Epitaxy of metals : concepts and specificities

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OUTLOOK

- Why thin metallic films ? Why epitaxy ?
- Chap.I - Specificities of metallic thin film growth
- Chap.II - Epitaxial mechanisms
- Chap.III - Metallic film growth strategies
- Chap.IV - Illustration by examples

Why thin metallic films ? Why epitaxy ?

Wide applications

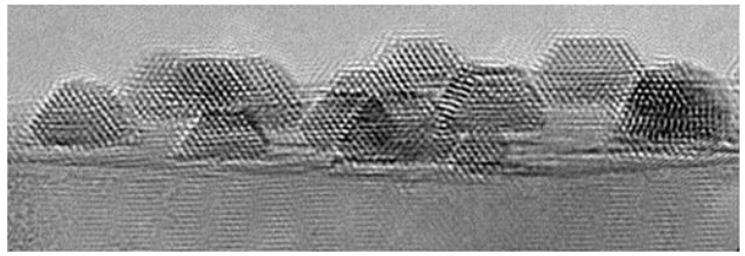
- Optics : filter, anti-reflective coatings, mirror,…
- Magnetism : computer reading heads, magnetic memory, spintronic
- Mechanics : protection to corrosion, hardness,…
- Chemistry : Catalysis, …

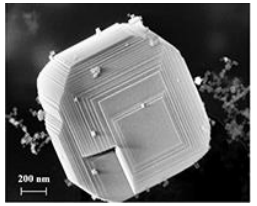
Epitaxy ?

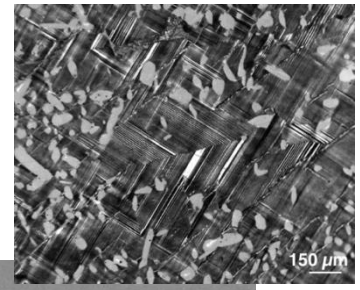
Often not needed (contrary to microelectronics)

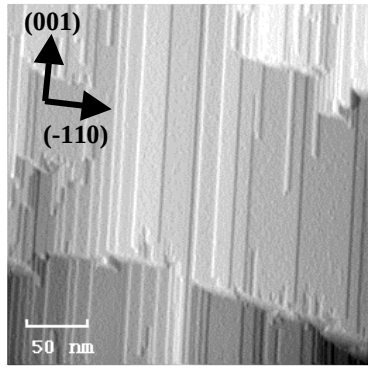
Epitaxy : model system to understand physics and validate new concepts

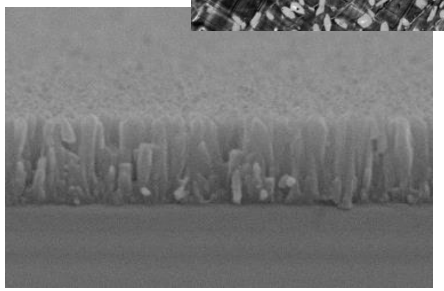
=> number of examples in spintronics

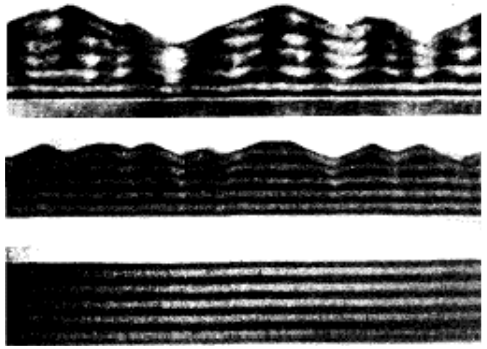


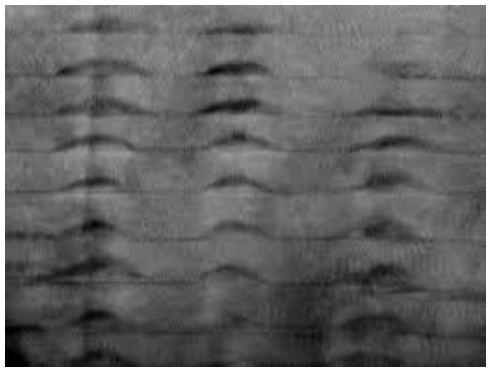












- Why thin metallic films ? Why epitaxy ?
- Chap.I - Specificities of metallic thin film growth

  choice of substrates, growth temperature

  Important energies and impact on metallic film growth:

    surface energy, model of first neighbor bonds

    Interface energy, wetting, adhesion (Dupré and Young formula)

    Bauer criterion for 2D growth

  Kinetical aspects : Adsorption, growth, percolation

Choice of substrates, growth temperature

In general, metals tend to mix, so 2 problems to get thin films stacks :

- Choice of the substrate to initiate the first layer growth
- Choice of the temperature of deposition

Substrate ?
Semiconductor : often intermixing at rather low temperature (ex: Si +metal form silicides) – not appropriate in general*
Oxide : often OK, intermixing but at high temperature : Al_2O_3, MgO, STO, ZnO, ….

** A pity for applications !*

Temperature for growth ?
- Adapted to initiate epitaxy
- stacks of different metallic layer : limited !
- alloys (no chemical order), compounds (chemical order) usually need heating

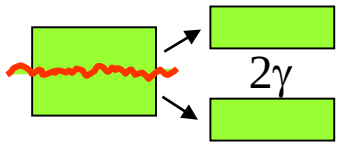
Depends on the system !

Growth of metals on oxyde substrate ? Go back to fundamentals

Important energies and impact on metallic film growth

surface energy, model of first neighbor bonds

Cut bonds model

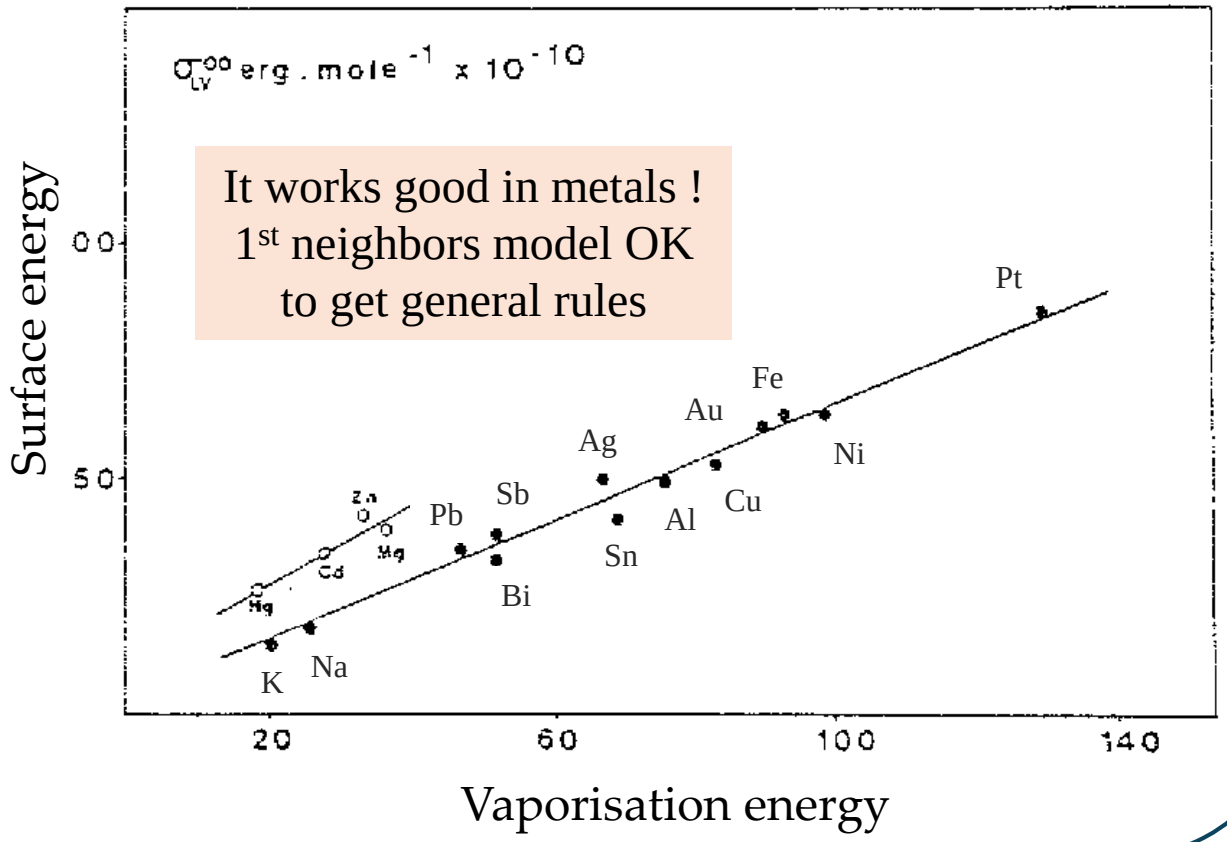


Surface energy = fraction of vaporisation energy (cohesion) = ratio of cut bonds in bulk and cut bonds at surface

Bulk : Z first neighbors = Z bonds
Surface : Z_s bonds (coordinence), so Z-Z_s cut bonds to create the surface

$$\gamma_{LV}^{0} = \left(\frac{Z - Z_s}{Z}\right)\Delta H_{vap}$$

Confrontation to CFC or HCP metals (12 first neighbors)



It works good in metals !
1st neighbors model OK
to get general rules

Important energies and impact on metallic film growth

How can we define interface energy ?

1st neighbors model : e_{AA}, e_{BB}, et e_{AB} bonding energy(<0)
s surface occupied by an atom

γ_A surface energy of A = - $e_{AA}/2s$
γ_B surface energy of B = - $e_{BB}/2s$

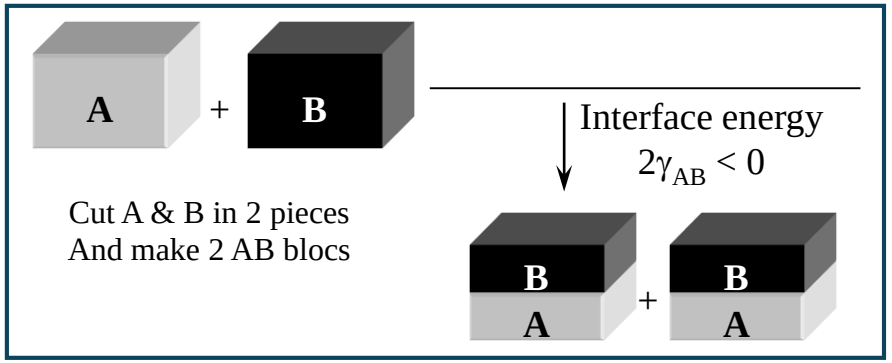
γ_{AB} interfacial energy AB = gain or loss of energy between on the one hand a AB interfacial bonding and on the other hand average energy of AA and BB (demixion):

$$\gamma_{AB}.s = e_{AB} - \frac{(e_{AA} + e_{BB})}{2}$$

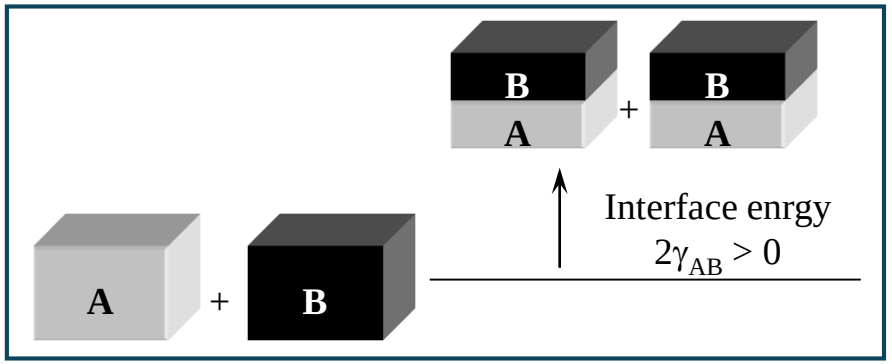
Similar to **mixing coefficient in metallurgy**.

$\gamma_{AB} > 0$: AA and BB better than AB (demixion)

$\gamma_{AB} < 0$: AB better than AA+BB (miscible)



Interface encouraged



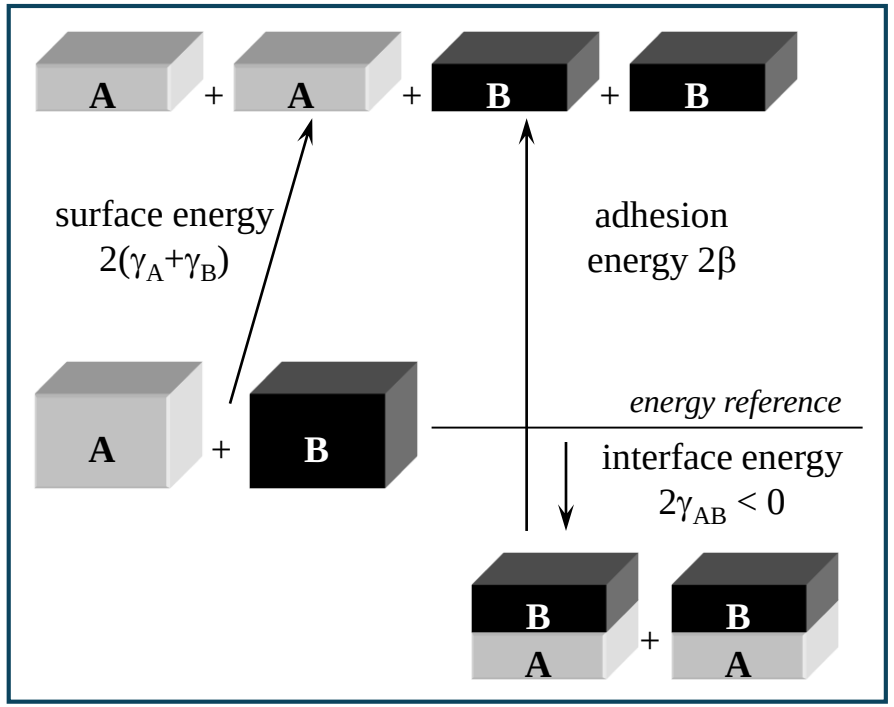
Demixion encouraged

Important energies and impact on metallic film growth

How can we define adhesion energy ?

β adhesion energy : energy to separate sticked one AB bloc

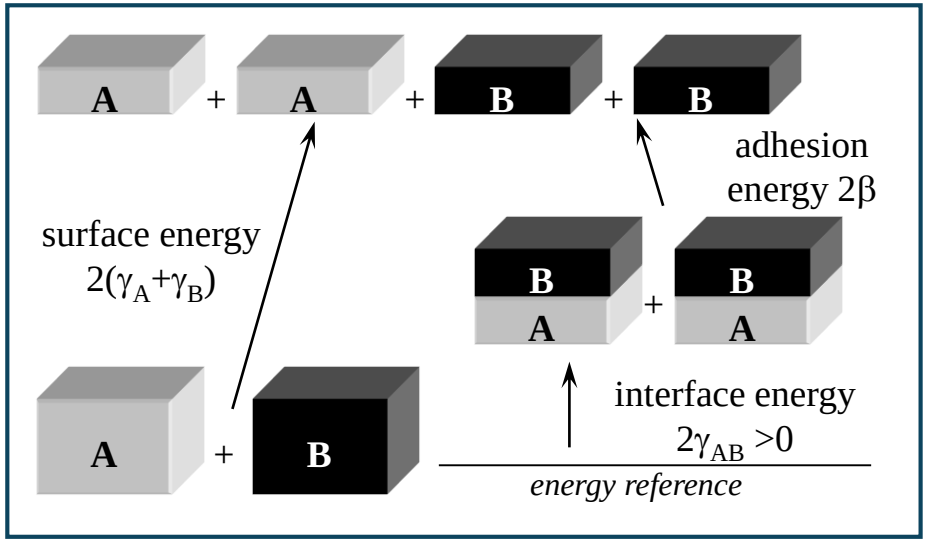
Dupré : $\gamma_{AB} + \beta = \gamma_A + \gamma_B$ so $\beta = \gamma_A + \gamma_B - \gamma_{AB}$



Strong adhesion

adhesion if β > 0

β <0 means energy gain by removing the layer = no adhesion

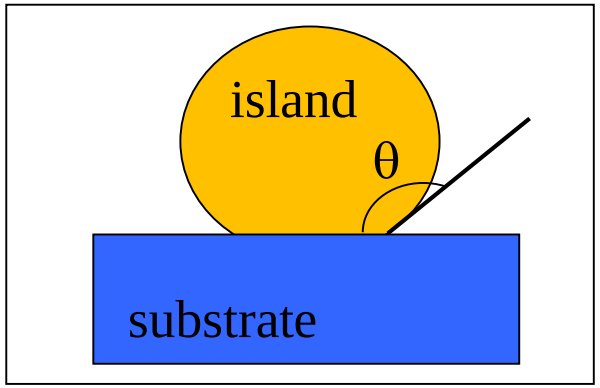


Weak adhesion
and if $\gamma_{AB} > \gamma_A + \gamma_B$ no adhesion at all !

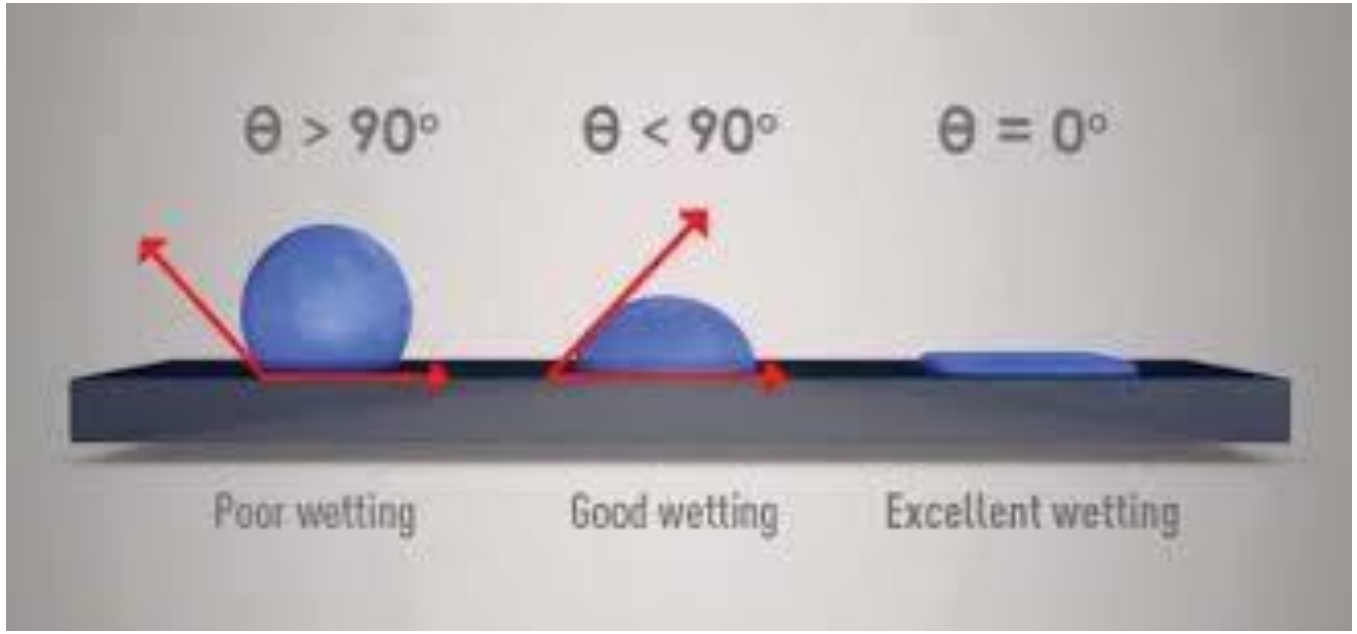
Important energies and impact on metallic film growth

Adhesion energy and wetting ?

