Crystal Growth: Physics, Technology and Modeling

Stanisław Krukowski & Michał Leszczyński
Institute of High Pressure Physics PAS
01-142 Warsaw, Sokołowska 29/37
e-mail: stach@unipress.waw.pl, mike@unipress.waw.pl

Zbigniew R. Żytkiewicz
Institute of Physics PAS
02-668 Warsaw, Al. Lotników 32/46
E-mail: zytkie@ifpan.edu.pl

Lecture 1. Epitaxy - introduction

22 February 2023

http://w3.unipress.waw.pl/~stach/cg-2022-23/

Epitaxy - introduction

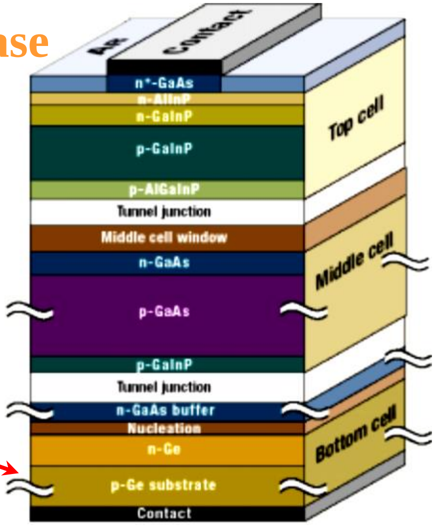
Outline

- **definitions**
- **methods of epitaxial growth**
- **lattice mismatch**
- **thermal strain**
- **antiphase domains (polar on non-polar growth)**
- **some methods to reduce defect density in lattice mismatched epitaxial structures**

bulk crystals

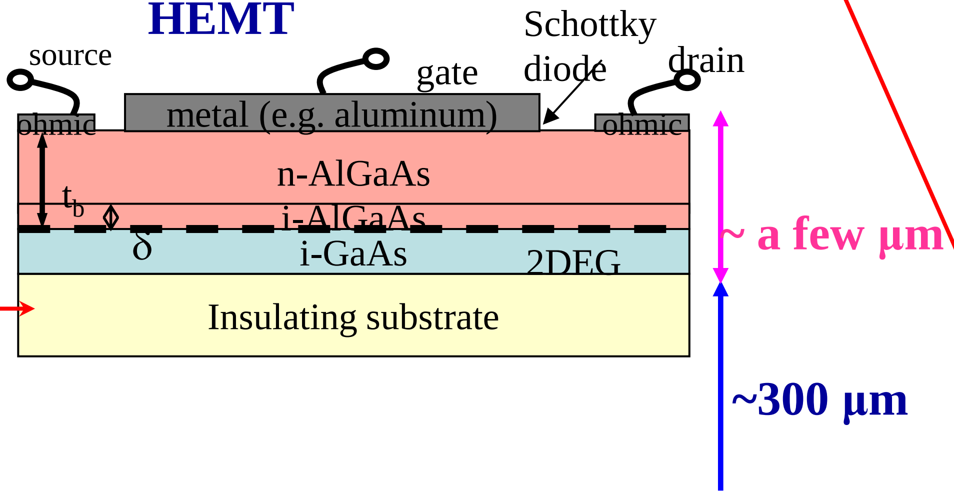
- melt grown
- solution grown
- grown from a gas phase
- ……

solar cell

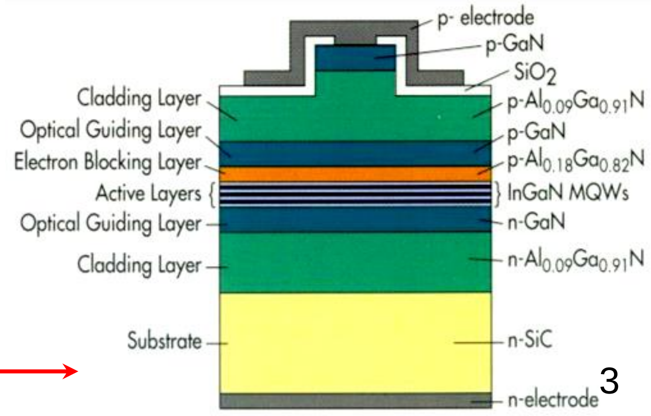


epitaxial structures

HEMT



laser diode



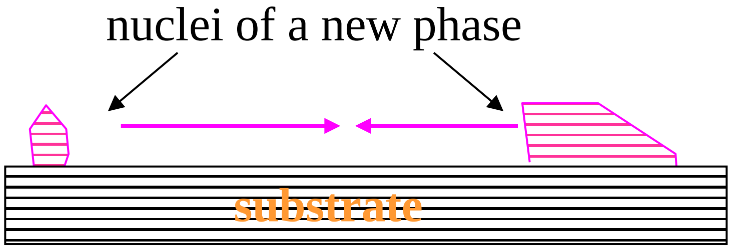
Definitions

- **Epitaxy =** growth of monocrystalline layers on the monocrystalline substrate in the way that crystalline structure of the layer is determined by the structure of the substrate

***epi* = on (above)**
***taxis* = an ordered manner**

MnTe(hex)/sapphire
MnTe(cub)/GaAs

GaN(hex)/ sapphire
GaN(cub?)/GaAs

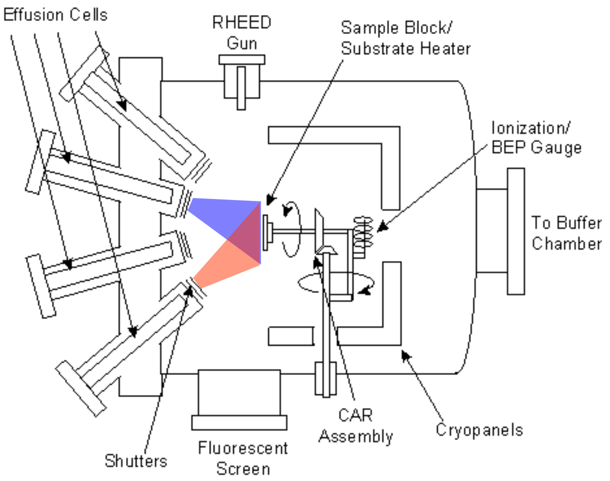


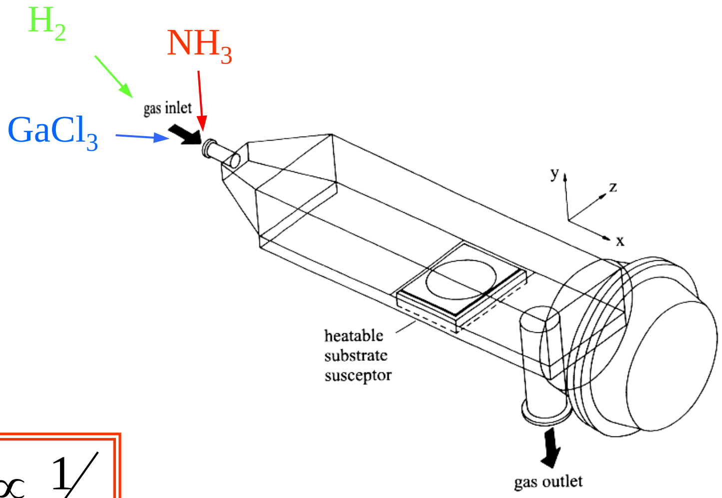
- **Homoepitaxy =** the layer and the substrate are the same
- **Heteroepitaxy =** the layer and the substrate are different (e.g. they differ by chemical composition)

Methods of epitaxial growth

- **Epitaxy from a gas phase (MBE, VPE, MOVPE, HVPE, ...)** $V_{gr} \sim \mu m/h$

next lectures: Z.R. Żytkiewicz i M. Leszczyński





$$\lambda_{swobodna} \propto {}^{1}\!/_{p}$$

non-equilibrium methods

in situ growth analysis possible

- **Liquid phase epitaxy (LPE, LPEE, ...)** $V_{gr} \sim \mu m/min$

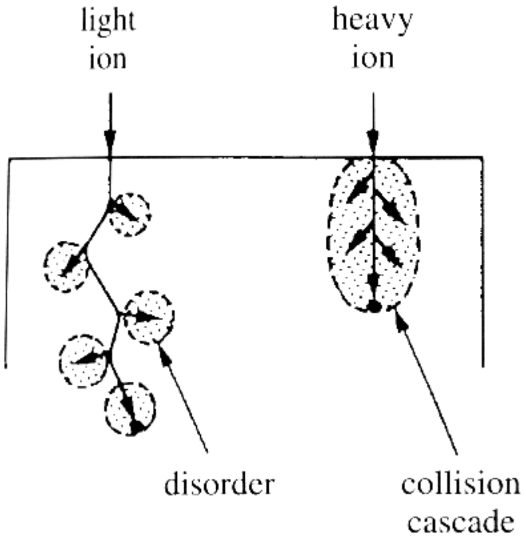
lecture: Z.R. Żytkiewicz 5 April 2023

Solid Phase Epitaxy

mass transport mechanism – solid state diffusion

Examples:

post implantation annealing



low-temperature buffer AlN (GaN)
(2-step growth)

GaN growth w/o the buffer
T ~ 1000°C

AlN nucleation
T ~ 600°C

atoms on the surface are mobile

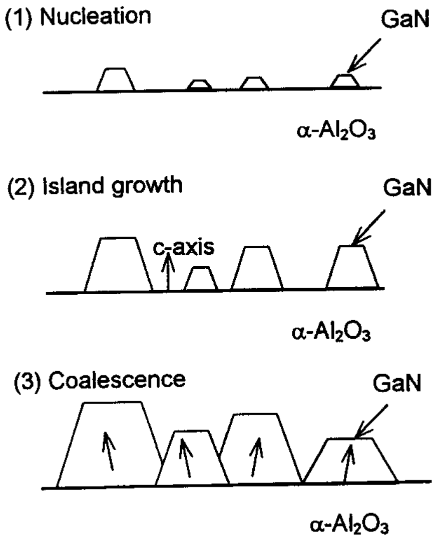


Figure 9. Schematic diagrams of the growth process of GaN on sapphire without an AlN buffer layer.

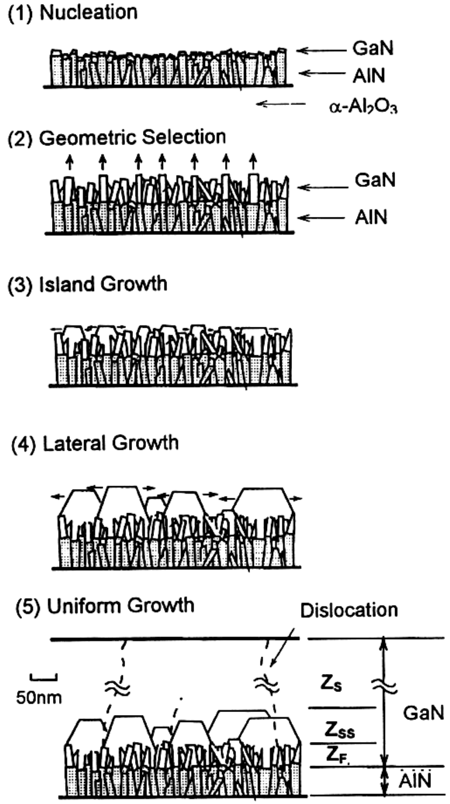
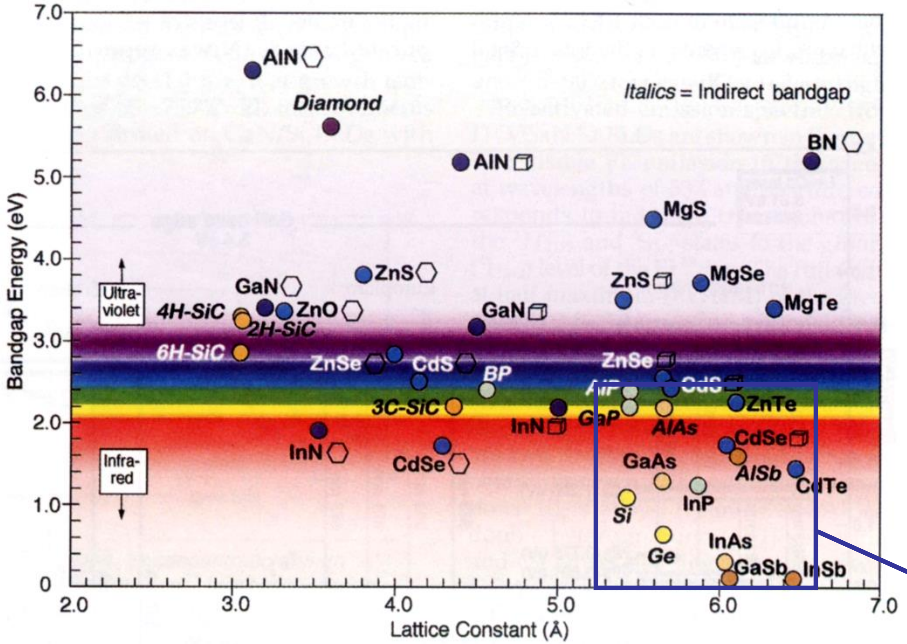


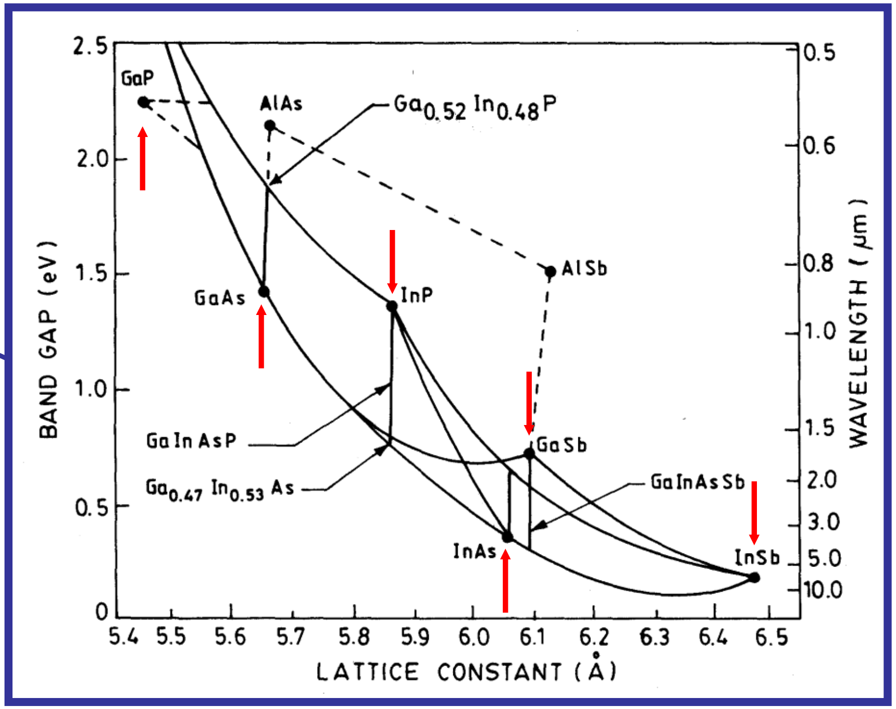
Figure 10. Schematic diagrams of the growth process of GaN on sapphire with an AlN buffer layer.

