Stuctural and chemical properties of hetero-epilayers

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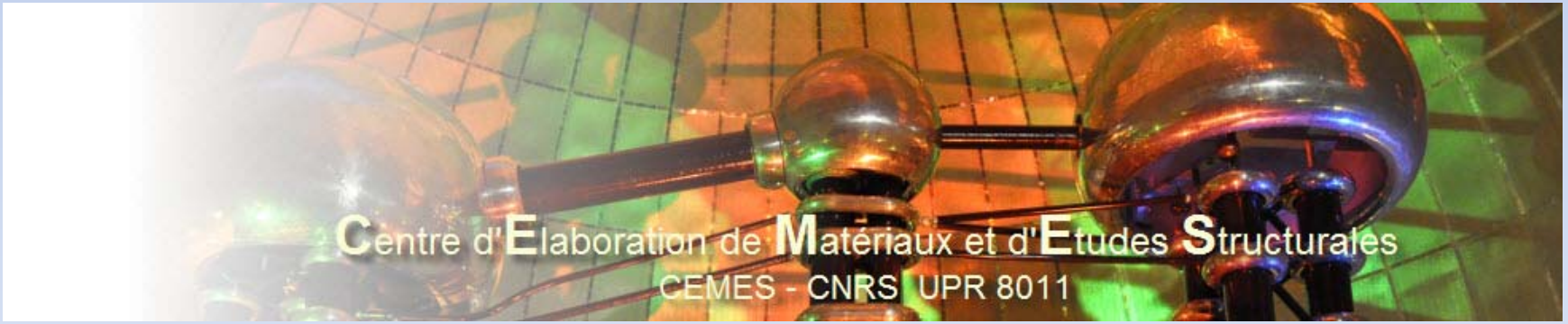


Stuctural and chemical properties of hetero-epilayers

epi (ἐπί) = above

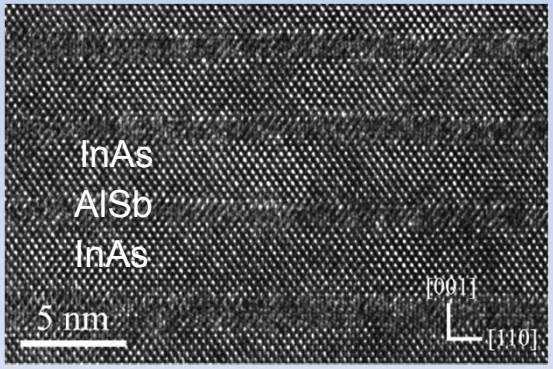
taxis (τάξις) = order, arrangement

hetero = different

Hetero-epitaxy = growth of a A crystal on a B crystal, A ≠ B
The 2 crystals share at least one common element of symetry

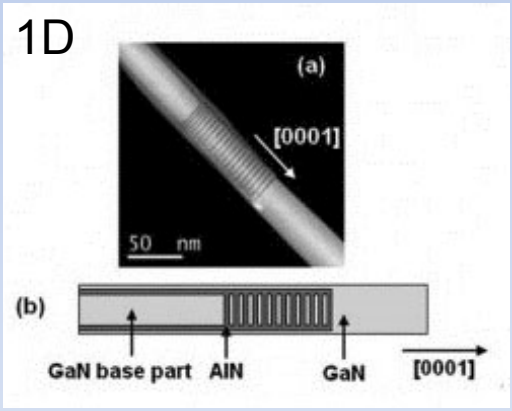
Artificial heterostructures (MBE, MOVPE, sputtering…)

2D



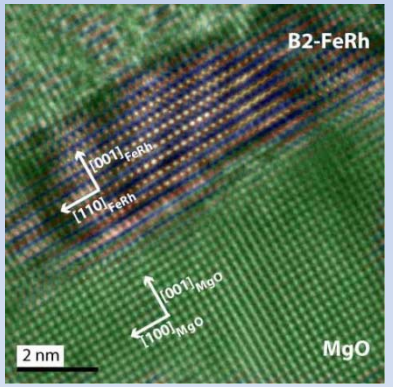
[InAs/AlSb] multilayer on an InAs substrate in a quantum cascade laser (IES-CEMES)

1D



[GaN/AlN] quantum disks in a nanowire PRB 83, 115417 (2011)

3D



FeRh nano-island on a MgO substrate (CEMES)

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The 2 crystals share at least one common element of symetry

Chalcopyrite on sphalerite (Kansas)

Rakovan, Rocks and Minerals, 61, 3170 (2006)

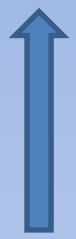
But also natural heterostructures

Although there are separated, the epitaxial cristallites have the same orientations !

Epitaxial Rutile on hematite (Brasil)

https://commons.wikimedia.org/wiki/File:Rutile-Hematite-171993.jpg

Origin of structural and chemical properties in heteroepitaxy ?



In heteroepitaxy, the 2 crystals share at least one common element of symetry but can differ by

- ✓ Their crystalline structures → epitaxial relationship
- ✓ Their lattice parameters: « lattice misfit »
  - ✓ Strain state (elastic energy)
  - ✓ Stress relaxation mechanisms
- ✓ Their chemical compositions → intermixing, preferential bonding at interfaces

Moreover, crystal growth

- ✓ is an out of equilibrium process
- ✓ involves interface and surface energies → growth modes, facetting = morphology

Outline

- ✓ Accomodation of the crystalline lattice of the epilayer with the substrate lattice
  - → same compound (homoepitaxy), two crystalline lattices: ex. of III-V compounds
  - → polar on non polar materials: exemple of III-V on Si
  - → epitaxial relationship: two exemples in the mineral world
- ✓ Accomodation of the lattice misfit
  - → elastic strain and internal stress in hetero-epitaxy
  - → plastic relaxation by extended defects (dislocations)
  - → can we measure the epitaxial strain by TEM ?
  - → can we measure the stress by TEM ?
- ✓ Chemical discontinuities at interfaces
  - → ex. strain and chemical composition in [InAs/AlSb] system
  - → some other exemples in semiconductors
- ✓ Role of surfaces and interfaces in the 3D morphology
  - → (SK growth modes in SC)
  - → exemple of « nano-epitaxy » of metallic core-shell particules (Fe-Au)

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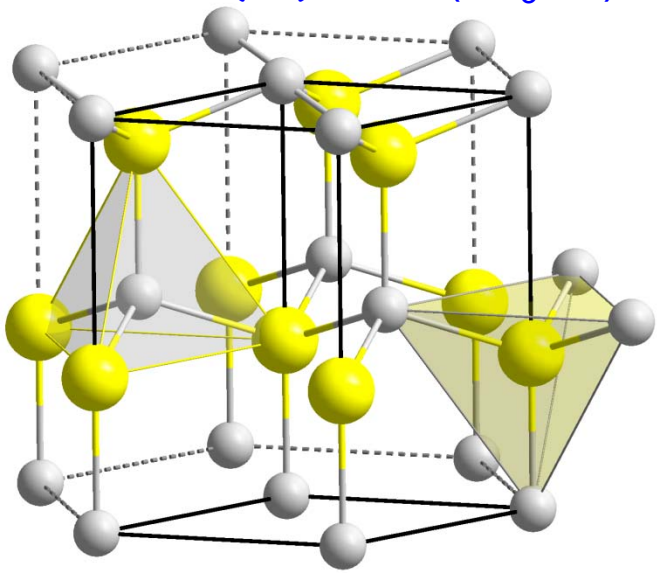
Same compound (homoepitaxy), two crystalline lattices: exemple of III-V

→ Most binary III-V and II-VI compounds can crystallize in two crystalline lattices

Same tetrahedrons - Same coordinance
But different stackings of atoms
Errors in the stacking are « easy »

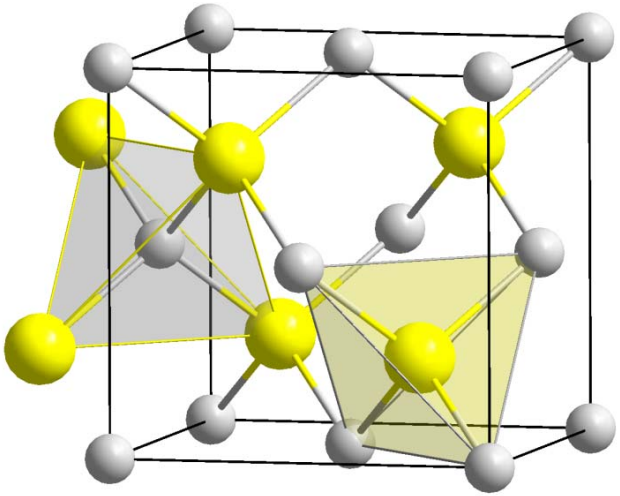
III-V	stable	metastable
AlN, GaN, InN	W	ZB
AlP, GaP, InP	ZB	W
AlAs, GaAs, InAs	ZB	W
AlSb, GaSb, InSb	ZB	W

Wurtzite (W) hexa ($P6_3mc$)



ABAB… stacking

Zinc blende (ZB) fcc (F-43m)

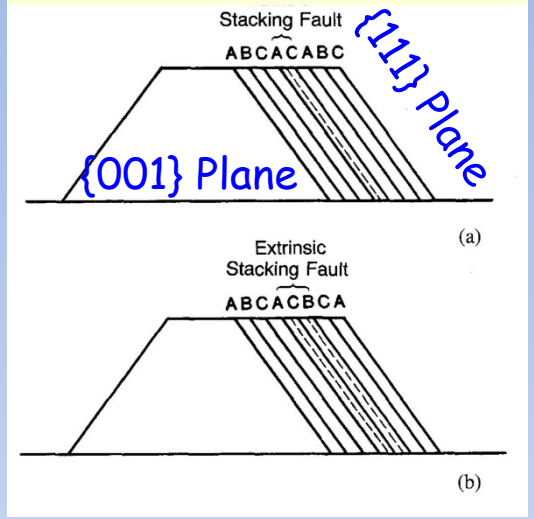


ABCABC… stacking

Same compound (homoepitaxy), two crystalline lattices: exemple of III-V

if errors occur in the stacking
in a <111> direction (ZB fcc structure)

Isolated stacking faults



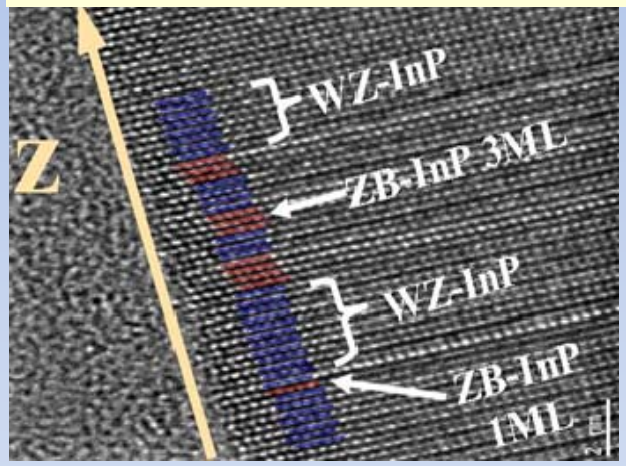
SF is a low energetical defect (3 meV/A^2 in GaP Cohen et carter 1999) but is ended by either a surface or a partial dislocation

ZB (fcc) ↔ W (hexa)

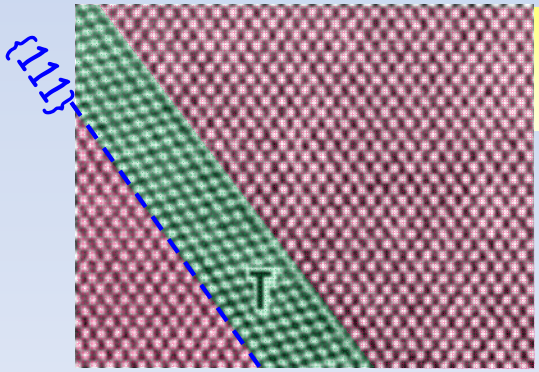
[111] ↔ [0001]

ABCABCABABABCABCABABAB..

Frequent in nanowires growth



Akopian et al Nano Lett. 2010, 10, 1198



twinning

ABCABCACBACBA

{111} Plane of symmetry

Twin = same structure than matrix
but rotation of 70° around a <110> direction

Ernst and Pirouz J. Mater. Res., 4, 834 (1989)

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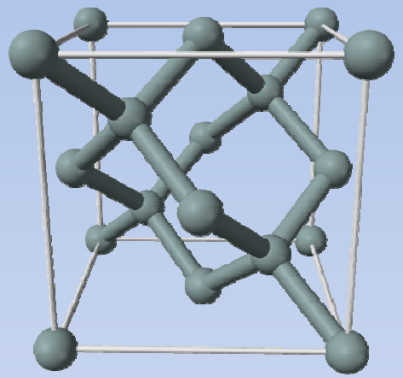
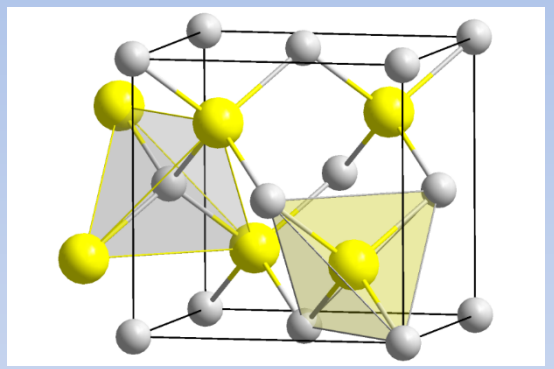
Polar on non polar materials: exemple of III-V on Si

group IV (C, Si, Ge and alloys SiGe)
→ cfc diamond structure (Fd3m)
→ unpolar material

III-V (except nitrides)
→ cfc zinc-blende structure (F-43m)
→ polar material

Si

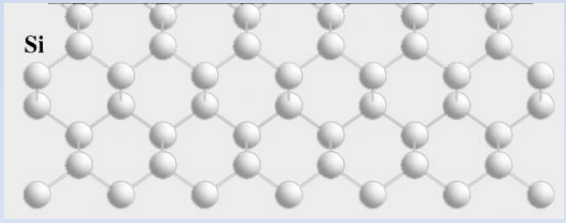




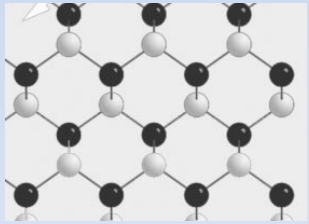
Ga
P

ex. GaP on Si (close lattice parameters: misfit 0.3%)

[001]



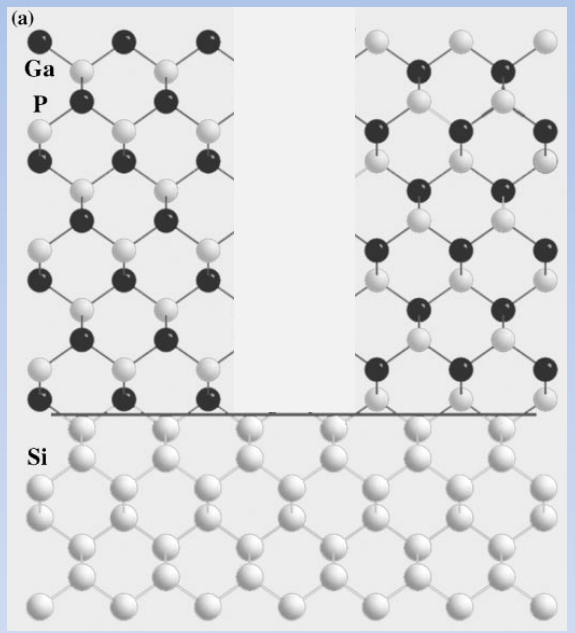
Projection in a
<110> direction



Ga
P

Polar on non polar materials: exemple of III-V on Si

Domain D1 Domain D2



2 variants of GaP !

