

# Crystal Growth: Physics, Technology and Modeling

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## Lecture 10. Selected methods of transmission electron microscopy 26 April 2022

<http://w3.unipress.waw.pl/~stach/cq-2021-22/>

# Transmission Electron Microscopy

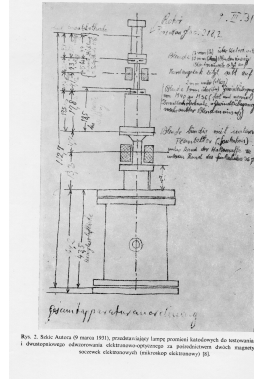
Direct information from inside of material on :

- type and density of defects
  - elemental and phase composition
  - strain field distribution (3D)
  - local electric and magnetic fields (up to 1 nm)
  - interfaces atomic structure
  - crystallography
- 
- resolution depending on the operating mode but below 35 pm is possible in some cases
  - Thin sample
  - Local info
  - Destructive

## The Genesis of TEM

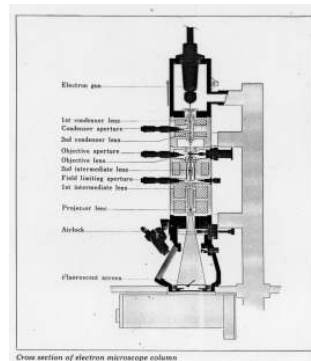
In 1923, Prince Louis de Broglie postulated the wave nature of matter.  
 In 1927, Hans Bush showed that magnetic coils can focus an electron beam in the same way as glass lenses to light.  
 In 1927 C.J. Davison and L.H Germer and G. P. Thompson and A. Reid independently demonstrated electron diffraction => the wave nature of electrons confirmed.  
 On April 7, 1931, Ernst Ruska and Max Knoll obtained the first TEM image using two magnetic lenses.  
 1936 - the first commercial TEM- Metropolitan-Vickers EM1.

## First experimental TEM



**Ernst Ruska and Max Knoll built the first electron microscope in 1931**  
 (Nobel Prize to Ruska in 1986)

## Conventional TEM like biological light microscope

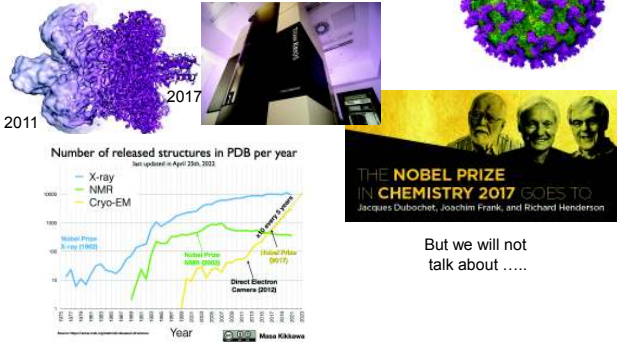


Jeol 2000EX IFAPM from 1989  
 200KV 0.27 nm Lab6 catode

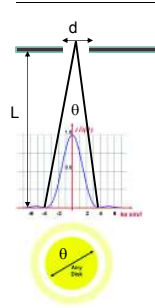
## Modern aberration corrected TEM/STEM

- X-FEG**
  - Monochromator
  - Condenser
  - Probe
  - Condenser
  - Aperture
  - Collector
- Extrema Field Emission Gun (X-FEG)**
  - Brightness (2.7 x 10<sup>10</sup> A/m<sup>2</sup>)
  - Current (2.5) x4 before monochromator
  - Current stability (0.1% over 7 days)
  - Small Coma
  - Toroidal Cathodes
  - Energy resolution (0.004 eV) without monochromator (0.02 eV)
- Monochromator**
  - Energy resolution at 200kV: 0.02 eV
- Accelerator**
  - 200 kV
- 3 Lens Condenser**
  - Large parallel illumination range (1.75 mm on axis)
  - Large convergence angle range (0.75 mrad)
- DCOR probe Cs corrector**
  - Correct high-order aberrations (2<sup>nd</sup>, 4<sup>th</sup> and 5<sup>th</sup> order aberrations)
- Super-Twin Objective Lens**
  - Probe Size: 0.05 mm
  - Large parallel (0.75 mrad)
- Photo Stage**
  - Probe size (0.05 mm) at axis (2.75 mm)
- Super-X Detector (4 Silicon Drift Detectors)**
  - Large collection angle (0.9 mrad)
  - 4 Detectors
  - High throughput rate (1-200 kcps)
  - Energy resolution (1.78 eV)
  - Direct electron readout (1000000)
- CETCOR Image Cs corrector**
- 4 Lens Projector system**
  - Compact power (high loading)
- Camera**
  - 70 x 45 CMOS based CCD camera
  - Illuminator: 2x 2.5W CCD
- Gatan Image Filter Quantum ERS**
  - High speed (1000 frames per second)
  - Large SLD (range 2000-400)

**Cryo-electron microscopy** innovators win 2017 Nobel Prize in Chemistry for developing cryo-electron microscopy for the high-resolution structure determination of biomolecules in solution Direct electron detection technology



Circular aperture Diffraction of photons or electrons- Diffraction limit



Airy Disk  
These rings are produced by Fraunhofer Diffraction by the circular aperture.  
 $L \gg \lambda$

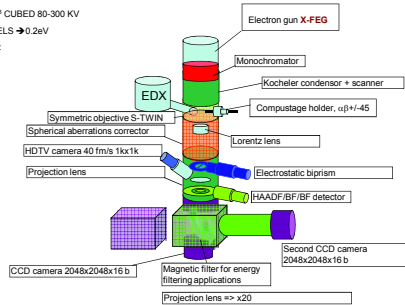
Using the small angle approximation  
Airy disk diameter  $\theta$  in radians

$$d \sin \theta = 1.22 \lambda$$

$$\theta \cong 1.22 \frac{\lambda}{d}$$

**50 YEARS OF** Electron Microscopy Group (EMG) of Institute of Physics Polish Academy of Sciences

IFPAN from September 2010 TITAN<sup>3</sup> CUBED 80-300 KV  
Resolution in TEM  $\rightarrow$  0.07 nm Energy resolution EELS  $\rightarrow$  0.2eV  
Electron Holography, EDX, STEM, HAADF, Lorentz



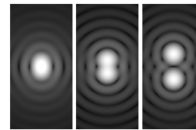
According to the Rayleigh Criterion, two point sources cannot be resolved if their separation is less than the radius of the Airy disk. The Airy disk is named for the English astronomer Sir George Biddell Airy, who served as the seventh Astronomer Royal from 1835-1881

Abbe Resolution =  $2\lambda/NA$  1873

$$d_0 = \frac{\lambda}{NA} = \frac{\lambda}{2n \sin \theta}$$

refined by Lord Rayleigh in 1896

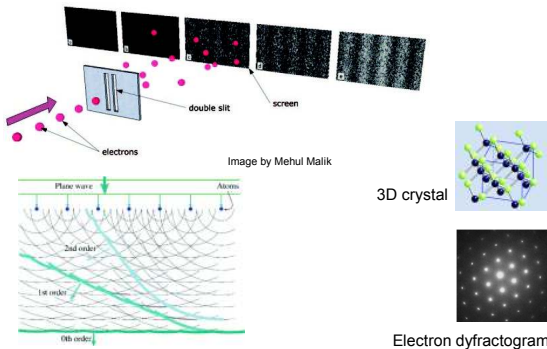
$$d_0 = \frac{0.61 \lambda}{n \sin \theta} \approx \frac{0.61 \lambda}{\sin \theta}$$



For electrons  $n=1$ , and small angles

So for better resolution  $\theta \uparrow$  and  $\lambda \downarrow$

Young's double-slit experiment performed with electrons .