Lattice mismatch



advantage of multicomponent systems

a = f(composition)



limited number of available substrate crystals!!!

epitaxy of layers lattice mismatched to the substrate - the most common case

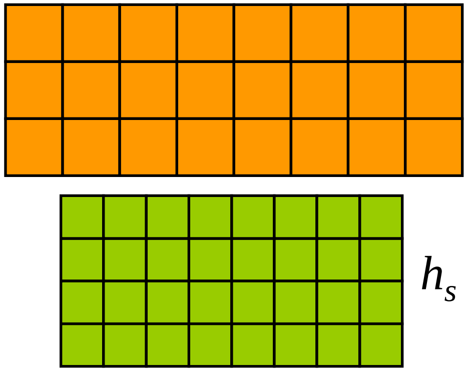
Lattice mismatch

assumptions: $\boxed{h_s = \infty}$ $\boxed{h_e < h_{cr}}$ $\boxed{a_e^{relax} > a_s}$

before epitaxy

after epitaxy

layer a_e^{relax}

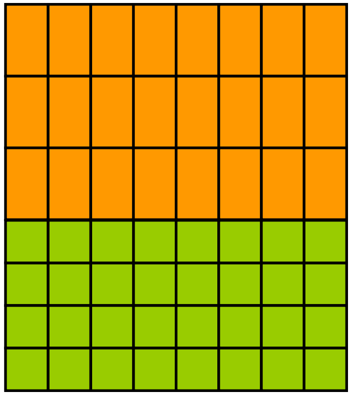


h_e

$h_s = \infty$

substrate a_s

strained layer



$a_e^{\parallel} = a_s < a_e^{relax}$

compression in the layer

$a_e^{\perp} > a_e^{relax}$

tetragonal lattice distortion

lattice misfit

$$\boxed{f = (a_e - a_s)/a_s}$$

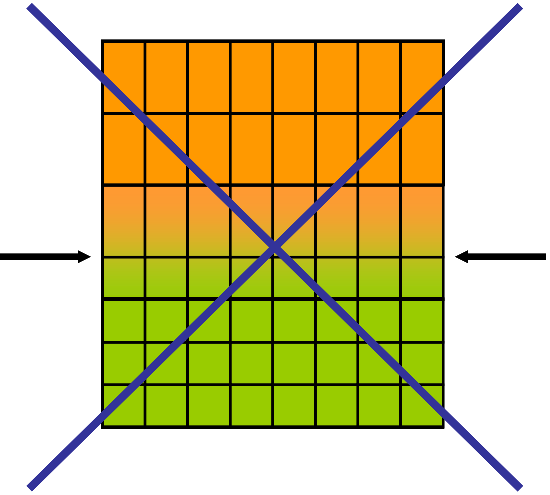
strain energy in the layer

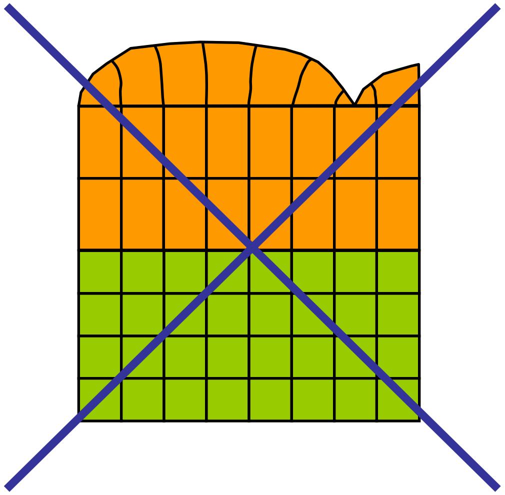
$$\boxed{E_{el} \propto f^2 \cdot h_e}$$

How to reduce lattice mismatch induced strain energy ?

interdiffusion

surface deformation



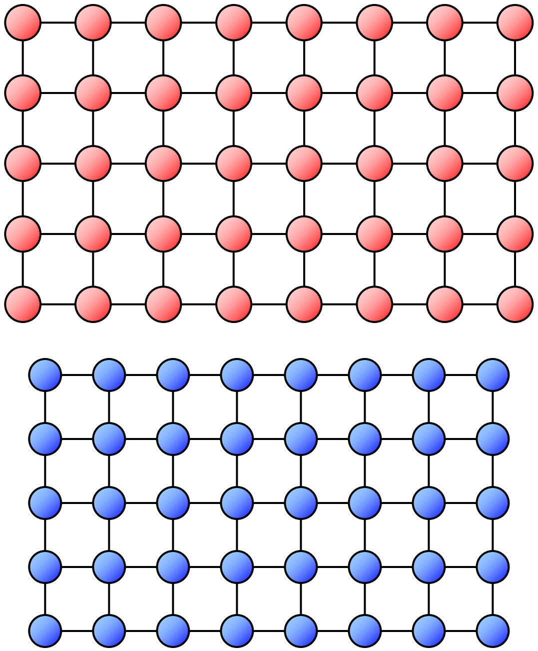


- very slow process
- less important in “thick” films
- important in nanostructures

- lattice relaxation at the surface
- important in nanostructures (QDs)
- less important in “thick” films

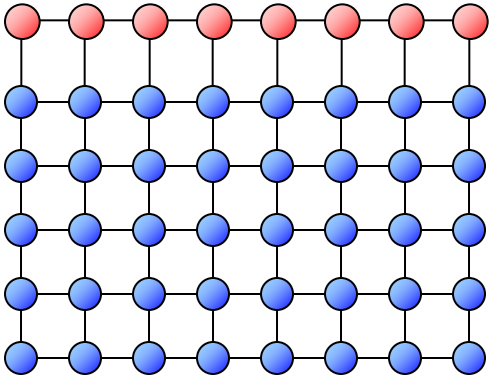
Generation of misfit dislocations

(misfit dislocations - MD)



separate A and B a(B) > a(A)

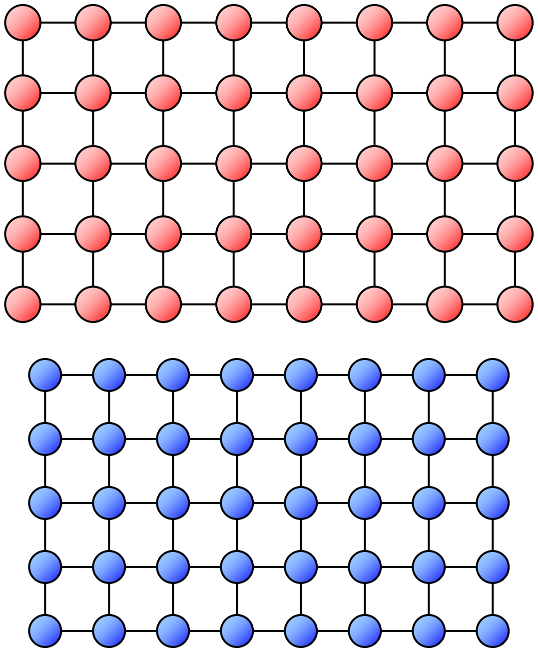
$E_e < E_D$ **pseudomorphic growth**



epitaxy of B on substrate A

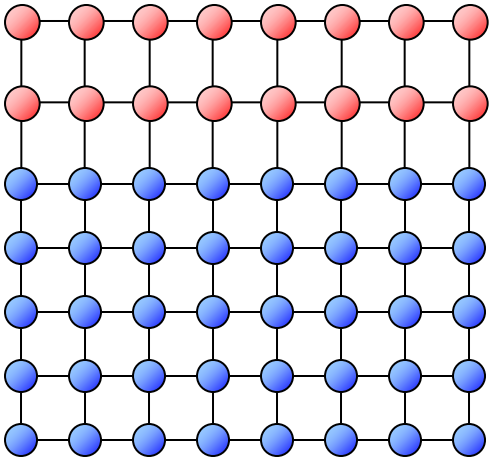
Generation of misfit dislocations

(misfit dislocations - MD)

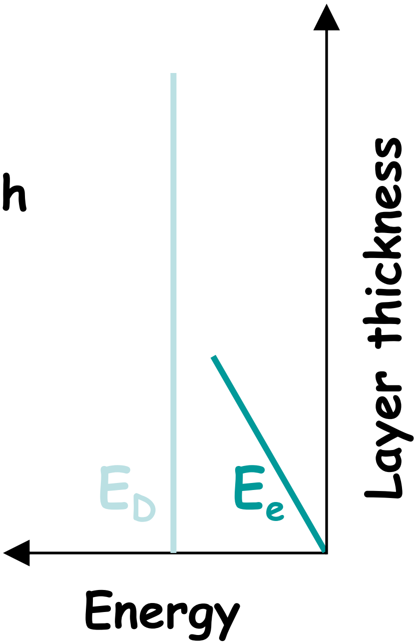


separate A and B a(B) > a(A)

$E_e < E_D$ **pseudomorphic growth**



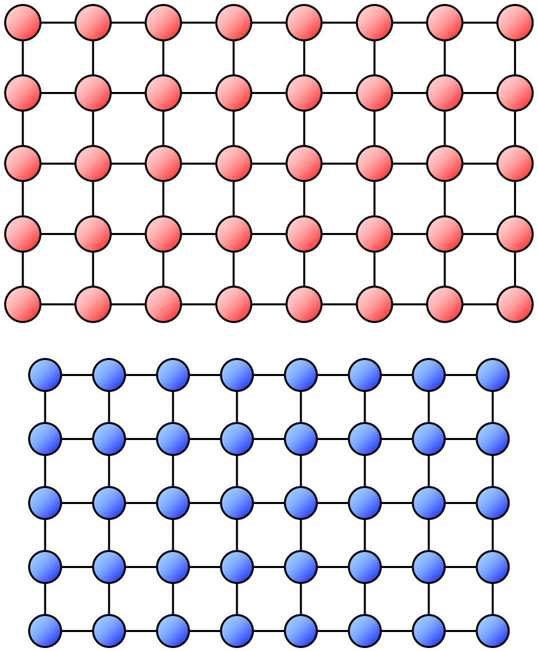
epitaxy of B on substrate A



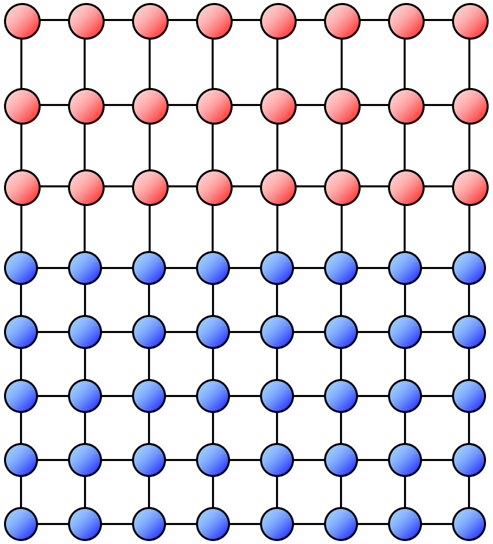
Generation of misfit dislocations

(misfit dislocations - MD)

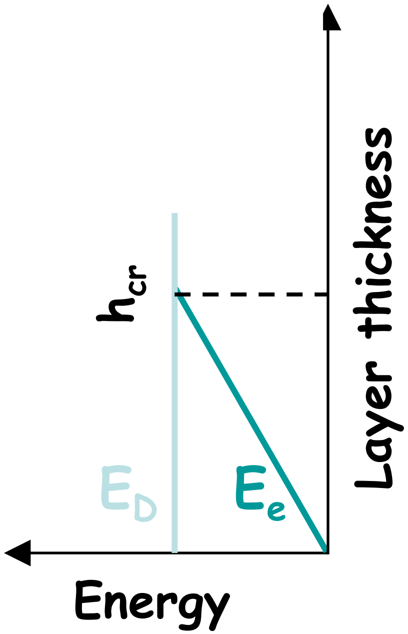
$E_e = E_D$



separate A and B a(B) > a(A)

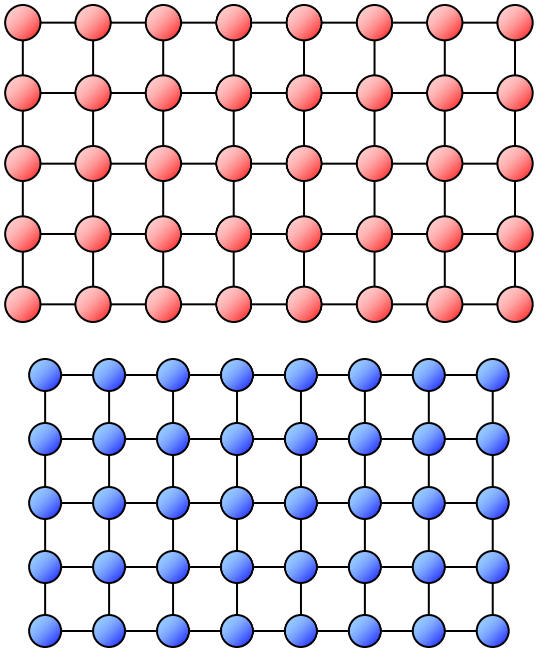


epitaxy of B on substrate A



Generation of misfit dislocations

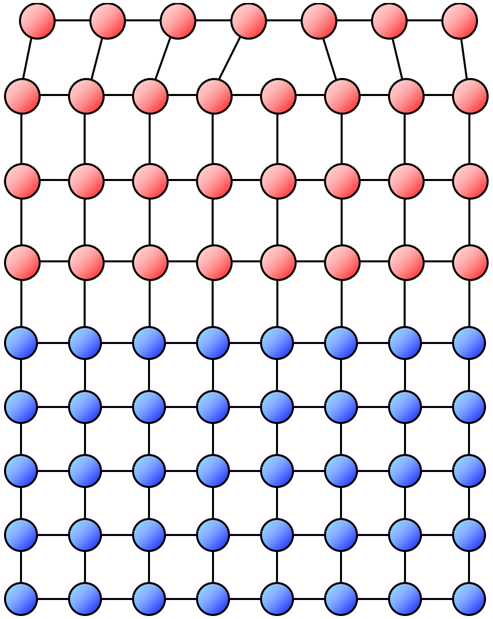
(misfit dislocations - MD)

