Crystal Growth: Physics, Technology and Modeling

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Lecture 10. Selected methods of transmission electron microscopy
28 April 2025

http://w3.unipress.waw.pl/~stach/cg-2022-23/

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 below 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.

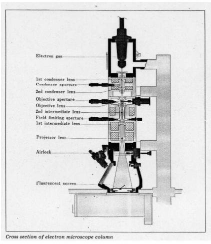
In 1927, Hans Bush showed that magnetic coils can focus an electron beam in the same way as glass lenses to light.

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.

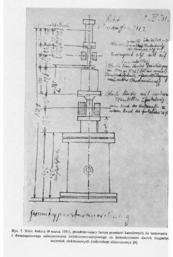
1936 - the first commercial TEM- Metropolitan-Vickers EM1.

Convectional TEM like biological light microscope



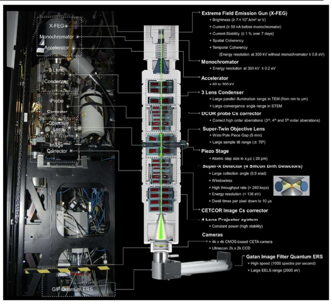
Jeol 2000EX IFAPN from 1989
200KV 0.27 nm Lab6 catode

First experimental TEM

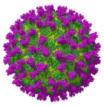


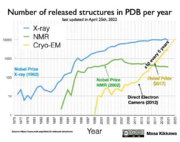
Ernst Ruska and Max Knoll built
the first electron microscope in 1931
(Nobel Prize to Ruska in 1986)

Modern aberation corrected TEM/STEM



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

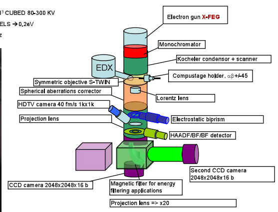




But we will not talk about …..

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

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 .

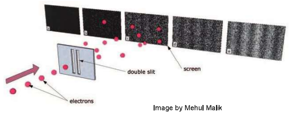
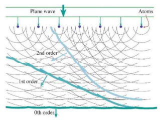
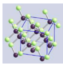
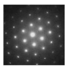


Image by Mehul Malik





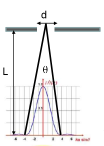
3D crystal



Electron dyfractogram

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- Diffraction 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

$$d\ sin\theta = 1.22\lambda \qquad \theta \cong 1.22\frac{\lambda}{d}$$

Resolution limit due to Diffraction

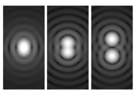
According to the Rayleigh Criterion, two point sources cannot be resolved if their separation is less than the radius of the Airy disk. The Airy disk is named for the English astronomer Sir George Biddell Airy, who served as the seventh Astronomer Royal from 1835-1881

Abbe Resolution = 2λ/NA2 1873

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

refined by Lord Rayleigh in 1896

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



For electrons n=1, and small angles

So for better resolution θ↑ and λ↓

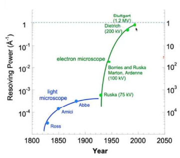
wavelength of electrons

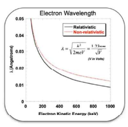
L. De Broglie 1924
Phil. Mag.,47 446
λ=h/p =h/mv

h Planc constant
p the momentum of the particle

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

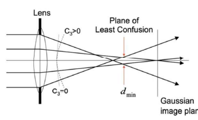
Accelartaion voltage	λ [nm]	λ (nm) relatywistic	% of c
100	0,00386	0,00370	0,54%
200	0,00273	0,00251	0,69%
300	0,00223	0,00197	0,77%





Resolution limit due to spherical aberration

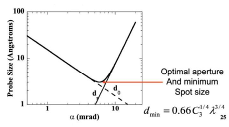
C_3 spherical aberration coefficient of objective lens



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 → d_{min}= 0.5 nm

Resolution limit due to spherical aberation minimum bem spot in STEM



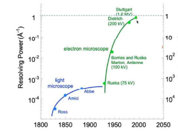
Optimal aperture
And minimum
Spot size

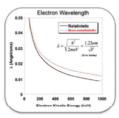
$$d_{\min} = 0.66C_3^{1/4}\lambda^{3/4}$$

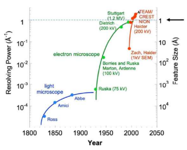
For a rough estimate of the optimum aperture size, convolve blurring terms
-If the point spreads were gaussian, we could add in quadrature:

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

Diffraction+abberations







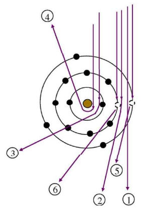
Aberration correction technology
Sub angstrom microscopy
Resolution in pm

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

After David A. Muller , Nature Materials 2009, https://www.paradim.org/2021_CU_SS

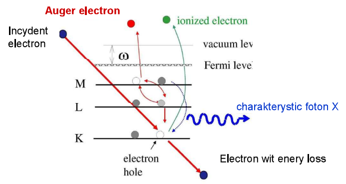
The interaction of high-energy electrons with an atom