Young formula



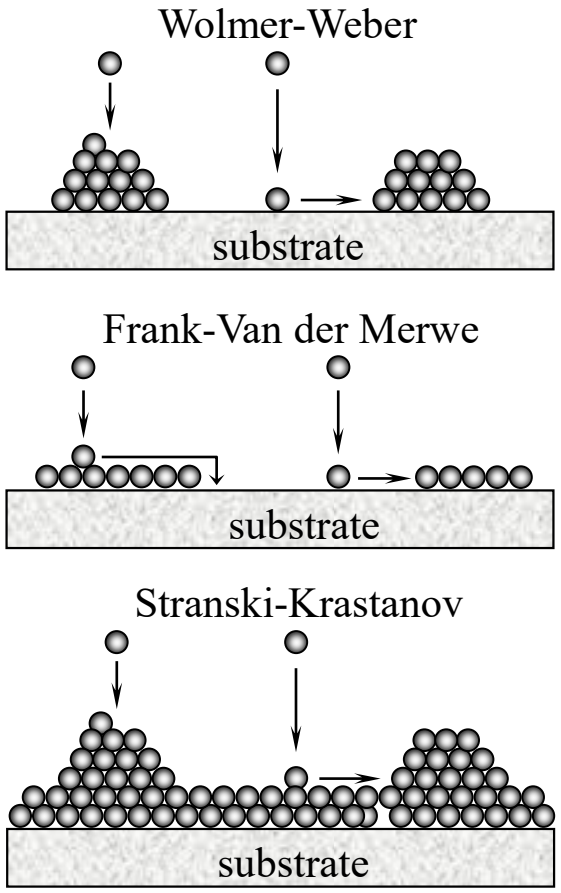
$$\cos\theta = \frac{\gamma_{Substrate} - \gamma_{Interface}}{\gamma_{\hat{i}sland}} = \frac{\beta}{\gamma_{\hat{i}lot}} - 1$$



$$\frac{\beta}{\gamma_{\hat{i}lot}} < 1 \qquad 1 \leq \frac{\beta}{\gamma_{\hat{i}lot}} < 2 \qquad \frac{\beta}{\gamma_{\hat{i}lot}} \geq 2$$

$\frac{\beta}{\gamma_{\hat{i}sland}} > 2$ with $\beta = \gamma_{island} + \gamma_{sub} - \gamma_{int}$ leads to $\gamma_{island} - \gamma_{sub} + \gamma_{int} < 0$ **Bauer criterion for 2D growth**

Important energies and impact on metallic film growth



Bauer criterion & 1st neighbors model

2D growth if $\gamma_{island} + \gamma_{interface} - \gamma_{sub} < 0$ + $\gamma_{interface} \cdot s = e_{island/sub} - \frac{(e_{island} + e_{sub})}{2}$

3D growth : Wolmer-Weber

$\gamma_{island} + \gamma_{interface} - \gamma_{sub} > 0$ $\gamma_{island} = -e_{island}/2s$ et $\gamma_{sub} = -e_{sub}/2s$ *

=> $e_{island} < e_{island/sub}$ => islands prefered, dewetting

2D growth : Frank Van der Merwe

$\gamma_{island} + \gamma_{interface} - \gamma_{sub} < 0$

=> $e_{island} > e_{island//sub}$ => interface prefered, wetting

transition 2D-3D : Stranski-Krastanov

Surface and interface energies not sufficient

Additonal energies : strain,…

** Do not forget that bonding energies e_{island} and $e_{sub} < 0$ (cohesion)*

Important energies and impact on metallic film growth

What Bauer criterion tells us ?

2D growth if $\gamma_{island} - \gamma_{sub} + \gamma_{interface} < 0$

A balance between =>

difference of energies From **SURFACE**

Surface energy 1 to 3J/M²
Difference can be small or large

difference of bonding energies **METALLURGY**

Usually small (<<1J/m2) (except for bad adhesion)

$$\gamma_{AB}\, s = e_{AB} - \frac{(e_{AA} + e_{BB})}{2}$$

« general » rules :

- if surface energies very different, $\gamma_{island} - \gamma_{sub}$ fix the growth mode => **surface predominant**
- if surface energies similar, $\gamma_{interface}$ fix the growth mode => **metallurgy predominant**
- Otherwise, competition between the 2

Important energies and impact on metallic film growth

What Bauer criterion tells us ?

2D growth if $\gamma_{island} - \gamma_{sub} + \gamma_{interface} < 0$

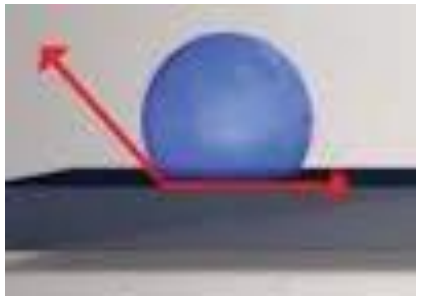
metals on oxide substrates

$\gamma_{oxides} \approx 1 \frac{J}{m^2}$ $\gamma_{metals} \approx 2 \frac{J}{m^2}$

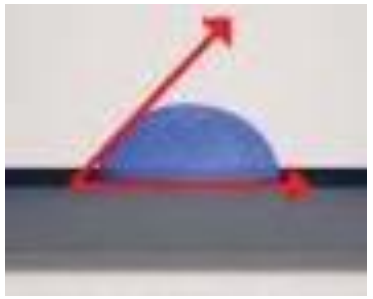
metals 3D on oxides
oxides 2D on metals

metals on oxide substrate :

$\gamma_{interface}$ fix 3D island morphology



Ag / oxides
Ag does not like O, e_{AgO} positive
$\gamma_{interface}$ large, poor adhesion

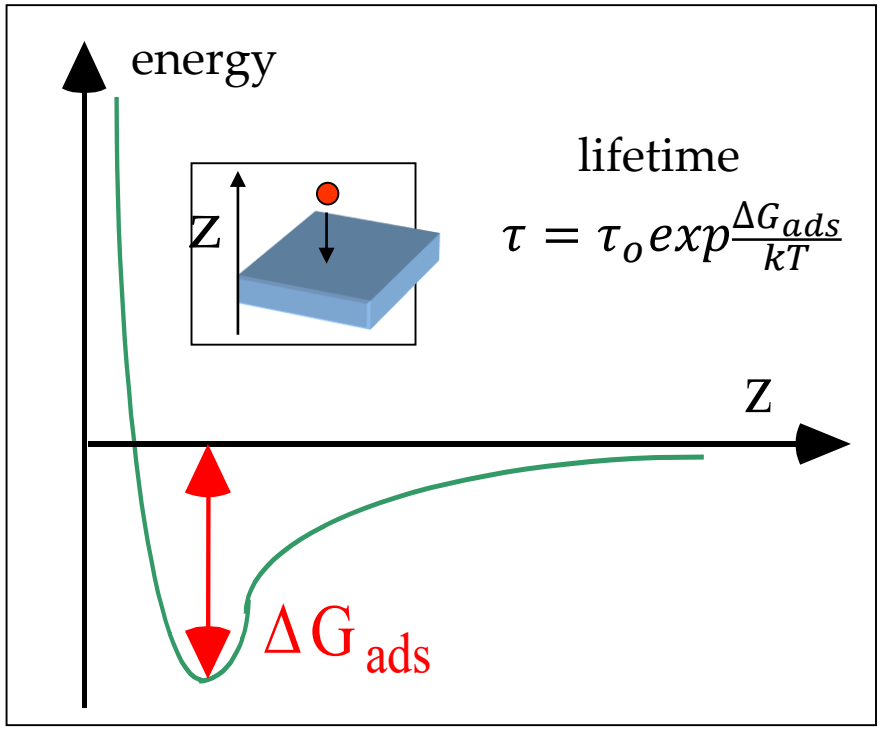


Fe / oxides
Fe likes O, e_{FeO} negative
good adhesion

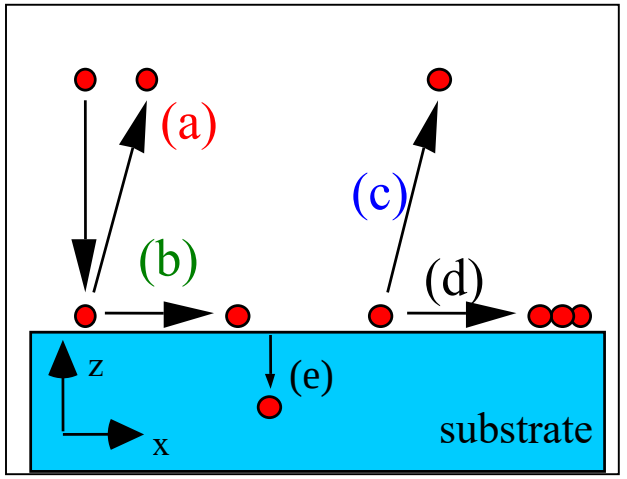
But we often need continuous thin film ! How can we do ? Kinetics !

Kinetical aspects : Adsorption, epitaxy, percolation

(1) Atoms attracted by the surface : adsorption



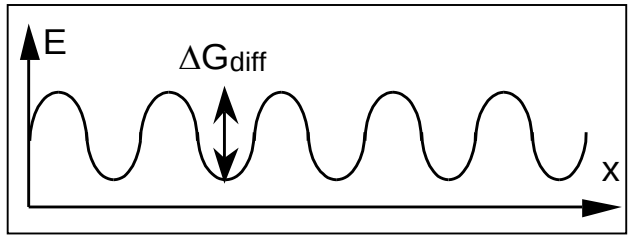
(2) Several mechanisms



(a): reflection
(b) : adsorption & diffusion
(c) : desorption
(d) : condensation
(e) : bulk diffusion

(3) Surface diffusion

Adatoms see prefered adsorption sites : periodic potential



ν hopping frequency

$$\nu = \nu_o \exp \frac{-\Delta G_{diff}}{kT}$$

x_s average diffusion length

$$x_s^2 = D_s \tau_{diff} = D_s / \nu$$

Kinetical aspects : Adsorption, epitaxy, percolation

Adsorption / desorption energy : 2 to 4 eV

Lifetime
at 300K : > 10^{20} s for 2eV
at 800K : 10^{12} s for 4eV, 1s for 2 eV
at 1300 K : 100s for 4eV, 10^{-6} s for 2eV

For metals around 4 eV + moderate growth temperature (avoid intermixing) : **desorption often negligible**

Surface diffusion energy : 0,1 to 1 eV

Hopping frequency at 300K :
10^{11} s^{-1} for 0.1eV (metals), 10^{-4} s^{-1} for 1eV (SC, oxide)

For metals around 0.1 eV, **fast surface diffusion**

Epitaxy needs fast surface diffusion / impinging growth flux
Semi-conductors and oxydes, epitaxial temperature high to increase surface diffusion
For metals, not necessary : epitaxy at room temperature possible !

Kinetical aspects : Adsorption, epitaxy, percolation

Surface diffusion easy for metals

system	Fe/ Fe(001)	Ni/ Ni(111)	Ag/ Ag(111)	Fe/ Mo(110)
E_{diff} (eV)	0.45	0.33	0.15	0.1

But be careful with intermixing !

system	Mn/Fe (001)	Ni/Fe (001)	Fe/Cu (001)	Mn/Ni (001)	Co/Fe (001)	V/Fe (001)	Nb/Fe (011)	Cr/Fe (001)	V/Fe (001)	Dy/Er (0001)	Sm/Nd (0001)
Intermixing temperature (°C)	100	200	150	RT	300	600	300	450	600	400	400

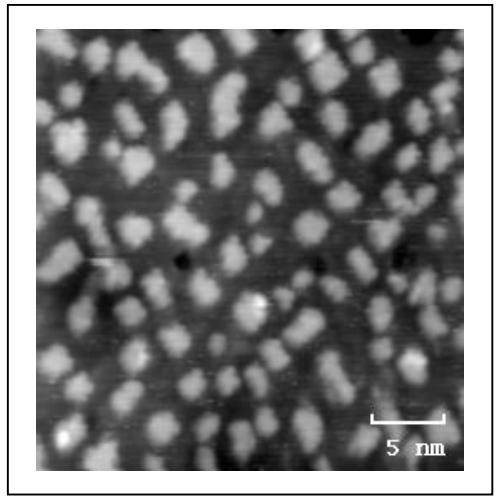
from" Molecular Beam Epitaxy: From Quantum Wells to Quantum Dots. From Research to Mass Production"
Chapter 20 : *"Epitaxial Magnetic Layers Grown by MBE : Model Systems to Study the Physics in Nanomagnetism and Spintronic"*
K. Dumesnil & S. Andrieu, Ed. M. Henini, ELSEVIER (2012)

low growth temperature often necessary

Kinetical aspects : Adsorption, epitaxy, percolation

Nucleation and percolation linked to surface diffusion

First step : nucleation
Distance between islands fixed by temperature

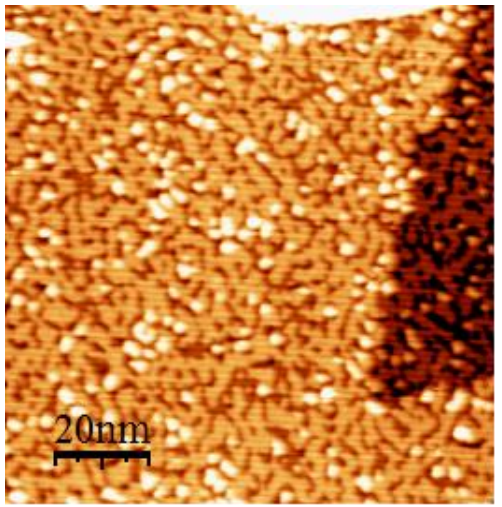


STM 0.25 ML Fe on Fe @RT

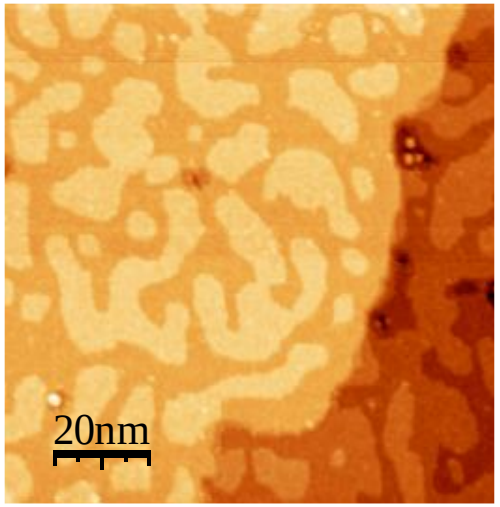
Higher is the temperature, lower the nucleation density and larger the island size (2D or 3D islands)

Example : STM for 0.5ML Ni on Fe(001)

300K



500K



To achieve early percolation, growth temperature as low as possible

summary

Prefered substrates for epitaxial metallic thin films : oxide

Metals / oxide : 3D growth in general

Metal on metal : 2D or 3D but be careful with intermixing !

Negative interface energy (metallurgy) preferred although bad adhesion

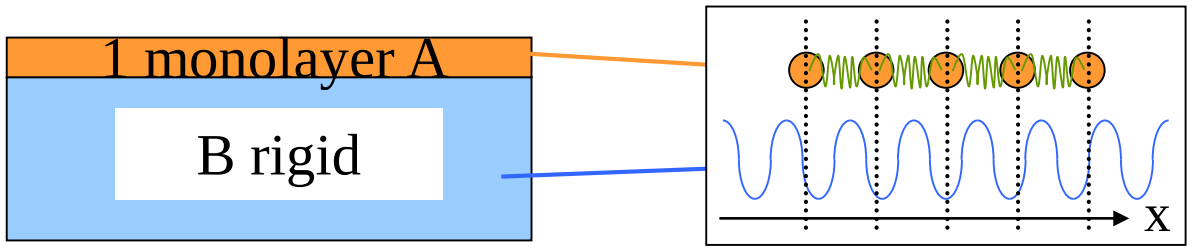
Growth temperature as low as possible
- to maximize islands density and minimize thickness for percolation
- to minimize intermixing

But now we need to get epitaxy !