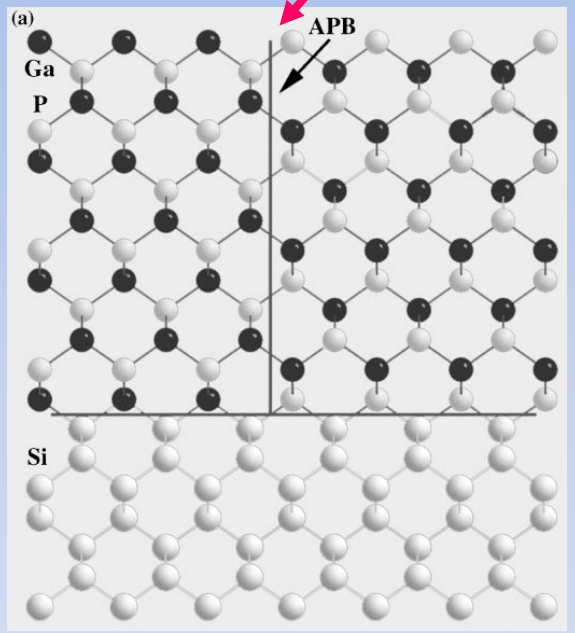
same structure,
same lattice parameter,
same composition,
but inversion of polarity

Projection in a <110> direction

Polar on non polar materials: exemple of III-V on Si

APB = antiphase boundary = III-III or V-V antisite bonds

Domain D1 Domain D2

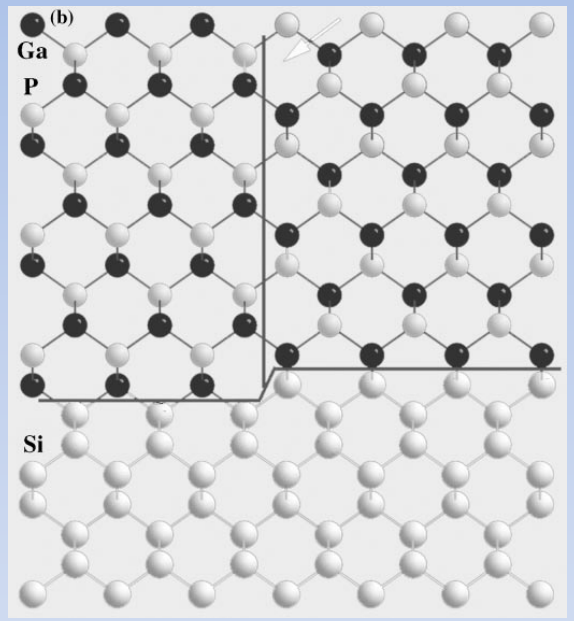


a

a/2

a/4

Domain D1 Domain D2



GaP
zinc blende

Si
diamond

2 variants of GaP !

same structure,
same lattice parameter,
same composition,
but inversion of polarity

2 antiphase domains

Projection in a <110> direction

Cohen et Carter, Journal of Microscopy 208, 84 (2002)

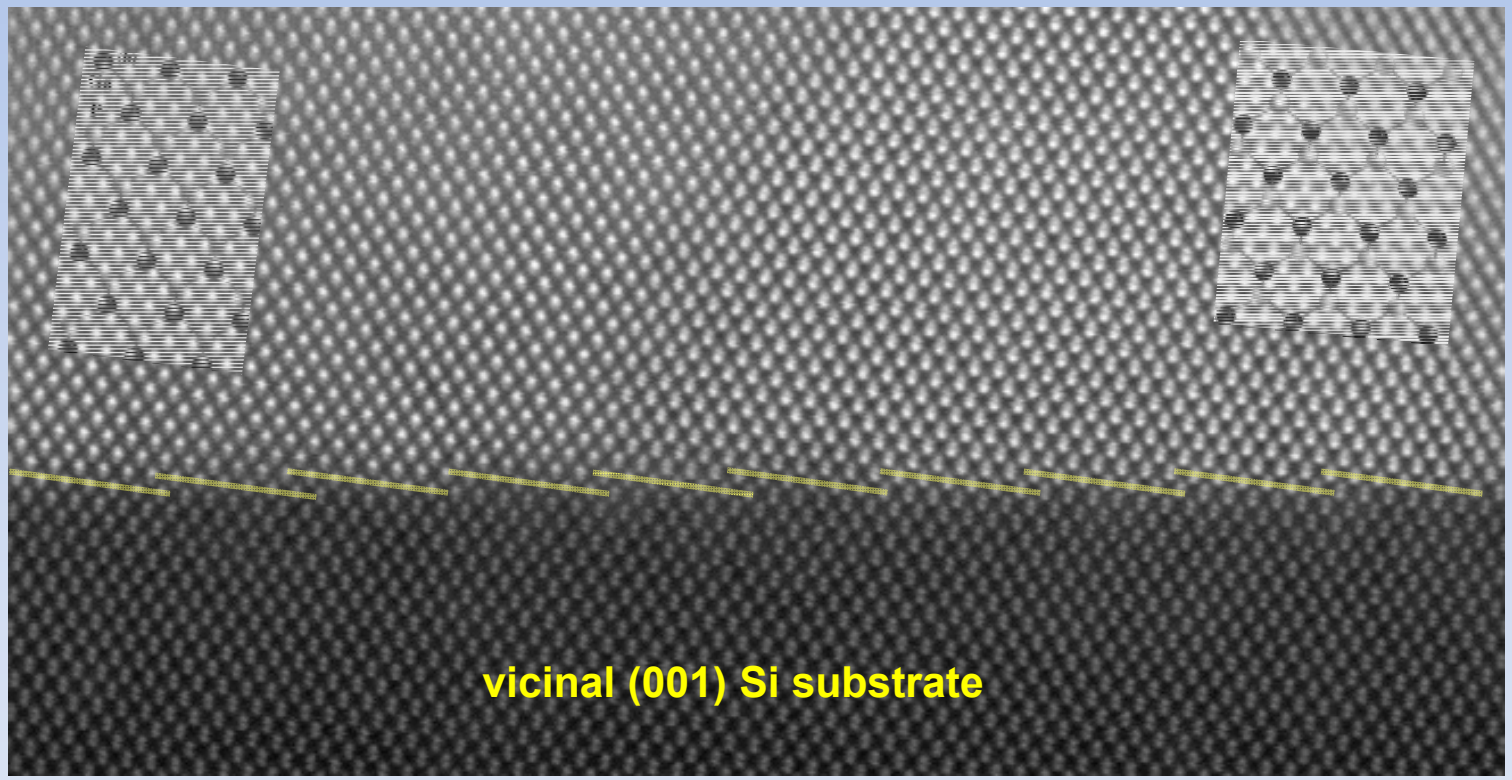
Polar on non polar materials: exemple of III-V on Si

MBE → GaP on vicinal Si (FOTON-INSA Rennes)

Observation of antiphase domains by STEM-HAADF in cross-section

APB

Atomic resolution, $I \sim Z^{1,7}$ → $I_{Ga} > I_P$
(CEMES Toulouse and Univ. Saragoza)

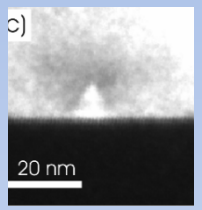


Polar on non polar materials: exemple of III-V on Si

MOVPE → GaP on Si

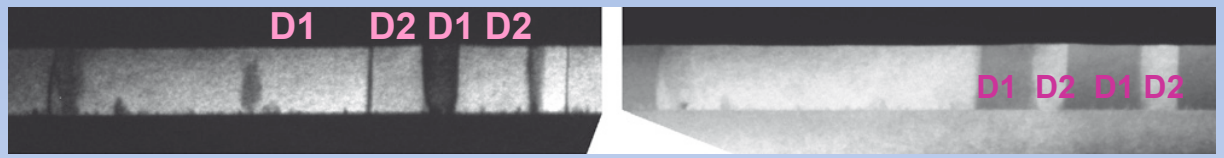
Observation of antiphase domains by conventional TEM in cross-section

g 002



g 002

g -1-11



Németh et al, J. Crystal Growth 310, 4763 (2008)

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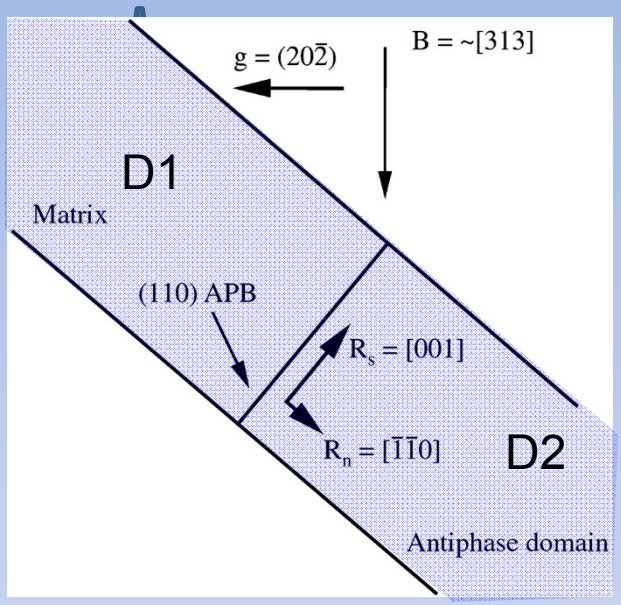
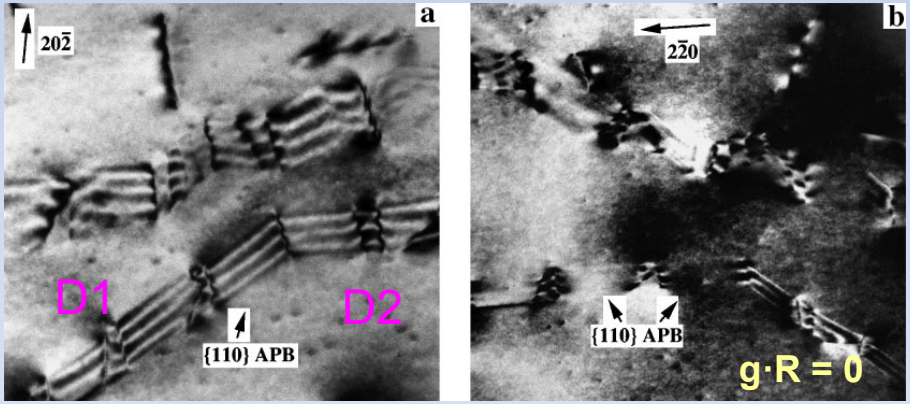




Thick GaP layer grown on Si: Conventionnal TEM observation after removing the Si (plane view)

Observation of antiphase boundary

α–fringes are related to a pure displacement D1 / D2

$\alpha = 2\pi (g \cdot R) = 2\pi (g \cdot (R_s + R_n))$

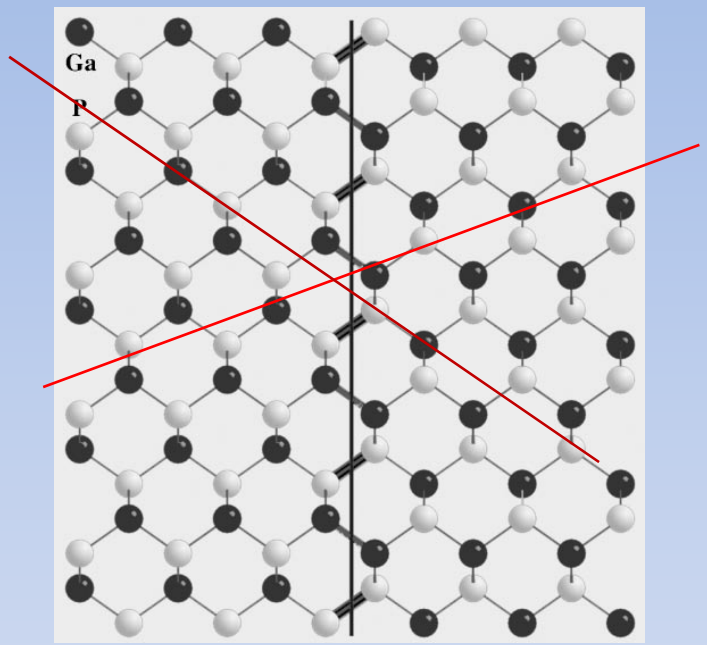
Fringes analysis of (110) APB →

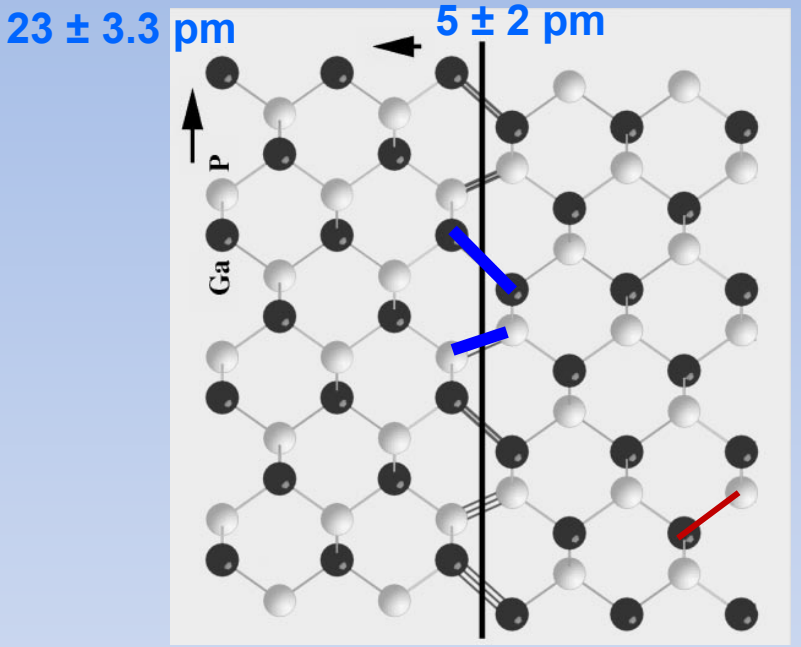
R_s = 23 ± 3 pm in [001]
R_n = 5 ± 3 pm in [-1-10]
0 ± 3 pm in [1-10]

Cohen et Carter, Journal of Microscopy 208, 84 (2002)

Polar on non polar materials: exemple of III-V on Si

This pure displacement accommodates the difference of bond lengths / Ga-P





→ Ga-Ga = 0.254 nm

and P-P = 0.227 nm

Ga-P = 0.234 nm

Cohen et Carter, Journal of Microscopy 208, 84 (2002)

Formation Energy of an (110) APB (antiphase boundary) eV/Å²	Unrelaxed (without displ.)	Relaxed (with displ).
Density Fonctional Theory - VASP (E. Tea et al FOTON/IRDEP)	0.041	0.030
DFT - WIEN2k Rubel and Baranovskii, Int. J. Mol. Sci., 10, 5104 (2009)	0.042	0.033

($E_{APB} \approx 10\ E_{SF}$)

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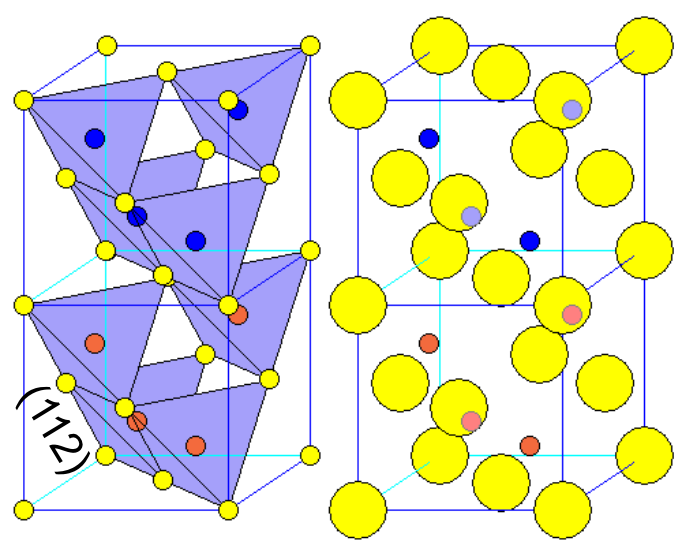
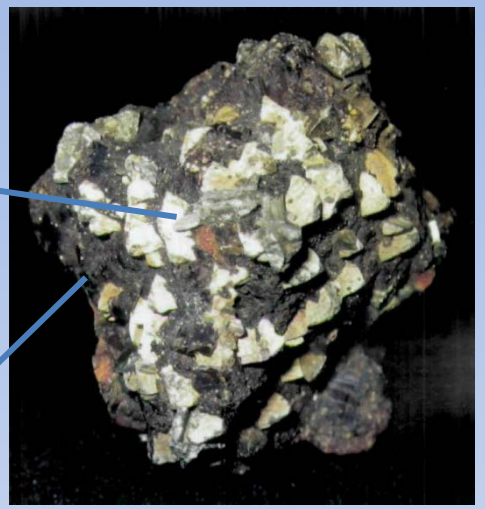
Epitaxial relationship: Chalcopyrite on sphalerite

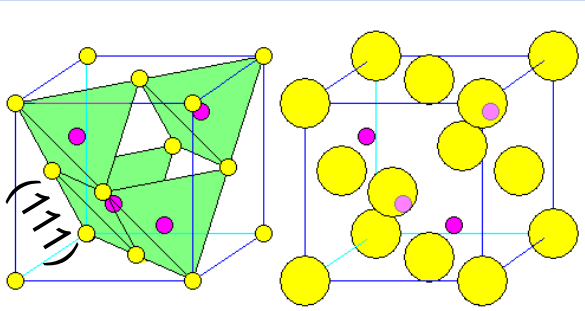


Chalcopyrite $CuFeS_2$ tetragonal

a = 0.528 nm
c = 1.041 nm



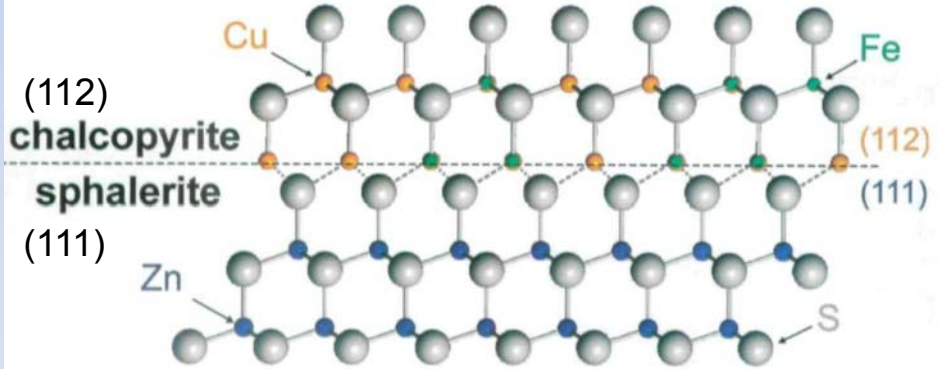
Rakovan, Rocks and Minerals, 61, 3170 (2006)



« Substrate » sphalerite ZnS
= zinc blende (fcc)

a = 0.541 nm

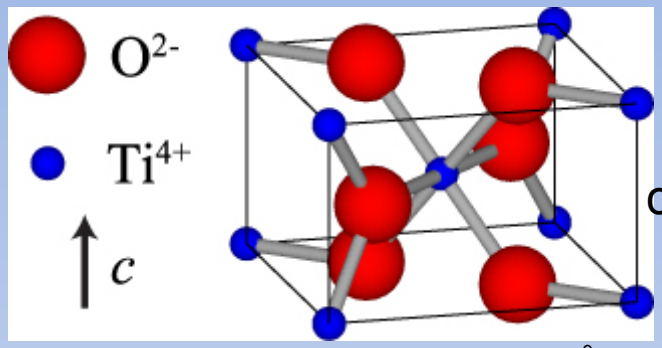
Tetrahedrons are preserved



https://www.uwgb.edu/dutchs/Petrology/Sphal-Chalc%20Structure.HTM

Epitaxial relationship: rutile on hematite

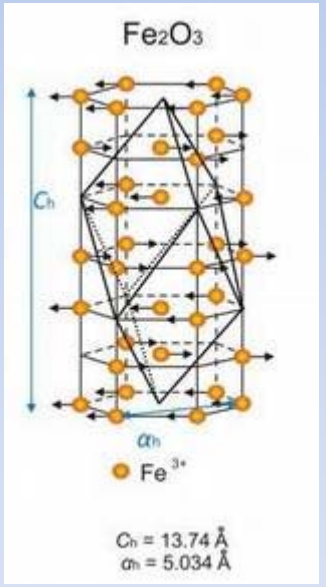
Rutile = TiO_2 (+ Fe, Tantalium, niobium, chromium, vanadium, Sn)
body-centered tetragonal (P 4_2/mnm)



c=2.953 Å

a=4.584 Å

How can the structures match ?



