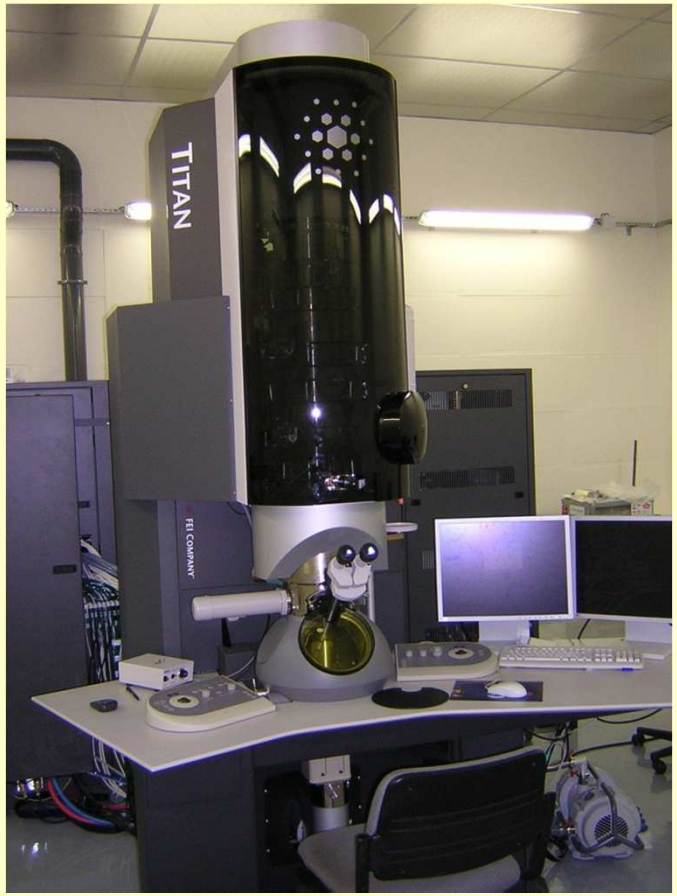

Structural Characterization of Nitrides : Electron Microscopy
(Transmission)

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Institut Néel CNRS Grenoble

GaNeX Summer School La Grande Motte June 2013

Structural informations about the sample

X-ray diffraction for a macroscopic investigation through Reciprocal Space data

To go further : 1) Image of the sample (Direct Space data)
2) At the local scale (up to atomic resolution)
3) Structural AND Chemical informations

In other words :

- ✓ Symmetry : hexagonal or cubic
- ✓ Polarity
- ✓ Defects (nature, position, orientation)
- ✓ Interfaces : with the substrate, in heterostructures
- ✓ Strain measurement
- ✓ Composition : in ternary or quaternary systems, interdiffusion,…

→ Need of a multi-technics instrument,
for informations at the local (nm or less) scale

→ Transmission Electron Microscope

Outline

I Transmission Electron Microscopy

1) Image at the local scale
2) Electrons-sample interactions
3) The different operation modes
4) TEM sample preparation

II Nitrides investigation

1) Structure of nitrides
2) Diffraction patterns: symmetry and orientation
3) Polarity
4) Defects
5) Interfaces
6) Chemical informations

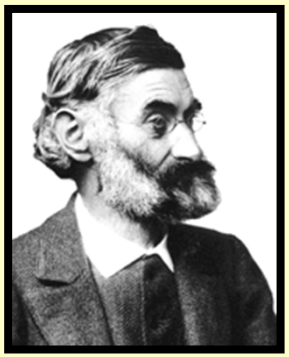
References

Part I

Transmission Electron Microscopy

1) Image at the local scale (up to atomic resolution) : Why using an ELECTRON microscope?

Resolution Power= 0.61 λ / n sin α

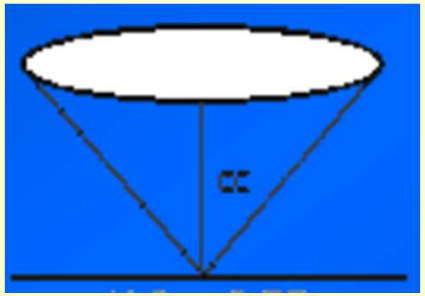


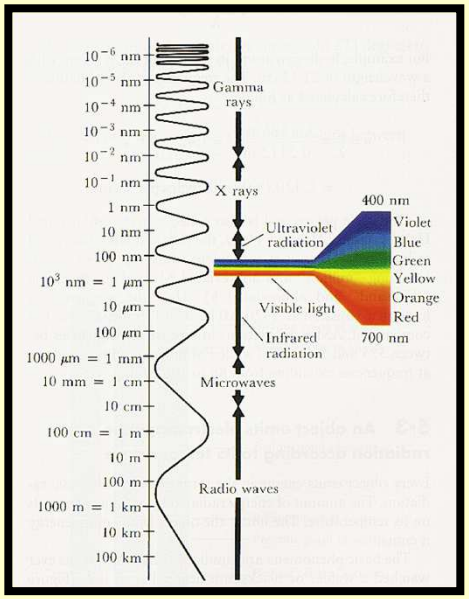
Ernst Abbe
1840 - 1905

λ = wavelength

n = refraction indice

α = half opening angle





⟶ To increase R.P (≈ ½ λ) :

Decreasing λ, but need to have lenses to deviate the beam in order to form an image

- **1923 : Louis de Broglie :**
the wavelength associated with moving electron is given by

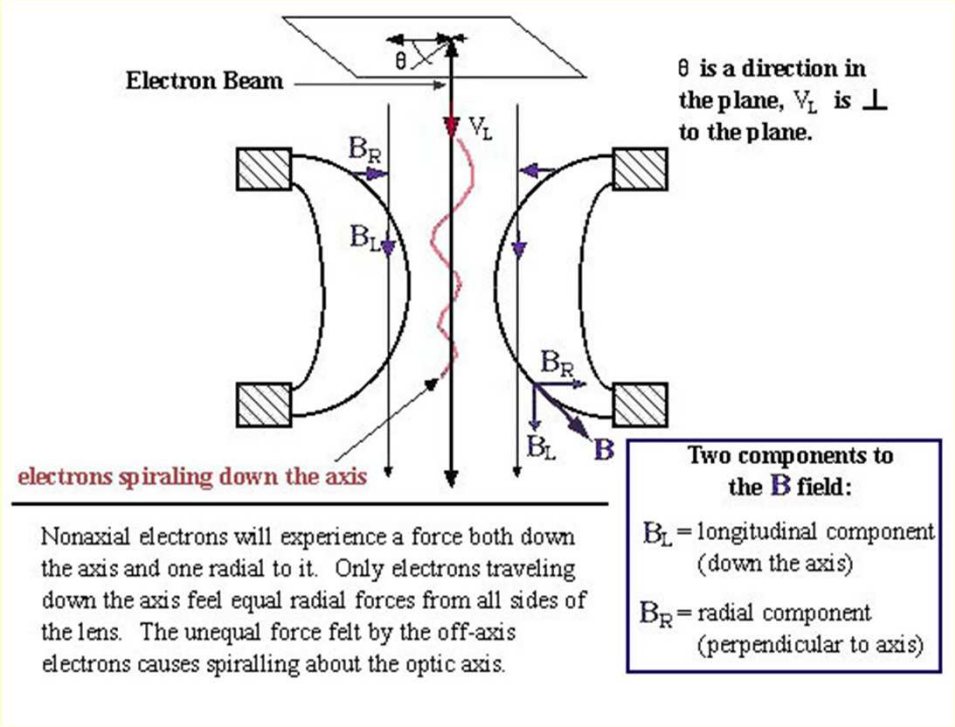
$\lambda = h / m v$ (v = velocity, m = mass)

or $\lambda\ (Å) = 12.22/\sqrt{V}$ (V = acceleration voltage)

V (kV)	100	200	300	400	1000
λ (Å)	0.0370	0.0251	0.0197	0.0164	0.0087

- **1926 : H. Busch : magnetic or electric fields can act as lenses for electron**
- **1932 : First electron microscope E. Ruska and M. Knoll**

Magnetic lens



Variable focus distance $f = K(V / i^2)$

V : acceleration voltage; i : current in the coil

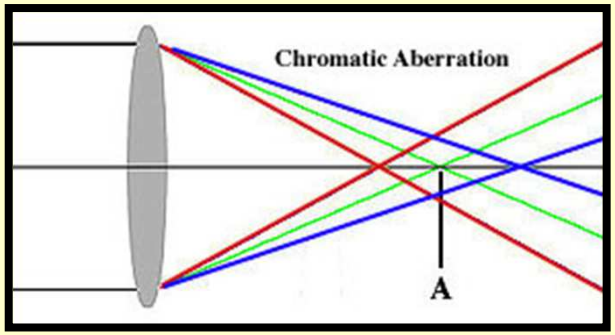
K : depends on the coil geometry

Lens aberrations : limit the microscope resolution power

- **Chromatic aberration**

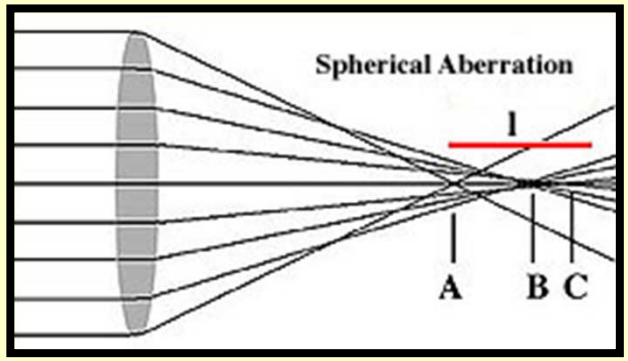
  → monochromatic beam

  (HT stability, monochromator, C_c corrector)



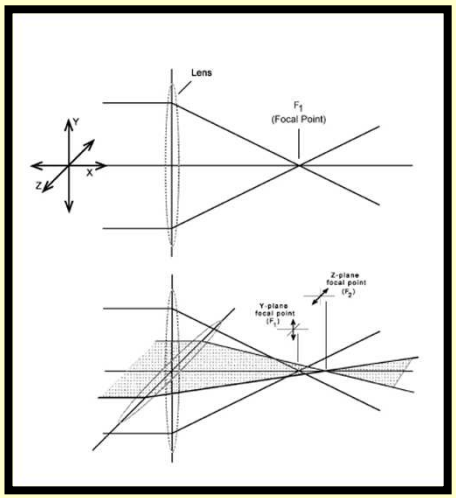
- **Spherical aberration**

  → C_s Corrector

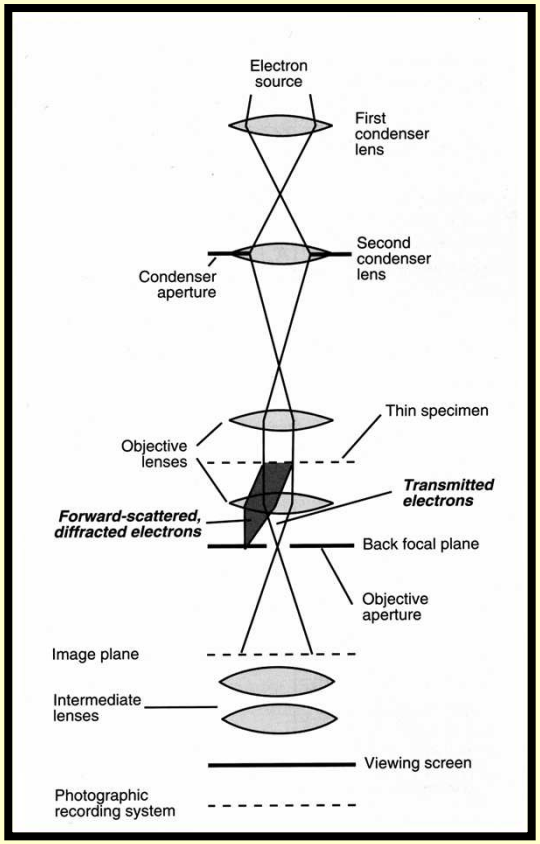


- **Astigmatism**

  → additionnal coils : stigmators



Transmission Electron Microscope

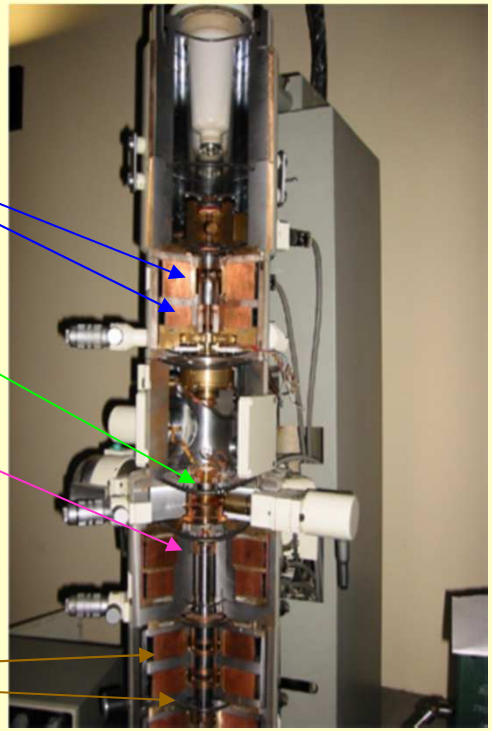


Condenser lenses :

Objectif lens:

Intermediate lens:

Projectors:



(Jeol 100CX ; CEMES)

2) electrons-sample interactions: Multi-technics instrument

2 types of interactions:

Elastic Interactions :

(backscattered, transmitted, elastically scattered electrons)

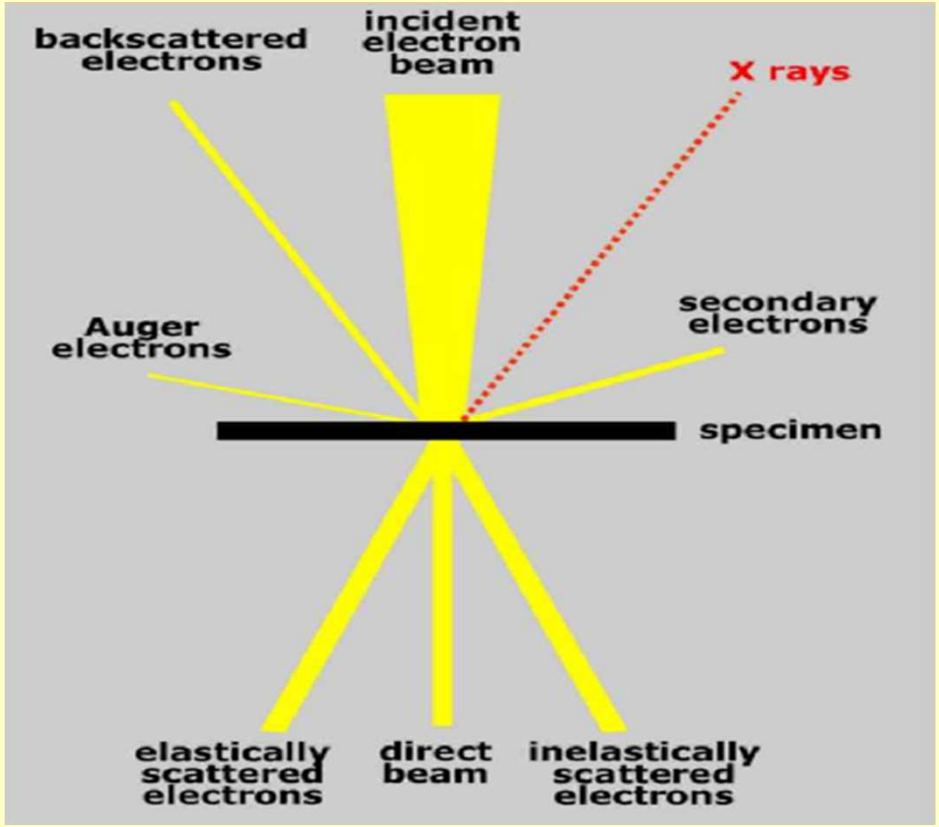
TEM or STEM imaging , Diffraction

Inelastic Interactions:

(X-rays, secondary, Auger, inelastically scattered electrons)

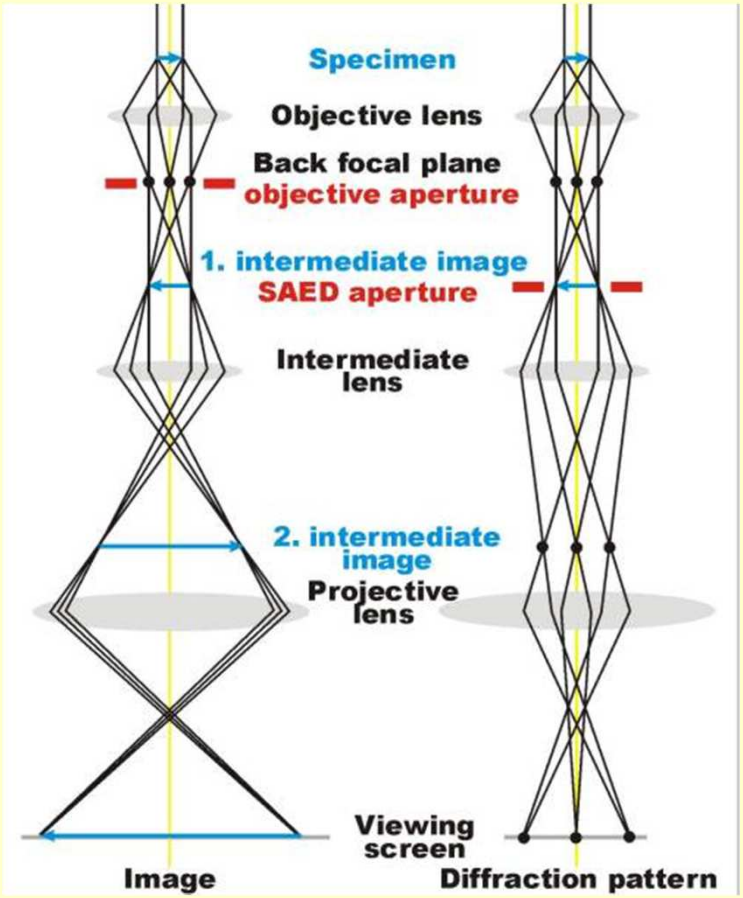
EFTEM imaging,

EELS, EDX spectroscopy



3) The different operation modes

A) Elastic scattering



Objectif lens:

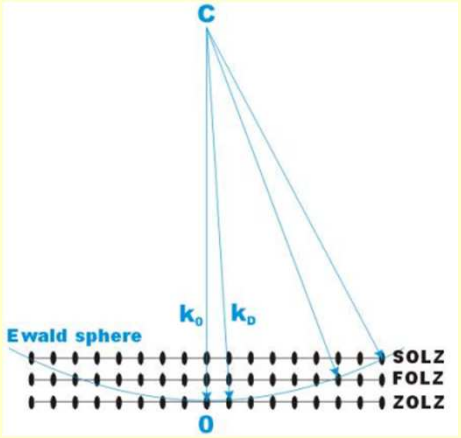
- First image of the sample in the image plane
- Diffraction pattern in the back focal plane

→ **Tuning of the intermediate lens:**

If object plane = first image
→ Image mode

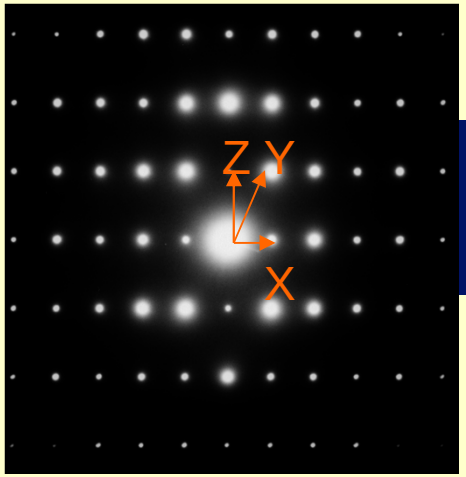
If object plane = diffraction pattern
→ Diffraction mode

a) Diffraction (parallel ED or convergent beam CBED)