OUTLOOK

- Why thin metallic films ? Why epitaxy ?
- Chap.I - Specificities of metallic thin film growth
- Chap.II - Epitaxial mechanisms
  - Frank Van der Merwe model
  - Confrontation of FVdM to metallic growth : localisation / delocalisation
  - Review on epitaxial relationships

Frank Van der Merwe model

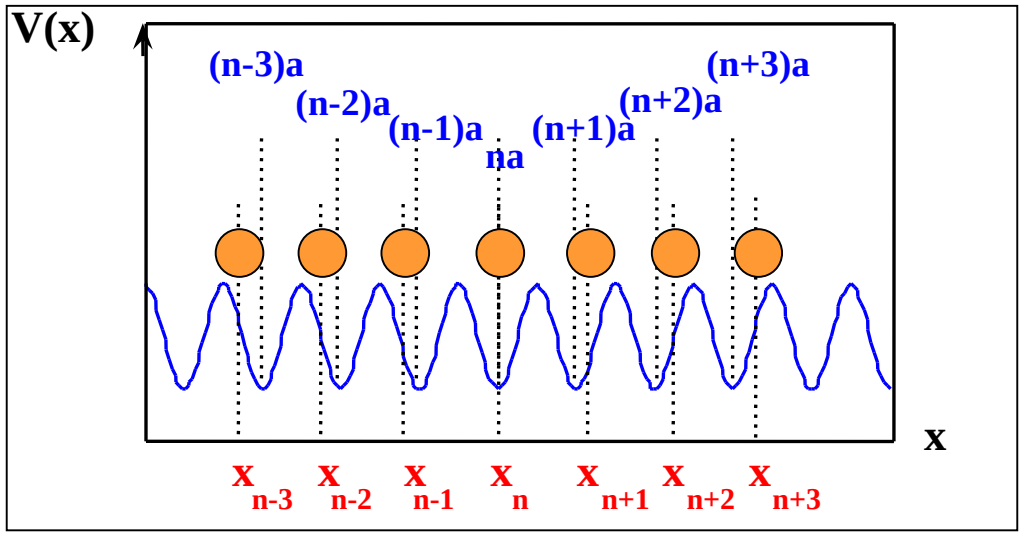


Competition between :
Potential height : linked to AB bond, so to interface
Spring stiffness : linked to AA bond

B lattice spacing b, totally rigid
A lattice spacing a in bulk

Preferential adsorption site $V = \frac{1}{2}W\left(1-\cos\frac{2\pi x}{b}\right)$

Bonding simulated by springs $\frac{1}{2}k(x-a)^2$



$$E_{tot} = \frac{1}{2}W\sum_{n=0}^{N-1}\left(1-\cos\left(\frac{2\pi x_n}{b}\right)\right) + \frac{1}{2}K\sum_{n=0}^{N-1}(x_n - x_{n-1} - a)^2$$

F.Frank, J.van der Merwe, Proc. Roy. Soc. London A198, (1949) 205 et 216

Frank Van der Merwe model

Choose ξ_n as $x_n=b(n+\xi_n)$ so :

$$E_{tot} = \frac{W}{2}\sum_{n=0}^{N-1}\left[\left(1-\cos 2\pi\xi_n\right)+2l_o^2\left(\xi_n-\xi_{n-1}-f\right)^2\right]$$

$$l_o = \sqrt{\frac{Kb^2}{2W}} \qquad f = \frac{a-b}{b}$$

misfit or mismatch between A & B

Minimization leads to
$\Delta^2\xi_n=\xi_{n+1}-2\xi_n+\xi_{n-1}$:

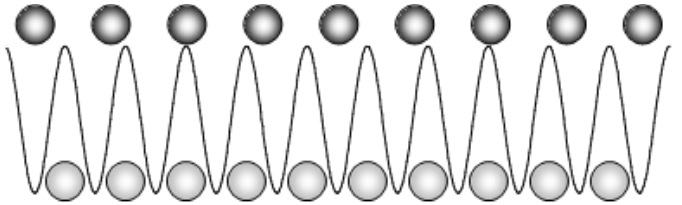
$$\Delta^2\xi_n = \frac{\pi}{2l_o^2}\sin 2\pi\xi_n$$

Minimization leads to
2 « trivial » solutions :

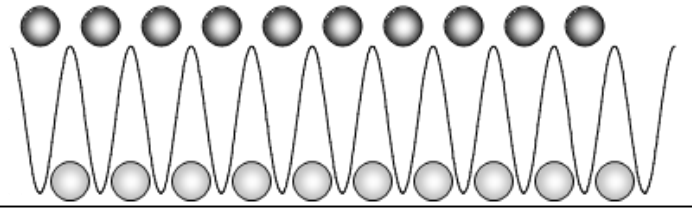
Numerisation
Vernier growth - delocalisation

A adopt the lattice parameter of B
Pseudomorphy –localisation
Possible up to $f \approx 13\%$

Vernier growth : uncommensurate



Pseudomorphy : commensurate



Frank Van der Merwe model

Other solution for small deformation ξ_n development in Taylor series (2nd order)

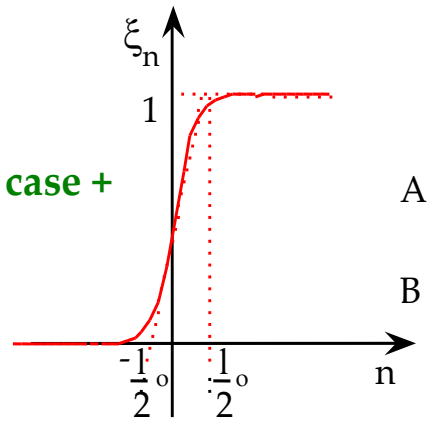
$$\Delta^2\xi_n \approx \frac{d^2\xi_n}{dn^2} = \frac{\pi}{2l_o^2}\sin 2\pi\xi_n$$

1st integration

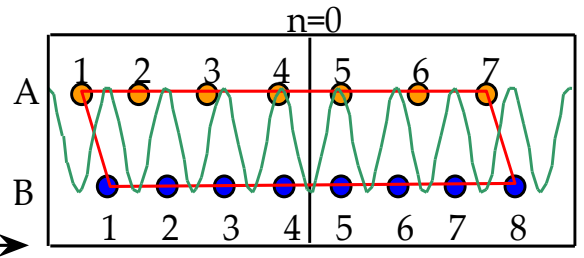
$$\frac{d\xi_n}{dn} = \pm\frac{1}{ql_o}\sqrt{\left(1-q^2\cos^2\pi\xi_n\right)}$$

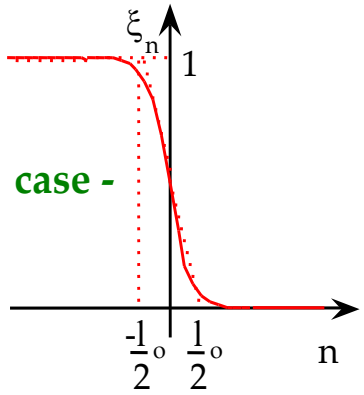
$$\frac{1}{q^2} = 1 + l_o^2\left(\frac{d\xi_n}{dn}\right)^2_{\xi_n=0}$$

particuliar case q=1 : $\xi_n = \frac{2}{\pi}arctg\left(\exp\pm\pi n/l_o\right)$

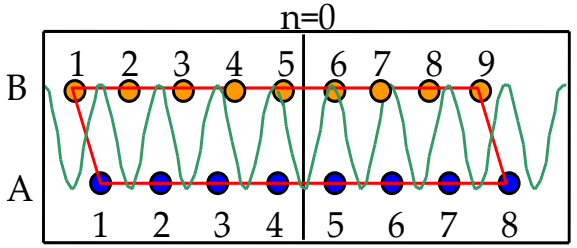


N-1 atoms A for N atoms B





N+1 atoms A for N atoms B



Dislocation

l_o size of the dislocation

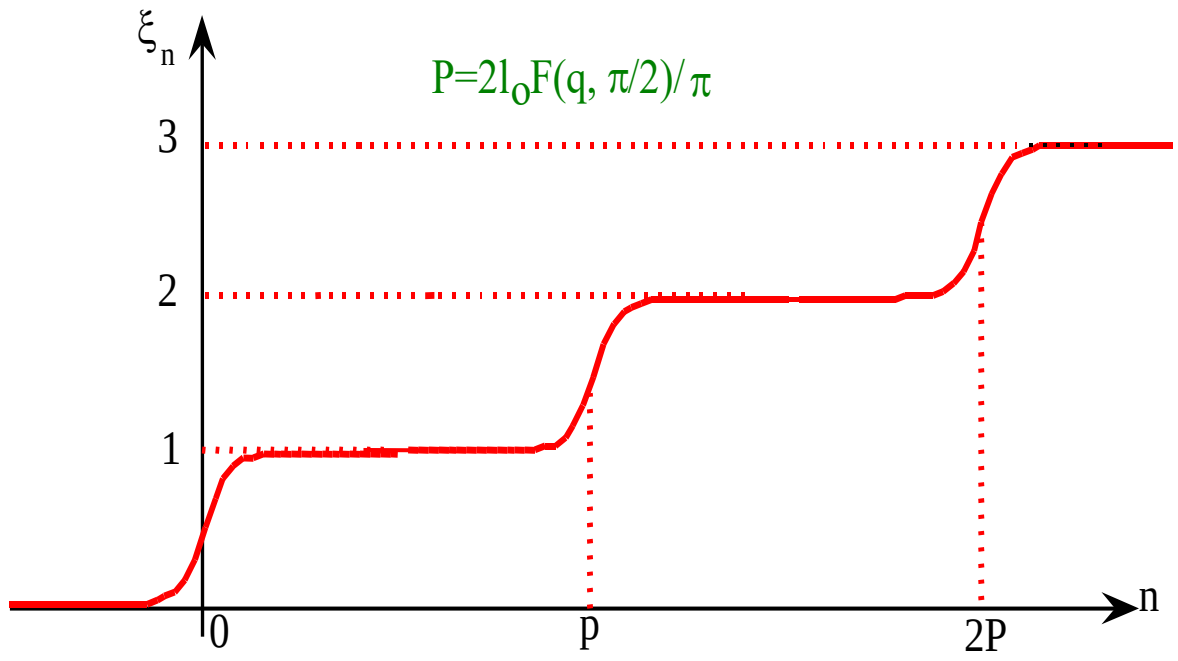
No more than several atomic distance

Pseudomorphic far from dislocation

Frank Van der Merwe model

Localisation & plastic relaxation : dislocation network thus appears

General case q > 1



Conclusion

For small deformation (localisation), always 2 mathematical solutions : which one stable ?

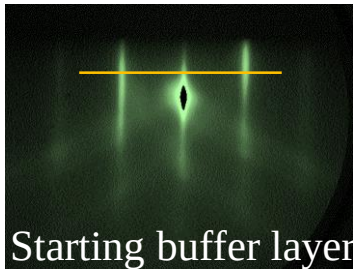
Smallest total energy

First, pseudomorphy, elastic energy increases ⇒ at a critical thickness, pseudomorphy total energy higher than dislocations relaxation

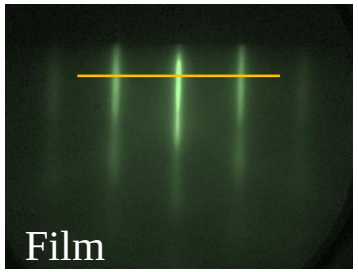
Critical thickness for plastic relaxation

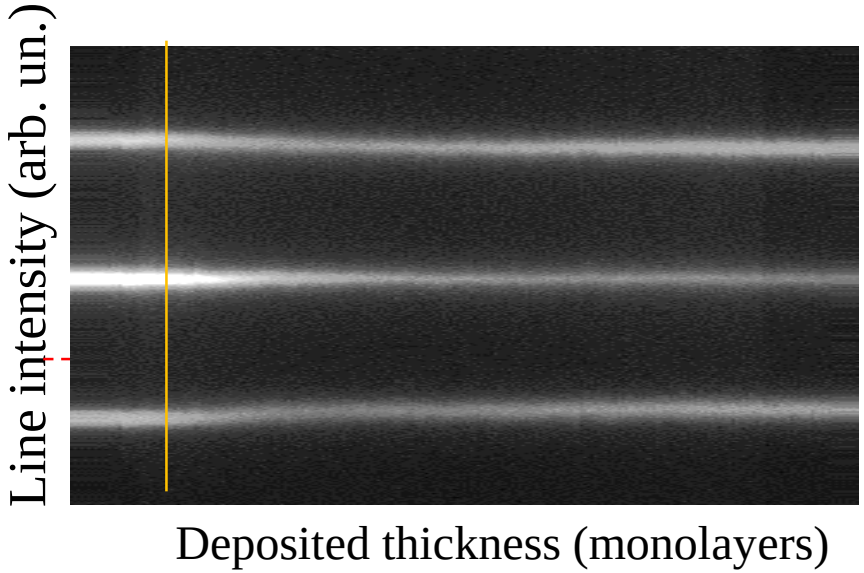
Confrontation of FVdM to metallic growth : localisation

Measurement of the average in-plane lattice spacing during the growth by RHEED

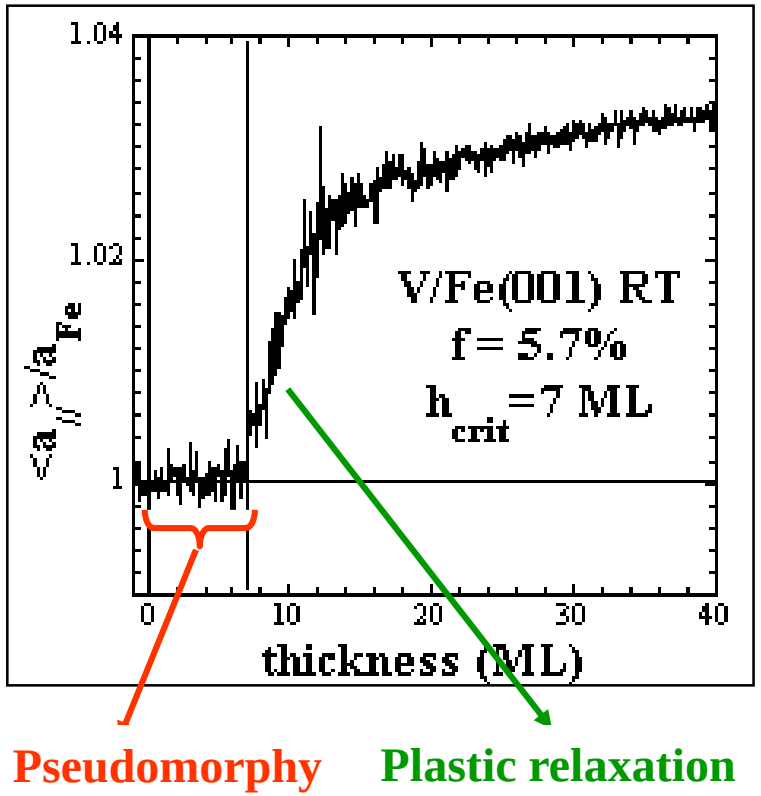


line profile followed during growth





Example : V growth on Fe(001)
V BCC a=0,303nm
Fe BCC a=0,287nm



Metal growth : many examples
See Turban et al, surf.sci. 446, p.241-253, (2000)

Semi-conductors :
f small 0.1 à 2%
h_c can reached several nm

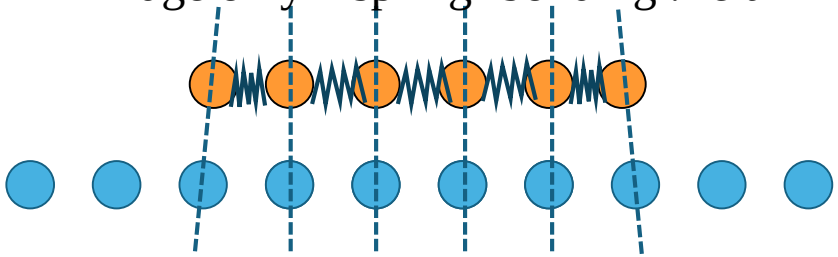
Metals : h_c always small:
a few atomic planes

(barrier height for dislocation creation lower than in SC)

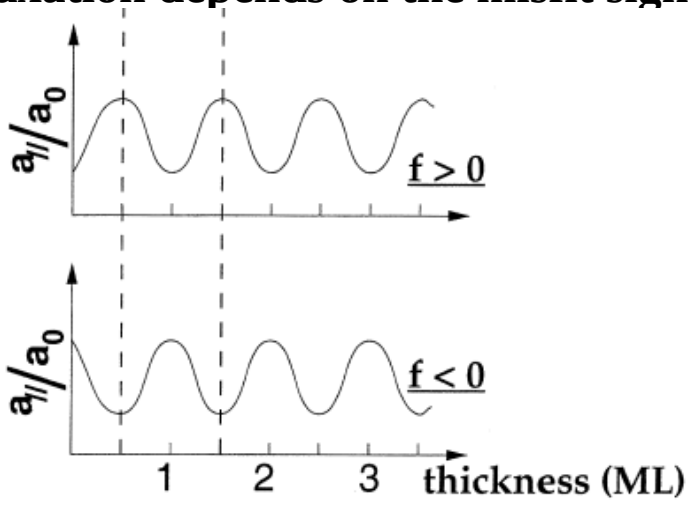
Confrontation of FVdM to metallic growth : localization, one step further

in-plane lattice spacing in subonolayer regime

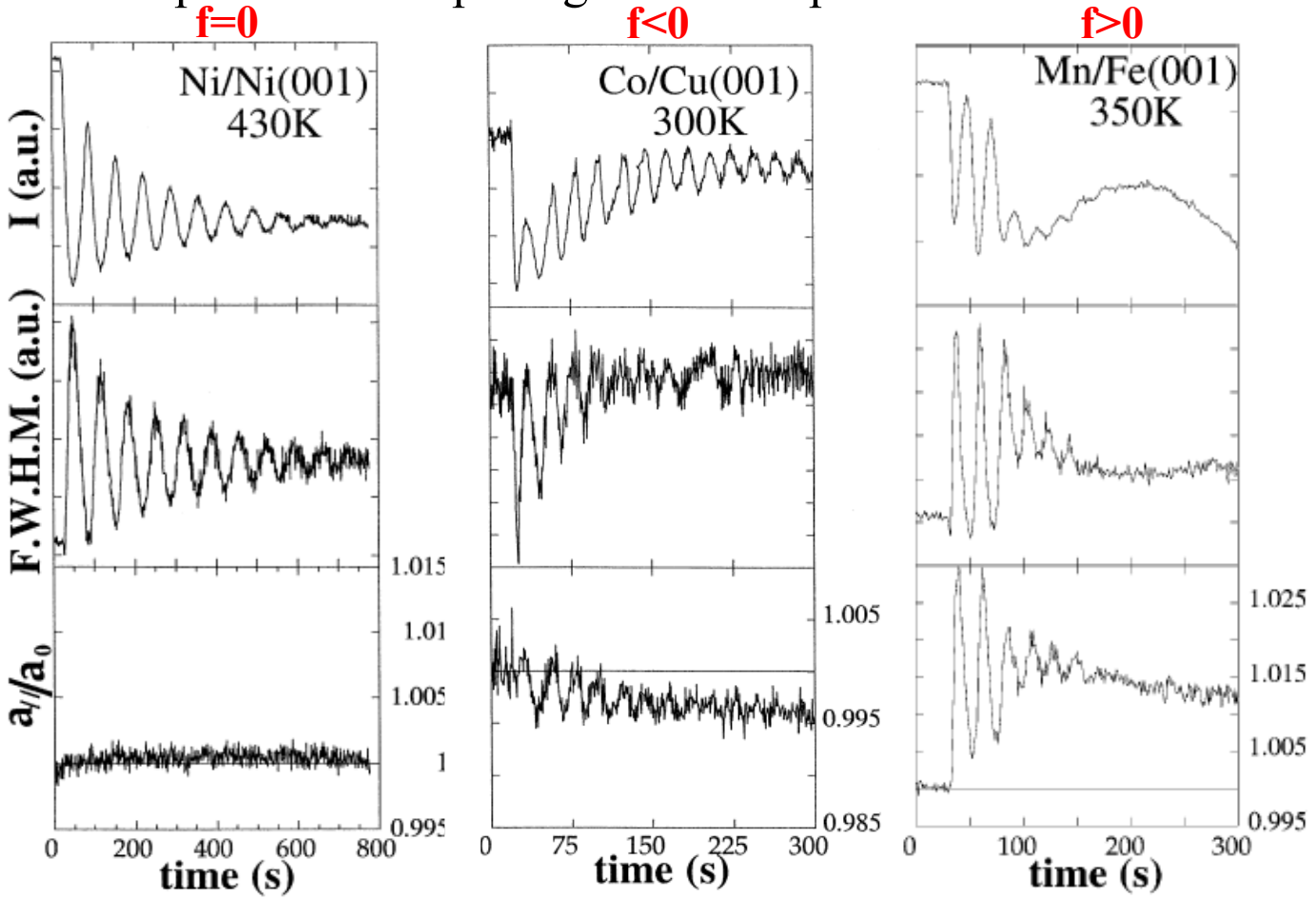
2D island :
- Middle : pseudomorphy : strained
- Edge only 1 spring=bonding : relax



