications

- 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

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

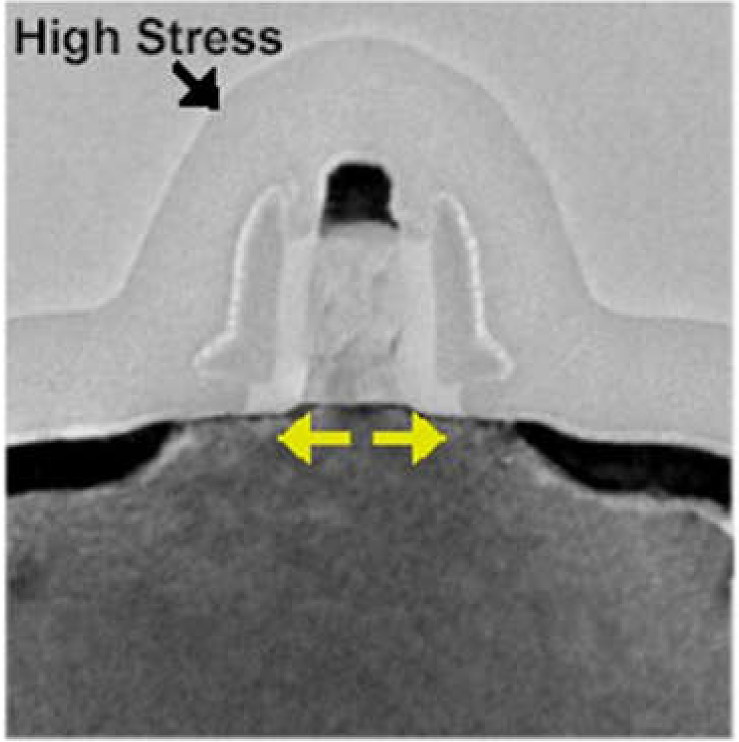



Fig. 3 TEM of NMOS transistor showing high tensile stress nitride overlayer.

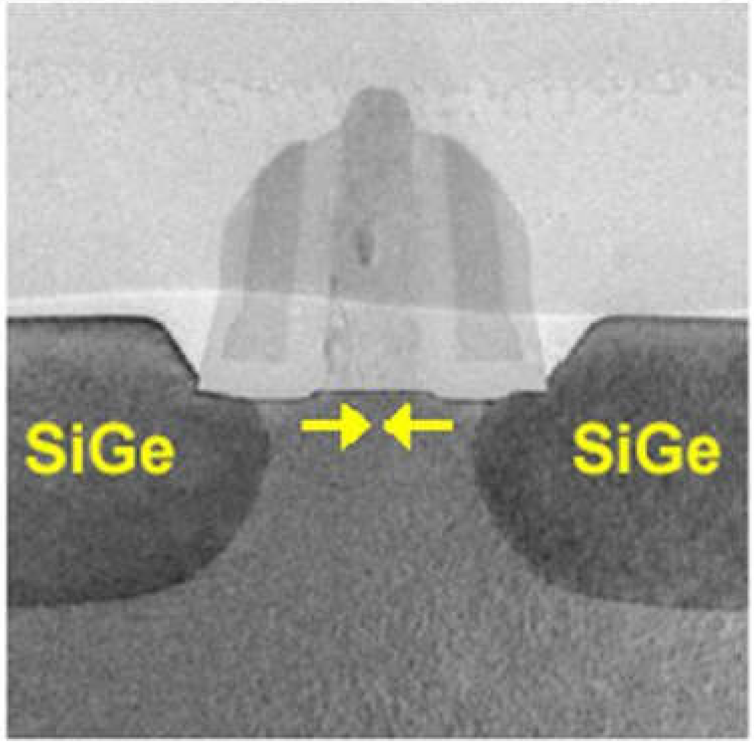



Fig. 4 TEM of PMOS showing SiGe heteroepitaxial S/D inducing uniaxial strain.

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

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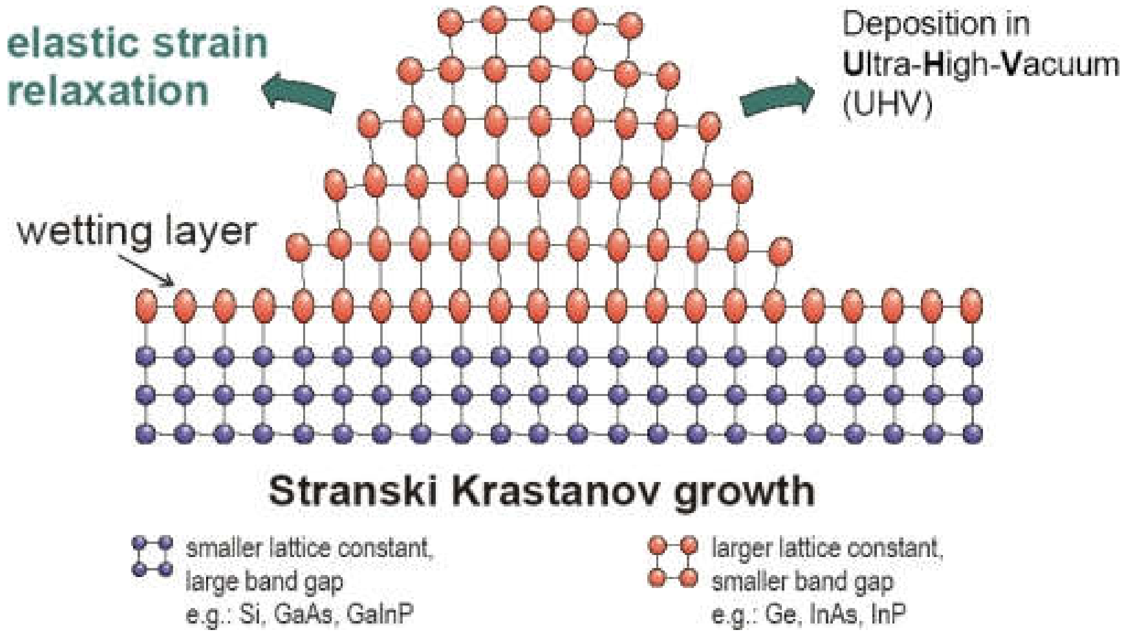
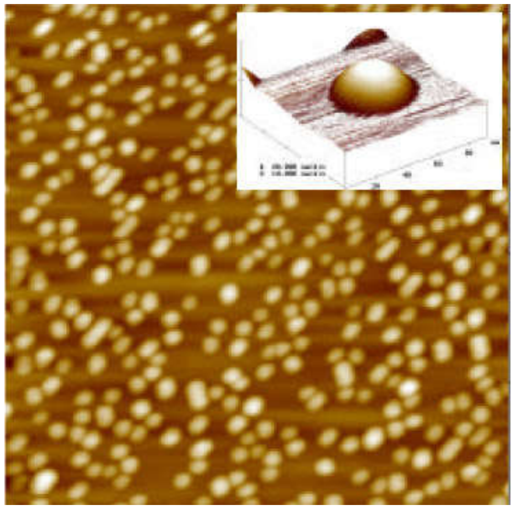
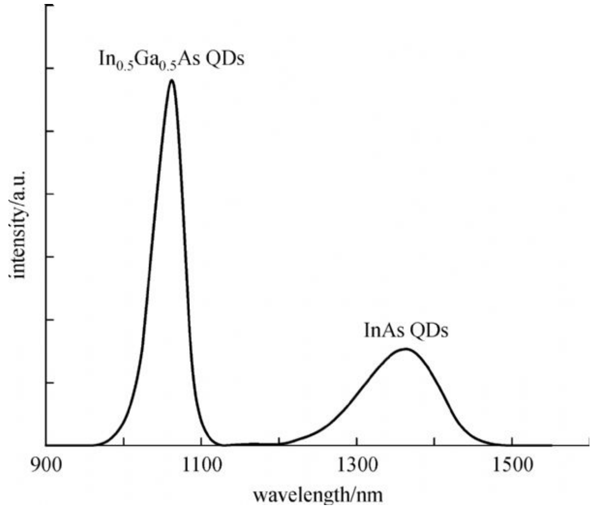
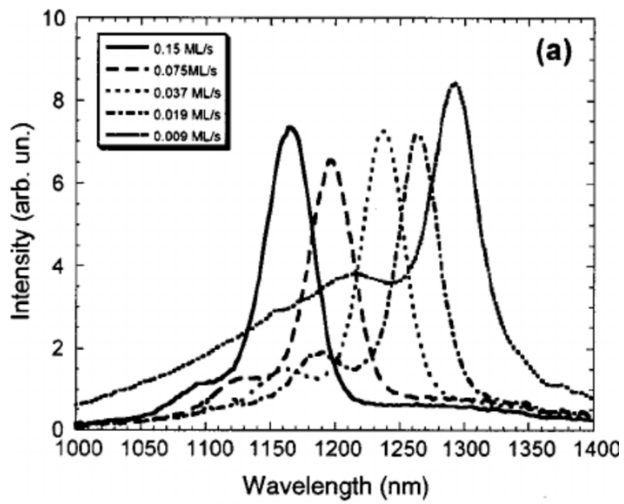
# III-V Quantum Dots