- energy 30-1000 KeV

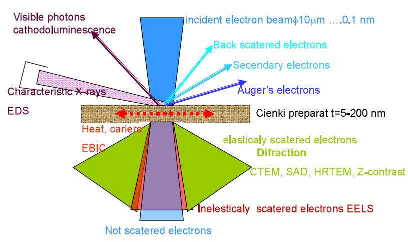


1. Not scattered electron
2. Low angle elastic scattering
3. High angle elastic scattering
4. Backward scatter
5. Inelastic scattering on outer shell
6. Inelastic scattering on inner shell

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 10^4 biger then 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

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

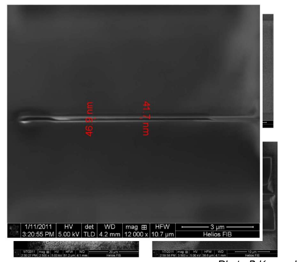
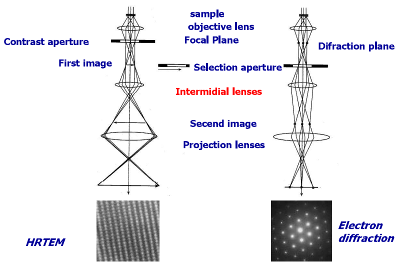
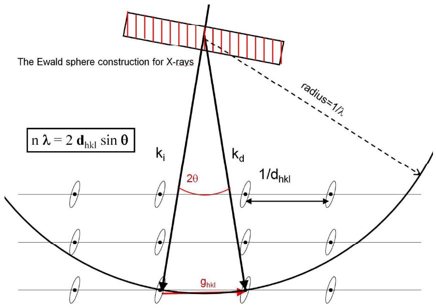


Photo B.Kurowska M.Klepka

Basic Modes of Operation of the TEM microscope

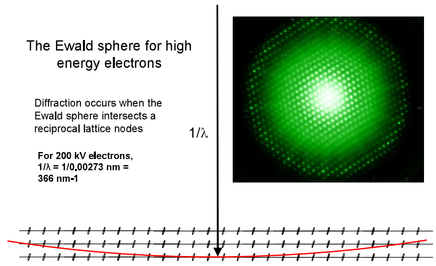




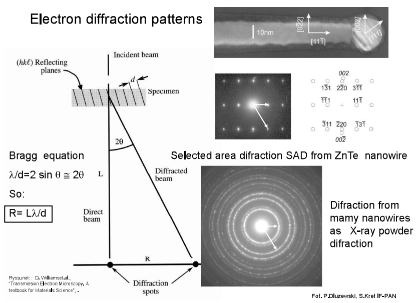
The Ewald sphere for high energy electrons

Diffraction occurs when the Ewald sphere intersects a reciprocal lattice nodes

For 200 kV electrons, 1/λ = 1/0,00273 nm = 366 nm-1



Electron diffraction patterns



Bragg equation

$\lambda/d=2 \sin\theta \cong 2\theta$

So:

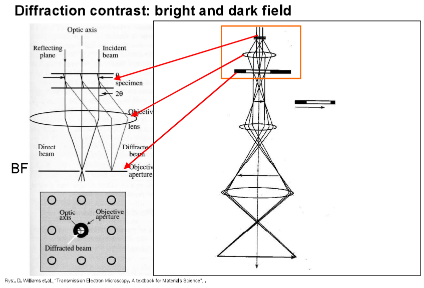
$R = L\lambda/d$

Selected area difraction SAD from ZnTe nanowire

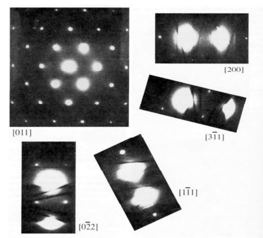
Diffraction from mamy nanowires as X-ray powder diffraction

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

Diffraction contrast: bright and dark field



Two-beam conditions for Si near 001 zone axis



Diffraction contrast: bright and dark field

Pd crystallites 5-15 nm

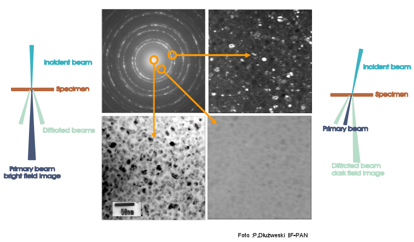
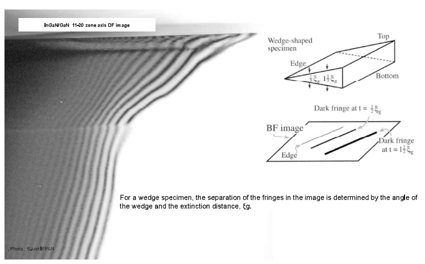


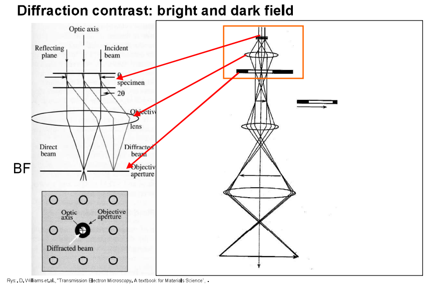
Foto :P.Dluzewski IF-PAN

PERFECT CRYSTALS → Thickness contours depend also of material



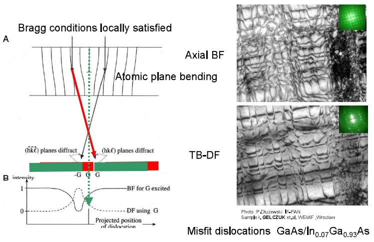
For a wedge specimen, the separation of the fringes in the image is determined by the angle of the wedge and the extinction distance, ξg.