Relaxation depends on the misfit sign



in-plane lattice spacing : RHEED profile in real time

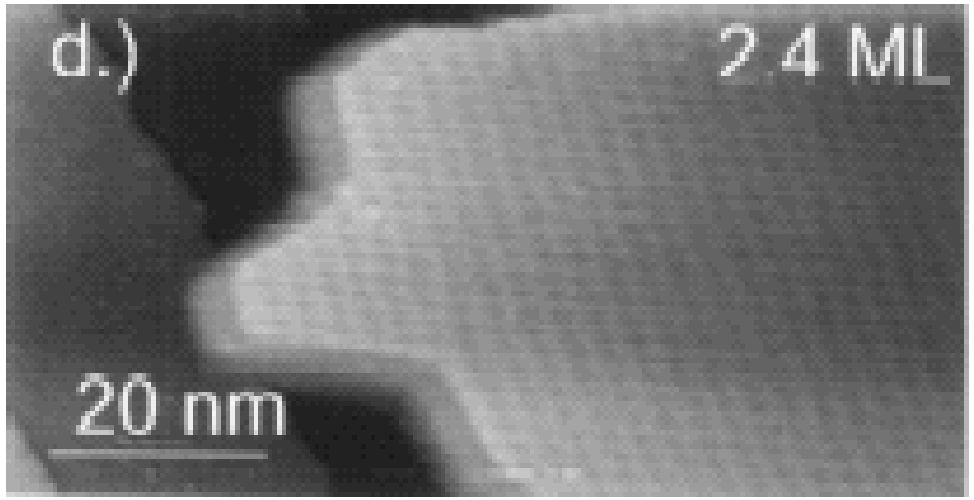


See Turban et al, surf.sci. 446, p.241-253, (2000)

Confrontation of FVdM to metallic growth : localisation

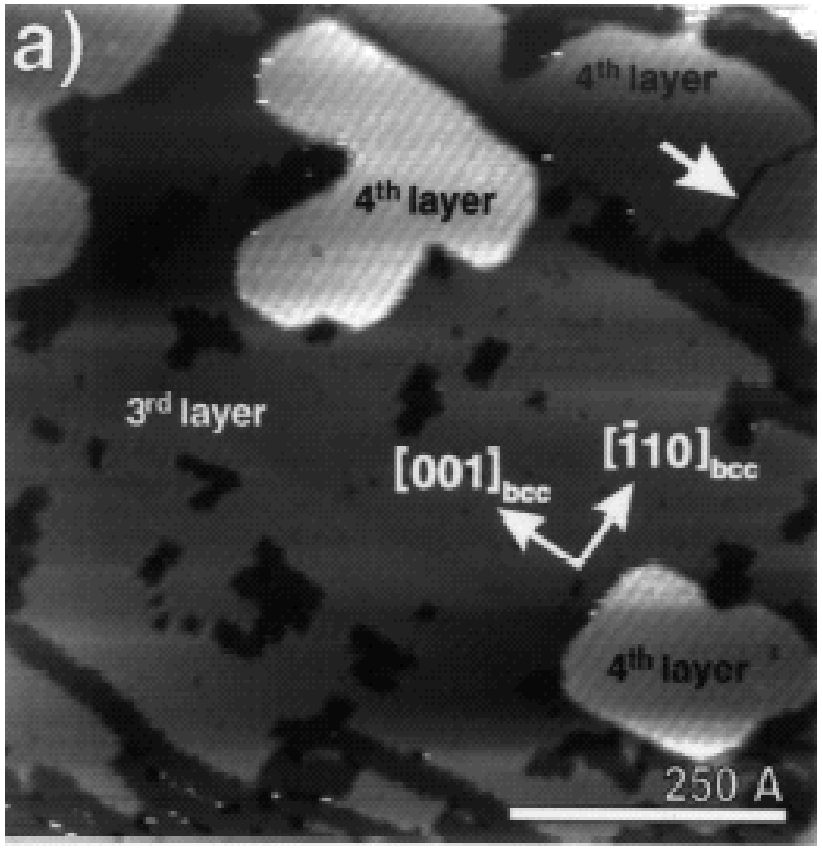
Dislocation network evidence by Scanning Tunneling Microscopy

Fe(110)/Mo(110) f=-8.7%



Malzbender, Surf. Sci. vol.414, 187 (1998)

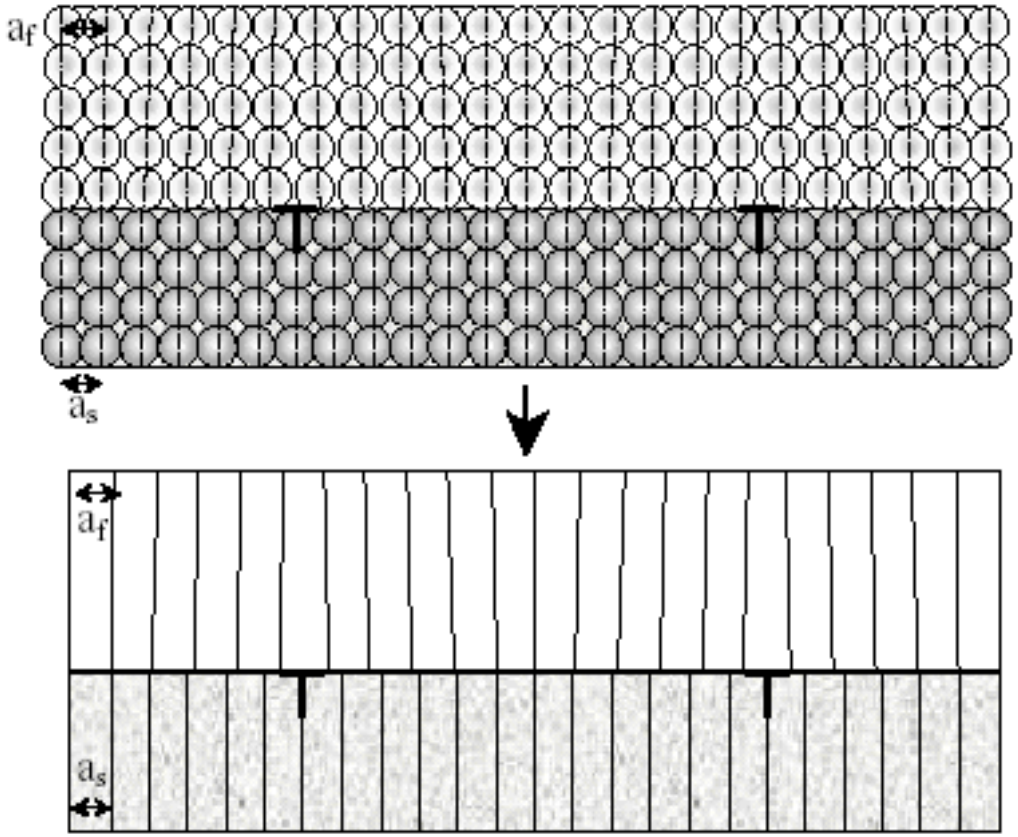
Cu(001) /W(110) misfit in only 1 direction

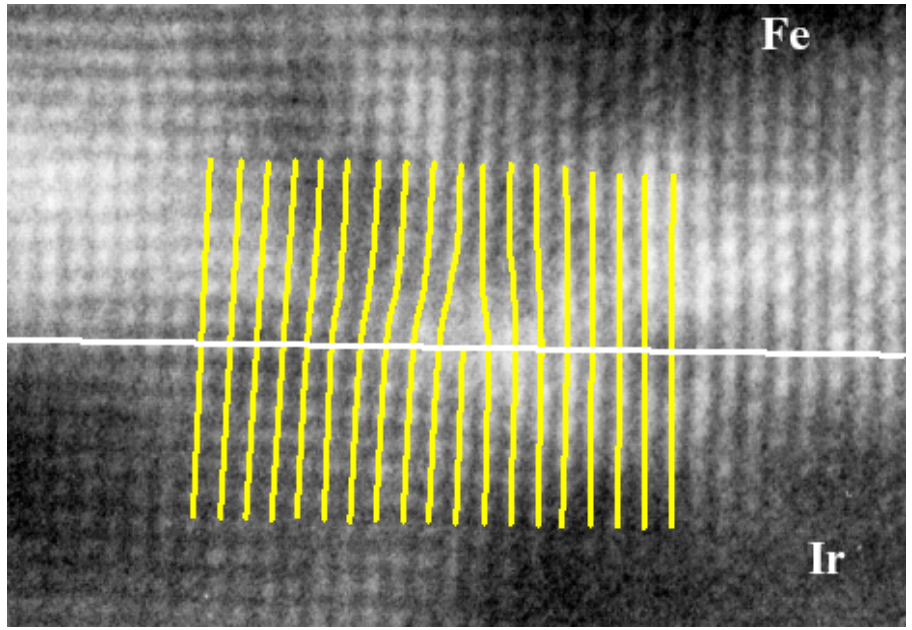


Reshöft , Surf. Sci., vol.421, 320 (1999)

Confrontation of FVdM to metallic growth : localisation

Dislocation evidence by Transmission Electron Microscopy

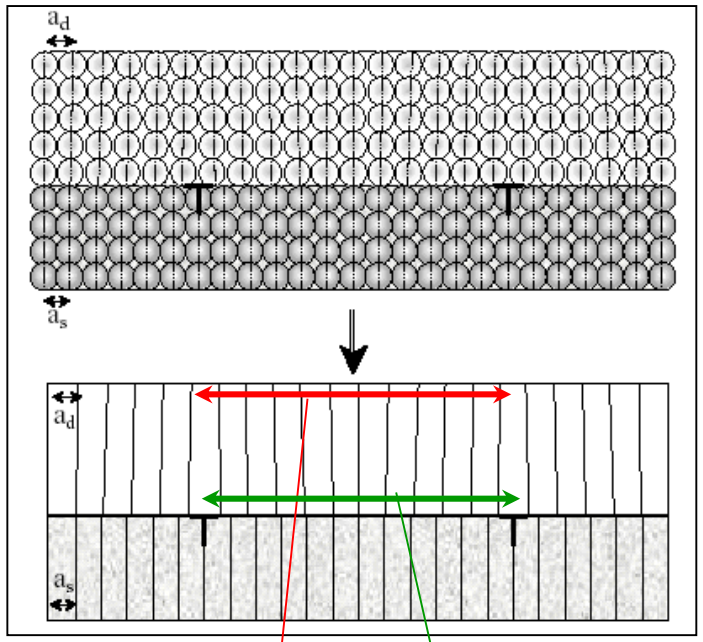




Andrieu et al, Phys. Rev. B 52, p.9938-9951, (1995)

Confrontation of FVdM to metallic growth : localisation

A rough estimation of distance between dislocations



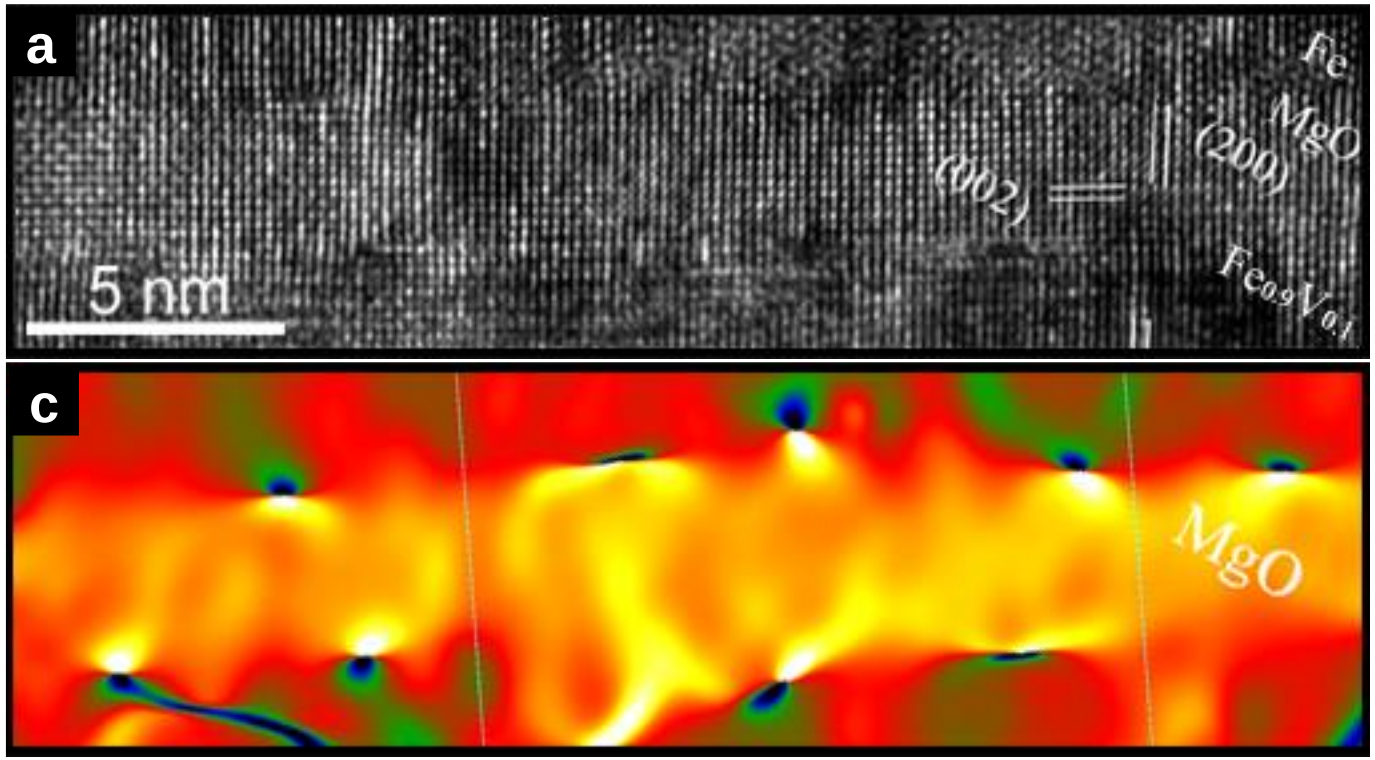
case $a_d > a_s$

$$(N-1)a_d = Na_s$$

$$N = \frac{a_d}{a_d - a_s} \Longrightarrow L = Na_s = \frac{a_s a_d}{a_d - a_s}$$

HRTEM : visu of strain => core dislocations

Bonell et al, Phys. Rev. B 82, 092405 (2010)



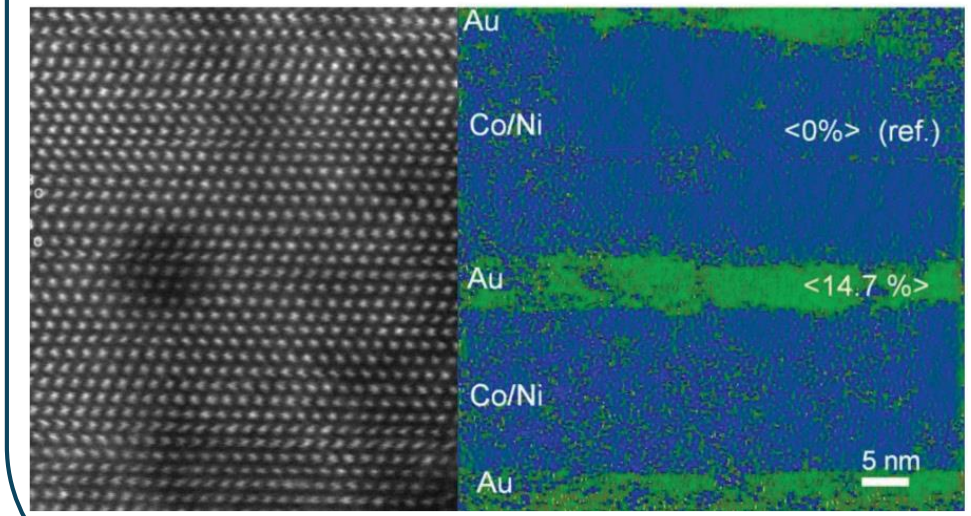
MgO / Fe(001) : $\langle L \rangle \cong 5\,nm$ OK with the model

Confrontation of FVdM to metallic growth : delocalisation

Spin valve : CoNi/Au/CoNi(111)

All FCC $a_{CoNi} = 0{,}36nm$ $a_{Au} = 0{,}408nm$ misfit 15,7%

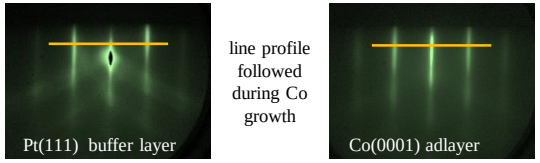
=> Au relaxed, Vernier growth

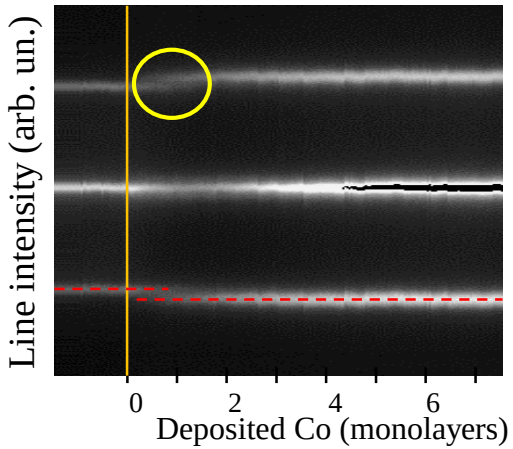


Phys. Rev. Materials **2**, *064410 (2018)*

Co on Pt(111) $a_{Co} = 0{,}251nm$ $a_{Pt} = 0{,}275nm$

=> $\mathbf{11.a_{Co} = 10.a_{Pt}}$!!!

