Crystal Growth: Physics, Technology and Modeling

Stanisław Krukowski & Michał Leszczyński Institute of High Pressure Physics PAS 01-142 Warsaw, Sokołowska 29/37

e-mail: stach@unipress.waw.pl, mike@unipress.waw.pl

Sławomir Kret

Institute of Physics PAS 02-668 Warsaw, Al. Lotników 32/46

E-mail: kret@ifpan.edu.pl

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

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

- resolution depending on the operating mode but belów 35 pm is possible in same cases
- Thin sample
- Local info
- Destructive

The Genesis of TEM

In 1923, Prince Louis de Broglie postulated the wave nature of matter.

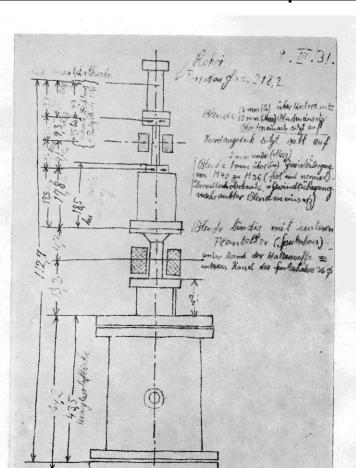
In 1927, Hans Bush showed that magnetic coils can focus an electron beam in the same way as glass lenses to light.

In 1927 C.J. Davisson 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



Rys. 2. Szkic Autora (9 marca 1931), przedstawiający lampę promieni katodowych do testowania jednoi dwustopniowego odwzorowania elektronowo-optycznego za pośrednictwem dwóch magnetycznych soczewek elektronowych (mikroskop elektronowy) [8].

Josan typeraturan oveling

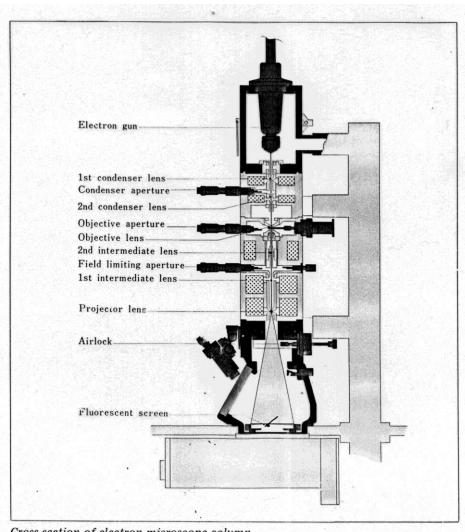




Ernst Ruska and Max Knoll built the first electron microscope in 1931

(Nobel Prize to Ruska in 1986)

Convectional TEM like biological light microscope

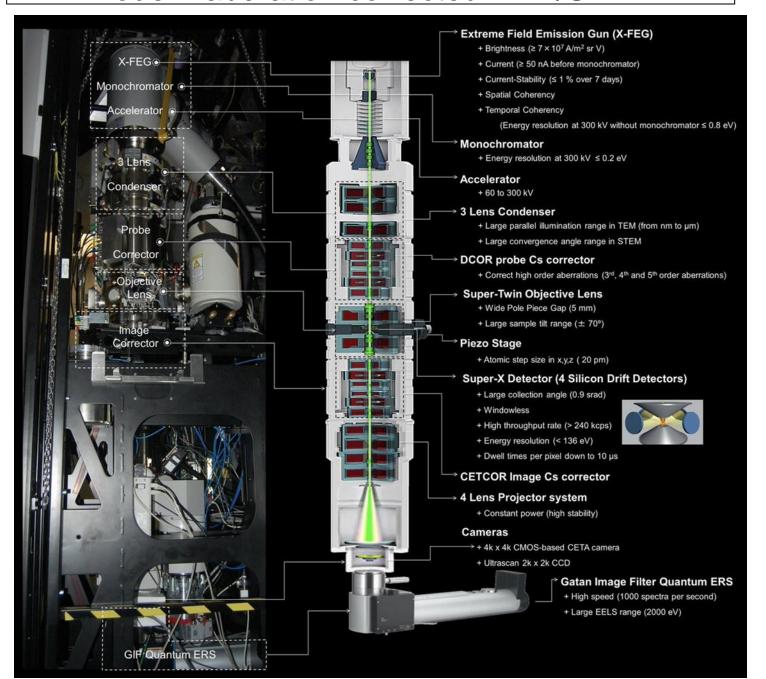


Cross section of electron microscope column



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

Modern aberation corrected TEM/STEM





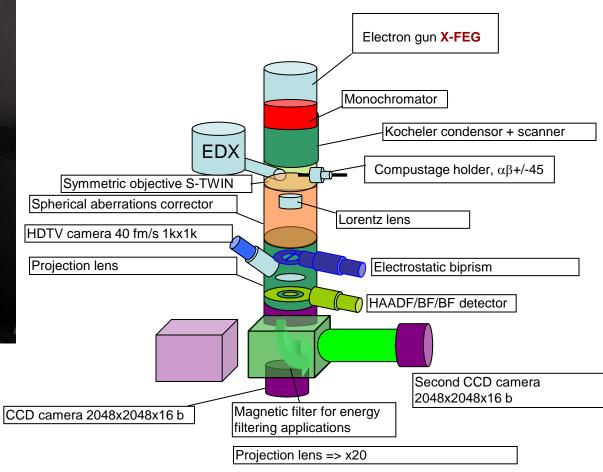
IFPAN from September 2010

TITAN3 CUBED 80-300 KV

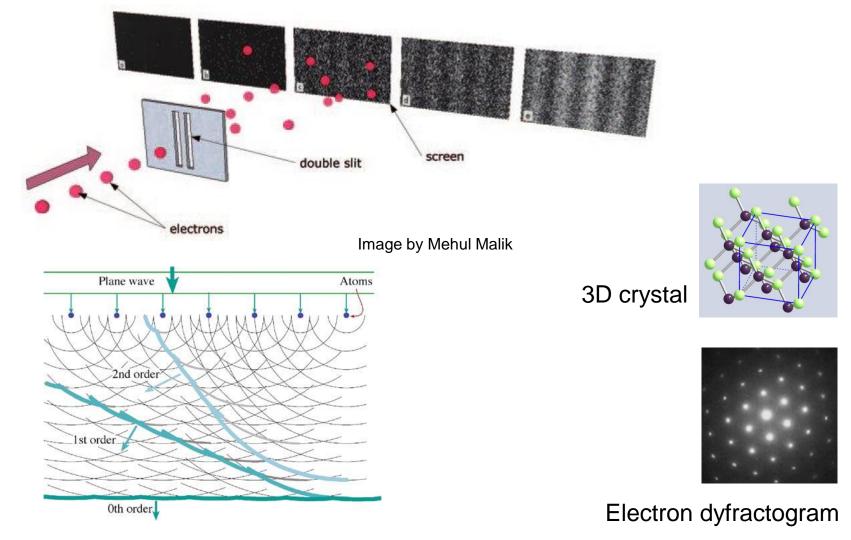
Resolution in TEM → 0.07 nm

Energy resolution EELS →0.2eV

Electron Holography, EDX, STEM, HADAF, Lorentz



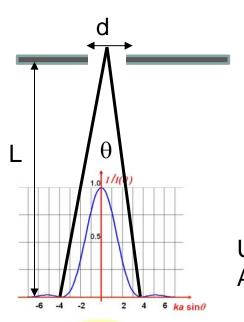
Young's double-slit experiment performed with electrons.



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.

Circular aperture Diffraction of fotons or electrons- Difraction limit



Airy Disk

These rings are produced by Fraunhofer Diffraction by the circular aperture. L>> λ

Using the small angle approximation Airy dysk diameter θ in radians



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

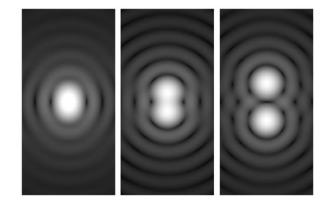
$$\theta \cong 1.22 \frac{\lambda}{d}$$

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 = $2\lambda/NA2$ 1873

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

refined by Lord Rayleigh in 1896

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



For electrons n=1, and small angles

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

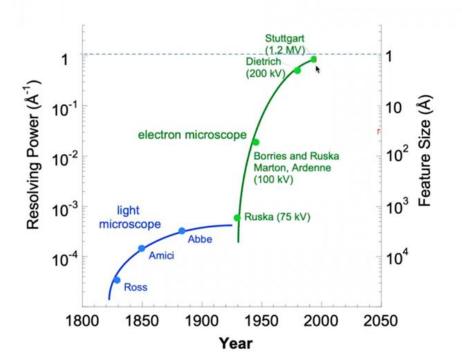
wavelength of electrons

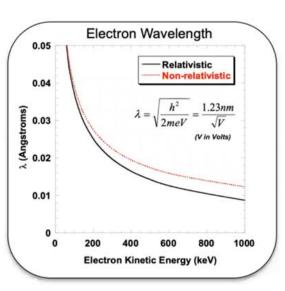
L. De Broglie 1924 Phil. Mag.,47 446 λ =h/p =h/mv

h Planc constantp the momentum of the particle

$$\lambda_B=rac{h}{mv}=rac{h}{\sqrt{1-rac{v^2}{c^2}}}v=rac{h\sqrt{1-rac{v^2}{c^2}}}{m_0v}$$

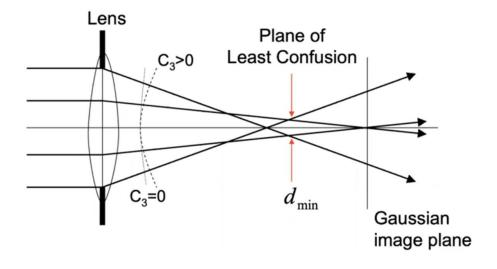
Accelartaion voltage	λ [nm]	λ (nm) relatywistic	% of c
100	0.00386	0.00370	0.54%
200	0.00273	0.00251	0.69%
300	0.00223	0.00197	0.77%





Resolution limit due to spherical aberation

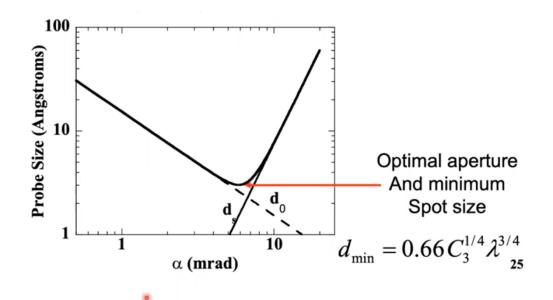
C₃ spherical aberration coefficient of objective lens



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

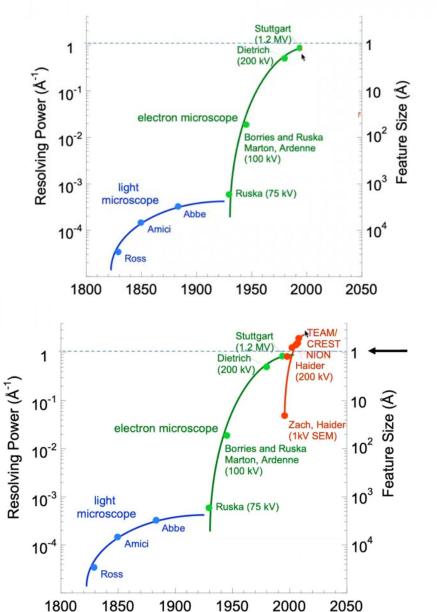
Typical TEM numbers: C_3 = 1 mm, α =10 mrad $\rightarrow d_{min}$ = 0.5 nm

Resolution limit due to spherical aberation minimum bem spot in STEM

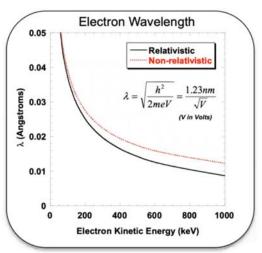


For a rough estimate of the optimum aperture size, convolve blurring terms -If the point spreads were gaussian, we could add in quadrature:

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



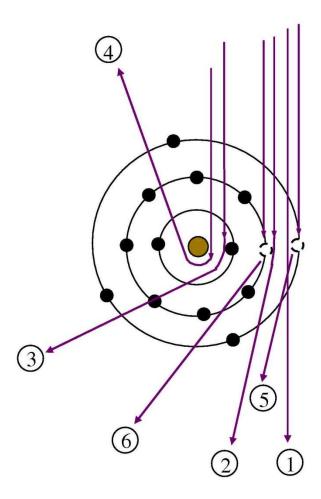
Year



Aberation corection technology Sub angstrom microscopy Resolution in pm

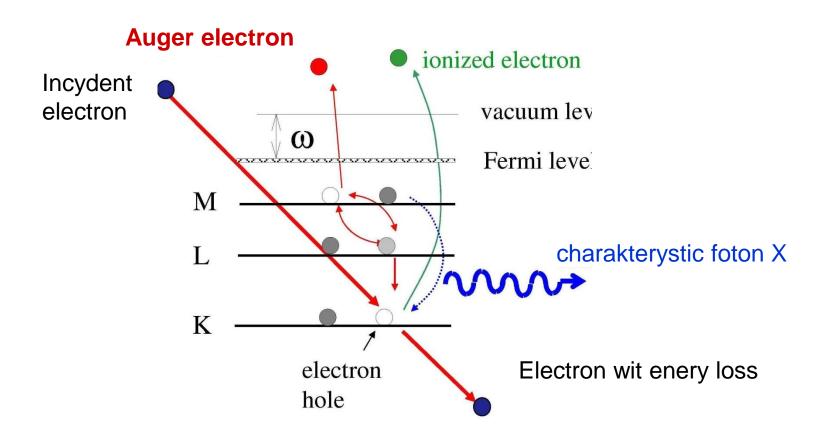
The interaction of high-energy electrons with an atom

- energy 30-1000 KeV

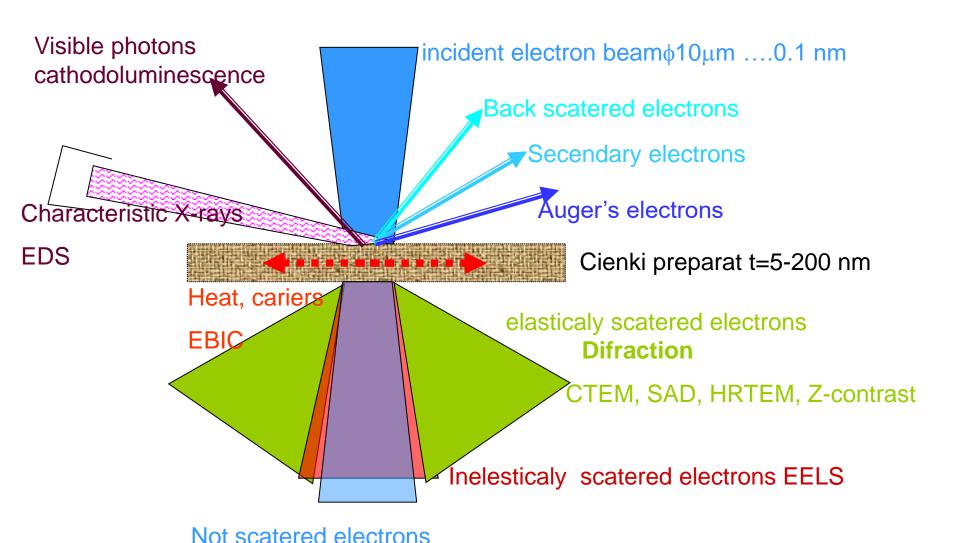


- Not scattered electron
- 2. Low angle elastic scattering
- 3. High angle elastic scattering
- 4. Backward scatter
- 5. Inelastic scattering on outer shell
- 6. Inelastic scattering on inner shell

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



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 lenght [nm]
Neutrons	nucleus	10 ⁷	10 ⁸
X-rays	electrons	10 ³	10 ⁵
electrons	potential	10	10 ²

Very strong interaction with matter

The signal from 1 atom in the sample for electrons is 10⁴ biger then for X-rays!!

Thin electron transparent sample: 10-50 nm grubości

- Ion milling

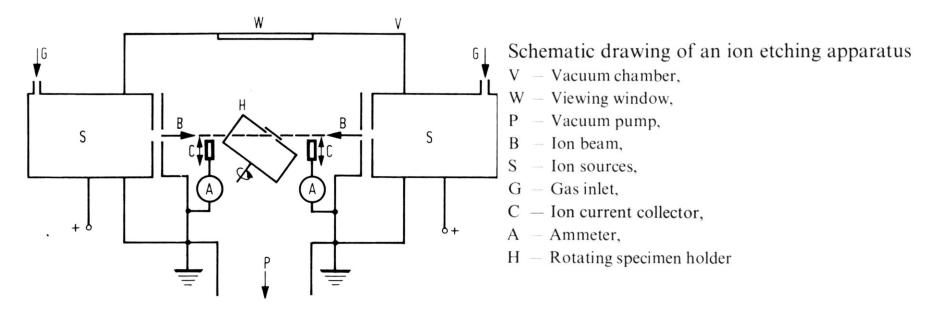


Image from: Electron Microscopy in Solid Stage Physics H.Bethge and J. Heydenreich , Elesevier 1987

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

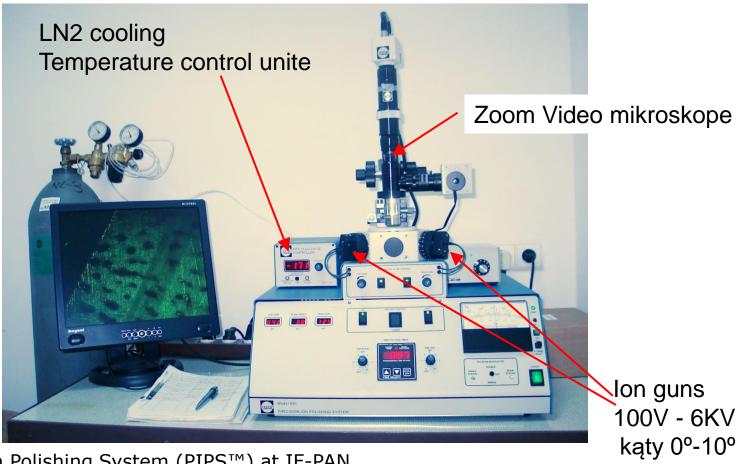
Accelerating voltage 4-9kV (200V- 8kV) time 1-48h

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

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

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



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

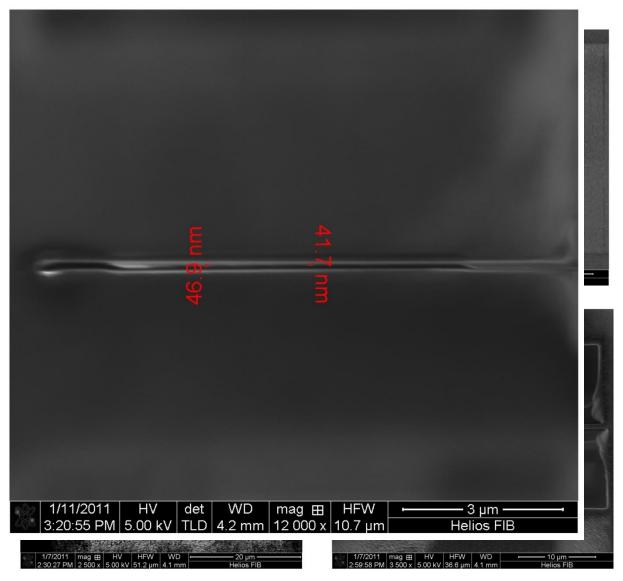
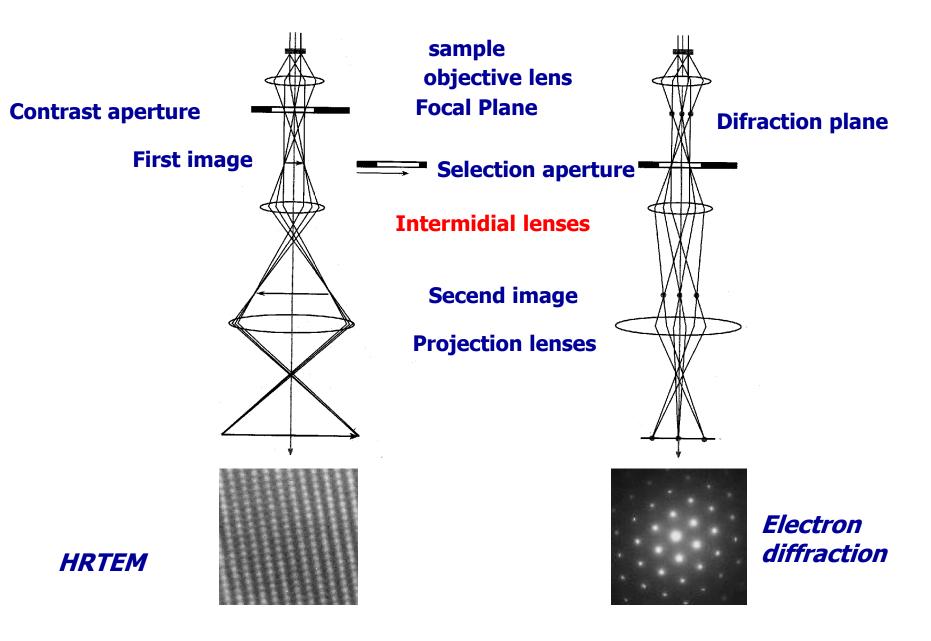
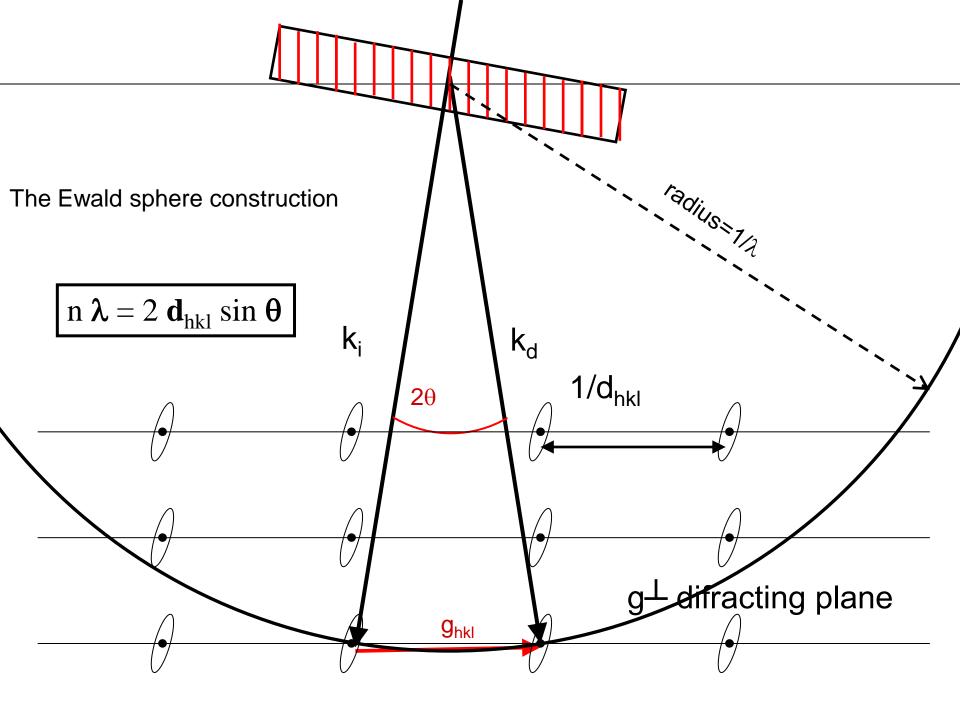