Diffraction contrast: bright and dark field



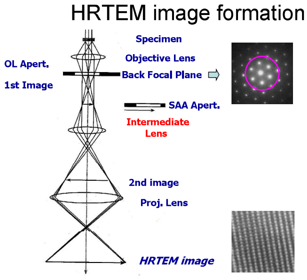
CRYSTAL WITH DEFECTS

Intuitive description of diffraction contrast of dislocation



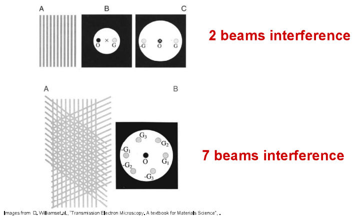
Misfit dislocations GaAs/$In_{0.07}Ga_{0.93}As$

HRTEM image formation



HRTEM image formation

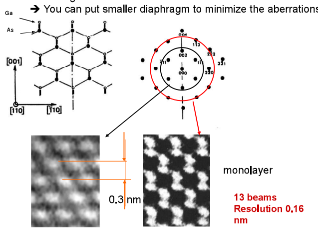
beams selection of on the diffraction pattern



HRTEM GaAs <110>

Don't forget about aberration of the lenses and MTF of the microscope

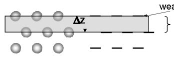
→ You can put smaller diaphragm to minimize the aberrations



HRTEM Simulation:

Stage 1 → high-energy electrons in a crystal

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



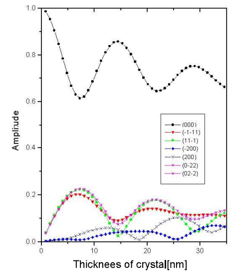
$$\Psi_{n+1}(\vec{r}) = [\Psi_n(\vec{r}) q_{n+1}(\vec{r})] * p_{n+1}(\vec{r})$$

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

Slice "transparency" function (n+1)

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

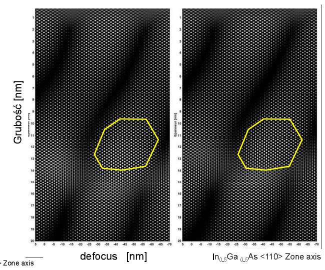
Propagator



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

GaAs incident beam direction <110>

Simulated HRTEMcontrast at 200 kV LaB_6



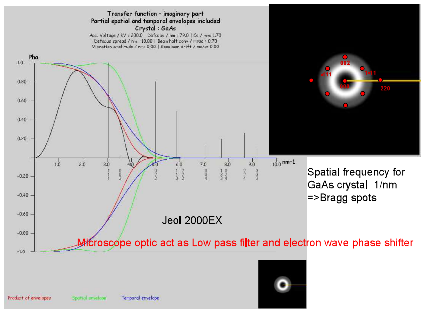
$In_{0.3}Ga_{0.7}As$ <110> Zone axis

HRTEM SIMULATION: STAGE II

→ electrons in the optical system of the microscope

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

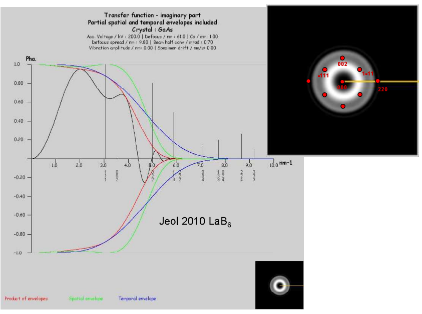
It takes into account the aberrations of the microscope optical system
→
Contrast Transfer Function (CTF) , Contrast transfer function



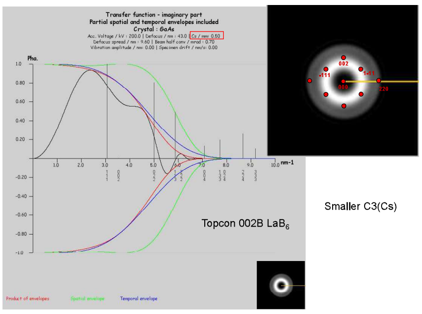
Spatial frequency for GaAs crystal 1/nm =>Bragg spots

Jeol 2000EX

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

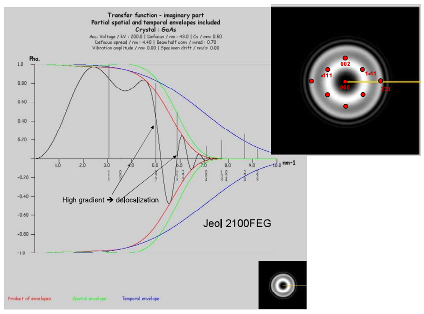


Jeol 2010 LaB_6



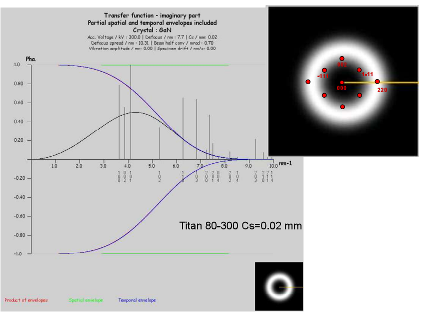
Topcon 002B LaB_6

Smaller C3(Cs)