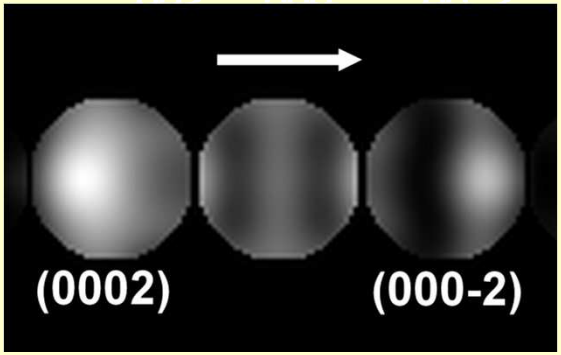


λ small (0.0197 Å at 300kV): Flat Ewald sphere; large number of reflexions visible:

Reciprocal Lattice Planes



Symmetry (cubic, hexagonal,….)
Orientation
Lattice parameters

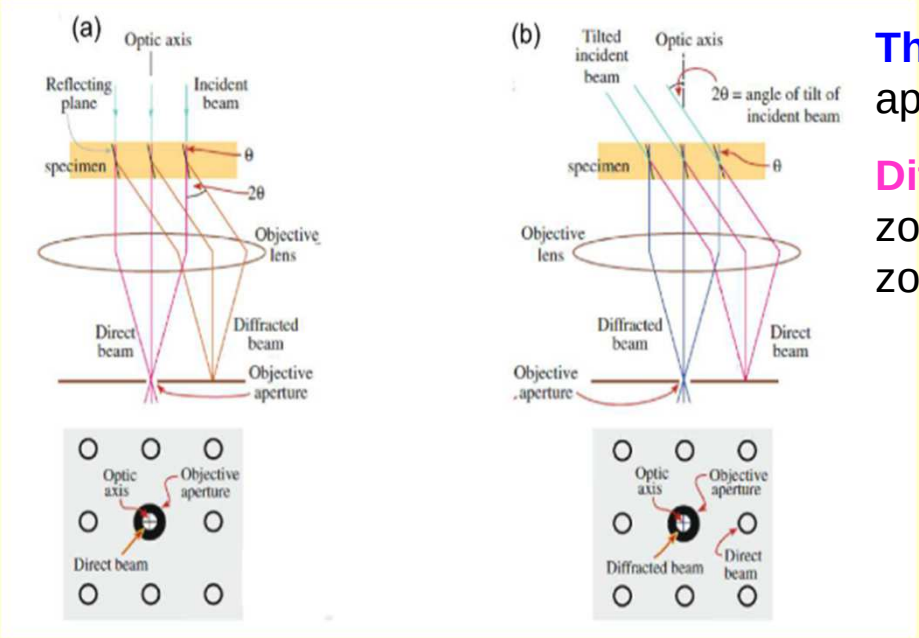


GaN 30nm

Polarity determination : features inside 0002 and 000-2 disks not equivalent

b) TEM Imaging (Conventional CTEM)

Bright Field **Dark Field**



From WILLIAMS et CARTER, 2009

Mass contrast: In BF, regions with higher Z atoms appear darker (stronger scattering)

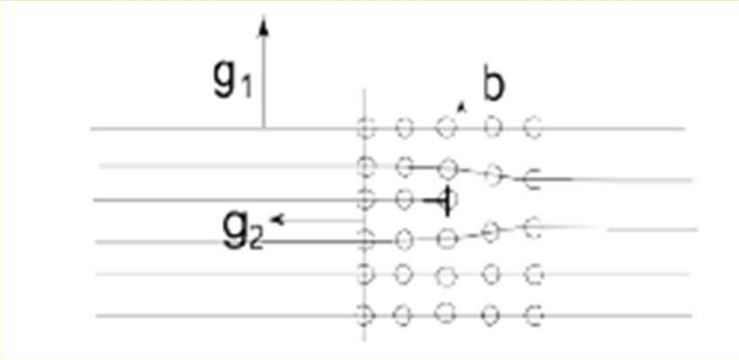
Thickness contrast: In BF, thicker regions appear darker (stronger scattering)

Diffraction contrast: regions oriented along a zone axis appear darker in BF ; in DF, bright zones corresponding to selected diffraction spot

Visualisation of defects (dislocations, stacking faults,…)
Qualitative informations on thickness, chemical composition, strain (comparison of different regions)

Defect with displacement field R : not appearing in dark field obtained with g (hkl) spot if $R.g = m$ integer

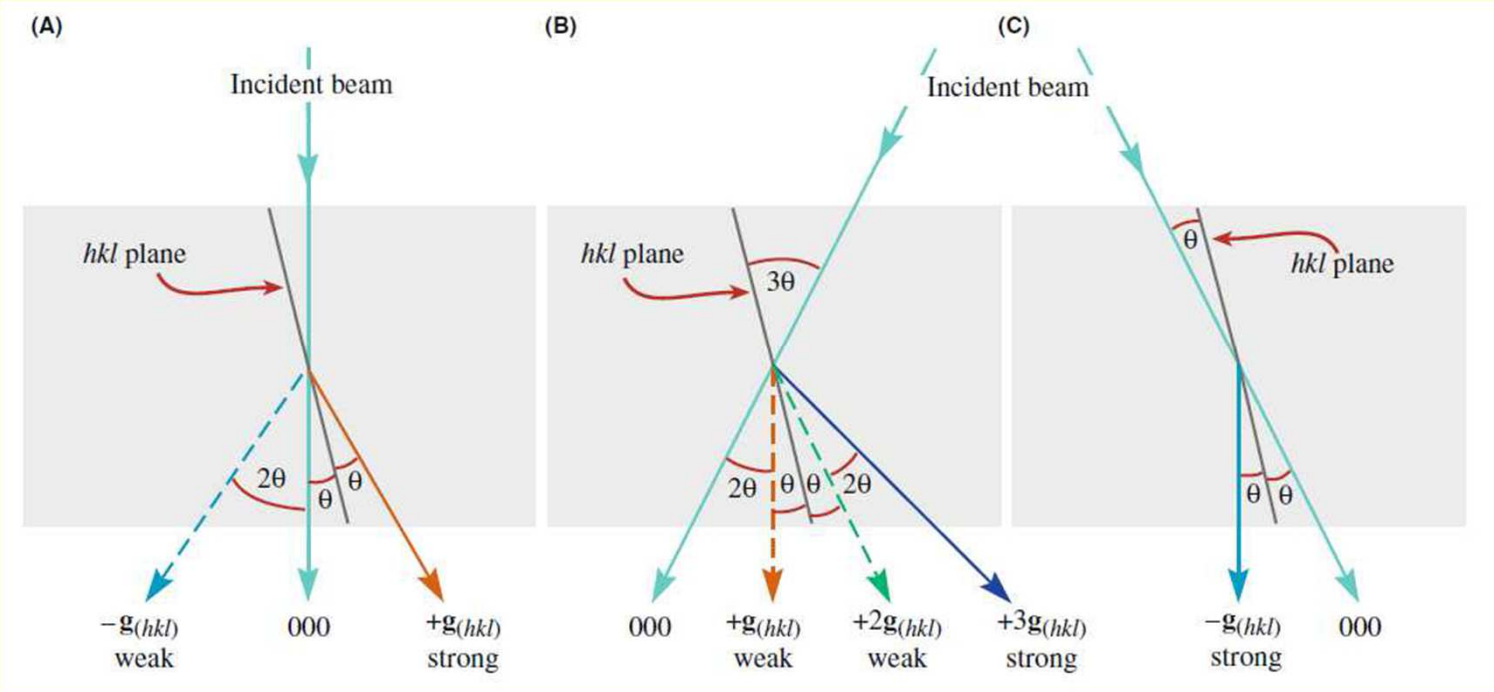
if $m = 0$, $R \perp g$



Example:
Edge dislocation
g1.b# 0
g2.b=0

If g1 and g2 found such R.g1 =0 and R.g2 = 0,
identification of R direction and nature of the defect

From WILLIAMS et CARTER, 2009



Bright Field

Weak beam (g-3g)
Defects bright

2 beams
Defects dark

Dark Field

From WILLIAMS et CARTER, 2009

c) High resolution HRTEM

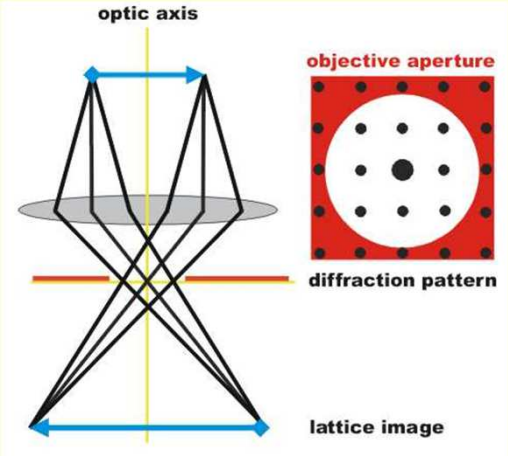
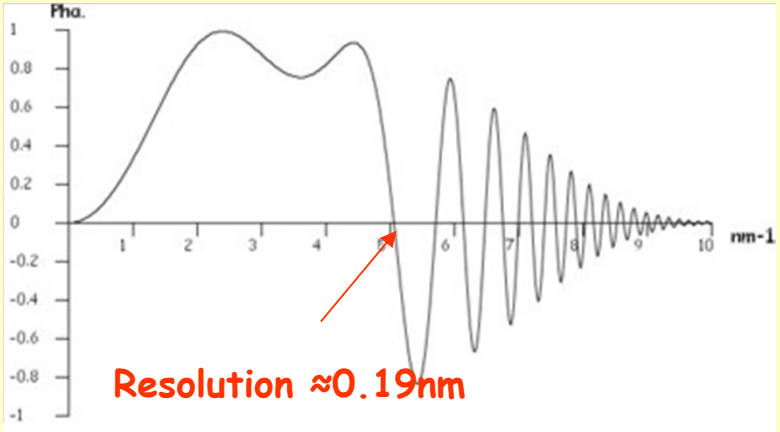


Image formed by interferences between transmitted and diffracted beams (zone axis orientation).

The contrast is linked to the modification of the phase of the incident beam when crossing the sample



Transfer function 300kv FEG; Cs=1.15mm ;

Scherzer defocus ($\Delta f_{scherzer} = -1.2\sqrt{C_s \lambda}$)

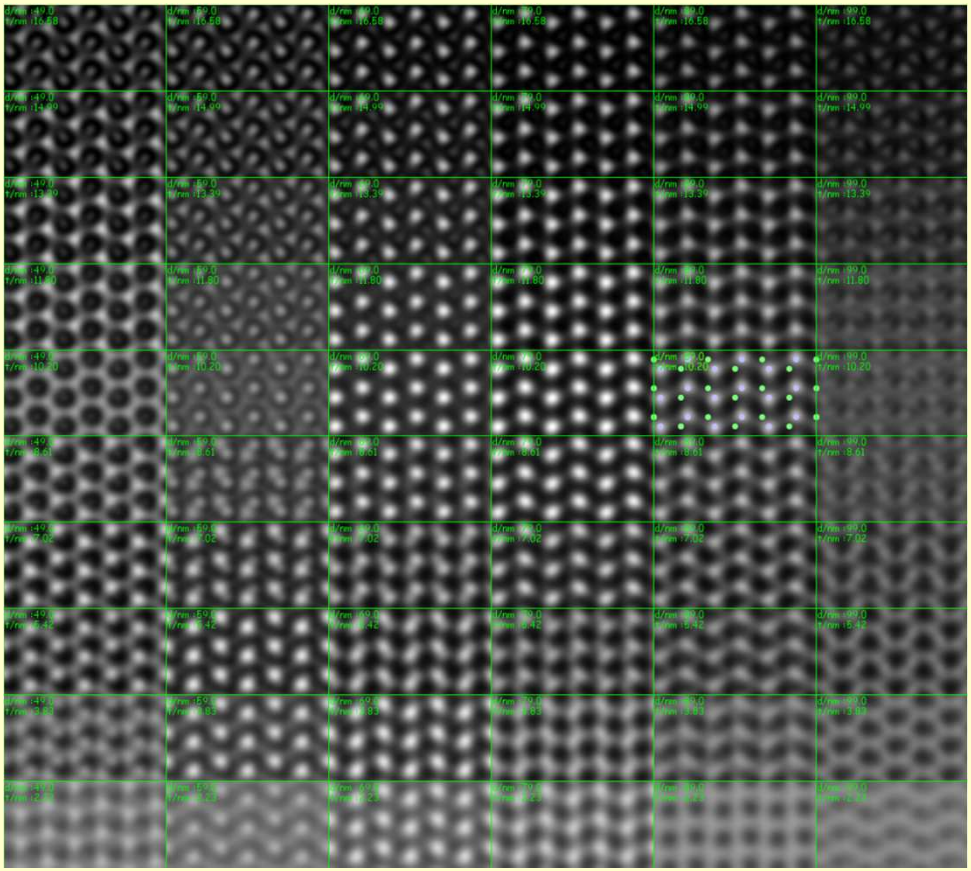
Lens aberrations decrease the image resolution (transfer function of the microscope, depends on defocus)

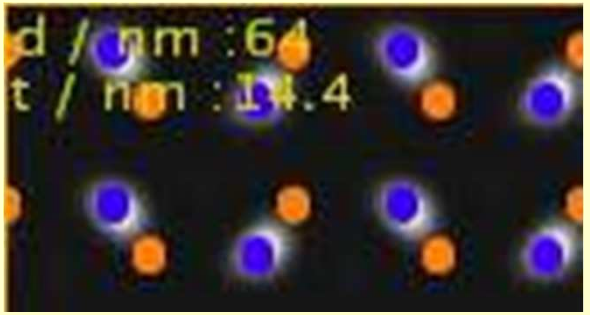
Point resolution= 0.66 $(C_s \lambda^3)^{1/4}$

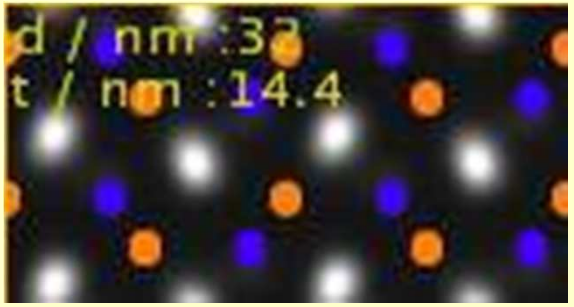
(maximum at Scherzer defocus)

defocus

thickness



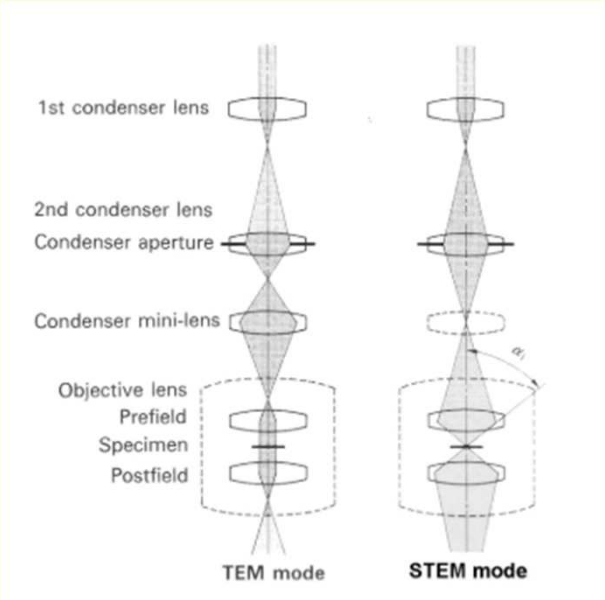


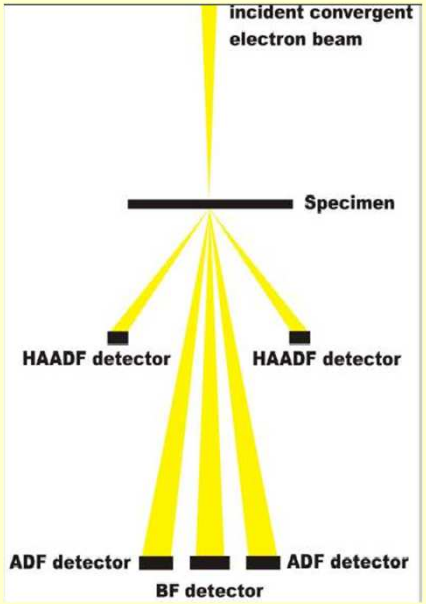


Atomic resolution possible but no direct interpretation of images : need to compare with simulations (dependence on thickness and defocus)

Image analysis (Geometrical Phase Analysis: Strain and/or composition)

d) High resolution Scanning Transmission Microscopy HR-STEM





Several detectors (BF and ADF as in TEM)

HAADF : incoherent scattering (Rutherford + Thermal Diffuse scattering).

Contrast proportionnal to $Z^{1.7}$

Heavier atoms appear brighter(Z contrast) ;

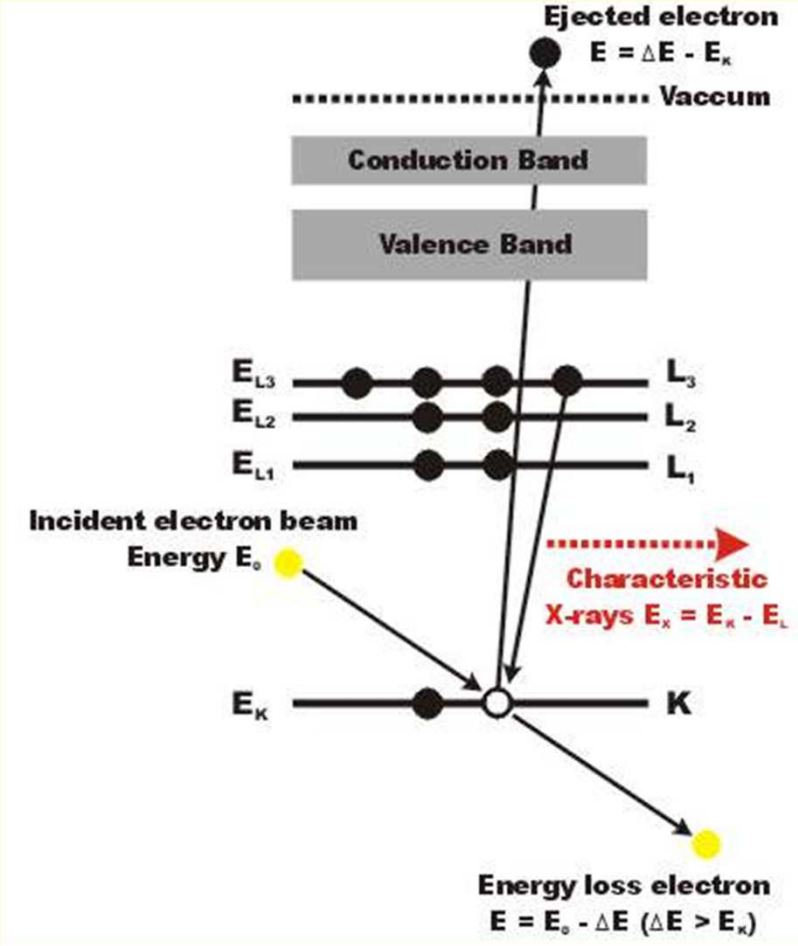
no diffraction contrast

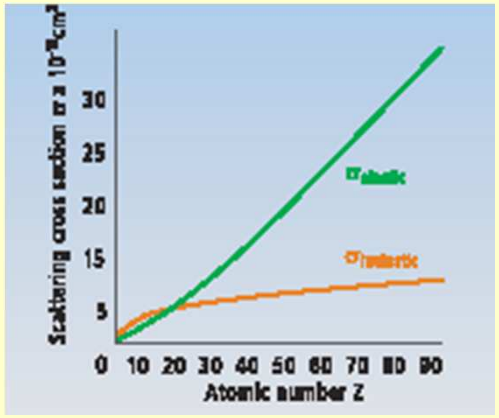
STEM : scanning a focussed probe across the sample

Atomic resolution possible ; direct (qualitative) interpretation of images (Z contrast)