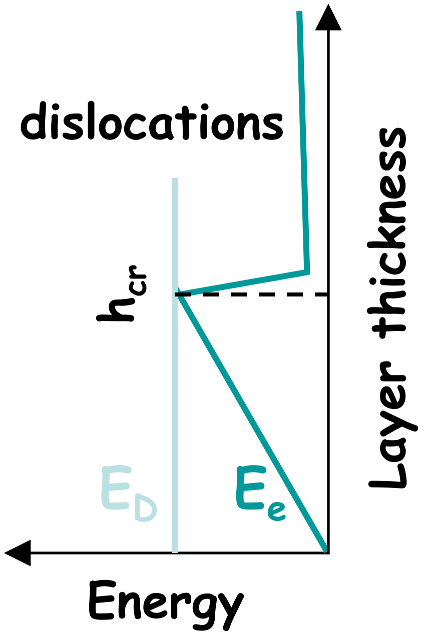


separate A and B a(B) > a(A)

E_e > E_D

relaxation - generation of dislocations

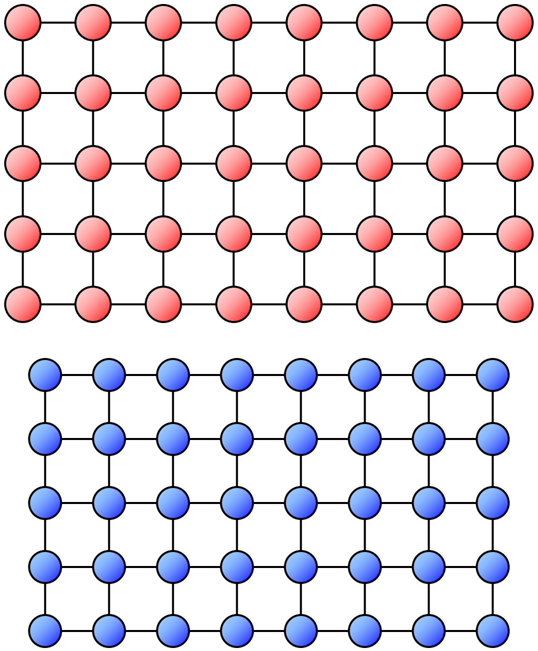




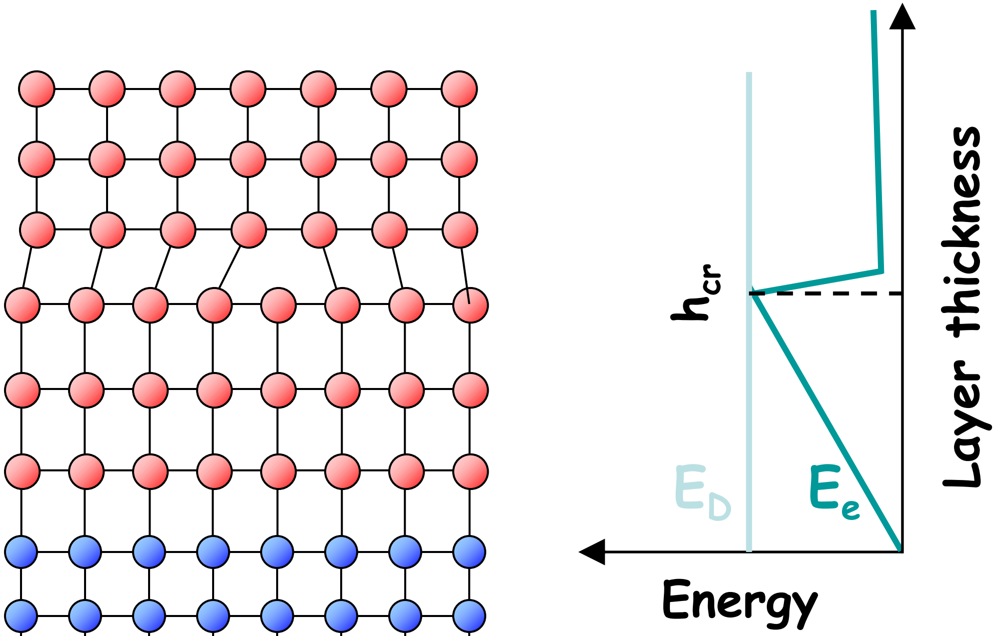
epitaxy of B on substrate A

Generation of misfit dislocations

(misfit dislocations - MD)



separate A and B a(B) > a(A)



epitaxy of B on substrate A

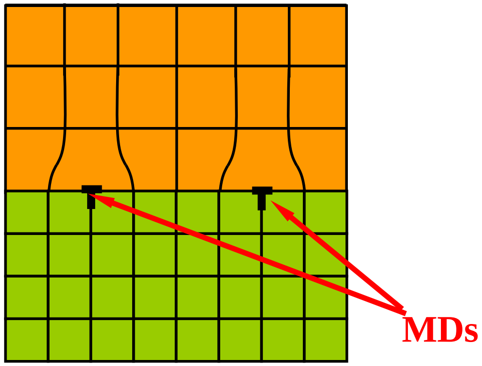
Generation of misfit dislocations

(misfit dislocations - MD)

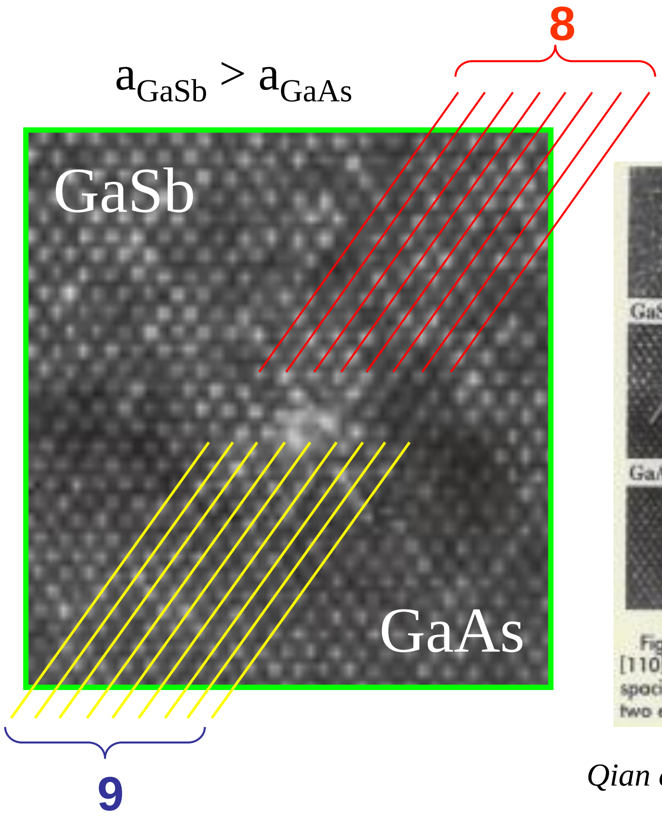
layer with misfit dislocations

$$\boxed{h_e > h_{cr}}$$

$$a_e^{II} \approx a_e^{\perp} \approx a_e^{relax}$$



$a_{GaSb} > a_{GaAs}$



Example: GaSb na GaAs

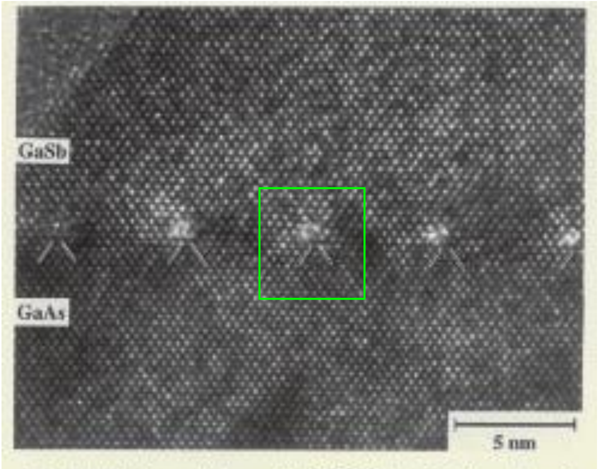


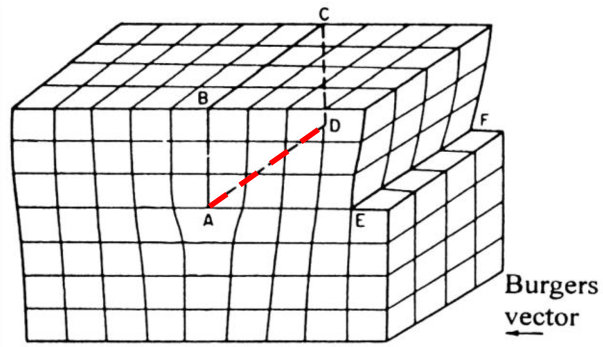
Fig. 1. Lattice image taken at the GaSb/GaAs interface along the [110] direction. A periodic array of 90° misfit dislocations with spacing of 5.7 nm are shown. Each dislocation is associated with two extra {111} planes as marked.

Qian et al. J. Electrochem. Soc. 144 (1997) 1430

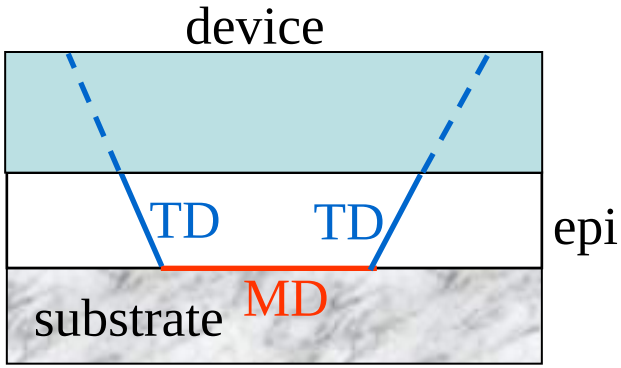
Do we like misfit dislocations ?

Threading dislocations

Dislocations cannot terminate inside the perfect crystal



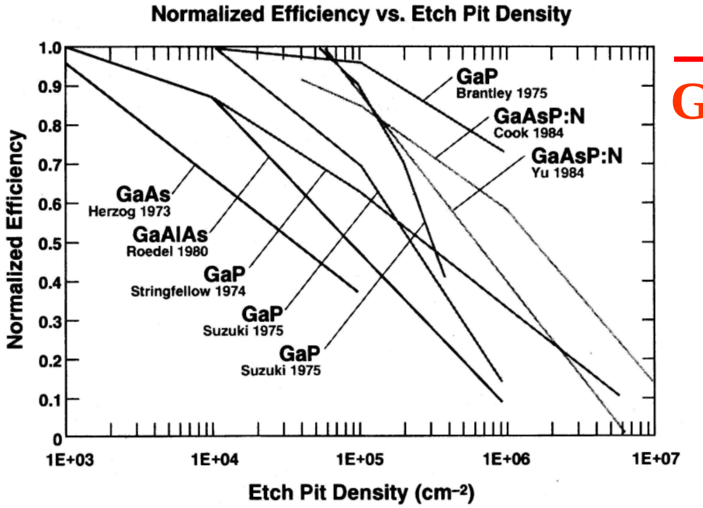
edge dislocations A-D;



MD = misfit dislocation
TD = threading dislocation

TD dislocations induce nonradiative recombination

Lester et al. APL 66 (1995) 1249



GaN

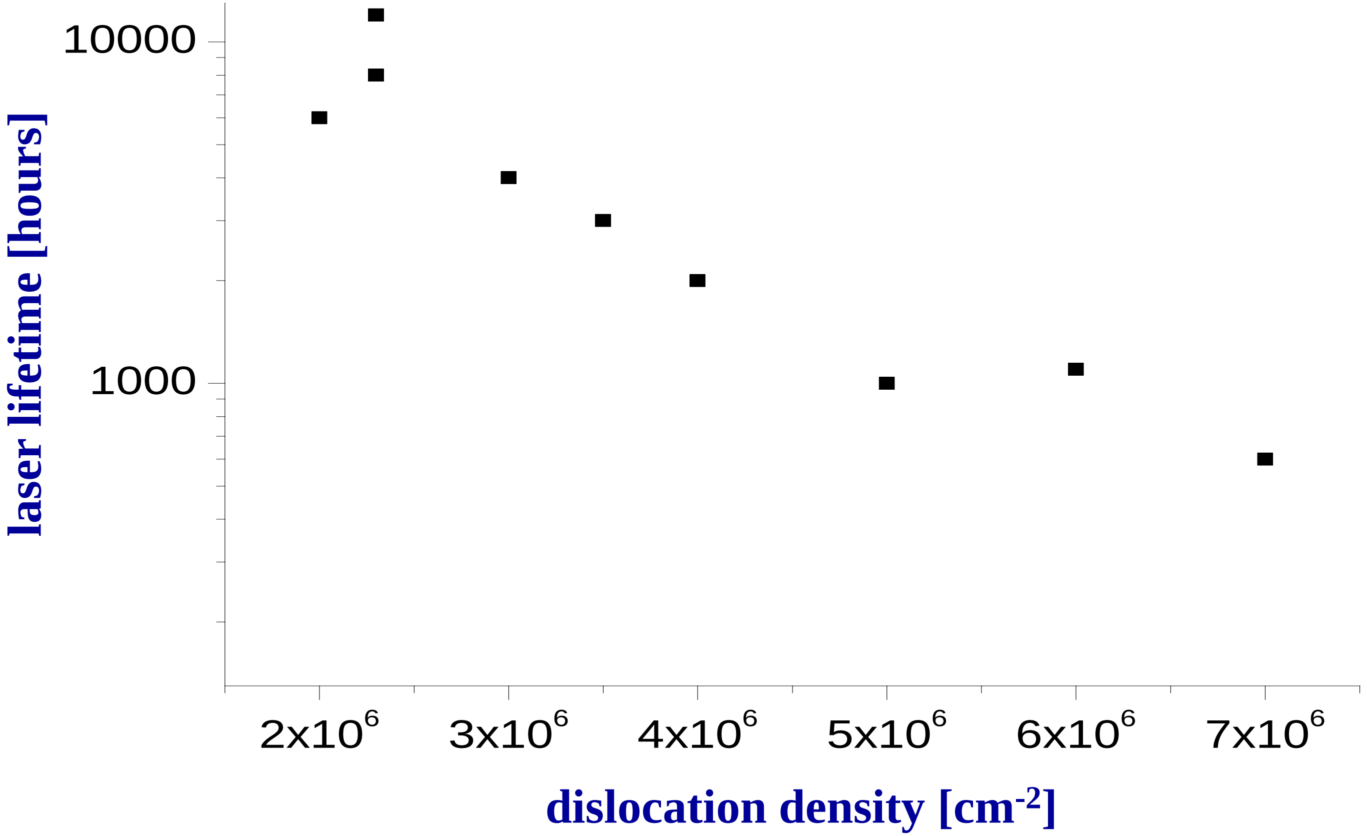
Fig. 3 Dependence of LED efficiency on dislocation density for devices made with a wide range of III–V materials [11].

catastrophic degradation

Do we like misfit dislocations ?