Hematite = α-Fe_2O_3 (+ Ti, Al, Mn, H_2O)
hexagonal

https://commons.wikimedia.org/wiki/File:Rutile-Hematite-171993.jpg

http://www.epm.ethz.ch/research/experimental_studies/min_mag/Hl_structure.jpg

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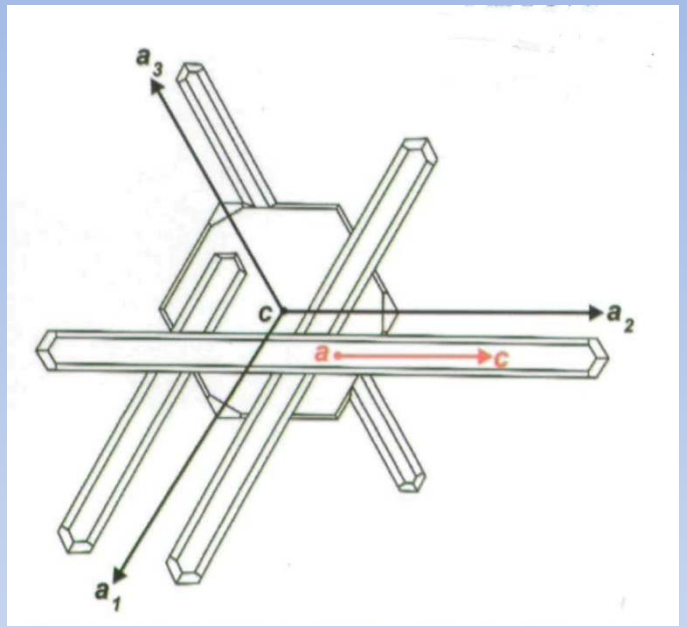

→ 3 rutile variants on one basal plane of hematite

Rakovan, Rocks and Minerals, 61, 3170(2006) and Herting-Agthe http://www.mineralogische-sammlungen.de/strohstern-engl.htm

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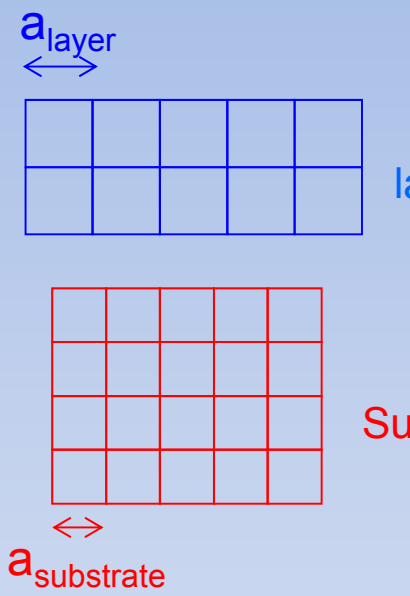
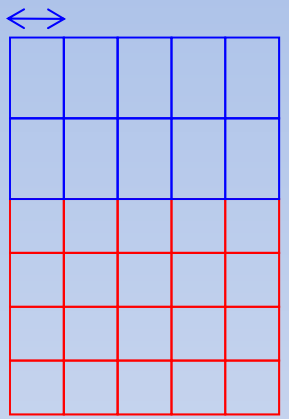
Elastic strain and internal stress in epitaxy

lattice misfit =
$(a_{layer} - a_{substrate}) / a_{substrate}$

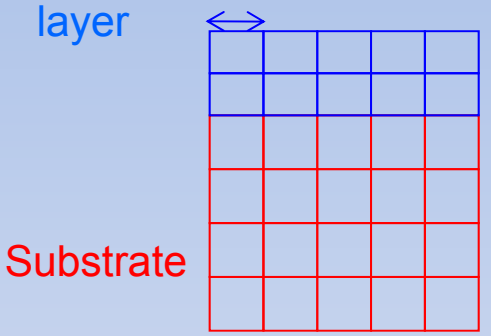


Accomodation through elastic strain and internal stress in the plane



$a_{layer} > a_{substrate}$

compressive stress



$a_{layer} < a_{substrate}$

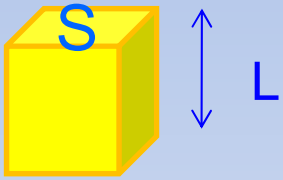
tensile stress

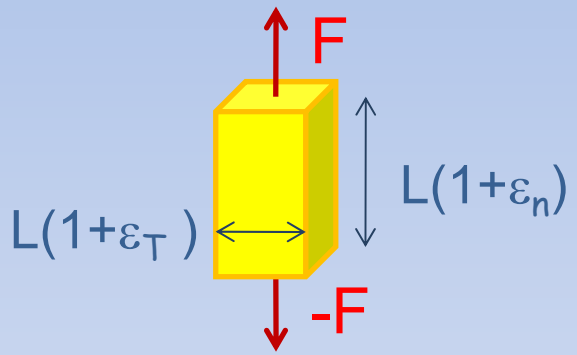
Elastic strain and stress: some basic notions

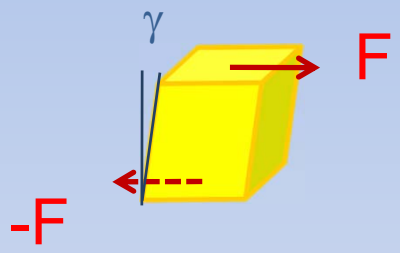
initial state

$\overrightarrow{F} \perp$ surface
→ Normal stress σ_n = F/S

$\overrightarrow{F}$ // surface
→ shear stress τ







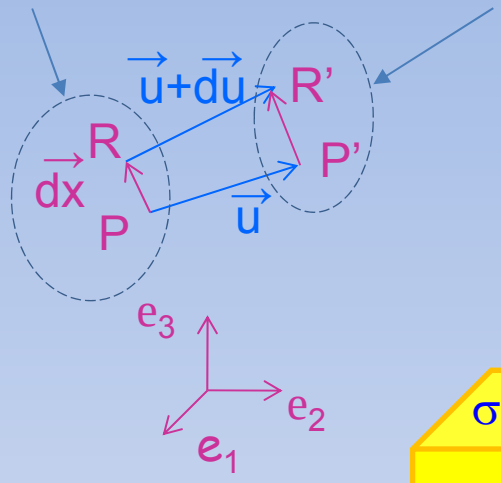
Strain components (ε_n, ε_T, γ) = « distortion » of the material / initial state, dimensionless

Stress components (σ, τ) = N/m^2 = Pascal

$$\overrightarrow{dF} = \sigma \,.\, \overrightarrow{dS}$$

Elastic strain and stress: some basic notions

initial state (relaxed) final state (strained)



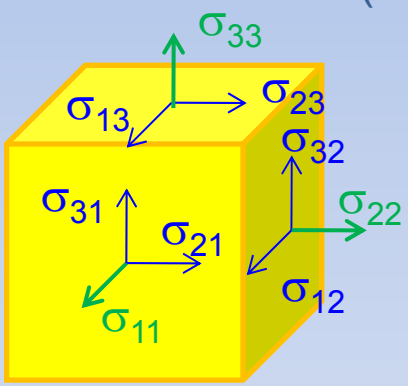
The strain is derived from the 3D displacement field $\vec{u}$

$$\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)$$

(small u)

$$\varepsilon = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{12} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{13} & \varepsilon_{23} & \varepsilon_{33} \end{pmatrix}$$

Length modification
Angular modification



$$\sigma = \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{13} & \sigma_{23} & \sigma_{33} \end{pmatrix}$$

3 « Normal » components
6 « Shear » components

Strain and stress are tensors of order 2

Symmetric → described by 6 independant components in a given coordinate system

Elastic strain and stress: some basic notions

$$\varepsilon = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{12} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{13} & \varepsilon_{23} & \varepsilon_{33} \end{pmatrix} \qquad \sigma = \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{13} & \sigma_{23} & \sigma_{33} \end{pmatrix}$$

The relationship between σ and ε constitutes the mechanical behavior law of the material

It depends on the material and on the level of strain

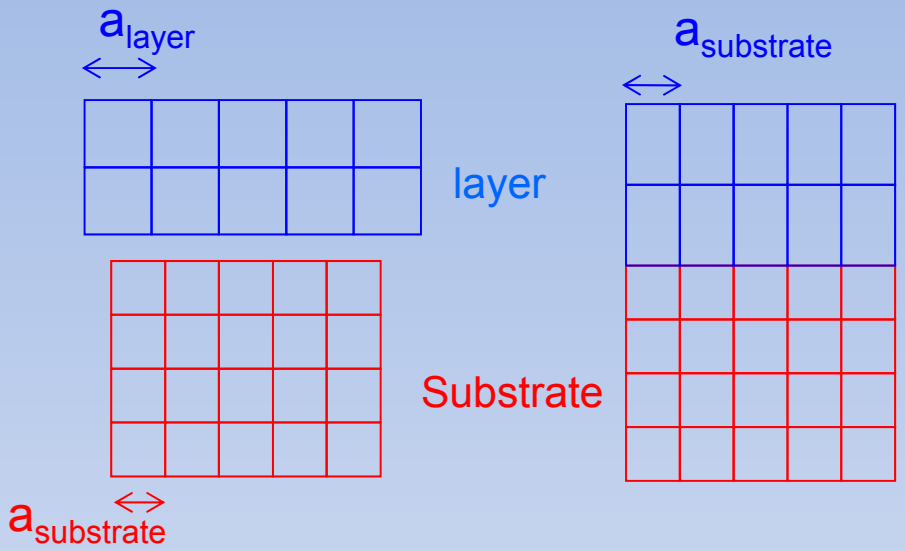
For crystals (anisotropic properties) at small strain
→ theory of linear elasticity
$\sigma = C\,\varepsilon$
C = elastic coefficients of the material (N/m^2 or Pa)

Stress and strain are tensors of order 2 → C is a tensor of order 4
C is symmetric → 21 ≠ coefficients in the general case (triclinic)
3 ≠ coefficients in cubic crystals C_{11}, C_{12}, C_{44}

For isotropic materials (ex. SiO_2), only two elastic constants are necessary (E, ν)

Elastic strain and internal stress: epitaxy of (001) cubic crystal

initial state (relaxed) final state (strained)



Growing the crystal creates the stress → Here, « initial state » = a virtual state !

The in-plane components of the strain are imposed by the lattice mismatch + symmetry in the (001) plane

$$\varepsilon_{11} = \varepsilon_{22} = (a_{substrate} - a_{layer}) / a_{layer} = -f$$

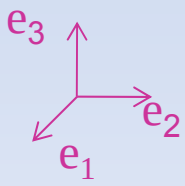
$$\sigma_{11} = \sigma_{22}$$

In the [100], [010], [001] basis:

$$\sigma = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \varepsilon = \begin{pmatrix} \varepsilon_{11} & 0 & 0 \\ 0 & \varepsilon_{22} & 0 \\ 0 & 0 & \varepsilon_{33} \end{pmatrix}$$

tetragonal strain, all shear components = 0

No stress along the growth direction ($\sigma_{33} = 0$)



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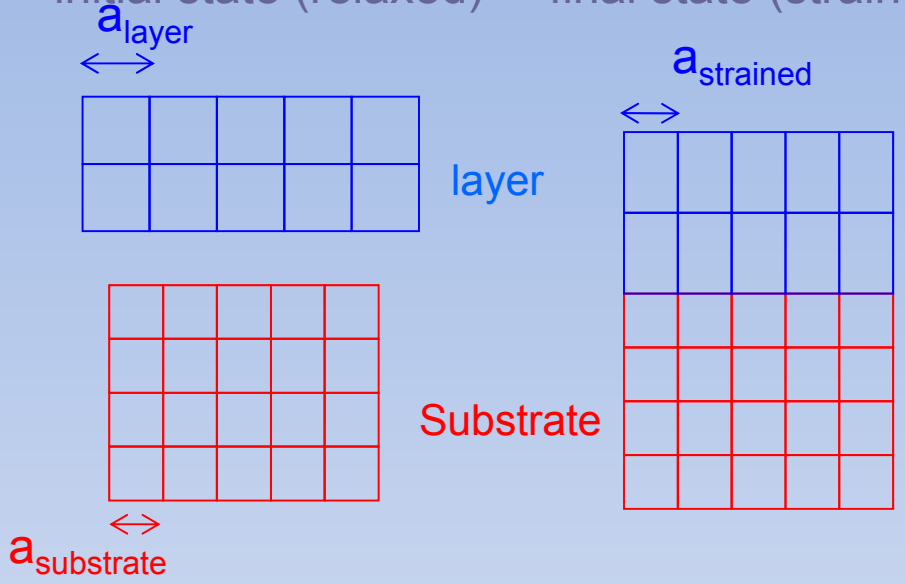

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$$\sigma_{11} = \sigma_{22}$$

Law of behavior

$$\sigma = C\,\varepsilon$$

Out-of plane strain $\varepsilon_{33} = -2(C_{12}/C_{11})\,\varepsilon_{11}$

In plane components of stress

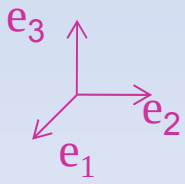
$$\sigma_{11} = \sigma_{22} = (C_{11}+C_{12}-2C^2_{12}/C_{11})\,\varepsilon_{11}$$

In the [100], [010], [001] basis:

$$\sigma = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \varepsilon = \begin{pmatrix} \varepsilon_{11} & 0 & 0 \\ 0 & \varepsilon_{22} & 0 \\ 0 & 0 & \varepsilon_{33} \end{pmatrix}$$

tetragonal strain, all shear components = 0

No stress perpendicular to the surface



Elastic strain and internal stress: epitaxy

Order of magnitude in SC

$\varepsilon_{33} = -2(C_{12}/C_{11})\,\varepsilon_{11}$

$\sigma_{11} = (C_{11}+C_{12}-2C^2_{12}/C_{11})\,\varepsilon_{11}$

	AlAs	InAs	InSb
C11 (GPa)	125.48	84.4	66.66
C12 (GPa)	53.54	46.4	36.41
C44 (GPa)	54.39	39.6	30.2
for $\varepsilon_{11} = -1\%$ ε_{33} (%)	0.9	1.1	1.1
σ_{11} (GPa)	-1.3	-0.8	-0.6

$$E_{elastic}(J) = \frac{1}{2}\int_{volume} \sigma.\varepsilon \quad \propto \quad f^2\, h_{epilayer}$$

↓

Mechanisms of stress release to reduce $E_{elastic}$

- $h_{epilayer} > h_{2D\text{-}3D}$ → SK growth mode = elastic relaxation by free surfaces
- $h_{epilayer} > h_{critical}$ → accommodation by misfit dislocations = plastic relaxation

Outline

- ✓ Accomodation of the crystalline lattice of the epilayer with the substrate lattice
  - → same compound (homoepitaxy), two crystalline lattices: ex. of III-V compounds
  - → polar on non polar materials: exemple of III-V on Si
  - → epitaxial relationship: two exemples in the mineral world
- ✓ Accomodation of the lattice misfit
  - → elastic strain and internal stress in hetero-epitaxy
  - → plastic relaxation by extended defects (dislocations)
  - → can we measure the epitaxial strain by TEM ?
  - → can we measure the stress by TEM ?
- ✓ Chemical discontinuities at interfaces
  - → ex. strain and chemical composition in [InAs/AlSb] system
  - → some other exemples in semiconductors
- ✓ Role of surfaces and interfaces in the 3D morphology
  - → (SK growth modes in SC)
  - → exemple of « nano-epitaxy » of metallic core-shell particules (Fe-Au)

Plastic relaxation by extended defects (dislocations)

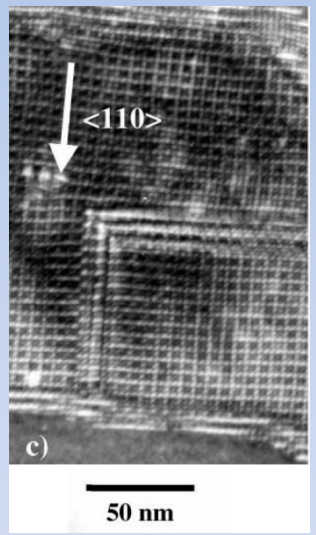
Ex. Growth of an highly mismatched system, GaSb on GaAs

a(GaAs)=0.565 nm
a(GaSb) = 0.6096 nm
f=7.9% → plastic relaxation

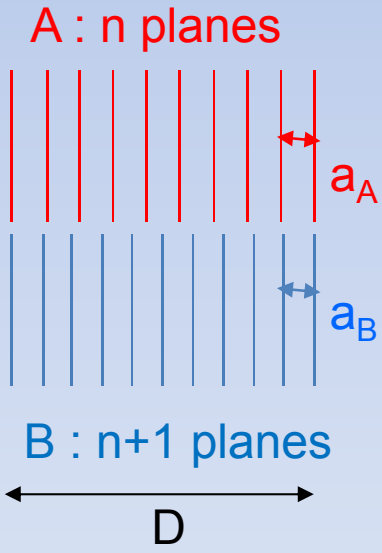
GaSb (7nm) / GaAs(001) MBE
Conventional TEM (weak beam) in plane view

↓

2 regular arrays of dislocations in the (001) interface
Spacing in [110] and [1-10] direction = 5.4 +/- 0.3 nm