Simulations for quantitative interpretation

B) Inelastic scattering : Chemical informations



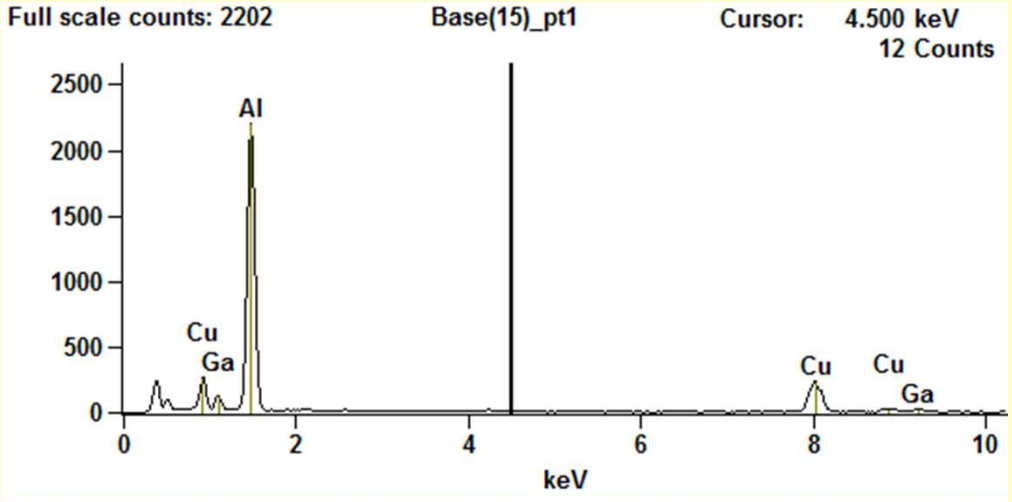


Signals weaker than for elastic interactions (except light elements)

→ intense beam needed or longer acquisition time

a) EDX

Spectrum mode



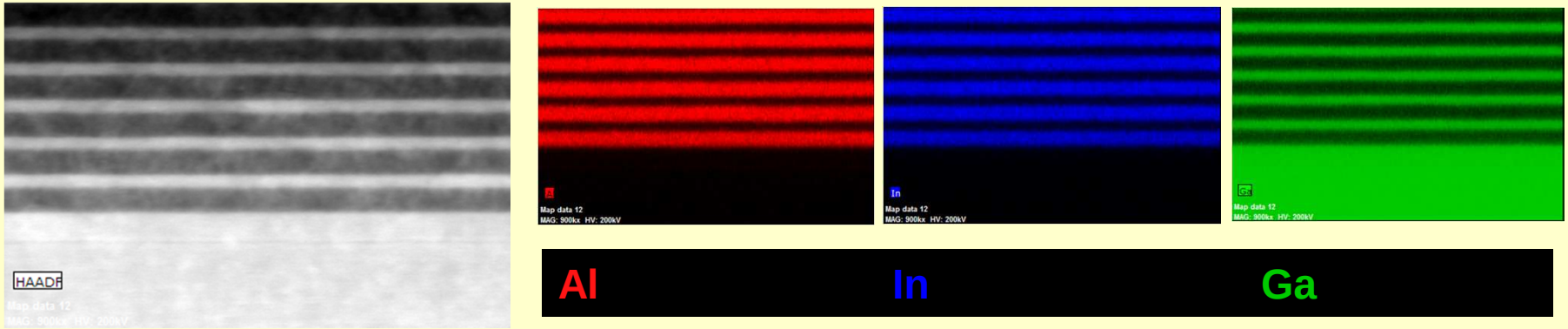
Not for light elements : ≈ Z<6 (C),
Energy resolution ≈ 100eV

Peak positions caracteristic of the chemical element
⟶ qualitative analysis

Quantitative analysis:

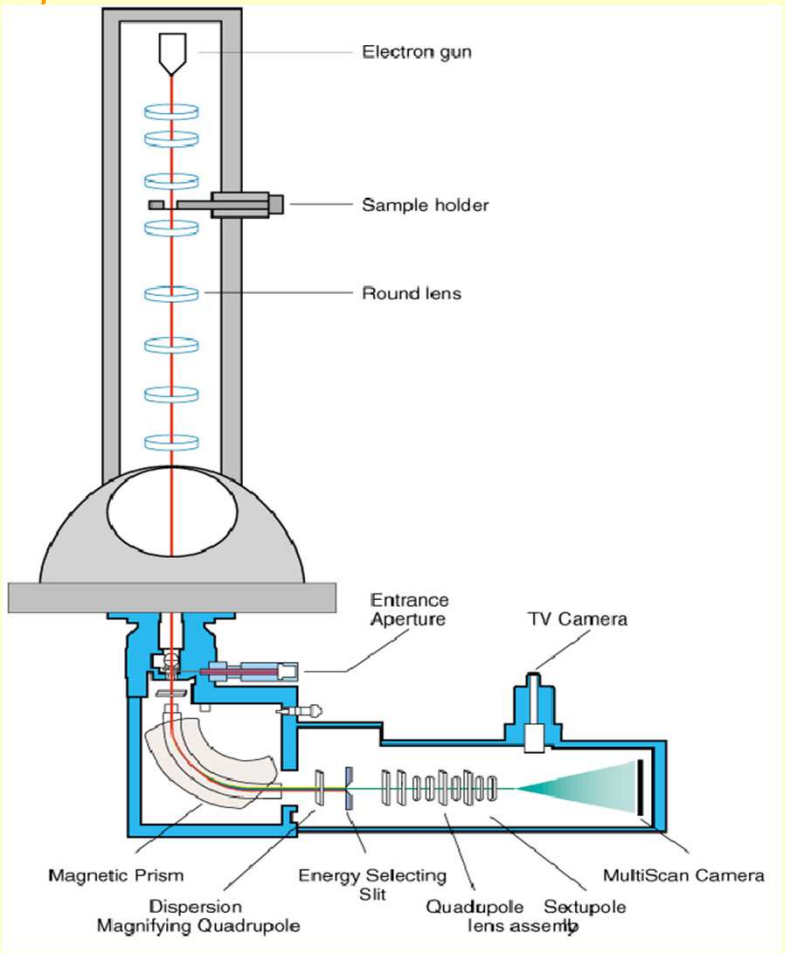
Need to introduce corrections and « standards »

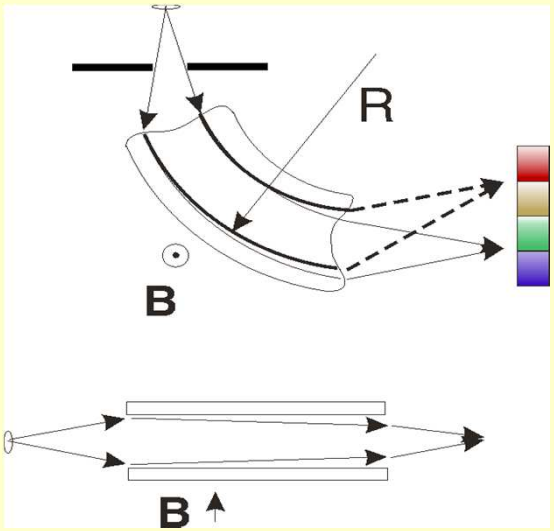
Chemical maps

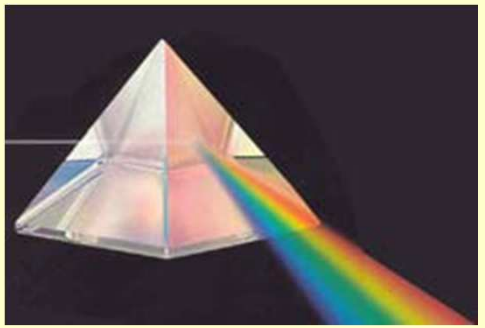


InAlN/GaN Multiple Quantum Wells

b) EELS and EFTEM







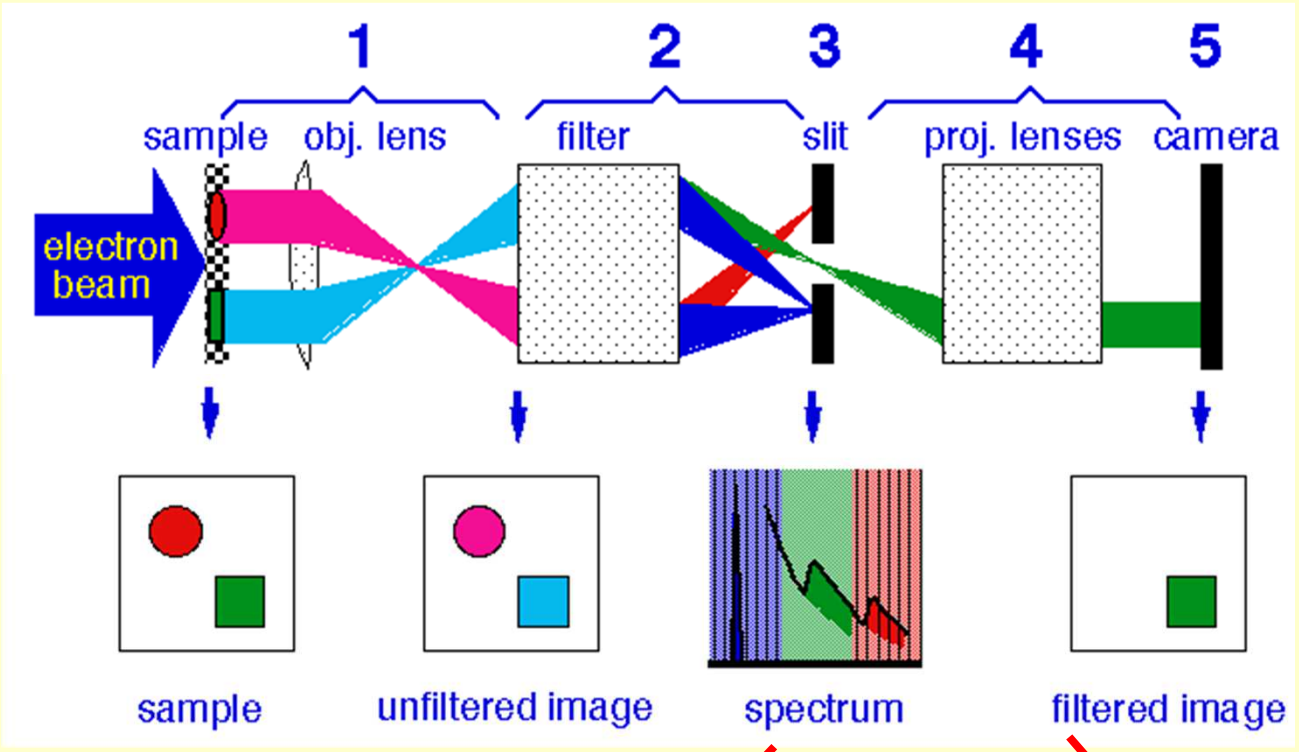
Magnetic prism to deviate electrons depending on their energy

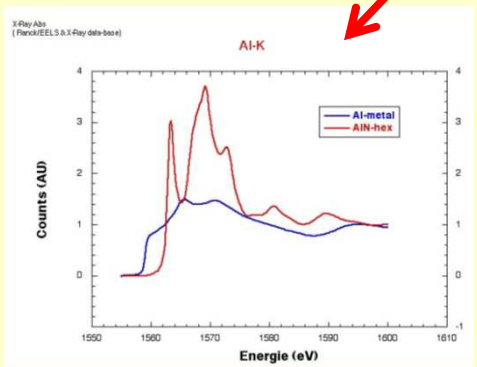
→ **spectrum mode (EELS)**

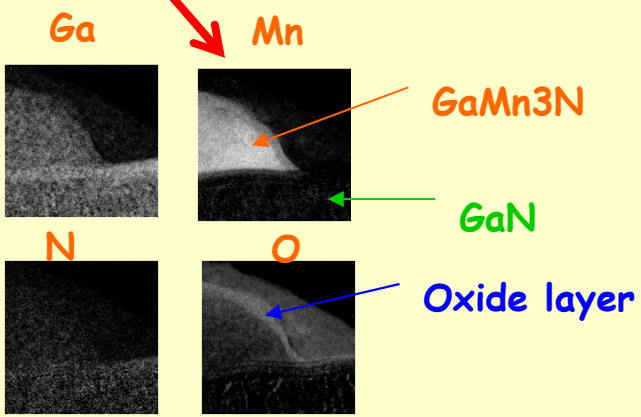
Image formation with electrons of an energy range (E+/-ΔE) (ΔE ≈qqs ev to qqs 10 ev)

→ **energy filtered mode (EFTEM)**

Ex : post-column filter


1
2
3
4
5
sample
obj. lens
filter
slit
proj. lenses
camera
electron beam
sample
unfiltered image
spectrum
filtered image


Al-K
Al-metal
AlN-hex
Counts (AU)
Energie (eV)


Ga
Mn
GaMn3N
GaN
N
O
Oxide layer

4) TEM sample preparation: need to have a thin sample (<300nm)

http://temsamprep.in2p3.fr

Long and often complex procedure

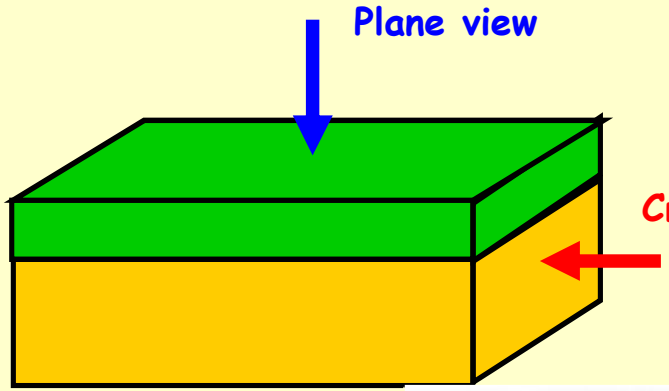
Destructive technic

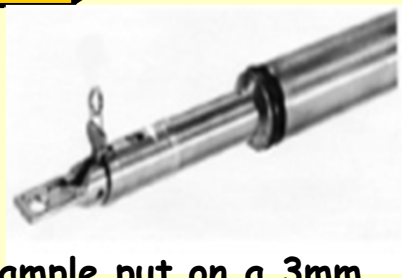
Only small volumes analyzed

(few $\mu m^2 \times$thickness)

Thin foil effect: strain relaxation possible

Best thickness range depends on the investigation method (CBED, HR-TEM, STEM, CTEM,….)



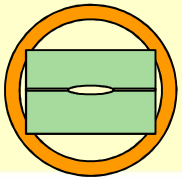


Thin sample put on a 3mm diameter ring

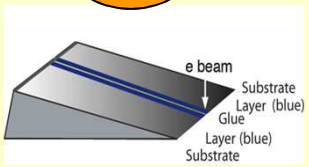
Preparation is a crucial step !!!!
Badly prepared samples will never lead to « good », useful images whatever the performances of the microscope and the ability of the microscopist

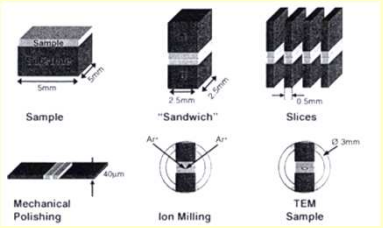
❖ Planar structures :

*Mechanical polishing + Ion Milling



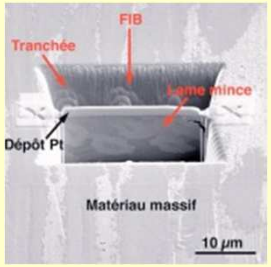
*Tripode polishing
(mechanical polishing to electrons transparency)





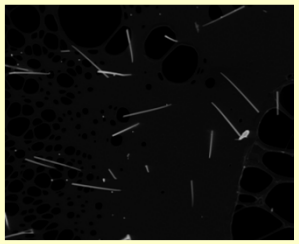
Cross section preparation
Sandwich technic

*Focus Ion Beam (FIB)
(parallel slice but
PB of beam damage, low voltage needed)

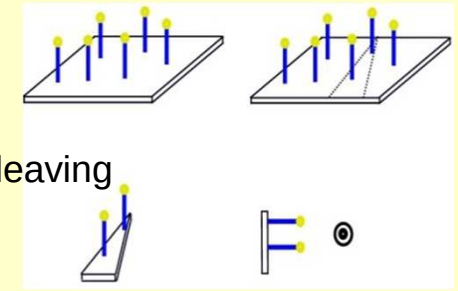


❖ Nanowires :

* Dispersion on a carbon coated grid
(mechanical or solvant + ultrasonic bath)



*Wedge cleavage



*FIB or ultramicrotomy for large wires

Part II

Nitrides Investigation

In other words :

- ✓ Symmetry : hexagonal or cubic
- ✓ Polarity
- ✓ Defects (density, nature, position, orientation)
- ✓ Interfaces : with the substrate, in heterostructures
- ✓ Strain measurement
- ✓ Composition : in ternary or quaternary systems, interdiffusion,…

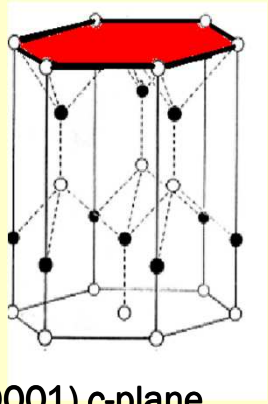
1) Structure of nitrides

- **Wurzite structure** : hexagonal $P6_3/mmc$ ABABAB stacking

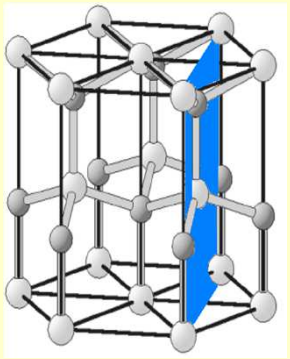
Ga (Al, In) (1/3, 2/3,1/4)

N (1/3, 2/3, 1/4+ u)

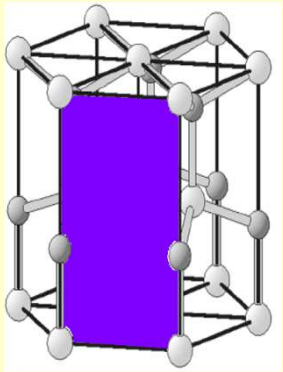
a=0.3189nm ; c=0.5185nm



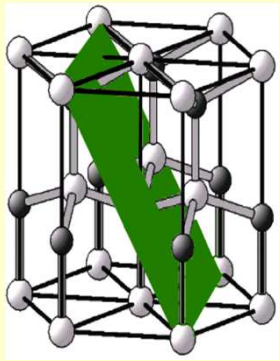
(0001) c-plane



(11$\underline{2}$0) *a*-plane



(1$\underline{1}$00) *m*-plane



(11$\underline{2}$2) plane

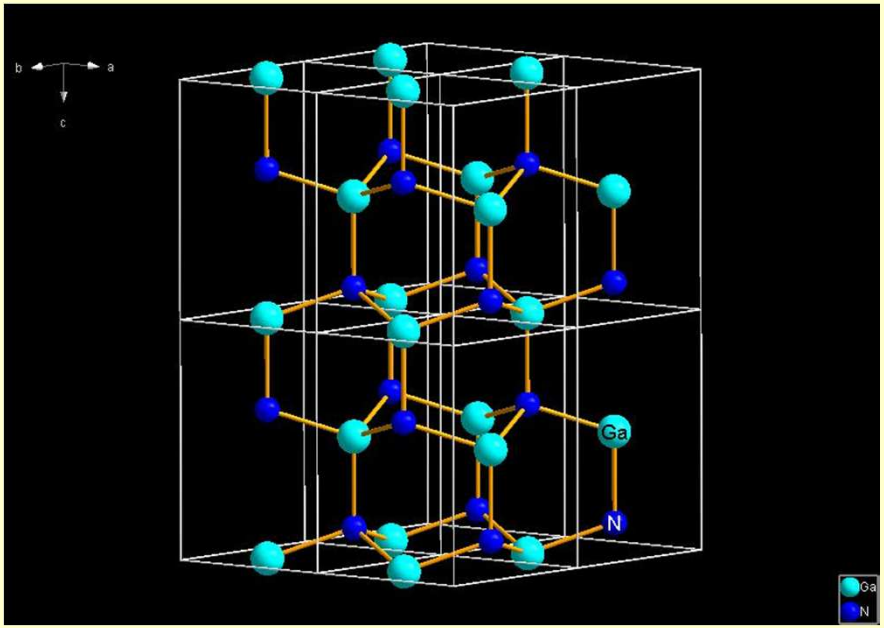
- **Zinc blende structure**: cubic F-43m ABCABCABC stacking