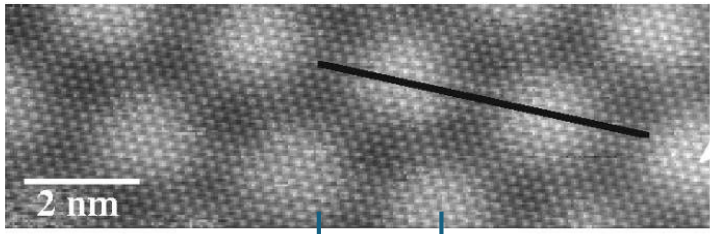


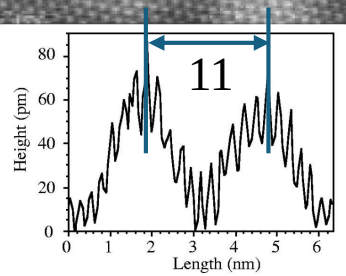


De Melo, Andrieu, in prep.

Seen by STM (2000) : Moiré pattern

Lunfgren et al, PRB 62, (2000)



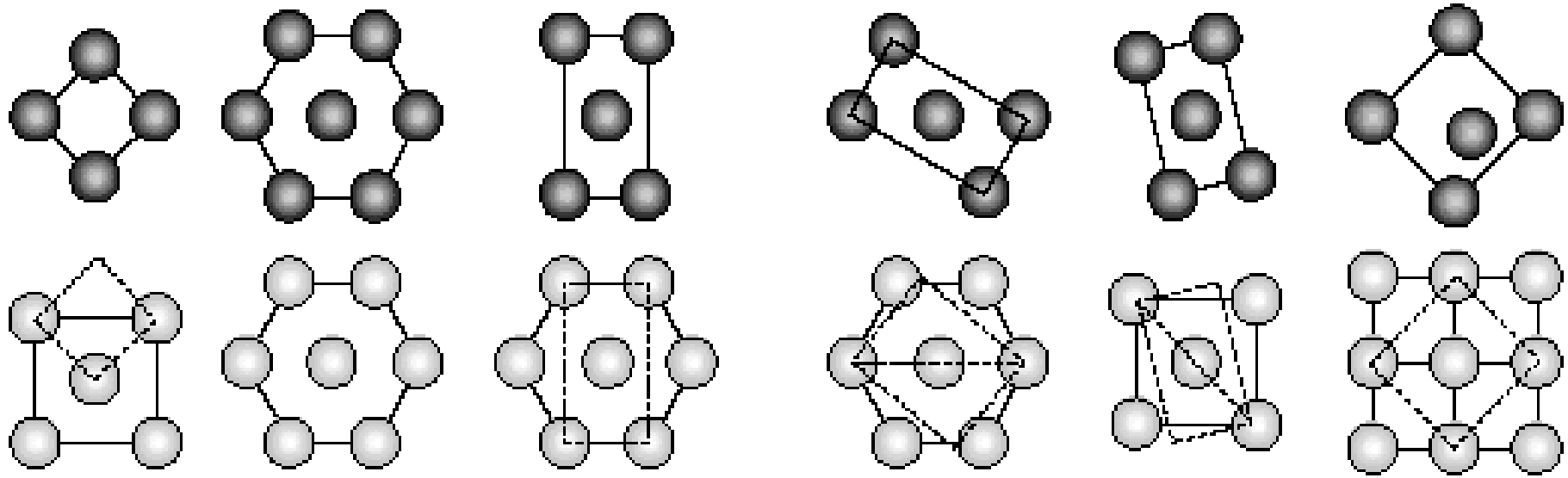


Super hexagon 11 Co on super hexagon 10 Pt, but they do not understand it as Vernier growth

Delocalisation also observed in metals

Review on epitaxial relationship

Some examples (not exhaustive)



Deposit lattice	substrate lattice	Epitaixial relationship	
CC	CFC		Fe/Au(001) Fe/Ag(001)
CFC	HEX		Ru/Ir(111) cfc Fe/Cu(001)
CC	CFC ou HEX	Nishiyama Wassermann	hexY/bccNb(110) Nb(110)/Cu(111)
CC	CFC ou HEX	Kurdjumov / Sachs	Fe/Ir(111) Fe/Ru(0001)
CC	CFC		Ni(110)/Fe(001)
HEX	CC ou CFC		Co(11$\bar{2}$0)/Fe(001)

from" Molecular Beam Epitaxy: From Quantum Wells to Quantum Dots. From Research to Mass Production"
Chapter 20 : *"Epitaxial Magnetic Layers Grown by MBE : Model Systems to Study the Physics in Nanomagnetism and Spintronic"*
K. Dumesnil & S. Andrieu, Ed. M. Henini, ELSEVIER (2012)

summary

General trends :

Epitaxial processes using metals follow the simple Frank Van der Merwe model

Main difference with Semi-Cond and oxides : easier to create defects in metals => lower critical thickness for plastic relaxation in metals

Epitaxy strongly linked to adhesion energy !

FVdM 2D model. Now combine epitaxy and growth modes

OUTLOOK

- Why thin metallic films ? Why epitaxy ?
- Chap.I - Specificities of metallic thin film growth
- Chap.II - Epitaxial mechanisms
- Chap.III – metallic film growth strategies
  - Choice of the substrate
  - Growth temperature, annealing
  - Metastable phase, superlattices growth
  - Alloys and compounds growth

Choice of the substrate

Examples of metallic layers "easy" to grow on oxide surfaces : MgO, STO, Al_20_3, ZrO_2, ZnO…

Growth on oxide	(001) BCC	(001) FCC	(111) FCC (0001) hcp	(110) BCC
substrate	MgO (001)	MgO(001)	Al_2O_3 (0001)	MgO(110) Al_2O_3 $(11\bar{2}0)$
layer	Cr, V, Fe, Nb, Mo, W	Rh, Pd, Re, Ir	Ir, Pt, Rh, Co, Ru	Cr, Fe, V, Nb, Mo, W

But single-crystalline epitaxy difficult to obtain for materials with bad wetting on oxide !

For instance Ag, Au, Cu because low adhesion, bad wetting
But also due to too large misfit : MgO(001) / Cu or Ni

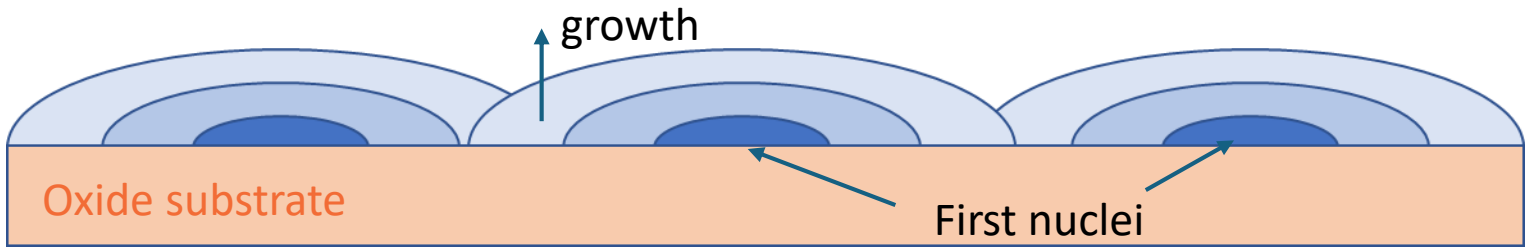
Solution : use a seed layer !

For instance MgO(001) /Rh (few Å) / Ni
Sapphire(0001)/ V(110) / Au(111)

Oxide substrate : growth temperature, annealing

Metals on oxides : 3D growth. How to obtain a continuous & flat surface ?

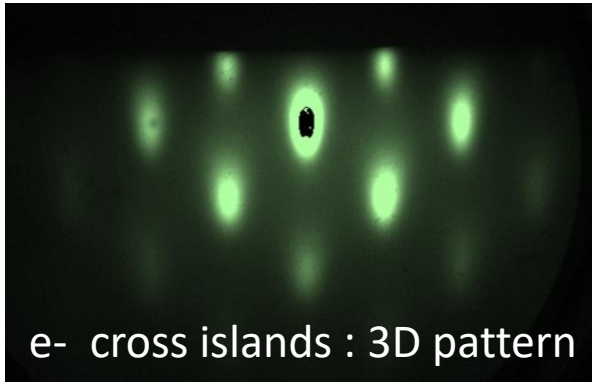
Growth at temperature as low as possible, reach the 3D islands percolation



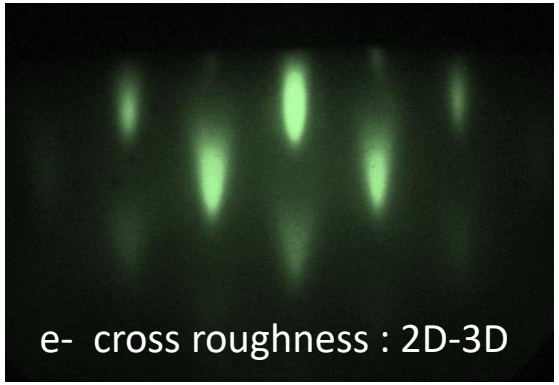
But surface rough after percolation ! Heat after percolation => minimize surface energy S.γ : flat surface

Controlled by RHEED
Islands : "spotty" rods
Smooth : continuous rods

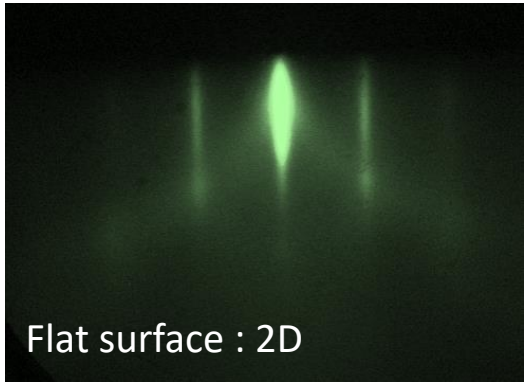
2nm Fe/MgO(001) @RT



20nm Fe/MgO(001) @RT



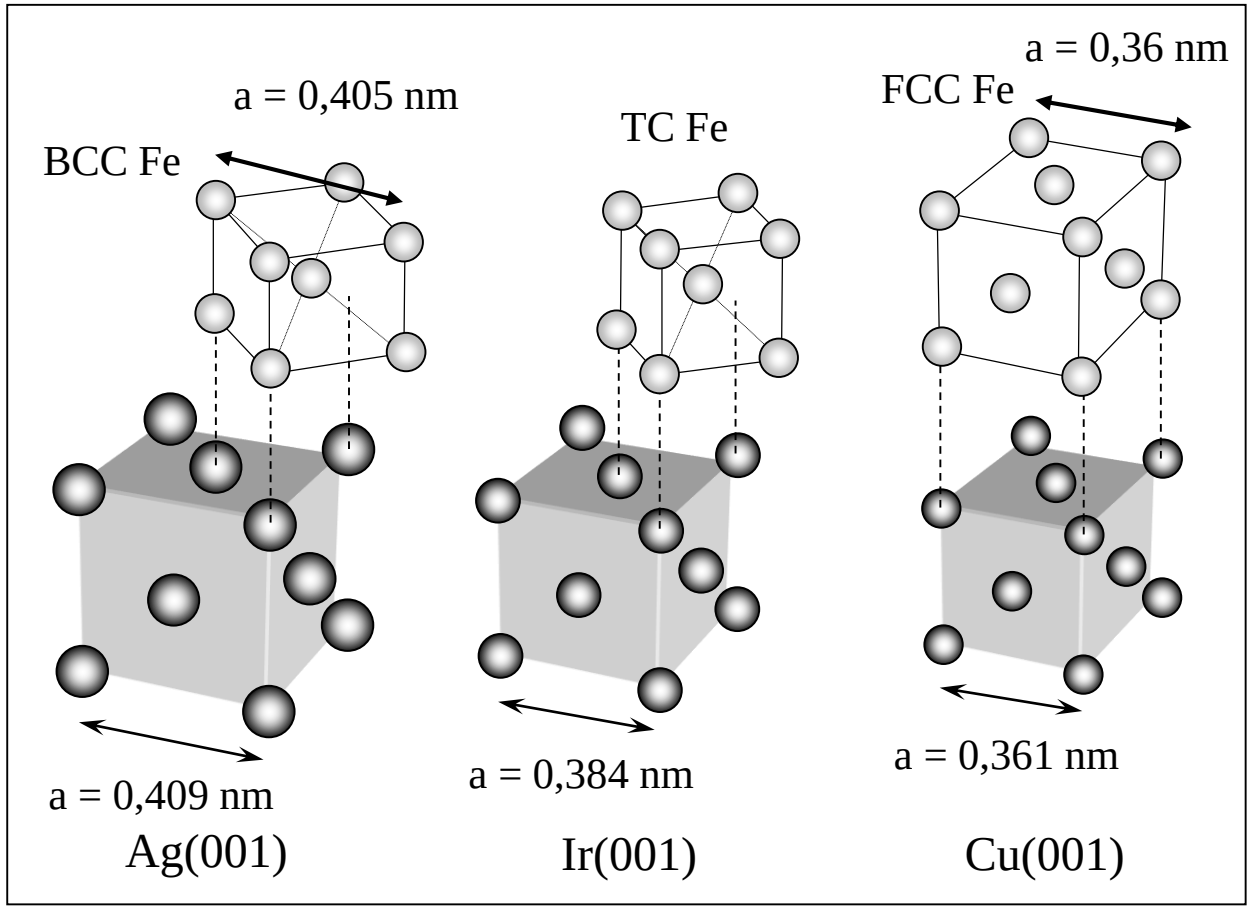
Annealed @450C



But be careful : heating too high => thermodynamics equilibrium : 3D islands => dewetting !

Metastable phase, superlattices

Using a buffer layer, one can grow phases not stable in normal condition : strain play the role of pressure



However, metastable phase vanish at critical thickness of plastic relaxation : few atomic planes, often too small for analysis

Solution : grow superlattices
But need some prerequisite !

Metastable phase, superlattices

Superlattices with flat interfaces should be great for metastable phase

Remind the Bauer Criterion : we need **A 2D over B and B 2D over A**. Is it possible ?

$$\gamma_A - \gamma_B + \gamma_{interface} < 0$$

and

$$\gamma_B - \gamma_A + \gamma_{interface} < 0$$

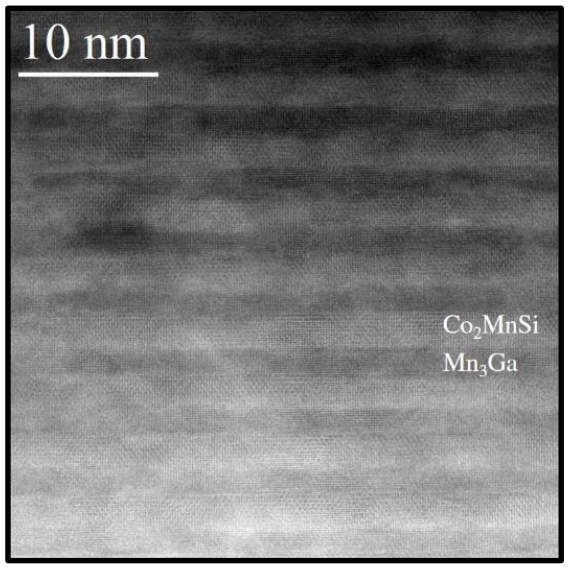
Possible if

$$|\gamma_{int}| < ||\gamma_A - \gamma_B|| \quad \textbf{AND} \quad \gamma_{int} < 0$$

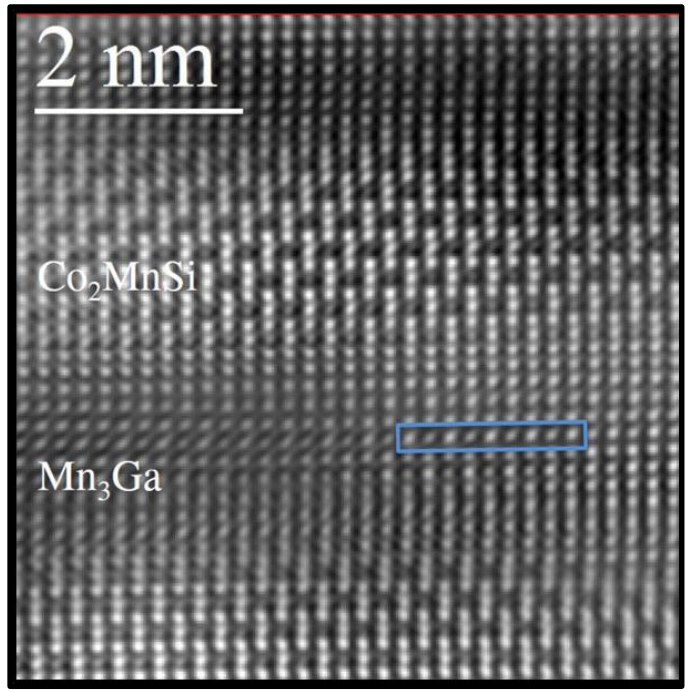
Not so rare !
Take 2 metals with similar surface energies and good bonding !

