Lectures:

Prof. Janne Ruokolainen, Dr. Hua Jiang, Dr. Jani Seitsonen, Dr. Ramzy Abdelaziz, Prof. Peter Liljeroth, Dr. Lide Yao

Schedule

17. 1. Introduction & Nanomicroscopy center (JR)
24. 1. TEM Basics (JR)
31. 1. Advanced TEM 1 (Hua)
7. 2. Advanced TEM 2 (Hua)
14. 2. Advanced TEM 3 (Hua)
21. 2. *no lecture (exam period at Aalto)*
28. 2. Cryo-TEM and Soft matter Sample preparation (JR)
7. 3. 3D-TEM-Tomography (Jani)
14. 3. STM/AFM (Peter)
21. 3. SEM (Ramzy)
28. 3. FIB and Sample preparation (Lide)

Summary:
Intro, Basic TEM, Cryo TEM ~ 3 lectures
Advanced TEM 2-3 lectures
(High resolution TEM and STEM, diffraction, spectroscopy EDX, EELS)
STM/AFM
FIB/sample preparation
SEM
Tomography

Additional Literature: (optional)

Book 1: *Transmission electron microscopy Basics I (David William and Barry Carter) 2nd edition*

Book 2: *G.H. Michler "Electron microscopy of polymers" (TEM, SEM, AFM..)*

Book 3: *A practical Guide to Tramsmission Electron Microscopy (Zhiping Luo)*

1

T E M —

the Transmission Electron Microscopy,

a Powerful Tool for Imaging, Diffraction and Spectroscopy in Materials Science

Lecture -- III

Dr. Hua Jiang

Hua.Jiang@aalto.fi

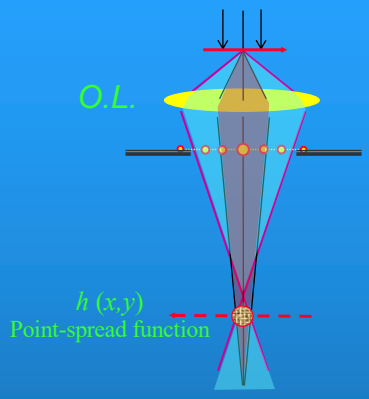
Nanomicroscopy Center, Aalto University

14 - 02 - 2023

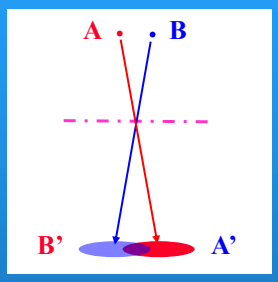
(to continue – Part 3)

2

A brief review: HR(T)EM image formation



$$g(x,y) = f(x,y) \otimes h(x,y)$$



f (x,y)

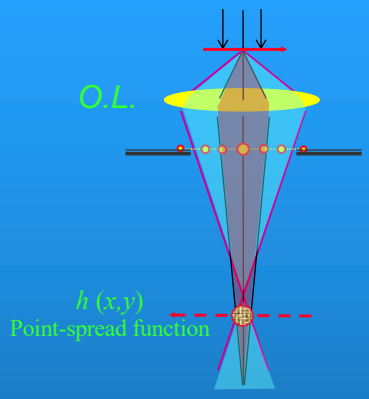
h (x,y)

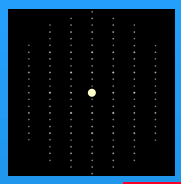
g (x,y)

Point-spread function (**PSF**) *h(x,y)* describes the lens performance in the real space.

3

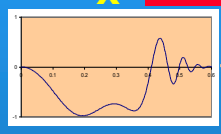
A brief review: HR(T)EM image formation





Diffraction:
the higher angle
the higher resolution

X **multiplied**



Lens CTF
higher angle

II

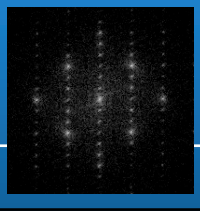


Image FFT
high resolution
information lost

Contrast transfer function (**CTF**) describes the lens performance in the reciprocal splace.