Ga (Al, In) (0,0,0)

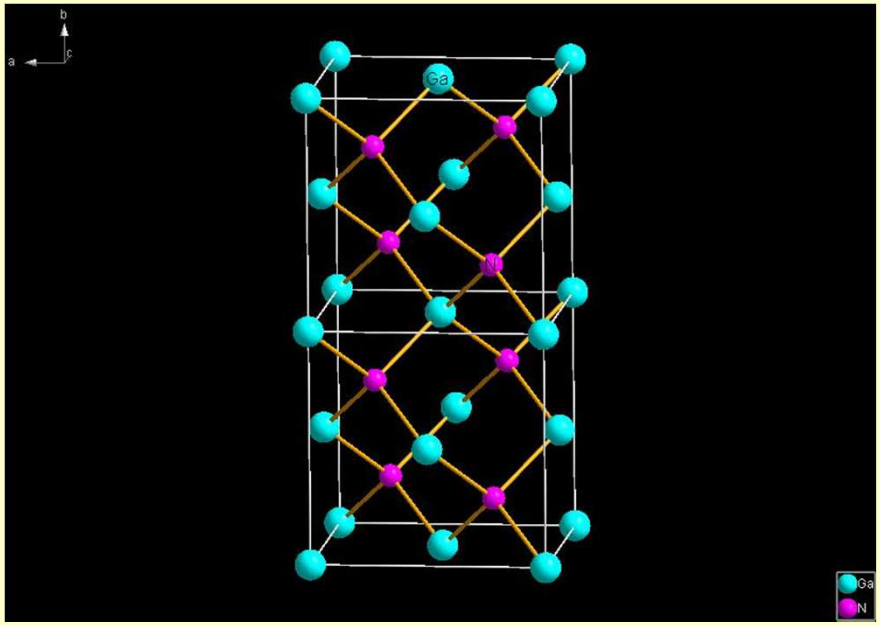
N (1/41/4, 1/4)

a=0.450nm

GaN wurzite

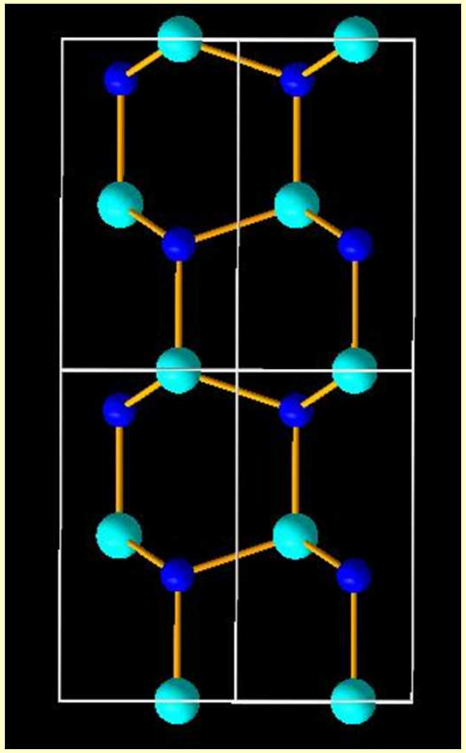


GaN zinc blende



Ga and N are both tetra-coordinated

[11-20] projection

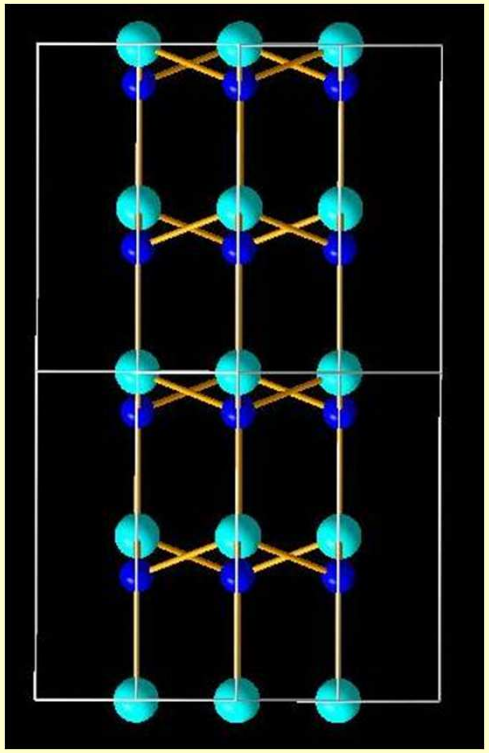


β N

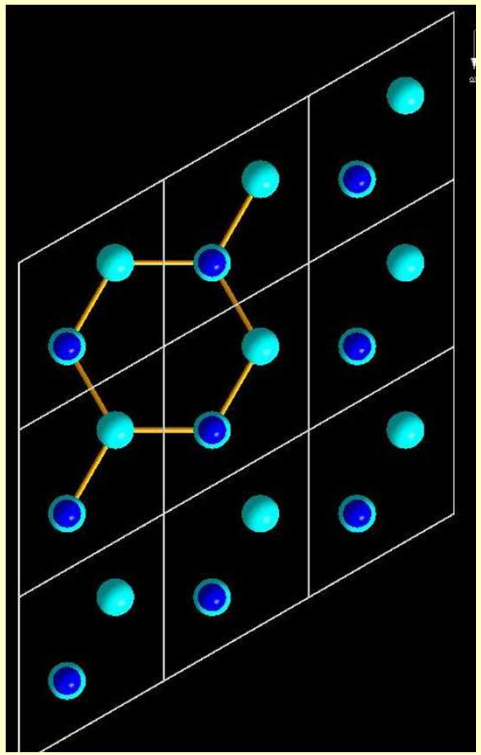
B Ga
α N

A Ga

[10-10] projection

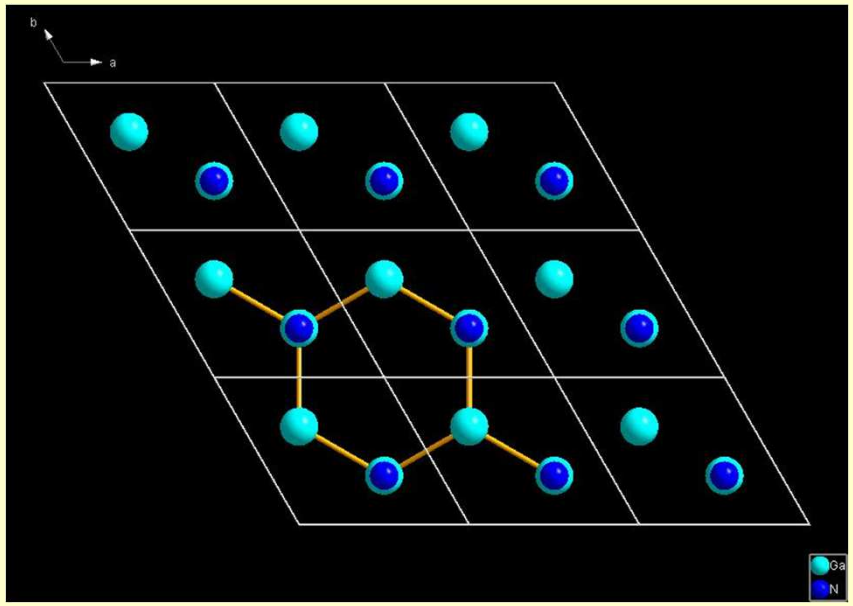


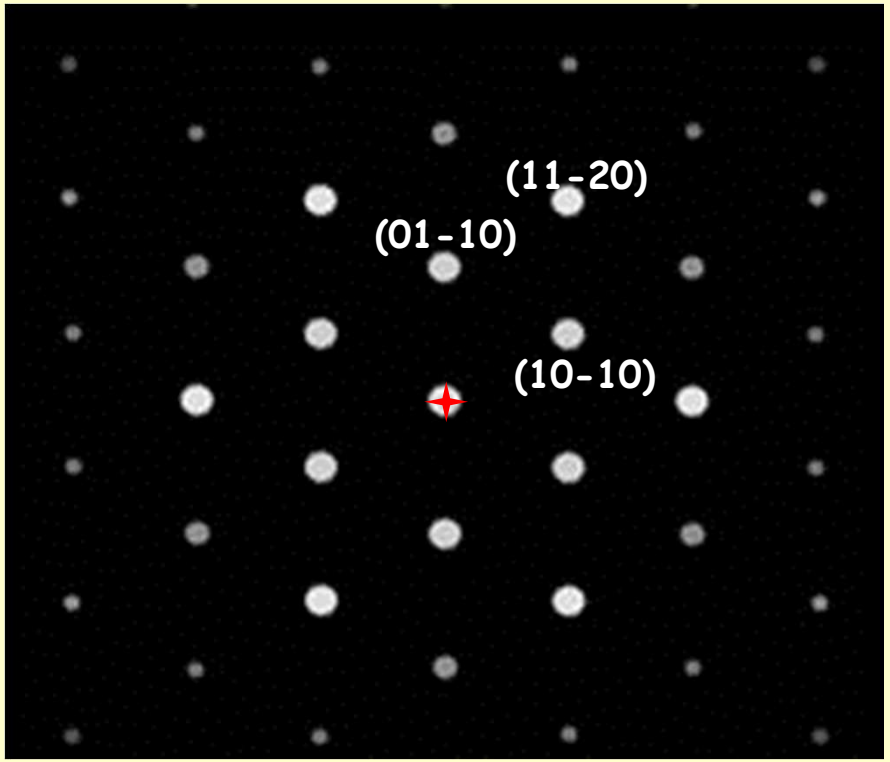
[0001] projection



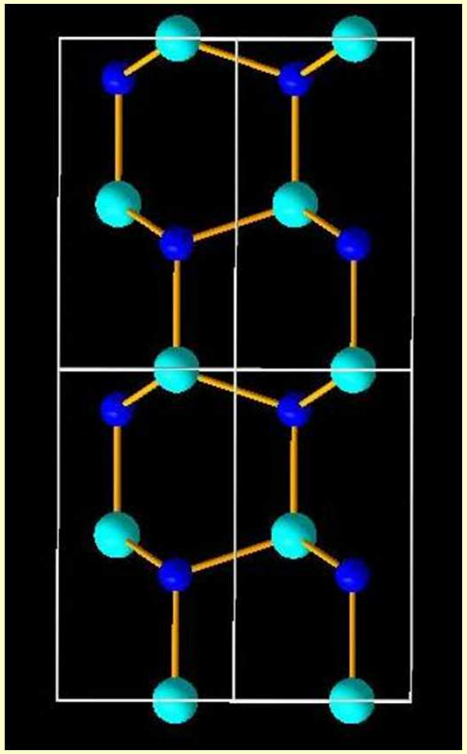
3 main projections of the wurzite structure

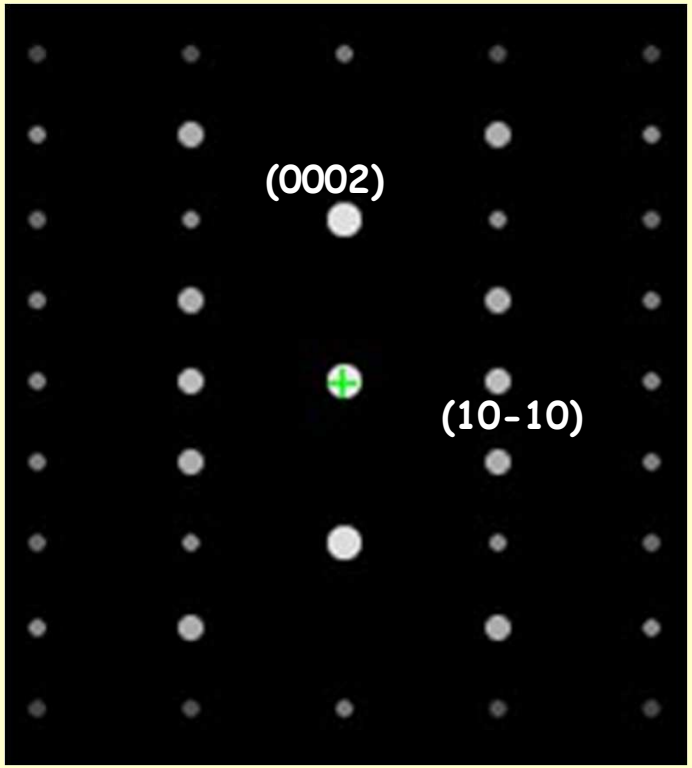
2) Diffraction patterns: symmetry and orientation



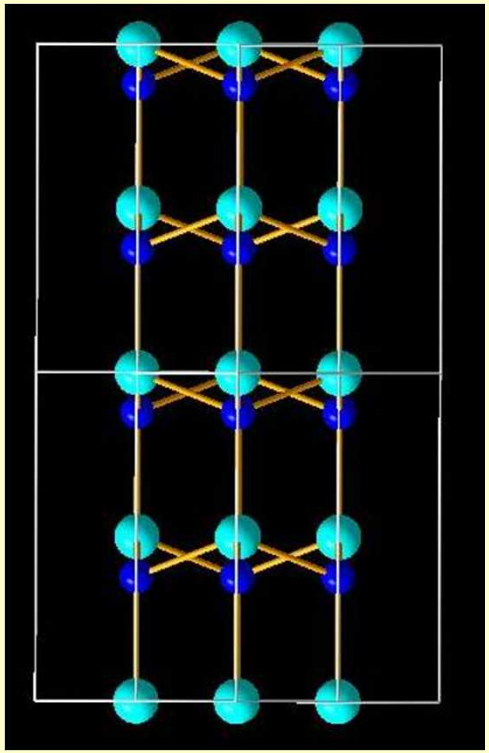


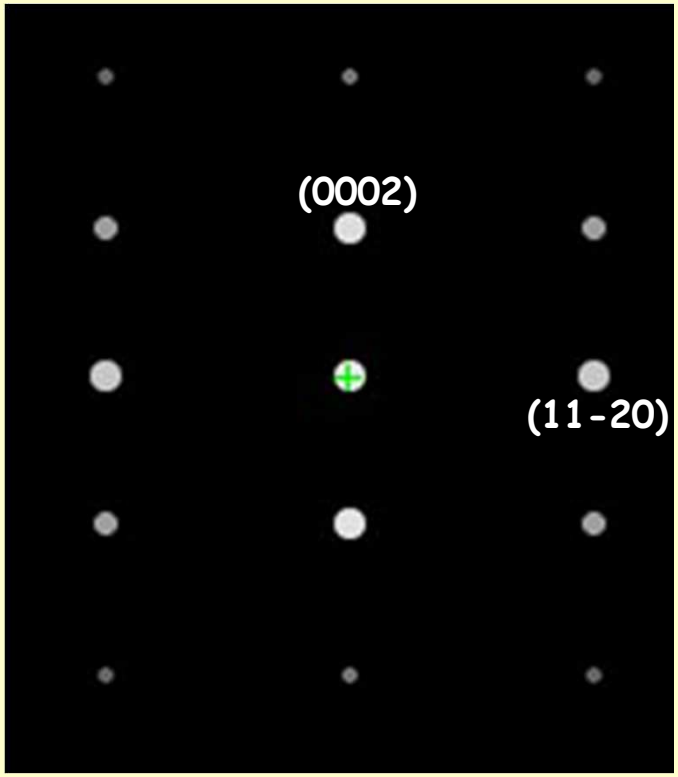
[0001] zone axis



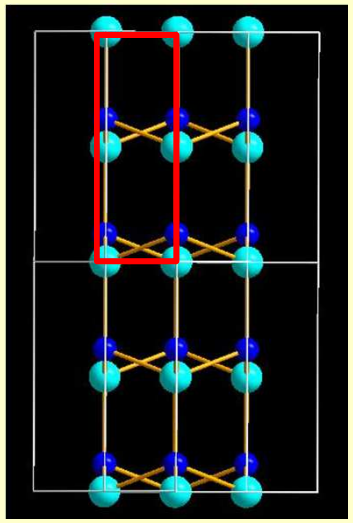


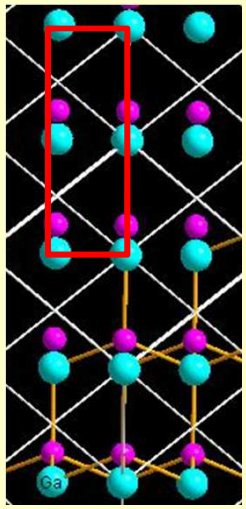
[11-20] zone axis





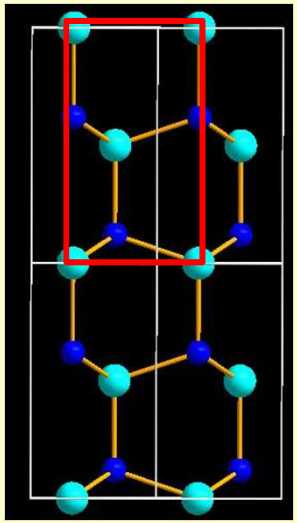
[10-10] zone axis

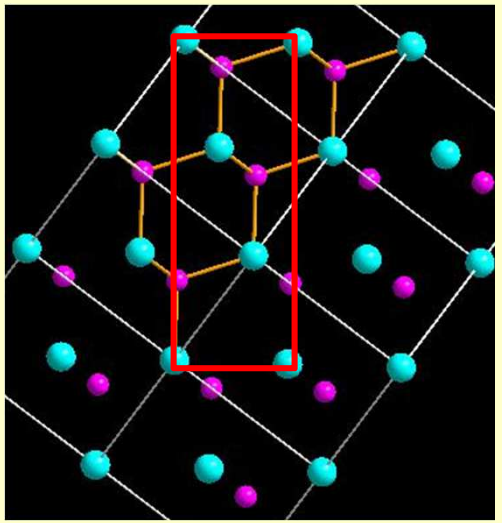




hexagonal [10-10] cubic [11-2]

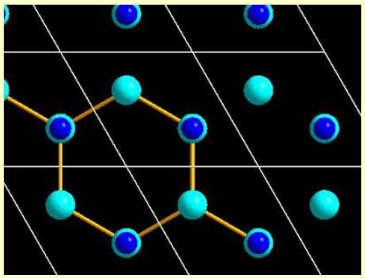
IDENTICAL

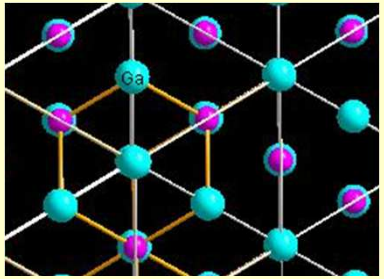




hexagonal [11-20] cubic [1-10]