Photo B.Kurowska M.Klepka

Basic Modes of Operation of the TEM microscope



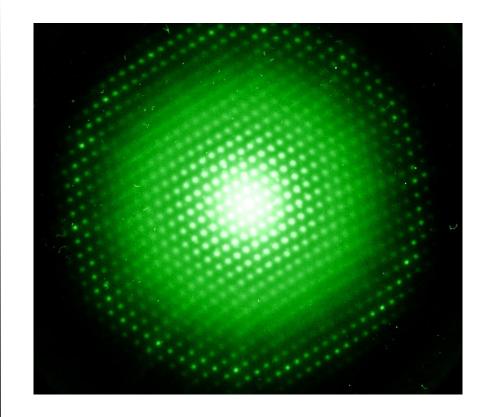


The Ewald sphere for high energy electrons

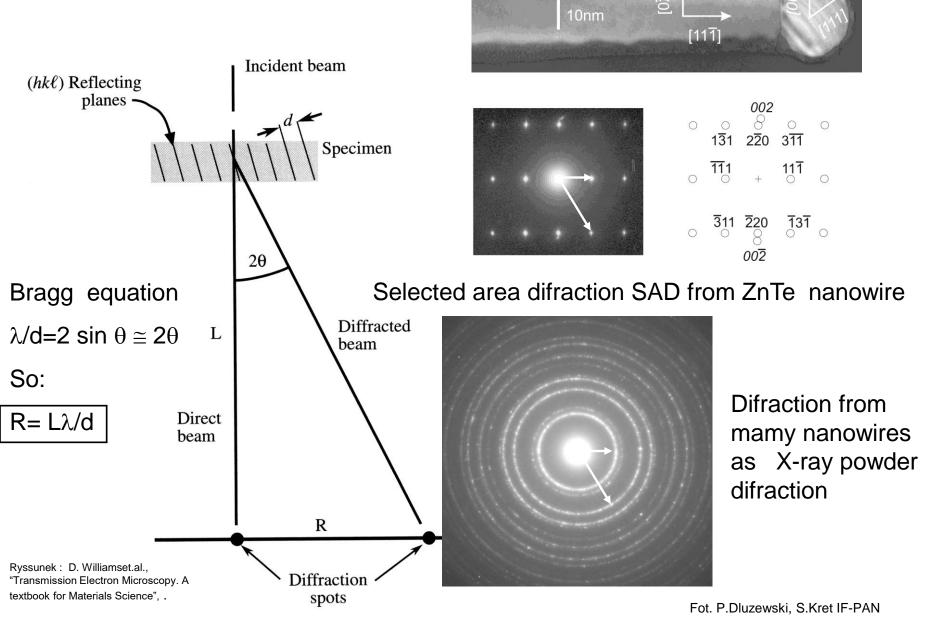
Diffraction occurs when the Ewald sphere intersects a reciprocal lattice nodes

1/λ

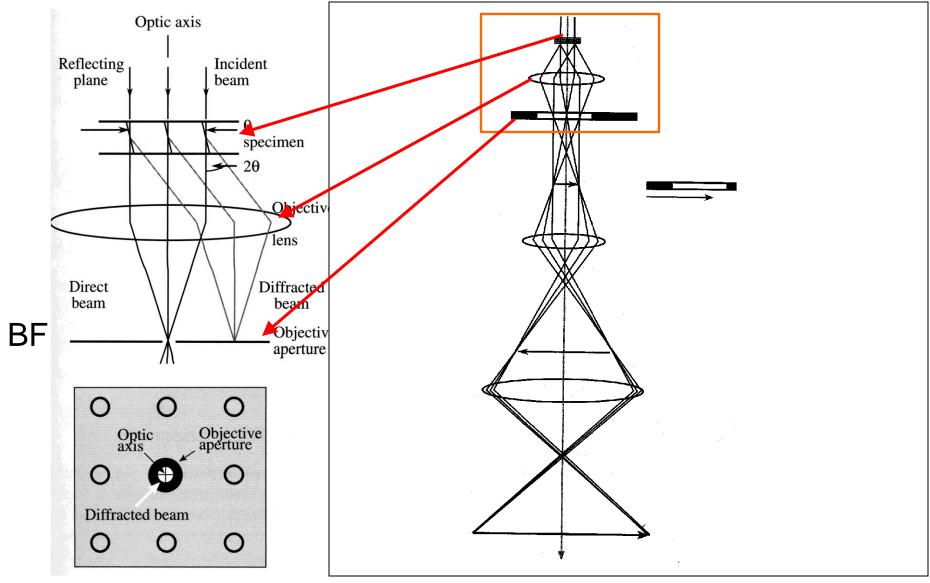
For 200 kV electrons, $1/\lambda = 1/0.00273 \text{ nm} = 366 \text{ nm}-1$



Electron difraction

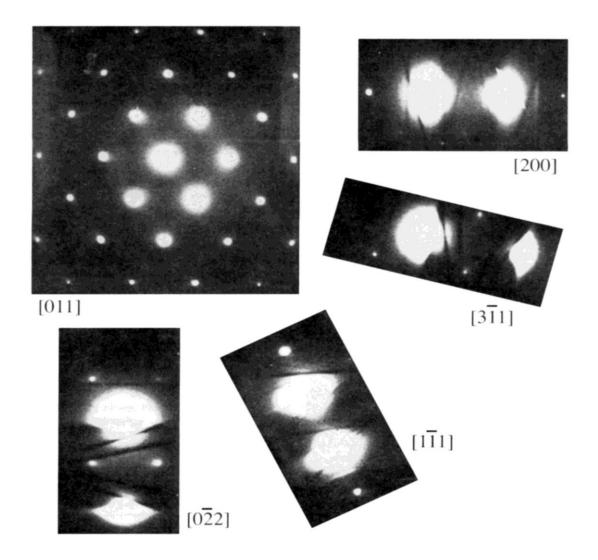


Diffraction contrast: bright and dark field



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

Two-beam conditions for Si near 001 zone axis



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

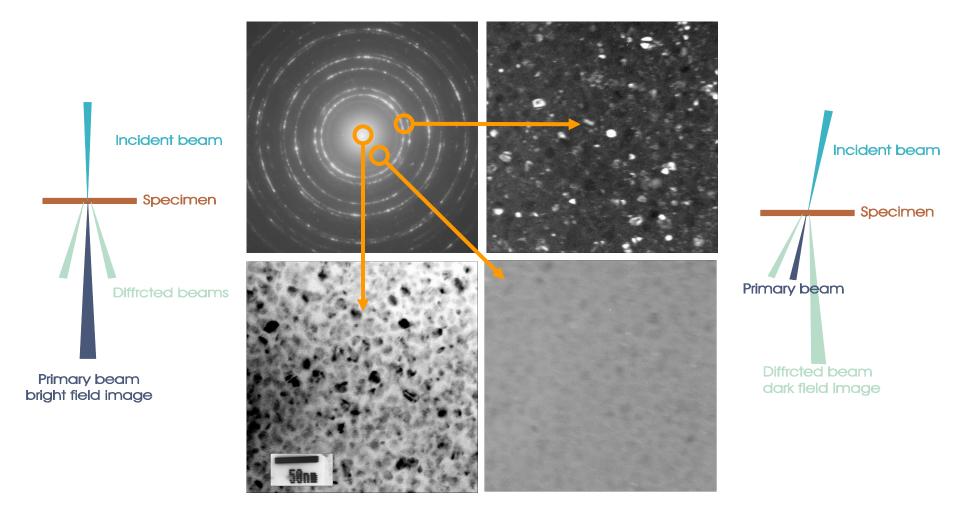
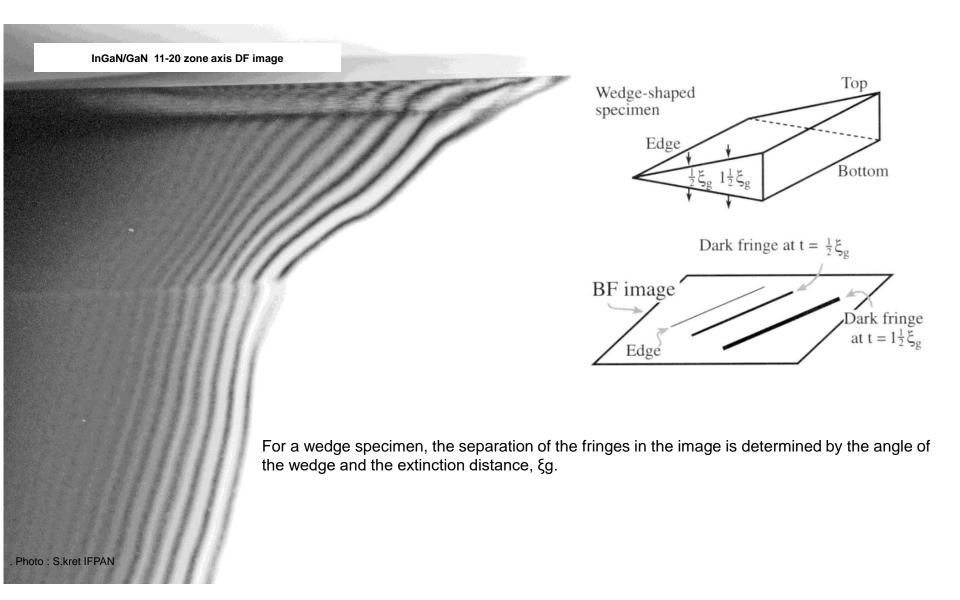


Foto:P.Dłużweski IF-PAN

PERFECT CRYSTALS → Thickness contours



The Howie-Whelan equations for two beams and perfect crystal

Description of the amplitude of diffracted ϕ_0 and ϕ_g as a function of z is given by:

Top
$$\frac{1}{dz} = \frac{i\pi}{\xi_0} \varphi_0 + \frac{i\pi}{\xi_g} \varphi_g \exp(2\pi i s_g z)$$

$$\frac{d\phi_0}{dz} = \frac{i\pi}{\xi_0} \varphi_0 + \frac{i\pi}{\xi_g} \varphi_g \exp(2\pi i s_g z)$$

$$\frac{d\phi_g}{dz} = \frac{i\pi}{\xi_g} \varphi_0 \exp(2\pi i s_g z) + \frac{i\pi}{\xi_0} \varphi_g$$
Bottom Diffracted beam beam
$$\frac{d\phi_g}{dz} = \frac{i\pi}{\xi_g} \varphi_0 \exp(2\pi i s_g z) + \frac{i\pi}{\xi_0} \varphi_g$$

Integration over the entire thickness gives the ϕ_0 and ϕ_g at exit surface of the specimen

The bright-field intensity is then given by $\varphi_0\phi_0^*$

The dark-field intensity is then given by $\varphi_g \phi_g^*$

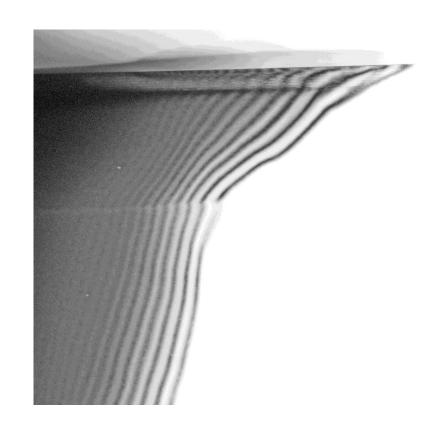
The extinction distance is given by:

$$\xi_g = \frac{\pi V_c \cos \theta_{\rm B}}{\lambda F_{\rm g}}$$

Analytical solution of the Howie-Whelan equations

$$Ig = |\phi_g|^2 = \phi_g \phi_g^* = \frac{\pi^2}{\xi_g^2} \frac{\sin^2 \pi t S_{eff}}{(\pi S_{eff})^2}$$

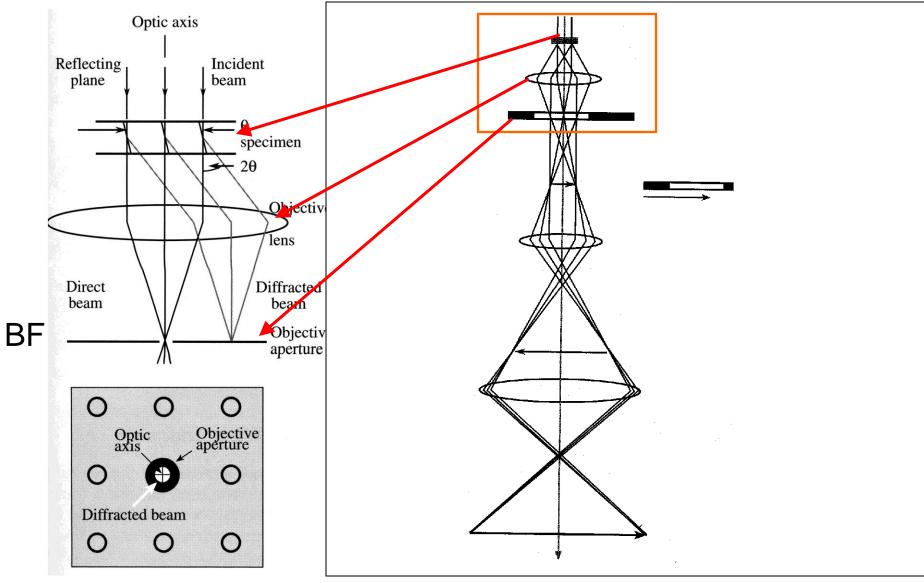
where
$$S_{eff} = \sqrt{s^2 + \frac{1}{\xi_g^2}}$$



"Absorption" high-angle scattering (elastic and/or inelastic) can be accounted for by replacing $1/\xi$ by $1/\xi+i/\xi$