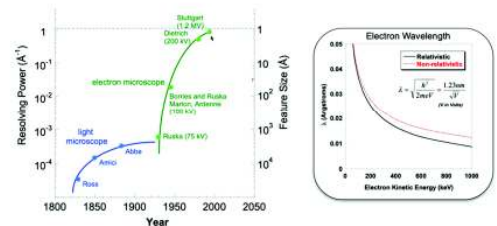
A plane, coherent electron wave generates secondary wavelets from a row of scattering centers (atoms)  
The secondary wavelets interfere, resulting in a strong direct (zeroorder) beam and several (higher order) beams scattered (diffracted) at specific angles.

wavelength of electrons

L. De Broglie 1924  
Phil. Mag. 47 446  
 $\lambda = h/p = h/mv$   
 $h$  Planck constant  
 $p$  the momentum of the particle

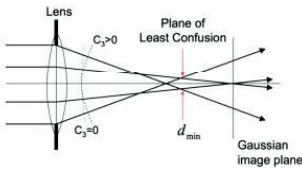
$$\lambda_{rel} = \frac{h}{mv} = \frac{h}{m_0 \gamma v} = \frac{h \sqrt{1 - \frac{v^2}{c^2}}}{m_0 v}$$

| Acceleration voltage | $\lambda$ [nm] | $\lambda$ (nm) relativistic | % of c |
|----------------------|----------------|-----------------------------|--------|
| 100                  | 0.00386        | 0.00370                     | 0.54%  |
| 200                  | 0.00273        | 0.00251                     | 0.69%  |
| 300                  | 0.00223        | 0.00197                     | 0.77%  |



Resolution limit due to spherical aberration

$C_3$  spherical aberration coefficient of objective lens

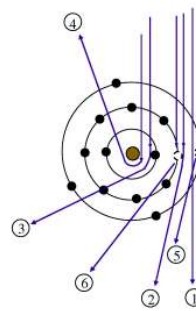


For a lens with aperture angle  $\alpha$ , the minimum blur is  $d_{min} = \frac{1}{2} C_3 \alpha^3$

Typical TEM numbers:  $C_3 = 1 \text{ mm}$ ,  $\alpha = 10 \text{ mrad} \rightarrow d_{min} = 0.5 \text{ nm}$

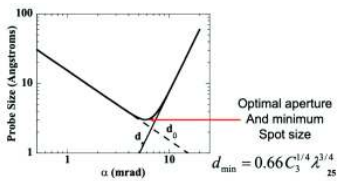
The interaction of high-energy electrons with an atom

- energy 30-1000 KeV



1. Not scattered electron
2. Low angle elastic scattering
3. High angle elastic scattering
4. Backward scatter
5. Inelastic scattering on outer shell
6. Inelastic scattering on inner shell

Resolution limit due to spherical aberration minimum beam spot in STEM

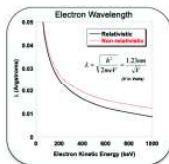
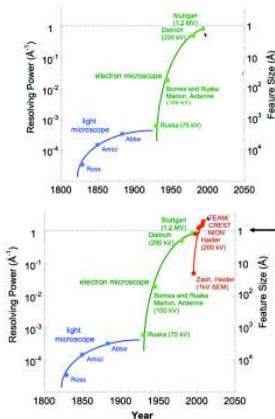
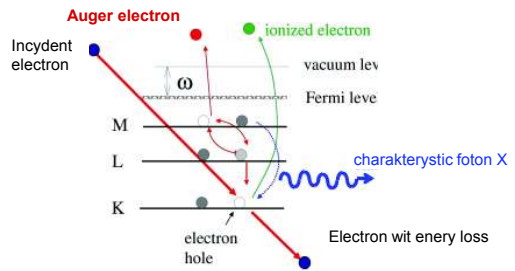


Optimal aperture  
And minimum  
Spot size  
 $d_{min} = 0.66 C_3^{1/4} \lambda^{3/4}$

For a rough estimate of the optimum aperture size, convolve blurring terms  
-If the point spreads were gaussian, we could add in quadrature:

$$d_{tot}^2 \approx d_0^2 + d_s^2 = \left(\frac{0.61\lambda}{\alpha_0}\right)^2 + \left(\frac{1}{2} C_3 \alpha_0^3\right)^2$$

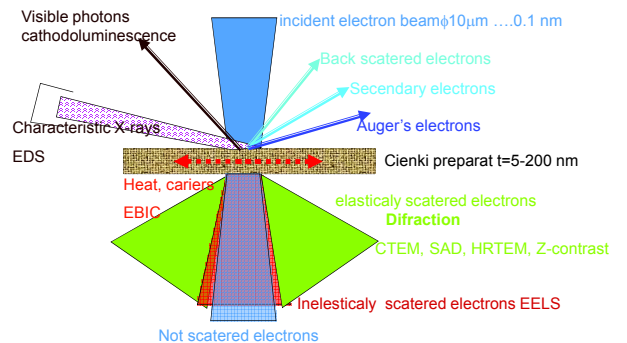
The interaction of high-energy electrons with a solid - inelastic scattering



Aberration correction technology  
Sub angstrom microscopy  
Resolution in pm

Aberration correctors are complex  
and computers are needed  
to optimize construction  
and for working

The signals produced by an electron probe in a thin crystal used for imaging and / or spectroscopy



Why are electrons so interesting?

|           | Scattered on : | Mean free path [nm] | Absorption length [nm]   |
|-----------|----------------|---------------------|--------------------------|
| Neutrons  | nucleus        | $10^7$              | $10^8$                   |
| X-rays    | electrons      | $10^3$              | $10^5$                   |
| electrons | potential      | <b>10</b>           | <b><math>10^2</math></b> |

Very strong interaction with matter

The signal from 1 atom in the sample for electrons is  **$10^4$  bigger** than for X-rays !!



**IFPAN from Jun 2010**

- Electron resolution
- 0.9 nm @ 15 kV
- 1.4 nm @ 1 kV
- Ion resolution
- 5.0 nm @ 30kV
- Ion energy 500V-30kV
- EDX
- Omiprobe
- GIS- Pt
- GIS-W

**Thin electron transparent sample : 10-50 nm grubości**

- Ion milling

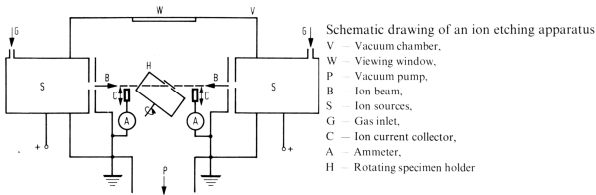


Image from: *Electron Microscopy in Solid State Physics H. Bethge and J. Heydenreich . Elsevier 1987*

Ion beam incidence angle 1-25° but <5° avoids selective etching

Accelerating voltage 4-9kV (200V- 8kV) time 1-48h

Argon ions, cooling with liquid nitrogen indirectly, (with a stream of inert gas)

vacuum 10-5 Torr (10-3 Torr when etching)

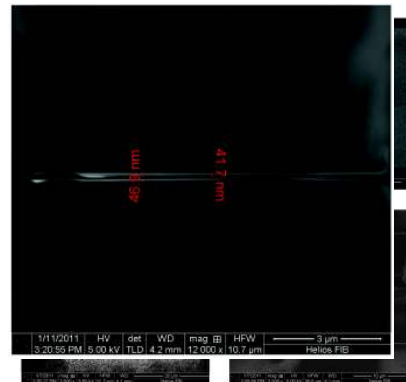
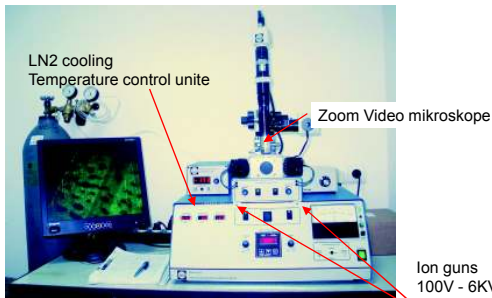


Photo B. Kurowska M. Klepka

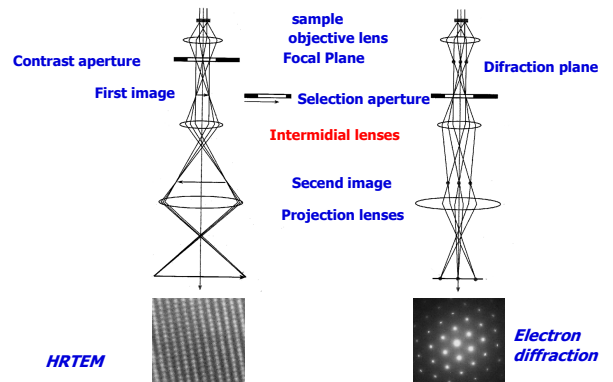
Ion milling => Radiation damage , surface amorphization