## InGaAs is not lattice matched to GaAs

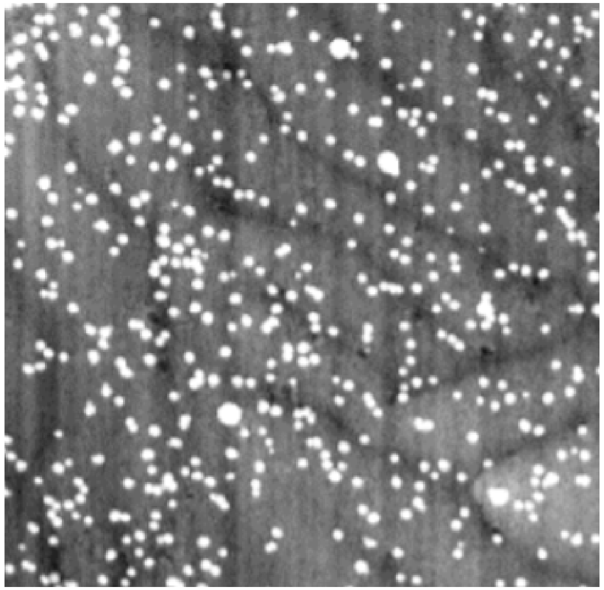



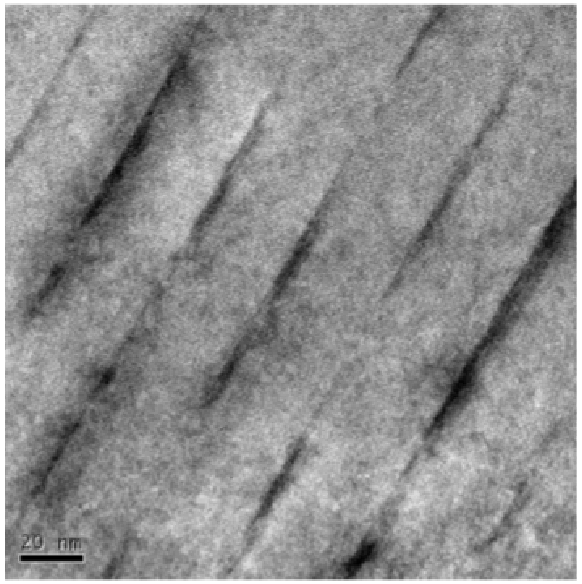





# III-V Quantum Dots






## InGaN quantum dot LEDs

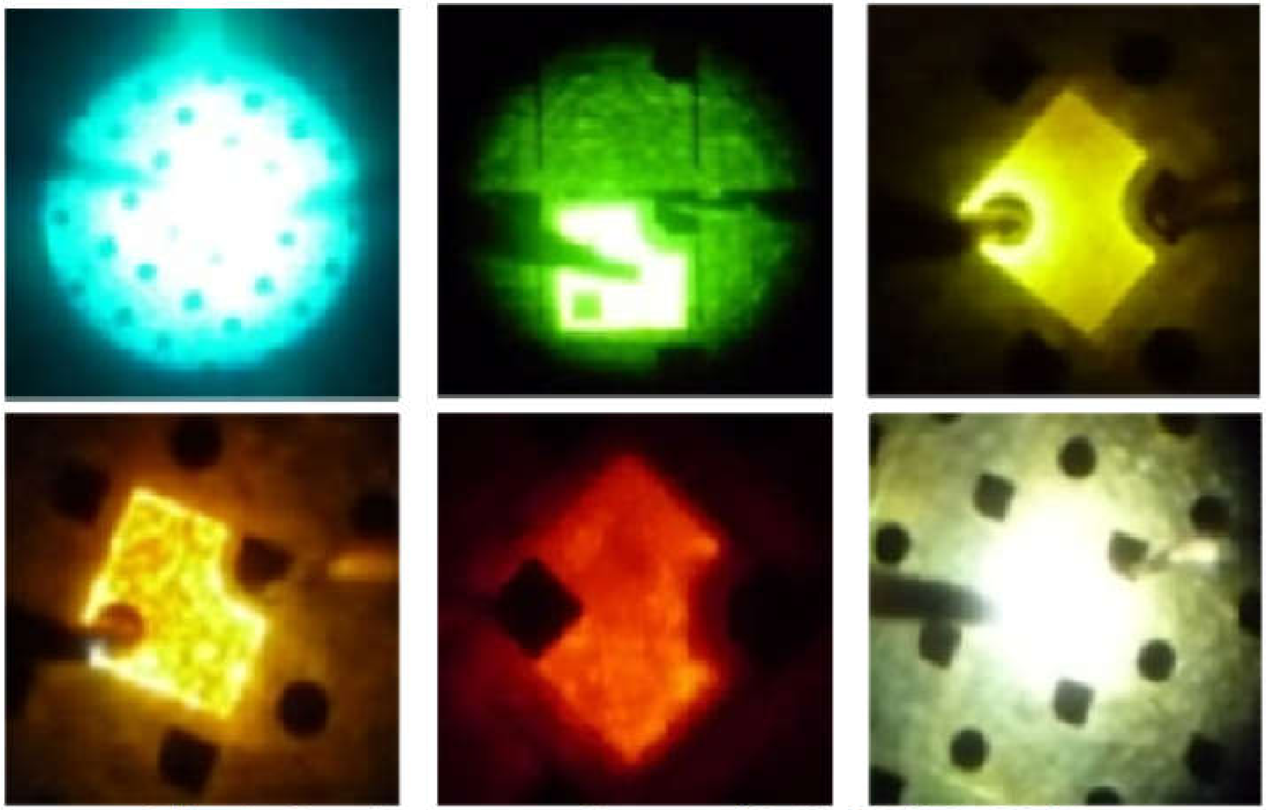
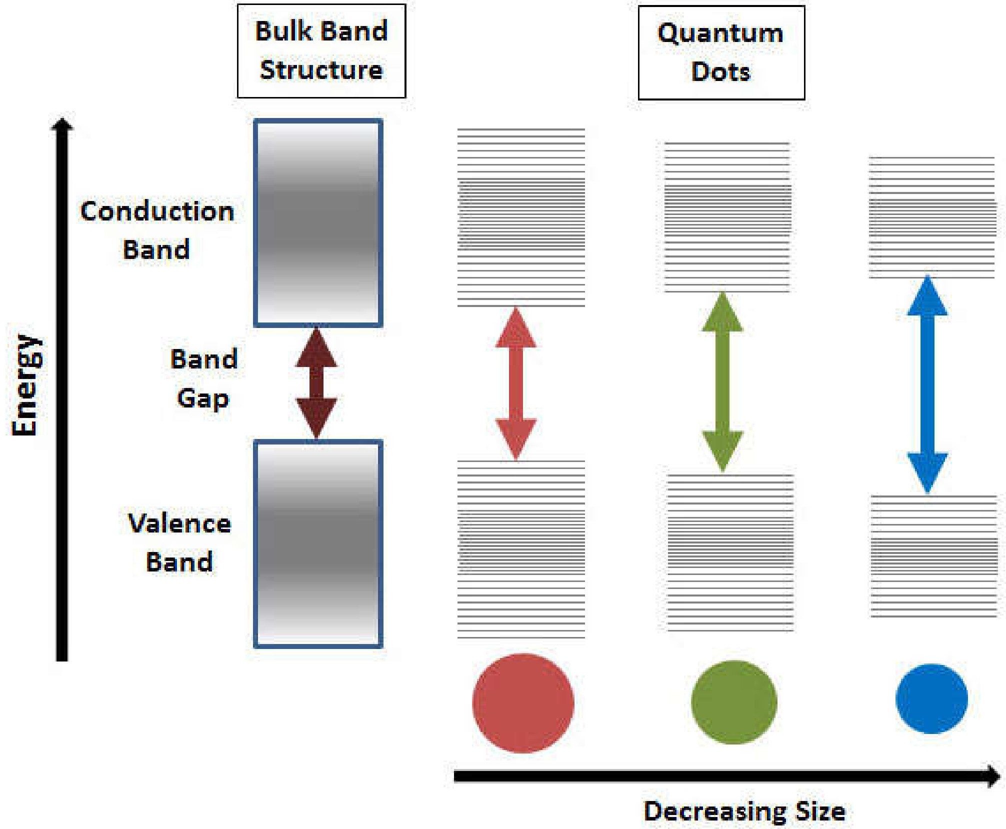
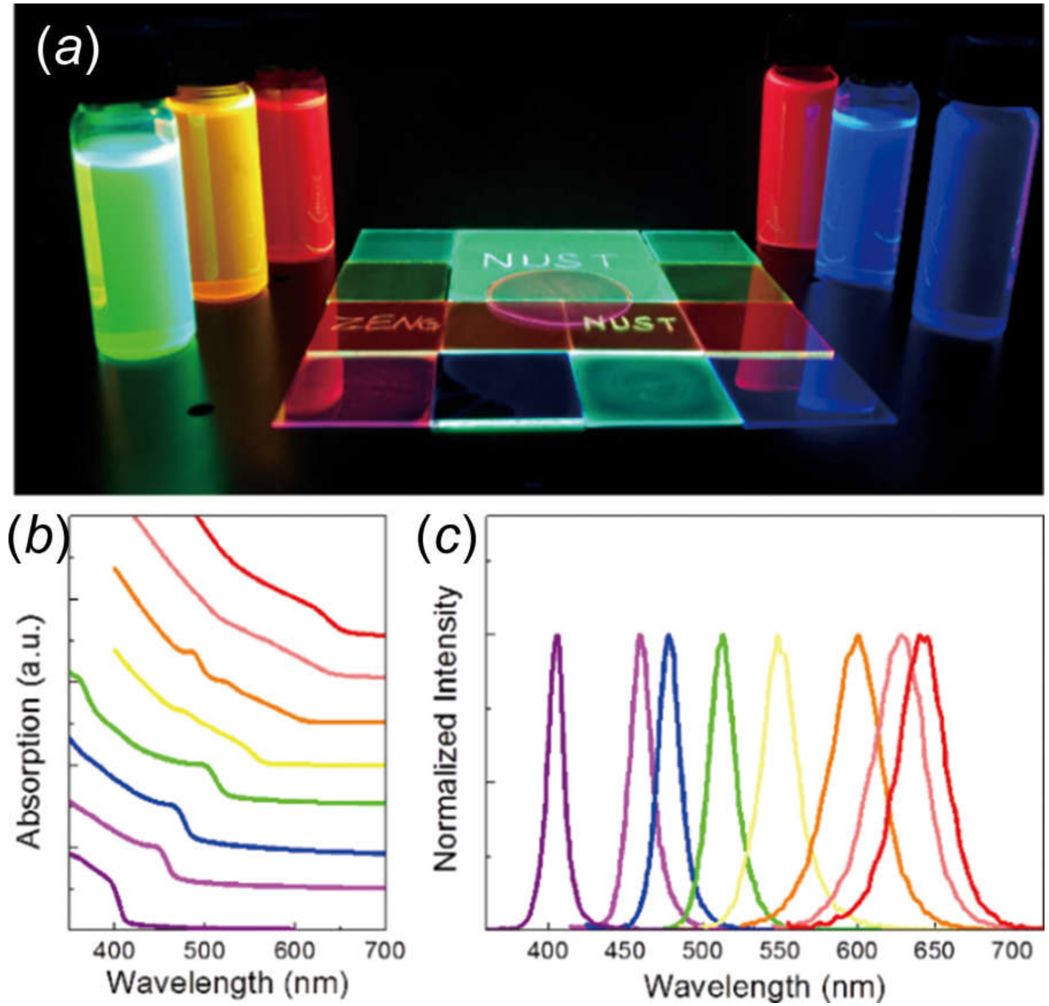


Fig. 2. Luminescence photos of InGaN QDs LEDs.