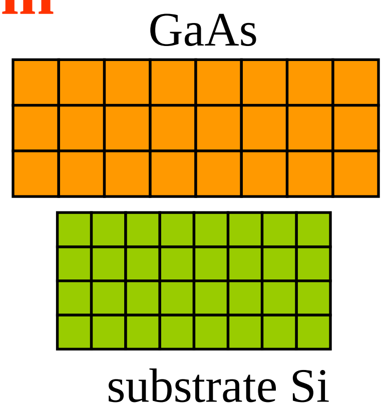
Threading dislocations

Lifetime of GaN/InGaN laser diodes as a function of dislocation density (from Sony)



Thermal strain

~~$a_{GaAs} > a_{Si} \Rightarrow$ compressive strain in GaAs grown on Si (???)~~



$$\varepsilon_{th} = (\alpha_{GaAs} - \alpha_{Si}) \cdot (T_{GT} - T_{RT})$$

tensile strain in GaAs on Si

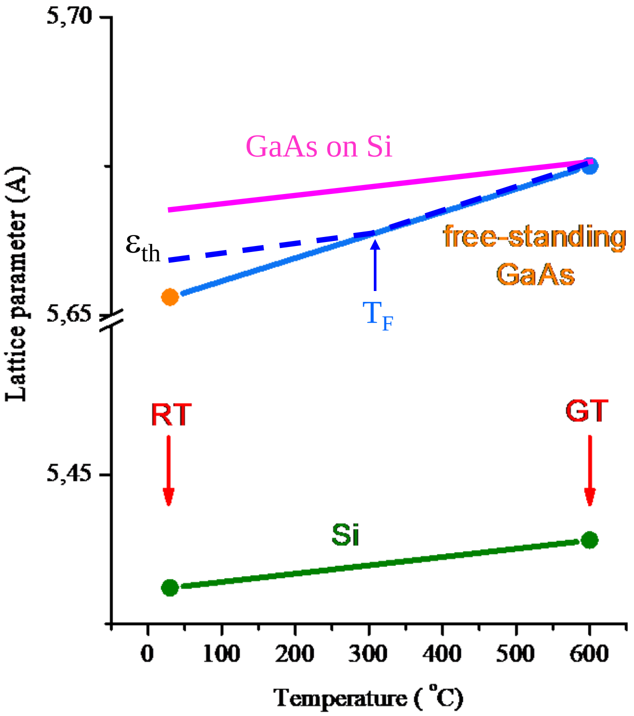
T_F

$$T_F = 450 \pm 90^o C \rightarrow GaAs/Si$$

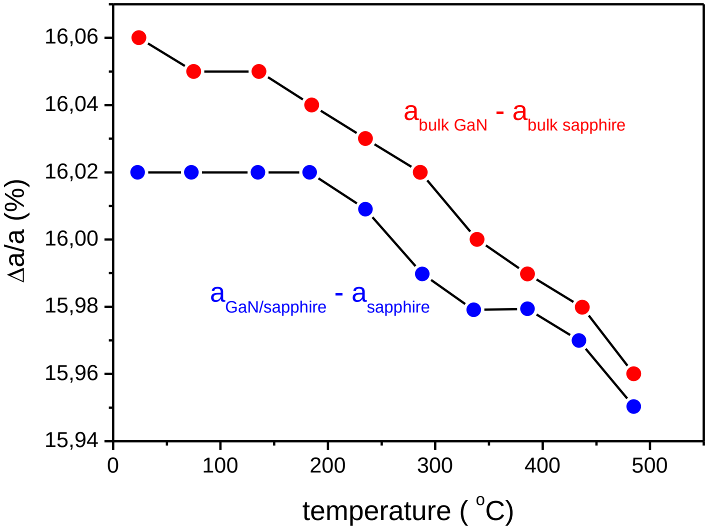
$$T_F = 250 \pm 100^o C \rightarrow InP/Si$$

Yamamoto & Yamaguchi '88

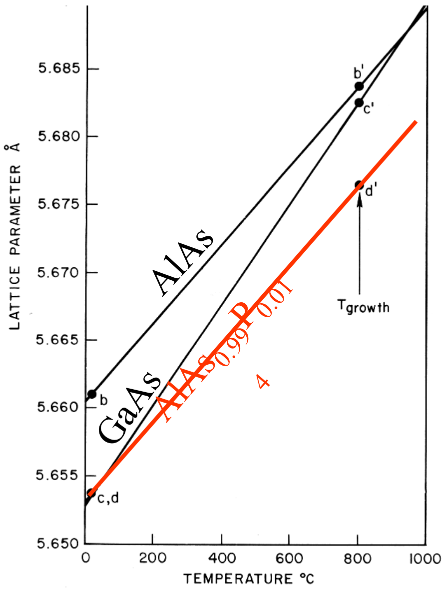
residual thermal strain

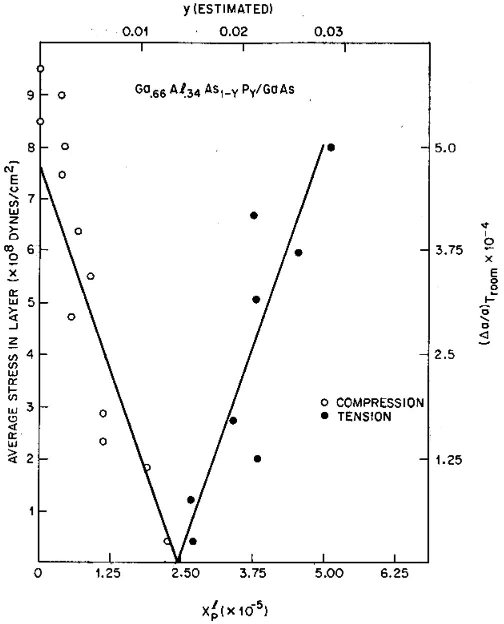


GaN/sapphire *Leszczynski et al. JAP '94*



Thermal strain cont.





- Laser DH GaAlAs/GaAs

Rozgonyi, Petroff, Panish JCG 27 (1974) 106.

AlGaAs/GaAs -

considered as an ideal laser system -

perfect lattice matching

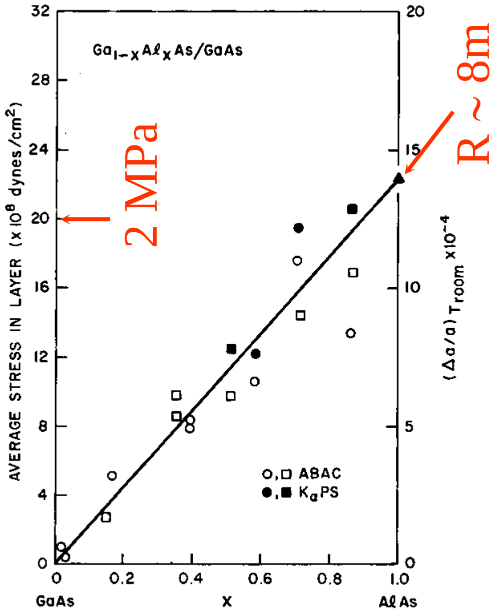


Fig. 6. Average film stress versus Al content data determined by ABAC (open circles and squares) and KαPS (solid circles and squares) techniques. Solid triangle at $x = 1.0$ is after Ettenberg and Paff[7].

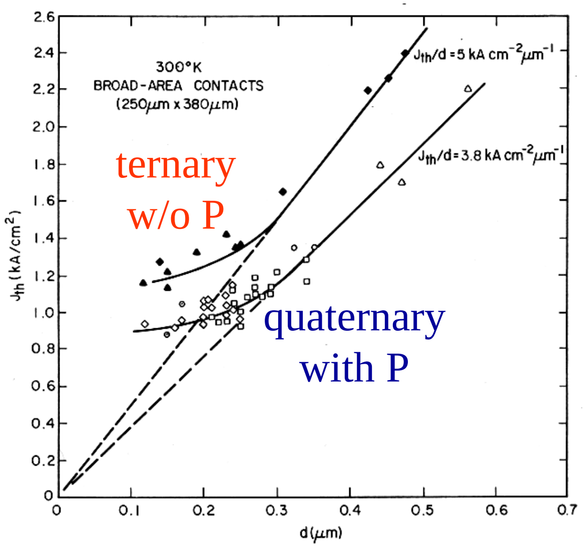


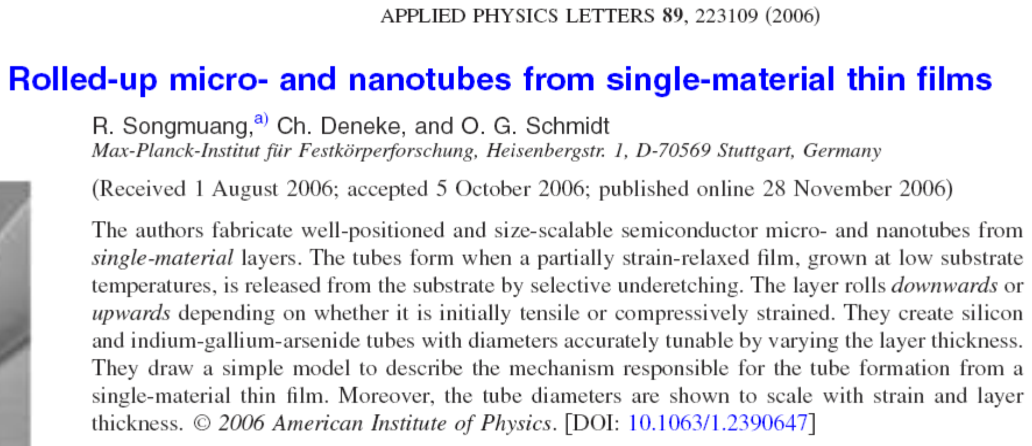
Fig. 12. Comparison of threshold current density data versus active GaAs layer thickness for lasers with ternary (closed symbols) and quaternary (open symbols) waveguiding layers (see text).

- GaAs on Si -

cracking of GaAs layers thicker than ~ 10 µm

10^9 dyn/cm^2 = 100 MPa

Lattice mismatch strain - application



APPLIED PHYSICS LETTERS **89**, 223109 (2006)

Rolled-up micro- and nanotubes from single-material thin films

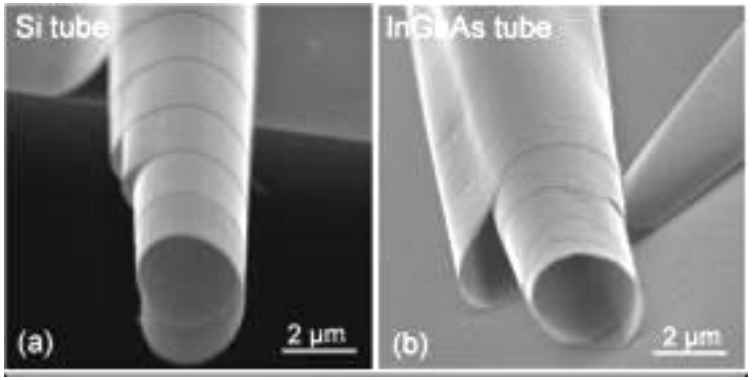
R. Songmuang,[a] Ch. Deneke, and O. G. Schmidt
Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany

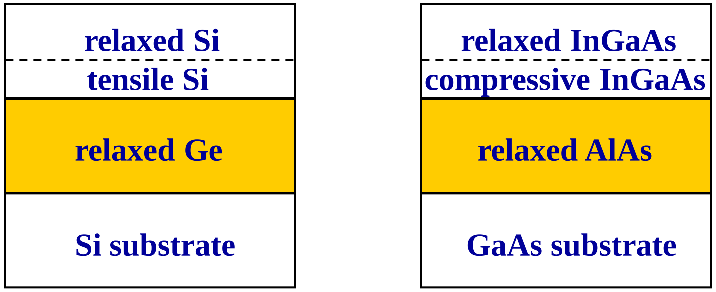
(Received 1 August 2006; accepted 5 October 2006; published online 28 November 2006)

The authors fabricate well-positioned and size-scalable semiconductor micro- and nanotubes from *single-material* layers. The tubes form when a partially strain-relaxed film, grown at low substrate temperatures, is released from the substrate by selective underetching. The layer rolls *downwards* or *upwards* depending on whether it is initially tensile or compressively strained. They create silicon and indium-gallium-arsenide tubes with diameters accurately tunable by varying the layer thickness. They draw a simple model to describe the mechanism responsible for the tube formation from a single-material thin film. Moreover, the tube diameters are shown to scale with strain and layer thickness. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2390647]