Mn_3Ga / Co_2MnSi (001) superlattices

HRTEM



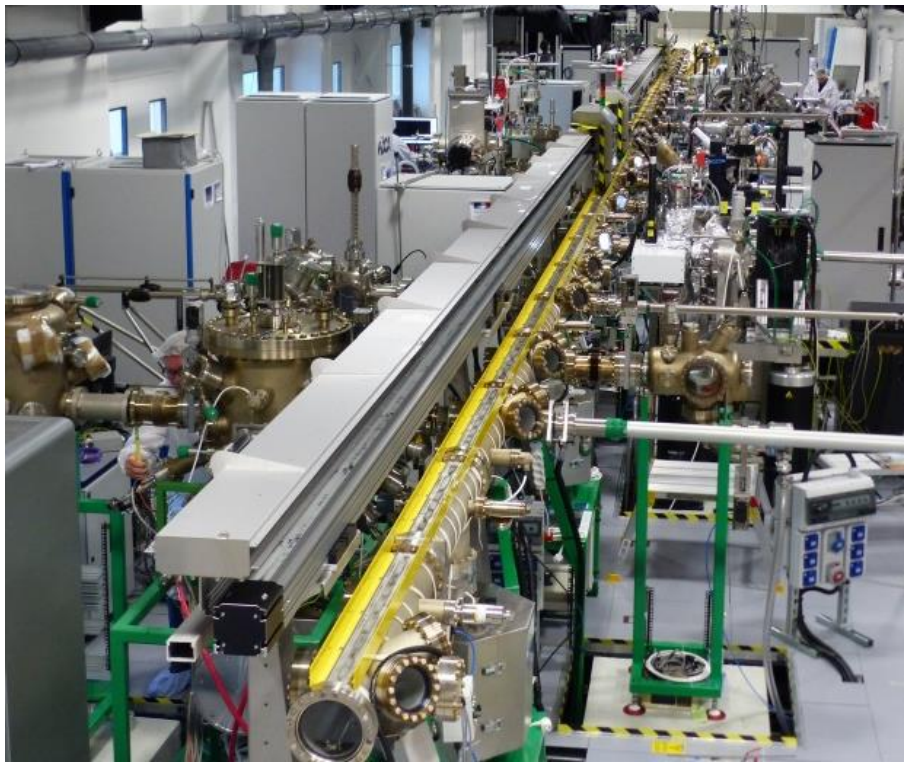
HAADF



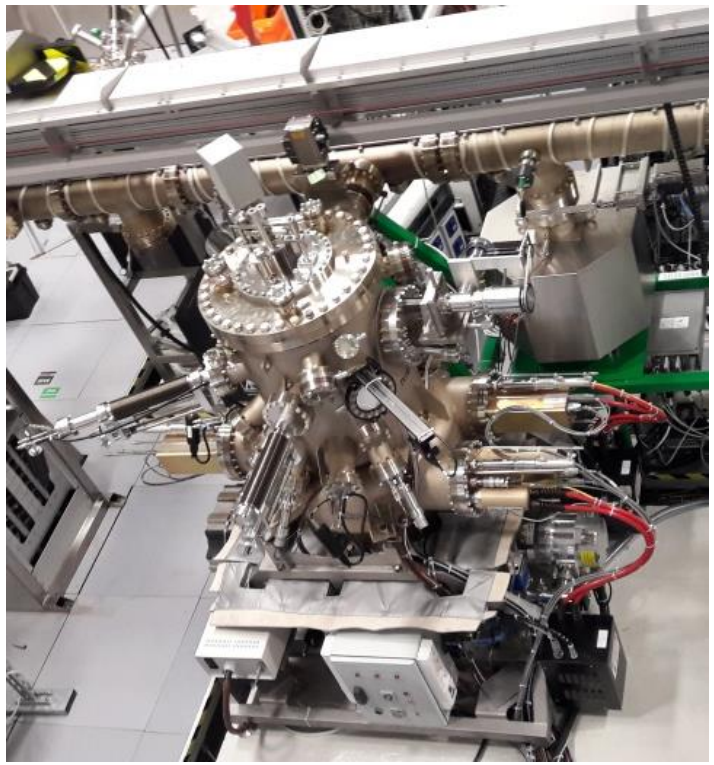
Palin et al, Phys. Rev. Appl.. 20, 054017 (2023)

Alloys and compounds growth

Special MBE machine designed for alloys and compounds : quaternary MBE on the Daum tube at IJL



70m long UHV tube : 30 connected machines
(MBE, Sputering, PLD, XPS-auger, ARPES, STM, Kerr)



MBE with 24 materials : 3 e-guns
6 pockets + 6 cells

Alloys and compounds growth

How to control accurately the stoichiometry ?

Fluxes absolute measurements using quartz µbalance located at the place of the sample : **sticking =1 assumed***

**be careful for material with low evaporation temperature / high vapor pressure*

$$\Phi_A = n_A . v_A = v_A \frac{\rho_A . \mathcal{N}_{avo}}{\mathcal{M}_A} \quad (at/m^2/s)$$

n_A atomic density ρ_A mass density
V_A growth rate M_A molar mass

ABC 1:1:1 ternary alloy : $\Phi_A = \Phi_B = \Phi_C$

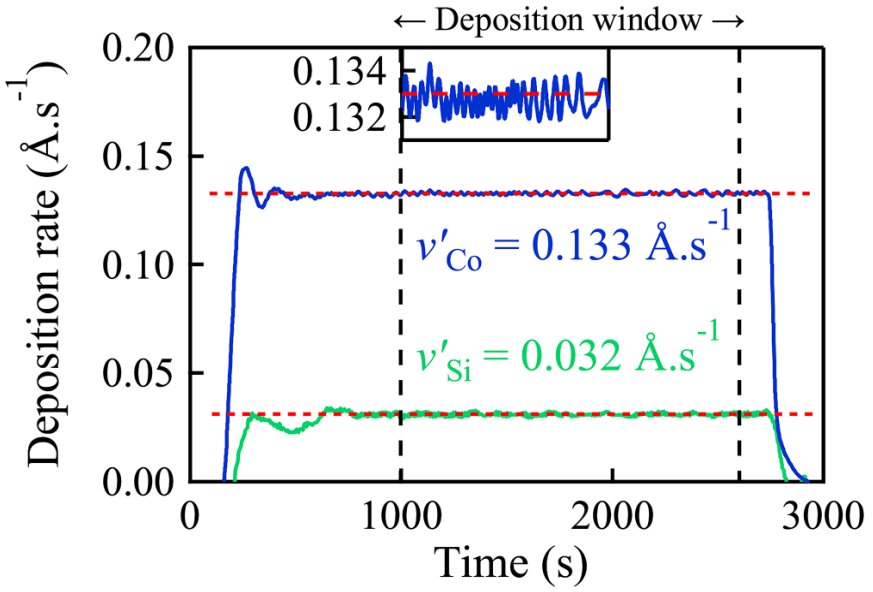
$$thick_{ABC} = \left(\frac{V_A \rho_A + V_B \rho_B + V_C \rho_C}{\rho_{ABC}} \right) . time$$

QCM mesure a mass, need mass density to convert in growth rate : choose an arbitrary mass density

$$\rho_A = \rho_B = \rho_C = \rho_{ABC}$$

$$thick_{ABC} = (V'_{Co} + V'_{Mn} + V'_Z) . time$$

Regulation of the flux using quartz connected to IC6 inficon : sensitivity 0,0008 Å/s



Guillemard et al,, J. Appl. Phys. tutorial 128, 241102 (2020)

Alloys and compounds growth

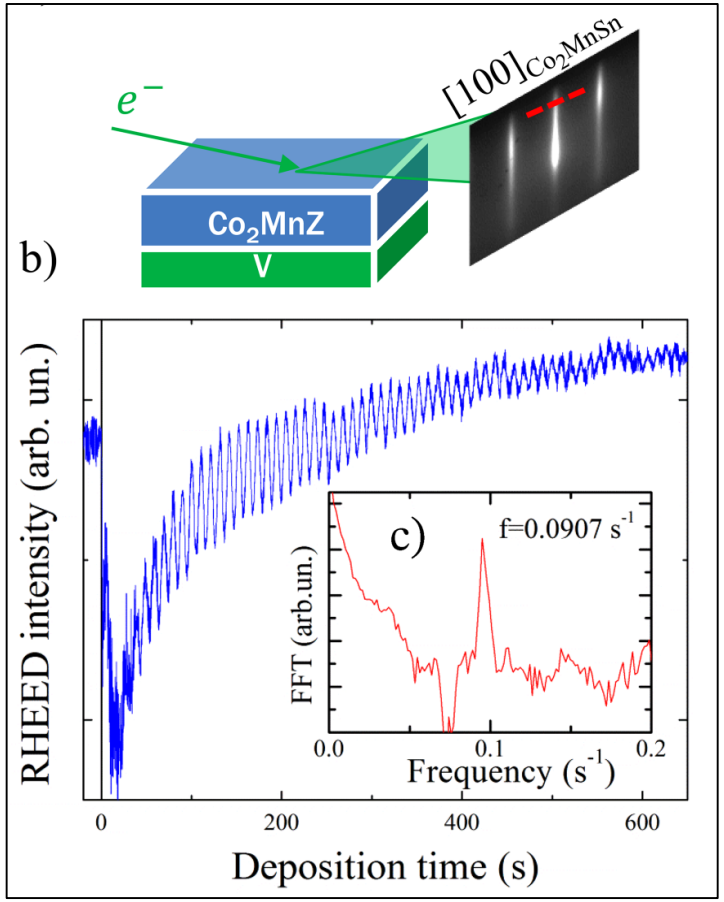
How to control accurately the stoichiometry ?

test the stoichiometry ? Use RHEED intensity oscillations

Using the flux and knowing the alloy density and structure, we can calculate the time to complete a monolayer. Comparison with RHEED oscillations

Test on full-Heusler compounds Co_2MnZ (Z=Si,Ge, Ga, Al, Sn, Sb)

CMZ grown on buffer layers (since 3D on oxides)



	buffer	a_{CMZ} (nm)	Calculated period (s) ± 4%	Observed period (s) ±3%	Diff. (%)
Co_2MnAl	Cr	0.574	12.14	12.0	-1.1
Co_2MnSi	Cr	0.566	12.49	12.45	~0
Co_2MnGa	Cr	0.575	12.1	11.6	-4.1
	V	0.575	12.1	12	-0.8
Co_2MnGe	Cr	0.576	12.05	12.0	~0
Co_2MnSn	V	0.599	11.15	11.0	-1.3
Co_2MnSb	V	0.592	11.41	11.4	~0

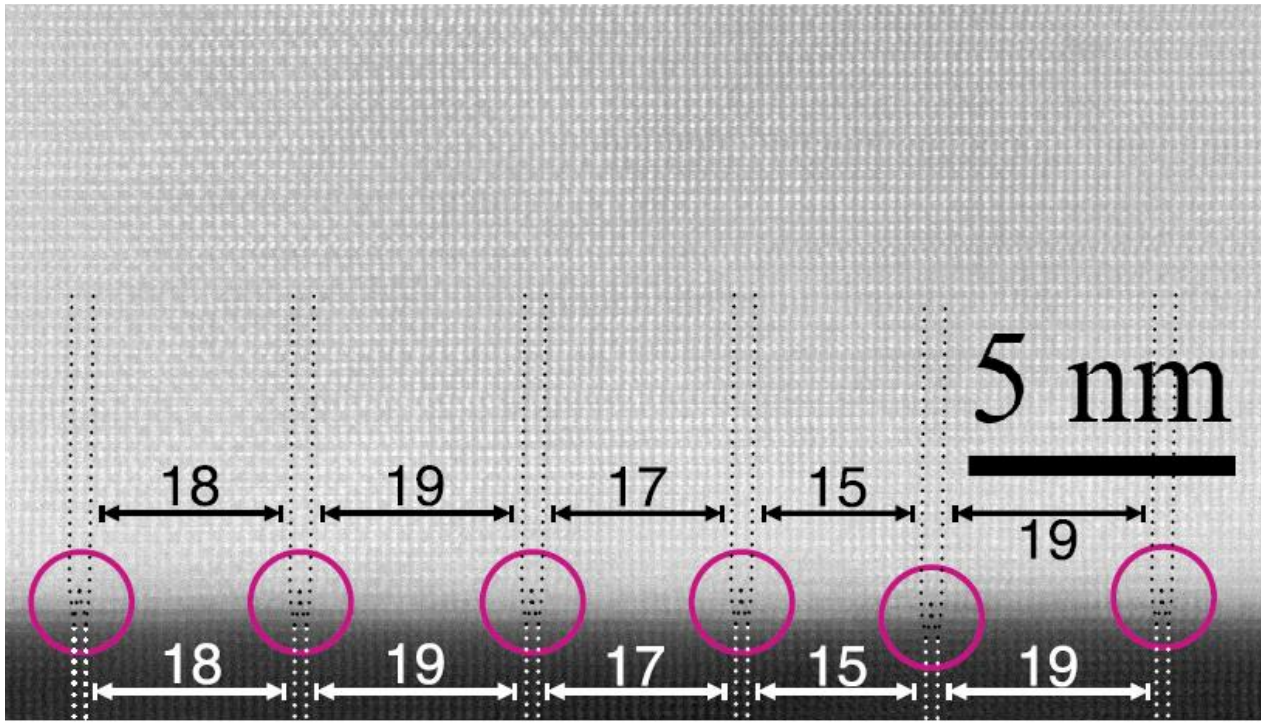
Excellent control of stoichiometry
But need perfect sticking on quartz

Alloys and compounds growth

FVdM : eleastic + plastic relaxation with dislocations ?

Co_2MnSi cubic a=0,566nm
on MgO(001) $a = \sqrt{2}.0{,}421 = 0{,}595\ nm$

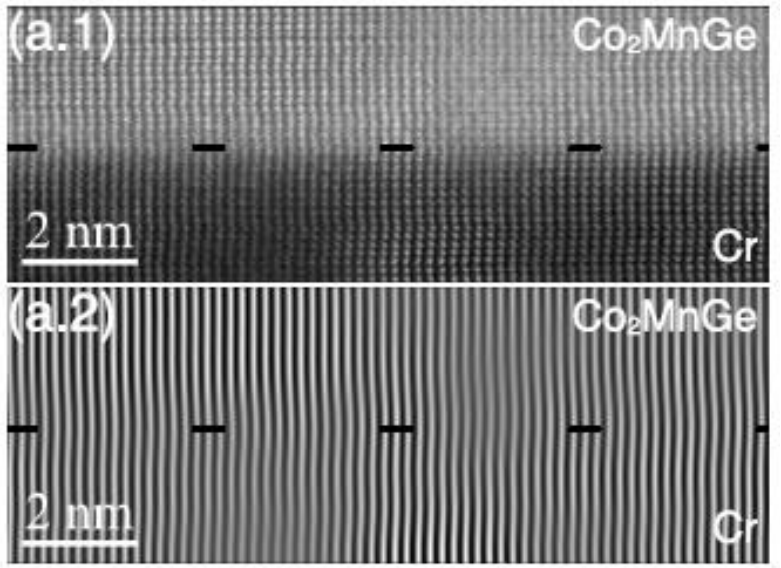
Misfit = -5%



FVdM => N=20 observed on a large scale N=19+/-3

Co_2MnGe cubic a=0,575nm
on Cr(001) $a = 2.0{,}288 = 0{,}576\ nm$

Misfit =0



No misfit dislocations observed

F-VdM model OK !

summary

Continuous flat metallic films on oxide : possible but below 10 nm thick difficult (dewetting)

Metastable phase, systems with large density of interfaces : grow superlattices. Full 2D growth (A/B and B/A) possible in many case at least

If an accurate stoichiometry in alloys and compounds necessary for physical properties, possible by MBE using quartz µcrobalance. Calibration often OK but be careful with light element or high vapor pressure

OUTLOOK

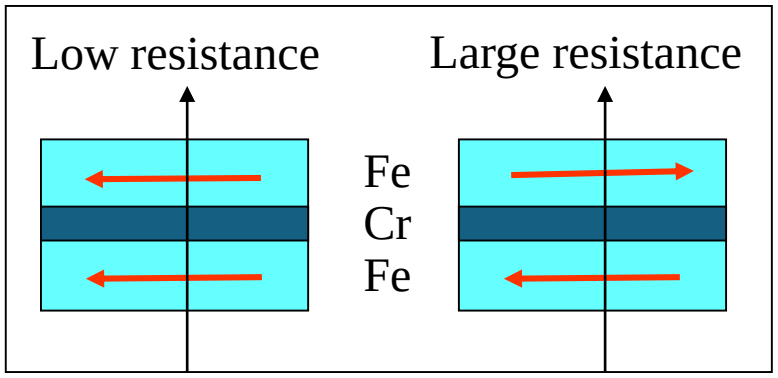
- Why thin metallic films ? Why epitaxy ?
- Chap.I - Specificities of metallic thin film growth
- Chap.II - Epitaxial mechanisms
- Chap.III - Growth mechanisms and strategies
- Chap.IV - Illustration by examples in spintronics
  - Giant MagnetoResistance in epitaxial Fe/Cr/Fe : A. Fert Nobel prize
  - Tunnel MagnetoResistance in epitaxial Fe/MgO/Fe(001)
  - Perpendicular Magnetic Anisotropy
  - Full Heusler compounds and spin gap
  - Topology and ternary compounds : search for non-centrosymmetric material

Giant MagnetoResistance GMR epitaxial Fe/Cr/Fe: **Albert FERT Nobel prize in Physics 2007**

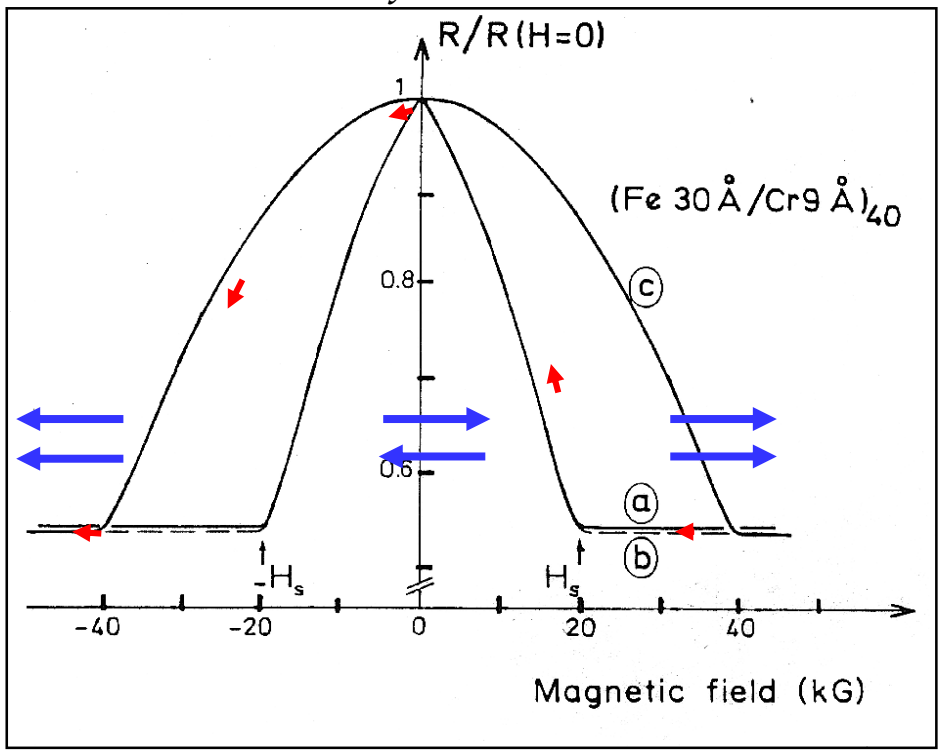
Fe/Cr/Fe (001) spin valve grown by MBE !

Fe BCC a=0,287nm,
Cr BCC a=0,288nm ideal !