L. Wang, *et al.*,. *Front. Optoelectron.* **7,** 293 (2014)

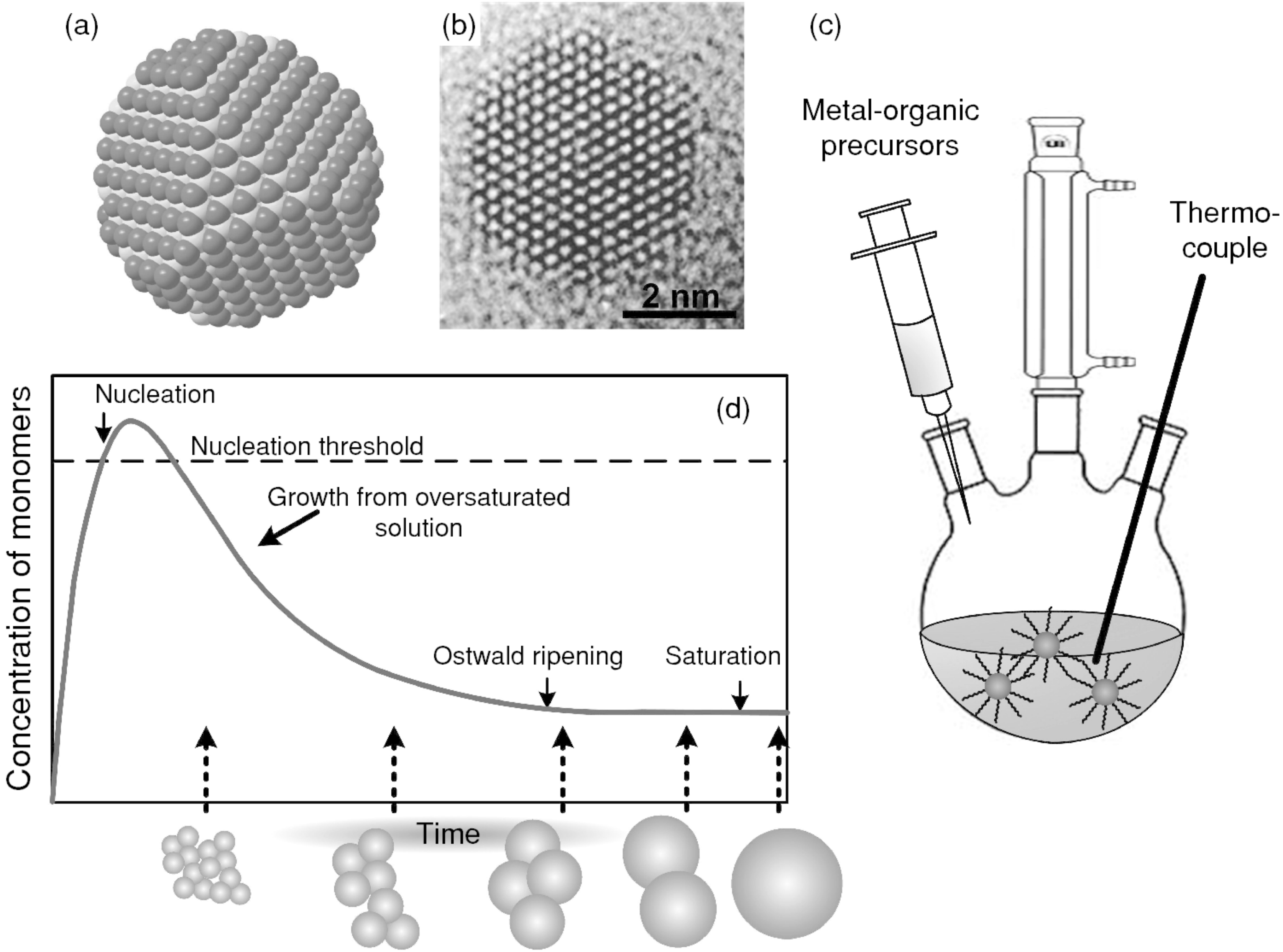
# Colloidal Quantum Dots



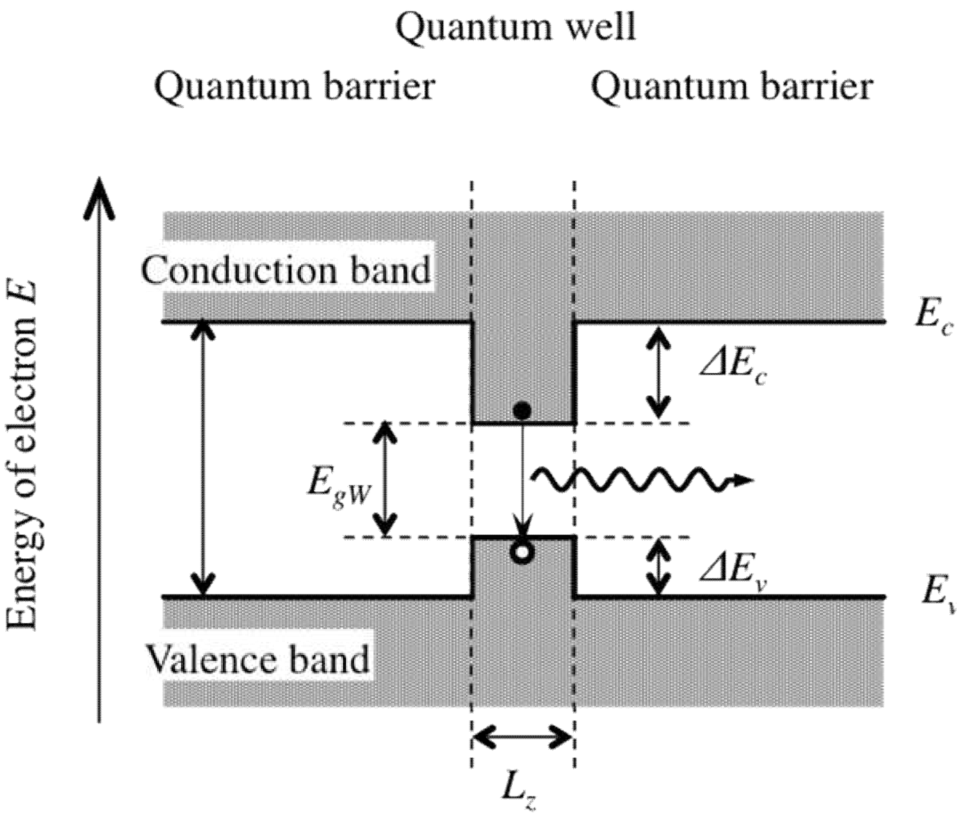




C. B. Murray, *et al.*,. *Annu. Rev. Mater. Sci.* **30,** 545 (2000)

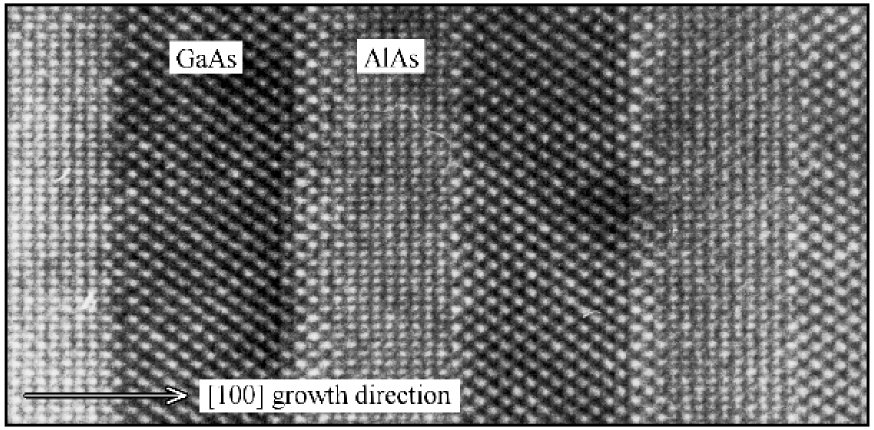
# Colloidal Quantum Dots

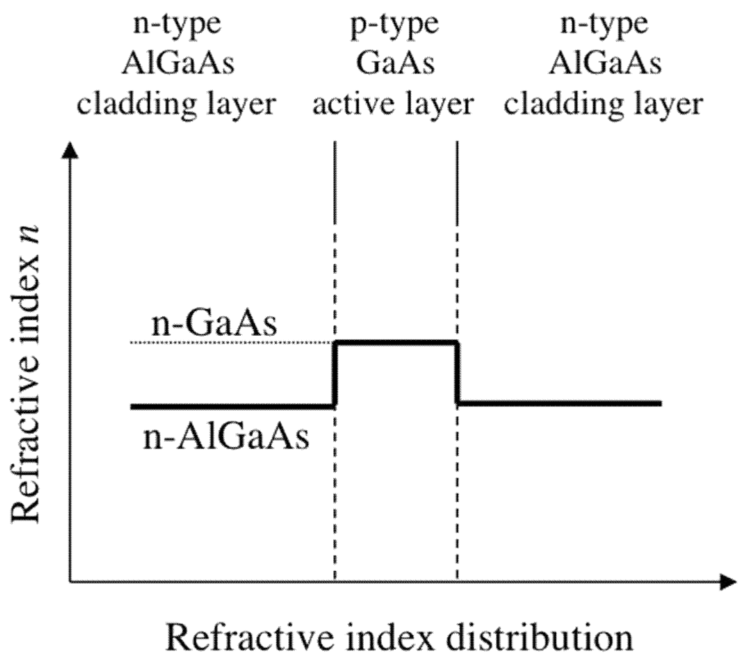


# Quantum Wells




## AlGaAs / GaAs quantum wells

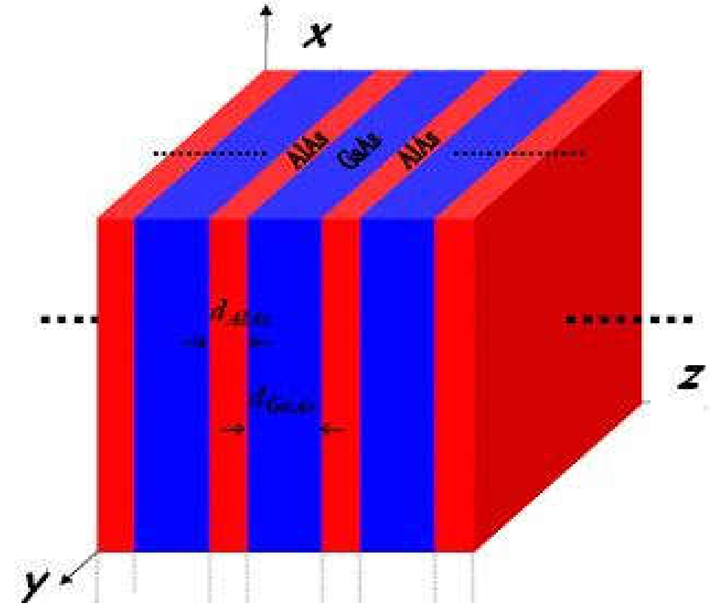


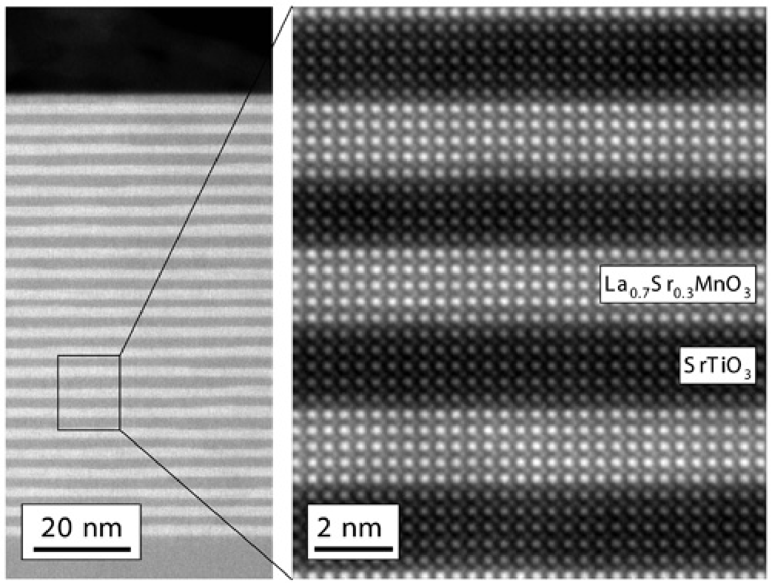