$a_{Si} < a_{Ge}$

$a_{InGaAs} > a_{AlAs}$

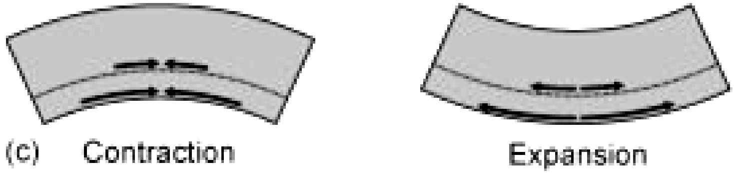


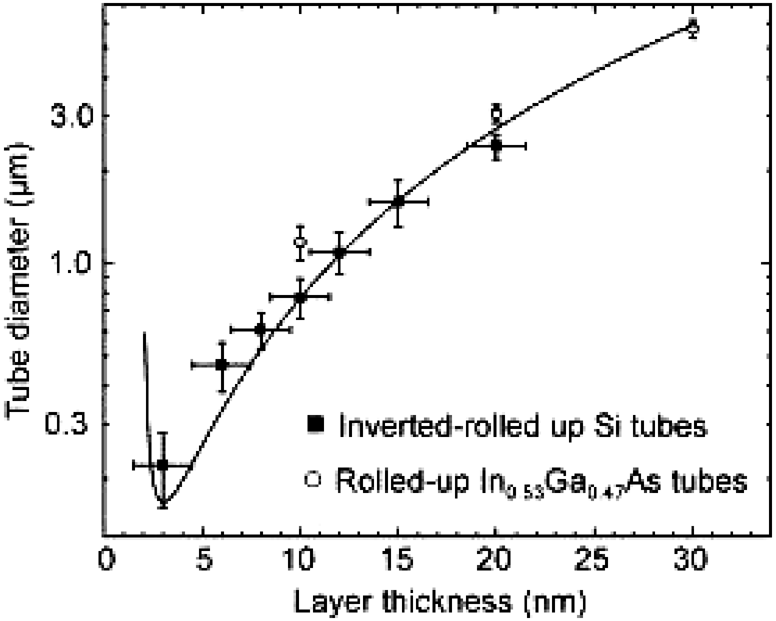


relaxed Si
tensile Si
relaxed Ge
Si substrate

relaxed InGaAs
compressive InGaAs
relaxed AlAs
GaAs substrate

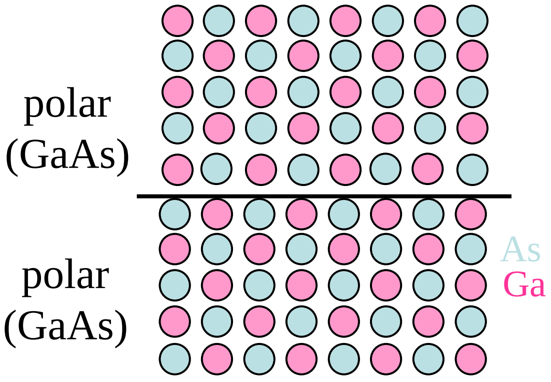
after release by etching 🟨

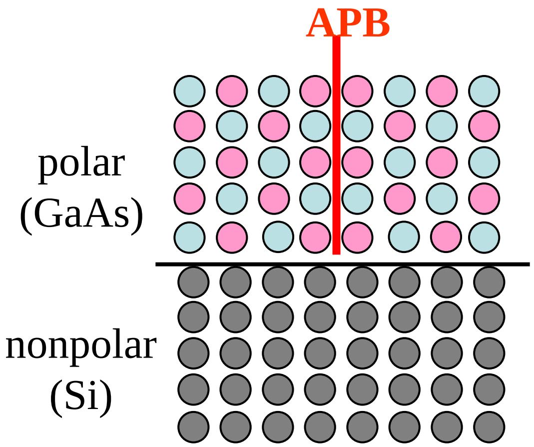




Antiphase domains (polar on nonpolar)

(antiphase domain boundaries - APB)





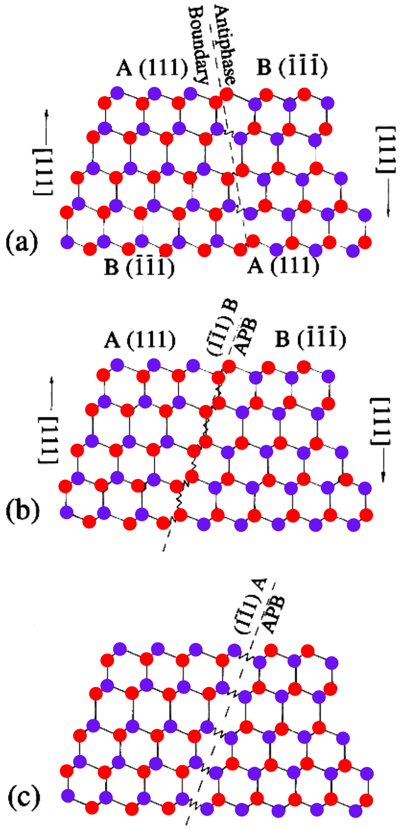
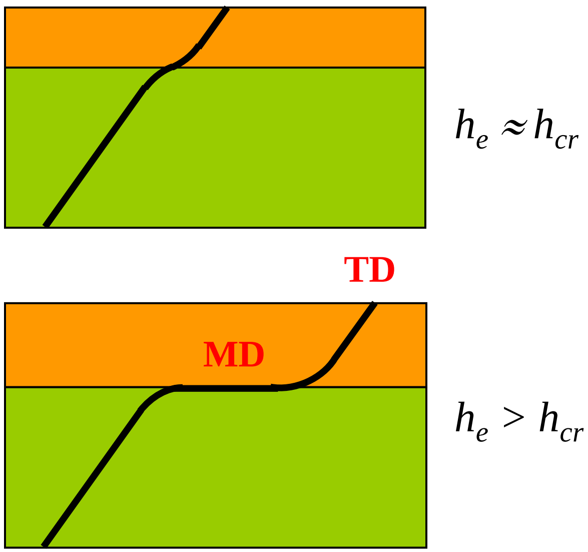


Fig. 2.11. Antiphase boundaries in the sphalerite structure [shown in the (1$\bar{1}$0) projection]. Zig-zag lines denote wrong bonds. (**a**) Type I APB on the ($\bar{1}\bar{1}$3) plane; (**b**) type II APB on the ($\bar{1}$1$\bar{1}$) plane involving wrong *B*-*B* bonds only and an excess of *B* atoms; (**c**) type II APB involving wrong *A*-*A* bonds with an excess of *A* atoms (taken from [2.20])

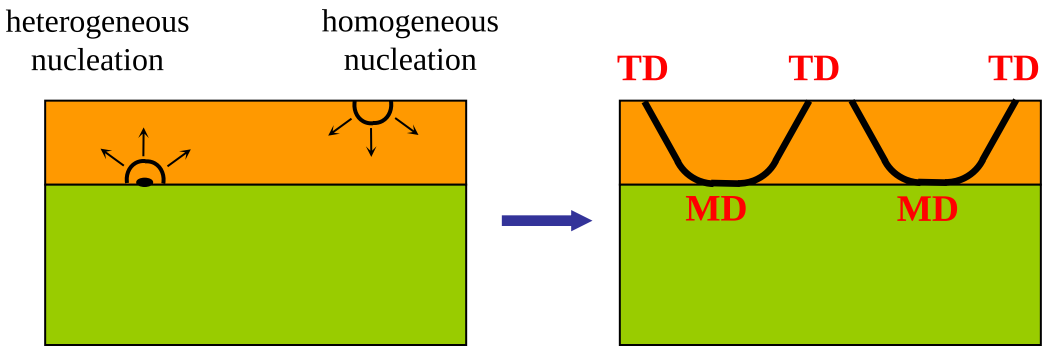
some tricks are needed (e.g. annealing of Si (111) substrate) to reduce density of APB

Generation of misfit dislocations: the mechanisms

bending of substrate TDs



generation of dislocation half-loops



$$N_{TD} \propto {}^{2}\!/_{l_{av}}$$

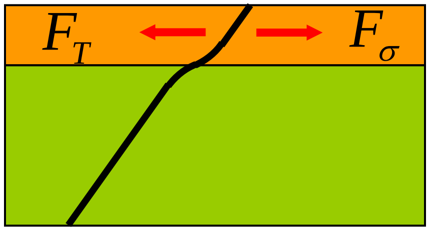
l_{av} - length of MD segment
$Ge_{0.25}Si_{0.75}$/Si l_{av} ~ 10 µm;

in lattice-mismatched structures
EPD ~ 10^{6} - 10^{10} cm^{-2}

Critical thickness for MD generation

Matthews & Blakeslee *Journal of Crystal Growth* *27 (1974) 118*

$h_e \approx h_{cr}$



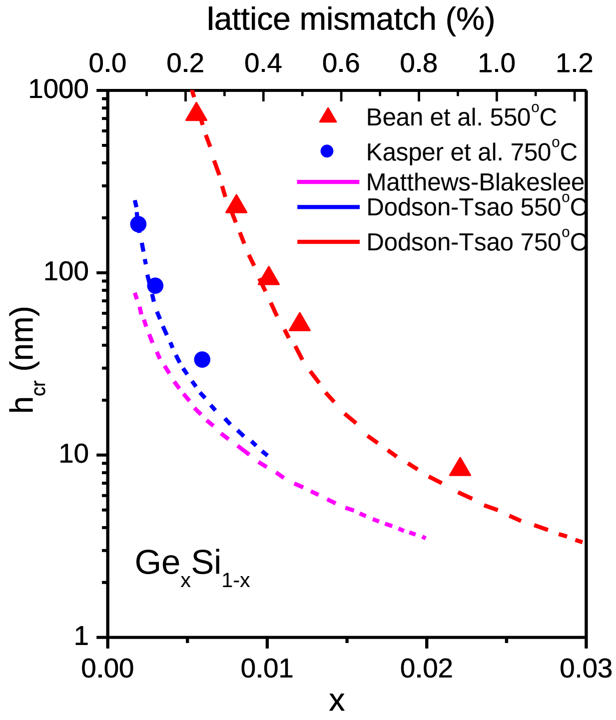
misfit stress force $F_\sigma \sim b \cdot h_e \cdot f$

dislocation line tension $F_T \sim b^2 \cdot \left[\ln\left({h_e}/{b} \right) + 1 \right]$

$F_\sigma > F_T \longrightarrow$ growth of MD segment

$F_\sigma = F_T \longrightarrow h_e = h_{cr}$ (onset of MD generation)

equilibrium model



Dodson & Tsao *APL 51 (1987) 1325; 52 (1988) 852*

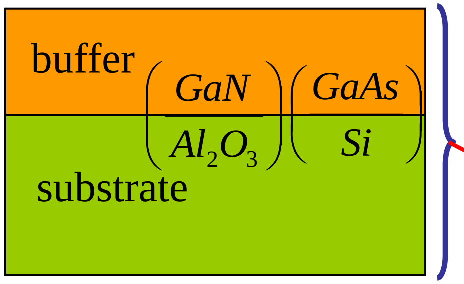
velocity of MD $\propto$ excess stress (actual stress - stress @ EQ)

$\downarrow$

strain = f (h_e, T, t, ...)

dynamical model

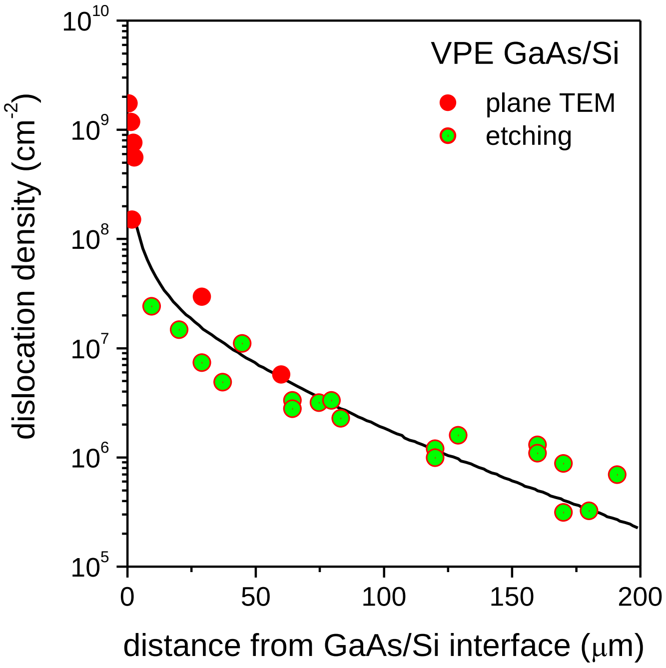
Buffer layers



buffer = fully (?) relaxed epitaxial layer with required value of the lattice parameter grown on available substrate wafer