Rocher et al. Appl. Surf. Sc. 188 (2002) 55



$(n-1)\ a_B = n\ a_A$
$n = a_B / (a_A - a_B) = 1/f$

$n = 1/f = 12.7$
→ between two dislocations
$D = 12.7 \frac{a_{GaSb}}{\sqrt{2}} = 5.47$ nm

↑
Lattice parameter in the [110] direction

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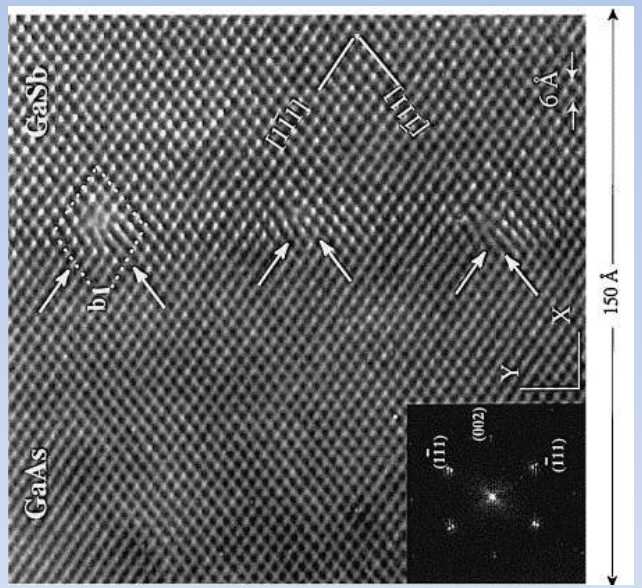
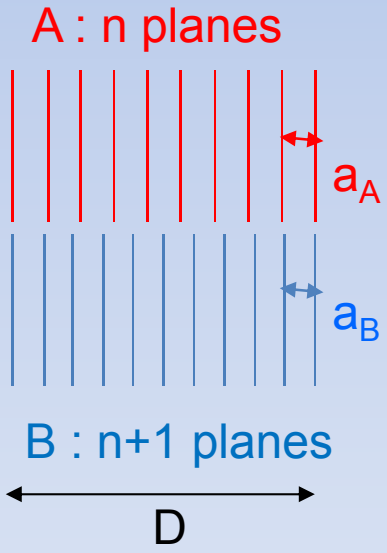


Rocher et al.
Thin Solid Films 319 (1998) 172

HRTEM (atomic resolution) in cross-section along [110]

↓

regular array of dislocations
about 12 GaSb lattice planes for 13 GaAs ones



$(n-1)\, a_B = n\, a_A$
$n = a_B / (a_A - a_B) = 1/f$

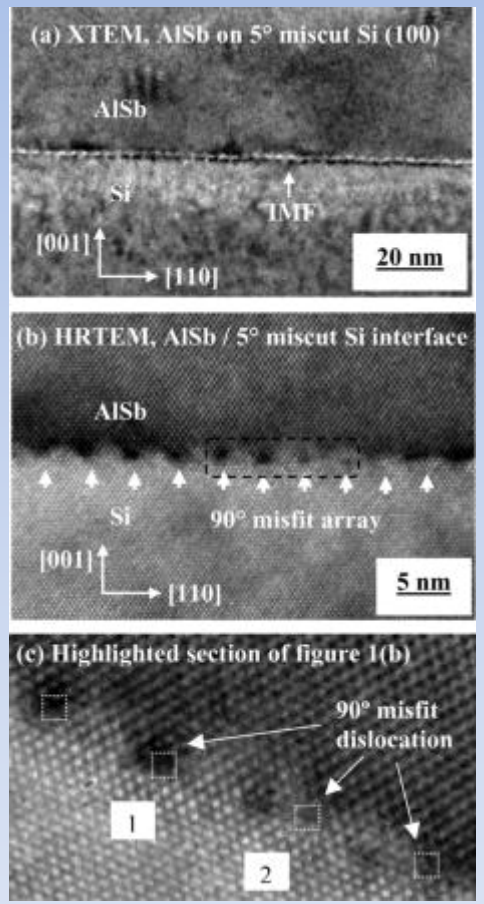
$n = 1/f = 12.7$
→ between two dislocations
$D = 12.7 \frac{a_{GaSb}}{\sqrt{2}} = 5.47$ nm

Lattice parameter in the [110] direction

Plastic relaxation by extended defects (dislocations)

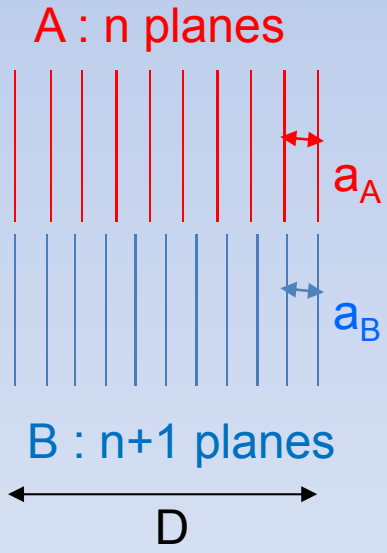
Another exemple

a(AlSb) = 0.61355 nm
a(Si) = 0.543 nm
f = 13%



Huang, Appl. Phys. Lett. 93, 071102 (2008)

TEM → D (dislocation separation) = 3.46 nm
HRTEM → 8 AlSb lattice sites grown on 9 Si lattice sites



$(n-1)\, a_B = n\, a_A$

$n = a_B / (a_A - a_B) = 1/f$

$n = 1/f = 7.7$

→ between two dislocations

$D = 7.7 \frac{a_{aAlSb}}{\sqrt{2}} = 3.3$ nm

Lattice parameter in the [110] direction

Outline

- ✓ Accomodation of the crystalline lattice of the epilayer with the substrate lattice
  - → same compound (homoepitaxy), two crystalline lattices: ex. of III-V compounds
  - → polar on non polar materials: exemple of III-V on Si
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  - → (SK growth modes in SC)
  - → exemple of « nano-epitaxy » of metallic core-shell particules (Fe-Au)

Can we measure the epitaxial strain by TEM ?

What do we measure in TEM ?

Atomic resolution images (HRTEM or HAADF-STEM)
→ Measure the local variation of lattice parameter / reference zone

Various methods (in the following exemples: geometrical phase analysis (GPA)
Hÿtch et al, Ultramicroscopy, 74, 131 (1998))

Can we measure the epitaxial strain by TEM ?

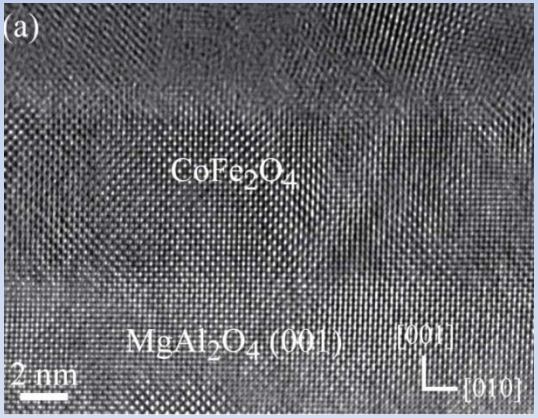
What do we measure in TEM ?

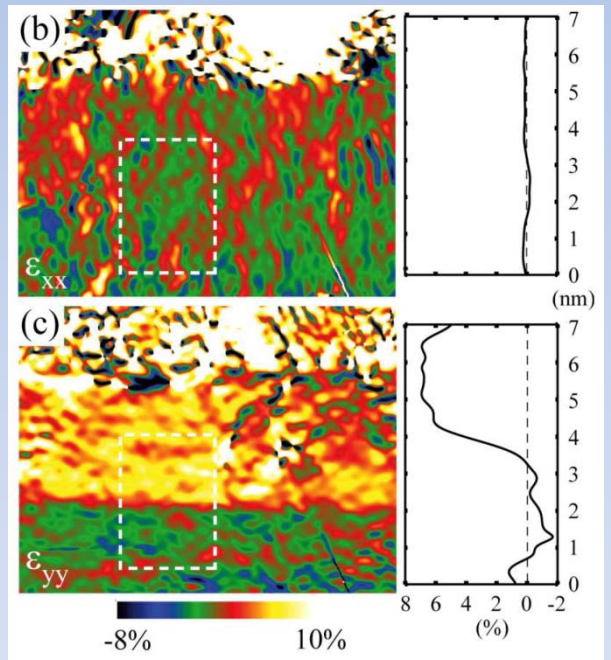
Atomic resolved images (HRTEM or HAADF-STEM)
→ Measure the local variation of lattice parameter / reference zone (the substrate)

One exemple: $CoFe_2O_4$ layer

on $MgAl_2O_4$ (001) substrate
(misfit f =3.8%)

Gatel et al. APL
103 (2013) 092405





in-plane lattice parametre variation:
measure/reference = 0%
→ in-plane strain in the layer
$\varepsilon_{11} = 0 - f = -3.8\%$

out-of-plane lattice parametre variation:
measure/reference = 6.7% +/- 0.3%
→ out-of-plane strain in the layer
$\varepsilon_{33} = 6.7 - f = 2.9\%$ +/- 0.3

C11 (GPa)	273
C12 (GPa)	106
C44 (GPa)	97

Calculated $\varepsilon_{33} = 2(C_{12}/C_{11})\, f = 2.8\%$

Strain measurement + no dislocations
→ The layer is fully elastically strained

Can we measure the epitaxial strain by TEM ?

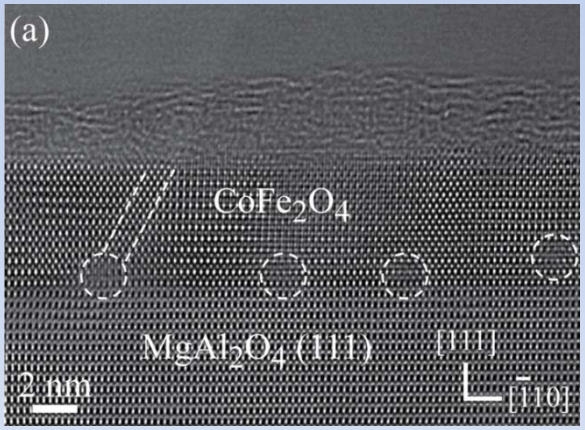
What do we measure in TEM ?

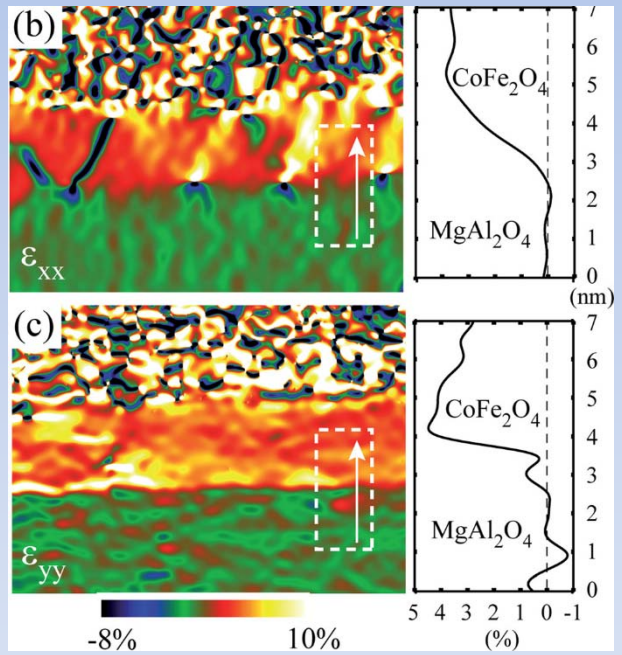
Atomic resolved images (HRTEM or HAADF-STEM)
→ Measure the local variation of lattice parameter / reference zone (substrate)

One exemple: $CoFe_2O_4$ layer

on $MgAl_2O_4$ (111) substrate
(misfit f =3.8%)

Gatel et al. APL
103 (2013) 092405





in-plane variation:
Measure/reference = 3.7%
→ in plane strain = 0%

out-of-plane variation:
Measure/reference = 3.7%
→ Out-of-plane strain = 0%

C11 (GPa)	273
C12 (GPa)	106
C44 (GPa)	97

Strain measurement + interfacial dislocations
→ The layer is fully relaxed

Can we measure the epitaxial strain by TEM ?

What do we measure in TEM ?

Atomic resolved images (HRTEM or HAADF-STEM)

→ Measure the local variation of lattice parameter / reference zone

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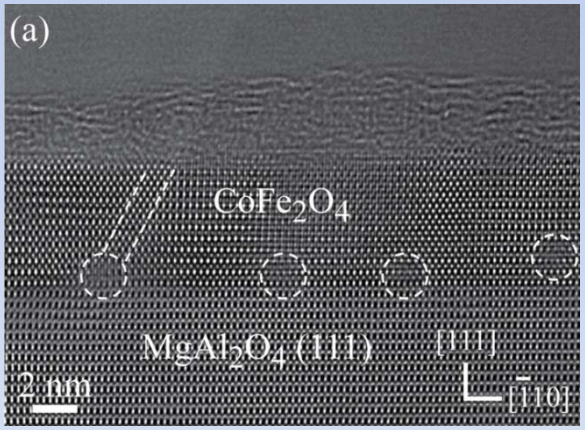
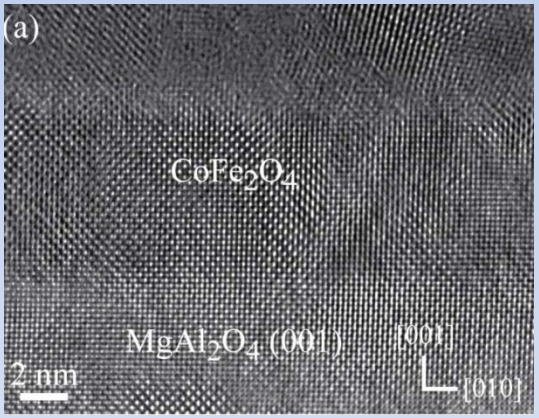
Gatel et al. APL
103 (2013) 092405

on $MgAl_2O_4$ (111) substrate



Magnetic properties degraded
(dislocations + APB)

on $MgAl_2O_4$ (001) substrate



Magnetic properties preserved / bulk
+ magnetoelastic effect (compressive stress)

Can we measure the epitaxial strain by TEM ?

What do we measure in TEM ?

Atomic resolved images (HRTEM or HAADF-STEM)
→ Measure the local variation of lattice parameter / reference zone

TEM is a powerfull approach:

- **Very local approach (nm)**
- **Applies to an individual object:**
  one nanometric layer, one QD, one nanowire….
- **Chemical and strain analysis possible at the same scale**
- **Defects also analysed**

Can we measure the epitaxial strain by TEM ?

What do we measure in TEM ?

Atomic resolved images (HRTEM or HAADF-STEM)
→ Measure the local variation of lattice parameter / reference zone

But not a direct or simple approach…

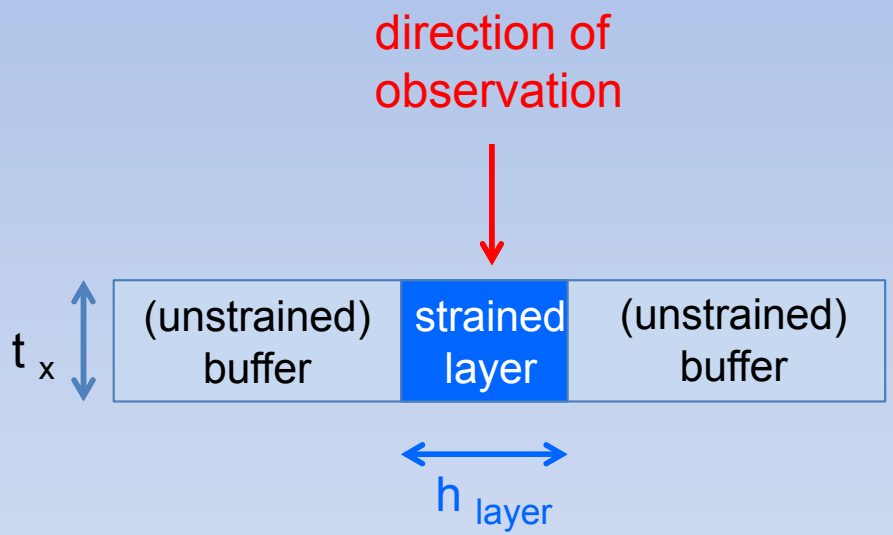
Image is not a simple 2D projection of the crystal (possible artefacts !)

Information can be lost by image analysis

- Strain knowledge needs to have a reference of the unstrained material
  → in TEM, the reference zone is generally the substrate and not the unstrained material
- Reconstitution of a 3D tensor from 2D data
- Thinning for TEM observation → modification / as grown sample (relaxation by free surfaces)

Can we measure the epitaxial strain by TEM ?

Cross-sectionnal sample thinned



2 “Historical articles” on surface relaxation

- ✓ Treacy, and Gibson (1986) The effects of elastic relaxation on transmission electron-microscopy studies of thinned composition-modulated materials. J. Vac. Sci. Technol. B, 4,1458–1466.
- ✓ Treacy, Gibson, and Howie (1985) On elastic relaxation and long wavelength microstructures in spinodally decomposed InxGa1xAsyP1y epitaxial layers. Philos. Mag. A, 51, 389.