**1. electronic confinement**
**2. optical confinement**

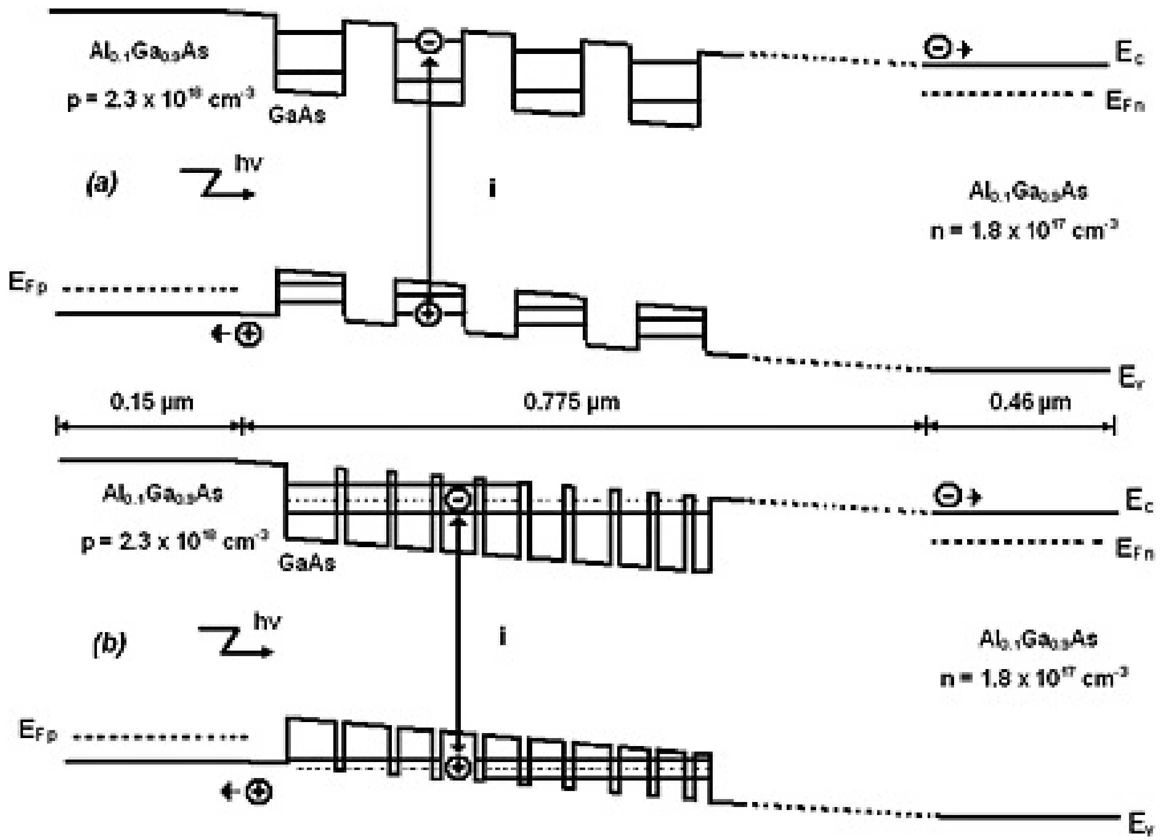
**2000 Nobel Prize in Physics**

# Superlattice



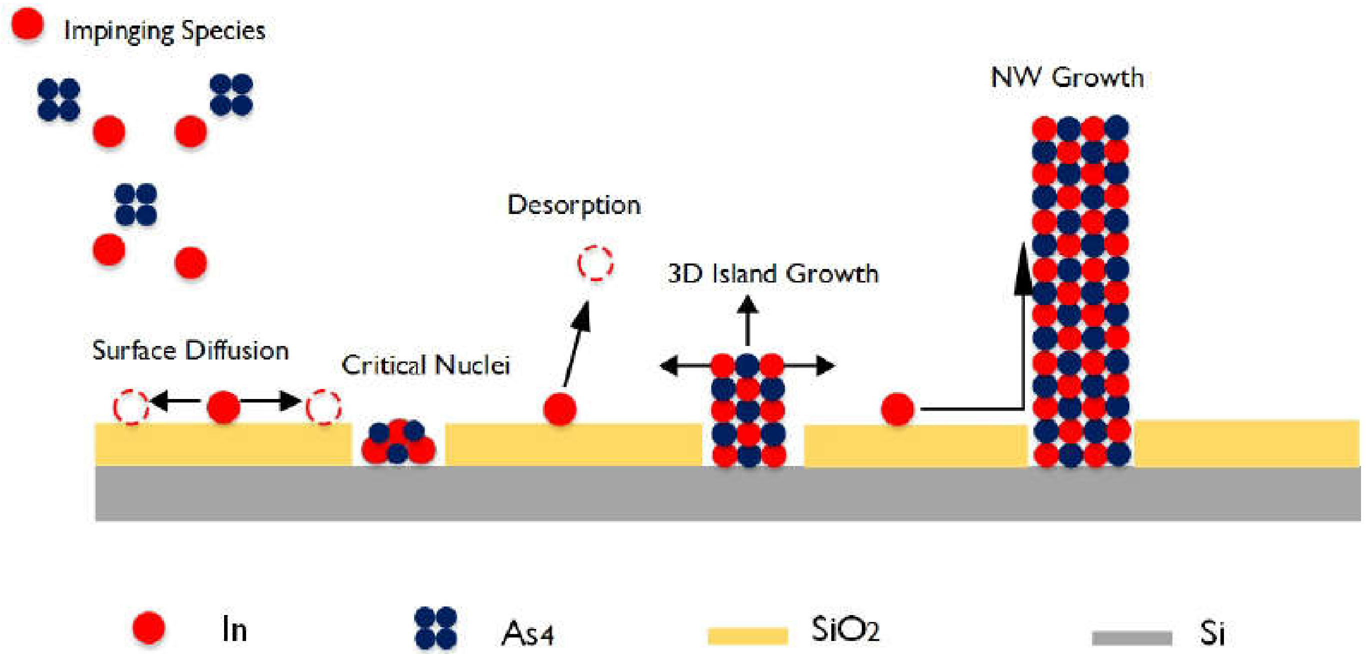

conventional quantum wells

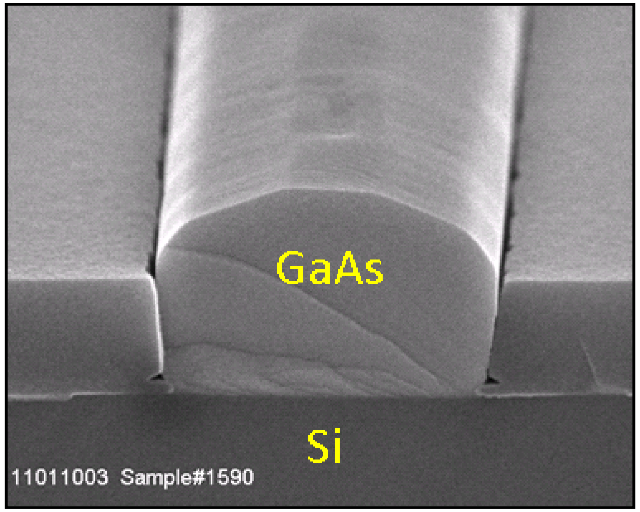


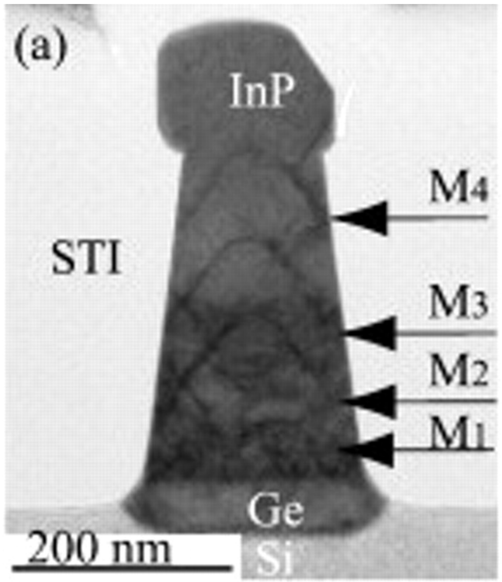

superlattice

# Selective Area Growth

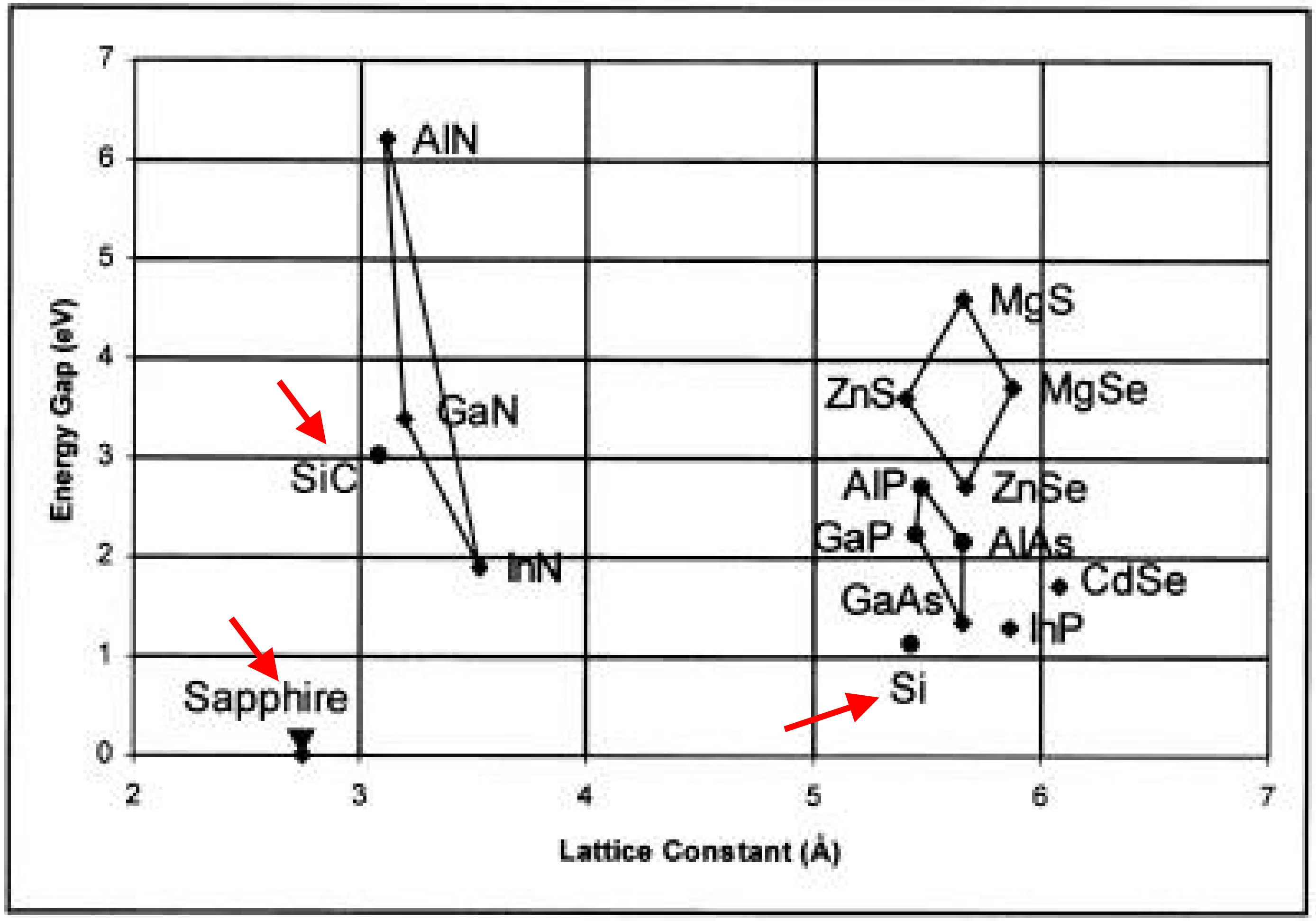
## At high T, Ge, III-Vs grow on Si, but not on $SiO_2$

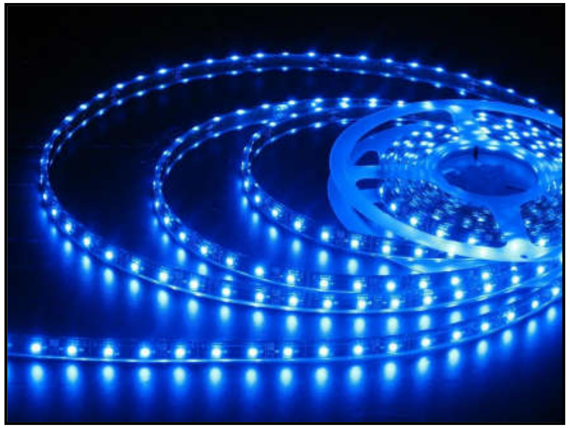


# GaN Growth



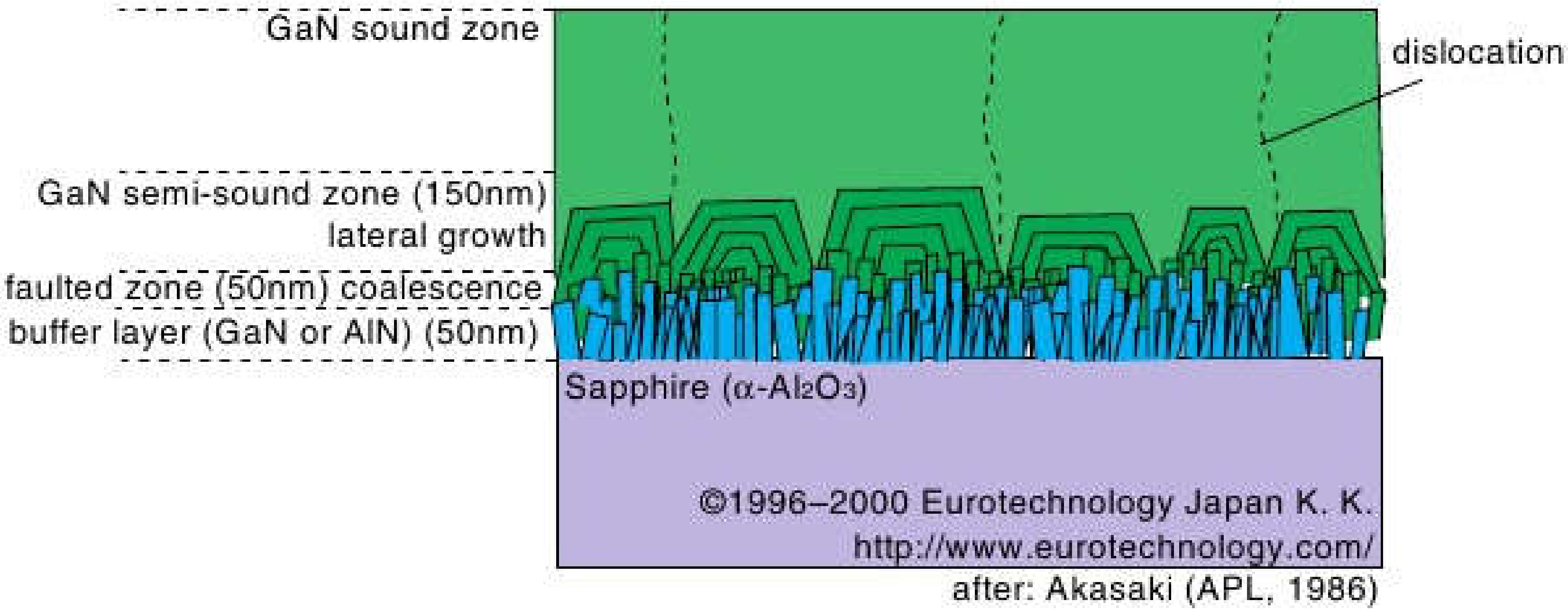