new substrate for next epitaxial growths

Tachikawa & Yamaguchi APL 56 (1990) 484



Qian et al. J. Electrochem. Soc. 144 (1997) 1430

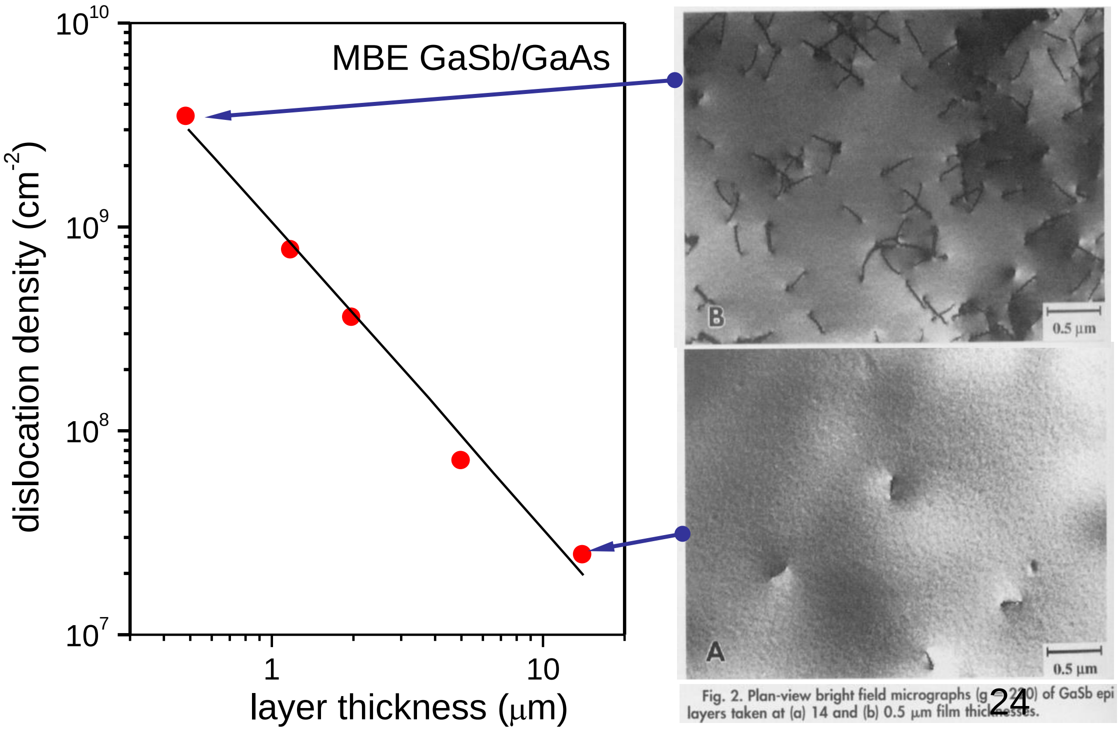
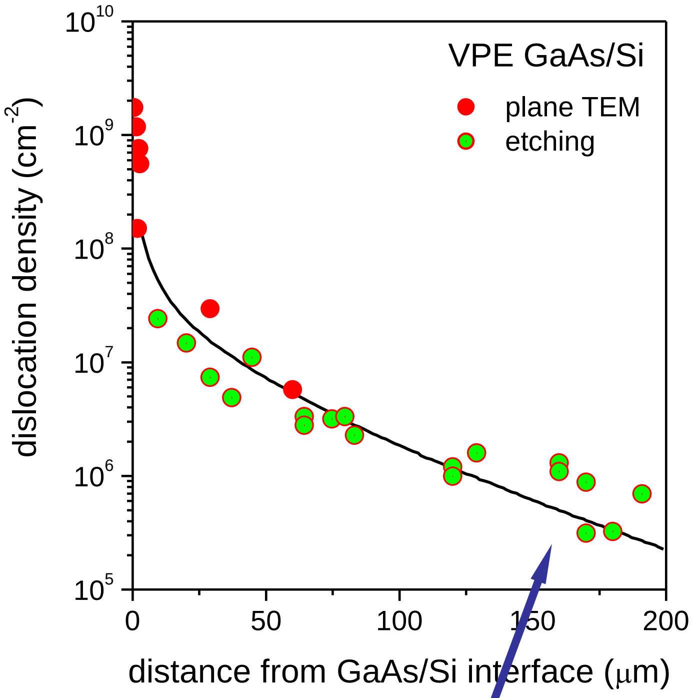


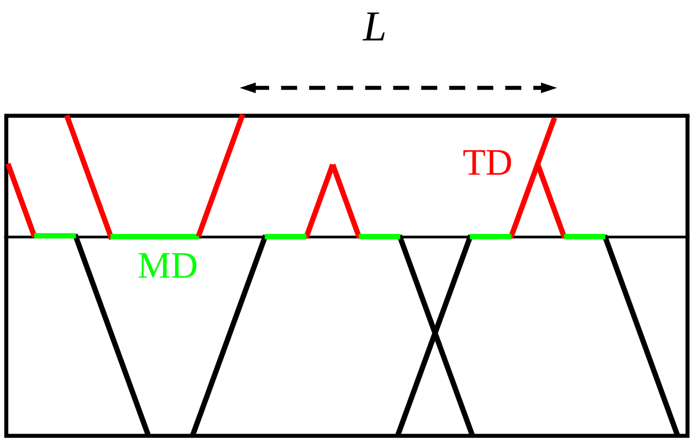
Fig. 2. Plan-view bright field micrographs (g = 220) of GaSb epi layers taken at (a) 14 and (b) 0.5 μm film thicknesses.

Threading dislocations in thick buffers

Tachikawa & Yamaguchi APL 56 (1990) 484



Why this plot saturates for thicker films ?



$$\boxed{L = 1/\sqrt{N_{TD}}}$$

$N_{TD} = 10^{10}\ \mathrm{cm}^{-2} \Rightarrow L = 100$ nm

reactions of dislocations highly efficient

$N_{TD} = 10^{6}\ \mathrm{cm}^{-2} \Rightarrow \mathrm{L} = 10\ \mu\mathrm{m}$

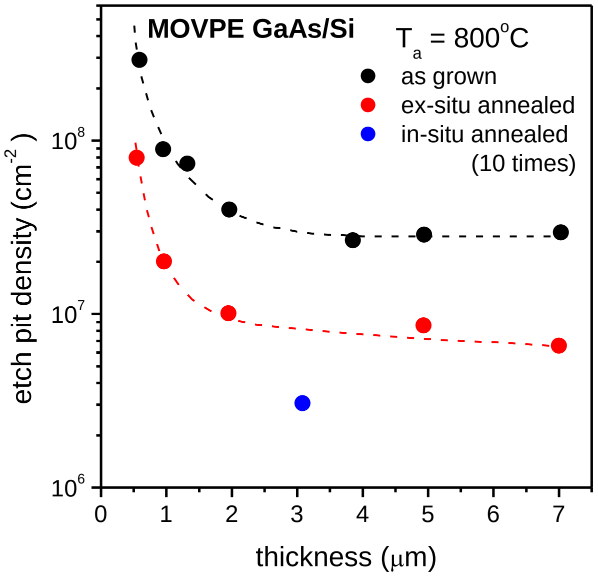
low efficiency of dislocation reactions

How to speed up reduction of EPD with buffer thickness?

Annealing

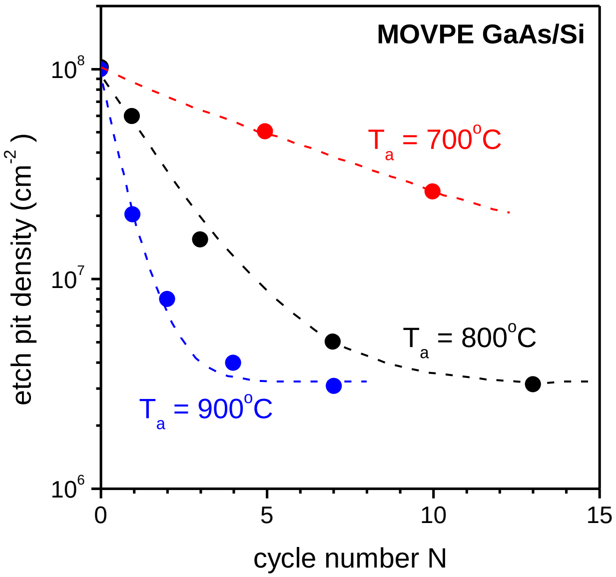
thermal strain ⇔ driving force for TD movement

Yamamoto & Yamaguchi MRS *116* *(1988) 285*



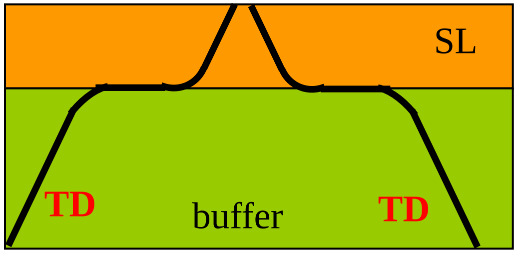
- annealing *in-situ*:
  - growth 1 μm GaAs
  - annealing ($T_{gr} \rightarrow RT \rightarrow T_a$) × N
  - growth 2 μm GaAs @ T_{gr}

Yamaguchi et al. APL *53* *(1988) 2293*



Filtration of TDs by strained superlattice

lattice mismatch strain ⇔ driving force of bending and movement of dislocations



Qian et al. J. Electrochem. Soc. *<u>144</u>* *(1997) 1430*

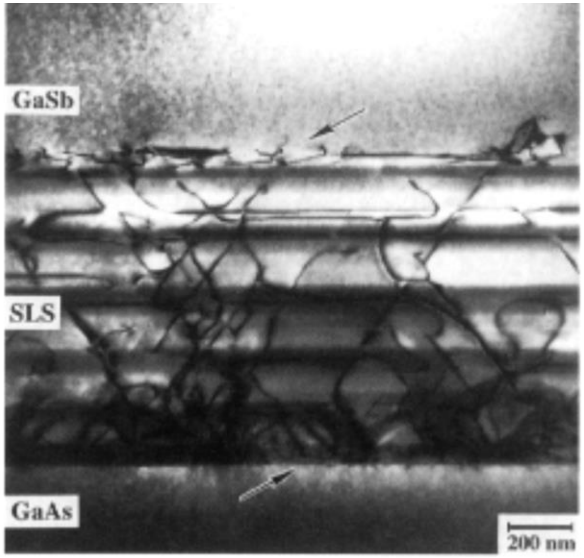
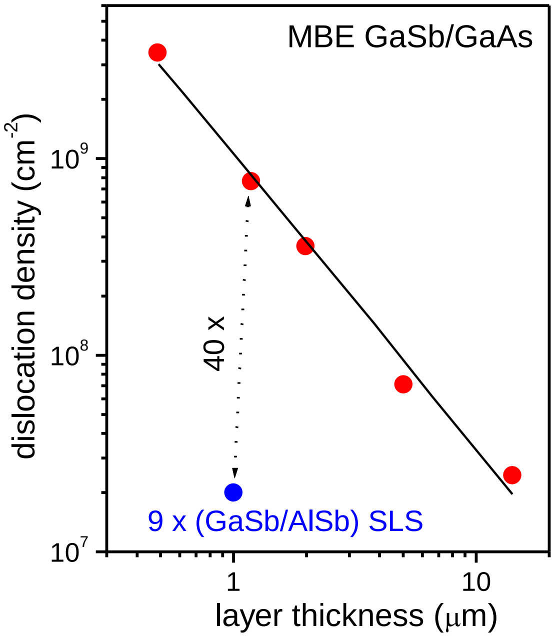


Fig. 5. Cross-sectional bright field micrograph shows the dislocation filtering of the GaSb/AlSb SLS. The majority of threading dislocations are bent by the SLS resulting in low defect density at the top GaSb layer.

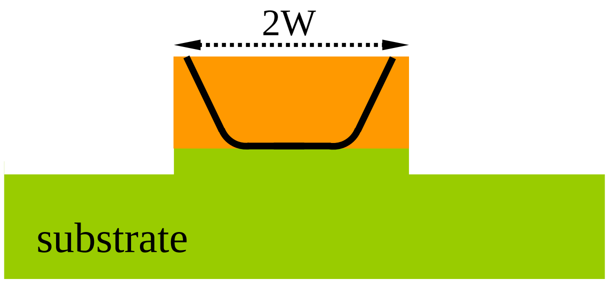


- SLS filter efficient for high TD densities
- careful growth needed (no new defects)
- sometimes annealing used in addition

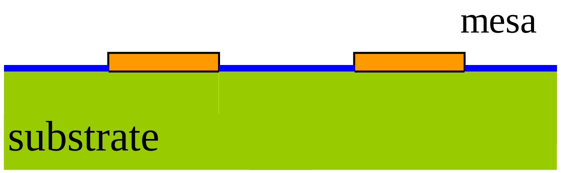
TD density < 10^6 - 10^7 cm^{-2}
not achievable in homogeneous buffers

Epitaxy on „small” substrates

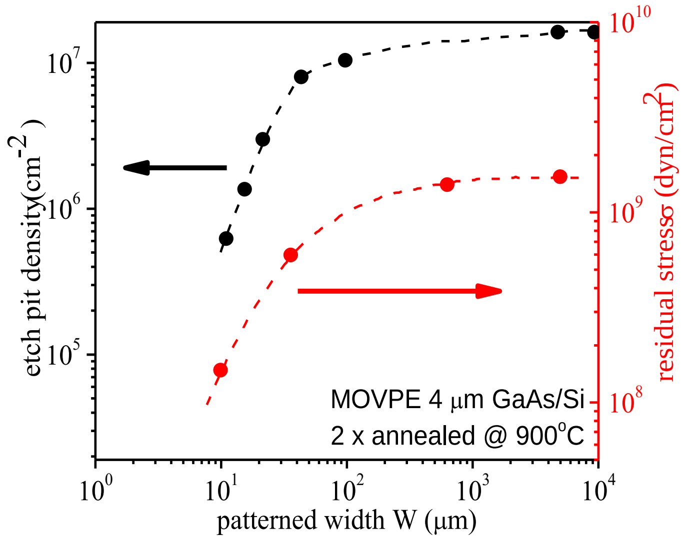
dislocations terminate at the sidewalls



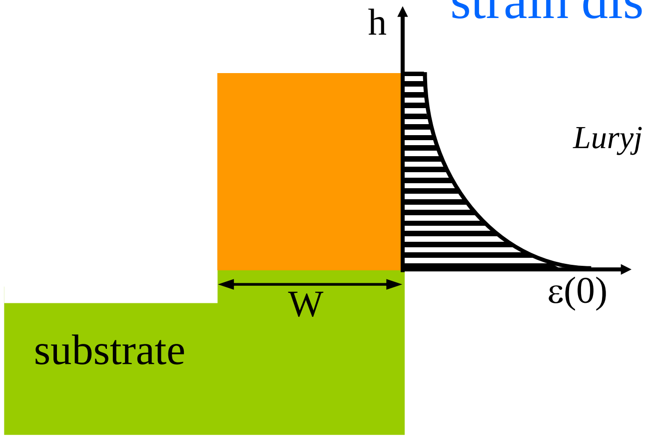
Selective Area Growth (SAG)
on masked substrate