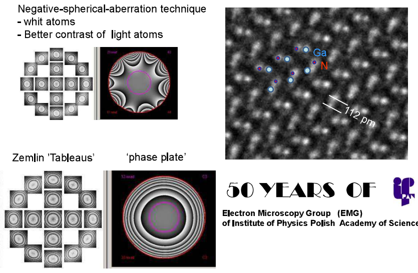
High gradient → delocalization

Jeol 2100FEG



Titan 80-300 Cs=0.02 mm

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



Zemlin 'Tableaus' 'phase plate'

24 mrad beam tilt

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 :

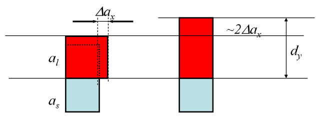
The positions of the intensity maxima may correspond to the location of the atomic columns or tunnels between lattice sites or neither of them. But this relation is constant in the whole analysed image .

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
- artifacts due to digitalisation, noise, filtering, interpolation

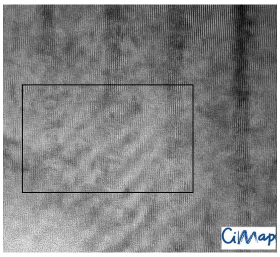
Pseudomorphic growth, tetragonal distortion, biaxial stress



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 $d_y > a_x$.

$$d_z = \alpha \Delta a_x + a_s$$

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



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

pseudomorphic

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

Chemical composition from Vegard`s Law

InGaN , GaN, InN, (ZnTe, CdTe)

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

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

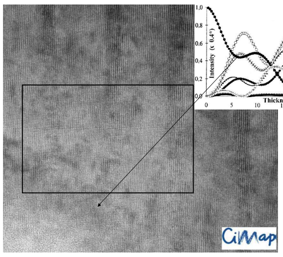
$\varepsilon = (d_y - a_s)/a_s = \alpha(a_s - a_s)/a_s$

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

a_x - relaxed lattice parameter for composition x
a_A - relaxed latitce 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:

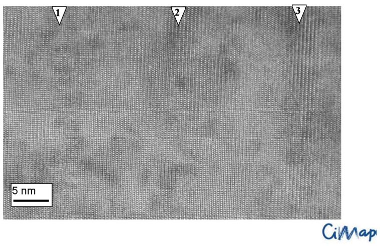
$$x(x,y) = \frac{a_s - a_x(x,y)}{a_A - a_S} = \frac{\Delta_{sx}}{\Delta_{AS}} = \frac{\varepsilon(x,y) a_s}{\alpha \Delta_{AS}}$$



Maine beam in the phase

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

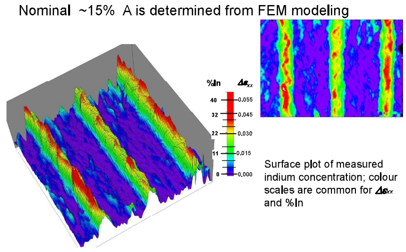
Thickness 5-10 nm



Thickness 5-10 nm

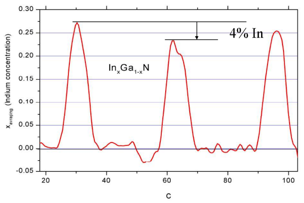
ε_{MAX}=0.030-0.038 ➔ A=720 ➔In_{Max}22-28%

Nominal ~15% A is determined from FEM modeling

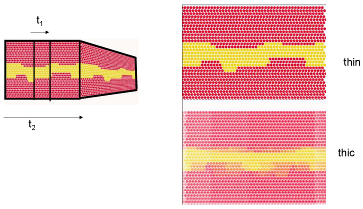


Surface plot of measured indium concentration; colour scales are common for Δa_{sx} and %In

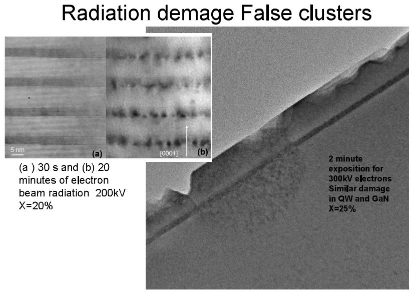
Average profile ➔ better S/N ratio



Averaging problem.

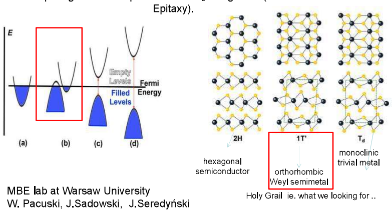


Radiation demage False clusters



(a) 30 s and (b) 20 minutes of electron beam radiation 200kV X=20%

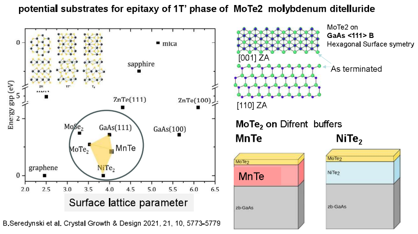
2D transition metal dichalcogenides (TMDs) – an attempt to grow the 1T' phase of $MoTe_2$ using MBE (Molecular Beam Epitaxy).