4

A brief review: HR(T)EM image formation

- The general concept:

$$g(x,y) = f(x,y) \otimes h(x,y)$$

- Simplifications – WPOA (*thin sample, weak phase object*):

$$I(x,y) = 1 + 2\sigma V_t(x,y) \otimes \mathcal{F}\{\sin \chi(\mathbf{u})\}$$

- Optimized imaging condition

$$\sin \chi(\mathbf{u}) \approx -1 \quad \rightarrow \quad \chi(\mathbf{u}) = \pi \Delta f \lambda u^2 + \frac{1}{2}\pi Cs \lambda^3 u^4$$

- Scherzer focus condition and the Structure Image:

$$I(x,y) = 1 - 2\sigma V_t(x,y) \quad \leftarrow \quad \Delta f = -1.2(Cs\lambda)^{\frac{1}{2}}$$

1. HRTEM image can be directly interpretable at an optimized imaging condition.
2. At arbitrary conditions, the image contrast need to be interpreted with care.

5

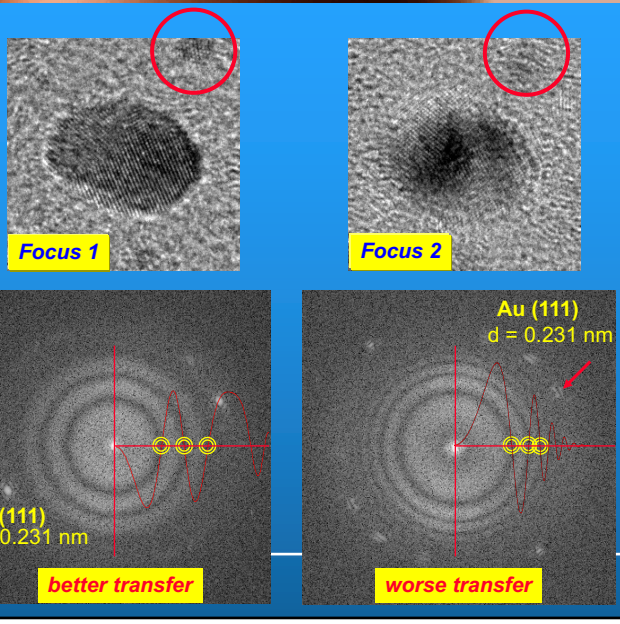
Understanding CTF

CTF --- Contrast transfer function

$$\sin \chi(\mathbf{u}) = \sin\left(\pi \Delta f \lambda u^2 + \frac{1}{2}\pi Cs \lambda^3 u^4\right)$$

6

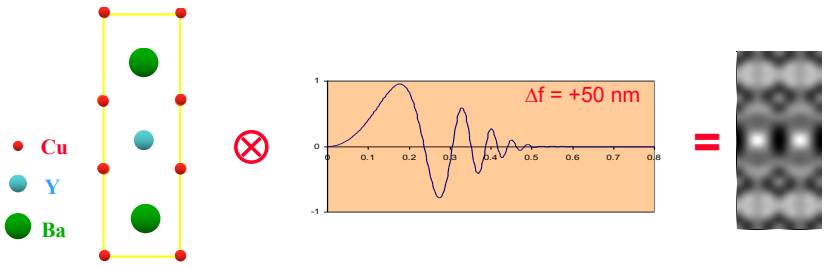
To view 2D transfer functions



7

"Image Calculation"
to simulate HREM imaging

Object: $f(x, y)$ ⊗ PSF: $h(x, y)$ = image: $g(x, y)$

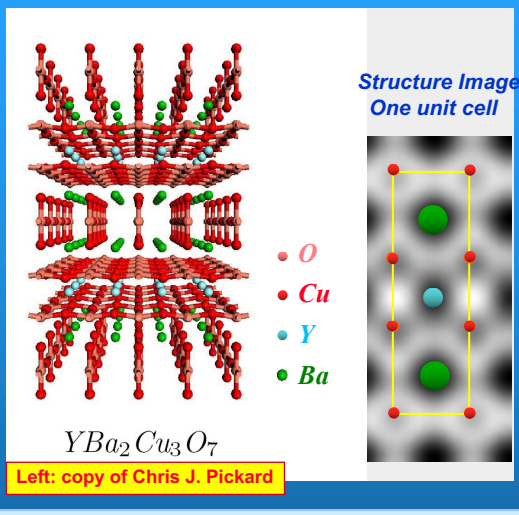


Please be noted that there is an obvious mistake in this slide

8

Atomic columns in crystals

A perspective of YBCO along [100]