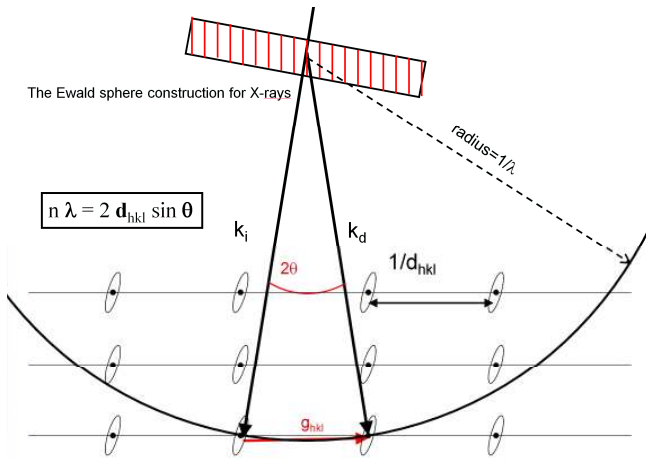
Damage limitation by: lower voltage, reducing the angle of incidence of the ion beam, cooling of sample



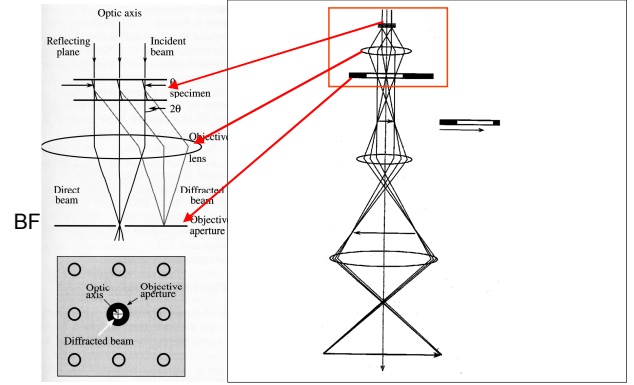
Precision Ion Polishing System (PIPS™) at IF-PAN

Basic Modes of Operation of the TEM microscope





### Diffraction contrast: bright and dark field



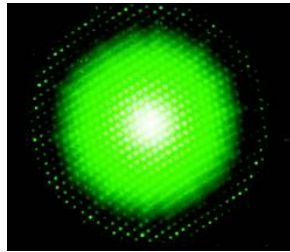
Rys: D. Williams et al., "Transmission Electron Microscopy: A textbook for Materials Science", .

### The Ewald sphere for high energy electrons

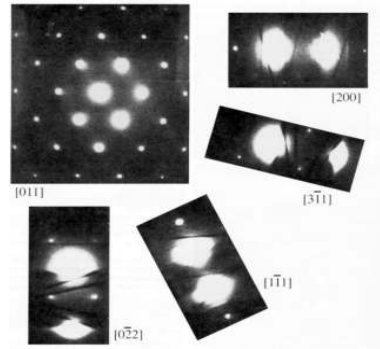
Diffraction occurs when the Ewald sphere intersects a reciprocal lattice nodes

For 200 kV electrons,  
 $1/\lambda = 1/0.00273 \text{ nm} = 366 \text{ nm}^{-1}$

$1/\lambda$

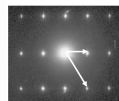
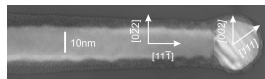
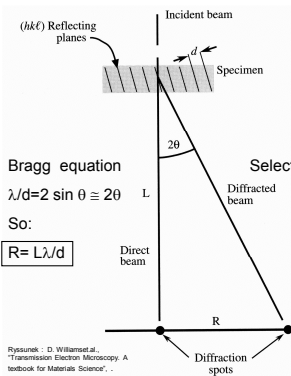


### Two-beam conditions for Si near 001 zone axis

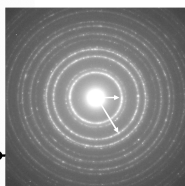


Photos from: D. Williams et al., "Transmission Electron Microscopy: A textbook for Materials Science", .

### Electron diffraction



Selected area diffraction SAD from ZnTe nanowire



Diffraction from many nanowires as X-ray powder diffraction

Rysunek: D. Williams et al., "Transmission Electron Microscopy: A textbook for Materials Science", .

Fot. P. Duzewski, S. Kret IF-PAN

### Diffraction contrast: bright and dark field Pd crystallites 5-15 nm

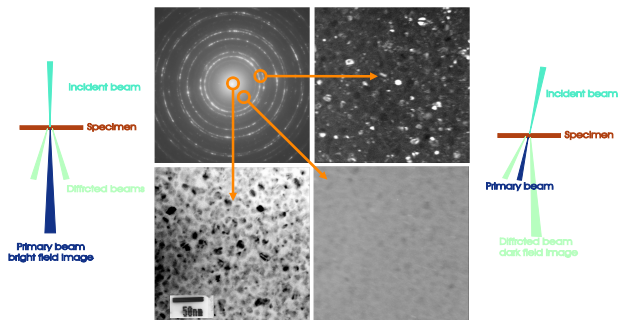
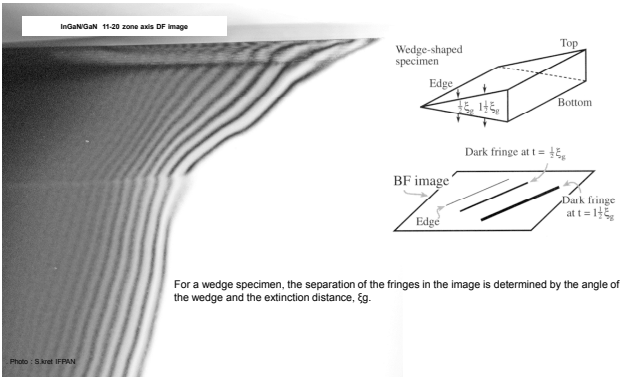
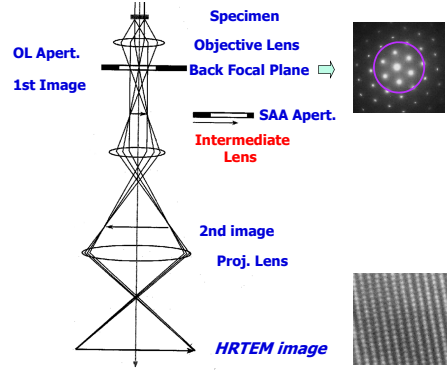


Foto: P. Duzewski IF-PAN

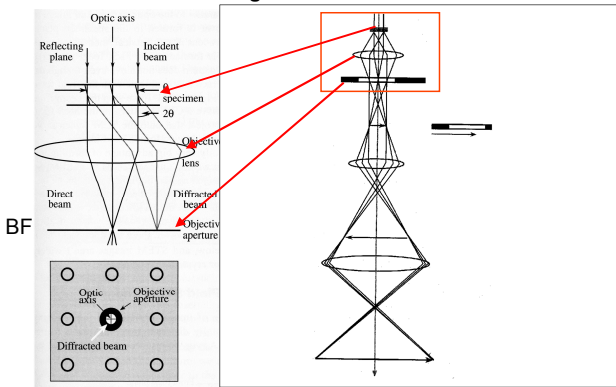
PERFECT CRYSTALS → Thickness contours depend also of material