MBE lab at Warsaw University
W. Pacuski, J.Sadowski, J.Seredyński

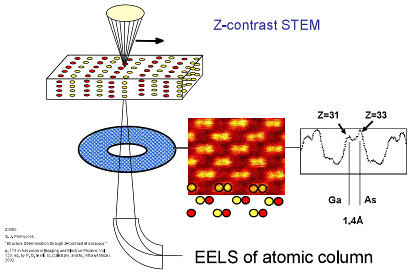
Holy Grail ie. what we looking for ..

potential substrates for epitaxy of 1T' phase of MoTe2 molybdenum ditelluride

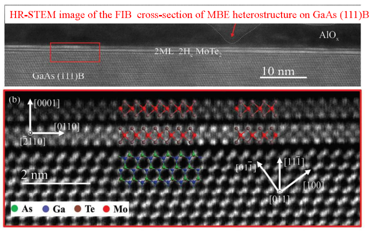


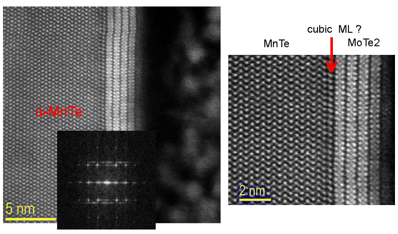
B.Seredynski et al. Crystal Growth & Design 2021, 21, 10, 5773-5779

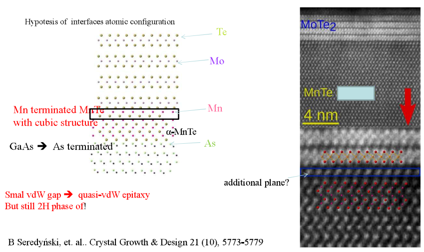
Z-contrast STEM



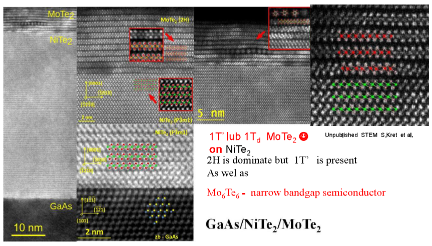
EELS of atomic column

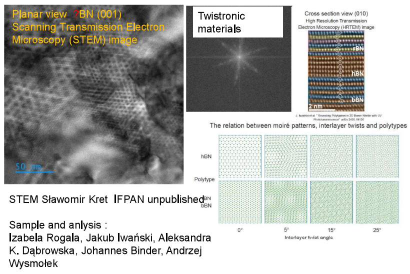


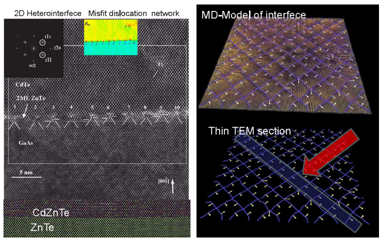


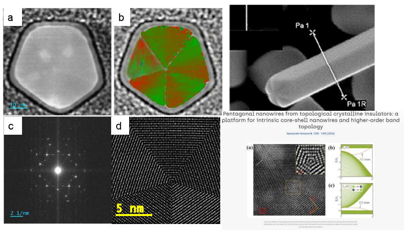


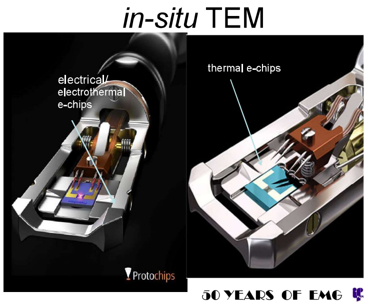
B Seredyński, et. al.. Crystal Growth & Design 21 (10), 5773-5779

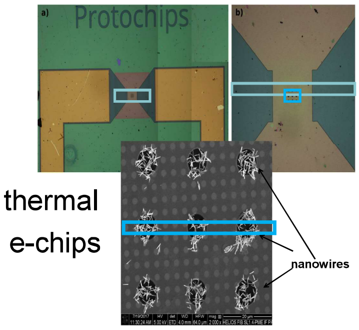

MoTe2
NiTe2
GaAs
10 nm
5 nm
2 nm
1T' lub 1Td MoTe2
on NiTe2
2H is dominate but 1T' is present
As wel as
Mo6Te6 - narrow bandgap semiconductor
Unpublished STEM S.Kret et al.
GaAs/NiTe2/MoTe2