Cr thin : 1 nm => AF coupling between Fe layers (RKKY)
+
Apply H : the 2 magnetization align
+
Current easier when the 2 magnetizations parallel than anti-parallel



from Baibich, Fert PRL 1990



Magnetoresistance

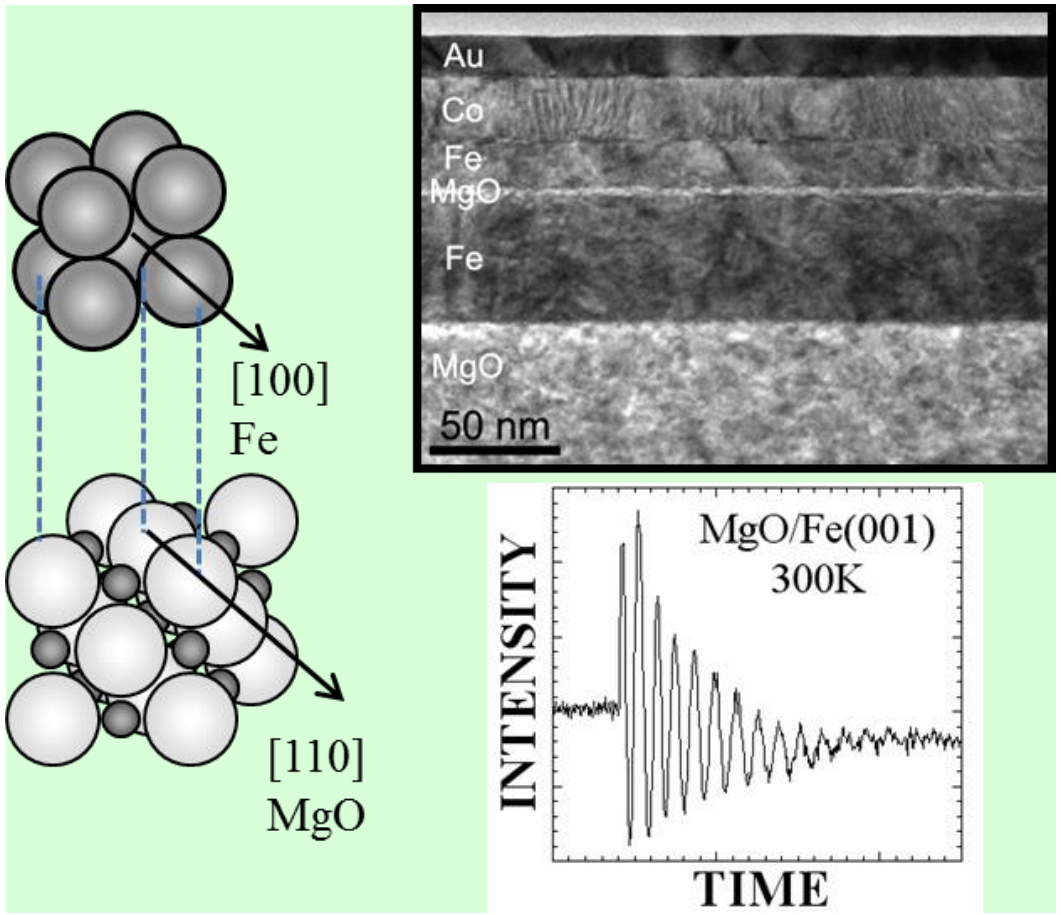
$$MR = \frac{R_{\uparrow\downarrow} - R_{\uparrow\uparrow}}{R_{\uparrow\downarrow}}$$

Few %, much larger than in bulk => **Giant magnetoresistance**

Birth of spintronics
Immediate application : read heads in computers

Tunnel MagnetoResistance (TMR)

Fe/MgO/Fe (001) grown by MBE



Cr (conductive) replaced by MgO (insulating)
= tunnel current through MgO

Remember : MgO on Fe (001) 2D ! (oxide on metal)

RHEED oscillations control of MgO thickness

Optimized MgO thickness : 2,4 nm

Huge magnetoresistance : around 200% at 300K

Can reach 500% with $FeCo_x$ alloys

*Bonell, Andrieu et al PRL**108**, 176602 (2012)*

*Andrieu et al, PRB **90**, 214406 (2014)*

So large effect, very small current, used in magnetic sensors, head and memories

Replication of the MBE knowhow in sputering

Tunnel MagnetoResistance (TMR) and dislocations in the barrier

Fe/MgO misfit =4% =>dislocations in MgO every 5nm : influence on TMR ???

Replace Fe by FeV_x alloys

Fe and V BCC miscible => FeV_x BCC alloys

$a_{Fe} = 0{,}287nm$ and $a_V = 0{,}303\ nm$

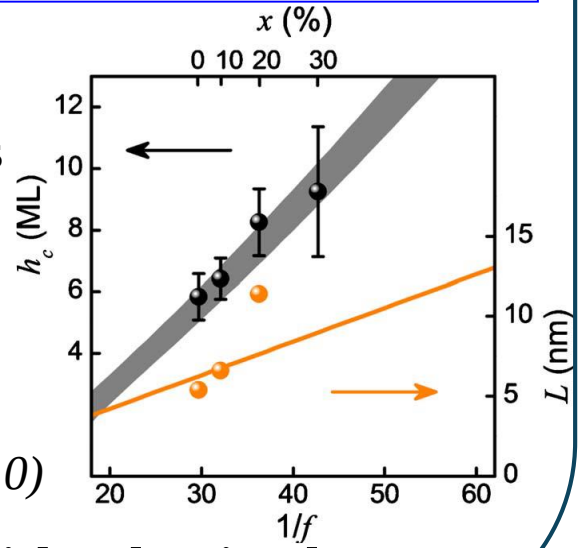
Vegard's law $a_{FexV} = (1-x)a_{Fe} + xa_V$

Perfect matching with MgO for 30% V

Increasing x decrease misfit so increase critical thickness of plastic relaxation

AND

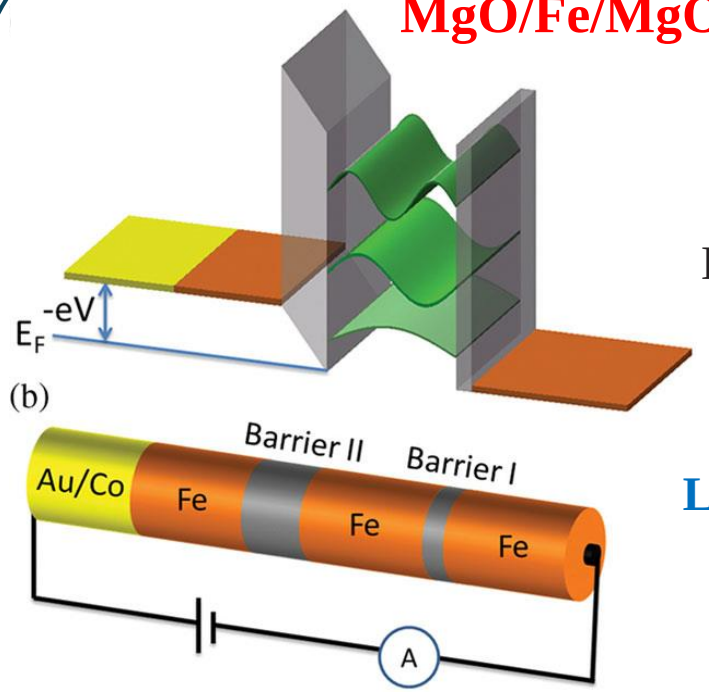
Increase distance between disloc L after relaxation



Phys. Rev. B ***82****, 092405 (2010)*

TMR increase when disloc density decrease

Dislocations & quantum wells in MgO/Fe/MgOAl



QW detected by TMR

Disloc density fixed by MgO (large misfit) or MgOAl (low misfit)

Lateral coherency fixed by desorder (disloc)

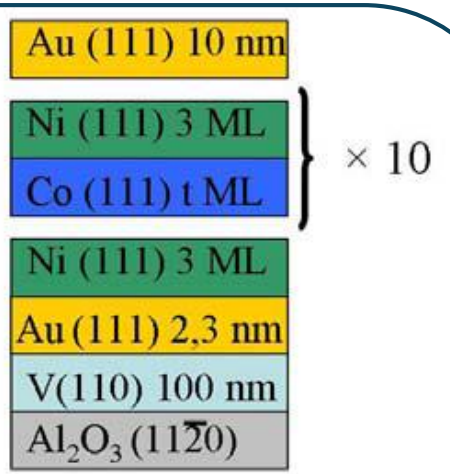
PRL 115, 157204 (2015)

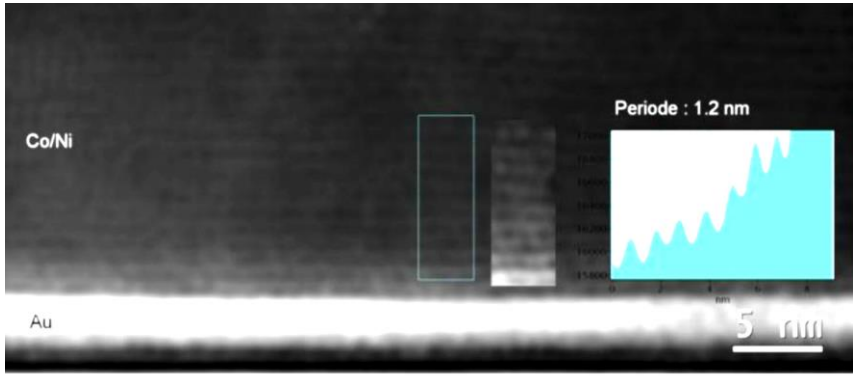
MgOAl misfit with Fe smaller => lower dislocation density => better QW lateral coherence, enhanced TMR !

Perpendicular Magnetic Anisotropy induced by Interfaces

Thin magnetic film : magnetization in-plane due to demag (disc). But perpendicular magnetization needed for devices !

Interfaces can bring perpendicular magnetic anisotropy

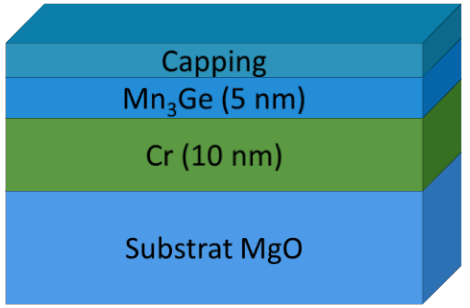


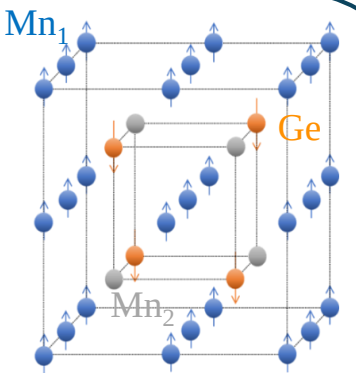


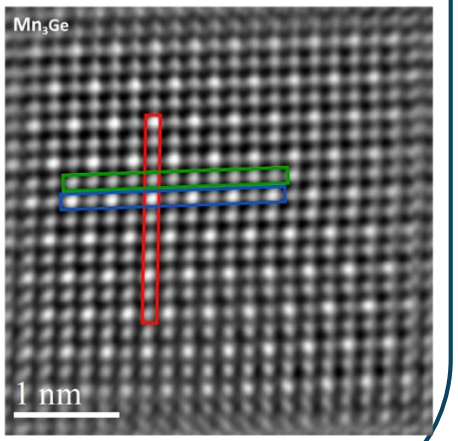
Phys. Rev. Materials ***2***, *064410 (2018)*

Or films with strong magnetocrystalline anisotropy (bulk)

Mn_3Ga, Mn_3Ge : Tetragonal, magnetic easy axis (001), grown on MgO





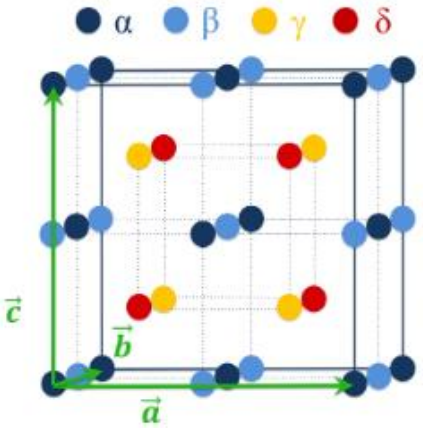


Phys. Rev. Appl.. ***20***, *054017 (2023)*

Half-Metal Magnet : full-Heusler compounds

Theory HMM: no minority spin @E_f,: **spin gap**
$\Rightarrow$ conductor for spin $\uparrow$ $\rightarrow$ fully polarized current !
$\Rightarrow$ insulator for spin $\downarrow$

Exploration of cubic Co_2MnZ compounds
Z=Si,Ge,Sn,Ga,Al,Sb on MgO(001)

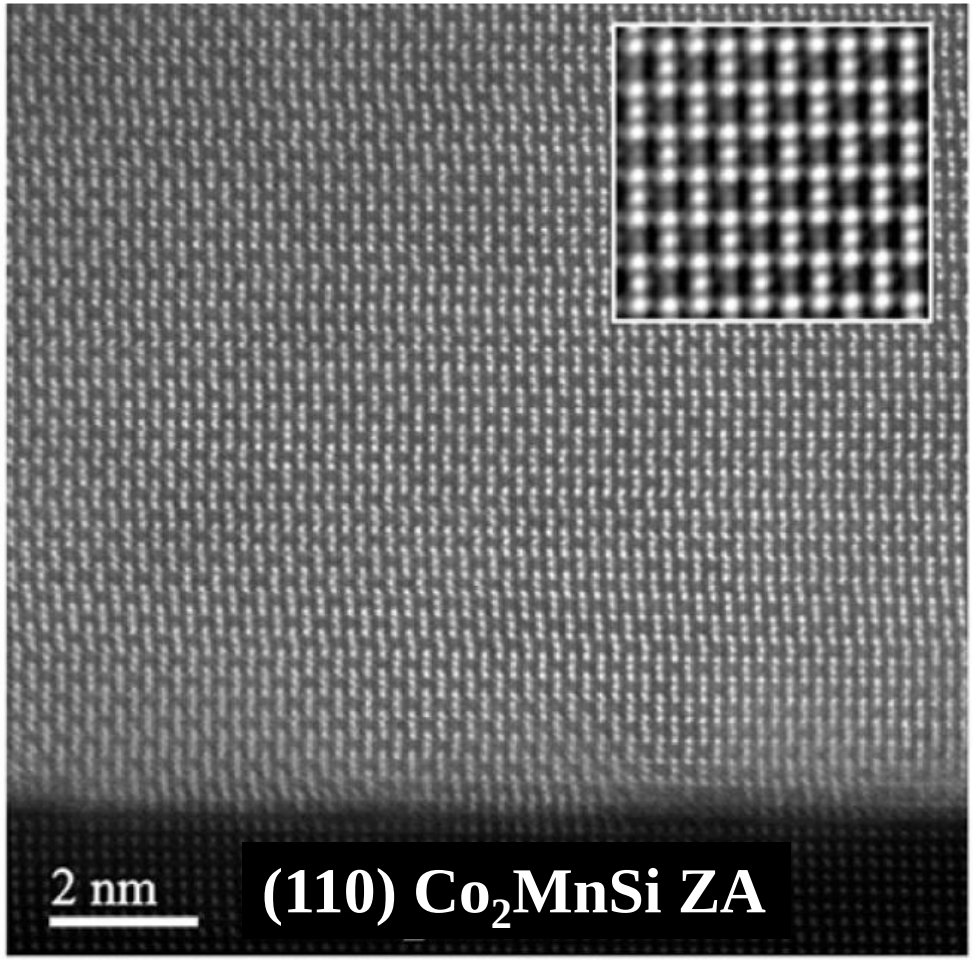


spin gap observed in CMSi, CMGe , CMSn
Extremely sensitive to stoichiometry

Phys. Rev. B ***93****, 094417 (2016)*
Phys. Rev. Appl.. 11, 064009 (2019)
Adv. Mat. 1908357 (2020)

Full spin polarization, ultra-low magnetic damping, very interesting for devices

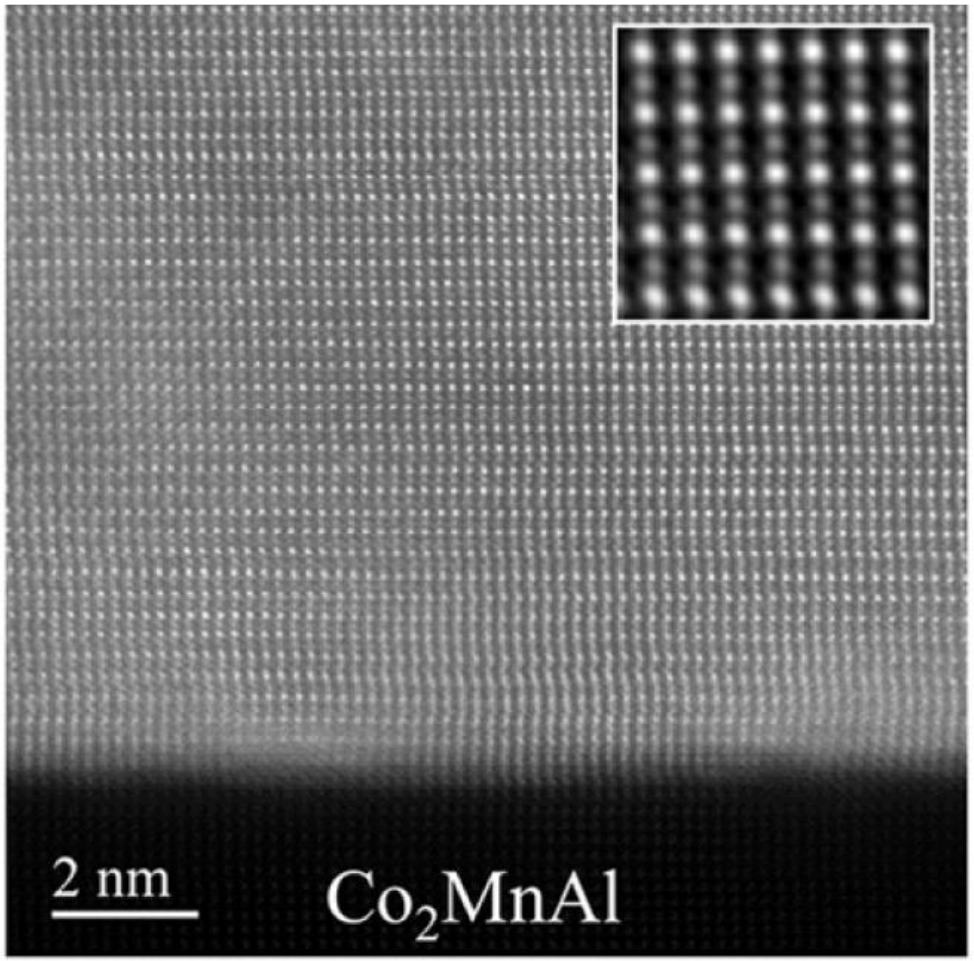
Epitaxy and chemical ordering : STEM-HAADF