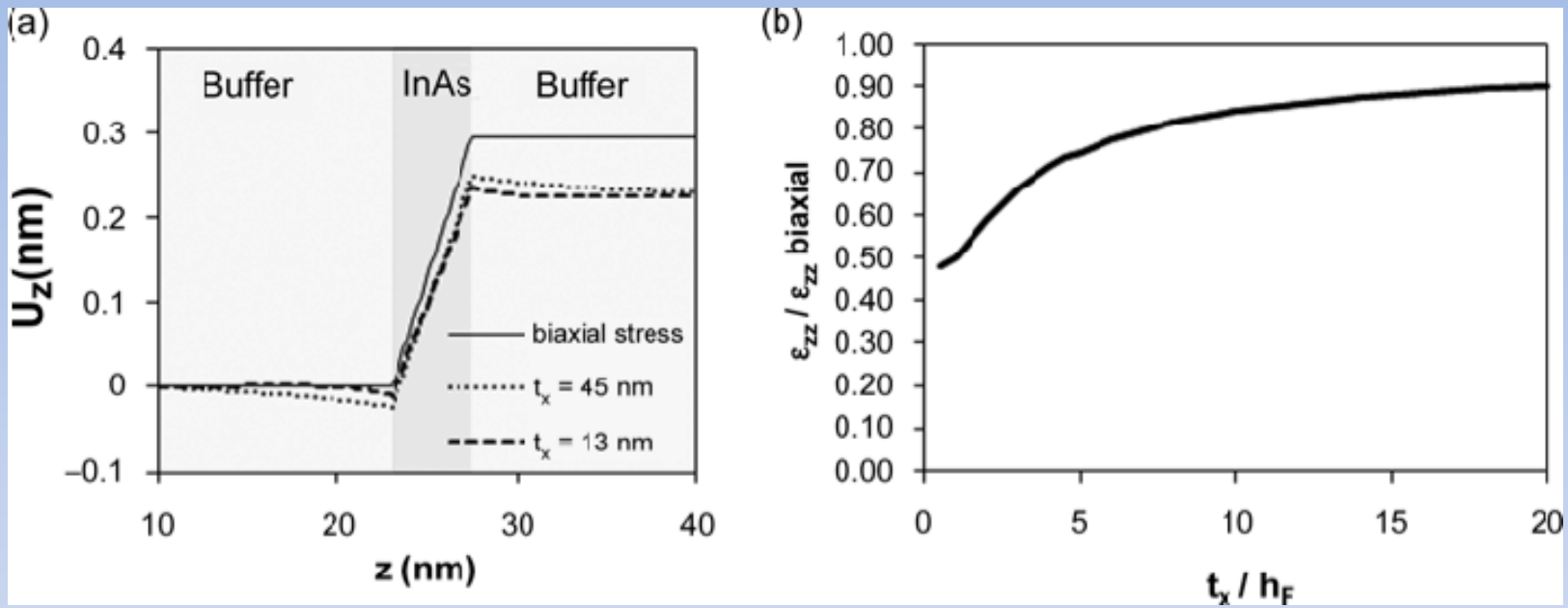
→ reduction of internal stress by surface relaxation

$t_x >> h_{layer}$ → bi-axial stress as in as-grown sample $\sigma_{11}=\sigma_{22}$ $\sigma_{33}=0$

$t_x << h_{layer}$ → uniaxial stress $\sigma_{11}=0$ σ_{22} $\sigma_{33}=0$

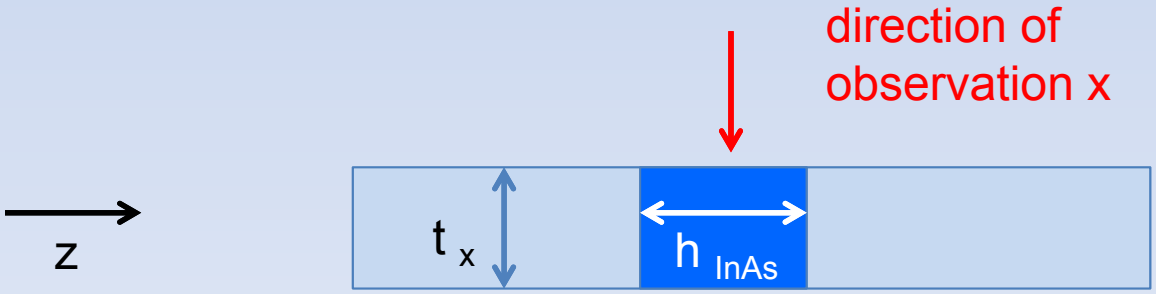
Can we measure the epitaxial strain by TEM ?

Finite element modeling (f = 3.2% h_{layer} = 5 nm)



out-of-plane displacements for unthinned sample, t_x=45 nm, t_x=13 nm

Reduction of out-of-plane strain with t_x/h_{layer}



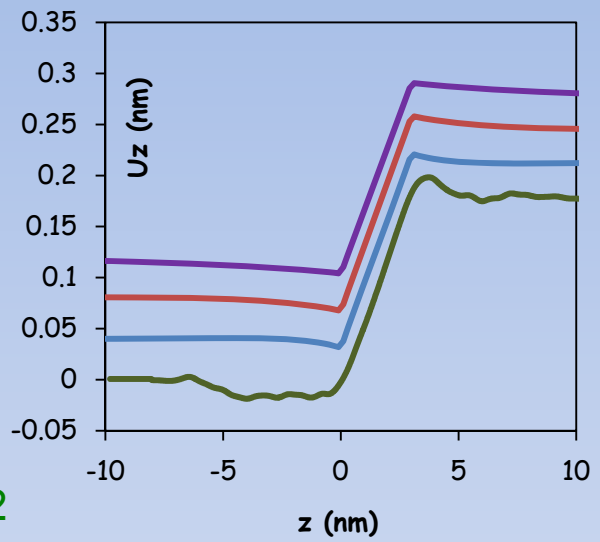
Gatel et al. Acta Mat 58, 3238 (2010)

Can we measure the epitaxial strain by TEM ?

Nominal value f = 0.032

→ dUz/dz = f + ε_{33} = $(1+2C_{12}/C_{11})$ f = 0.067

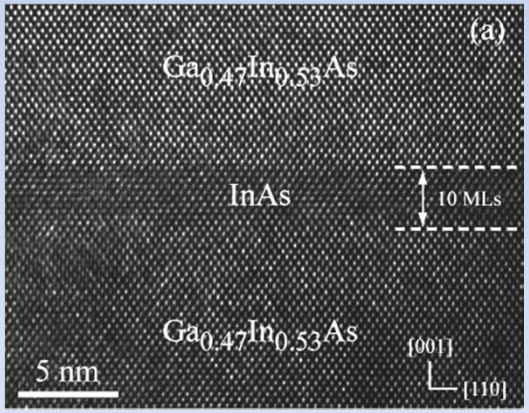
displacement field U_z in the growth direction



t_x = 50 nm f = 0.032 dU/dz = 0.063
t_x = 18 nm f = 0.035 dU/dz = 0.063
t_x = 9 nm f = 0.037 dU/dz = 0.063

Modeling by finite element

Experimental
dUz/dz = 0.063 +/- 0.002



→ Uz can be reproduced with the nominal value (f=0.032) but also with neighboring values !

Gatel et al. Acta Mat 58, 3238 (2010)

Can we measure the epitaxial strain by TEM ?

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Mechanical model of the sample with several hypothesis :
- mechanical behavior law
- geometry model of the sample (shape, thickness, boundaries conditions)
- a reference for relaxed state (misfit)

Ponchet et al in “Mechanical Stress on the nanoscale”, Wiley-VCH Berlin (2011)

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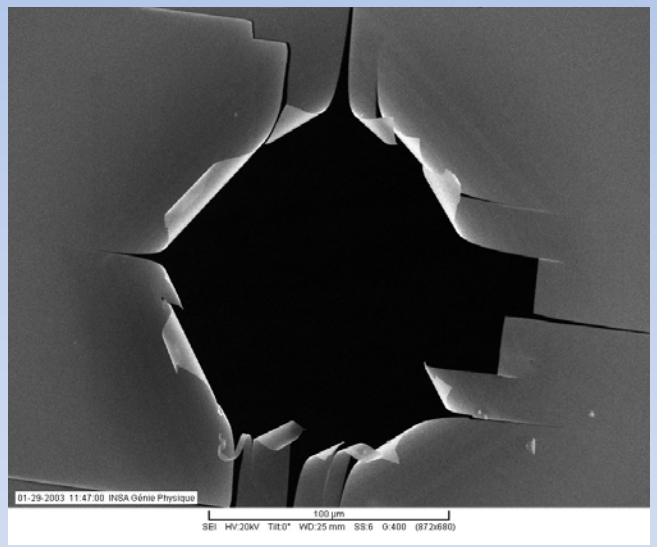
- ✓ Role of surfaces and interfaces in the 3D morphology
  - → (SK growth modes in SC)
  - → exemple of « nano-epitaxy » of metallic core-shell particules (Fe-Au)

Can we measure the stress by TEM ?

Up to now, we have considered the substrate either infinite or not deformable

exemple 10 nm $Ga_{0.8}In_{0.2}As$ layer epitaxially grown on GaAs substrate
thinning by the substrate side for plan view TEM



MEB observation

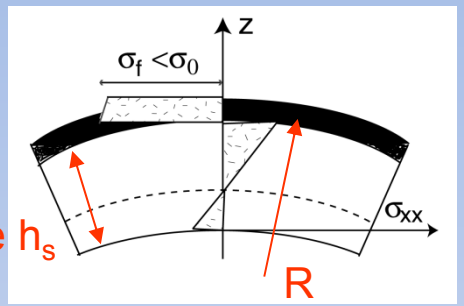
Bending is a direct consequence of stress !
It is a relaxation effect due to specimen thinning

Actually, the substrate has a finite size and is deformable
a good way to evidence the stress of an epilayer !

Can we measure the stress by TEM ?

Film h_f

Substrate h_s



In-plane stress in the film σ_f

$$= \frac{E_s}{6(1-\nu_s)} \frac{h_s^2}{h_f R} F\left(\frac{h_f}{h_s}\right)$$ Timoshenko 1926

$$= \frac{E_s}{6(1-\nu_s)} \frac{h_s^2}{h_f R}$$ Stoney 1906 if $h_f << h_s$

Independent on the origin of the stress (epitaxial stress, thermal stress…)

Curvature is used for a long time to measure the stress of a layer

- XR
- Optical measurement

Can we measure the stress by TEM ?

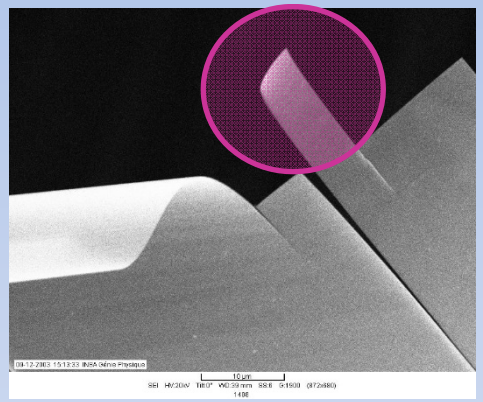
1) Plane view thinning

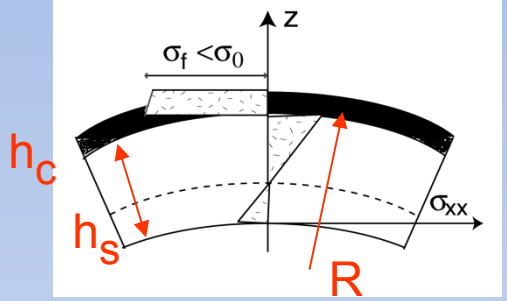
h_c = 10 nm $Ga_{0.8}In_{0.2}As$ sur GaAs (MBE LAAS)

Cabié et al, APL 84, 870 (2004)
and 86, 191901 (2005)

2) Select a suitable lamella

(50 nm < h_s < 300 nm)

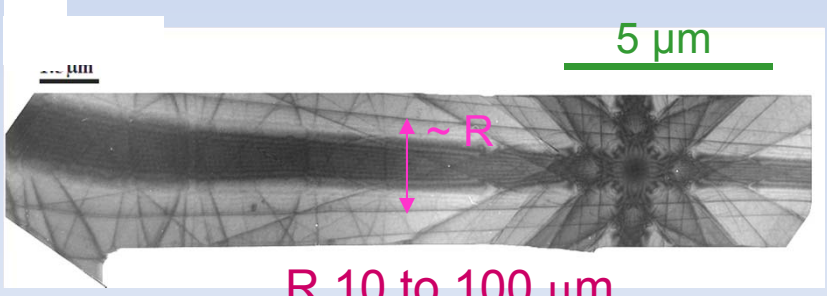




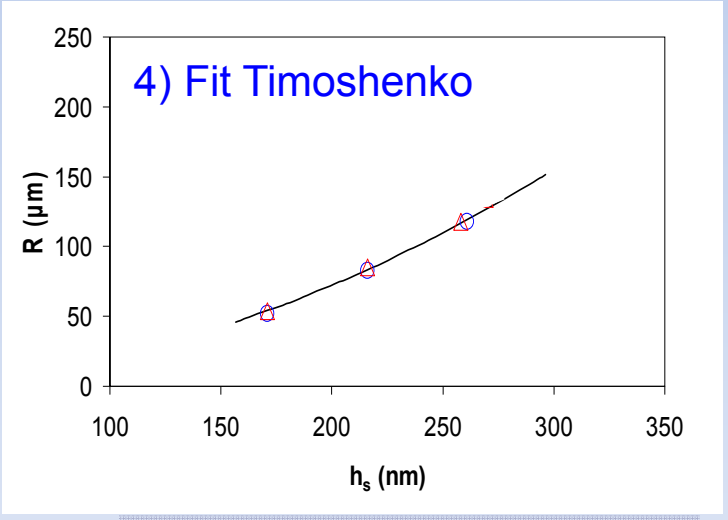
$$\sigma = \frac{E_s}{6(1-\nu_s)} \frac{h_s^2}{h_c R} F\left(\frac{h_c}{h_s}\right)$$

Can not be neglected (→ 30%)

3) TEM → R and h_s measured from bend contours (diffraction contrast)



R 10 to 100 µm



→ σ_{exp} = -1.30 GPa +/- 0.16

Can we measure the stress by TEM ?

- Avantage: Surface relaxation is completely controlled → very good approach of the stress before thinning
- Well adaped to *nanometric* layers with *stress* around 1GPa ($f \approx 10^{-2}$)
- Less local than strain measurement from atomic resolution images

Outline

- ✓ Accomodation of the crystalline lattice of the epilayer with the substrate lattice
  - → same compound (homoepitaxy), two crystalline lattices: ex. of III-V compounds
  - → polar on non polar materials: exemple of III-V on Si
  - → epitaxial relationship: two exemples in the mineral world
- ✓ Accomodation of the lattice misfit
  - → elastic strain and internal stress in hetero-epitaxy
  - → plastic relaxation by extended defects (dislocations)
  - → can we measure the epitaxial strain by TEM ?
  - → can we measure the stress by TEM ?
- ✓ Chemical discontinuities at interfaces
  - → ex. strain and chemical composition in [InAs/AlSb] system
  - → some other exemples in semiconductors
- ✓ Role of surfaces and interfaces in the 3D morphology
  - → (SK growth modes in SC)
  - → exemple of « nano-epitaxy » of metallic core-shell particules (Fe-Au)

Strain and chemical composition at interfaces: [InAs/AlSb] system

2) Consider AlSb on InAs:
- same crystalline lattice
- same family (III-V)
- AlSb/InAs = 1.3%
- but no atoms in common

Interface ? Al-As or In-Sb bonds
- Chemical discontinuity
- Strong change in bond length

1) Consider $Ga_{1-x}In_xAs$ on GaAs:
- same crystalline lattice
- same family (III-V)
- InAs/GaAs misfit 7% → f % = x * 7

Interface ? Ga-As or In-As bonds
- segregation of In / Ga → possible gradient of composition
- but progressive variation of lattice parameter

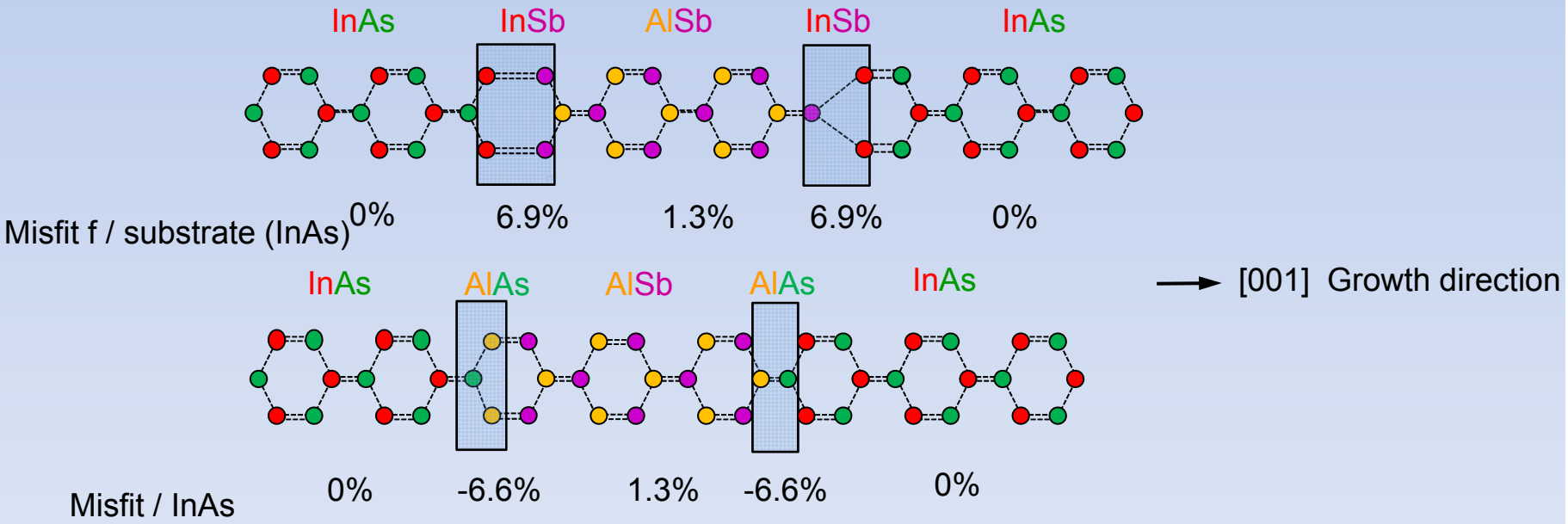
Strain and chemical composition at interfaces: [InAs/AlSb] system

Consider AlSb on InAs:
- same crystalline lattice
- same family (III-V)
- AlSb/InAs f = 1.3%
- but no atoms in common

Interface ? Al-As or In-Sb bonds
- Chemical discontinuity
- Strong change in bond length

Possible types of interfaces :
- In-Sb like = under compressive stress
- Al-As like = under tensile stress
- Mixed (alloy)

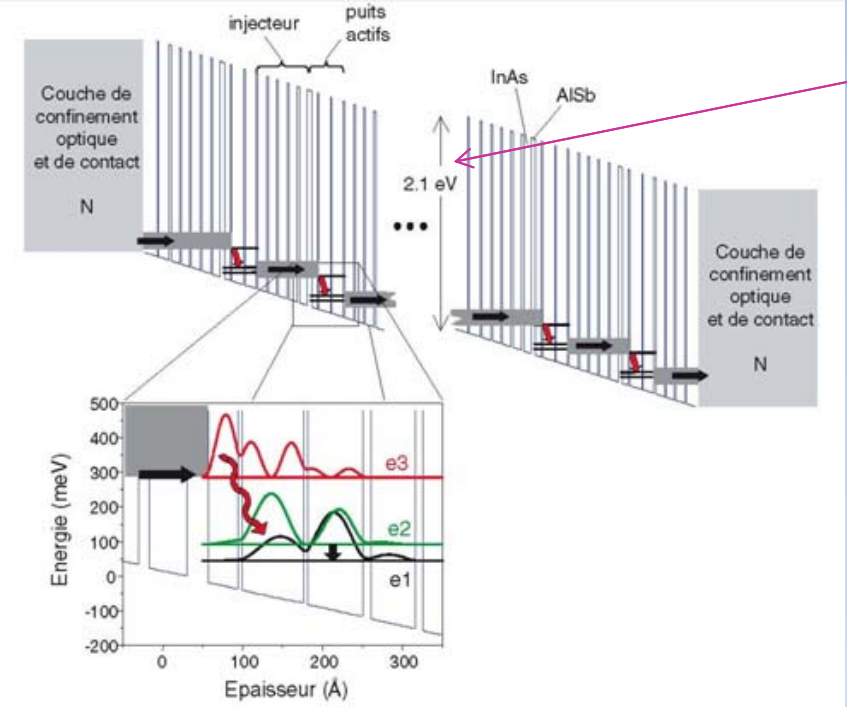
Do interfacial layers exist ?
Can we observe them ?
How stressed are the interfaces ?