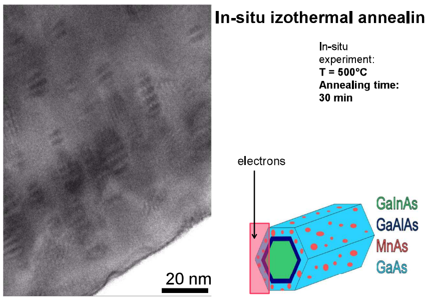

Planar view hBN (001)
Scanning Transmission Electron Microscopy (STEM) image
Twistronic materials
The relation between moiré patterns, interlayer twists and polytypes
STEM Sławomir Kret IFPAN unpublished
Sample and anlysis :
Izabela Rogala, Jakub Iwański, Aleksandra K. Dąbrowska, Johannes Binder, Andrzej Wysmołek

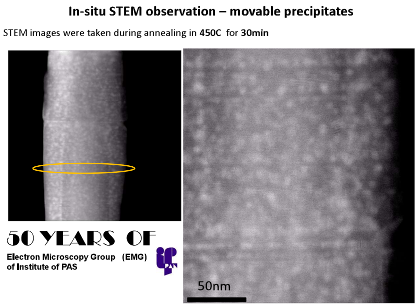

2D Heterointerface Misfit dislocation network
MD-Model of interface
Thin TEM section
CdZnTe
ZnTe
5 nm

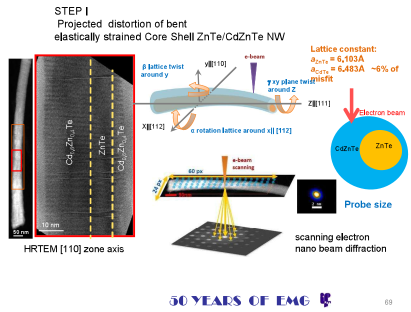

a
b
c
d
5 nm
Pentagonal nanowires from topological crystalline insulators: a platform for intrinsic core-shell nanowires and higher-order band topology

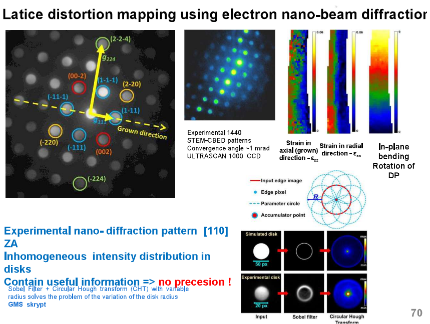

in-situ TEM
electrical/ electrothermal e-chips
thermal e-chips
Protochips
50 YEARS OF EMG

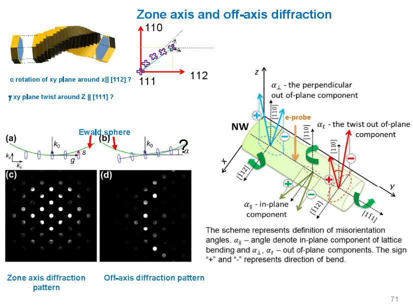

Protochips
a)
b)
thermal e-chips
nanowires

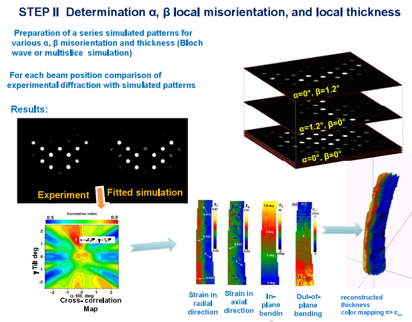

In-situ izothermal annealin
In-situ experiment:
T = 500°C
Annealing time:
30 min
electrons
GaInAs
GaAlAs
MnAs
GaAs
20 nm

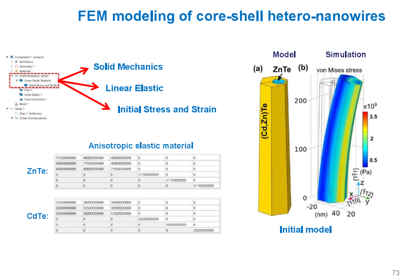

In-situ STEM observation – movable precipitates
STEM images were taken during annealing in 450C for 30min
50 YEARS OF
Electron Microscopy Group (EMG) of Institute of PAS
50nm

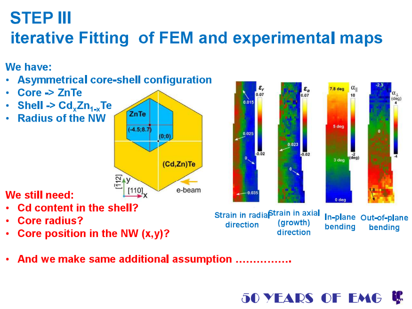

STEP I
Projected distortion of bent elastically strained Core Shell ZnTe/CdZnTe NW
Lattice constant:
a_{ZnTe} = 6,103A
a_{CdTe} = 6,483A ~6% of misfit
Electron beam
CdZnTe
ZnTe
Probe size
HRTEM [110] zone axis
scanning electron nano beam diffraction
50 YEARS OF EMG

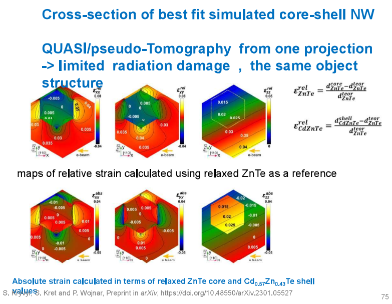

Latice distortion mapping using electron nano-beam diffraction
Experimental 1440 STEM-CBED patterns
Convergence angle ~1 mrad
ULTRASCAN 1000 CCD
Strain in axial (grown) direction
Strain in radial direction
In-plane bending
Rotation of DP
Experimental nano- diffraction pattern [110] ZA
Inhomogeneous intensity distribution in disks
Contain useful information => no precesion !
70