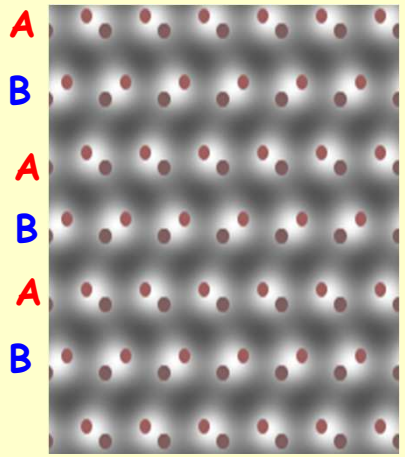
DIFFERENT

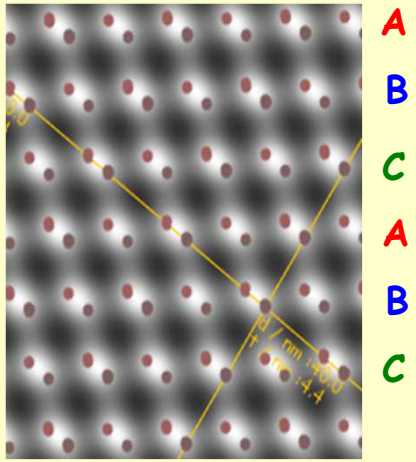




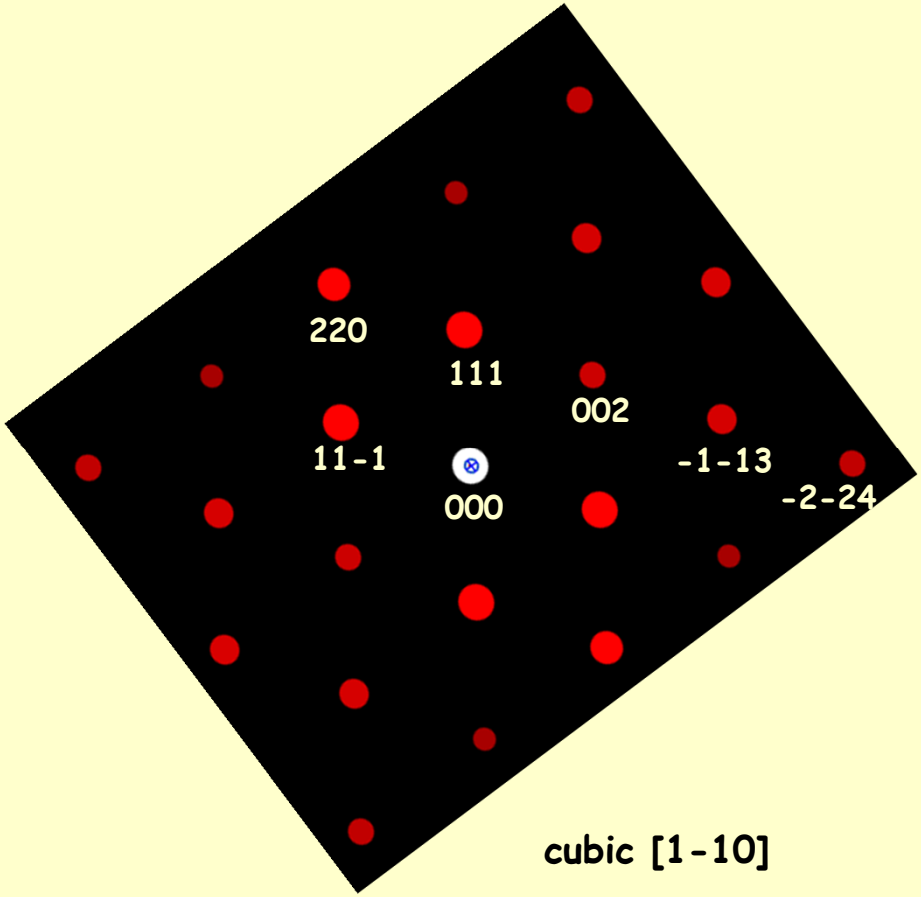
hexagonal [0001] cubic [111]

DIFFERENT

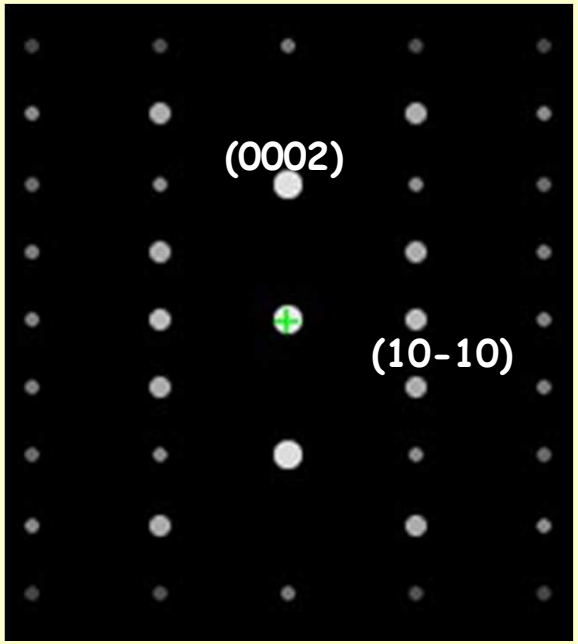




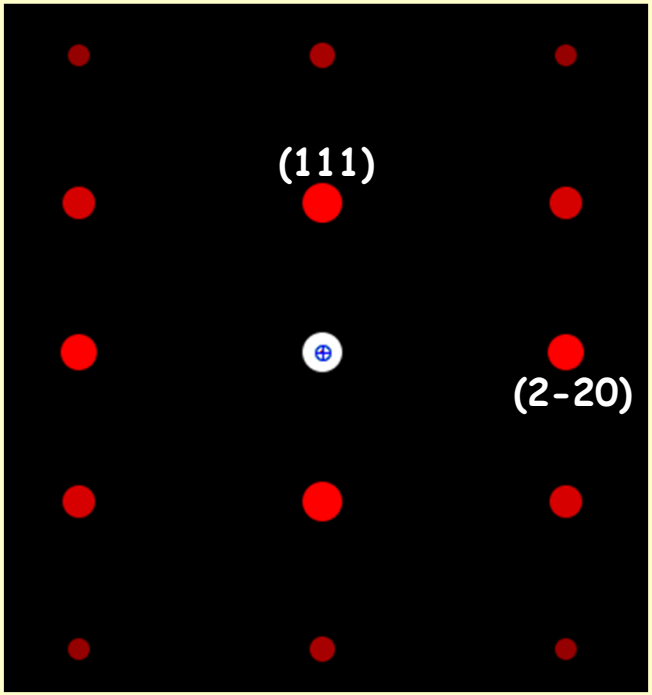
Diffraction patterns



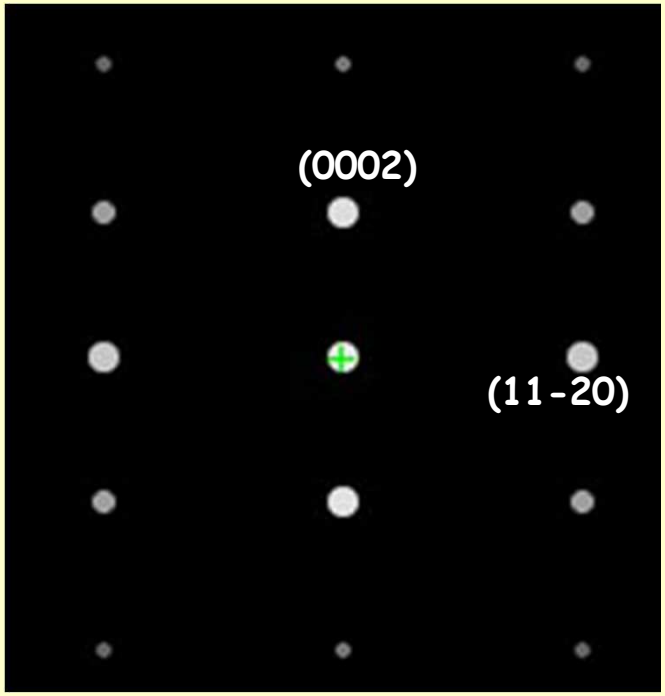
cubic [1-10]



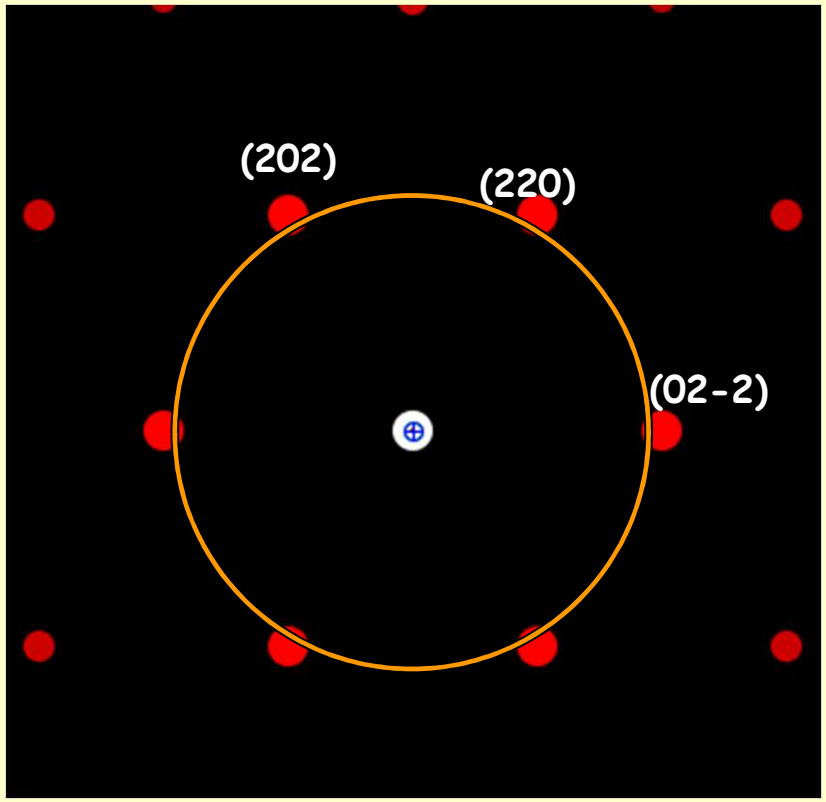
hexagonal [11-20]



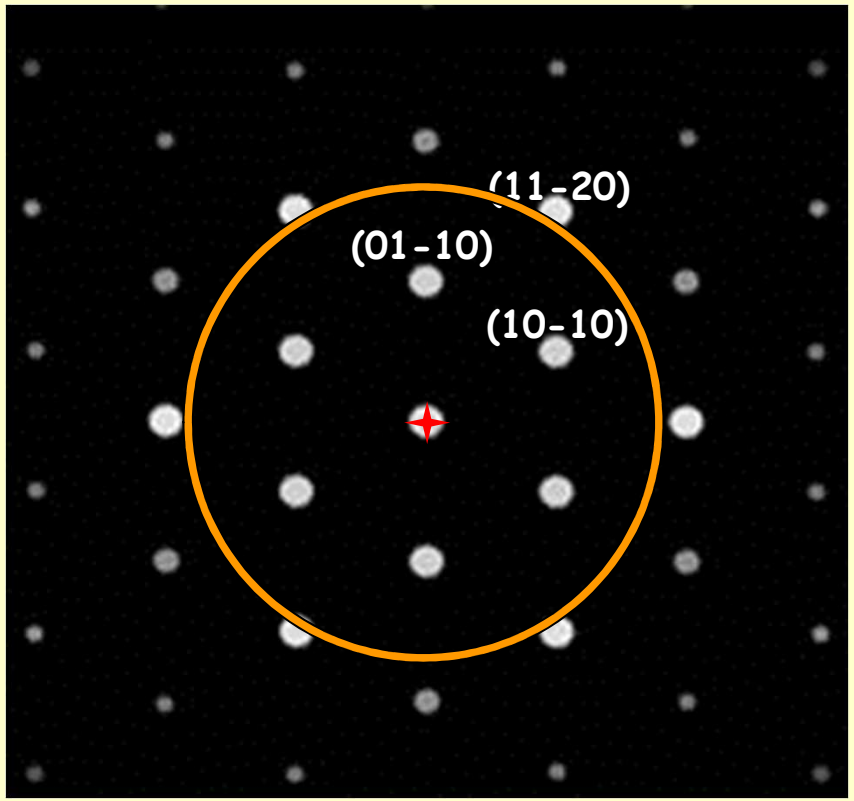
cubic [11-2]



hexagonal [10-10]



cubic [111]

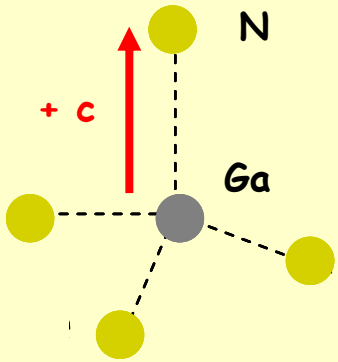


hexagonal [0001]

3) Polarity

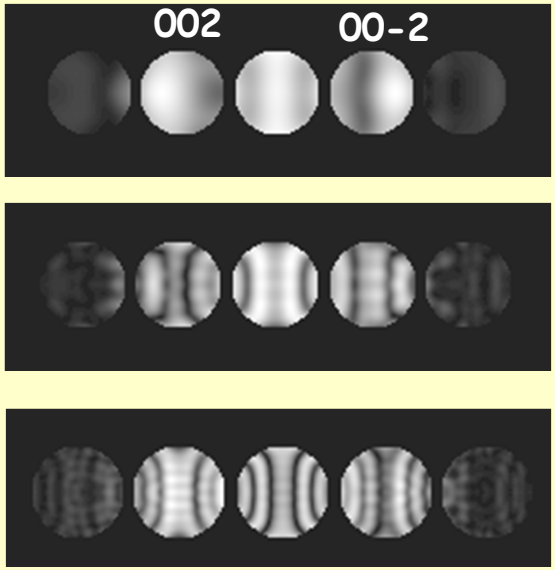
non – centrosymmetrical cell

+c defined by Ga → N vector



A) Determination from CBED (ex GaN @200kV)

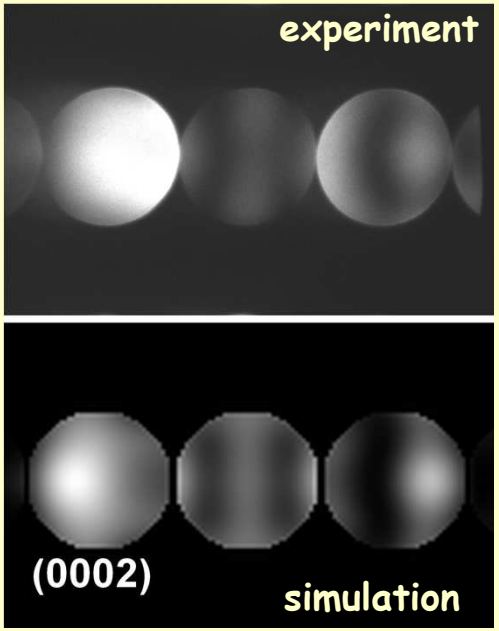
+g and –g disks not symmetric



30nm

90nm

150nm



Simulation fromJEMS software

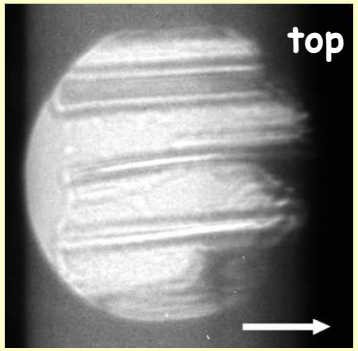
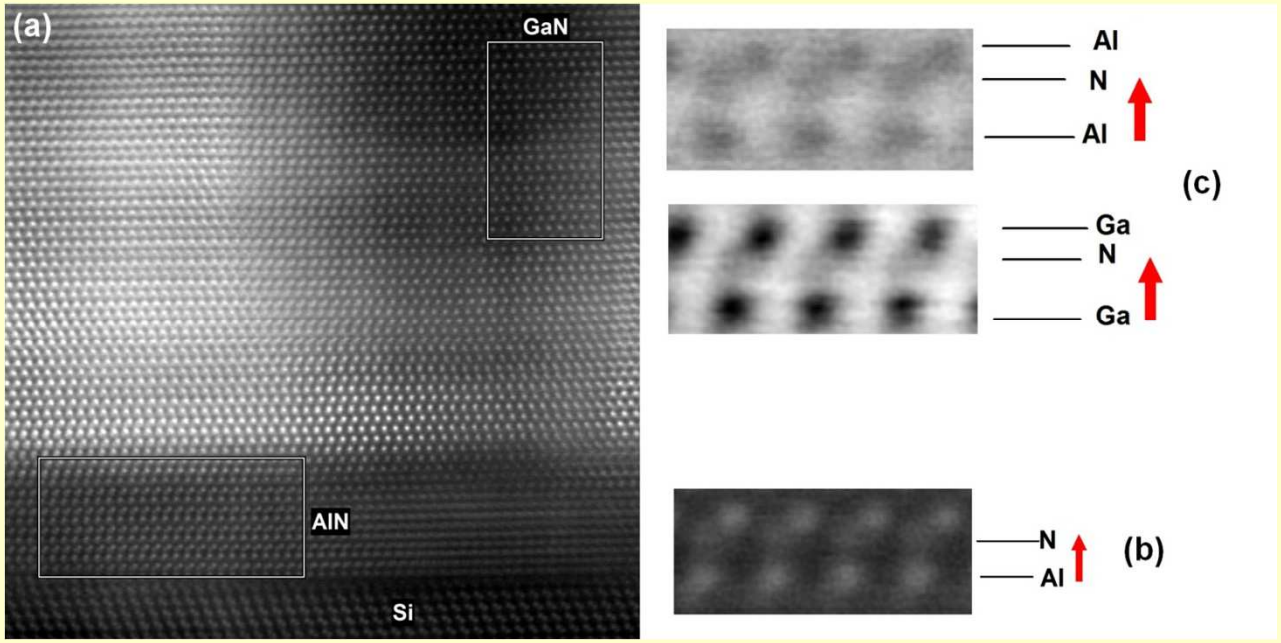


Image of NWs:
growth direction =-c
(N-polar)

Need to calibrate the rotation angle between diffraction and image mode

B) Determination from HR-STEM images : direct imaging of the atoms



Titan Ultimate probe-corrected microscope at @200kV
a) And b) HAADF images
c) ABF detector used
(courtesy JL Rouvière CEA Grenoble)

4) Defects

CM Drum, Phil Mag 11 3/3, p 313 (1965)
Rutérana et al. phys.stat.sol.(b*) 227, No.1, 177–228 (2001)*
Komninou et al. phys. stat. sol. (a) 202, No. 15, 2888–2899 (2005)

Usually studied by a Combination of :

- **CTEM : visualisation, orientation, density,..**
- **and HR-TEM (or HR-STEM) : atomic arrangement (+ chemical information)**

A few examples :

- *** stacking faults**
- *** dislocations**
- *** V defects**
- *** Inversion domains**