Yamaguchi et al. APL 56 (1990) 27



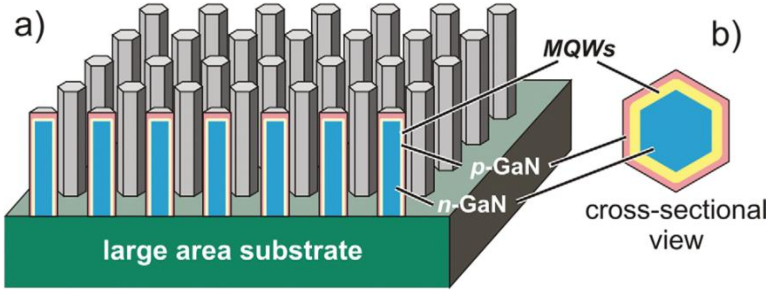
strain distribution in mesa



Luryj & Suhir APL 49 (1986) 140

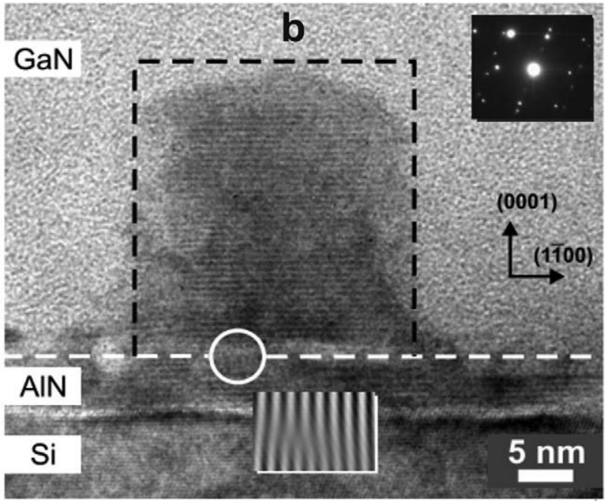
$$E_{strain}(h,W) \leftrightarrow E_{dislocation} \Rightarrow h_{cr} \text{ decreases with } W$$

Epitaxy on „small” substrates - Nanowires (NWs)



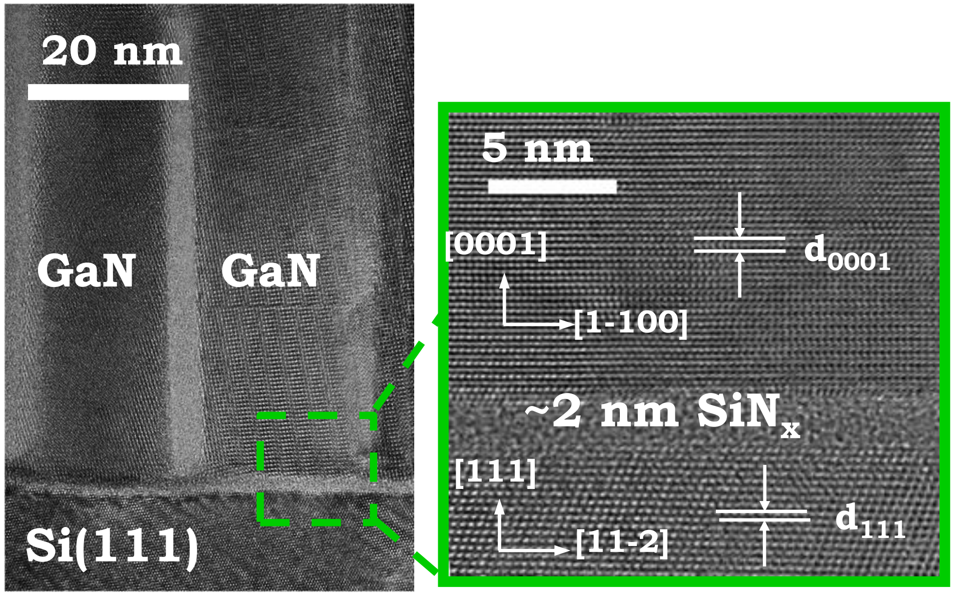
small NW footprint
(small contact area with the substrate)

GaN NWs on AlN/Si



Consonni et al. PRB 81 (2010) 085310

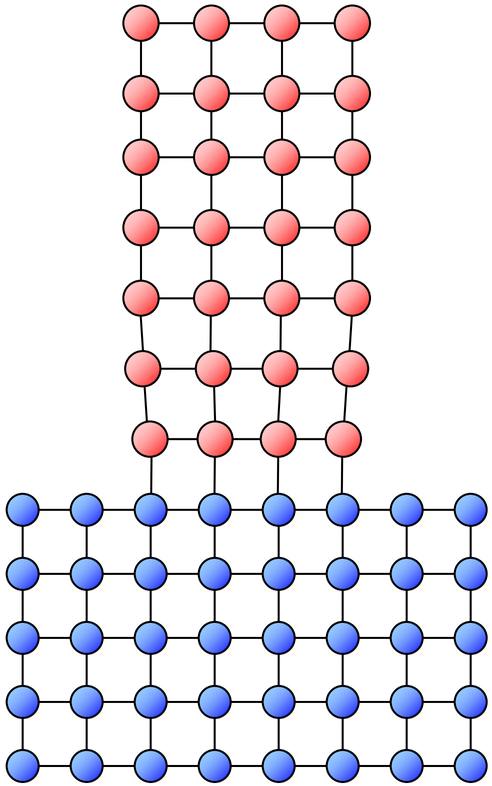
GaN NWs on nitridated Si



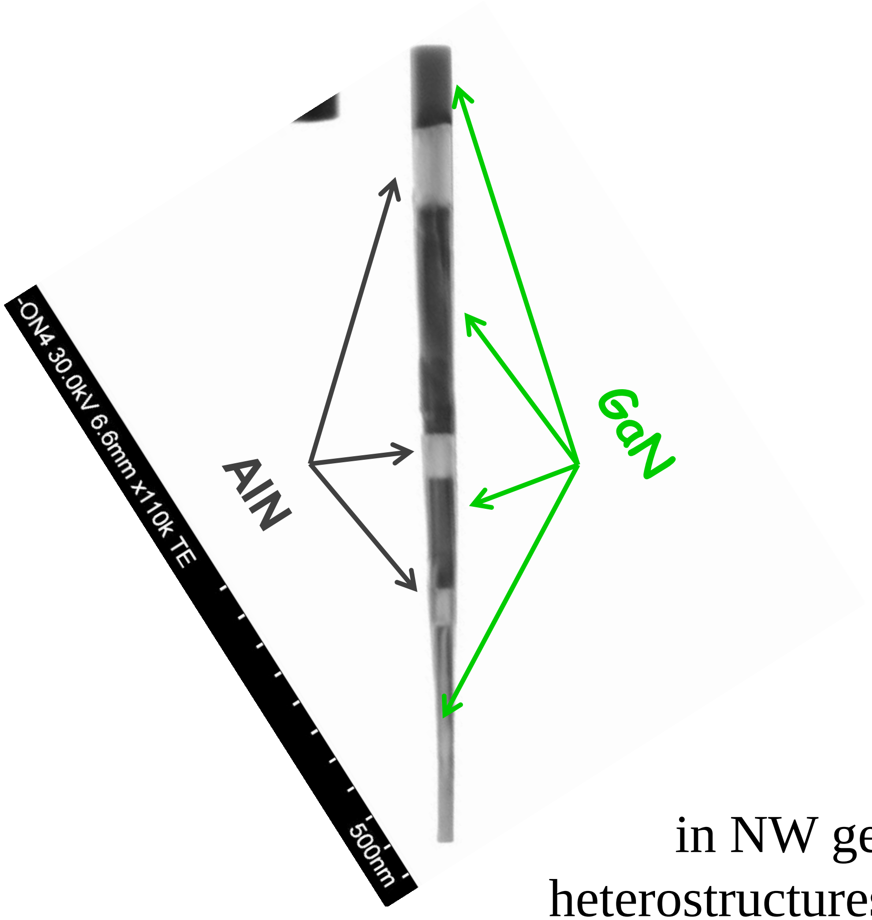
A. Wierzbicka, et al. Nanotechnology 24 (2013) 035703

perfect structural quality of NWs despite their large lattice mismatch with the substrate

Epitaxy on „small" substrates - Nanowires (NWs)

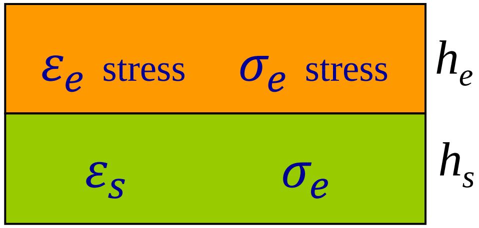


nanowire A on substrate B
a(B) > a(A)



in NW geometry
heterostructures with quality
not available in planar form
can be fabricated

Growth on „thin” substrates – concept of compliant substrates



equal forces in both parts

$$\sigma_e \times h_e = \sigma_s \times h_s$$

Hook’s law

$$\sigma \propto \varepsilon$$

$$\varepsilon_0 = \varepsilon_e + \varepsilon_s = \frac{\Delta a}{a}$$

$$\boxed{\frac{\varepsilon_e}{\varepsilon_0} = \frac{h_s}{h_e + h_s}}$$

$$\boxed{h_s = h_e \Leftrightarrow \varepsilon_e = \varepsilon_s}$$

partial transfer of strain from epi to substrate

⇓

larger critical thickness

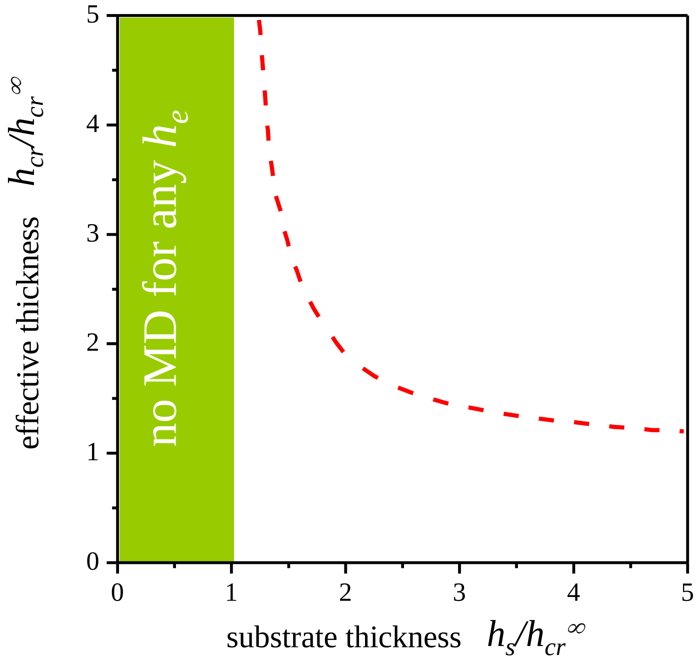
Y.H. Lo, APL 59 (1991) 2311

$$\boxed{\frac{1}{h_{cr}} = \frac{1}{h_{cr}^{\infty}} - \frac{1}{h_s}}$$

for $h_s > h_{cr}^{\infty}$

h_{cr} critical thickness

$$h_{cr}^{\infty} = h_{cr}(h_s = \infty)$$



$$h_s < h_{cr}^{\infty} \Rightarrow h_{cr} = \infty$$

⇔

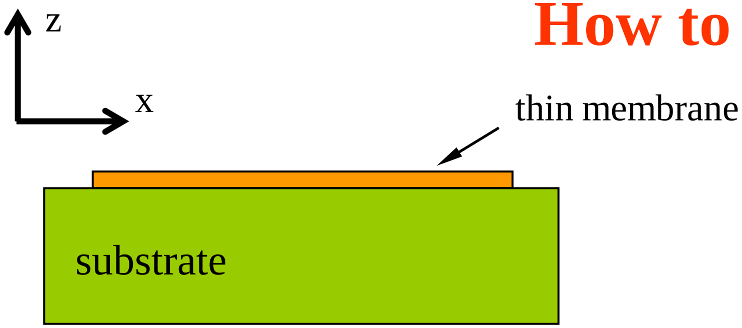
substrate

↳ layer

layer

↳ substrate

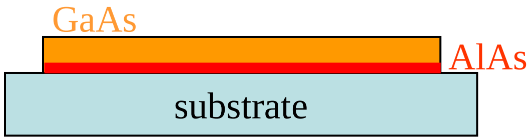
How to produce thin substrate membranes?

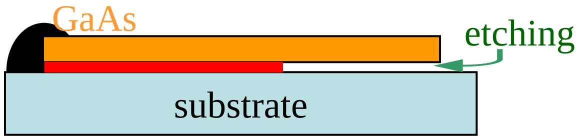


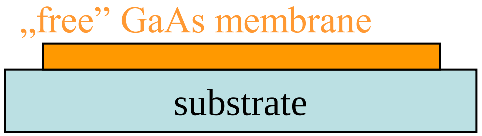
Requirements:

- strong bonding with the substrate in the z direction
  - to avoid rolling up of the membrane
- weak bonding with the substrate in the x direction
  - sliding of the membrane on the substrate possible
- large area and small thickness of the membrane

patterning + mesa release & deposition

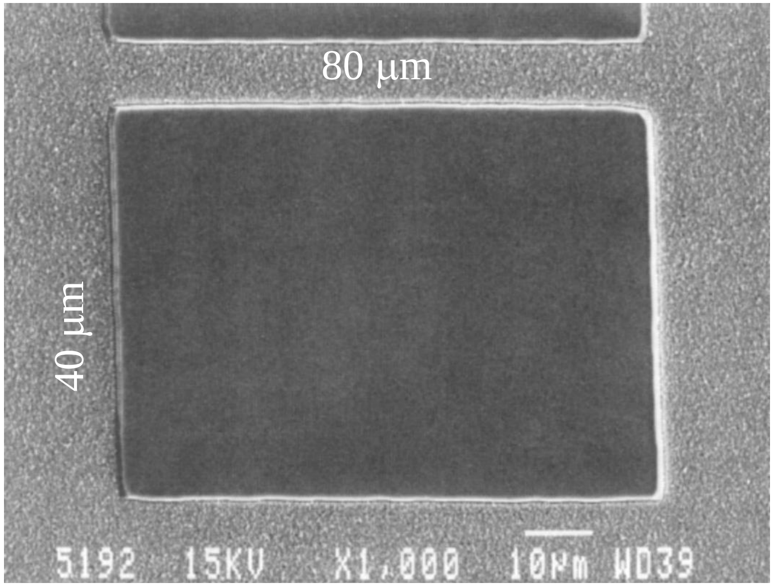






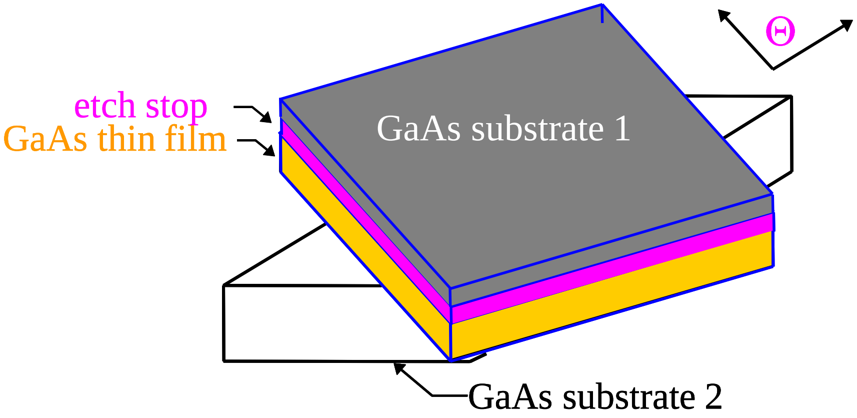
De Boeck et al. JJAP <u>30</u> (1991) L423