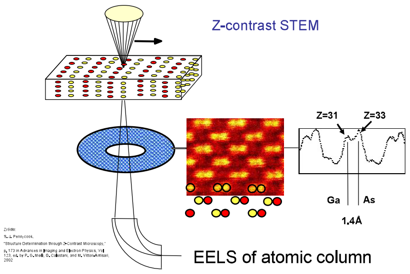

Zone axis and off-axis diffraction
110
112
111
Ewald sphere
NW
The scheme represents definition of misorientation angles.
Zone axis diffraction pattern
Off-axis diffraction pattern
71


STEP II Determination α, β local misorientation, and local thickness
Preparation of a series simulated patterns for various α, β misorientation and thickness (Bloch wave or multislice simulation)
For each beam position comparison of experimental diffraction with simulated patterns
Results:
Experiment
Fitted simulation
Cross- correlation Map
Strain in radial direction
Strain in axial direction
In-plane bendin
Out-of-plane bending
reconstructed thickness


FEM modeling of core-shell hetero-nanowires
Solid Mechanics
Linear Elastic
Initial Stress and Strain
Anisotropic elastic material
ZnTe:
CdTe:
Model
Simulation
von Mises stress
Initial model
73

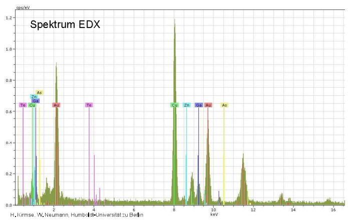

STEP III
iterative Fitting of FEM and experimental maps
We have:
Asymmetrical core-shell configuration
Core -> ZnTe
Shell -> $Cd_xZn_{1-x}Te$
Radius of the NW
We still need:
Cd content in the shell?
Core radius?
Core position in the NW (x,y)?
And we make same additional assumption ....
Strain in radial direction
Strain in axial (growth) direction
In-plane bending
Out-of-plane bending
e-beam
50 YEARS OF EMG

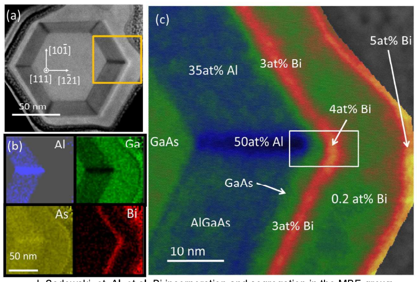

Cross-section of best fit simulated core-shell NW
QUASI/pseudo-Tomography from one projection
-> limited radiation damage , the same object structure
maps of relative strain calculated using relaxed ZnTe as a reference
Absolute strain calculated in terms of relaxed ZnTe core and $Cd_{0.57}Zn_{0.43}Te$ shell values
75



Spectroscopic methods

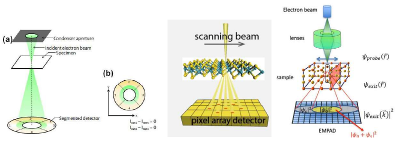
Characteristic X-ray spectroscopy (EDX)





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)

differential phase contrast, 4D STEM , and ptychography

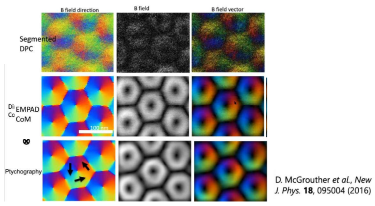


Central beam deflection
Due to magnetic /electric fields
Difference between segments
give signal for each pixel

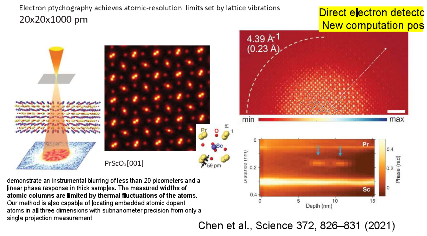
For every beam position
diffraction pattern is captured
Separated disks

Overlapping disks !
Phase information can be
captured for spots
corresponding to spatial frequencies
beyond the limitations of the lens

Magentic Skyrmions in FeGe after field cooling to 94

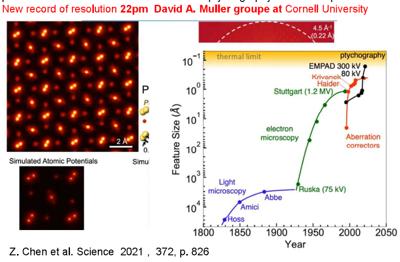


D. McGrouther et al., New J. Phys. 18, 095004 (2016)



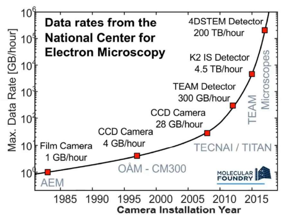
Chen et al., Science 372, 826–831 (2021)