InGaN blue LEDs

substrate price

| | |
|---|---|
| GaN | $$$$ |
| SiC | $$$ |
| sapphire | $$ |
| silicon | $ |

# GaN Growth on Sapphire



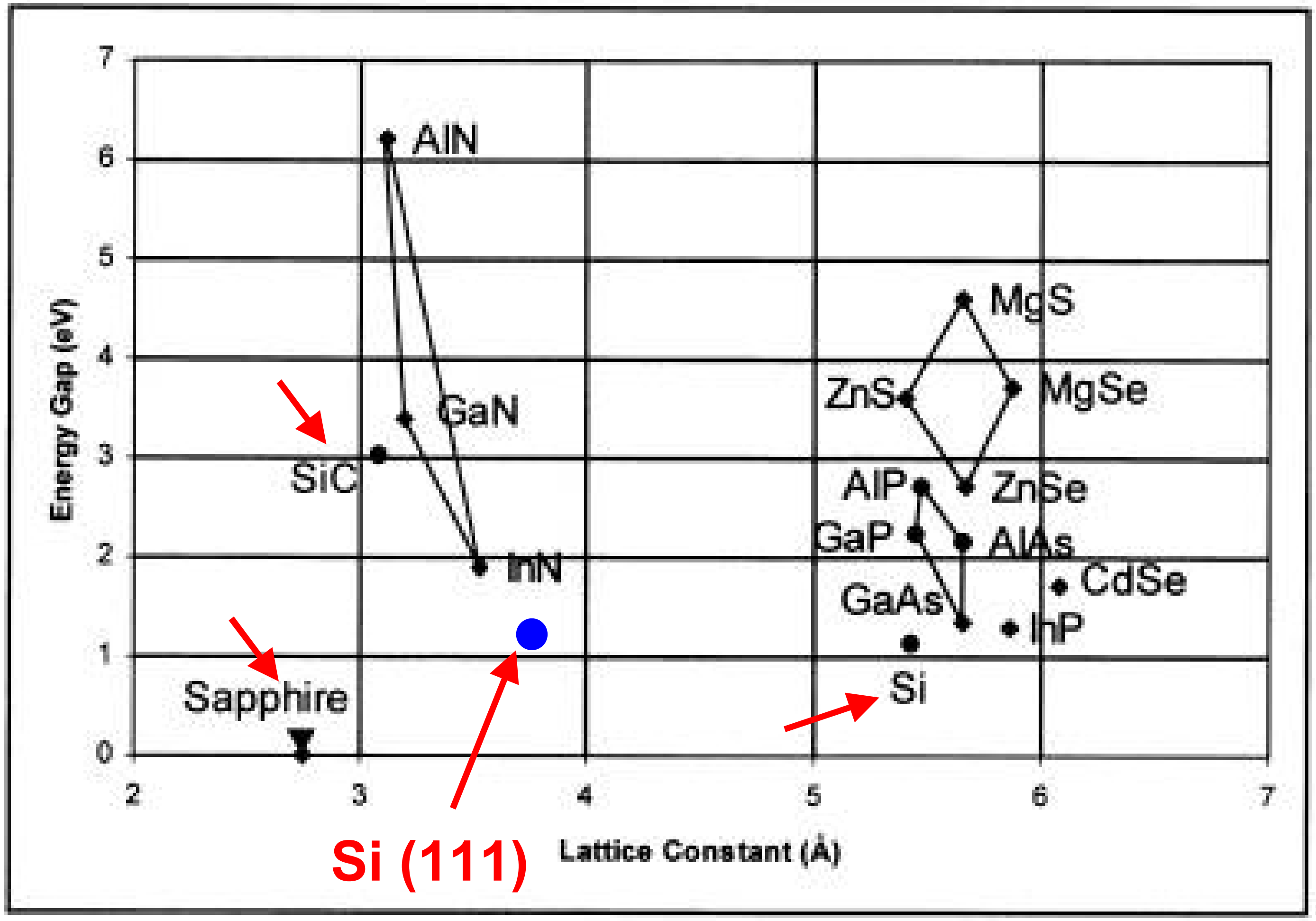

I. Akasaki H. Amano S. Nakamura

**2014 Nobel Prize in Physics**

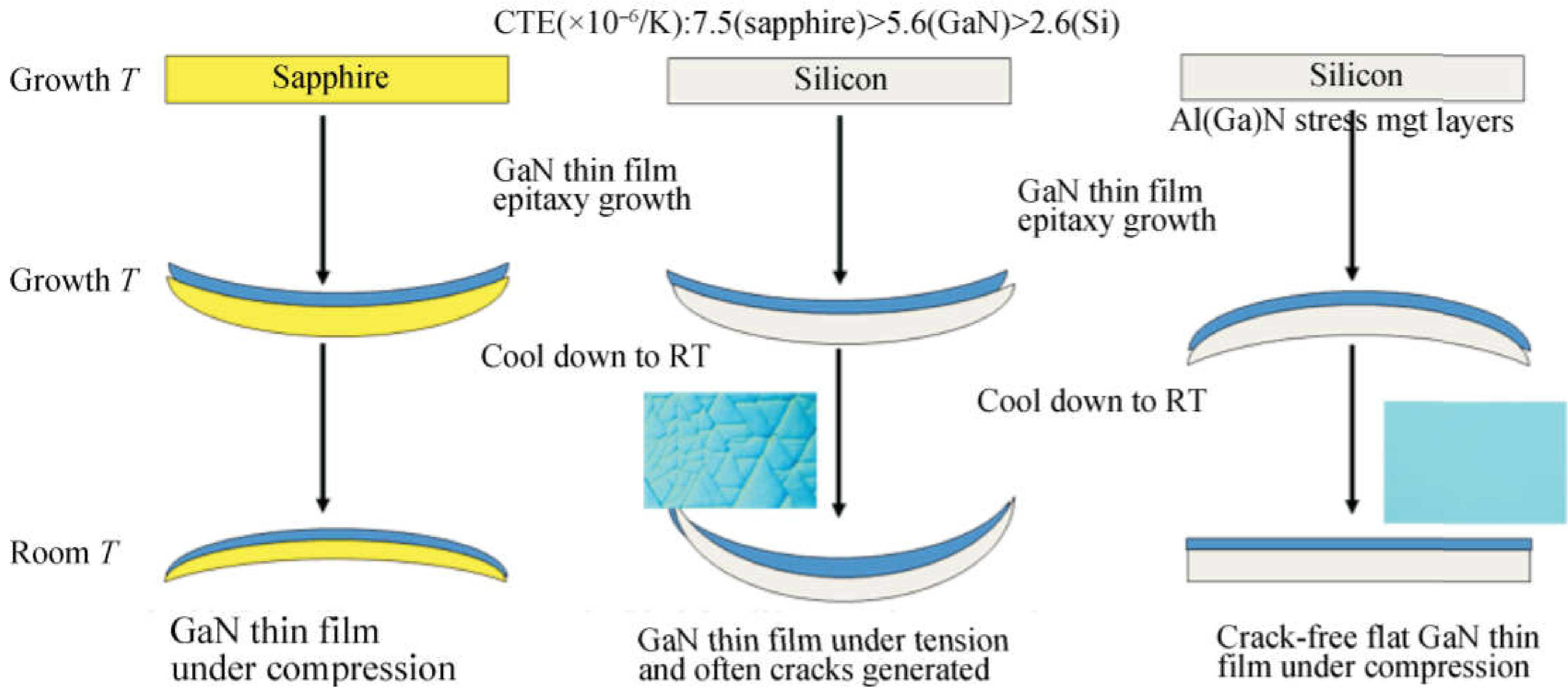
H. Amano, *et al.*,. *Appl. Phys. Lett.* **48,** 353 (1986)
H. Amano, *et al.*, *Jpn. J. Appl. Phys.* **28,** L2112 (1989)
S. Nakamura, *et al.*, *Appl. Phys. Lett.* **64,** 1687 (1994)