### HRTEM image formation

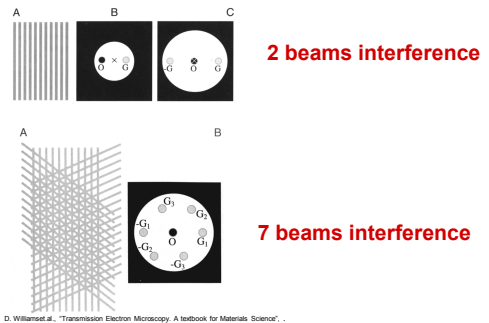


### Diffraction contrast: bright and dark field



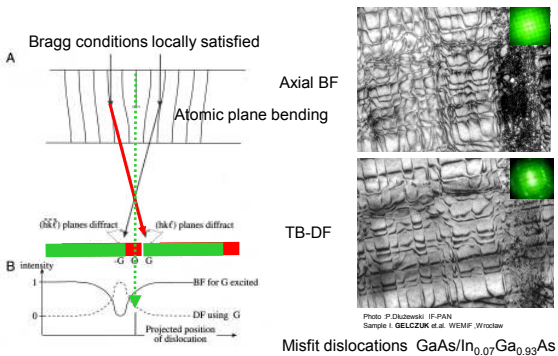
### HRTEM image formation

beams selection of on the diffraction pattern



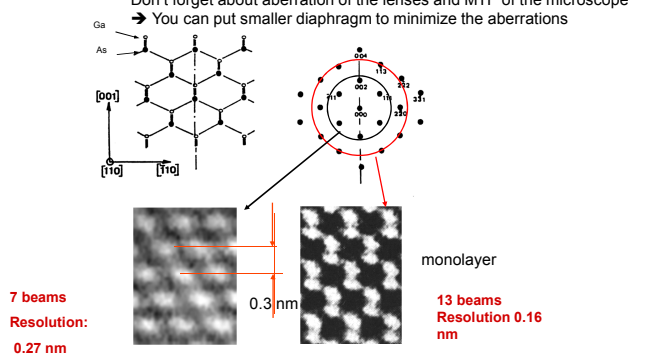
### CRYSTAL WITH DEFECTS

Intuitive description of diffraction contrast of dislocation



### HRTEM GaAs <110>

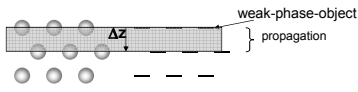
Don't forget about aberration of the lenses and MTF of the microscope  
→ You can put smaller diaphragm to minimize the aberrations



HRTEM Simulation:

Stage 1 → high-energy electrons in a crystal

metoda " multislice " : dividing a thick crystal into slices  
 "weak-phase-object approximation"  
 Cowley and Moodie (1957)



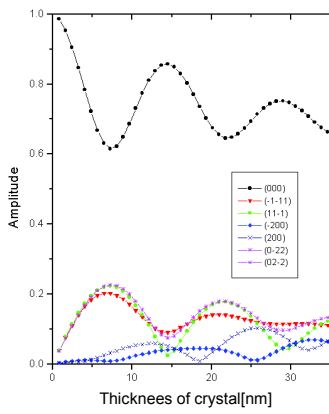
$$\Psi_{n+1}(\vec{r}) = [\Psi_n(\vec{r})q_{n+1}(\vec{r})] * p_{n+1}(\vec{r})$$

$$q_{n+1}(\vec{r}) = \exp\left[i \frac{\pi e}{\lambda E} \int_0^{\Delta z} V(x, y, z) dz\right]$$

$$p_{n+1}(\vec{r}) = \exp\left[-i \frac{k_z}{2\Delta z} (x^2 + y^2)\right]$$

Slice "transparency" function (n+1)

Propagator



Primary beam amplitudes and the main beams are deflected (no absorption)

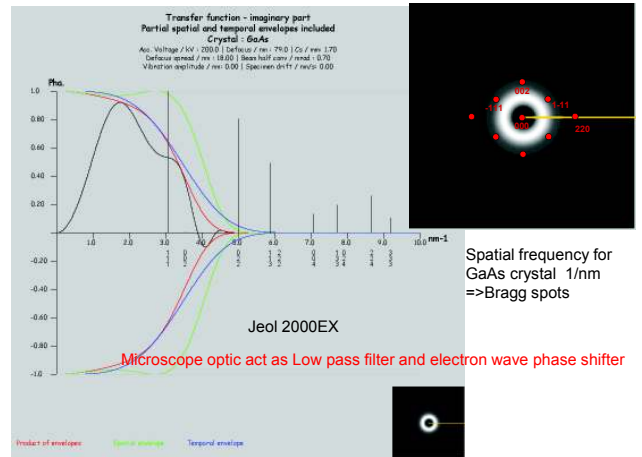
GaAs incident beam direction <110>

HRTEM SIMULATION: STAGE II

→ electrons in the optical system of the microscope

nonlinear image formation approximation  
 in partially coherent illumination K. Ishizuk 1980

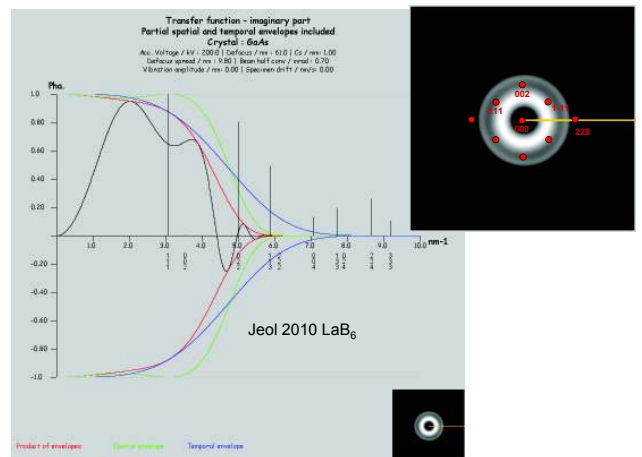
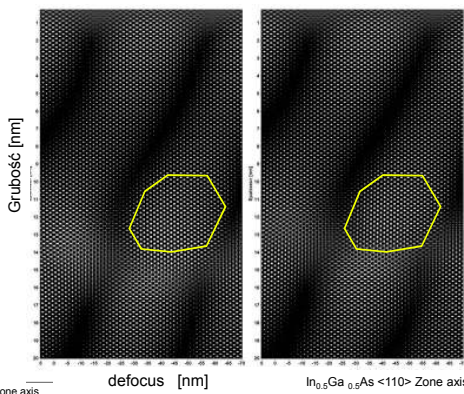
It takes into account the aberrations of the microscope optical system  
 → Contrast Transfer Function (CTF), Contrast transfer function

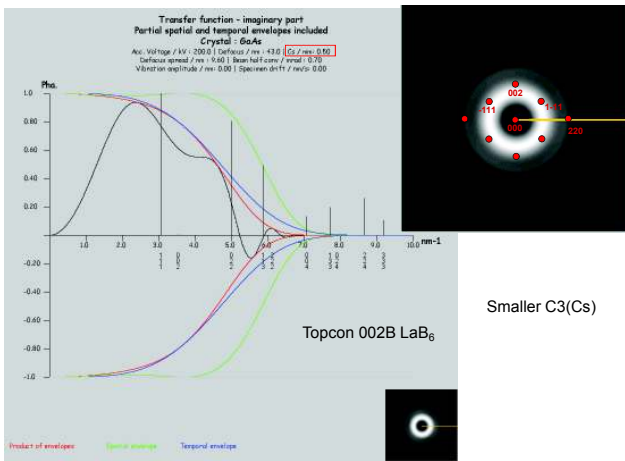


Spatial frequency for GaAs crystal 1/nm =>Bragg spots

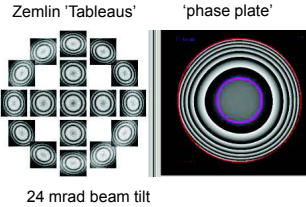
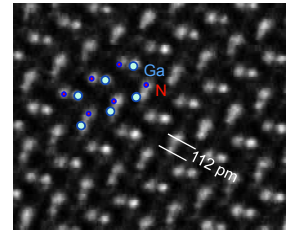
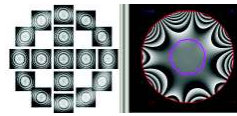
Microscope optic act as Low pass filter and electron wave phase shifter

Simulated HRTEMcontrast at 200 kV LaB<sub>6</sub>

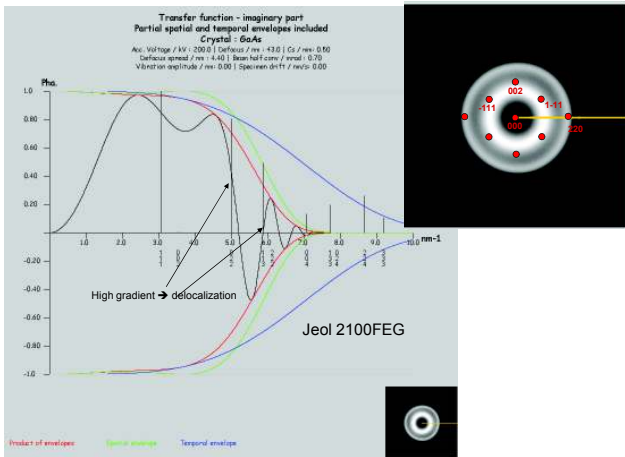




Negative-spherical-aberration technique  
- whit atoms  
- Better contrast of light atoms



**50 YEARS OF**   
Electron Microscopy Group (EMG)  
of Institute of Physics Polish Academy of Sciences



### Local strain measurement is a simple and popular method of QHRTEM

#### The main assumption :

The positions of the intensity maxima may correspond to the location of the atomic columns or tunnels between lattice sites or neither of them.  
But this relation is constant in the whole analysed image .