Strain and chemical composition at interfaces: [InAs/AlSb] system

AlSb-InAs is an important system for quantum cascade lasers emitting in the middle infra-red range (> 2 μm)

Cathabard et al APL 96, 141110 (2010)



Very large conduction band offset

interfaces

→ λ controlled by the layer thicknesses (fraction of a ML !)

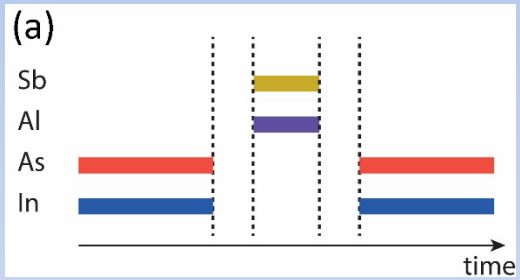
→ Very thin wells AND barriers (up to 1 MLs)

Recently, extension to longer wavelengths (19 μm) by reduction of the barrier thickness → 0.5 ML Chastanet et al APL 104, 021106 (2014)

Strain and chemical composition at interfaces: [InAs/AlSb] system

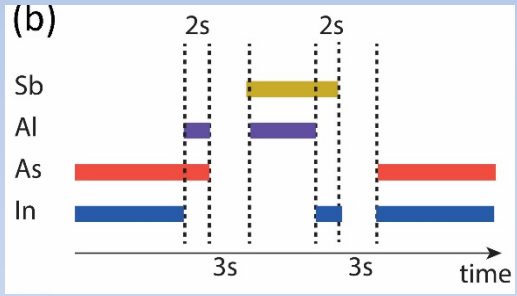
[InAs(20 nm)/AlSb(4 nm)] MBE (IES Montpellier)

3 different procedures at interfaces

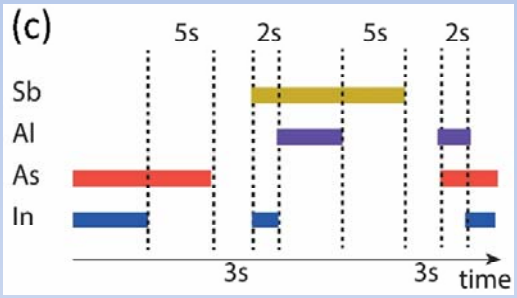


InAs / No fluxes / AlSb / No fluxes / InAs

spontaneaous formation of interfaces



InAs / Al-As forced / AlSb / In-Sb forced / InAs



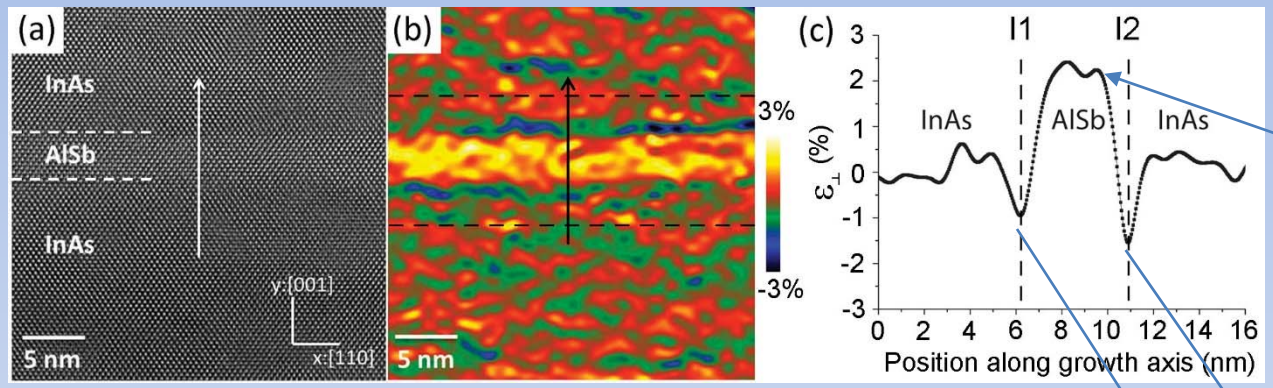
InAs / In-Sb forced / AlSb / Al-As forced / InAs

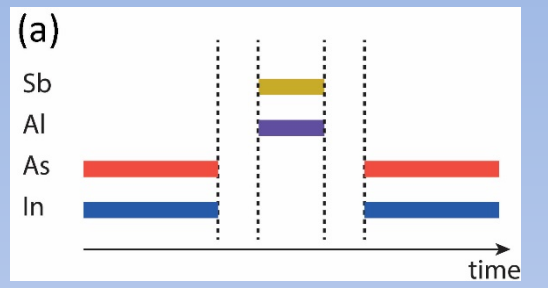
Interfacial sequences 0.7 ML

Strain and chemical composition at interfaces: [InAs/AlSb] system

1) Spontaneous formation of interfaces ?

Out of plane strain analysis from HREM images

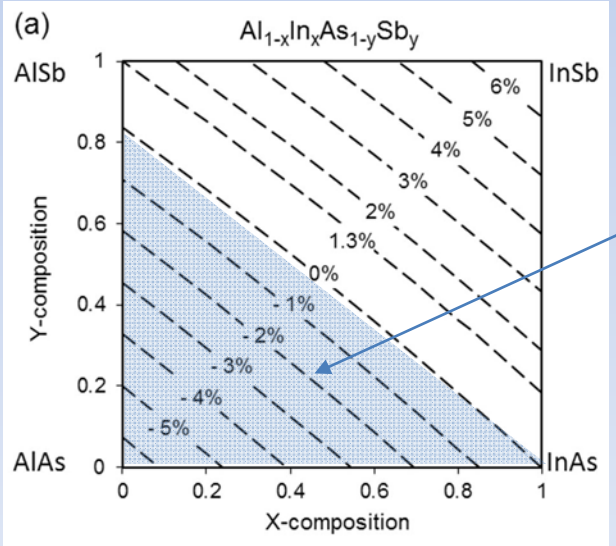




AlSb layer:
measured 2.5%
→ out-of-plane strain
2.5 – f = 1.2%
calculated = $2(C_{12}/C_{11})f$ = 1.3 %

→ compressive stress

Interfaces:
out-of-plane ε < 0
→ tensile stress

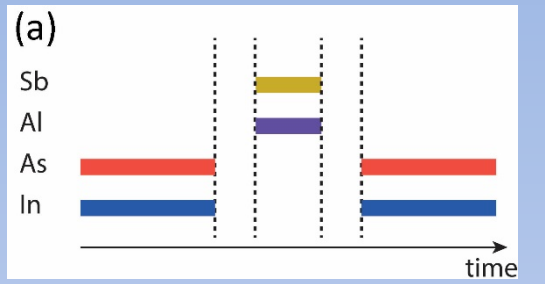


Quaternary alloy
Iso misfit curves

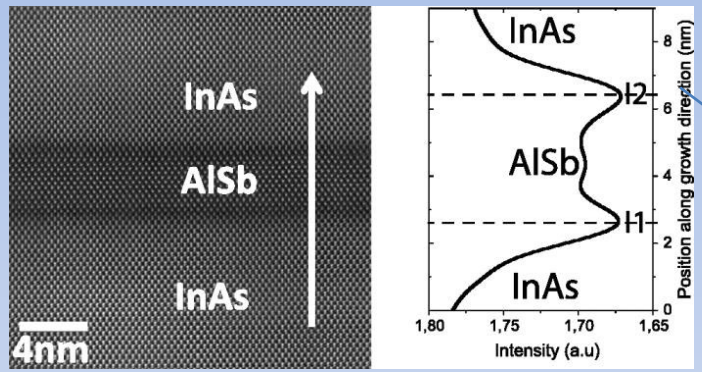
($f_{AlSb\ on\ InAs}$ = 1.3%)

Strain and chemical composition at interfaces: [InAs/AlSb] system

1) Spontaneaous formation of interfaces ?

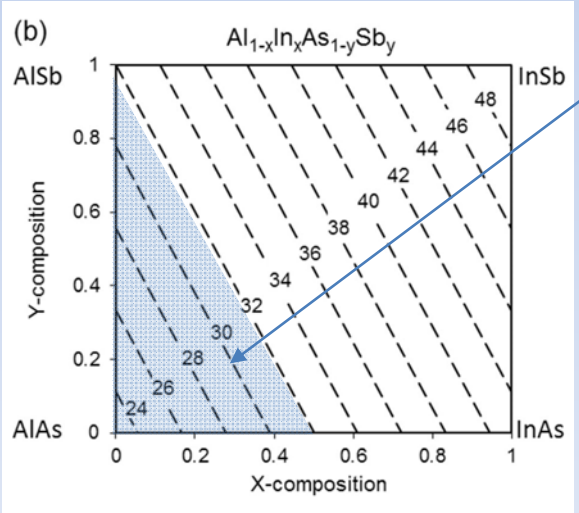


Chemical analysis from HAADF STEM Image (Saragoza)



« Z » contrast
Intensity $\propto Z^n$ (here $n \approx 1.7$)

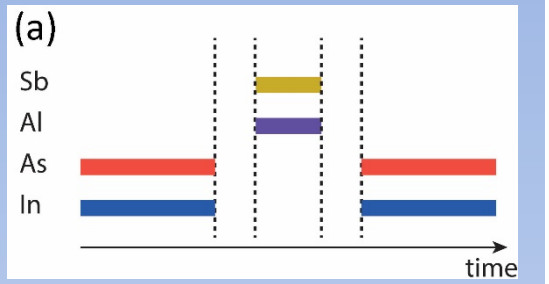
Interfaces → $Z_{interfaces} < Z_{AlSb} < Z_{InAs}$



Iso Z curves of quaternary alloys

Strain and chemical composition at interfaces: [InAs/AlSb] system

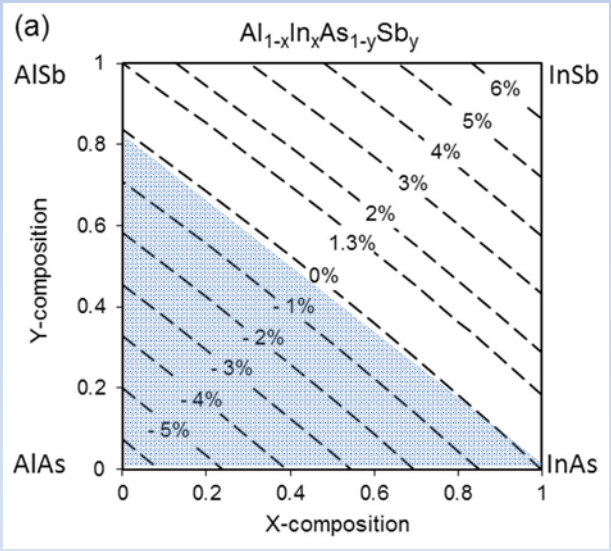
1) Spontaneous formation of interfaces ?



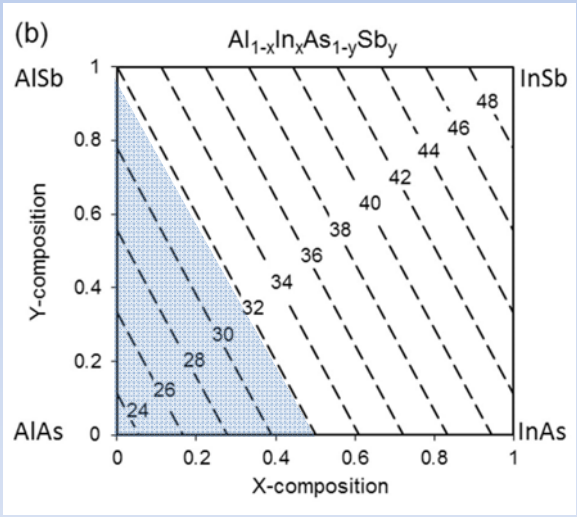
Combining Strain + Chemical analysis

→ AlSb is compressively strained on InAs following linear elasticity law

→ Interfaces are under moderate tensile stress with an Al-As rich tendency



Iso misfit

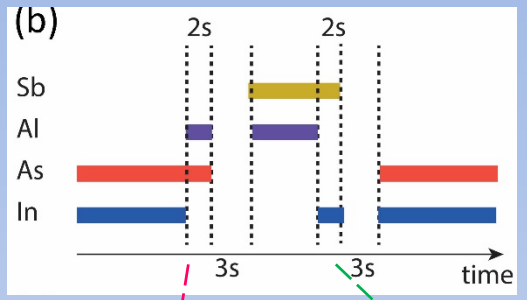


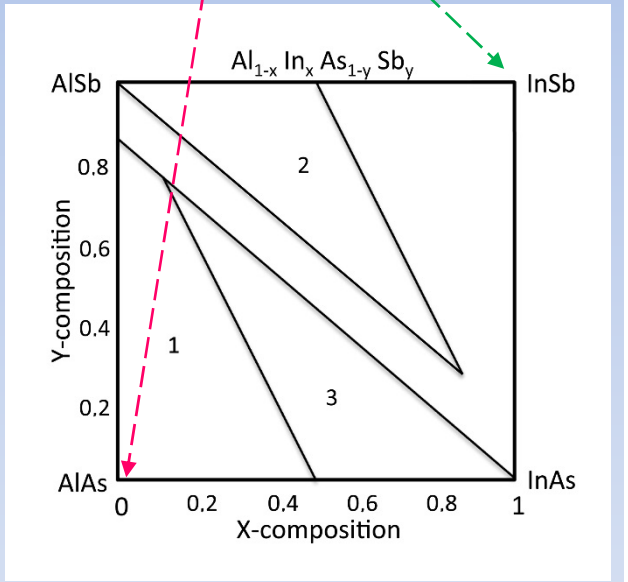
Iso Z

Nicolaï et al APL 104, 031907 (2014)

Strain and chemical composition at interfaces: [InAs/AlSb] system

2) Interfaces forced (sample B) ?

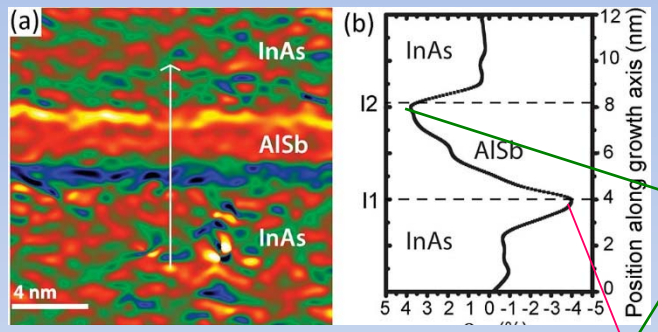




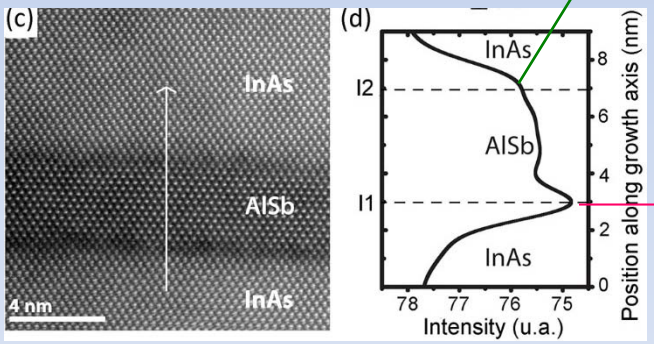
Strain and chemical composition at interfaces: [InAs/AlSb] system

2) Interfaces forced (sample B) ?