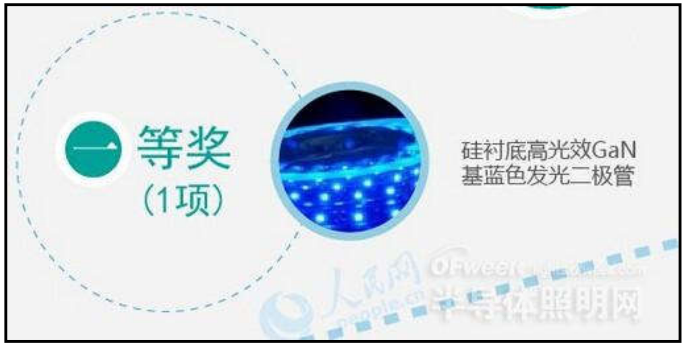
1. **growth with AlN buffer**
2. **GaN p-type doping**
3. **GaN blue LED!**

# GaN Growth on Silicon



# GaN Growth on Silicon



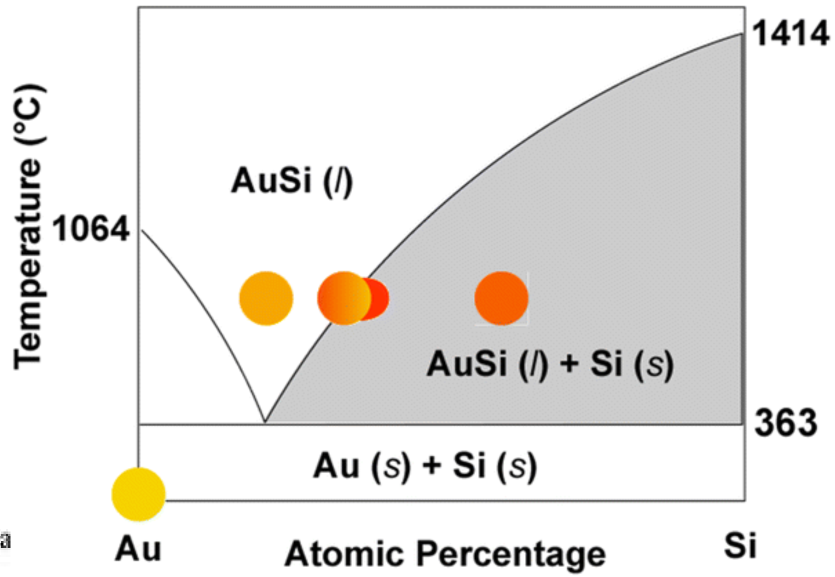



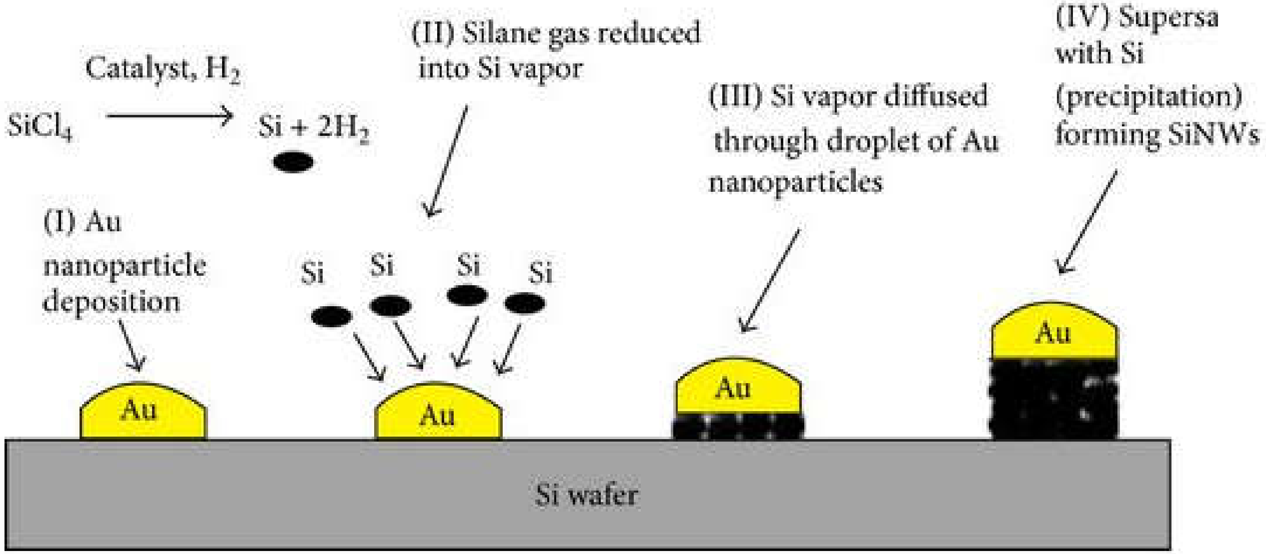

Q. Sun, *et al.*,. *J. Semicon.* **37,** 044006 (2016)

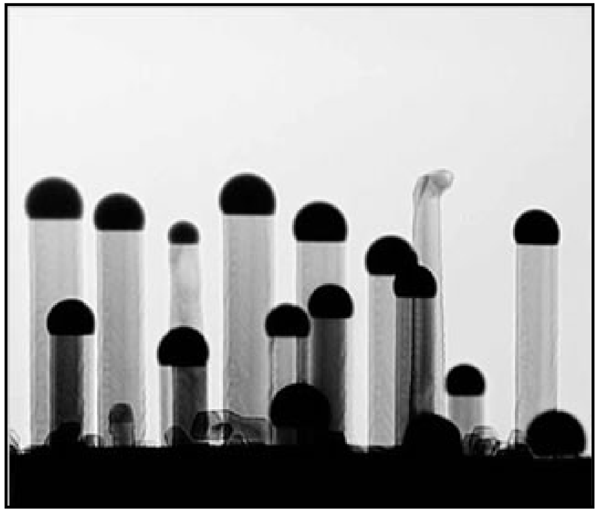
**2015年中国技术发明一等奖**

# Si Nanowire Growth

***VLS:*** ***Vapor-Liquid-Solid***

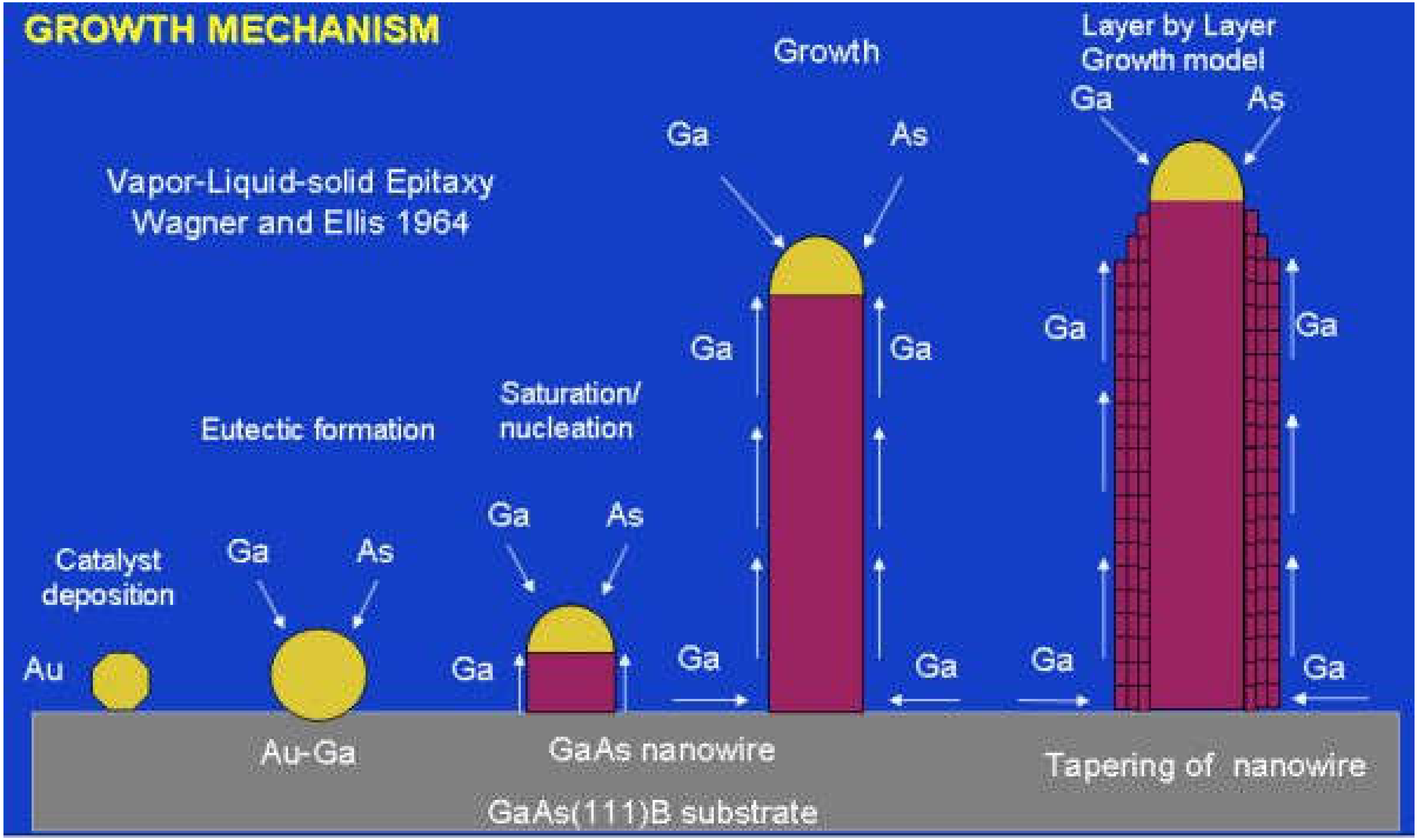


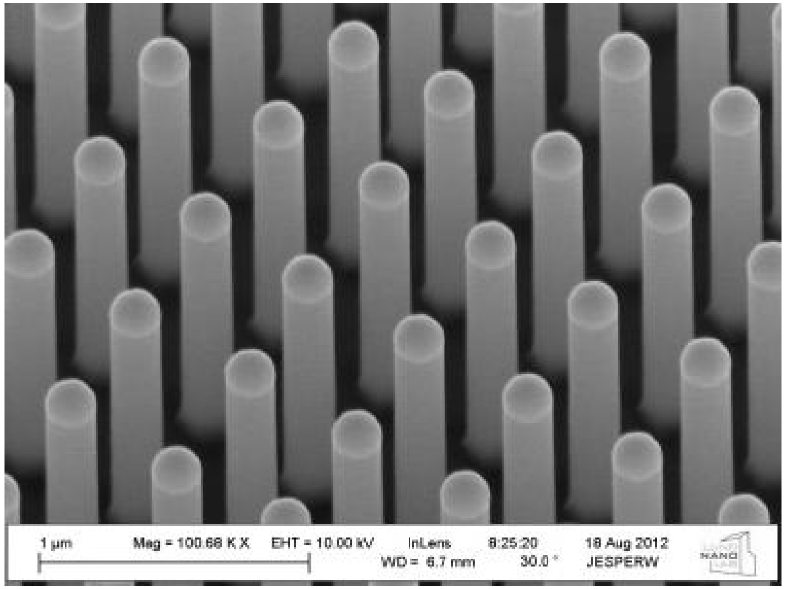
**Au-Si eutectic alloy**

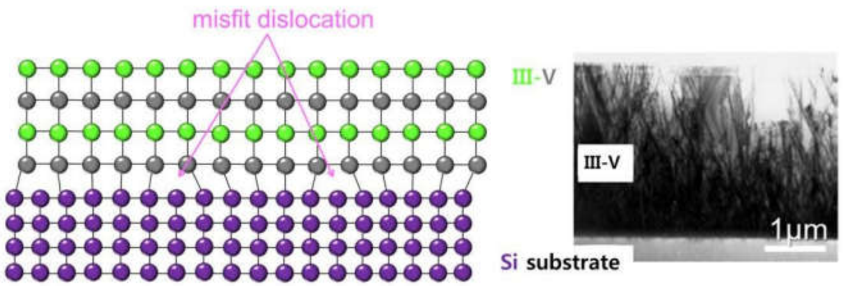
# III-V Nanowire Growth

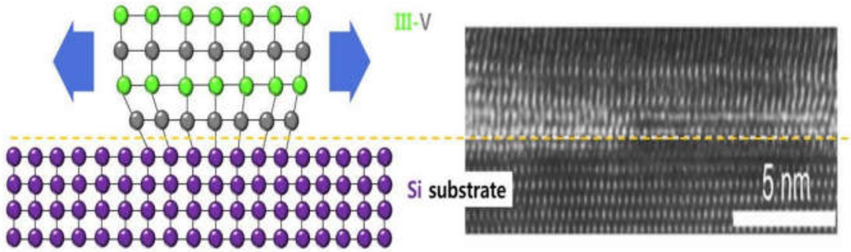



***metal catalysts reduce growth temperature***

# III-V Nanowire Growth



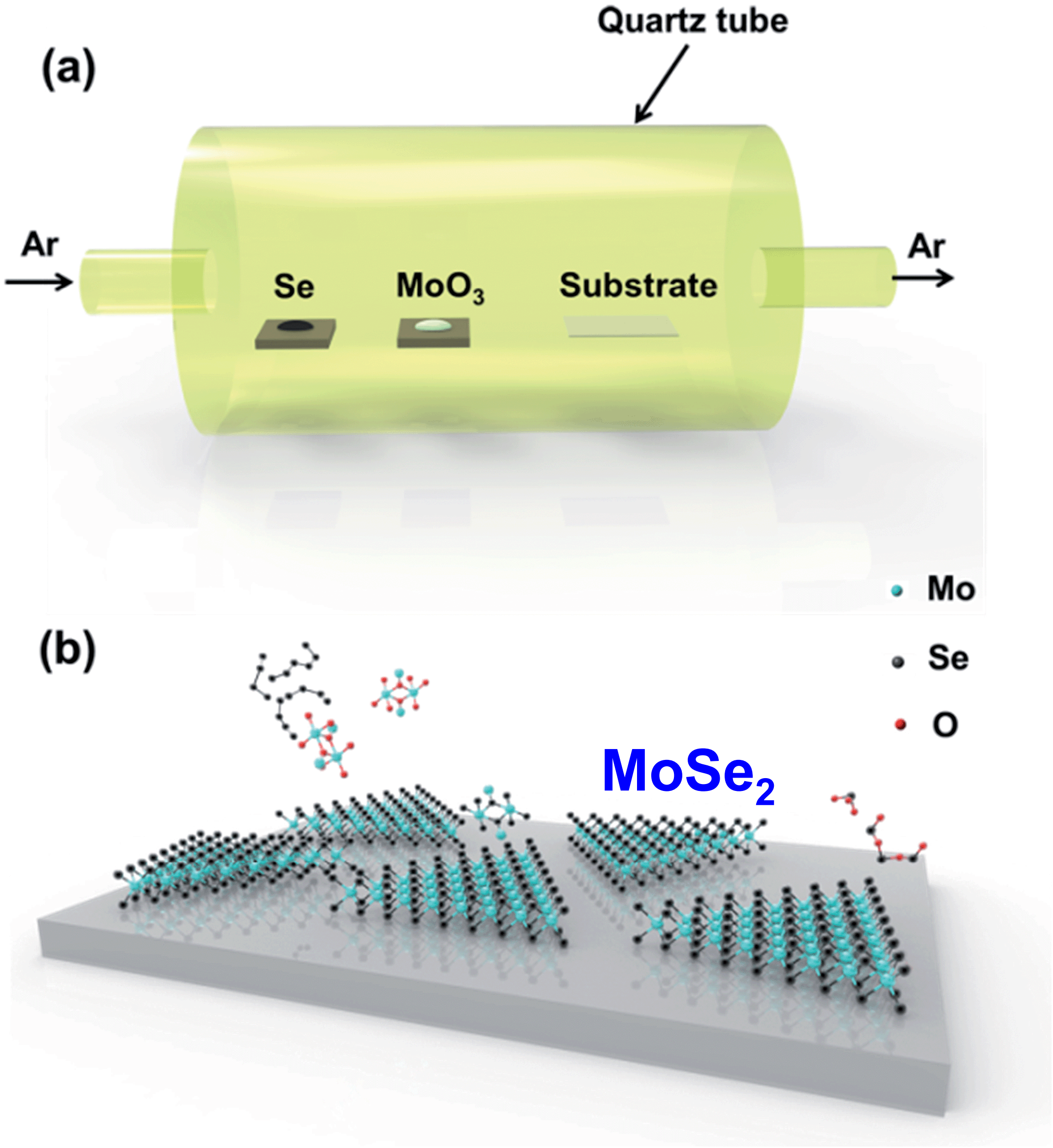



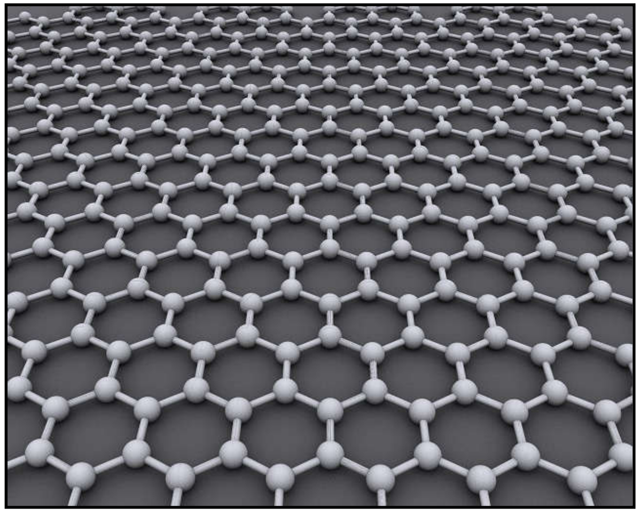



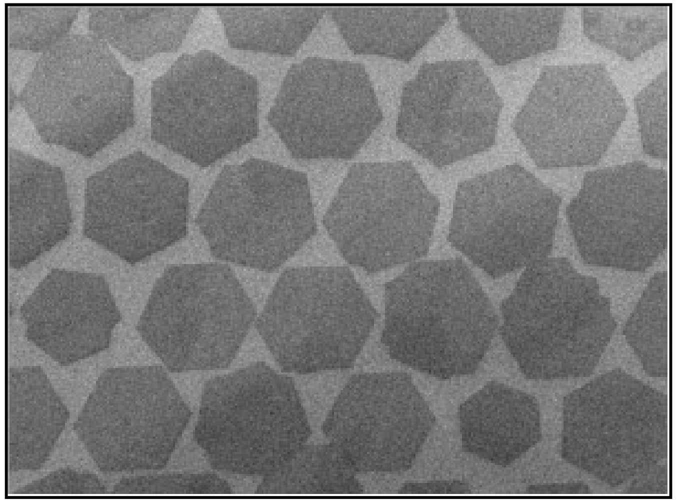

- **Direct growth of III-V film on Si:**
  Creation of massive threading dislocation due to the large lattice mismatch strain between III-V and Si