^{&#}x27;" a parameter ξ ' which is usually about 0.1ξ is really a fudge factor that modifies H-W equations to fit the experimental observations,

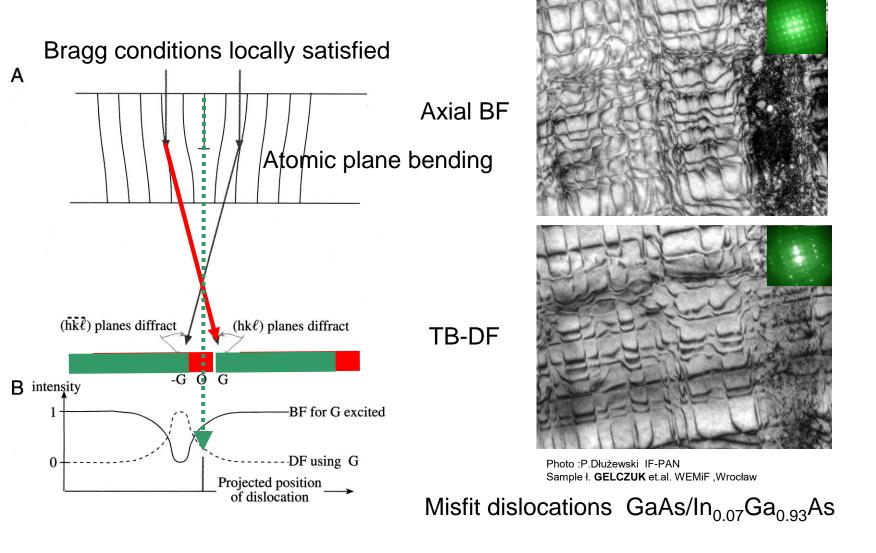
Diffraction contrast: bright and dark field



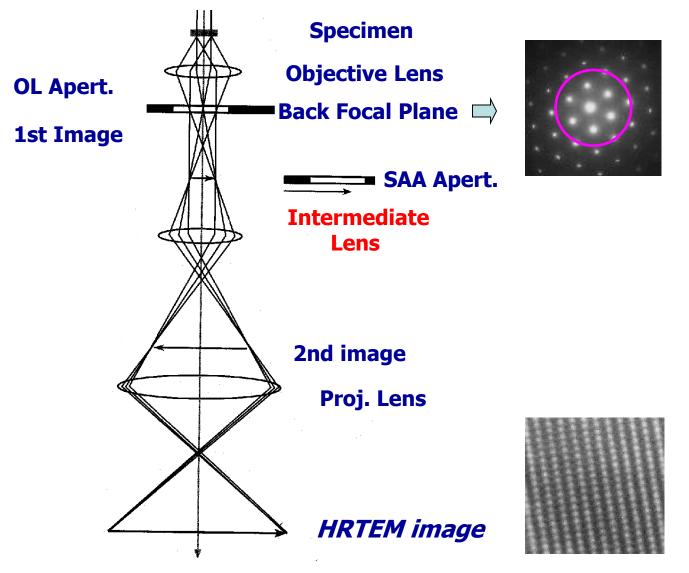
 $Rys:.\ D.\ Williams\ et. al.,\ "Transmission\ Electron\ Microscopy.\ A\ textbook\ for\ Materials\ Science",\ .$

CRYSTAL WITH DEFECTS

Intuitive description of diffraction contrast of dislocation

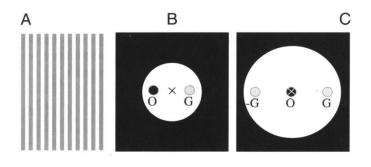


HRTEM image formation

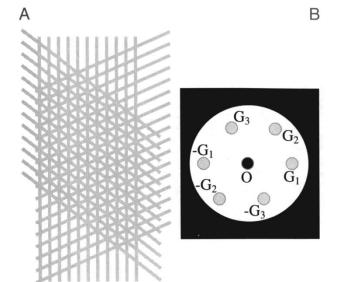


HRTEM image formation

beams selection of on the diffraction pattern



2 beams interference

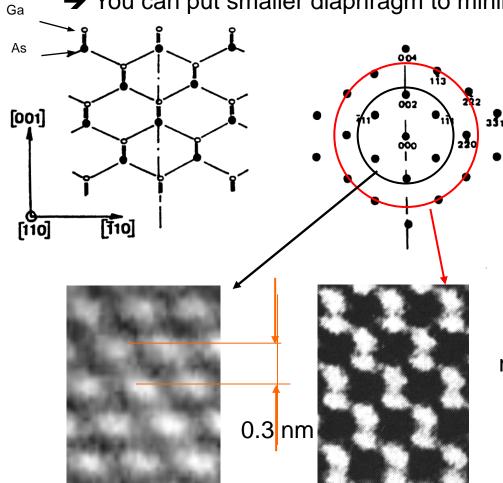


7 beams interference

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



monolayer

13 beams
Resolution 0.16
nm

7 beams

Resolution:

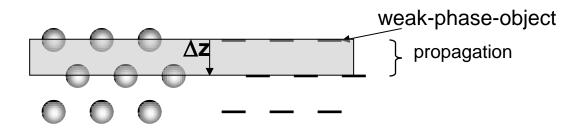
0.27 nm

HRTEM Simulation:

Stage 1 → high-energy electrons in a crystal

metoda " multislice " : dividing a thick crystal into slices "weak-phase-object aproximation"

Cowley and Moodie (1957)



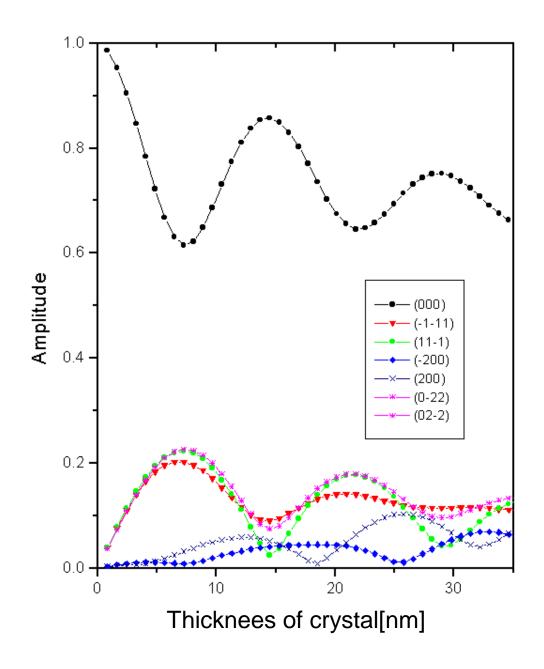
$$\Psi_{n+I}(\vec{r}) = [\Psi_n(\vec{r})q_{n+I}(\vec{r})] * p_{n+I}(\vec{r})$$

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

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

Slice "transparency" function (n+1)

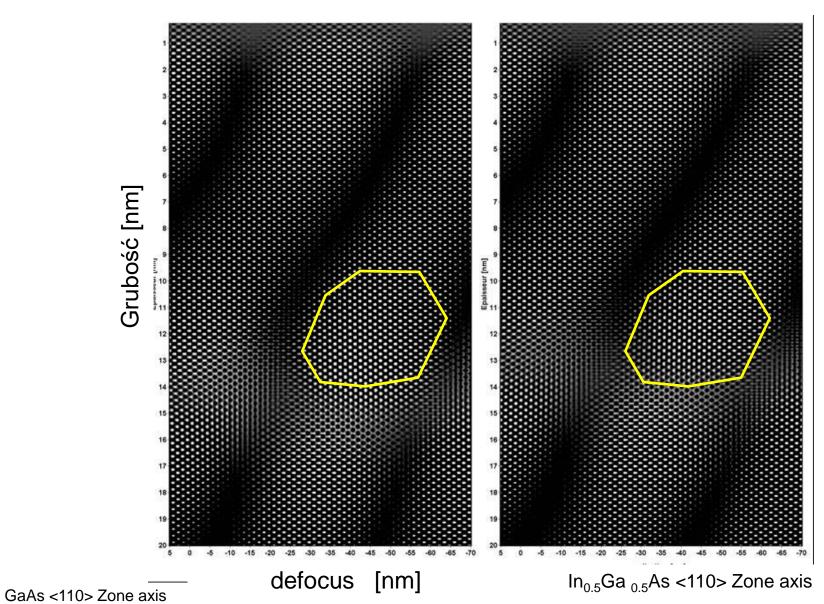
Propagator



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

GaAs incident beam direction <110>

Simulated HRTEMcontrast at 200 kV LaB₆



HRTEM SIMULATION: STAGE II

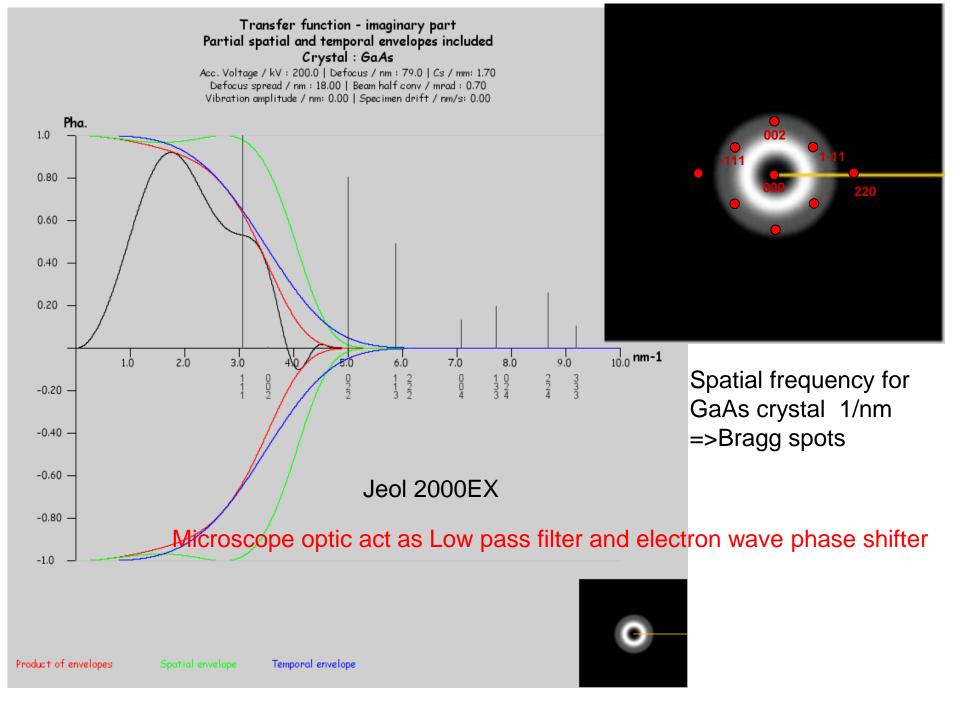
→ electrons in the optical system of the microscope

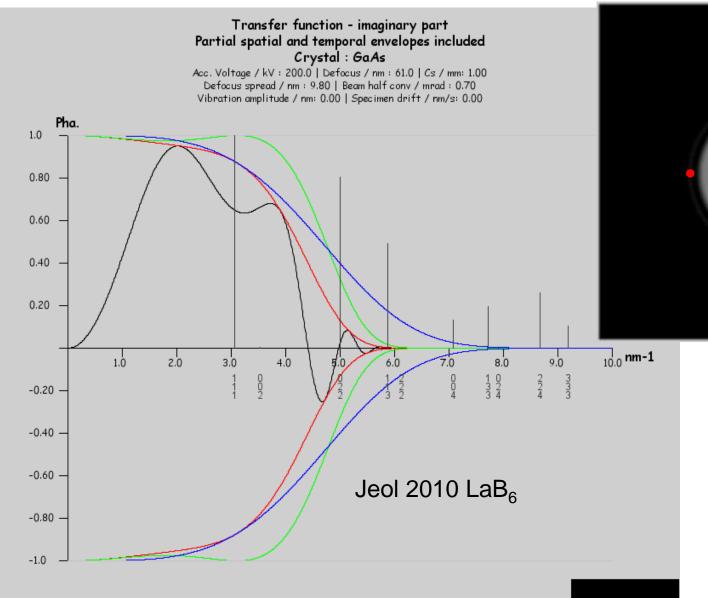
nonlinear image formation approximation in partially coherent ilumination K. Ishizuk 1980