A) Stacking faults

Basal stacking faults (BSF) are the most common planar defects in nitrides

Intrinsic: lattice translation

I_1: ABABABCBCBCB

I_2: ABABABCACACA

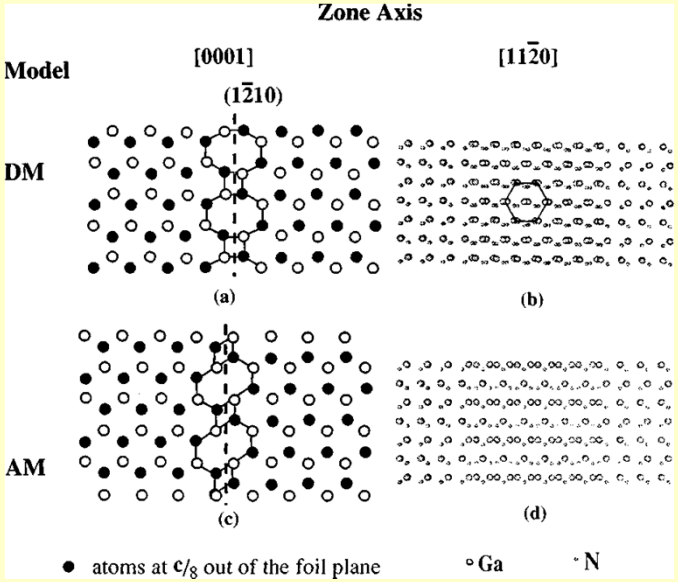
Extrinsic: additional plane

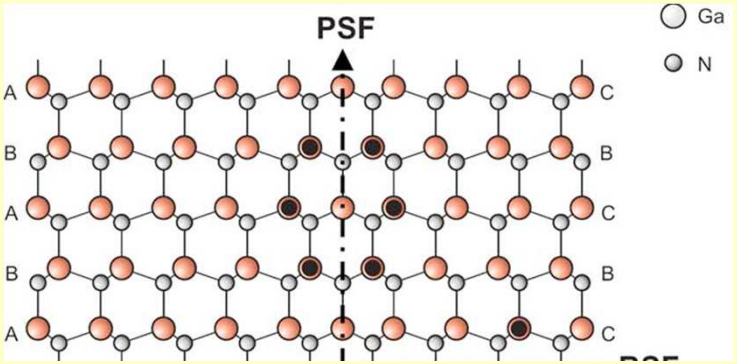
E: ABABACBABAB

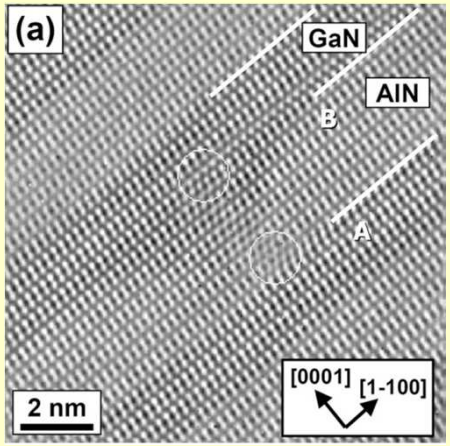
Ξ Cubic sequence in hexagonal lattice

SF

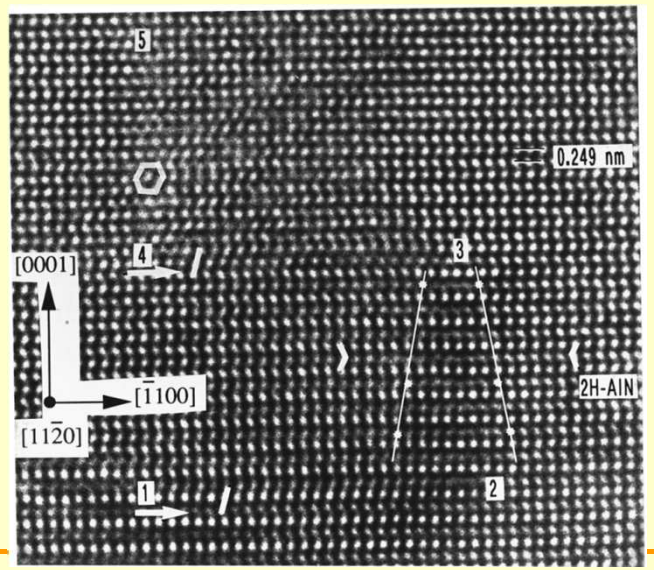
Prismatic SF (may result from islands coalescence)







From P. K. Kandaswamy JAP 106, 013526 2009



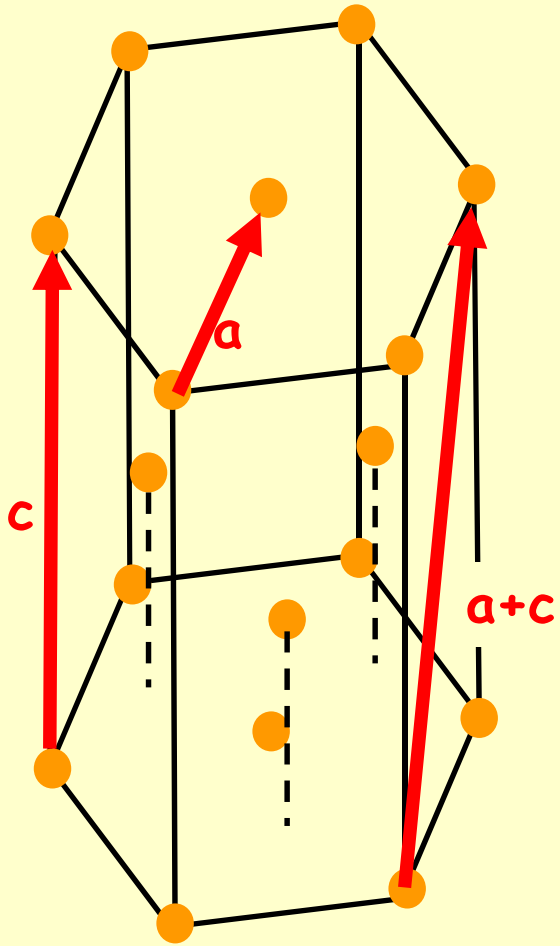
High resolution image showing
the simultaneous occurrence of the two models (2)/(3): AM prismatic stacking (Amelinckx)
(4)/(5):DM prismatic stacking fault (Drum)
(from P. Vermaut, et al APL. 74, 694 (1999))

B) Dislocations

Edge a type b = 1/3<11-20>

Screw c type b = <0001>

Mixed a+c type b = 1/3<11-23>

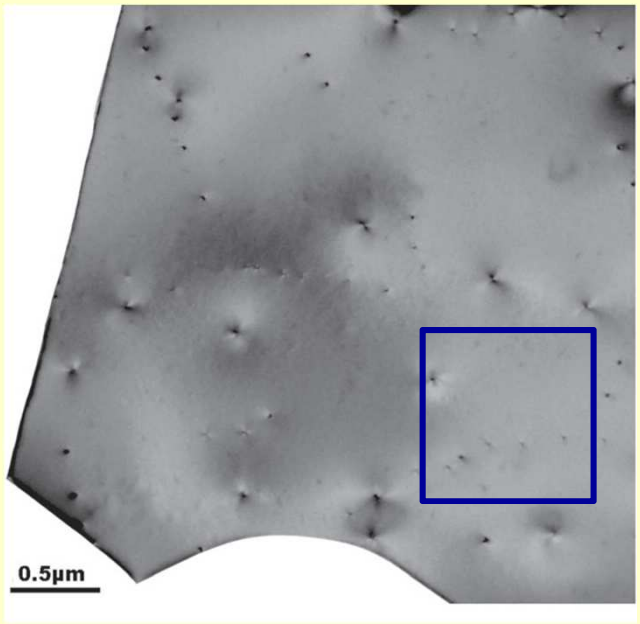


g/b	a	c	a+c
{11-20}	visible	No contrast	visible
{0002}	No contraste	visible	visible

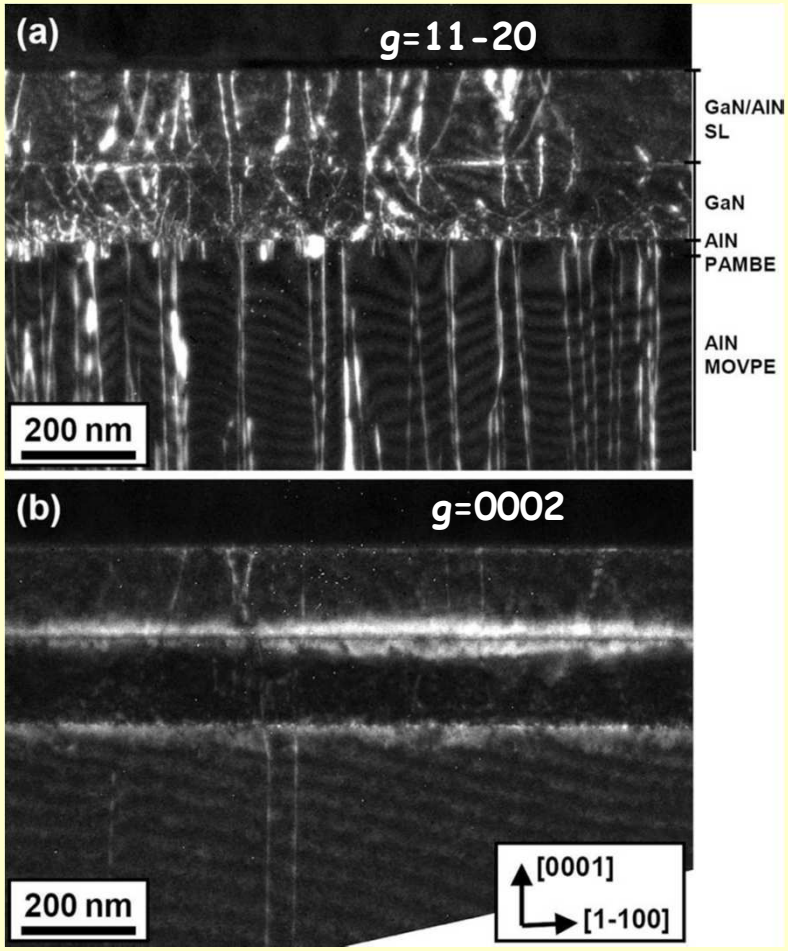
Threading dislocations : propagate from the interface to the sample surface

Low magnification : weak beam : identification (a,c,a+c)

Dislocation density (threading dislocations)
Low magnification plane view
BF 2 beams with g = (11-20)
(from Vennegues et al. Semicond. Sci. Technol. 28 (2013) 035006)

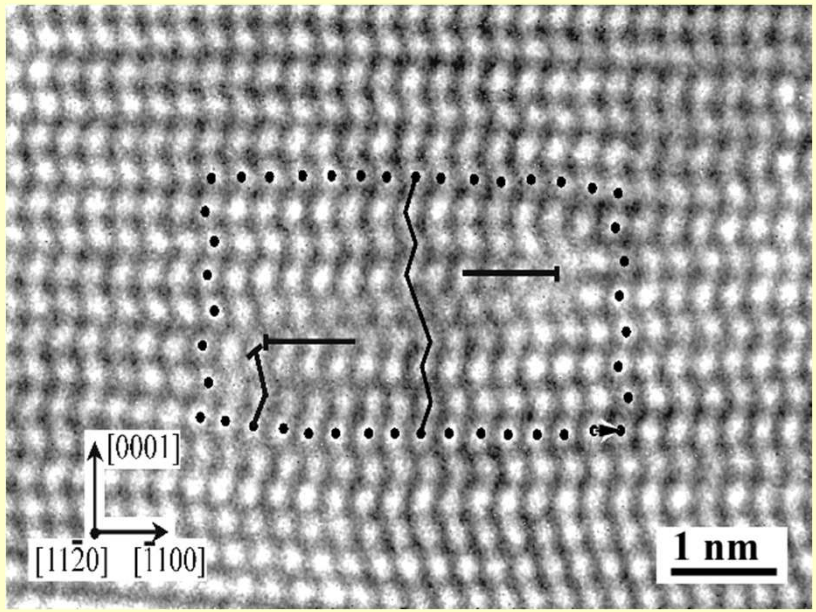


10^8 dislocation.cm^{-2} = 1 dislocation.µm^{-2}.



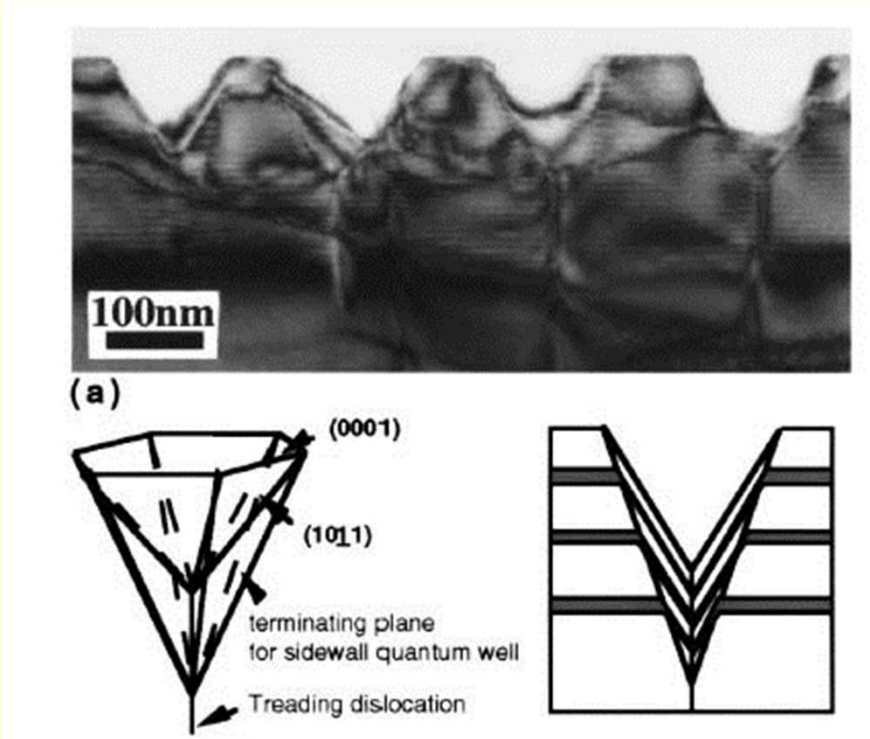
*From Kandaswamy et al. J. Appl. Phys. **106**, 013526 (2009)*

Dislocation from HR-TEM : Burger circuit



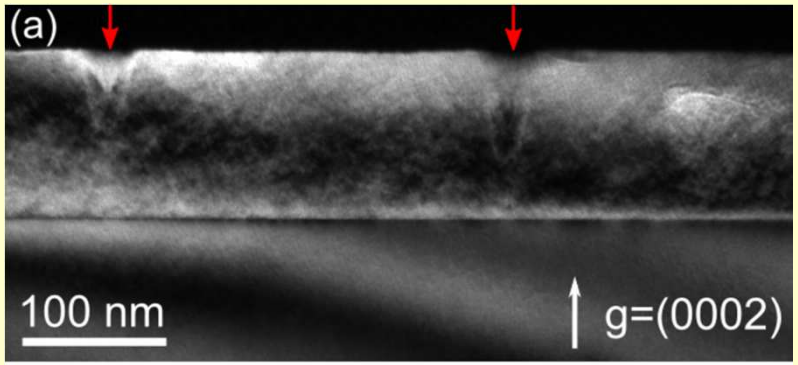
I1 stacking fault, closure failure, 1/3 [10110]
(*from Ruterana et al. phys.stat.sol.(b) 227, No.1, 177–228 (2001)*)

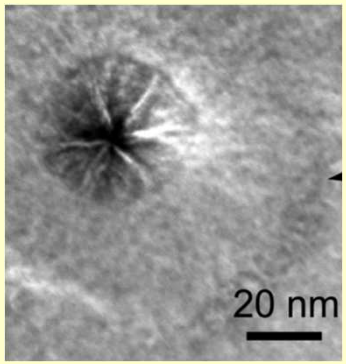
C) V-defects



From X.H. Wu et al, APL. 72 (1998) 692.

V-defects are inverted pyramids with {10-11} facets. There are located close to the surface, often above threading dislocations



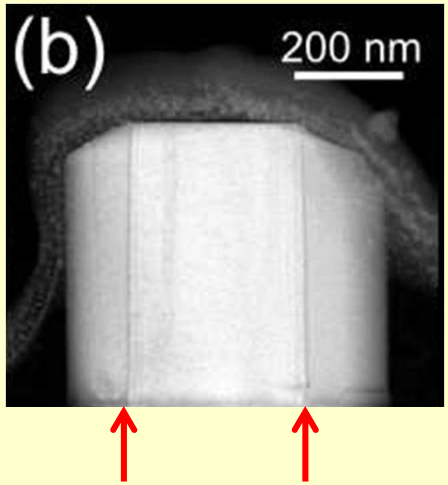


V defects in InAlN layer
Cross section DF image and Plane view

From G. Perillat et al, APL. 113, 063506 (2013)

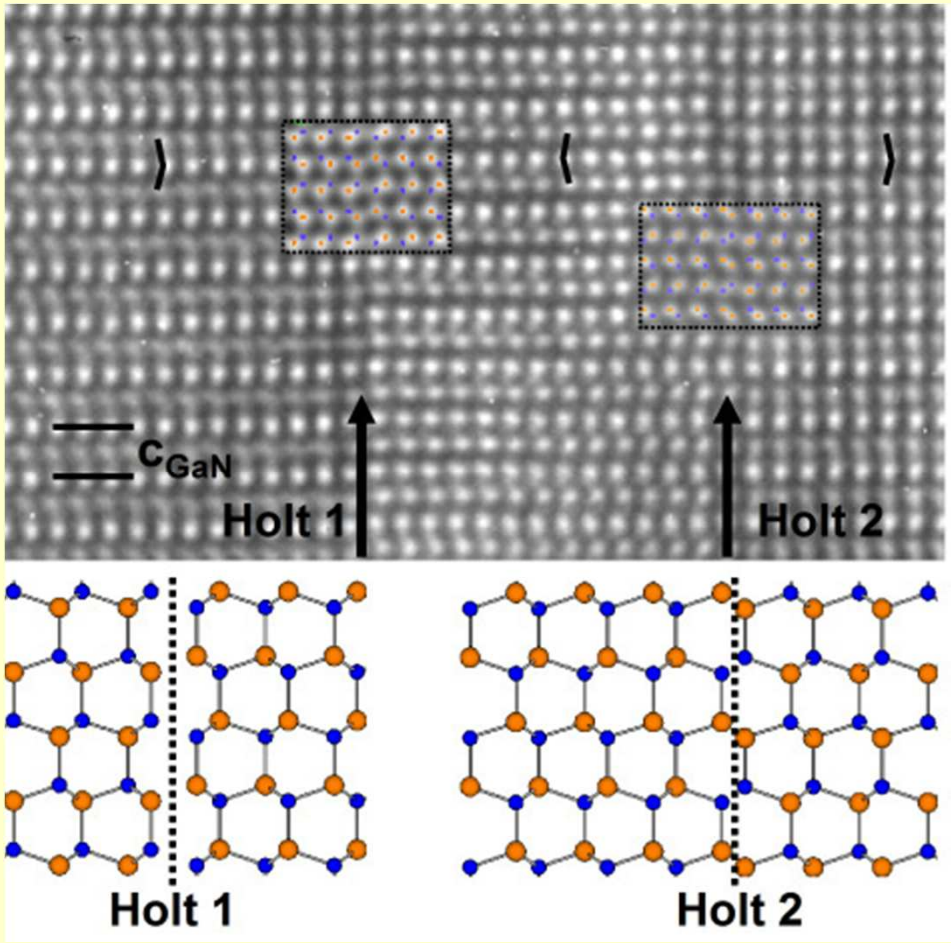
D) Inversion domains

DF low magnification: visualisation



From G. Perillat Thesis
Université Grenoble

HR-TEM : identification of the ID type



From Sarigiannidou et al. Semicond. Sci. Technol. ***21*** *(2006) 612-618*

5) Interfaces (with the substrate or in heterostructures)

→ orientation

→ Strain relaxation

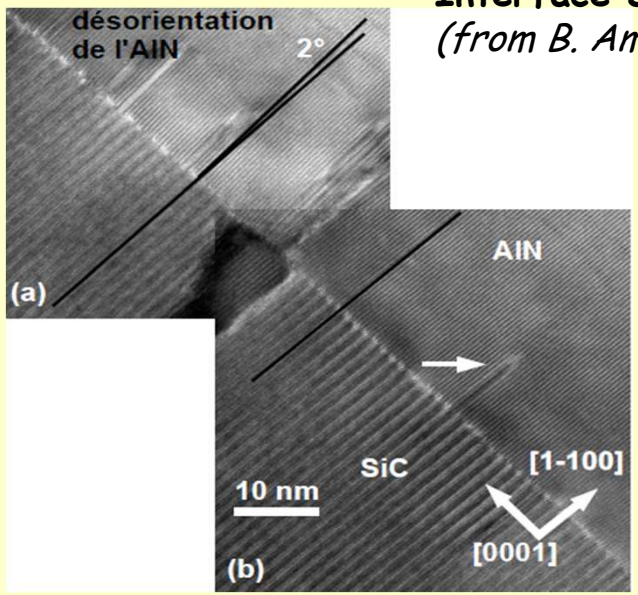
A)Elastic relaxation (Strain analysis)

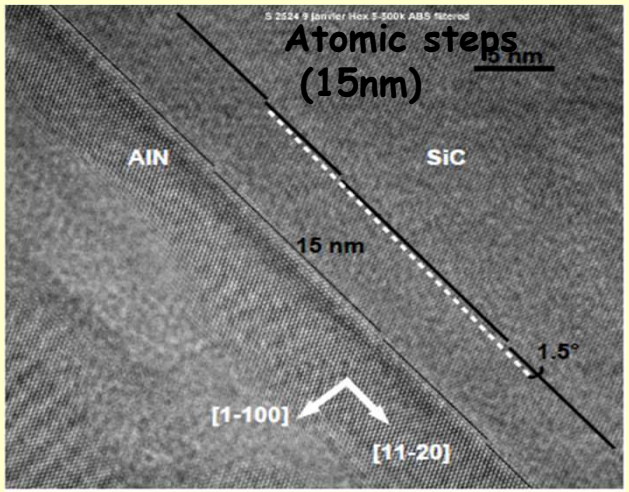
B)Plastic relaxation (Misfit dislocations, cracks,…)