Strain analysis (from HREM image)



Chemical analysis (HAADF STEM)



high compressive stress

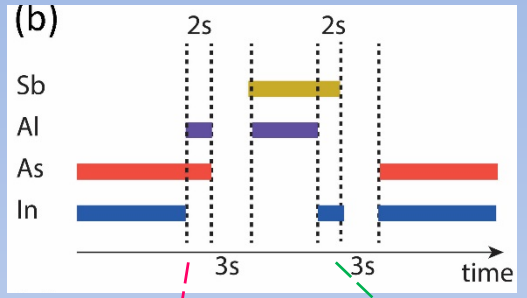
$Z_{AlSb} < Z_{interfaces} < Z_{InAs}$

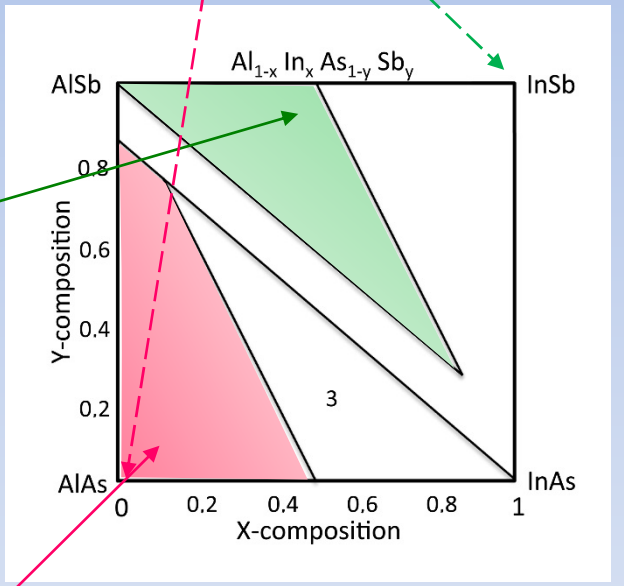
→ interface mixed $(Al_{0.5}In_{0.5})$-Sb like

high tensile stress

$Z_{interfaces} < Z_{AlSb} < Z_{InAs}$

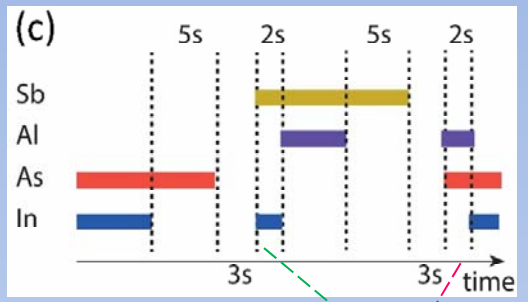
→ interface Al-As like

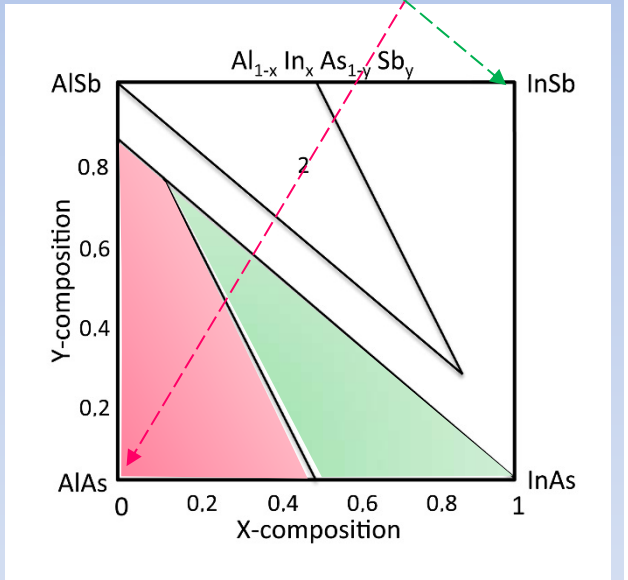




Strain and chemical composition at interfaces: [InAs/AlSb] system

2) Interfaces forced (sample C) ?

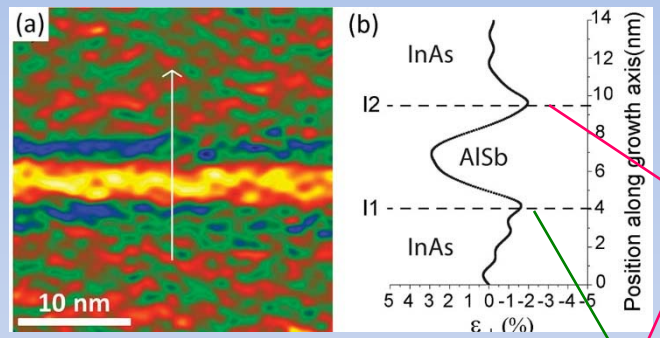




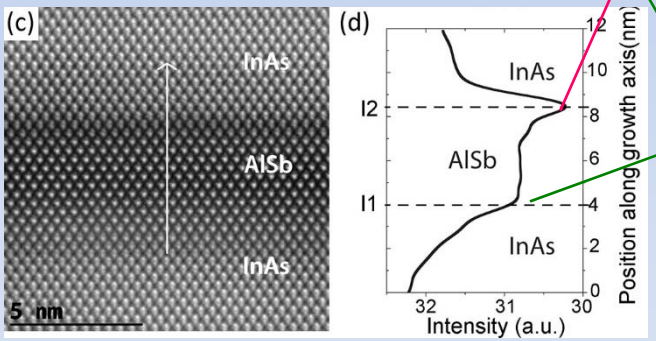
Strain and chemical composition at interfaces: [InAs/AlSb] system

2) Interfaces forced (sample C) ?

Strain analysis (from HREM image)



Chemical analysis (HAADF STEM)



tensile stress

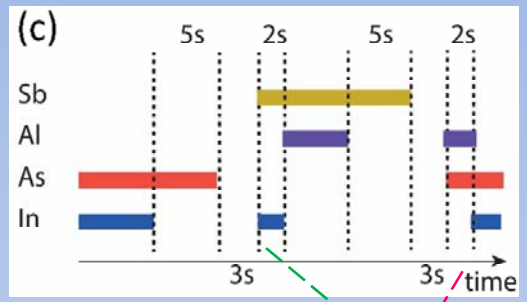
$Z_{interfaces} < Z_{AlSb} < Z_{InAs}$

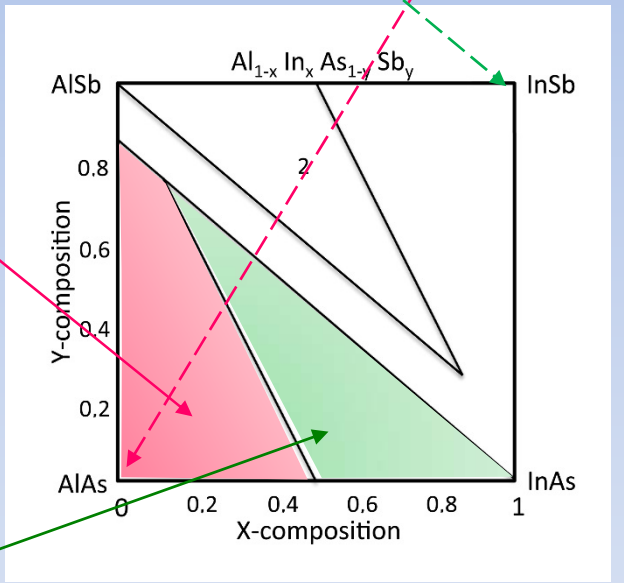
→ Interface Al-As like

sligth tensile stress

$Z_{AlSb} < Z_{interfaces} < Z_{InAs}$

→ Interface mixed ($Al_{0.5}In_{0.5}As$?)





Strain and chemical composition at interfaces: [InAs/AlSb] system

- Tendancy to Al-As like interface is spontaneously favoured
- Intentional insertion of Al-As interfacial sequence is successful at both interfaces
- Intentional insertion of In-Sb interfacial sequence is
  - only partially successful at InAs on AlSb interface
  - inoperative at AlSb on InAs interface
- Interfacial strain can be larger than average strain

Crystal	Melting Point (K)	Cohesive energy (eV)
AlAs	2013	6.8
AlSb	1338	6.6
InAs	1215	5.4
InSb	800	4.7

Higher stability of AlAs compared to InSb (bulk)

Nicolaï et al JAP 118, 035305 (2015)

Outline

- ✓ Accomodation of the crystalline lattice of the epilayer with the substrate lattice
  - → same compound (homoepitaxy), two crystalline lattices: ex. of III-V compounds
  - → polar on non polar materials: exemple of III-V on Si
  - → epitaxial relationship: two exemples in the mineral world
- ✓ Accomodation of the lattice misfit
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  - → plastic relaxation by extended defects (dislocations)
  - → can we measure the epitaxial strain by TEM ?
  - → can we measure the stress by TEM ?
- ✓ Chemical discontinuities at interfaces
  - → ex. strain and chemical composition in [InAs/AlSb] system
  - → some other exemples in semiconductors
- ✓ Role of surfaces and interfaces in the 3D morphology
  - → (SK growth modes in SC)
  - → exemple of « nano-epitaxy » of metallic core-shell particules (Fe-Au)

Strain and/or chemical composition at interfaces: some other systems

- InAs-AlSb on InAs(001) (MBE) Nicolaï APL-2014 and JAP-2015
  → tensile Al-As like interface favored compared to In-Sb like
  Attributed to the higher stability of AlAs

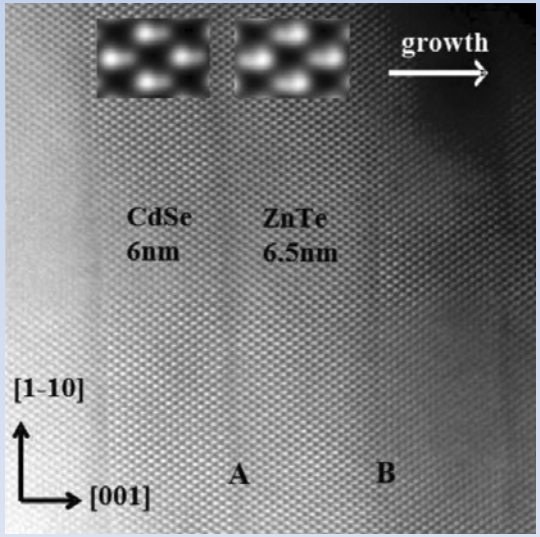
Crystal	Cohesive energy (eV)
AlAs	6.8
AlSb	6.6
InAs	5.4
InSb	4.7

- InAs-GaSb on GaSb(001) → tensile Ga-As like interface favored compared to In-Sb like

Mahalingam et al, Ultramicroscopy 127, 70 (2013).

- Also in II-VI system: ZnTe/CdSe (no strain in this system) (MBE)

→ Zn-Se like thin transition layer - Never Cd-Te like Bonef et al, APL 106, 051904 (2015)



Crystal	Cohesive energy (eV)
ZnSe	2.7
CdSe	2.5
ZnTe	2.4
CdTe	2.2

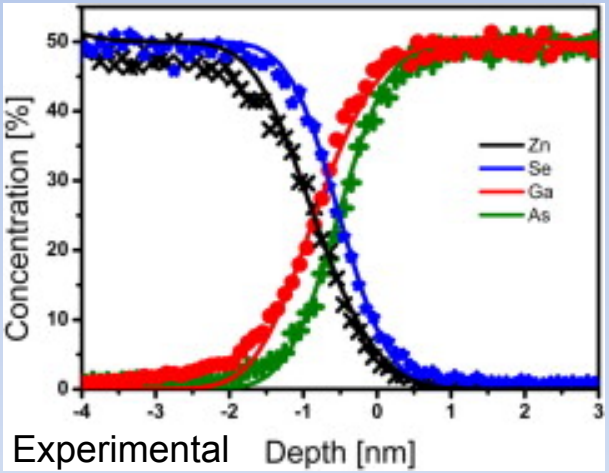
Attributed to the higher stability of ZnSe

Strain and/or chemical composition at interfaces: some other systems

- II-VI on III-V: ZnSe on GaAs(001) (MBE)

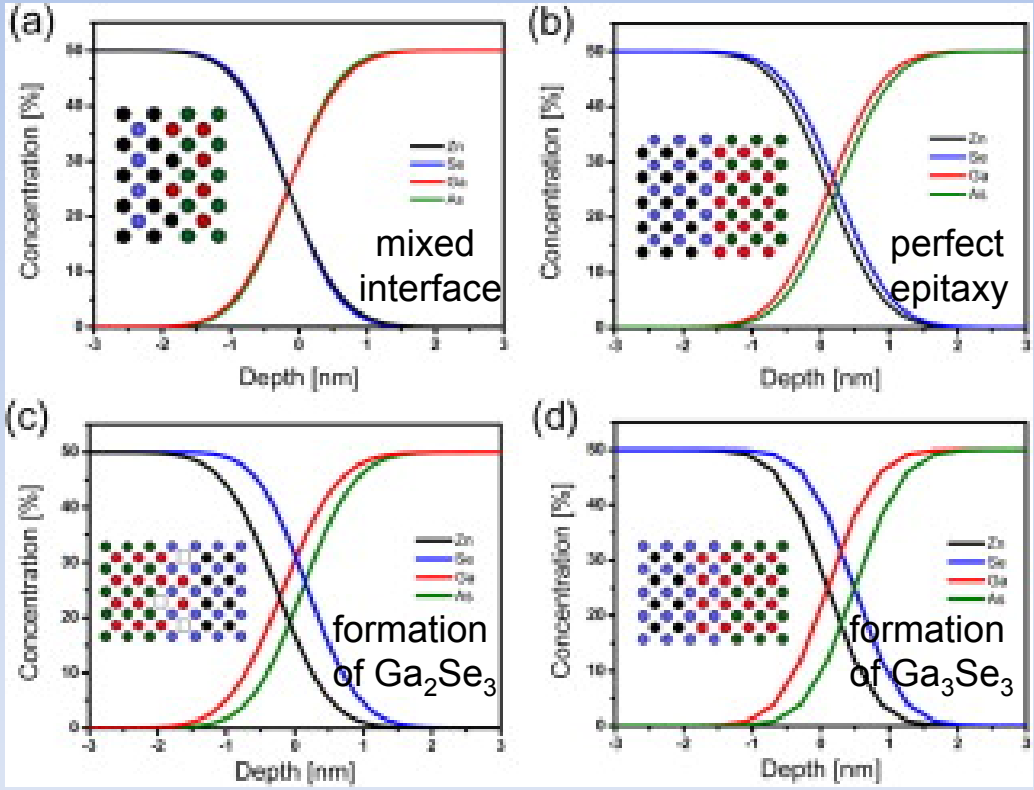
→ formation of an interfacial layer attributed to $Ga_{2+x}Se_3$ compound

Benallali et al, Scripta Materialia 69 (2013) 505



Experimental

Atom probe tomography profiles



Simulations

Outline

- ✓ Accomodation of the crystalline lattice of the epilayer with the substrate lattice
  - → same compound (homoepitaxy), two crystalline lattices: ex. of III-V compounds
  - → polar on non polar materials: exemple of III-V on Si
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- ✓ Accomodation of the lattice misfit
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  - → can we measure the epitaxial strain by TEM ?
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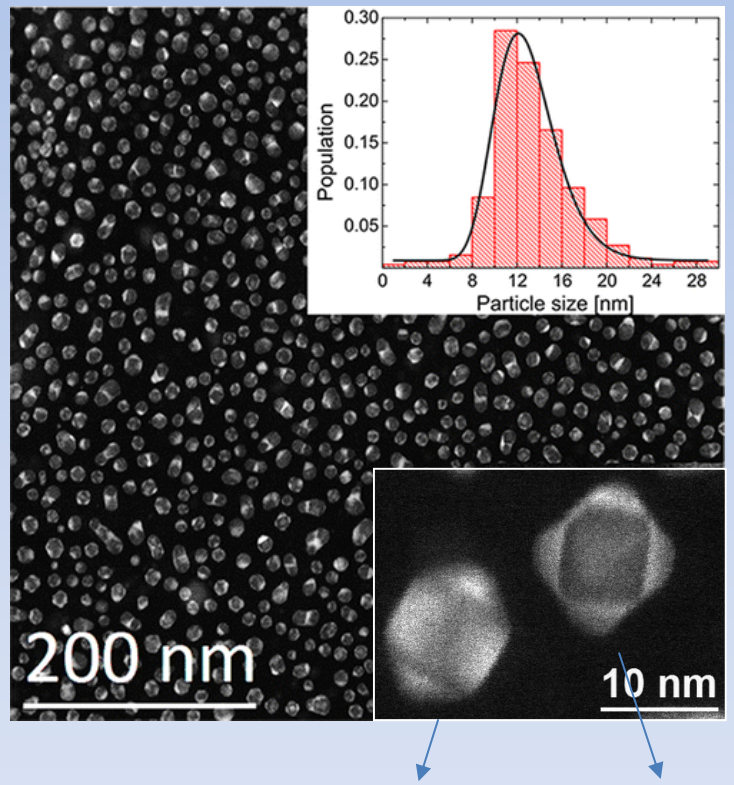
  - → ex. strain and chemical composition in [InAs/AlSb] system
  - → some other exemples in semiconductors
- ✓ Role of surfaces and interfaces in the 3D morphology
  - → (SK growth modes in SC)
  - → exemple of « nano-epitaxy » of metallic core-shell particules (Fe-Au)

« nano-epitaxy » of metallic core-shell particules (Fe-Au)

Deposit of Fe(2 nm) then Au (1 nm) on an amorphous Al_2O_3 film
Magnetron sputtering (UHV, growth mechanims ~ MBE)
800°C (Fe and Au not miscible)



Observed along [110]Fe and [001]Fe

→ Core-shell Fe@Au nanoparticles

Core = cube of iron, faces {100}
Shell = 6 symmetric pyramids of gold

Wulff construction for bcc metals →
Stable shape of Fe = rhombic dodecaedron
Saito, JCG 53 (1981) 273

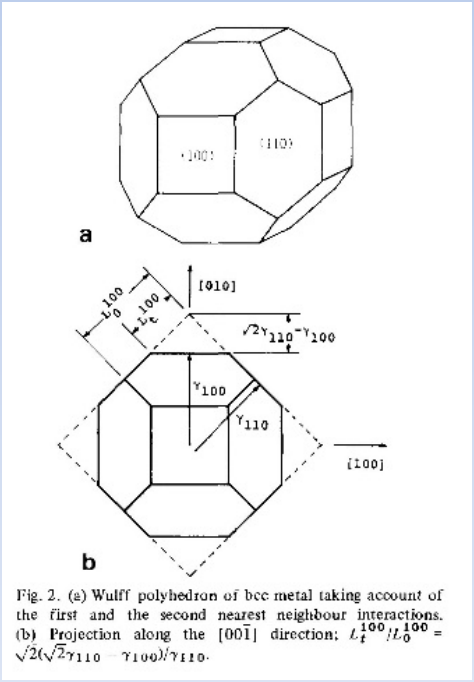
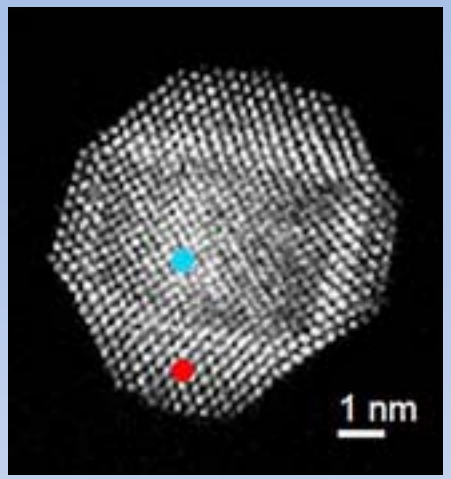


Fig. 2. (a) Wulff polyhedron of bcc metal taking account of the first and the second nearest neighbour interactions. (b) Projection along the [00$\bar{1}$] direction; $L_t^{100}/L_0^{100} = \sqrt{2}(\sqrt{2}\gamma_{110} - \gamma_{100})/\gamma_{110}$.