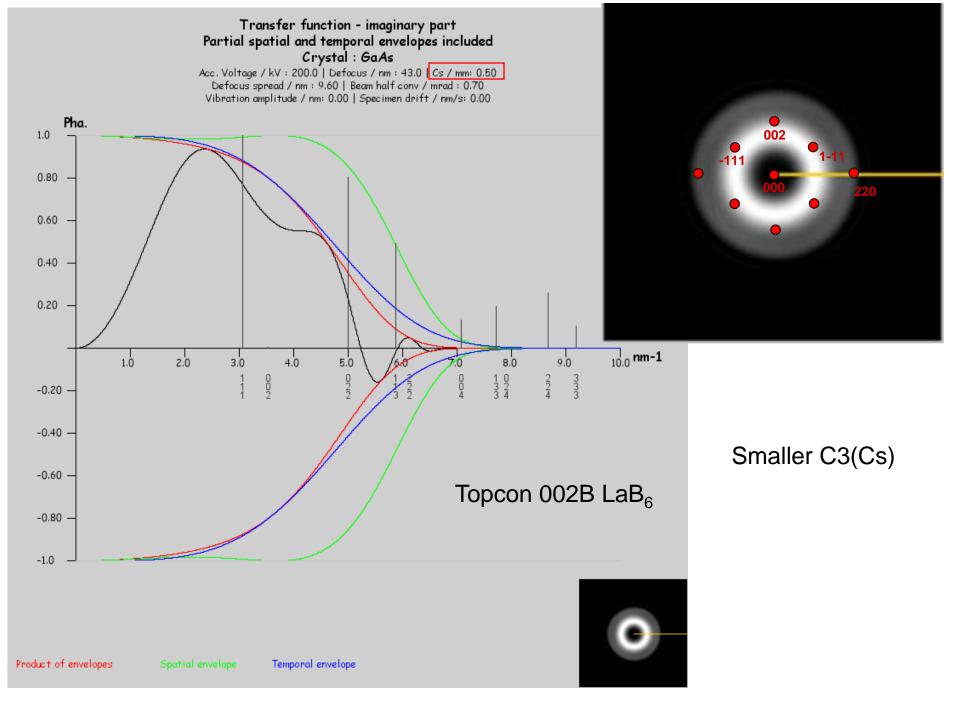
It takes into account the aberrations of the microscope optical system

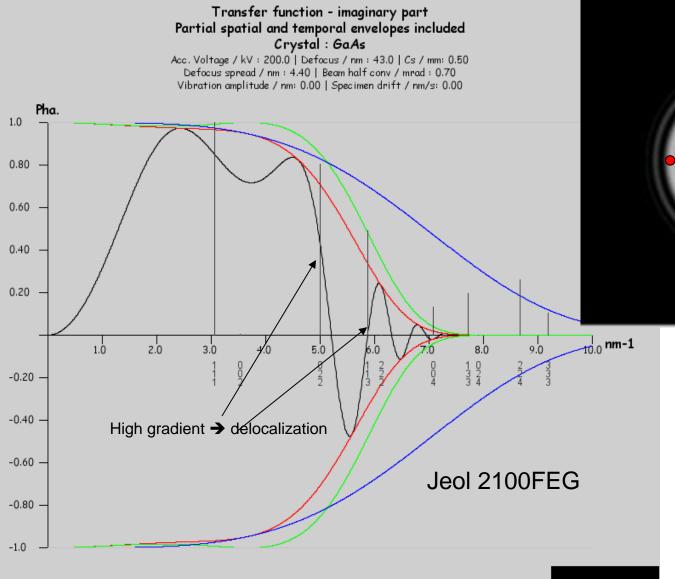


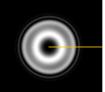
Contrast Transfer Function (CTF), Contrast transfer function



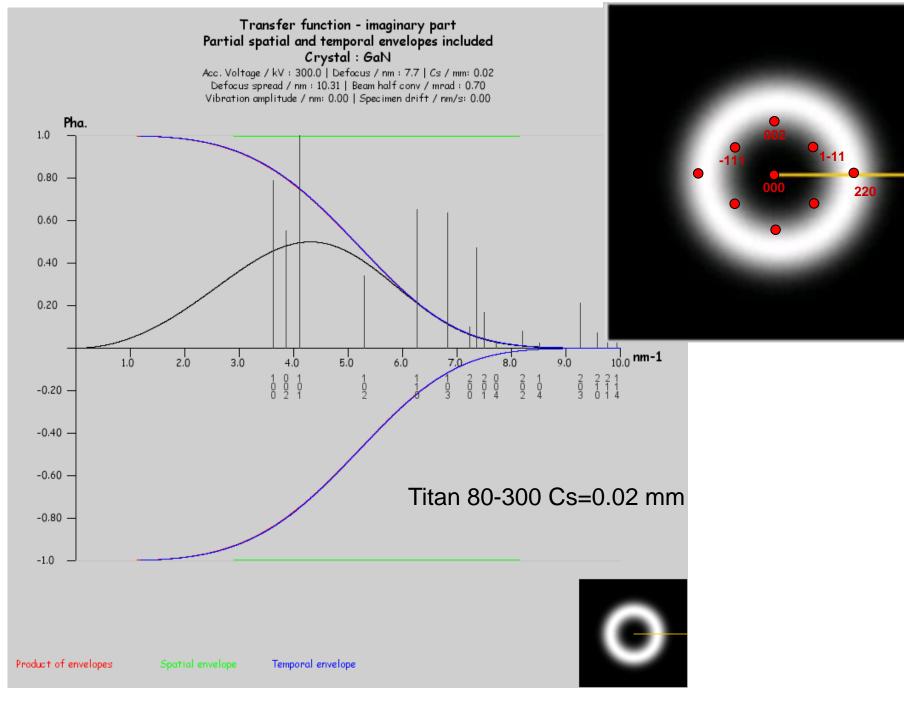






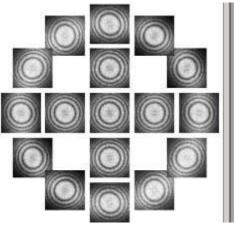


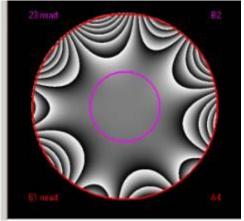
002



Negative-spherical-aberration technique

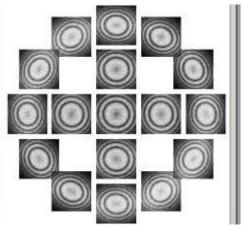
- whit atoms
- Better contrast of light atoms

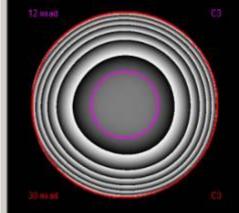




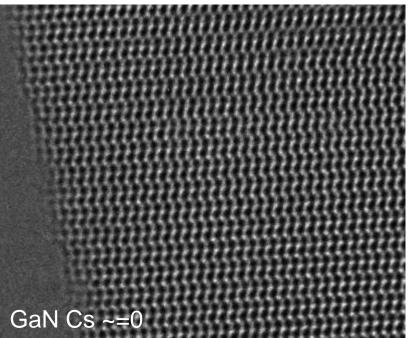
Zemlin 'Tableaus'

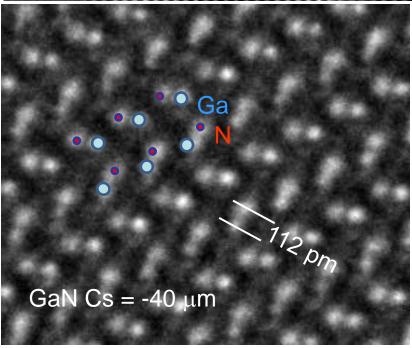
'phase plate'





24 mrad beam tilt





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.

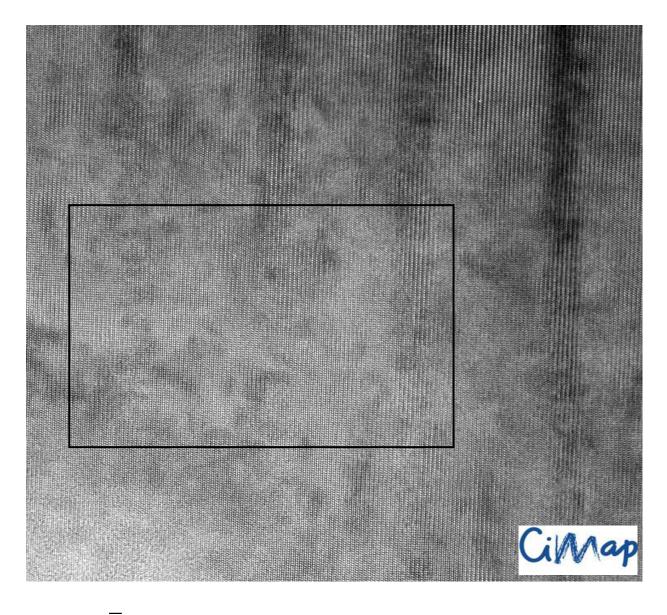
Image simulations for axial HRTEM show that the measured lattice spacing depends locally on the imaging conditions (local foil misalignment and thickness variation) particularly for non-centrosymmetric structures/projection!!

Real word effect:

- surface relaxation
- artefacts due to sample preparation

Errors in processing:

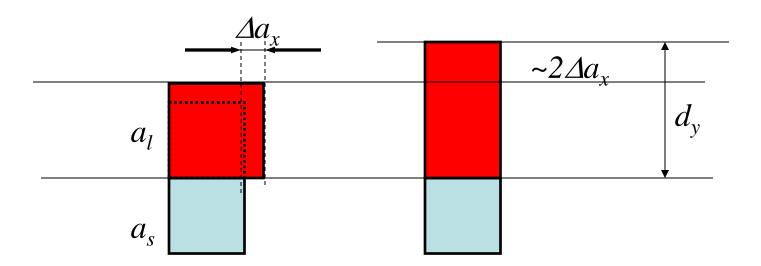
- loss of information
- artifacts due to digitalisation, noise, filtering, interpolation



 $In_{0.15}Ga_{0.8}N/GaN$ pseudomorphic

[1120] zone axis HRTEM image of InGaN (MBE) MQWs.

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 $d_y > a_x$.

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

Chemical composition from Vegard's Law

InGaN, GaN, InN, (ZnTe, CdTe)

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

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

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

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

 a_x - relaxed lattice parameter for composition x

a_{A.} - relaxed lattice parameter for component A

a_B - relaxed latitce parameter for component B

a_s - relaxed lattice parameter for substrate

 $a_B = a_s$

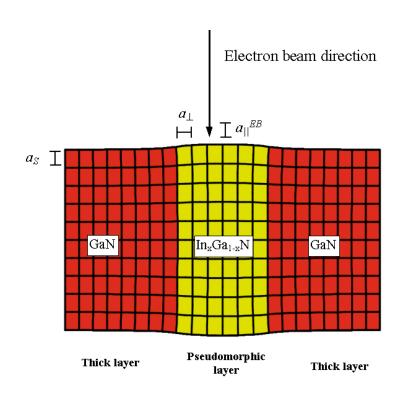
α – relaxation parameter

Local composition:

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

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

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

40%

What is α ?

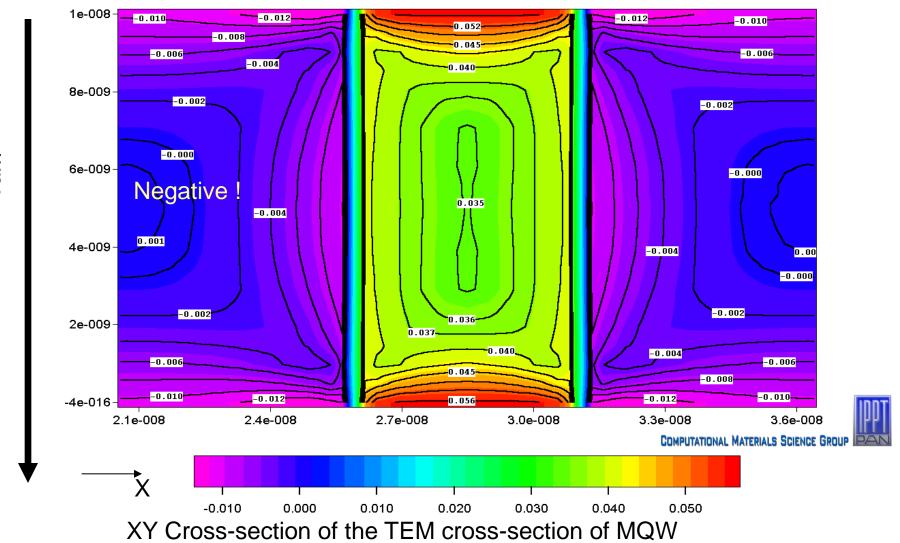
Biaxial or uniaxial?