- **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



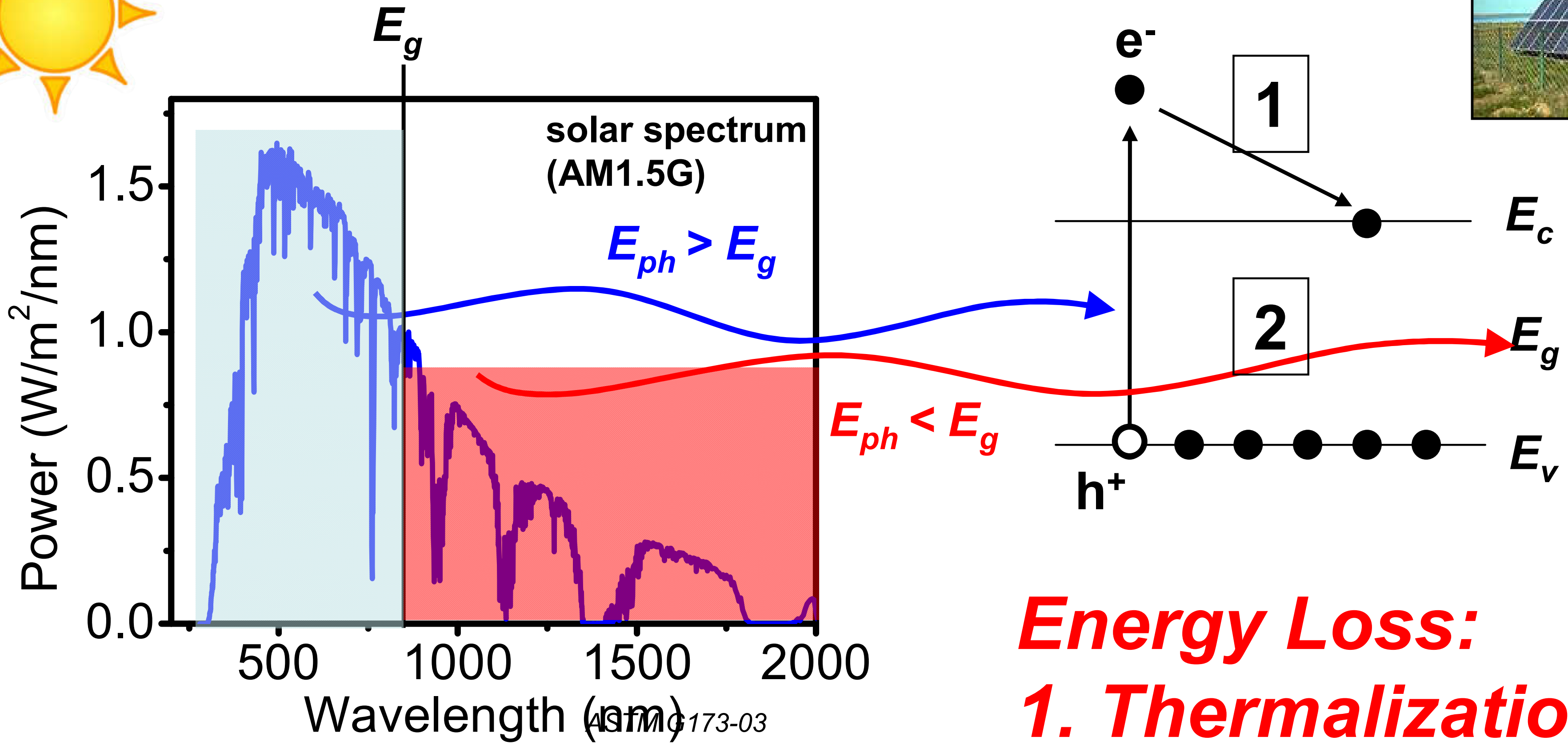





**grain boundaries exist**

***lattice match is not restrict for monolayers***

# Solar Cells




***Energy Loss:***

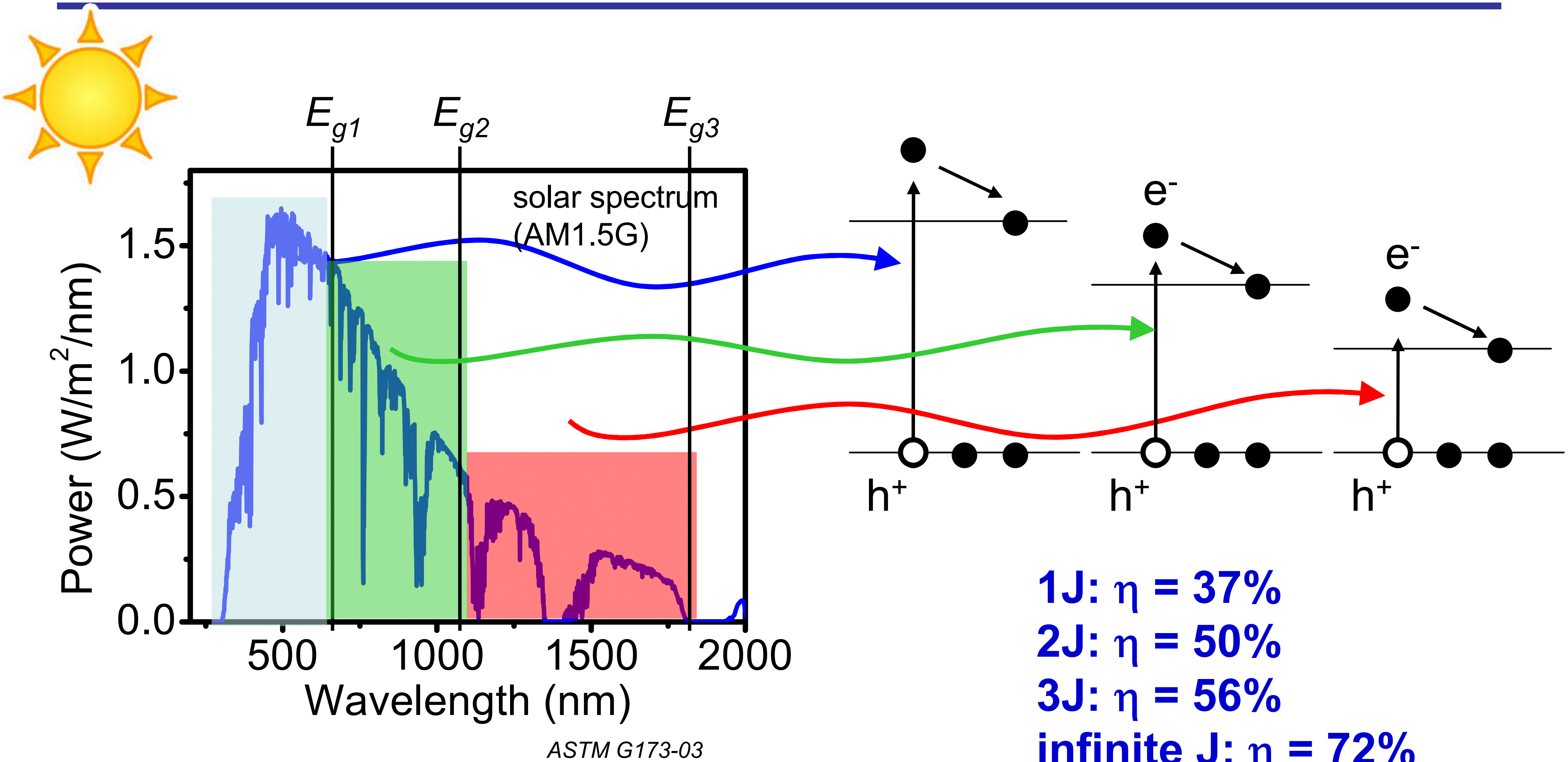
***1. Thermalization***

***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



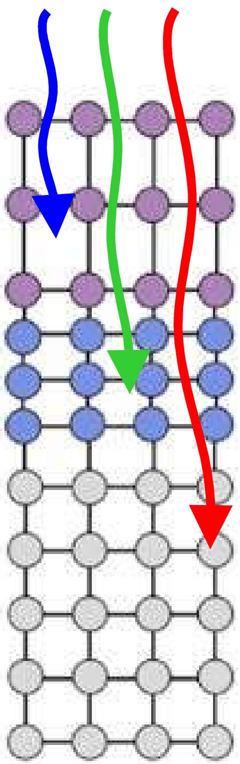

**1J: $\eta$ = 37%**
**2J: $\eta$ = 50%**
**3J: $\eta$ = 56%**
**infinite J: $\eta$ = 72%**

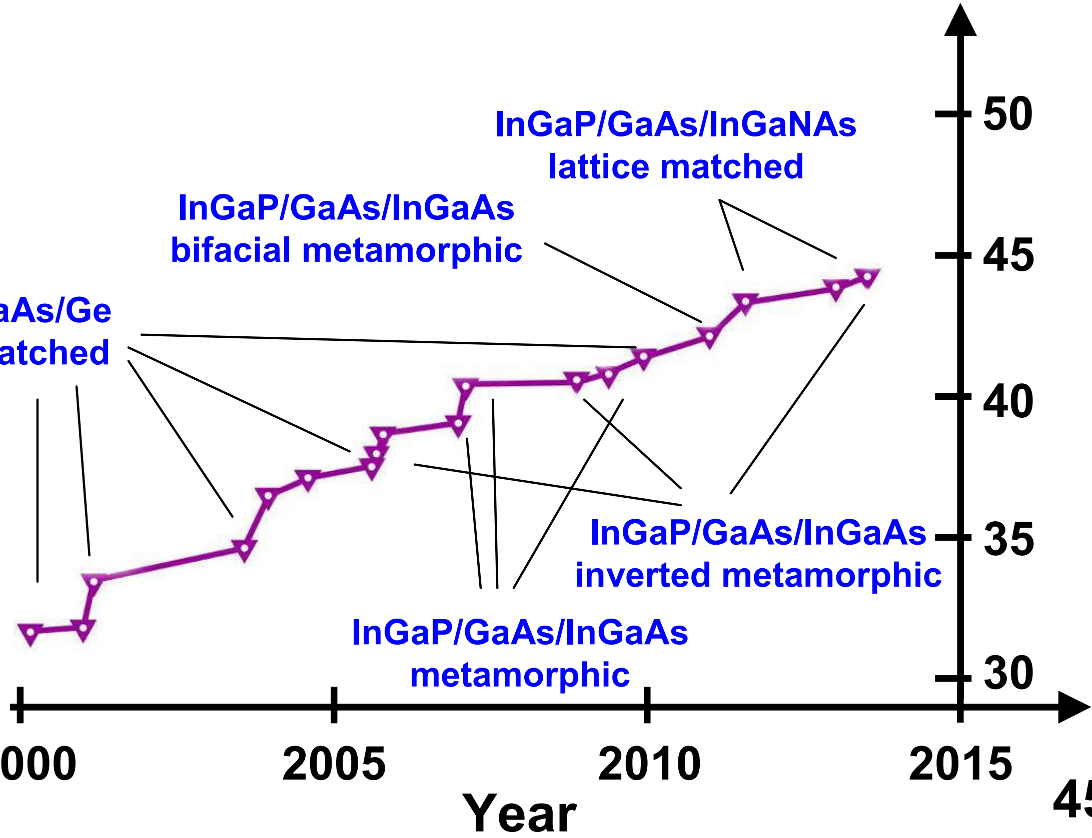
***Use the entire solar spectrum***


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

# Multijunction Solar Cells

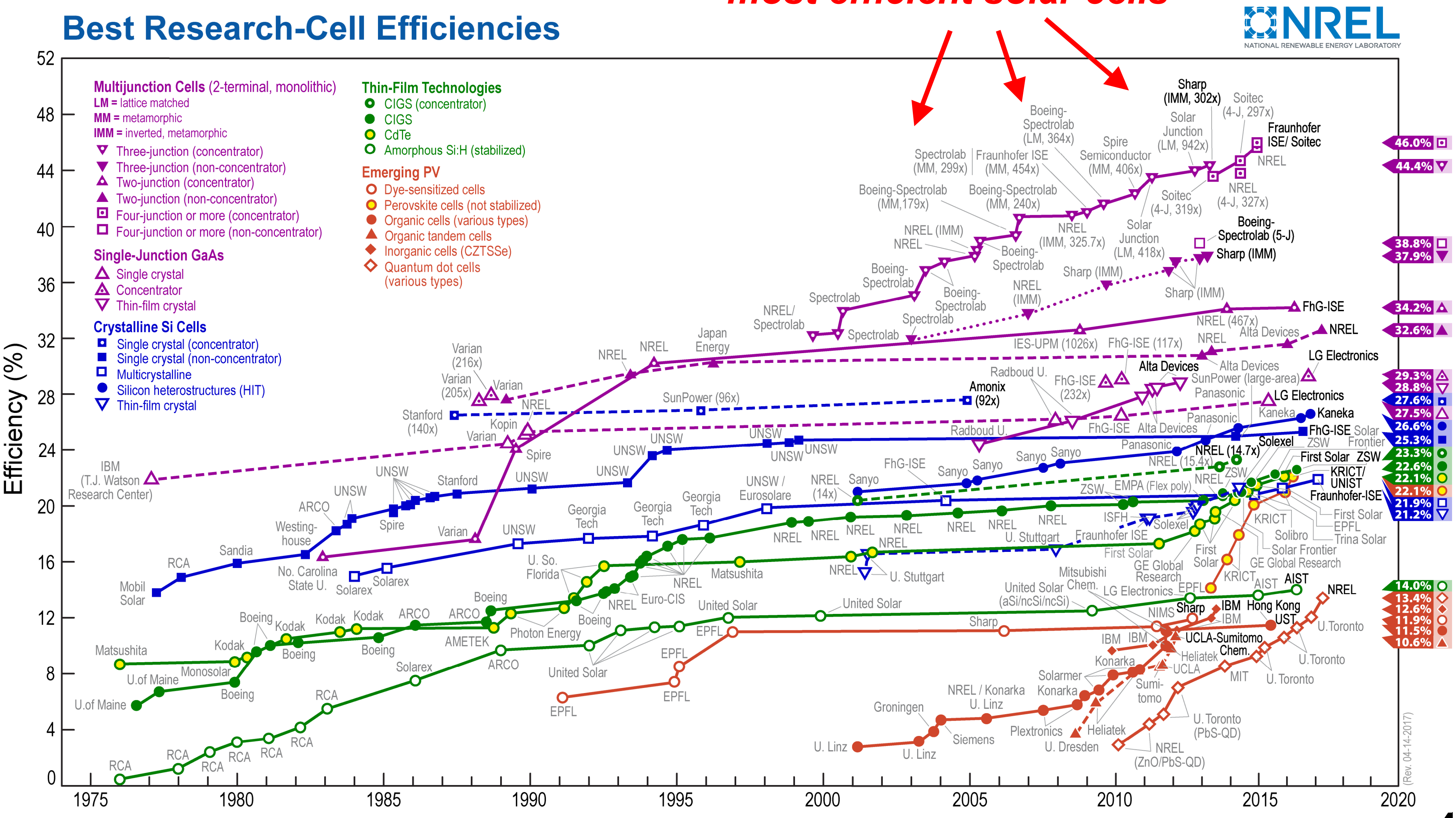
- Lattice matched epi-growth (MOCVD or MBE)
- Current matching
- Suitable bandgaps