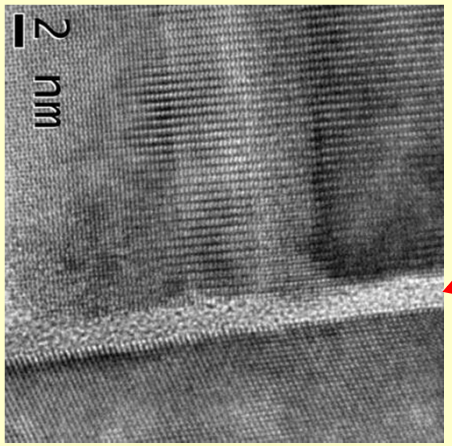
→ abruptness

A) orientation

Interface SiC/m-plane AlN
(from B. Amstatt Thesis Université Grenoble)







Amorphous layer at the Si_GaN NW interface

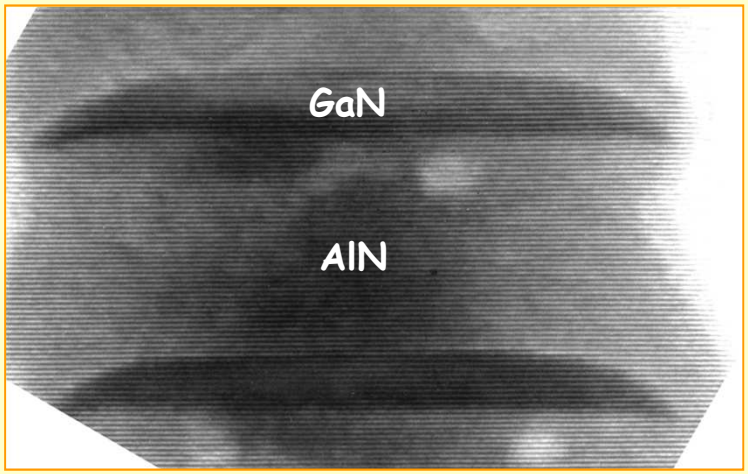
B) Strain relaxation

a) Elastic relaxation

Strain Analysis by the Geometrical Phase Analysis Method GPA (analysis in the Fourier space from a HR-TEM image)

*M. J. Hytch, E. Snoeck, and R. Kilaas, Ultramicroscopy **74**, 131 1998*

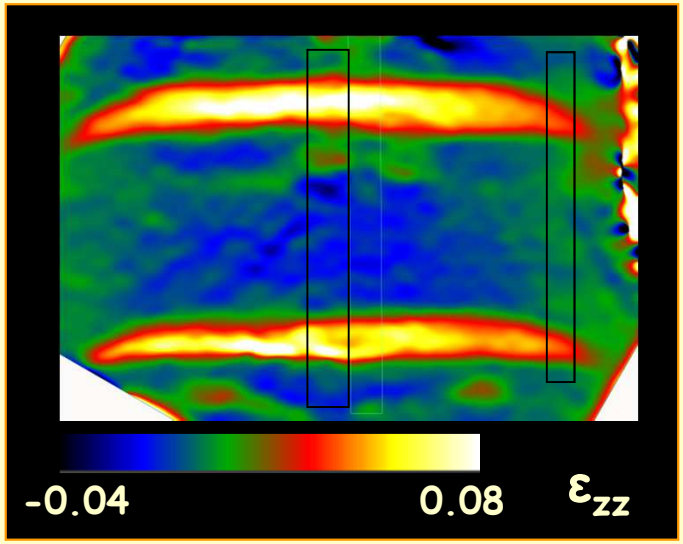
GaN/AlN in a nanowire : HREM image tilted (10°) from [11-20] zone axis



(from Bougerol et al. Nanotechnology20, 295706, (2009))

Variation of c_{002} → $\varepsilon_{zz} = (c - c_{ref})/c_{ref}$

Relative deformation map

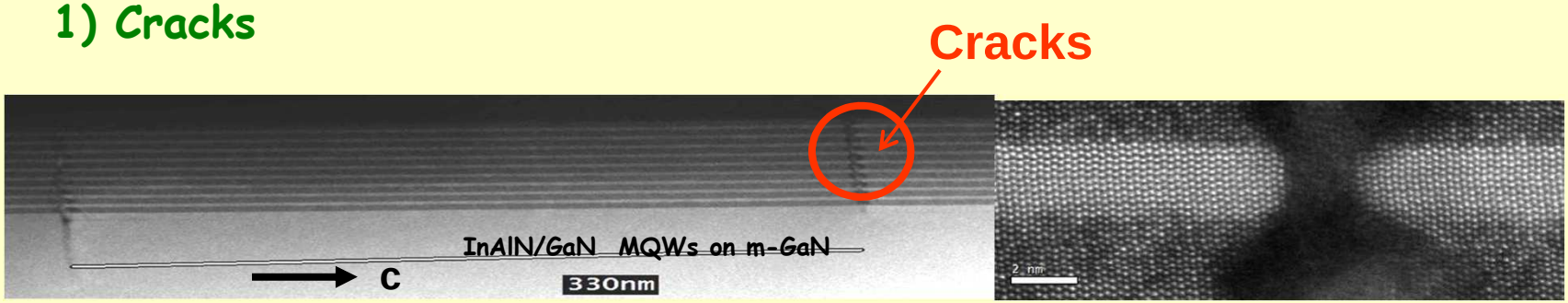


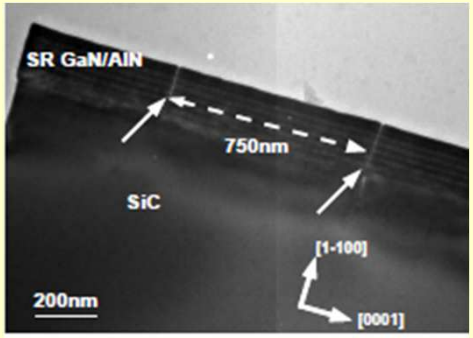
$C_{ref} = C_{AlNbulk}$

Image = projection
Lattice parameters maps: depends on strain AND composition

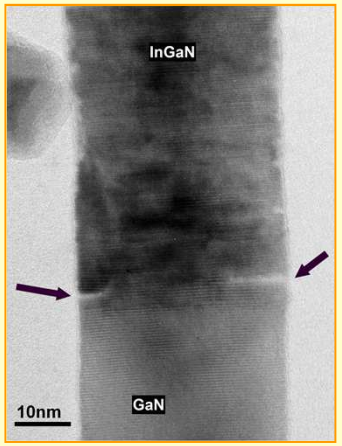
b) Plastic relaxation

1) Cracks



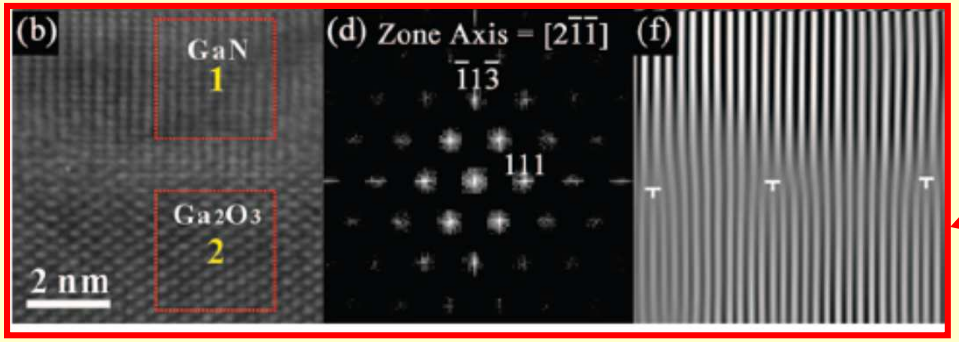


GaN/AlN m-plane growth on SiC



GaN/InGaN Nanowires with high In content *(from G. Tourbot et al. Nanotechnology, 22, 75601 (2011))*

2) Misfit dislocations (additional lattice plane on one side of the interface)

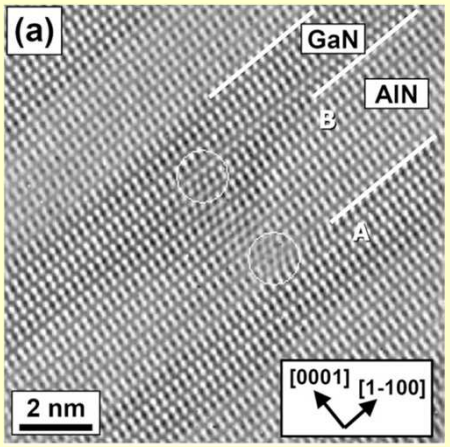


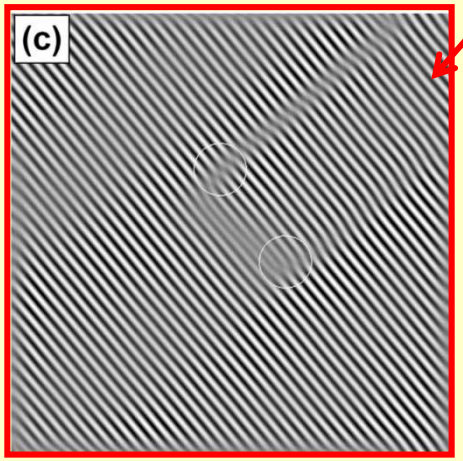
Regular array of dislocations observed by :

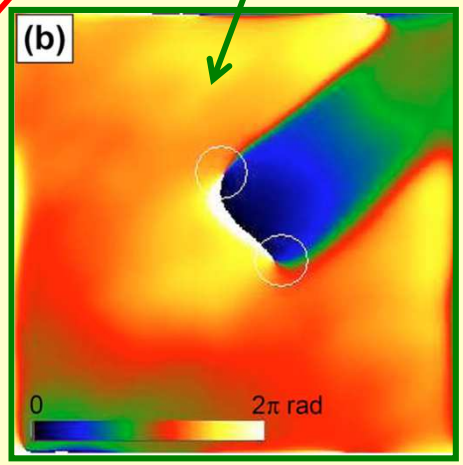
Fourier filtering
(selection of a given g)

or GPA analysis (2Π phase shift)

coaxial Ga_2O_3/GaN nanowires Nanoletters 8(10),3288, 2008







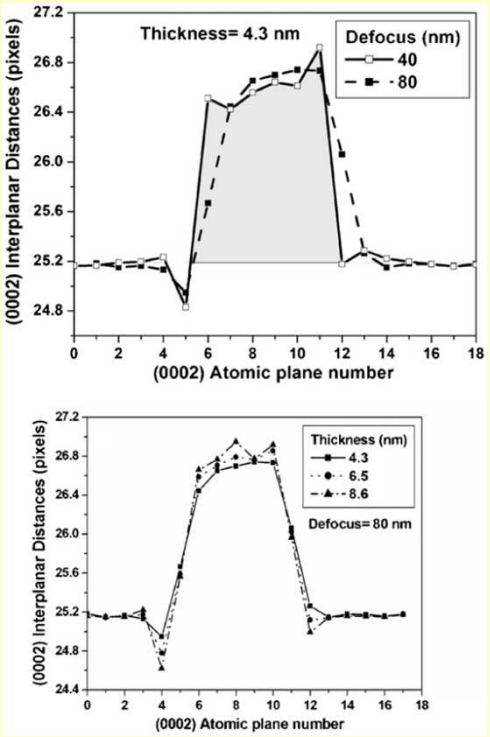
From P. K. Kandaswamy JAP 106, 013526 (2009)

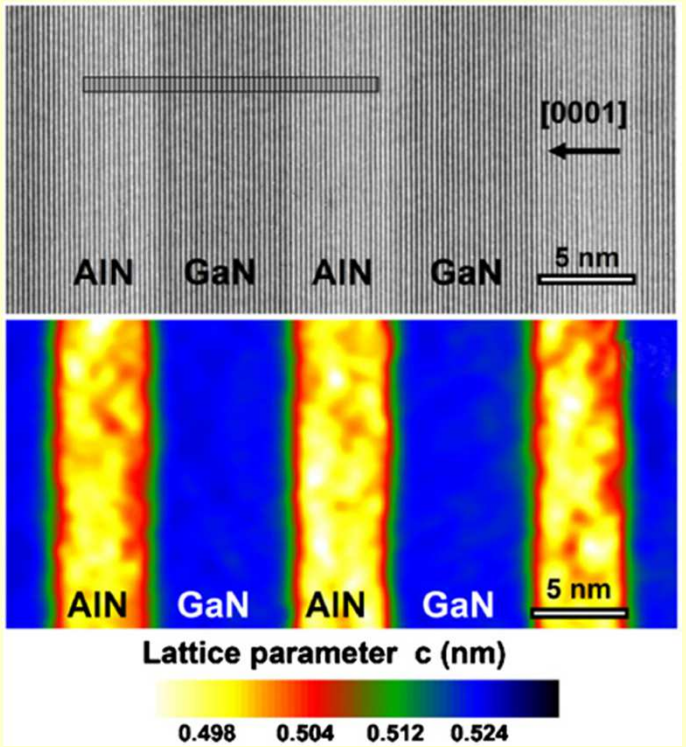
Need to have images with well defined planes (otherwise artefacts from FF or GPA)

C) Interface abruptness

Analysis of HR-TEM images : based on the variation of the lattice parameter
* in the direct space lattice fringes profiles
* in the reciprocal space GPA

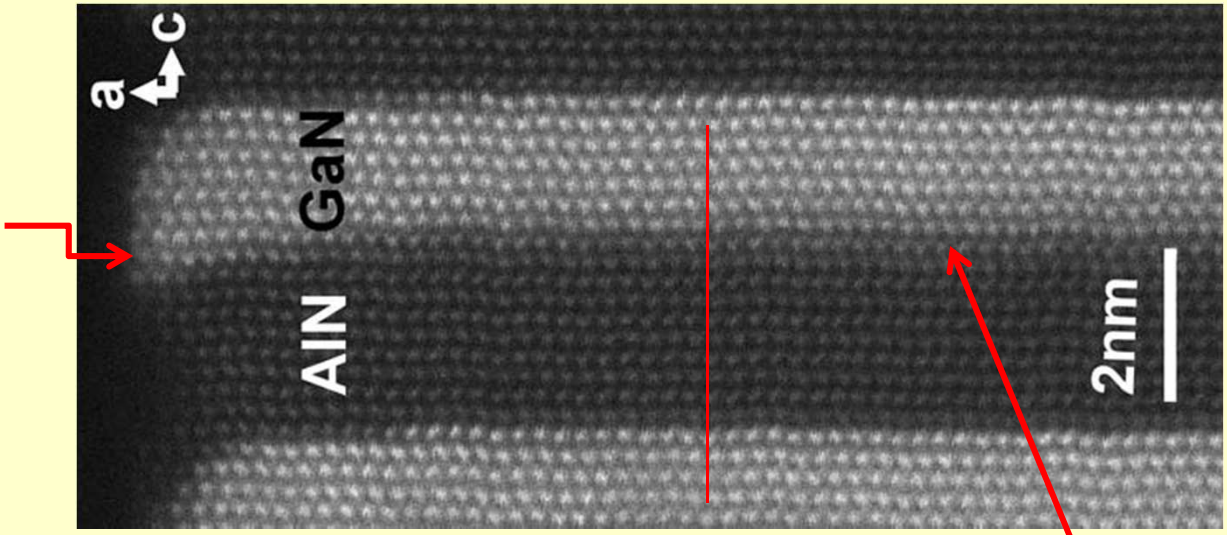
Need to compare with simulations if quantitative analysis needed : interface width affected by experimental conditions (defocus and thickness)

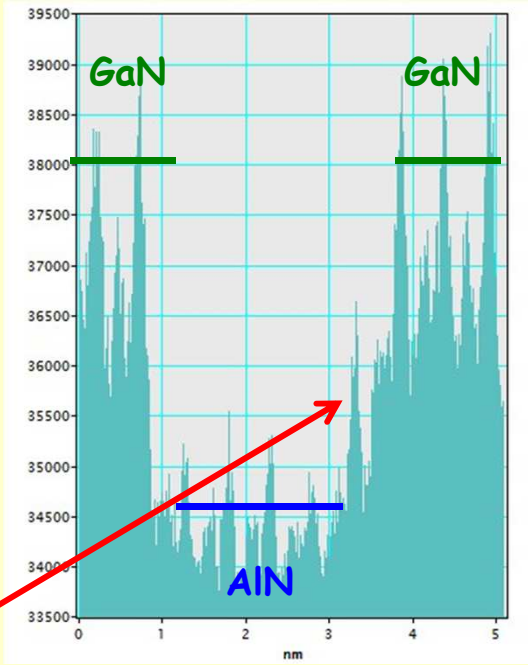




*(from Sarigiannidou et al, Semicond. Sci. Technol. **21** (2006) 612-618)*

Analysis of HR-STEM images : variation of the lattice parameter + contrast





No interdiffusion between Al and Ga

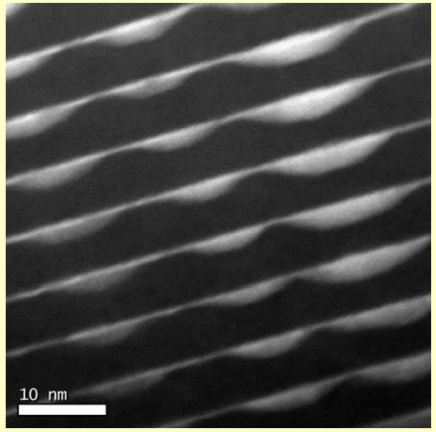
Greyish layer due to projection of GaN from the periphery and not to intermixing

Don't forget the analyzed image is a projection

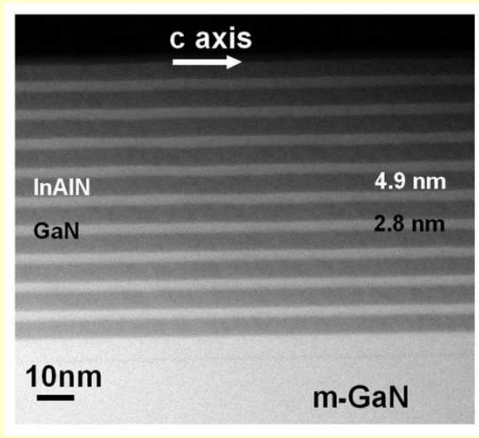
6) Chemical informations

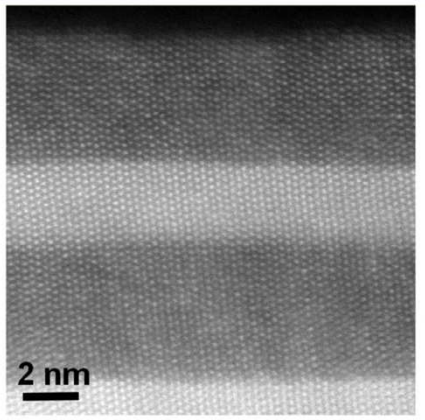
A) HAADF-STEM

Contrast proportionnal to $Z^{1.7}$

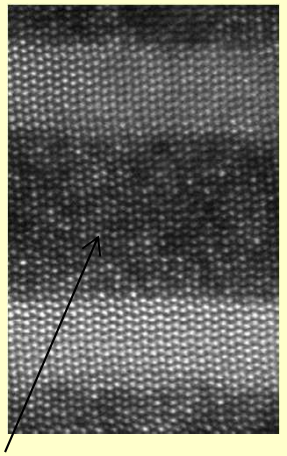


GaN QDs (bright) in AlN (dark)