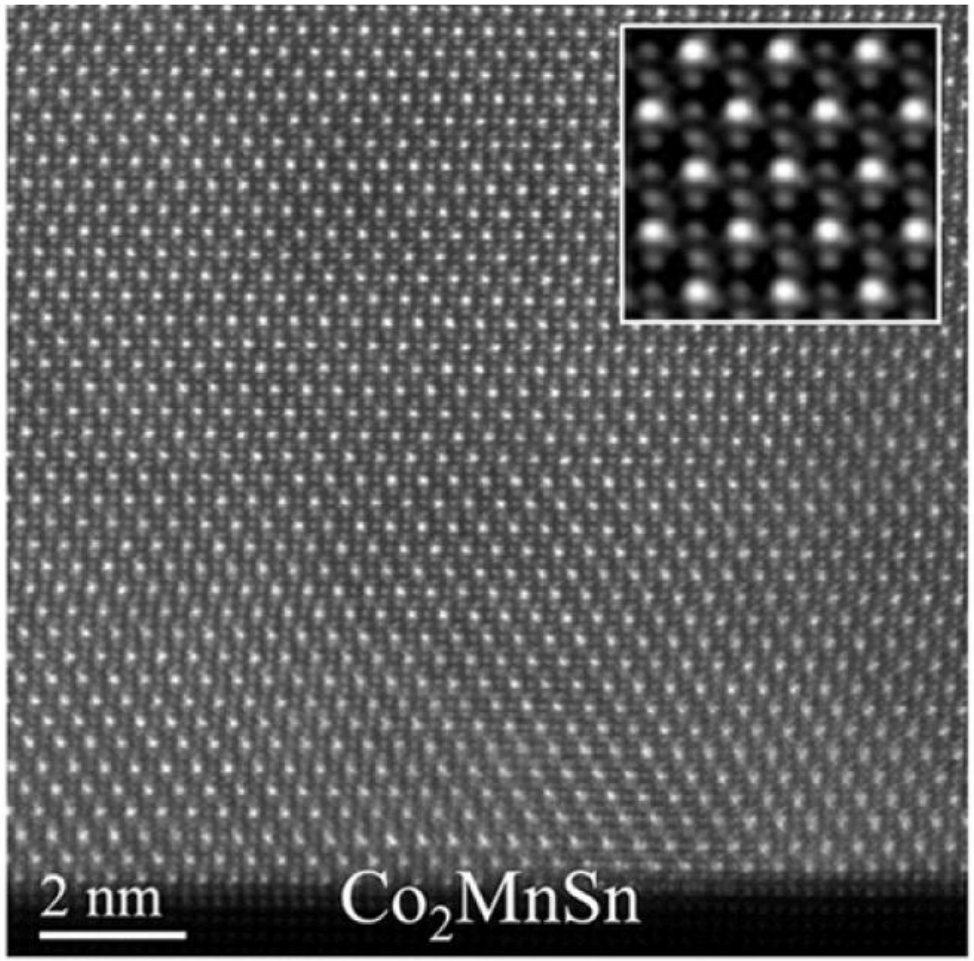


$L2_1$ chem.ordering : α,β : Co δ: Mn γ: Si

Half-**M**etal **M**agnet : full-Heusler compounds

Epitaxy and chemical ordering : STEM-HAADF





B2 : α,β : Co δ, γ: 50% Al 50% Mn Inverse Heusler : α: Co, β : Sn δ: Co γ: Mn

Topology and ternary compounds : search for non-centrosymmetric material

Spin-charge conversion in spintronics : create a spin current in a non-magnetic material (from a feromagnetic layer) that is converted in charge current & vice-versa

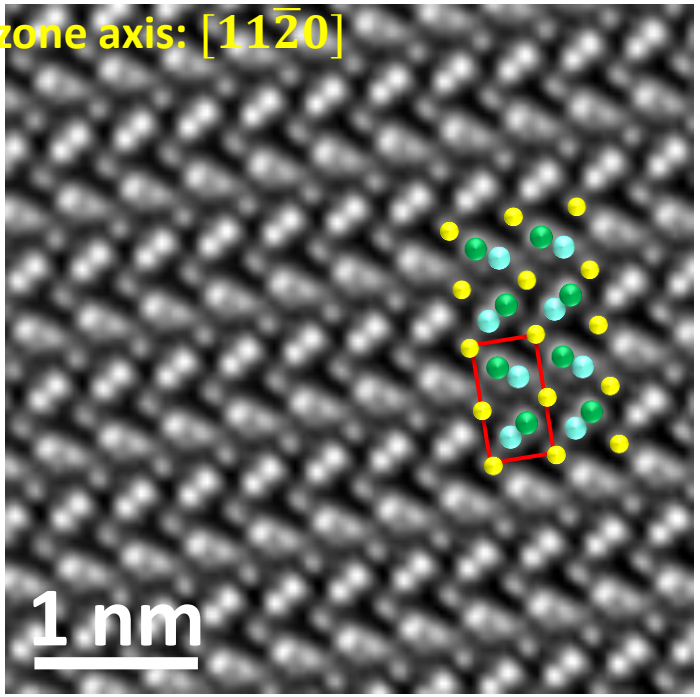
Ingredient : need strong spin-orbit coupling + non-centrosymmetric structure

Half-Heusler compounds XYZ OK
Explore 30 alloys with :
X=**Ti,Y, Sc**
Y=**Ru,Rh,Pd,Pt, Au** (heavy metal SOC)
Z=**Bi, Sn**
Substrate sapphire(0001)

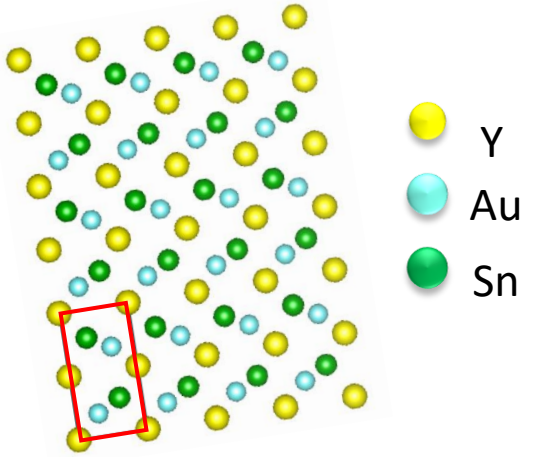
We obtained 17 epitaxial compounds !
some Half-Heusler, but other structures also

1st example : YAuSn (find $P6_3mc$ in bulk)

STEM-HAADF



Simulation of YAuSn $P6_3mc$

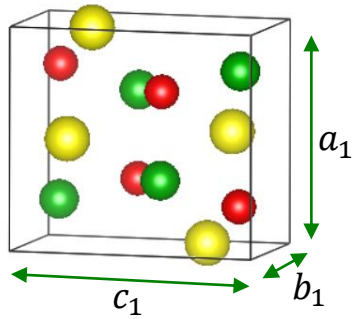


Confirmation of $P6_3mc$
Never grown in thin film
Not yet published

YAuSn $[11\bar{2}0](0001)$ // Al_2O_3 $[11\bar{2}0](0001)$.

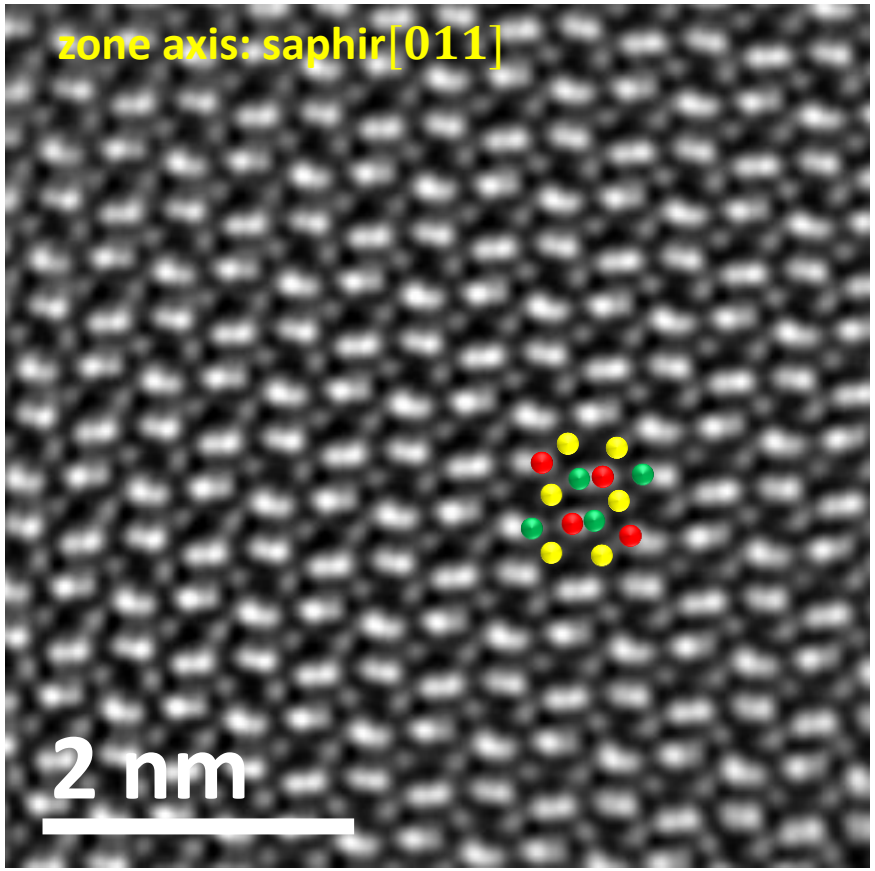
2nd example : YPtSn (find Pnma in bulk), YPdSn (nothing published)

YPtSn
Known in bulk,
space group Pnma

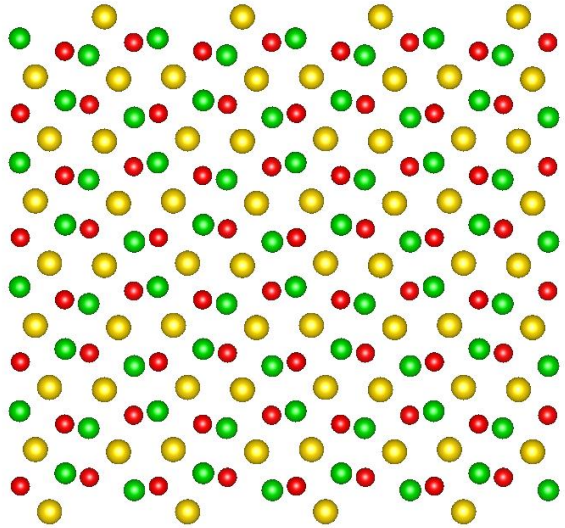


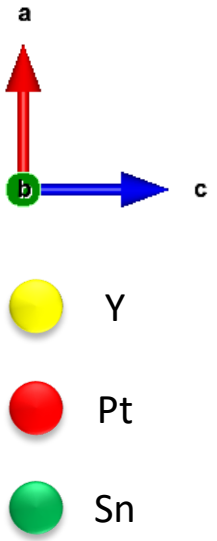
$a_1 = 7{,}16$ Å
$b_1 = 4{,}54$ Å
$c_1 = 7{,}95$ Å

STEM-HAADF



Simulation YPtSn Pnma



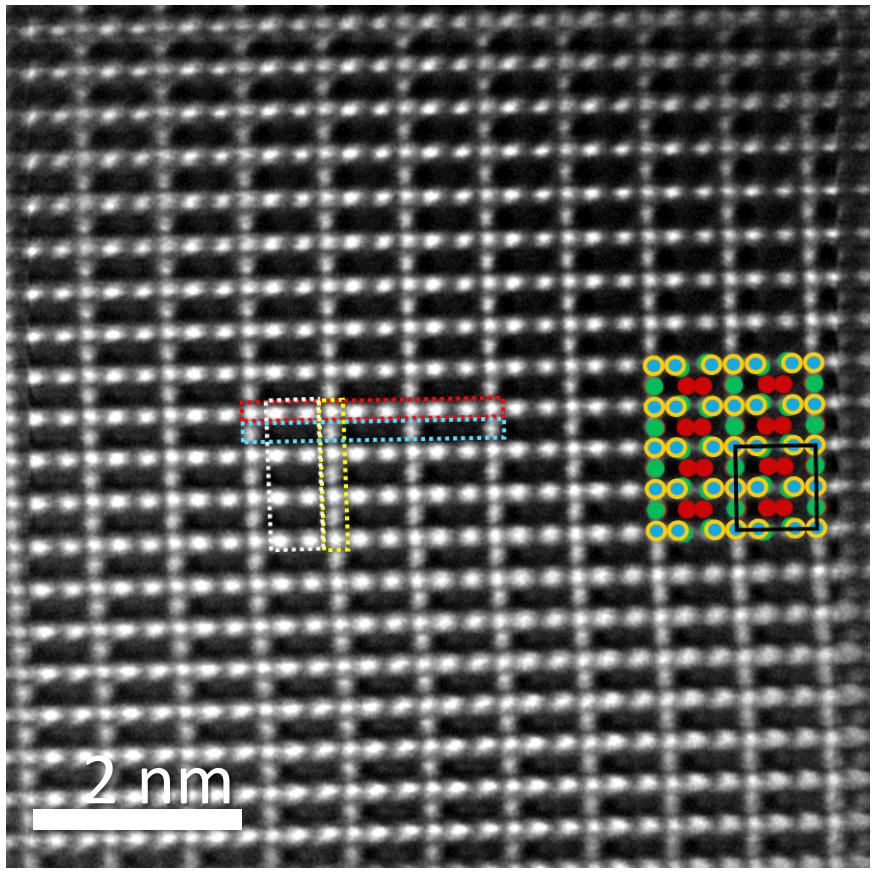


Axe de zone : [010]

Confirmation of ***Pnma***
Never grown in thin film
Not yet published

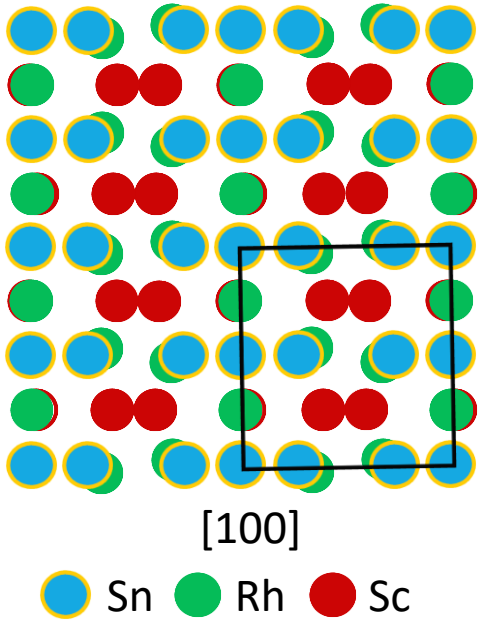
Very nice epitaxy ! Similar with YPdSn (never grown even in bulk) But Pnma is centrosymmetric….

3rd example : ScRhSn (no publi) ScPdSn (find P-62c in bulk)



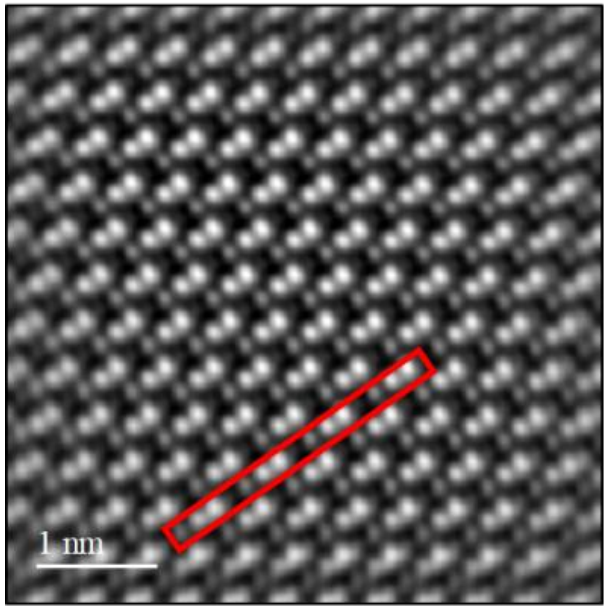
Not yet published

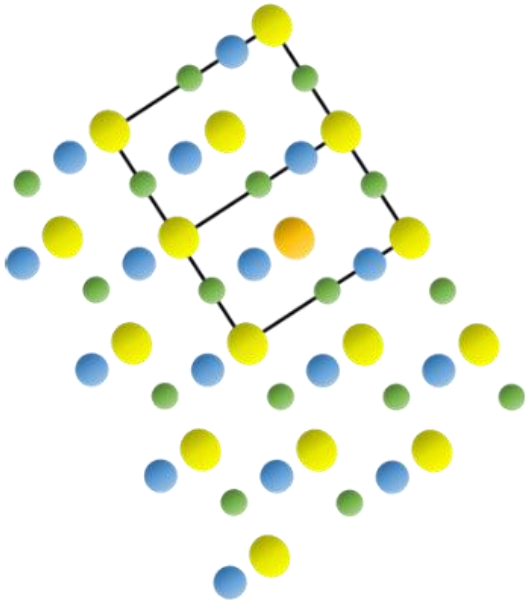
ScRhSn indexed in a hexagonal *P*-62*c* lattice with $a = b = 6.43$ Å, and $c = 6{,}71$ Å.

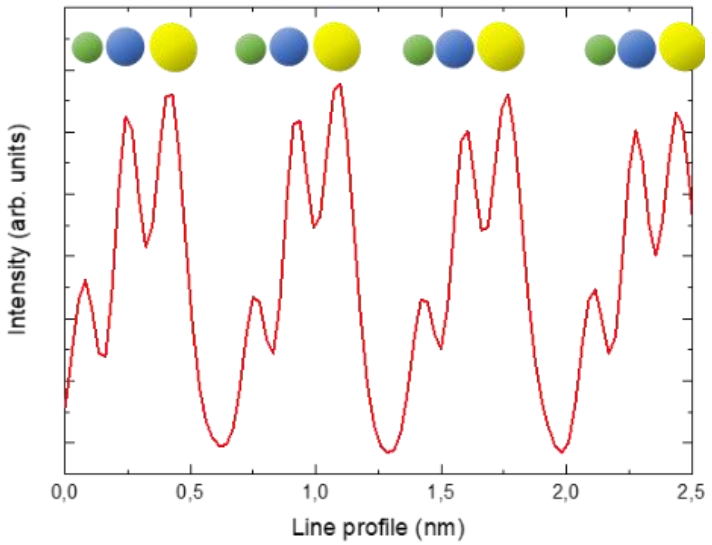


Very nice epitaxy ! And non centro-symmetric !

4th xample : Half-Heusler F-43m: YPdBi, YPtBi, TiRhSn, TiPtSn, ScPtSn, ScAuSn







YPdBi & YPtBi : Palin et al, Phys. Rev. Materials 7, 104203 (2023), Other compounds not yet published

Many systems, but sometimes bad chemical ordering, or multidomains
Can destroy the non centro-symmetry.

CONCLUSIONS

Many possibilities to grow metalic thin films even in complex structures

Metastable phases can be obtained

Superlattices allow to multiply the number of interfaces : new functionalities due to interface engineering

Model systems that allowed to go into details and understand new physics

Alloys / compounds : so many unexplored systems !

This lecture : general idea, needs theory (DFT, Monte Carlo, link to band structure) to get good numbers on specific systems

Challenge for applications : replication using semi-conductor substrates

MBE thin metallic film still pertinent to understand physics in polycristalline films often grown by sputtering (ex: High Entropy Alloys)

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Thank you for your attention

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Questions?