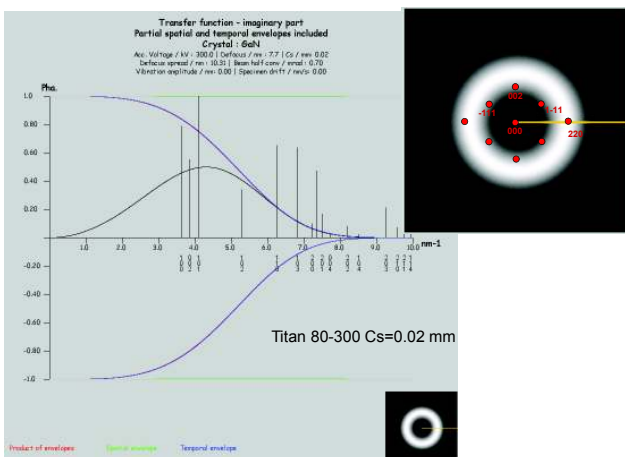
Image simulations for axial HRTEM show that the measured lattice spacing depends locally on the imaging conditions (local foil misalignment and thickness variation) particularly for non-centrosymmetric structures/projection !!

#### Real word effect :

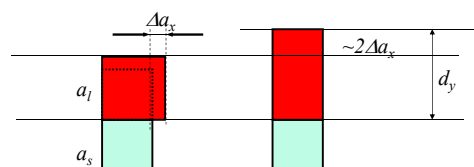
- surface relaxation
- artefacts due to sample preparation

#### Errors in processing:

- loss of information
- artefacts due to digitalisation, noise, filtering, interpolation



### Pseudomorphic growth, tetragonal distortion, biaxial stress

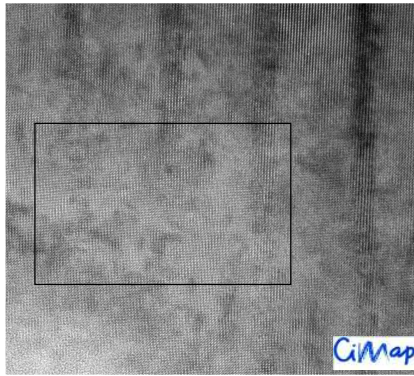


During pseudomorphic growth of a material with lattice parameter  $a_x$  on a substrate with lattice parameter  $a_s$  the lattice parameter  $a_{x||} = a_s$ . However the lattice parameter in the y direction is  $d_y > a_x$ .

$$d_x = \alpha \Delta a_x + a_x$$

Dilatation of lattice in y is  $d_y - a_x = \alpha \Delta a_x = \alpha (a_x - a_s)$  where  $\alpha = \left(1 + 2 \frac{c_{12}}{c_{11}}\right) = \frac{1+\nu}{1-\nu} \approx 2$





In<sub>0.15</sub>Ga<sub>0.8</sub>N/GaN  
pseudomorphic

[11̄20] zone axis HRTEM image of InGaN (MBE) MQWs.

## 2D FE modeling

Geometry and border conditions similar as experimental

In function of the Indium concentration and *t* foil thickness

Homogeneous Indium distribution in QW

## Chemical composition from Vegard's Law

InGaN, GaN, InN, (ZnTe, CdTe)

$$a_{In_xGa_{1-x}N} = xa_{InN} + (1-x)a_{GaN}$$

$$a_x = xa_A + (1-x)a_B$$

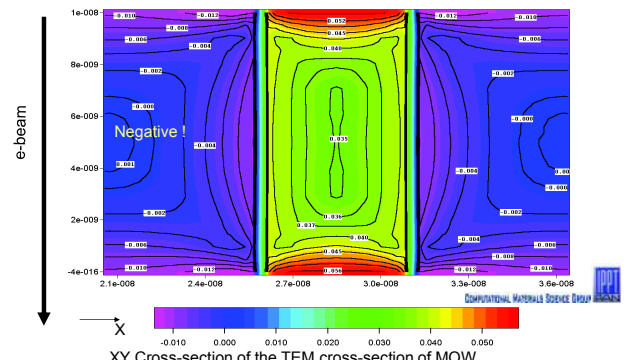
$$\varepsilon = (a_y - a_s) / a_s = \alpha(a_x - a_s) / a_s$$

$$\varepsilon = \alpha \Delta_{sx} / a_s \rightarrow \Delta_{sx} = \varepsilon a_s / \alpha$$

$a_x$  - relaxed lattice parameter for composition *x*  
 $a_A$  - relaxed lattice parameter for component A  
 $a_B$  - relaxed lattice parameter for component B  
 $a_s$  - relaxed lattice parameter for substrate  
 $a_B = a_s$   
 $\alpha$  - relaxation parameter

Local composition:

$$x(x, y) = \frac{a_s - a_x(x, y)}{a_A - a_s} = \frac{\Delta_{sx}}{\Delta_{AS}} = \frac{\varepsilon(x, y) a_s}{\alpha \Delta_{AS}}$$



XY Cross-section of the TEM cross-section of MQW  
 Calculated distribution  $\varepsilon_{xx}(x, y)$  after stress relaxation for In concentration %In=30 (QW/barriers geometry, in relation to GaN)

## Thin foil effect

~Uniaxial stress ?

$$d_y = \alpha \Delta a + a_s$$

For (110) surface relaxation

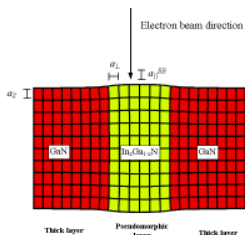
$$\alpha = 1 + 4 \frac{C_{44} C_{12}}{C_{11}^2 + 2C_{11} C_{44} + C_{11} C_{12} - C_{12}^2}$$

For CdTe/ZnTe

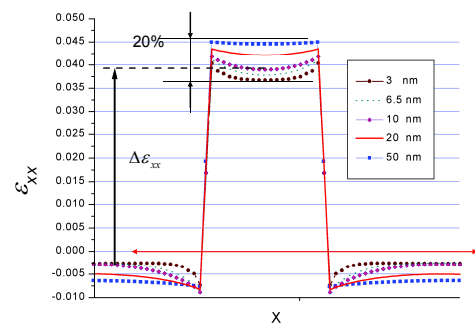
$$\alpha_{ter} \approx 2.25 \quad \alpha_{uniax} \approx 1.6$$

40%

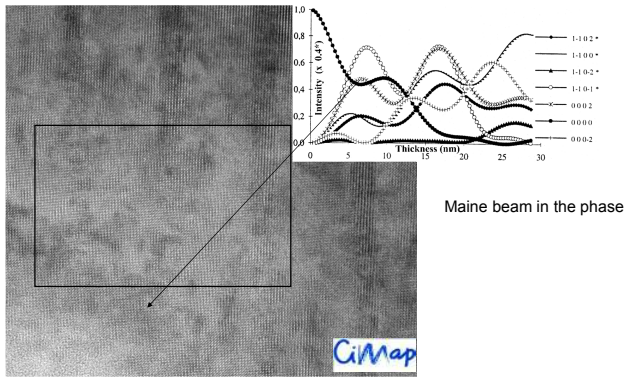
Biaxial or uniaxial ?



What is  $\alpha$  ?

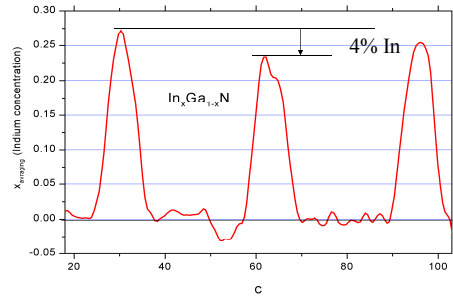


Profiles of  $\varepsilon_{xx}(x)$  obtained by averaging  $\varepsilon_{xx}(x, y)$  along the *y* direction for 30% indium concentration and *t*=5, 10, 15, 30 nm.