« nano-epitaxy » of metallic core-shell particules (Fe-Au)

Atomic resolution observations along the [001] $_{Fe}$

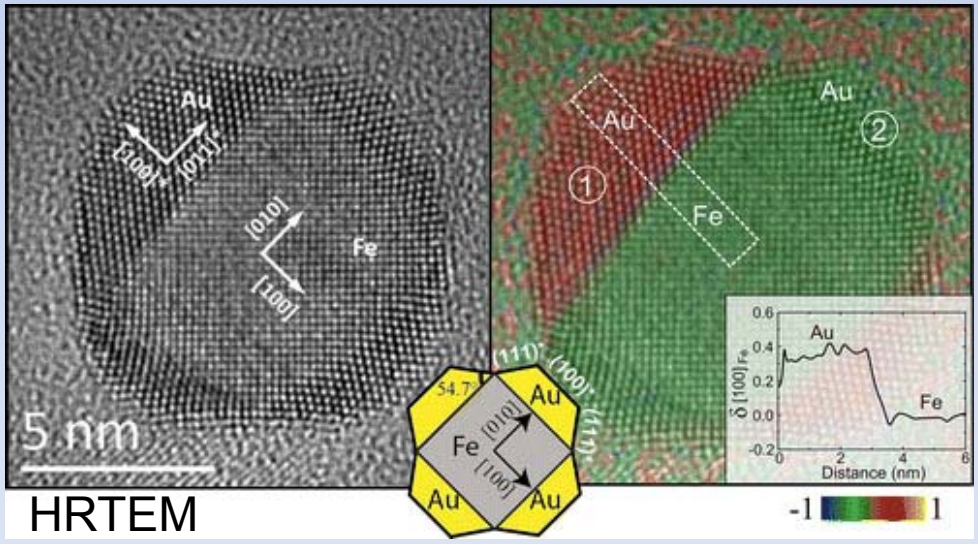
STEM HAADF



→ Core-shell Fe@Au nanoparticles

- Core = cube of iron
- Shell = 6 symmetric pyramids of gold

- Quasi-perfect interfaces (no dislocations)
- Quasi-perfect facetting of the gold shell



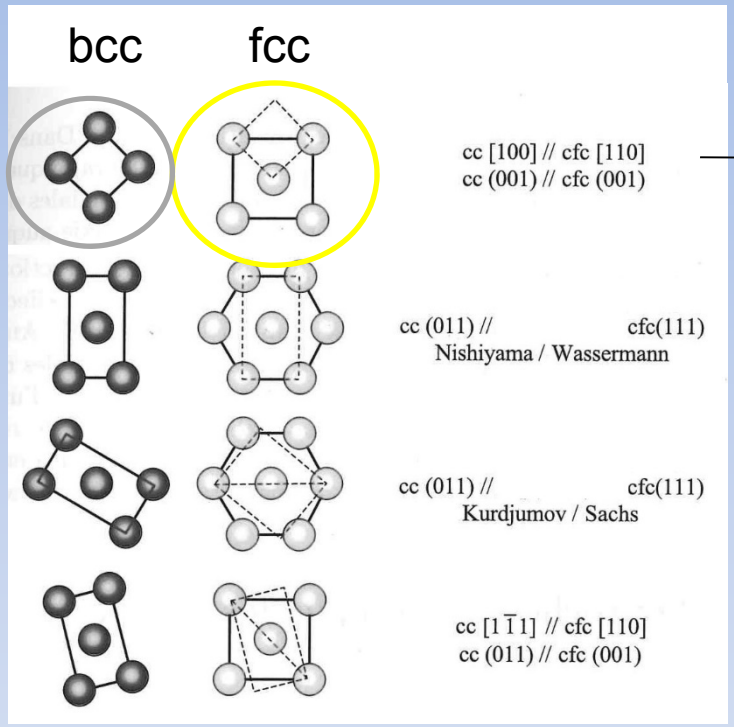
HRTEM

Not the same structure
Fe = bcc
Au = fcc

Very large misfit
a_{Fe} = 0.28665 nm
a_{Au} = 0.40784 nm

« nano-epitaxy » of metallic core-shell particules (Fe-Au)

Possible epitaxial relationships for epitaxy of fcc on bcc metals



Au (100)[011] / Fe(100)[010]

a_{Au} = 0.28665 nm a_{Fe} = 0.28665 nm

fcc bcc

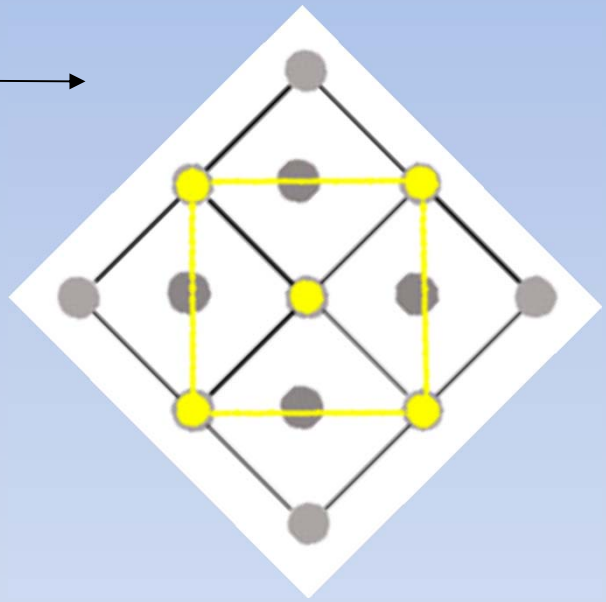


Fig. from Andrieu et Müller, Les surfaces solides : concepts et méthodes (2005)

$$\frac{a_{Au}}{a_{Fe}} = 1.42 \approx \sqrt{2} \quad \rightarrow \text{after rotation of } 45°,$$

$$\text{misfit} = \frac{a_{Au} - \sqrt{2}\, a_{Fe}}{\sqrt{2}\, a_{Fe}} = 0.6\%$$

Langlois et al, Nano Lett., 15, 5075 (2015)

« nano-epitaxy » of metallic core-shell particules (Fe-Au)

Can we explain the Au (100)[011] / Fe(100)[010] interfaces ?

Factors favoring

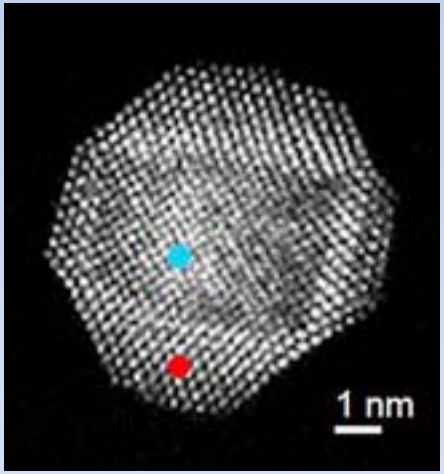
- Suitable relationship
- Low misfit within this relationship
- DFT calculation → This interface energy was found as low as 356 mJ·m−2

Benoit et al Phys. Rev. B. 86, 075460 (2012)

Can we explain this core-shell morphology ?

On each Au pyramid,
(001) top facet and (111) lateral facets

Surface energies		
Fe	2400 J·m−2	Exp. Tyson et al Surf. Sci. 1977, 62, 267
Au(111)	1500 J·m−2	Exp. Tyson et al Surf. Sci. 1977, 62, 267
Au(100)	1800 J·m−2	DFT Benoit et al Phys. Rev. B. 86, 075460 (2012)



Favor the full coverage of iron by gold
(wetting phenomenon)

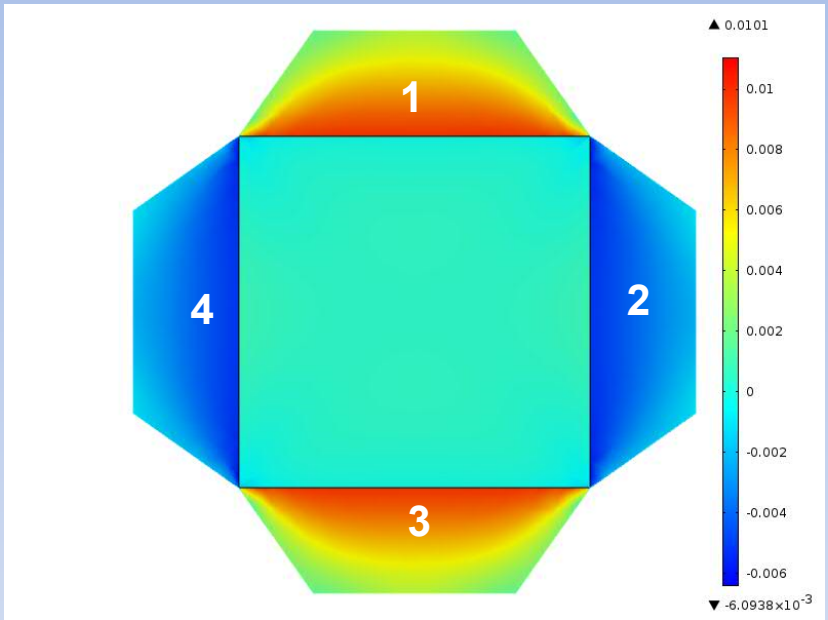
« nano-epitaxy » of metallic core-shell particules (Fe-Au)

Elastic properties / surfaces properties

1) Finite element modeling of the strain

Hypothesis:

- Fe cube / 6 identical Au pyramids
- Misfit = 0.6%
- No dislocations (system fully strained)
- Linear elasticity



Strain in the vertical direction =
Out-of-plane strain in pyramids (1) and (3)
In plane strain in pyramides (2) and (4)

« nano-epitaxy » of metallic core-shell particules (Fe-Au)

Elastic properties / surfaces properties

At interfaces, strain is close to the (virtual) case of 2D Au layer on infinite Fe substrate

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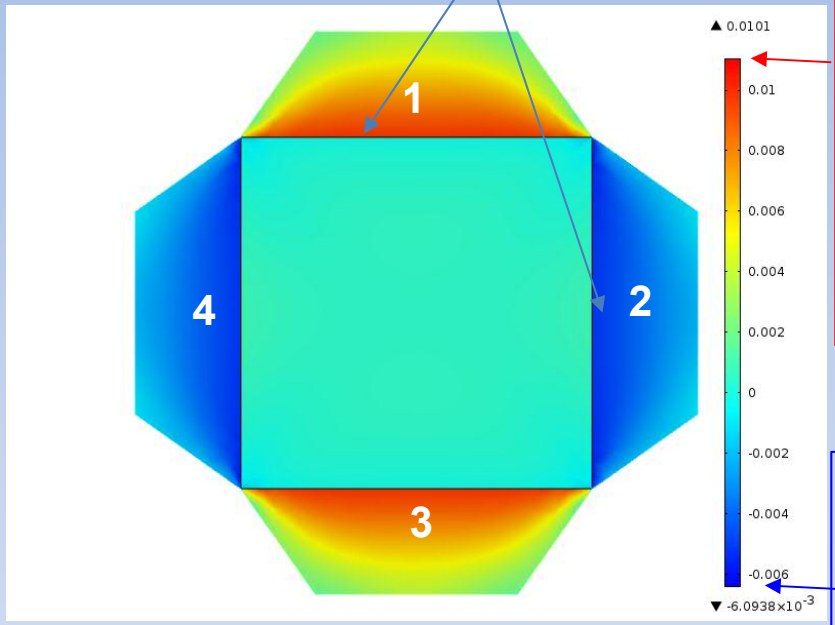

2D: $\varepsilon_{out\text{-}of\text{-}plane}$ = 0.0116 = 1.16%

2D: $\varepsilon_{in\text{-}plane}$ = -0.006 = -f

Strain in the vertical direction =
Out-of-plane strain in pyramids (1) and (3)
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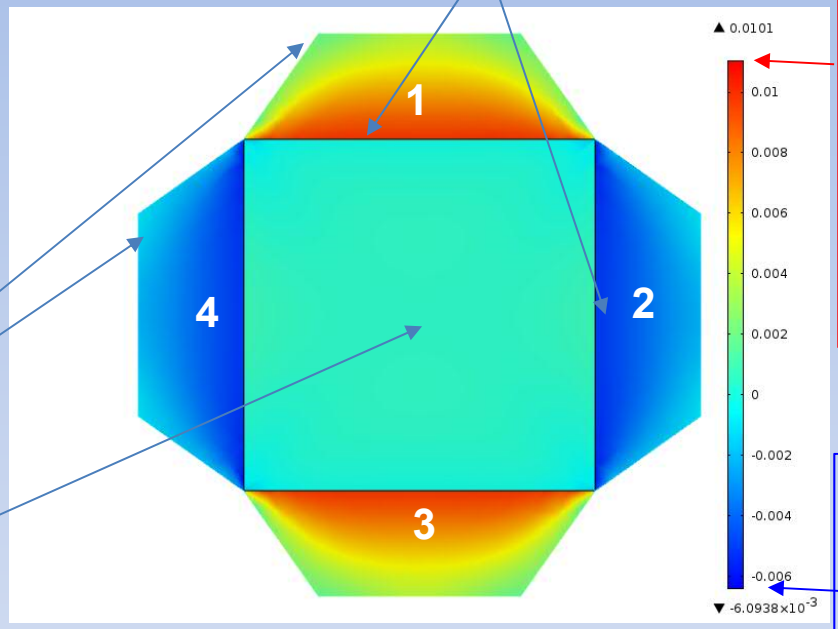


2D: $\varepsilon_{out\text{-}of\text{-}plane}$ = 0.0116 = 1.16%

2D: $\varepsilon_{in\text{-}plane}$ = -0.006 = -f

Full relaxation at the top of gold pyramids

iron is slightly strained
→ Stress shared between core (10% of E_{elas}) and shell (90%)

Strain in the vertical direction =
Out-of-plane strain in pyramids (1) and (3)
In plane strain in pyramides (2) and (4)

Very similar to island growth in semiconductors systems
(for instance Ponchet et al. APL 72, 2984 (1998))

Langlois et al, Nano Lett., 15, 5075 (2015)

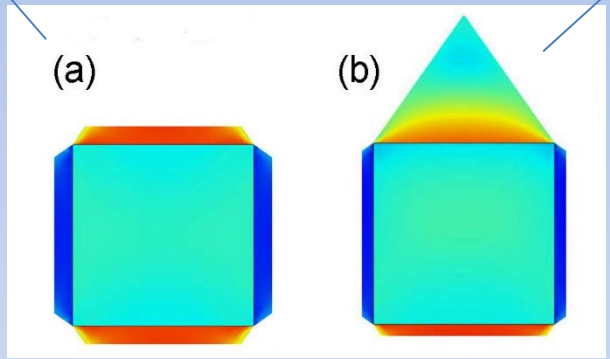
« nano-epitaxy » of metallic core-shell particules (Fe-Au)

Elastic properties / surfaces properties

2) Strain-induced or surface-induced morphology ?

6 identical troncated pyramids
Favored by reduction of surface energy

1 full + 5 identical troncated pyramids
Favored by reduction of elastic energy



For the same quantities of gold and iron

Here size = 8 nm, f = 0.006 → E surface >> E elastic
morphology determined by surface properties (symmetrical shape, facetting)

If (size = 800 nm, f = 0.006) or (size = 8 nm, f = 0.06) → E surface << E elastic
morphology determined by elastic properties (asymmetrical morphology)

Langlois et al, Nano Lett., 15, 5075 (2015)

Some conclusions…

- Epitaxial relationship
  - → very simple …..or very complex
  - → close crystalline lattices can generate « strong » defects (ex. ZB / diamond → APD)
  - → a suitable epitaxial relationship can minimize the misfit

- Strain/Stress measurement by TEM
  - → **stress** can be measured directly through curvature
  - → powerfull approach of the **strain** at a very local scale
  - → possible investigation of **strain**, chemistry, defects at a the same scale
  - → but **strain** is never directly measured

    keep in mind that one uses a mechanical model including
    - ➢ a law of mechanical behavior of the material (for instance linear elasticity…)
    - ➢ a reference for relaxed state (for strain measurement)
    - ➢ a geometrical model of the thinned sample (shape, thickness…)

    try to estimate an error bar

- Chemical discontinuity → possible interfacial ultra thin layers
  - → with specific composition
  - → specific strain (can be > average strain !)
  - → very sensitive to growth procedure

- Competition surface, interface and elastic energies → determines 3D morphology
  - → SK island growth (SC) but also « nano-epitaxy » of metallic core-shell particules

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