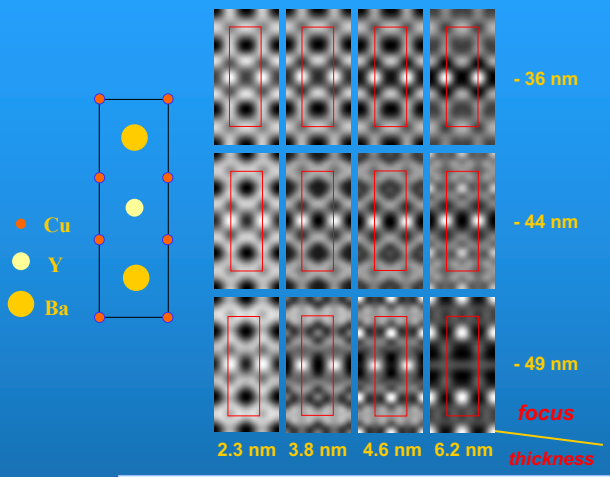
Left: copy of Chris J. Pickard

How does the sample thickness affect image contrast ?

9

"Image Calculation"

to simulate HREM imaging



Note: by comparing the contrast of experimental images with that of the simulated ones, we obtain info of both specimen thickness and focusing conditions, and also check the structure mode.

Image simulation needs a structure modeling first before it can be carried out !!

10

"Image Processing"

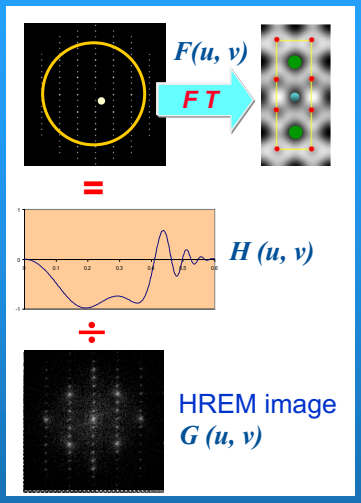
to extract structure informatiton from images

image $\otimes h(x,y)$

$$G(u,v) = F(u,v) \cdot H(u,v)$$

$$F(u,v) = \frac{G(u,v)}{H(u,v)}$$

structure $FT^{-1}\left[F(u,v)\right]$



Resolution is limited due to the aberrations !!

11

"Image Processing"

to remove lens contribution and extract structure info from an image

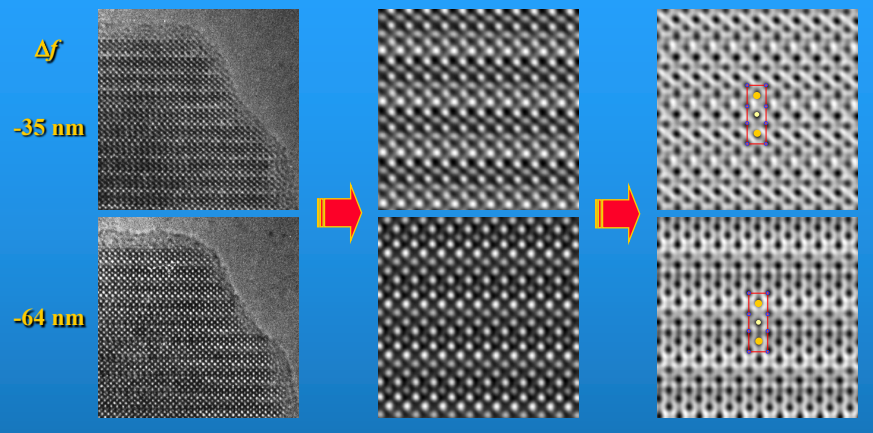
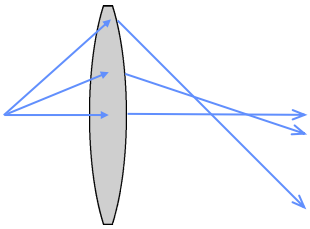