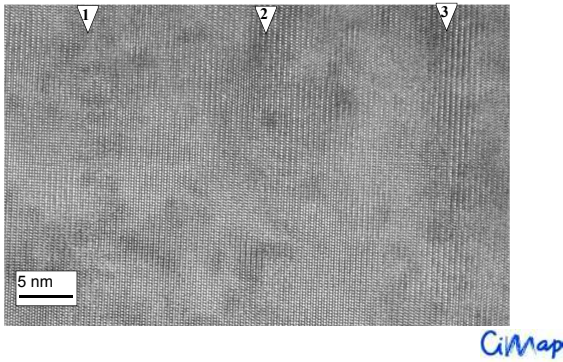


$[1\bar{1}20]$  zone axis HRTEM image of InGaN (MBE) MQWs .

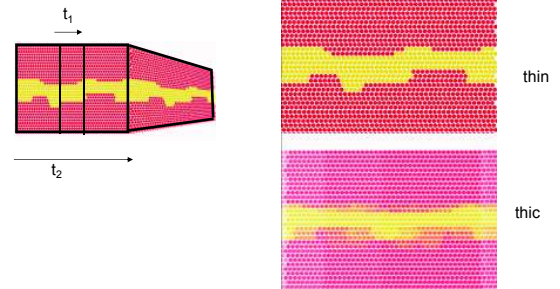
Average profile  
 → better S/N ratio



Thickness 5-10 nm



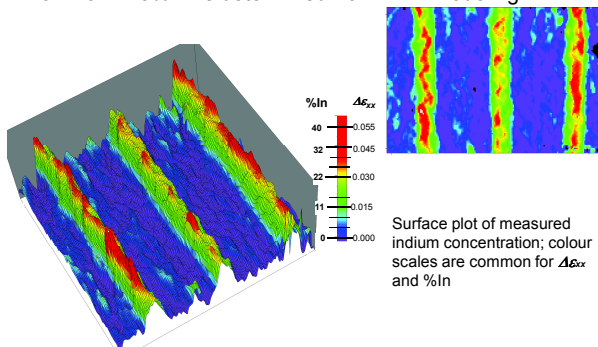
Averaging problem.



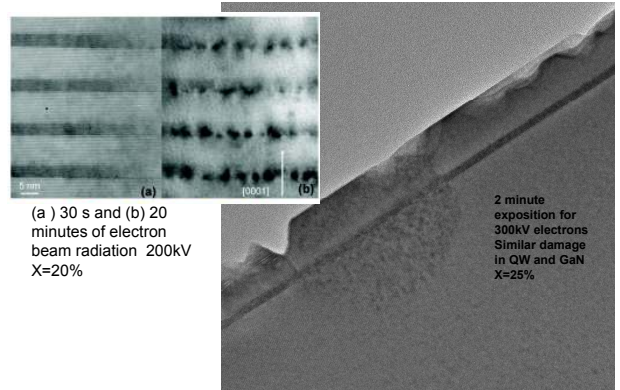
Thickness 5-10 nm

$\epsilon_{MAX}=0.030-0.038 \rightarrow A=720 \rightarrow In_{MAX}22-28\%$

Nominal ~15% A is determined from FEM modeling

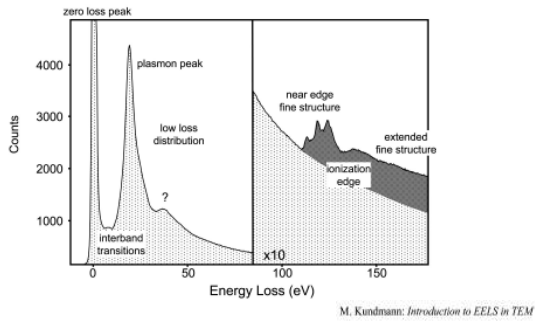


### Radiation damage False clusters

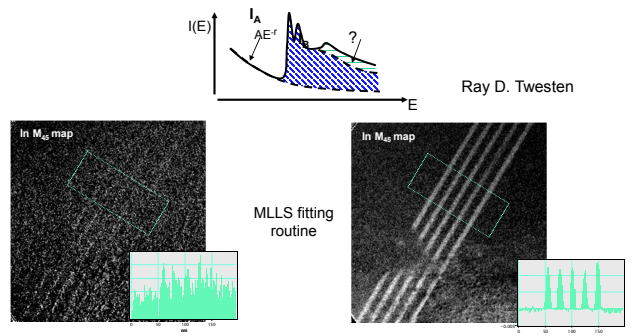


## Electron energy loss spectroscopy and mapping the chemical composition

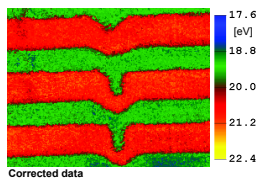
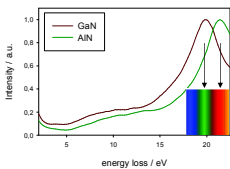
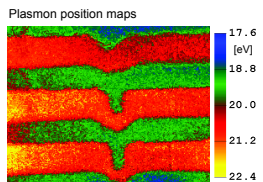
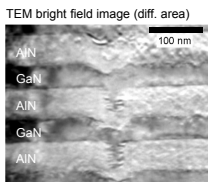
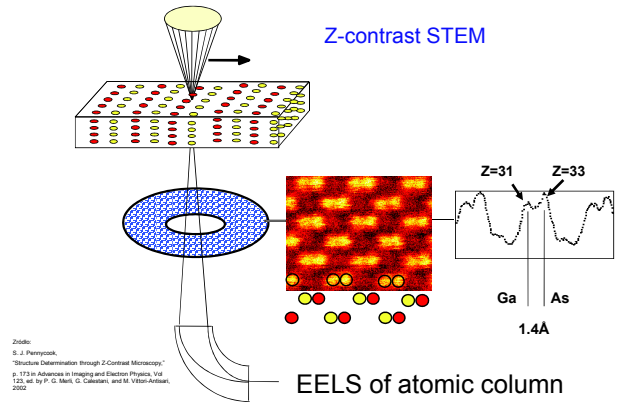
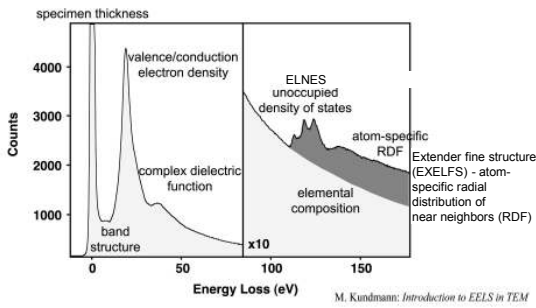
Electrons lose different amounts of energy depending on what they scattered



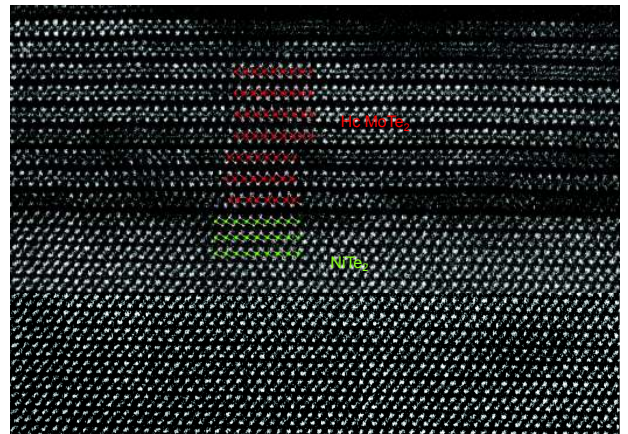
## Multiple linear least-squares fitting Mapping of Indium M<sub>45</sub> Edge



Such information can be obtained on a nanometric scale

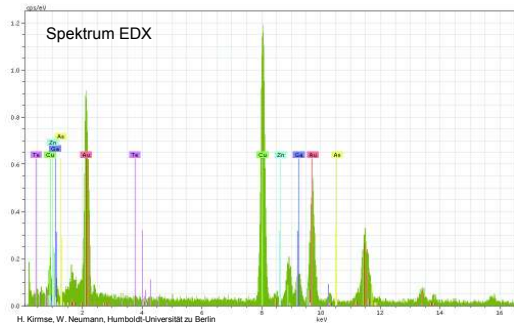


B. Schaffer, G. Kohlheitner, W. Grogger published in Ultramicroscopy



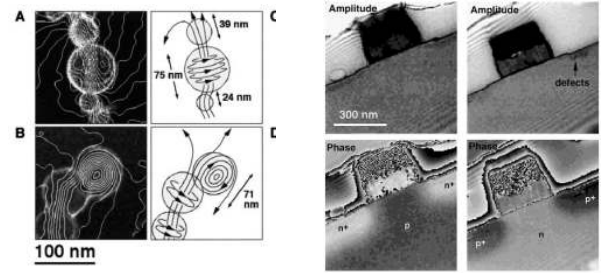
## Spectroscopic methods

Characteristic X-ray spectroscopy (EDX)