2D FE modeling

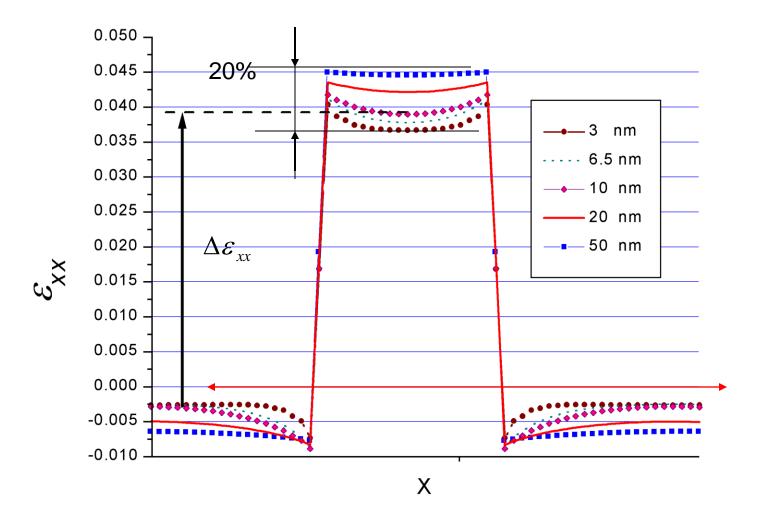
Geometry and border conditions similar as experimental

In function of the Indium concentration and t foil thickness

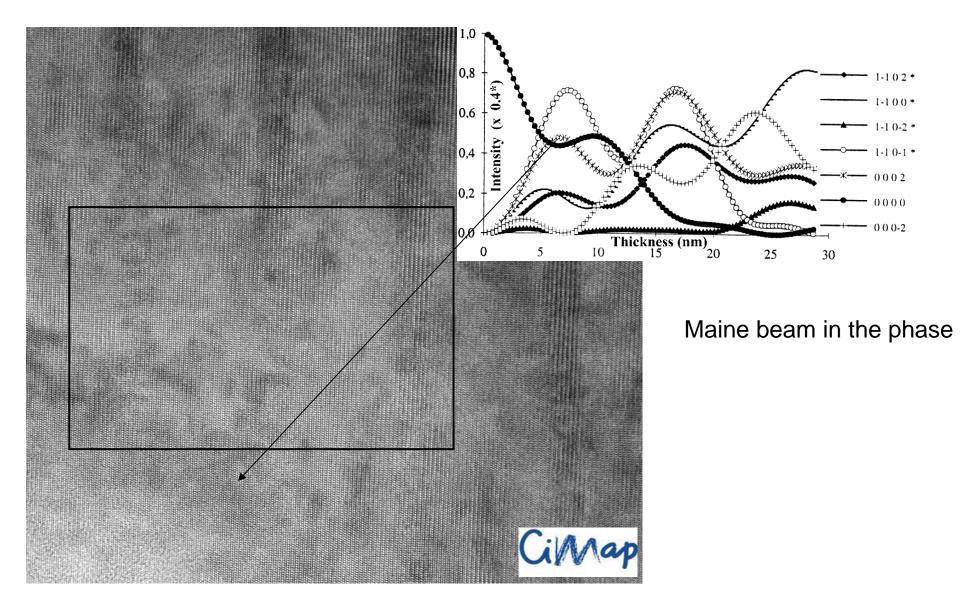
Homogeneous Indium distribution in QW



Calculated distribution $\varepsilon_{xx}(x, y)$ after stress relaxation for In concentration %In=30 (QW/barriers geometry, in relation to GaN)

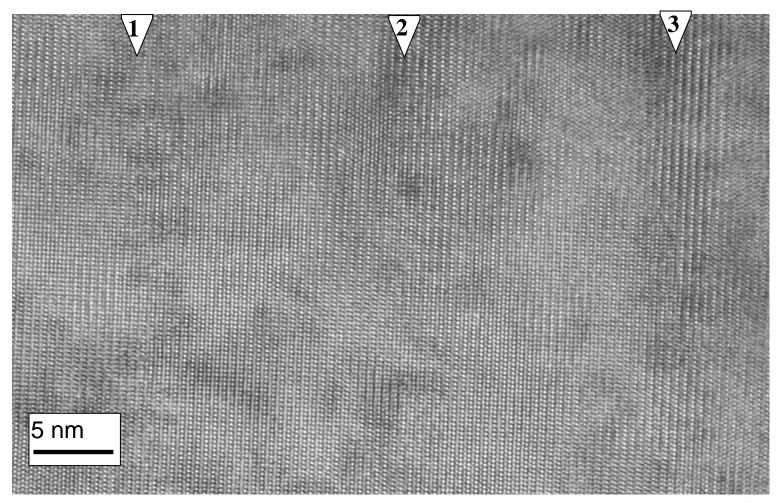


Profiles of $\varepsilon_{xx}(x)$ obtained by averaging $\varepsilon_{xx}(x,y)$ long the y direction for 30% indium concentration and t=5, 10, 15, 30 nm.



[$11\overline{2}0$] zone axis HRTEM image of InGaN (MBE) MQWs .

Thickness 5-10 nm

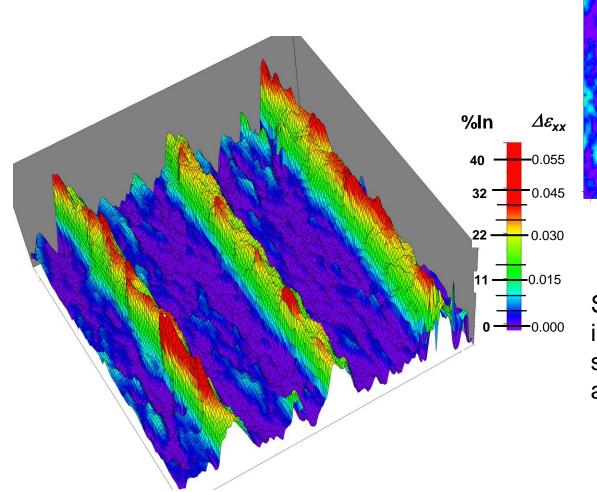


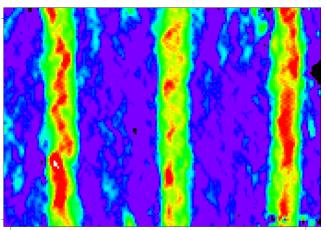


Thickness 5-10 nm

$$\mathcal{E}_{MAX} = 0.030 - 0.038 \rightarrow A = 720 \rightarrow \ln_{Max} 22 - 28\%$$

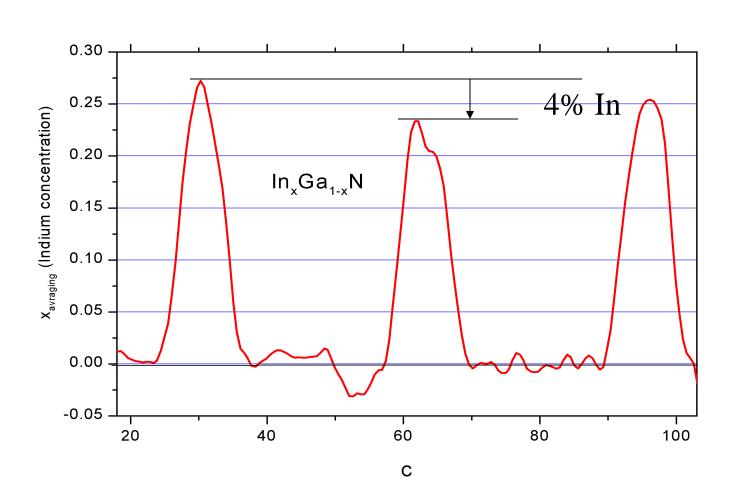
Nominal ~15%



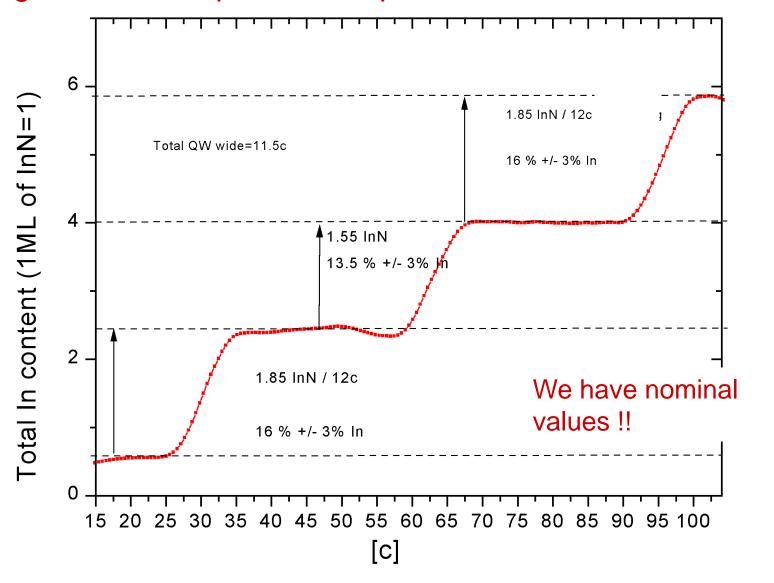


Surface plot of measured indium concentration; colour scales are common for $\Delta \varepsilon_{xx}$ and %In

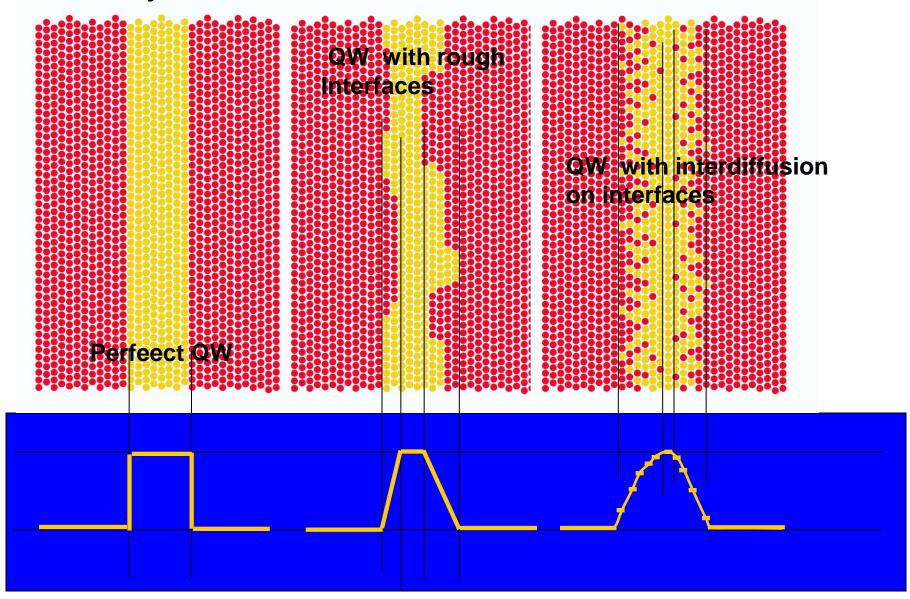
Average profile→ better S/N ratio



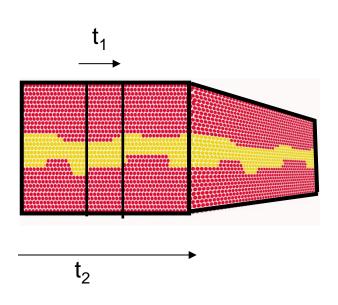
Integration of composition maps → total In content in QW!!