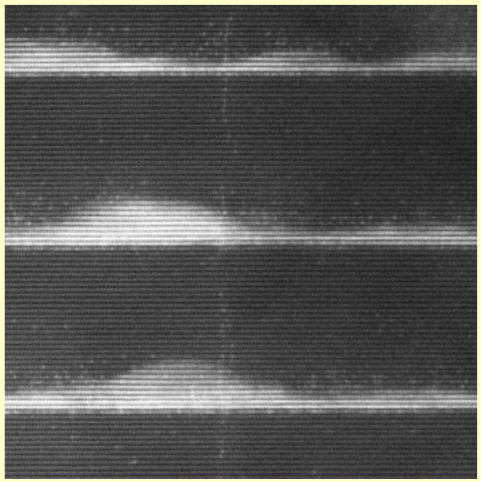




InAlN/GaN MQWs



In (bright) and Al (dark)

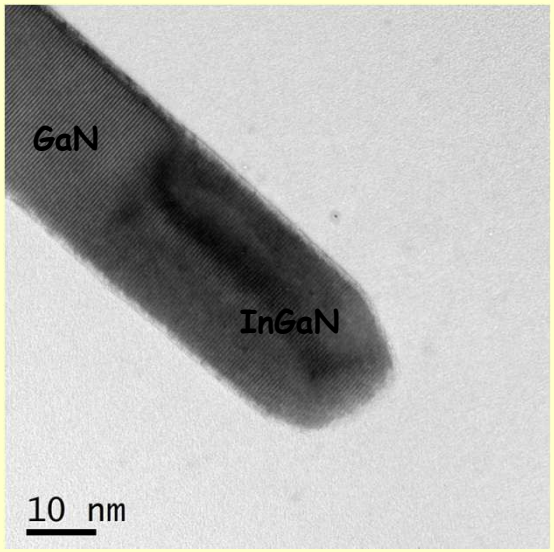


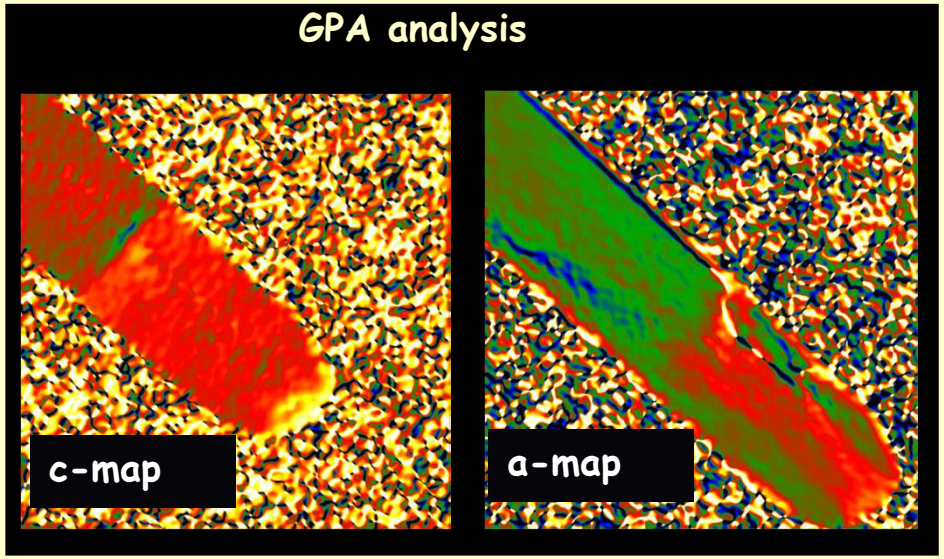
(courtesy PH Jouneau CEA Grenoble)

Tm atoms in AlN barrier above GaN QDs and along a dislocation

Quantitative analysis requires simulations
(no commercial software)

B) From GPA analysis of HR-(S)TEM





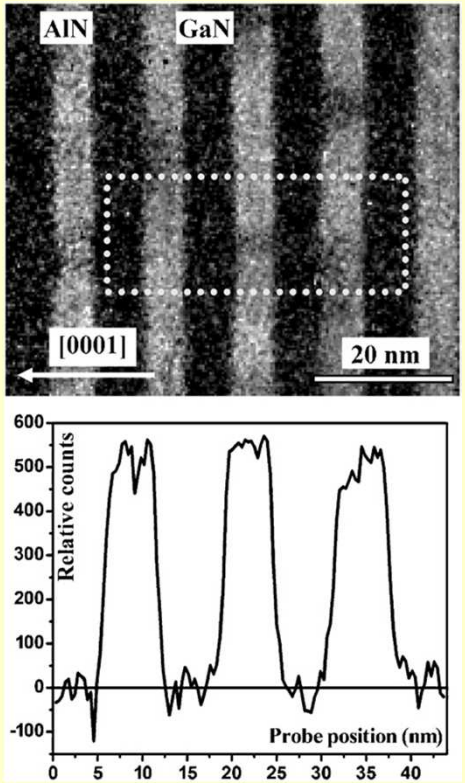
GaN NWs with InGaN thick layer at the top : c and a maps not equivalent

As mentionned before, depends on strain and composition

C) Analytical methods

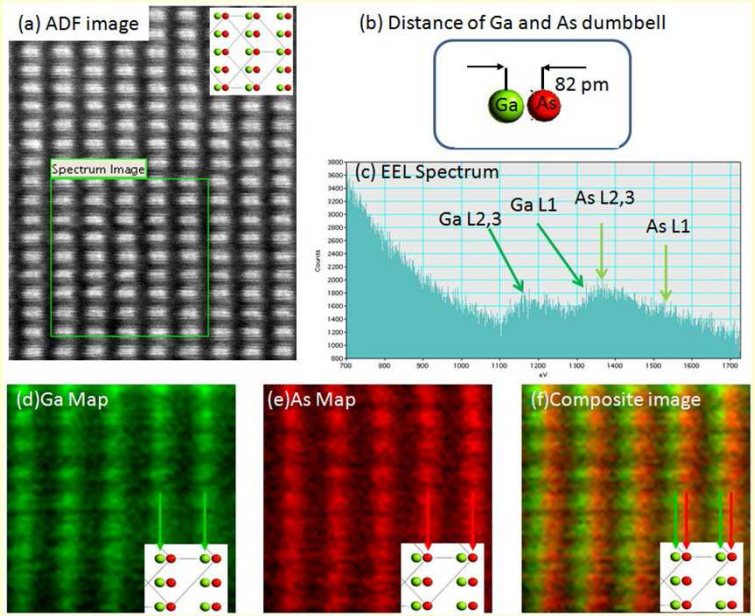
a) EELS and Energy Filtered TEM (EFTEM)

Intensity of inelastic electrons strongly decreases with increasing energy loss
⟶ intensity of electrons with losses >1KeV very small
⟶ need of high intensity of e-beam ⟶ risk of sample damage



*(from Sarigiannidou et al, Semicond. Sci. Technol. **21** (2006) 612-618)*

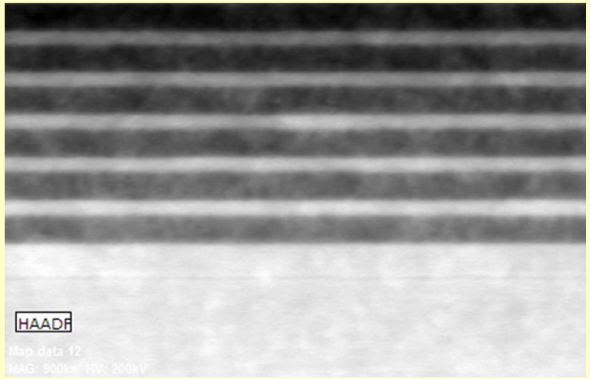
Atomic resolution reported with probe-corrected microscopes



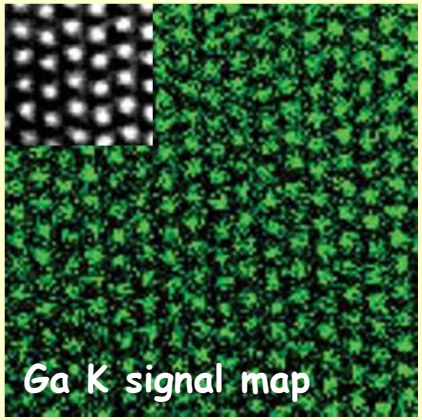
(from Eiji Okunishi et al. (Jeol) et EMC2012 conference)

b) EDX (Energy Dispersive X-ray)

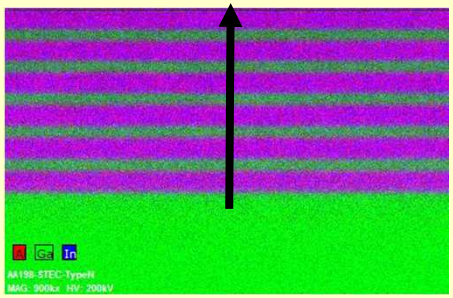
Improvement with new high sensitivity detectors (ex 4 quadrant SSD EDX FEI)

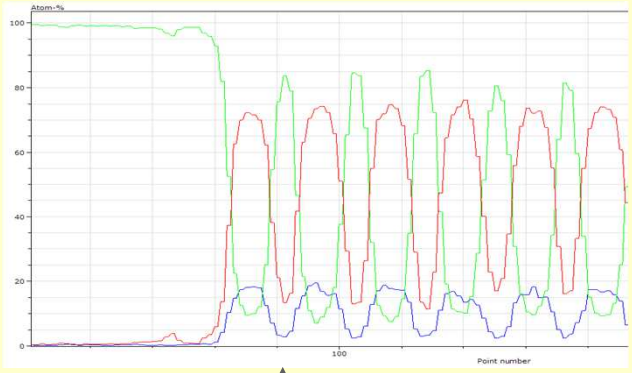


Atomic resolution reported with probe-corrected microscopes



(from Arno Meingast T U Graz)





Spatial resolution depends on the voltage,probe size, sample thickness,(typically less than 1nm on TEM 200kV compared to ~ 5nm in SEM 20kV)

Quantitative analysis requires to use standards

Conclusion

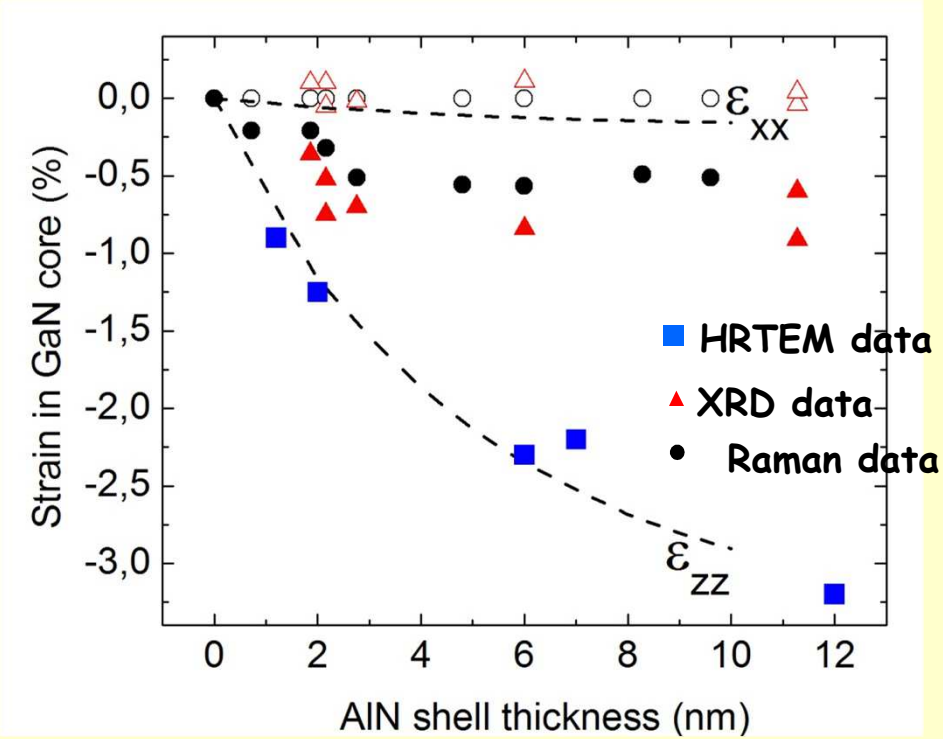
Symmetry, orientation	Diffraction HR-(S)TEM (Haute résolution)
Polarity	CBED HR-STEM with probe corrected microscope
Strain	GPA on HR-(S)TEM if known composition
Defects	CTEM (low mag) : density, orientation,… HR-(S)TEM
Chemical mapping	EDX EFTEM/ STEM-EELS GPA if no or known strain

Don't forget

1)electron microscopy = local scale investigation

Is the analyzed region representative of the whole sample? Unbiased selection?

Need to combine with macroscopic methods such as X-ray diffraction, Raman spectroscopy,…

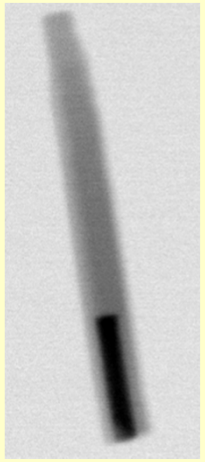


Valence Force Field model to simulate strains in core-shell NWs

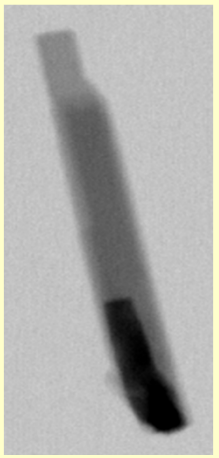
Example from Hestroffer et al.
Nanotechnology 21, 415702 (2010)

Dicrepancy between macroscopic and microscopic data?

Selection of NWs with regular shell = dislocation free



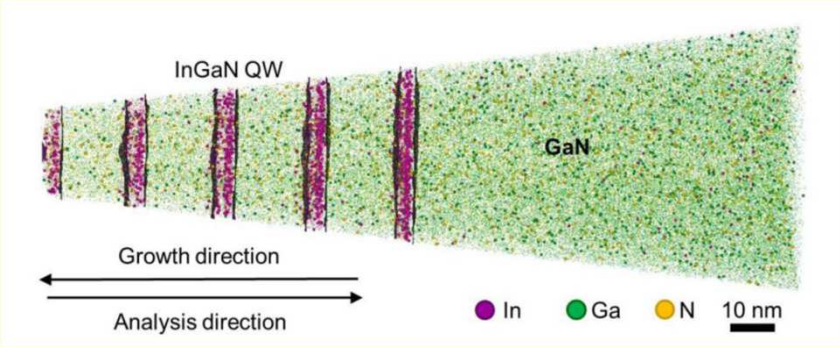
elastic relaxation



plastic relaxation

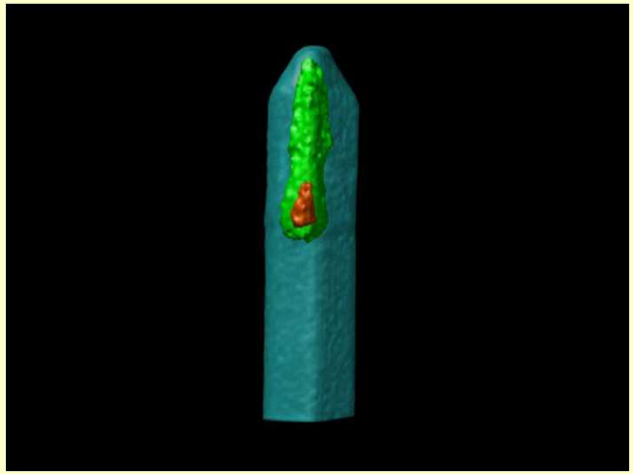
2) electron microscopy = projection method

Need to combine several projections
Or to combine with tomography methods such as **Atom Probe Tomography**



(from A. Rosenauer, Bremen university)

Or Electron tomography



GaN/InGaN NW (G. Tourbot et al. Nanotechnology, 22, 75601 (2011)

A few references

*Transmission Electron Microscopy - Basics by D.B.Williams and C.B.Carter

*High-resolution transmission electron microscopy : the ultimate nanoanalytical technique

J. Thomas, P. Midgley, Chem. Commun., 1253-1267 (2004)

*http://www.matter.org.uk/tem/

*http://temsamprep.in2p3.fr

*On line dictionary of crystallography: http://reference.iucr.org/dictionary/Main_Page

*Quantitative measurement of displacement and strain fields from HREM micrographs (GPA)

MJ Hÿtch, E. Snoeck, R. Kilaas, Ultramicroscopy 74 131-146, (1998)

*Atomic Structure of Extended Defects in Wurzite GaN Epitaxial Layers

P. Ruterana and G. Nouet, Phys. Stat. Sol (b) 1, 177-228, (2001)

Appendix 1 crystallographics indices

(*hkl*) = designates a crystal face or a family of planes throughout a crystal lattice.

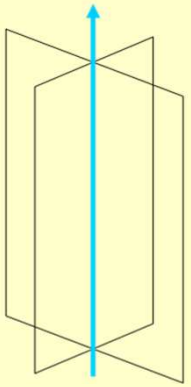
[*hkl*] = designates a direction in the lattice from the origin to a point.

{*hkl*} = designates a set of face planes that are equivalent by the symmetry of the crystal. {100} in the cubic class includes (100), (010), (001), (-100), (0-10) and (00-1).

d_{hkl}-spacing is defined as the distance between adjacent (hkl) planes.

A zone axis is a lattice row parallel to the intersection of two (or more) families of lattices planes. It is denoted by [*u v w*]. A zone axis [*u v w*] is parallel to a family of lattice planes of Miller indices (*hkl*) if:
$uh + vk + wl = 0$
The indices of the zone axis defined by two lattice planes (h_1, k_1, l_1), (h_2, k_2, l_2) are given by:

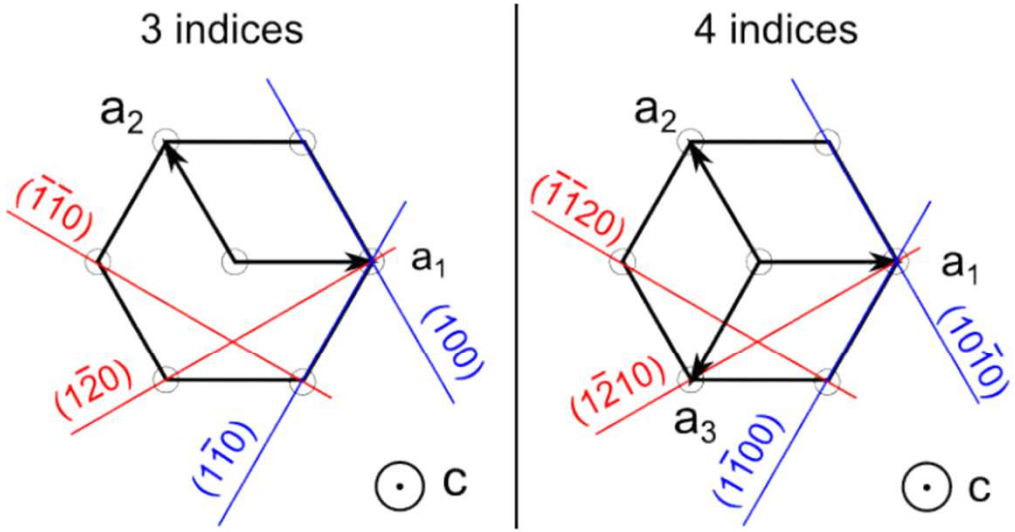
$$\frac{u}{\begin{vmatrix} k_1 & l_1 \\ k_2 & l_2 \end{vmatrix}} = \frac{v}{\begin{vmatrix} l_1 & h_1 \\ l_2 & h_2 \end{vmatrix}} = \frac{w}{\begin{vmatrix} h_1 & k_1 \\ h_2 & k_2 \end{vmatrix}}$$



Three lattice planes have a common zone axis (*are in zone*) if their Miller indices (h_1, k_1, l_1), (h_2, k_2, l_2), (h_3, k_3, l_3) satisfy the relation:

$$\begin{vmatrix} h_1 & k_1 & l_1 \\ h_2 & k_2 & l_2 \\ h_3 & k_3 & l_3 \end{vmatrix} = 0$$

Appendix 2



	Notation à trois indices	Notation à quatre indices
Plans	H = h K = k	h = H k = K i = - (h + k)
Planes	L = l	l = L
Directions	U = 2 u + v V = 2 v + u	u = (2U - V)/3 v = (2V - U)/3 t = - (u + v)
	W=w	w=W