## Holografia elektronowa (niskiej rozdzielczości)

- precyzyjne pomiary zmiany fazy fali elektronowej
- wizualizacja lokalnych pól magnetycznych i elektrycznych,

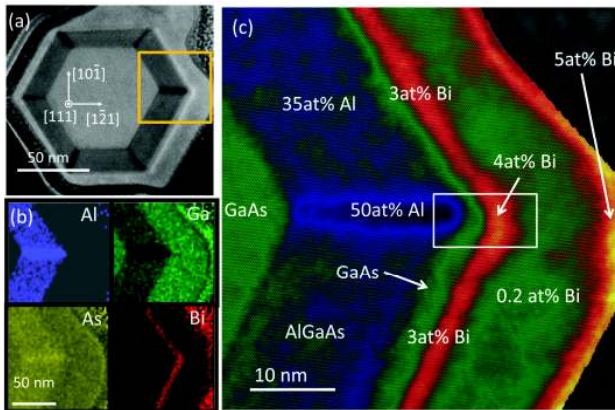


Nanocząski FeNi, wiry magnetyczne

Tranzystory 0.3μm NMOS i PMOS  
Amplituda i faza

RAFAL E. DLININ-BORKOWSKI et al. MICROSCOPY RESEARCH AND  
TECHNIQUE 64:390-402 (2004)

W.D.Rau et al. phys. Stat. Sol. (b) 222, 213 (200)



J. Sadowski, et. Al. et al. Bi incorporation and segregation in the MBE-grown GaAs-(Ga,Al)As-Ga(As,Bi) core-shell nanowires. Sci Rep 12, 6007 (2022)

ALLOYEAU et al.

PHYSICAL REVIEW B 80, 014114 (2009)

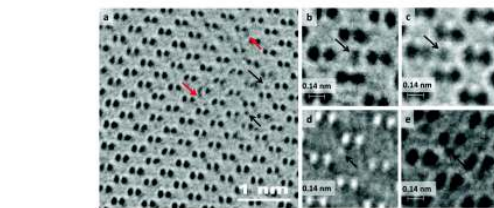
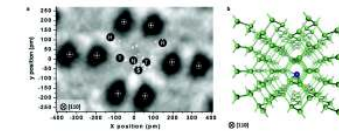
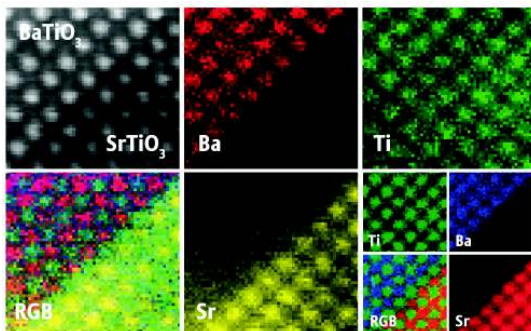


FIG. 1. (Color online) (a) Aberration-corrected images of a thin Ge crystal oriented along the [110] direction [black arrows show occupied interstitial sites, red arrows (dark gray) show column vibrations occurring during the acquisition time]. Magnified areas where an interstitial atom is observed, (b) and (c) in *T* sites, (d) in an *H* site that overlaps with a bond-centered site when the crystal is oriented along the [110] zone axis, (e) in an off-center site. Electron dose:  $4.0 \times 10^6$  electrons/nm<sup>2</sup>. Range of focus from -1 to -8 nm.



Phase Contrast  
Single interstitial  
Atom of Ge imaged and tracked !!



Atomic resolution STEM/EELS map on BaTiO<sub>3</sub>/SrTiO<sub>3</sub> interface at 80 and 200 kV acceleration voltage.

Gatan Image filter Fei Titan 80KV

## Projection problem

→ Tomography

H. Ripstein et al. / Microtechnol. Reprogram 65(2003) 171-187

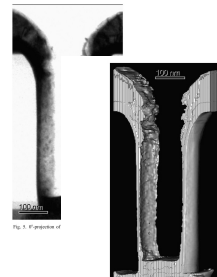
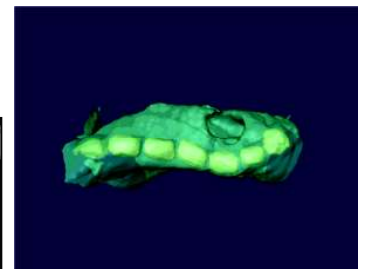
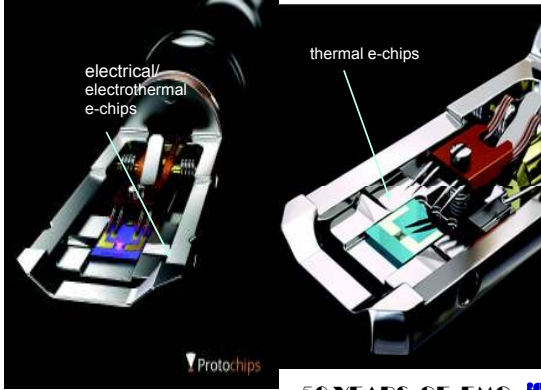


Fig. 3. 3D projection of

Fig. 3. Surface rendering of the 3D reconstruction of the tested curved sample 1.

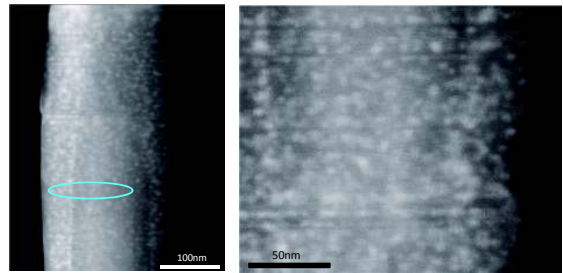


# in-situ TEM



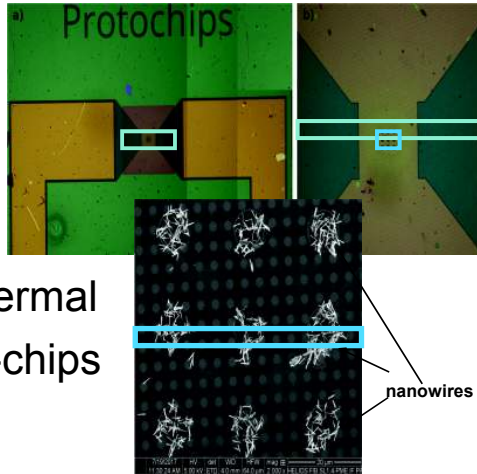
50 YEARS OF EMG

# In-situ STEM observation – movable precipitates



50 YEARS OF EMG

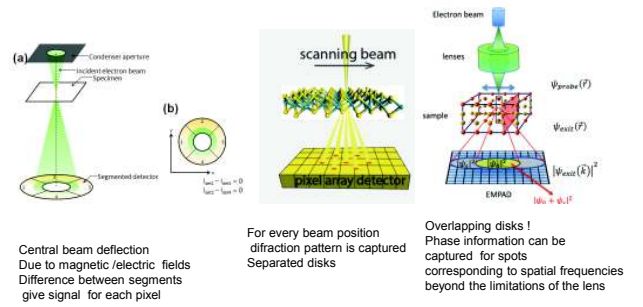
STEM and Image processing  
A.Kaletka & S.Kret