MBE 1.3 µm GaAs/Si;
patterning + mesa release & deposition
MBE growth of 1 µm GaAs



PL: no strain in GaAs grown on the membrane
large strain in GaAs grown on bulk Si

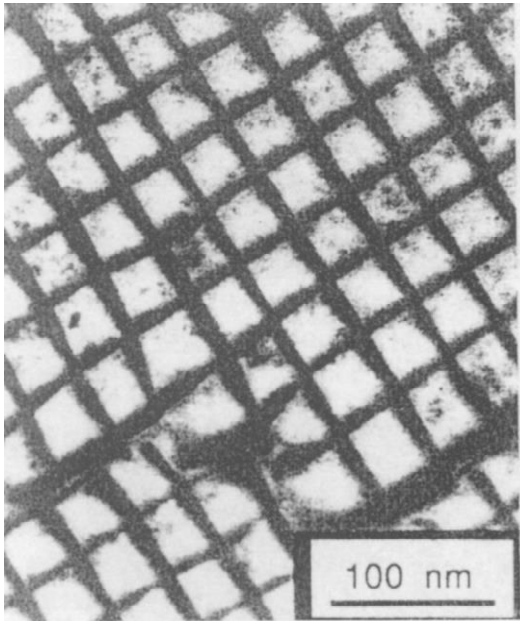
Formation of thin substrates by wafer bonding



- connection: T ~ 550° C in H_2 or UHV
- pressure: ~ 200 g/2 inch wafer
- etching to remove the host substrate
- twist angle Θ: 0 - 45°
- very thin layers (10 ML) can be bonded

Twist-bonded interface

Benemara et al. Mat. Sci. Eng.B 42 (1996) 164



Plane-view TEM
of bonded Si wafers
(Θ ~ 0.6°)

dense network of screw dislocations
⇓
"soft" connection
distance between dislocations = f(Θ)
no threading dislocations

Problems:

- gas bubbles at the joint leading to cracks
- residual contaminations at the joint
- problems with cleaving
- difficult technology

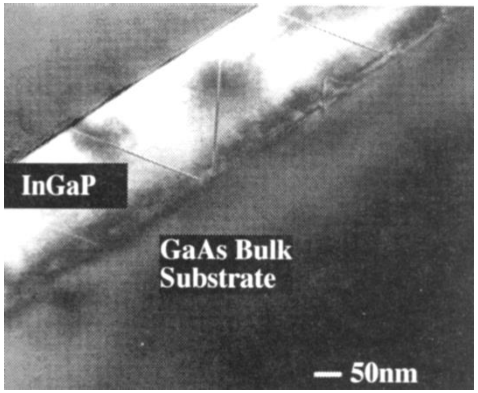
Universal compliant substrate

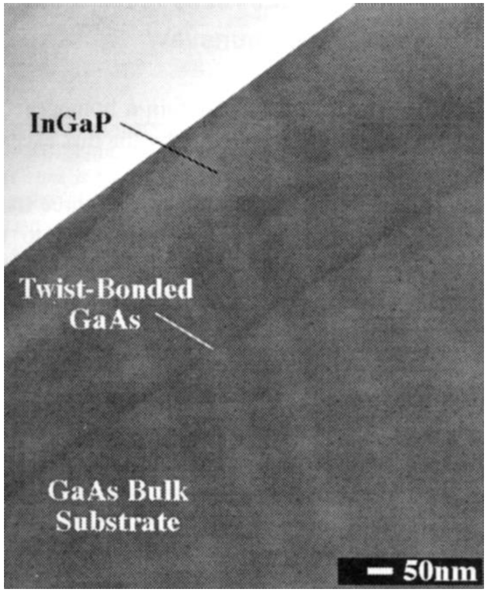
Ejeckam et al. APL 70 (1997) 1685

film GaAs 10 nm; $\Theta \sim 17^{o}$ in H_2

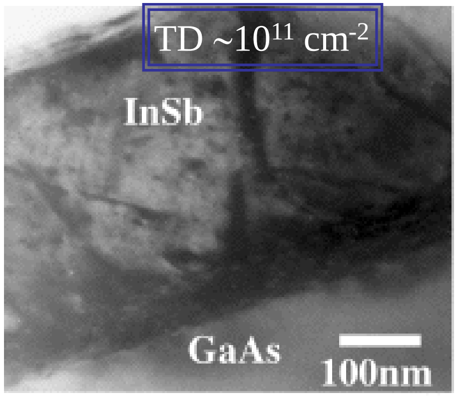
300 nm of InGaP on GaAs by MOVPE

f = 1% $\Rightarrow h_e = 30 \times h_{cr}^{\infty}$ (10 nm)

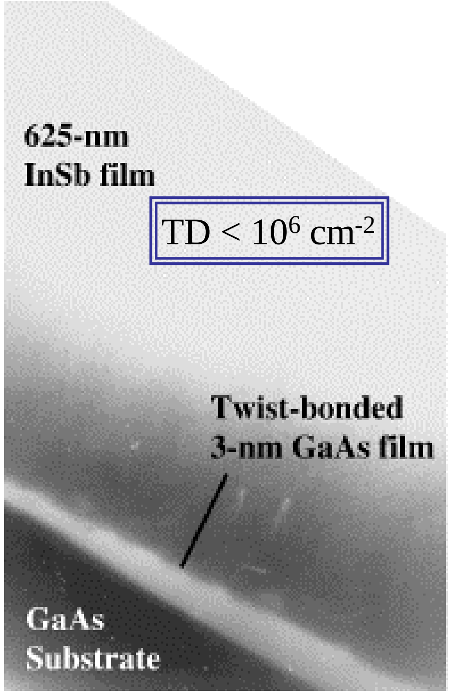




Lo et al. Cornell Sci. News 1997;
Ejeckam et al. APL 71 (1997) 776



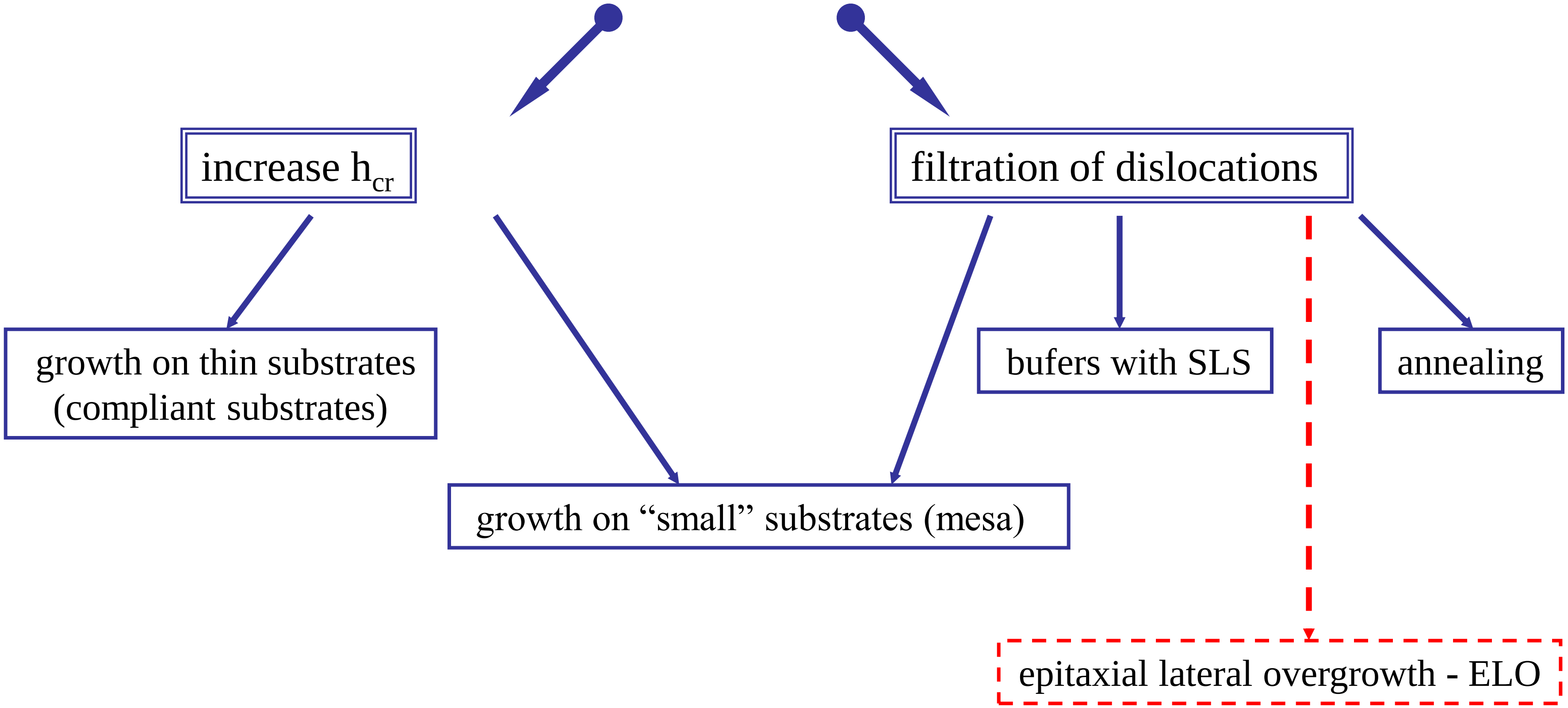
InSb on GaAs f = 14.7%



Conclusion:

- spectacular laboratory results;
- nice confirmation of the effect of strain transfer from epilayer to the thin substrate
- difficult technology
- no reports on a wide application in the industry

Methods to reduce defect density in lattice mismatched epitaxial structures - summary



increase h_{cr}

filtration of dislocations

growth on thin substrates (compliant substrates)

growth on “small” substrates (mesa)

bufers with SLS

annealing

epitaxial lateral overgrowth - ELO

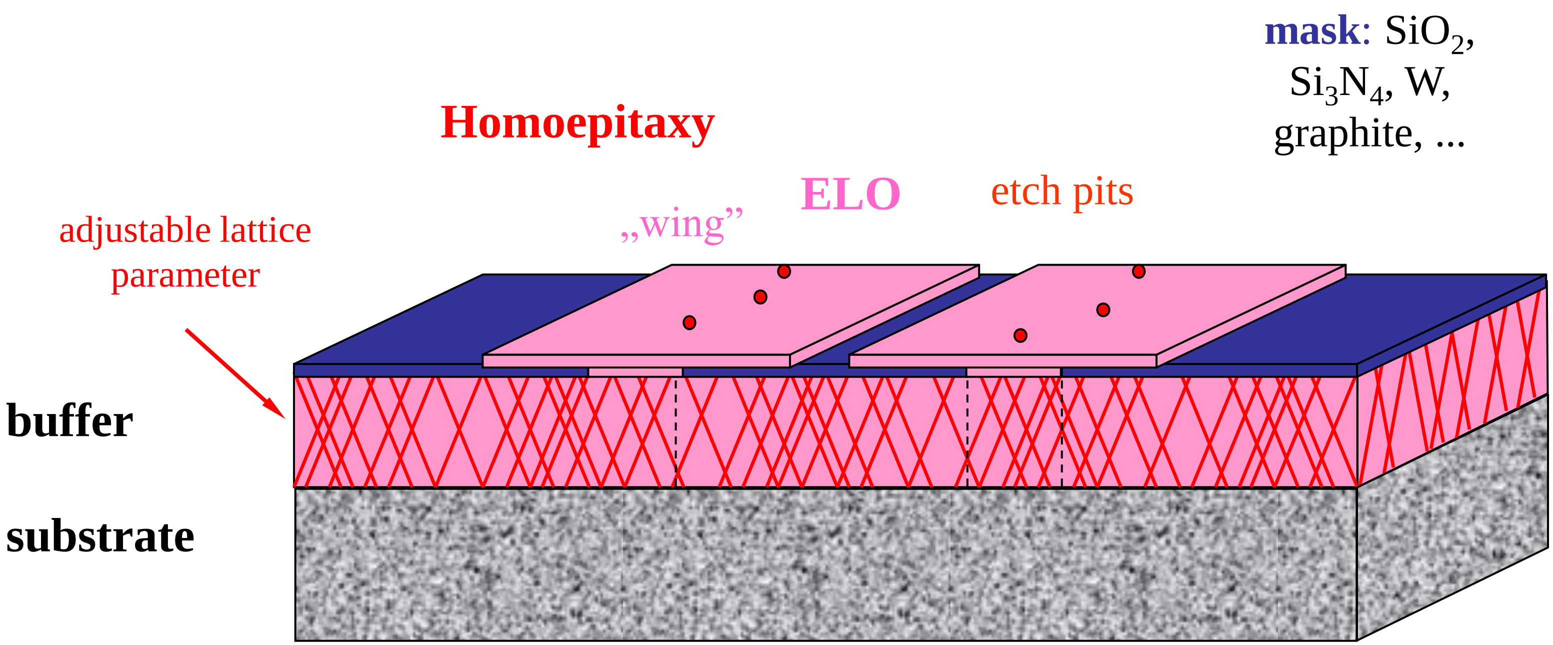
There are no universal method to reduce dislocation density in lattice mismatched heterostructures;

The best way is to avoid lattice mismatch – find the suitable substrate !!!

Epitaxial Lateral Overgrowth - ELO

How to grow low EPD homoepitaxial layers
on heavily dislocated substrates ?

→ **ELO**



MOVPE GaN: S = 5 – 20 µm; W = 2 - 5 µm
LPE GaAs: S = 100 – 500 µm; W = 6 - 10 µm