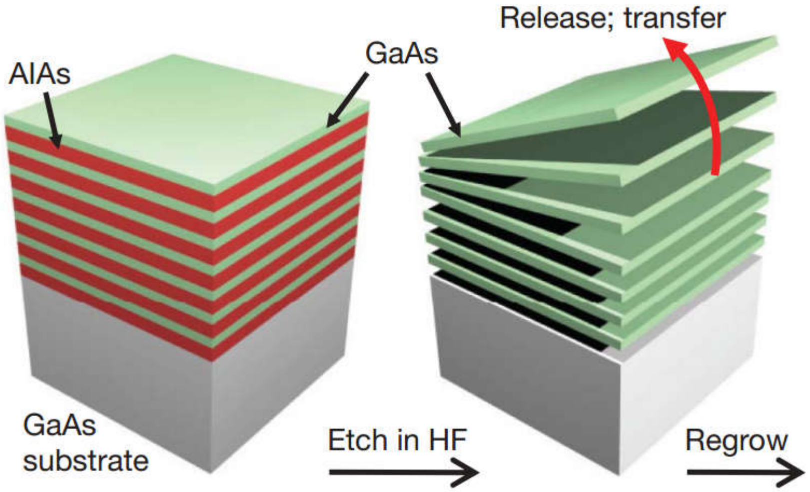
# Multijunction Solar Cells

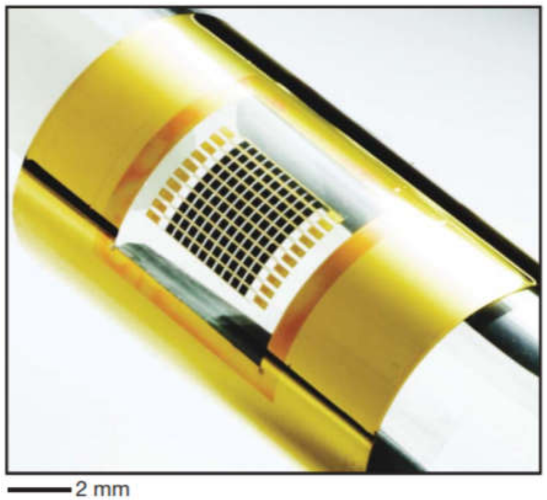
*most efficient solar cells*



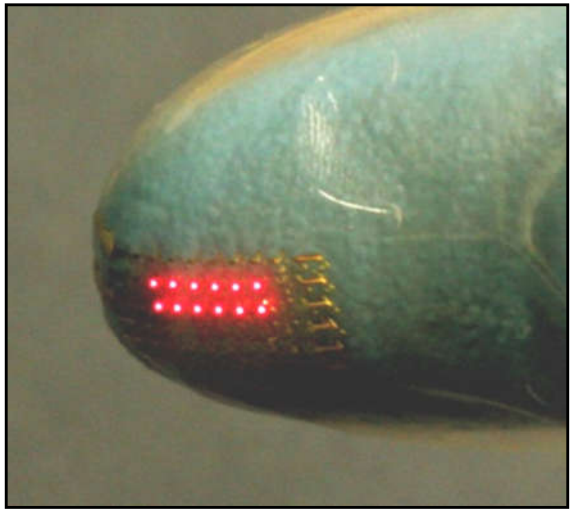
# Epitaxy Liftoff

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

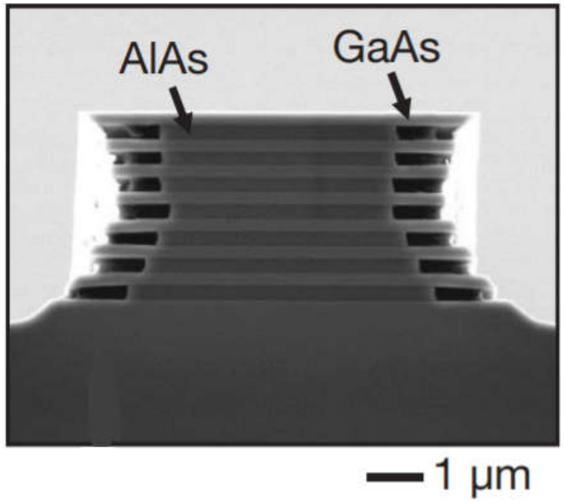



solar cells

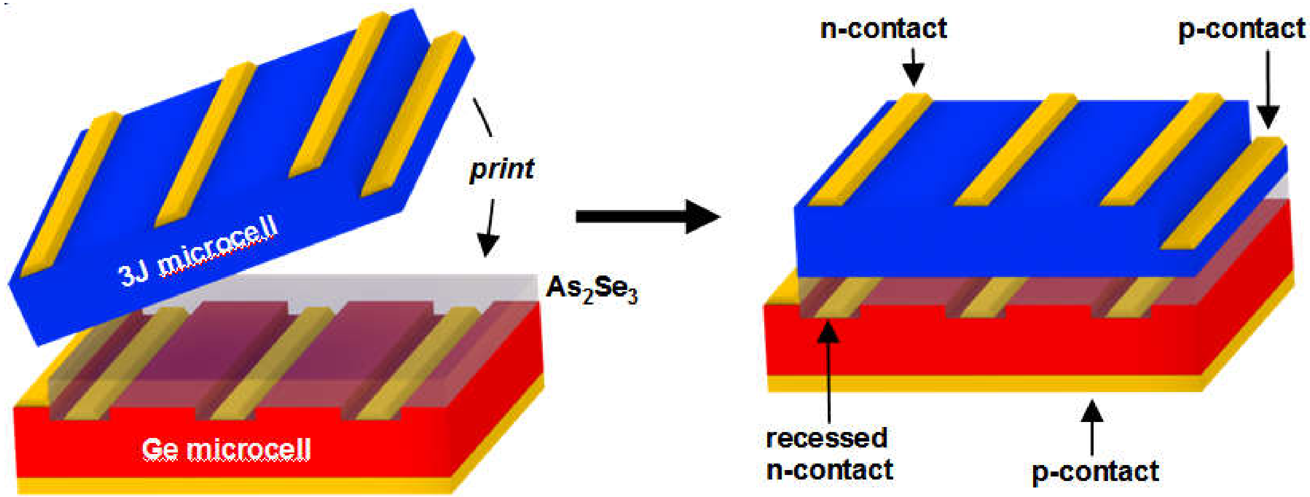


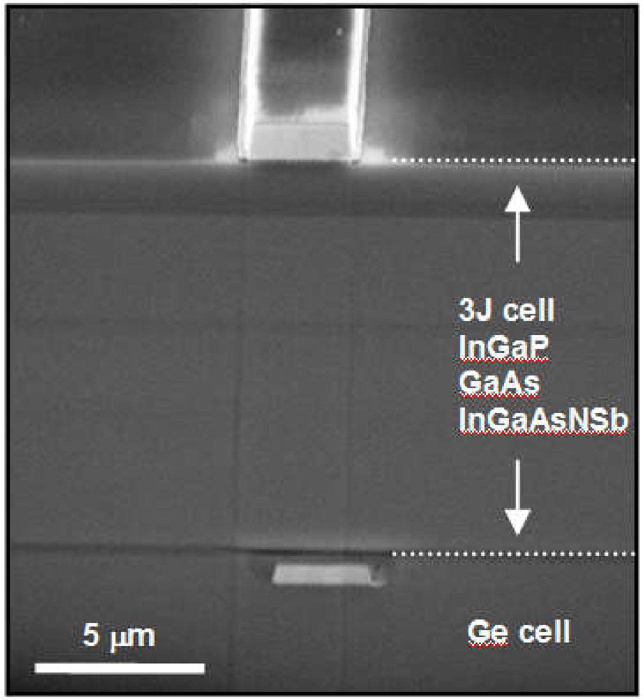
LED

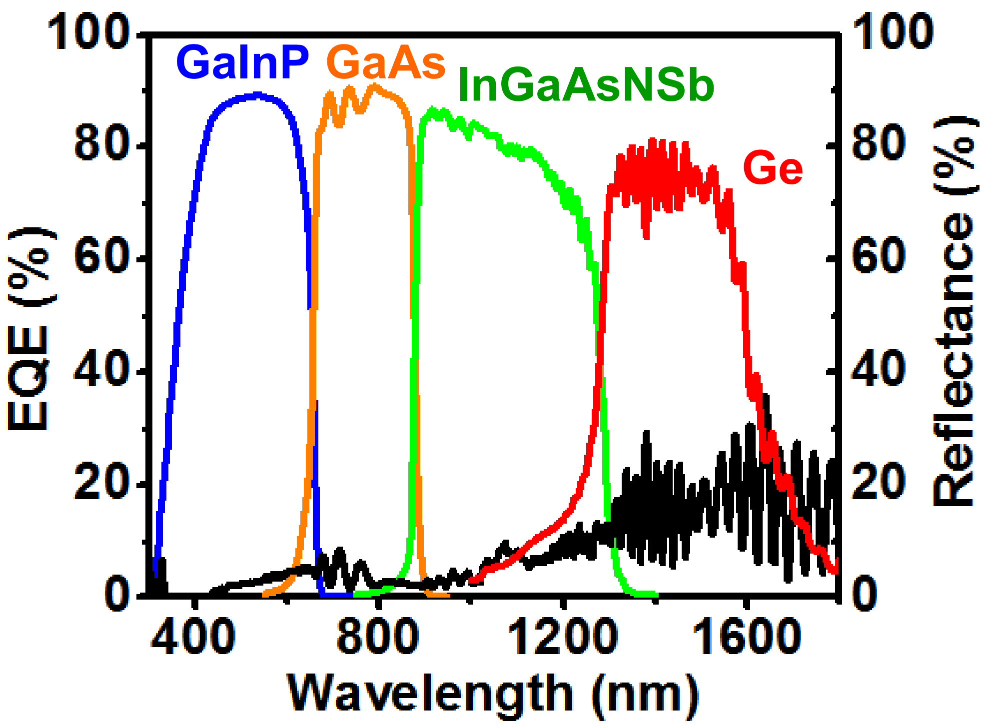



S. I. Park, *et al.*, *Science* **325,** 977 (2009)
J. Yoon, *et al.*, *Nature* **465,** 329 (2010)

# Stacked MJ Solar Cells



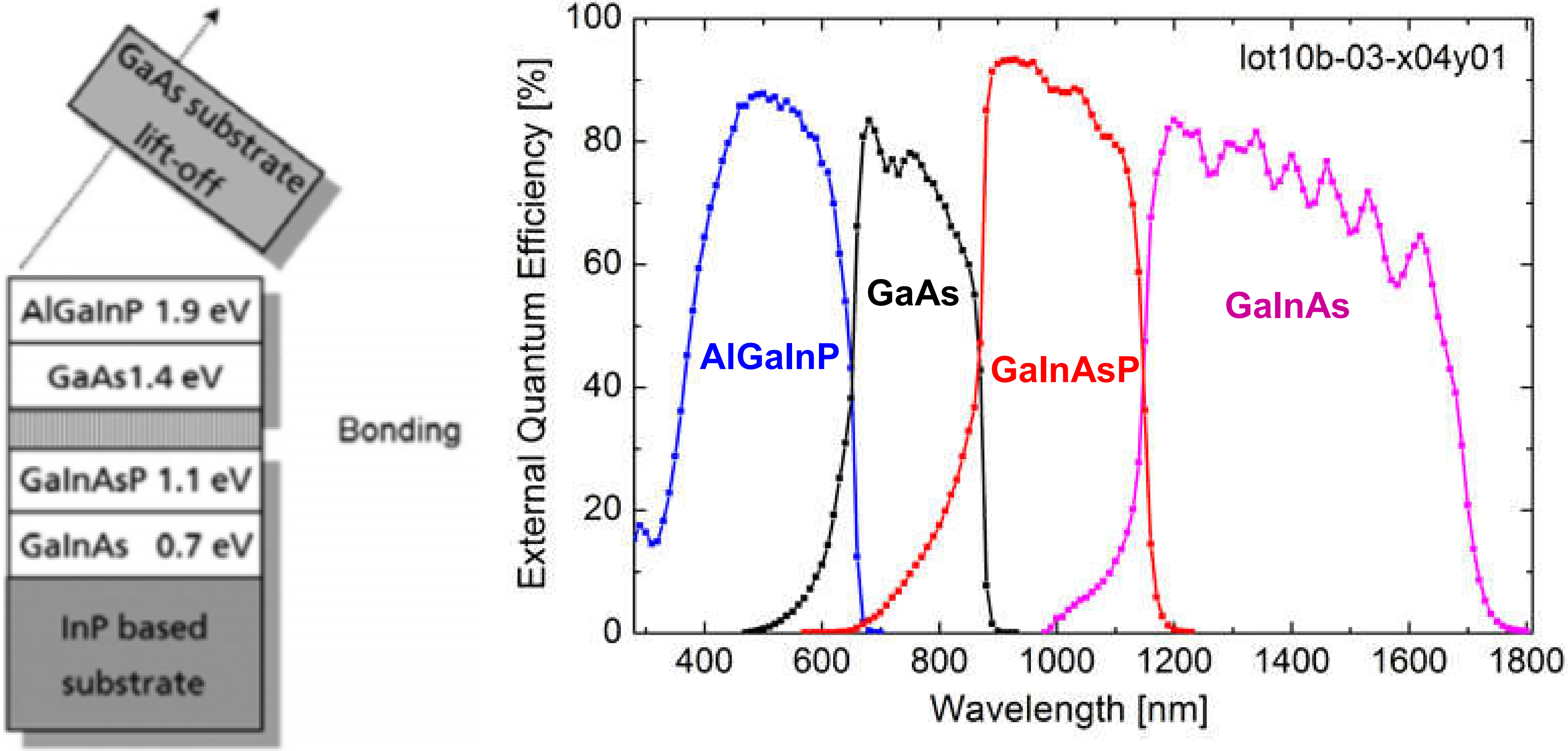

**stacked GaInP/GaAs/InGaAsNSb // Ge solar cells**

***Efficiency: 44%***

X. Sheng, *et al.*, *Nature Mater.* **13**, 593 (2014)

# Stacked MJ Solar Cells

**bonded AlGaInP/GaAs // GaInAsP/GaInAs solar cells**



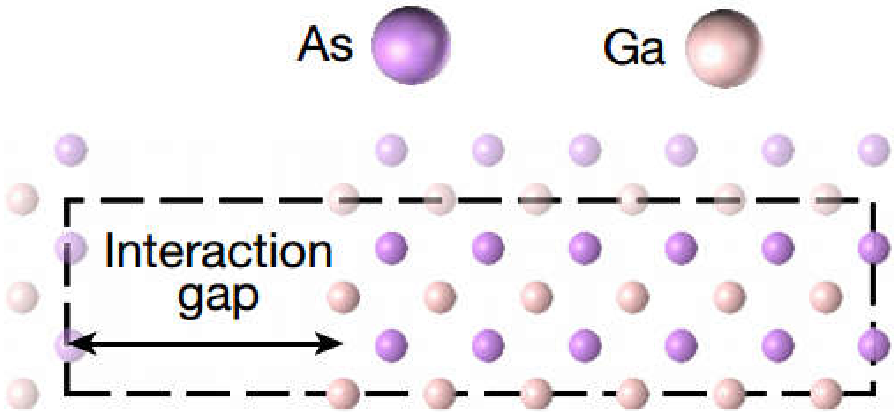

***World record efficiency: 46%***

F. Dimroth, *et al.*, *IEEE J. Photovolt.* **6**, 343 (2016)

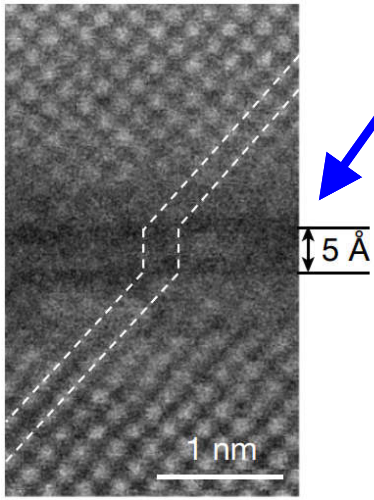
# 'Remote' Epitaxy

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

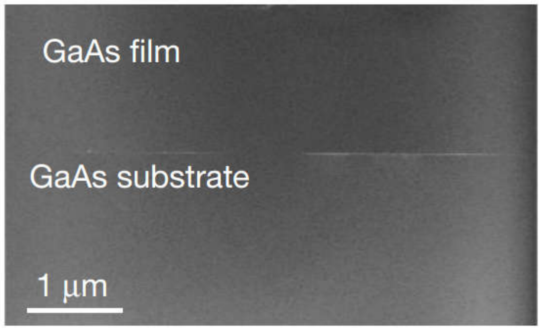
Yunjo Kim[1]*, Samuel S. Cruz[1]*, Kyusang Lee[1]*, Babatunde O. Alawode[1], Chanyeol Choi[1], Yi Song[2], Jared M. Johnson[3], Christopher Heidelberger[4], Wei Kong[1], Shinhyun Choi[1], Kuan Qiao[1], Ibraheem Almansouri[1,5], Eugene A. Fitzgerald[4], Jing Kong[2,6], Alexie M. Kolpak[1], Jinwoo Hwang[3]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

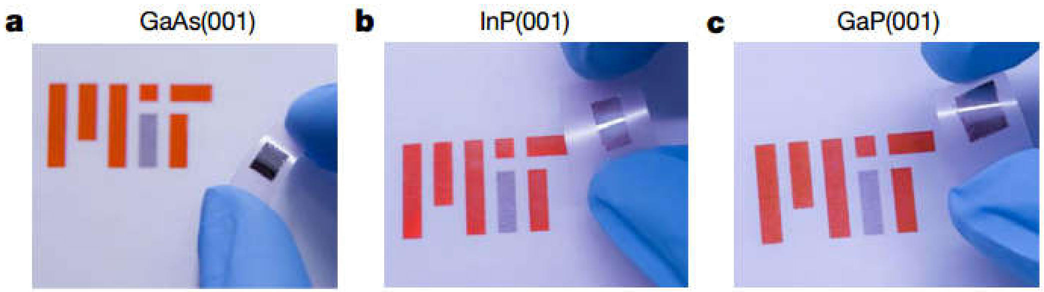







graphene interlayer




Y. Kim, *et al.*, *Nature* **544,** 340 (2017)

***Thank you for your attention***