thermal e-chips

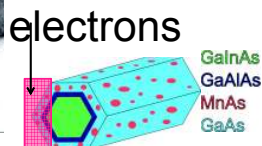
nanowires

# differential phase contrast, 4D STEM, and ptychography



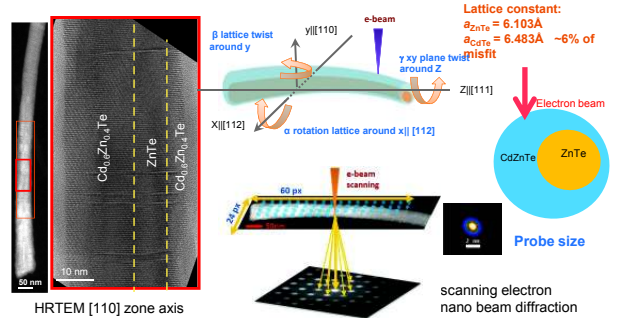
# In-situ isothermal annealing

In-situ experiment:  
T = 500°C  
Annealing time:  
30 min



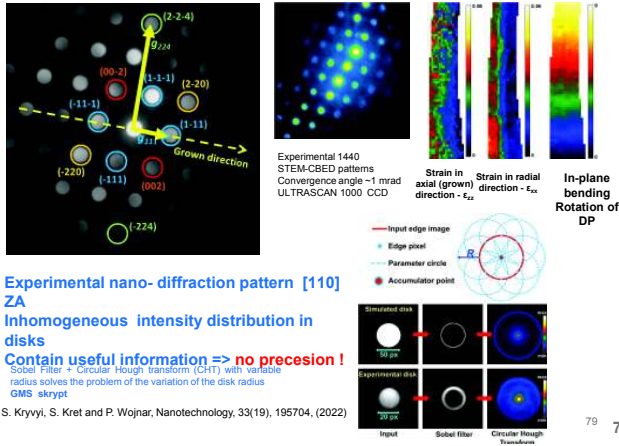
50 YEARS OF EMG

# STEP I Projected distortion of bent elastically strained Core Shell ZnTe/CdZnTe NW



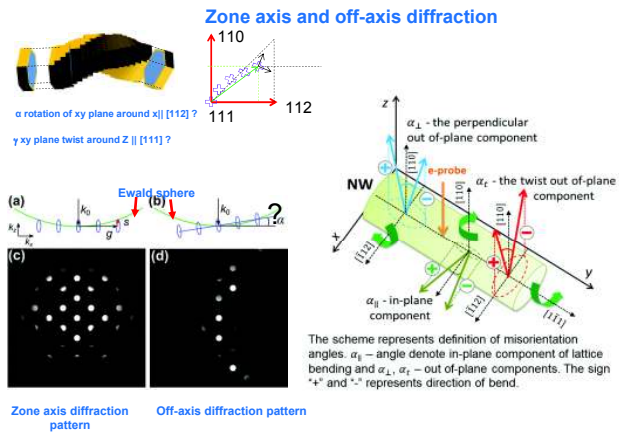
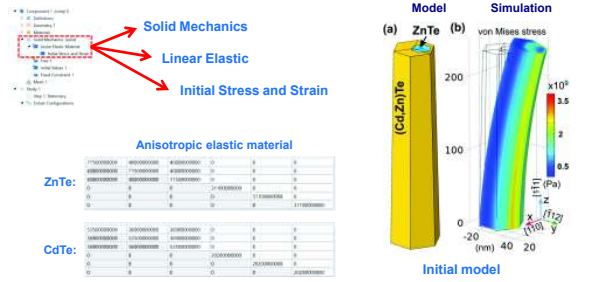
50 YEARS OF EMG

## Lattice distortion mapping using electron nano-beam diffractor

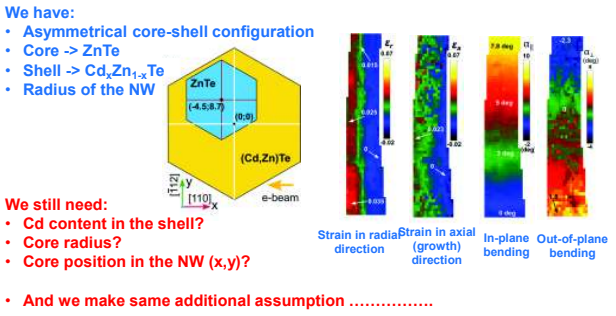


Experimental nano-diffraction pattern [110] ZA  
Inhomogeneous intensity distribution in disks  
Contain useful information => no precision!  
Sobel Filter + Circular Hough Transform (CHT) with variable radius solves the problem of the variation of the disk radius  
GMS skript  
S. Kryvyi, S. Kret and P. Wojnar, Nanotechnology, 33(19), 195704, (2022)

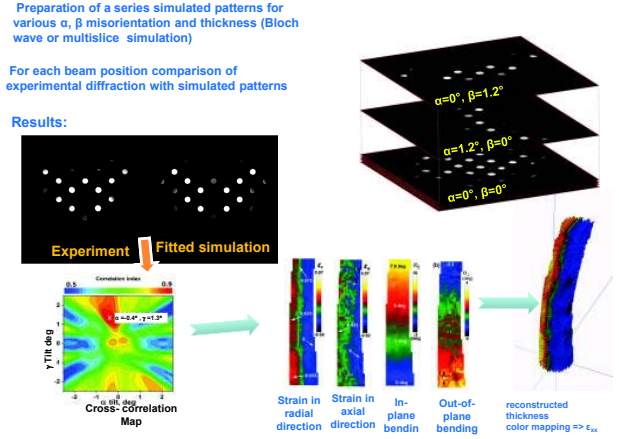
## FEM modeling of core-shell hetero-nanowires



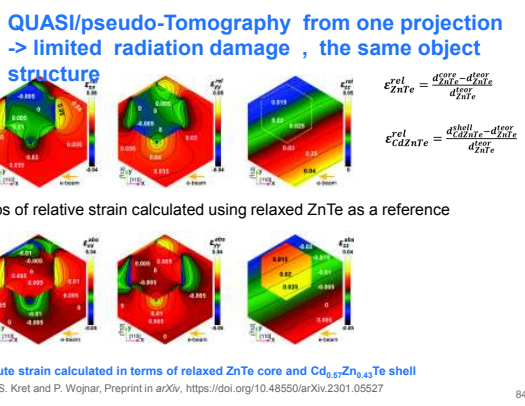
## STEP III iterative Fitting of FEM and experimental maps



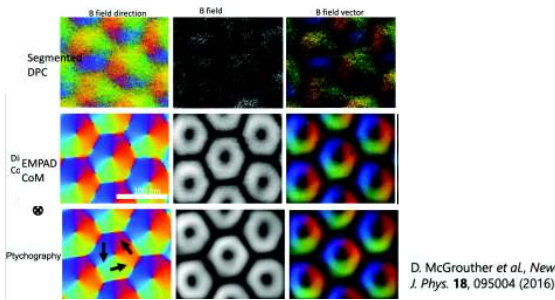
## STEP II Determination $\alpha$ , $\beta$ local misorientation, and local thickness



## Cross-section of best fit simulated core-shell NW



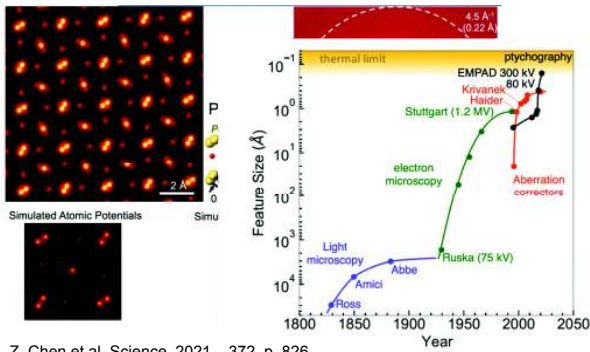
## Magnetic Skyrmions in FeGe after field cooling to 94



## Some weak points of TEM

- Necessity to perform the preparation
- Destruction of the material
- Poor sampling local information only from electron-transparent regions but up to 0.1-0.5 mm<sup>2</sup> for the best samples preparation protocols
- Preparation artifacts
- stress relaxation in a thin foil
- amorphization, radiation defects by ions during preparation
- radiation damage with electrons during observation
  
- the sample is no longer representative due to
- ionization and destruction of chemical bonds heating and diffusion of components in poorly conducting samples, knockout or shifting atoms, spraying
  
- high costs of equipment,
- time-consuming preparation of thin cross-sections
- complicated "keyboardology" and data interpretation
  
- imagination and knowledge of a microscopist (still needed)

Ultimate lateral resolution – better than the thermal vibration of atoms with a perovskite – PrScO<sub>3</sub> - structure. Multi-Slice ptychography for this sample  
**New record of resolution 22pm David A. Muller groupe at Cornell University**



Z. Chen et al. Science 2021 , 372, p. 826

TEM methods are the most powerful fast progressing characterization tools for crystalline nanomaterials with few limitations