Ultimate lateral resolution – better than the thermal vibration of atoms with a perovskite – PrScO3 - structure. Multi-Slice ptychography for thic sample
New record of resolution 22pm David A. Muller groupe at Cornell University



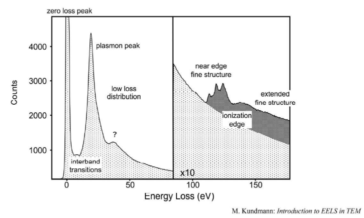
Z. Chen et al. Science 2021 , 372, p. 826

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

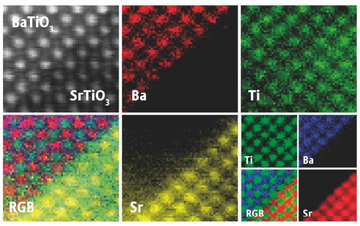


Electron energy loss spectroscopy and mapping the chemical composition

Electrons lose different amounts of energy depending on what they scattered



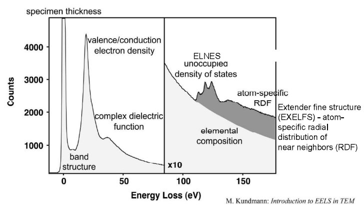
M. Kundmann: Introduction to EELS in TEM



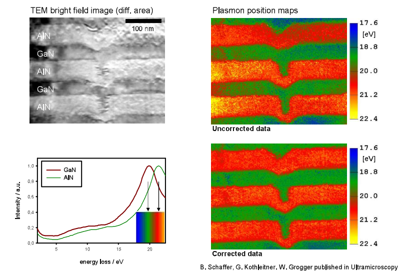
Atomic resolution STEM/EELS map on $BaTiO_3/SrTiO_3$ interface at 80 and 200 kV acceleration voltage.

Gatan Image filter Fei Titan 80KV

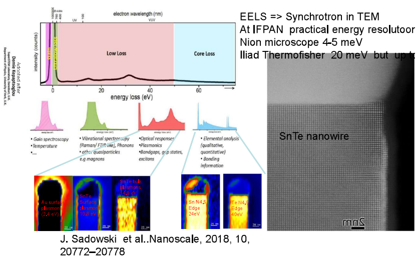
Such information can be obtained on a nanometric scale



M. Kundmann: Introduction to EELS in TEM



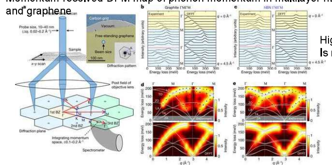
B. Schaffer, G. Kothleitner, W. Grogger published in Ultramicroscopy



EELS => Synchrotron in TEM
At IFPAN practical energy resolutoor
Nion microscope 4-5 meV
Iliad Thermofisher 20 meV but up t

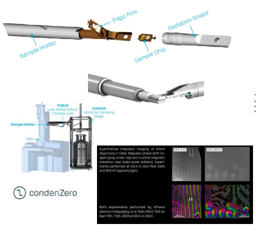
J. Sadowski et al..Nanoscale, 2018, 10, 20772–20778

Momentum-resolved DPM map of phonon momentum in multilayer hBN and graphene

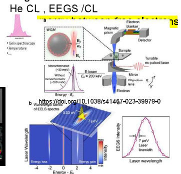


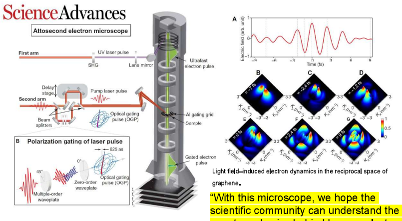
High Energy resolu
Is needed

Pseudocolor intensity maps of multilayer hBN (left) and monolayer graphene (right), constructed from the
measured EELS spectra, shown with the simulated phonon dispersion curves (solid lines).
a good agreement between the measured and calculated dispersion of phonons.



EBIC
Hall effect
Superconductors electrical mesurm
Magnetic fields visualization
He CL , EEGS /CL

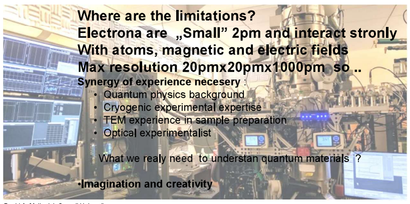




Light field–induced electron dynamics in the reciprocal space of graphene.

"With this microscope, we hope the scientific community can understand the quantum physics behind how an electron behaves and how an electron moves."

Hui et al., Sci. Adv. 10, eadp5805 (2024) 21 August 2024



Where are the limitations?
Electrona are „Small" 2pm and interact stronly
With atoms, magnetic and electric fields
Max resolution 20pmx20pmx1000pm so ..

Synergy of experience necesery :

- Quantum physics background
- Cryogenic experimental expertise
- TEM experience in sample preparation
- Optical experimentalist

What we realy need to understan quantum materials ?

•**Imagination and creativity**

David A. Muller lab Cornell University

•**Financial suport investyment/maintance/operationmal cost**

•**Dedicated TEM not useful for standard characterization**

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 Ions during preparation
➔ radiation damage with electrons during observation

➔ the sample is no longer representative due to
➔I 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)