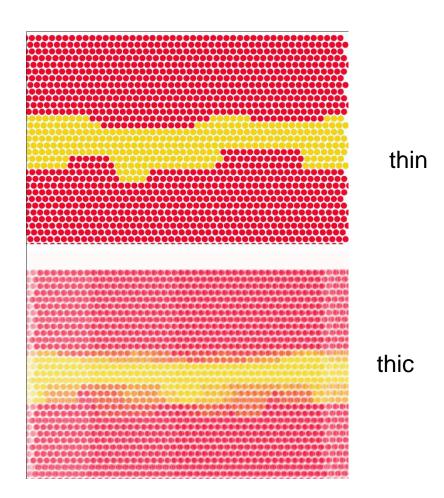


What you want to know about QW

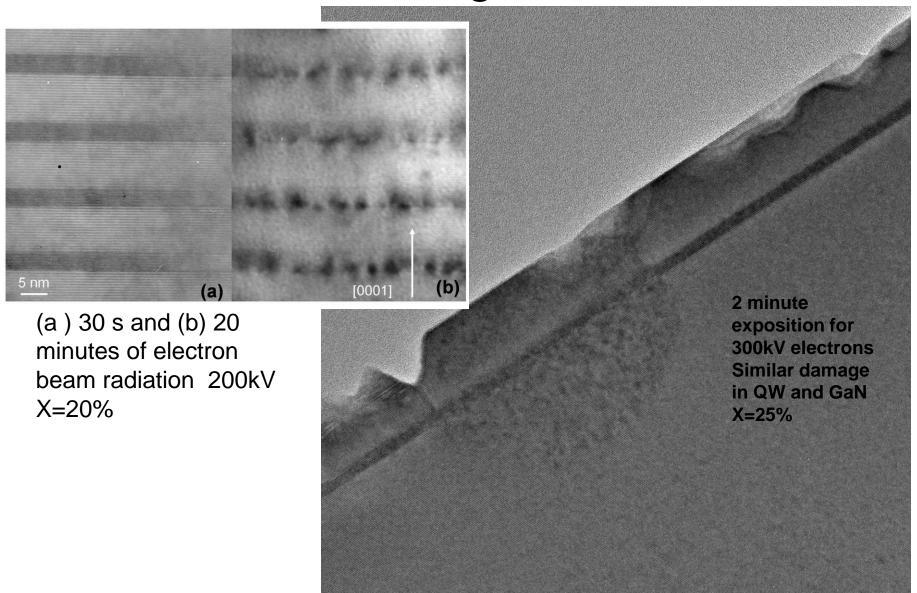


Averaging problem.



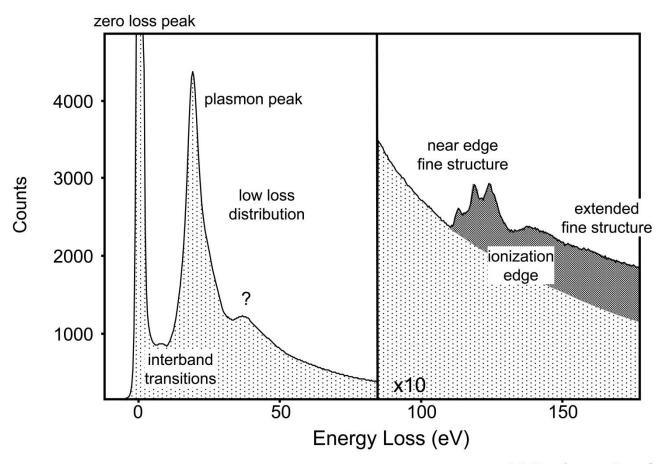


Radiation demage False clusters

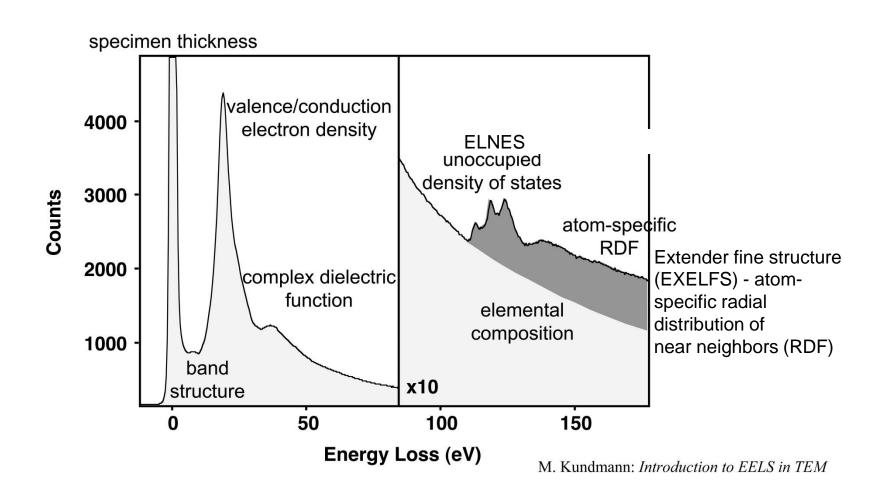


Electron energy loss spectroscopy and mapping the chemical composition

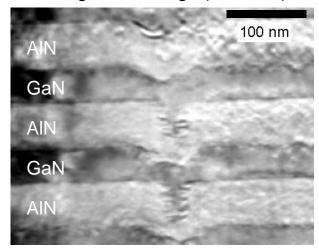
Electrons lose different amounts of energy depending on what they scattered

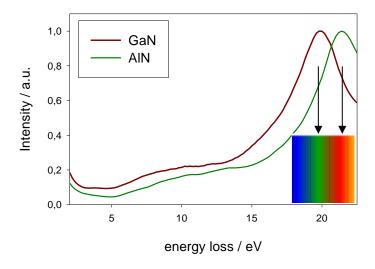


Such information can be obtained on a nanometric scale

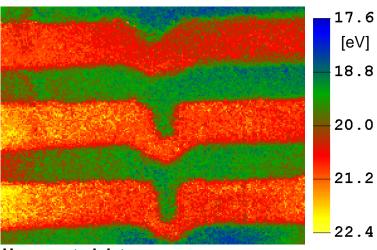


TEM bright field image (diff. area)

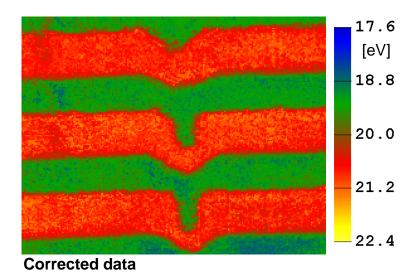




Plasmon position maps

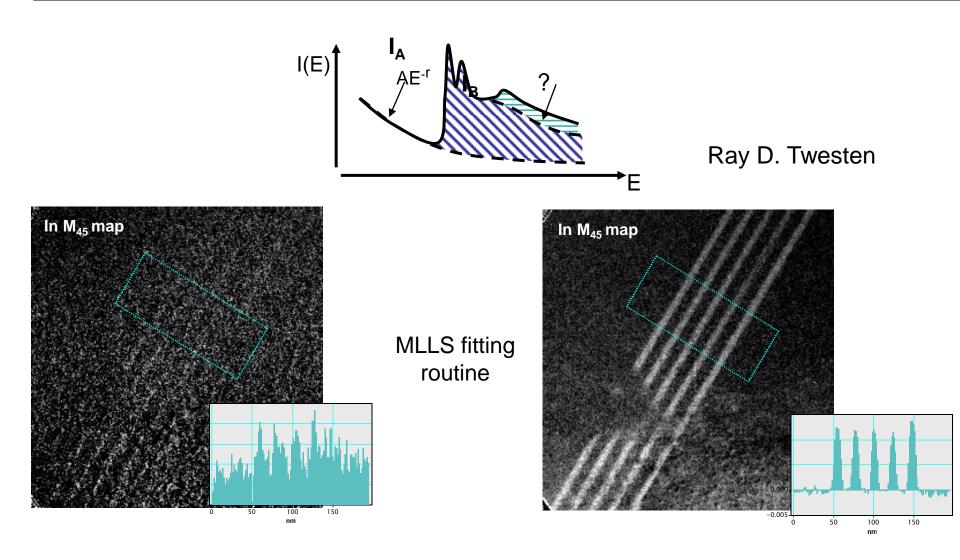


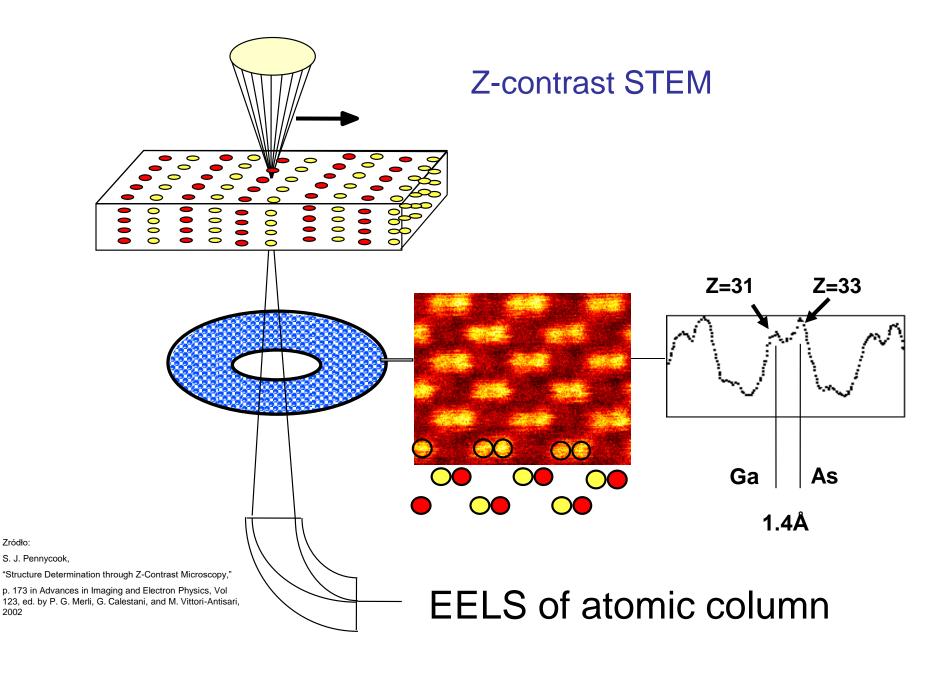
Uncorrected data



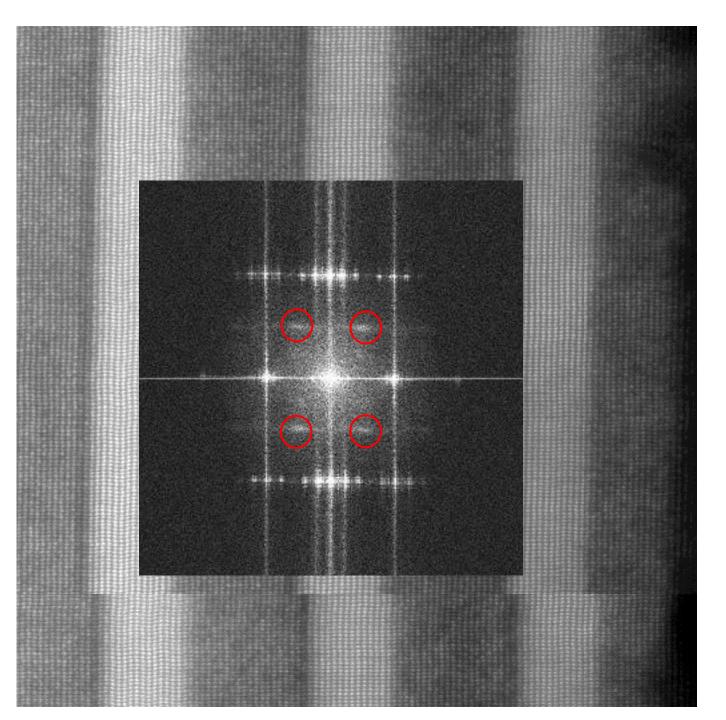
B. Schaffer, G. Kothleitner. W. Grogger published in Ultramicroscopy

Multiple linear least-squares fitting Mapping of Indium M₄₅ Edge



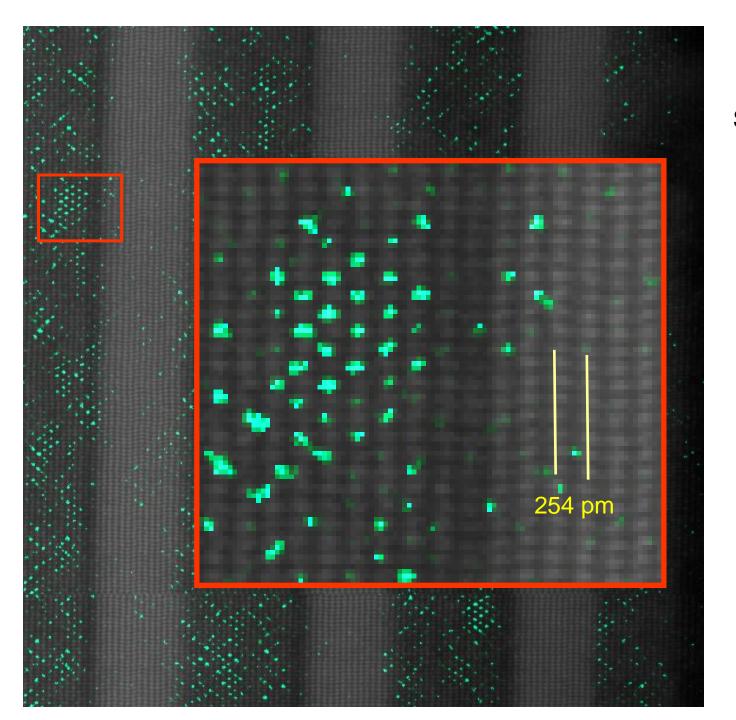


Zródło:

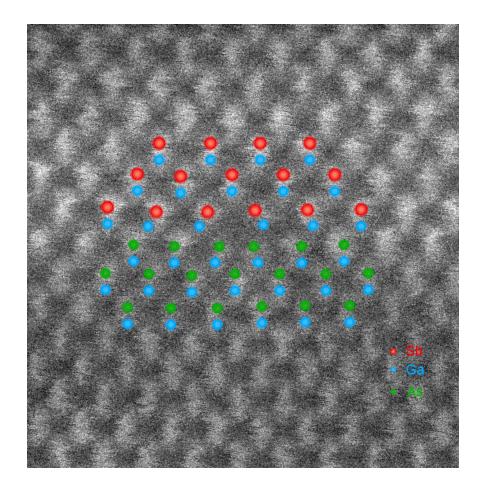


HR-STEM

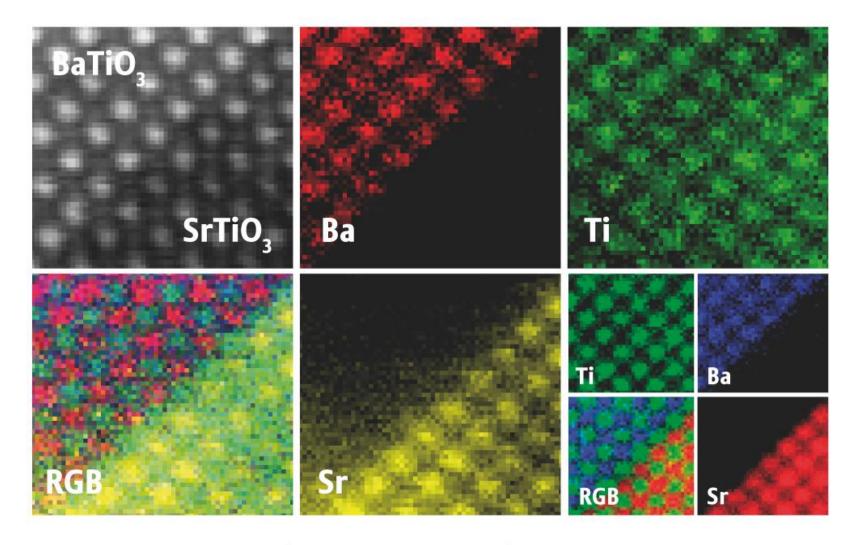
Sample A (N3075)



Sample A (N3075)



Wysokorozdzielcze zdjęcie STEM –HAADA otoczenia rdzenia dyslokacji Lomera z doskonałym rdzeniem 5/7 na granicy GaAs/GaSb .

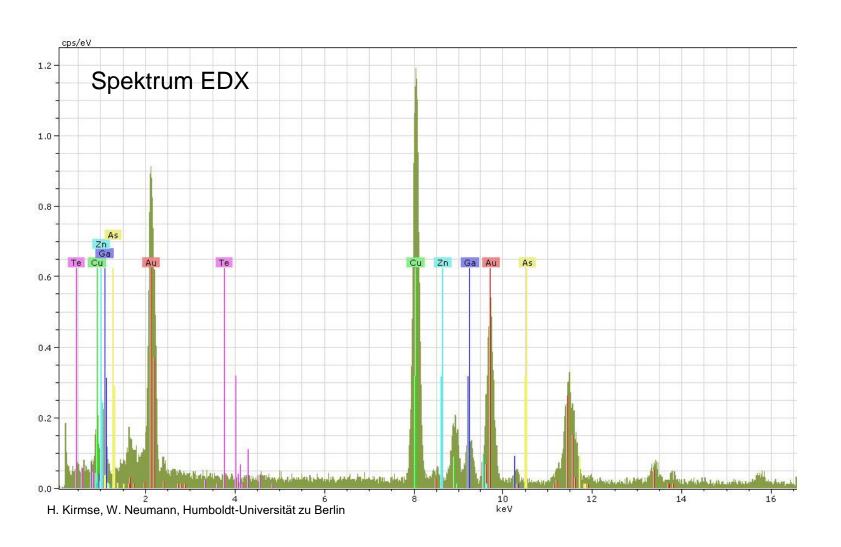


Atomic resolution STEM/EELS map on BaTiO₃/SrTiO₃ interface at 80 and 200 kV acceleration voltage.

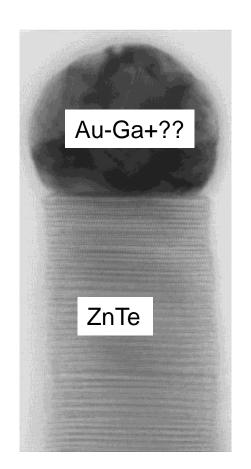
Gatan Image filter Fei Titan 80KV

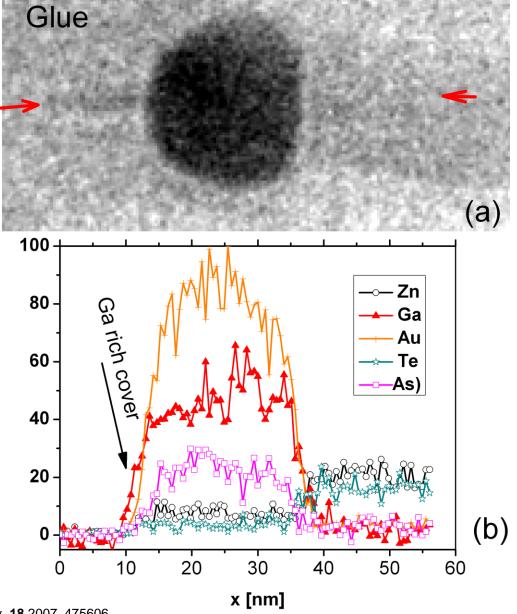
Spectroscopic methods

Characteristic X-ray spectroscopy (EDX)



FEG-EDX
Liniowy profil składu
nanodrut ZnTe/katalizator

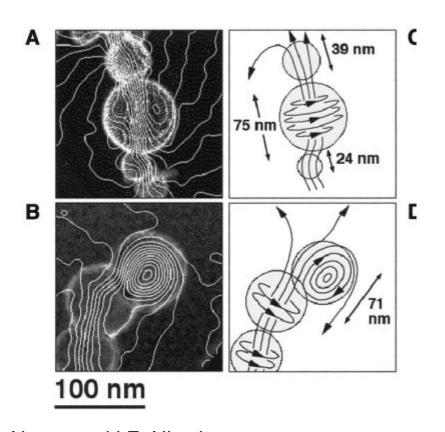




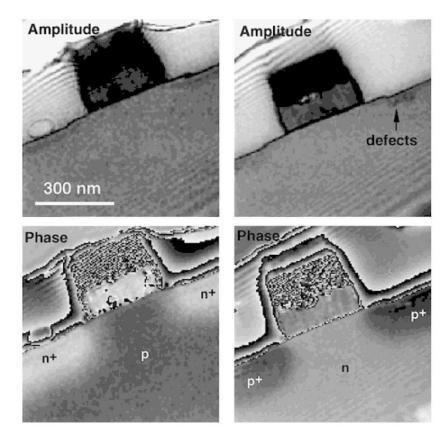
E.Janik at al.. Nanotechnology, 18,2007, 475606,

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

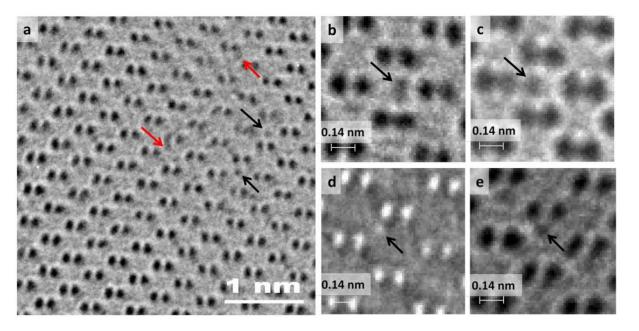
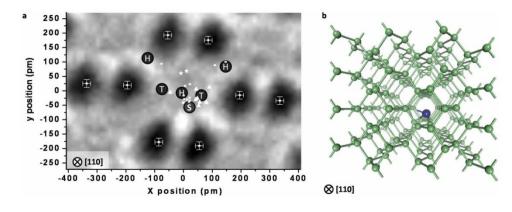
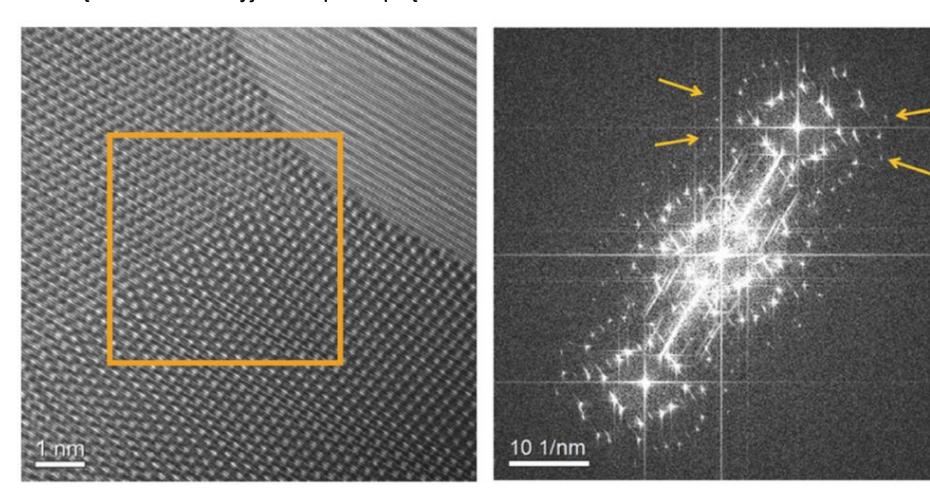


FIG. 1. (Color online) (a) Aberration-corrected images of a thin Ge crystal oriented along the [110] direction [black arrows show occupied interstitial sites, red arrows (dark gray) show column vibrations occurring during the acquisition time]. Magnified areas where an interstitial atom is observed, (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: 4.0×10^4 electrons/nm². Range of focus from -1 to -8 nm.



Kontrast Fazowy
Międzywęzłowy pojedynczy
Atom Ge zobrazowany i
namierzony!!

Holografia elektronowa (wysokiej rozdzielczości) Prążki interferencyjne 54 pm 3 prążki na atom



Prof. M. Lehmann, M. Linck, Dr T. Niermann of TU Berlin, Germany, Prof. Hannes Lichte of TU Dresden, Germany, and Dr B. Freitag of FEI Company, The Netherlands

Problem rzutu i uśredniania

→Tomografia



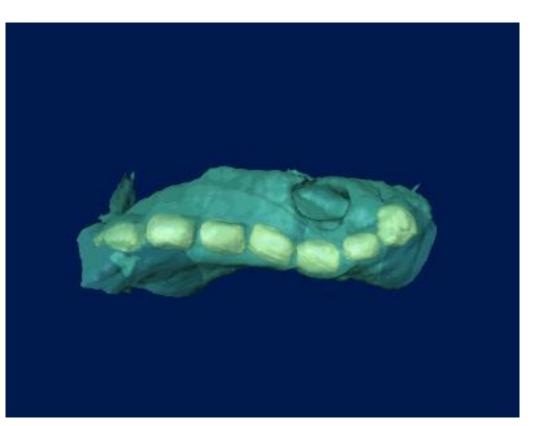


Fig. 3. Surface rendering of the 3D reconstruction of Ta-barrier/Cu-seed sample 1.

Some week 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 mm2 for the best samples preparation protocols
- → Preparation artifacts
- → stress relaxation in a thin foil
- → amorphization, radiation defects by lons during preparation
- → radiation damage with electrons during observation
- → the sample is no longer representative due to
- → jonization and destruction of chemical bonds heating and diffusion of components in poorly conducting samples, knocout 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)