Image processing corrects the image contrast, but does not increase its resolution !! ***How to further improve HRTEM image resolution?***

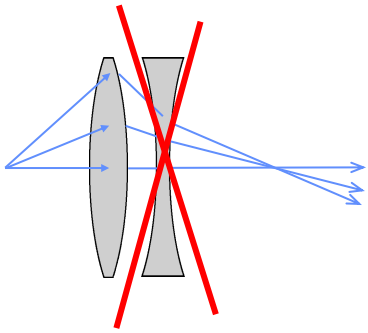
12

Cs (aberration) correction for optical lens

A converging lens



A doublets of
a converging and a diverging lens



No simple diverging round lenses available for electrons !

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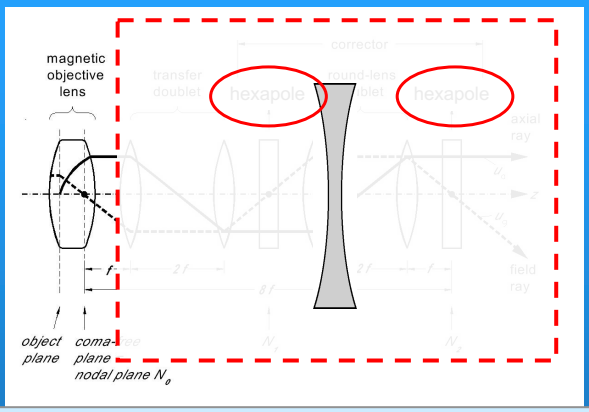
Cs (Aberration) correction for TEM



After 50 years endeavor, Cs aberration corrector for TEM has been successfully developed, which acts like a diverging lens to compensate the spherical aberration.

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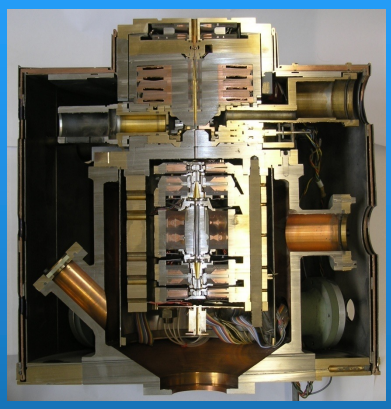
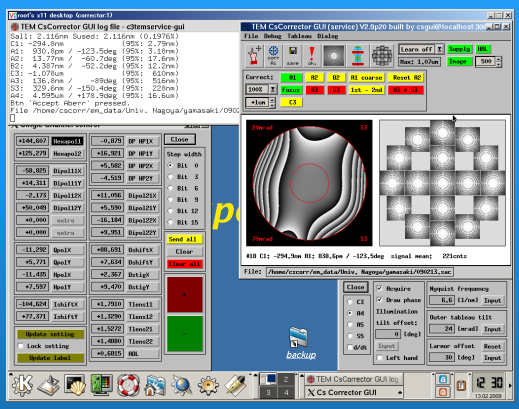
Cs corrector: Hardware + Software

Cs - corrector

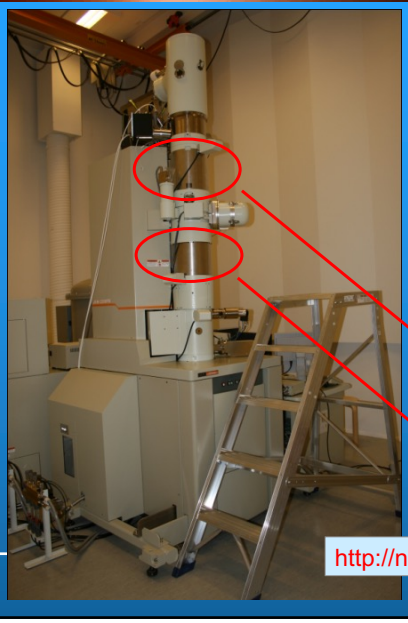


Cs – corrector GUI



15

JEOL-2200FS Double Cs-corrected TEM/STEM at Aalto



Probe-forming Cs corrector

Imaging Cs corrector

http://nmc.aalto.fi/en/

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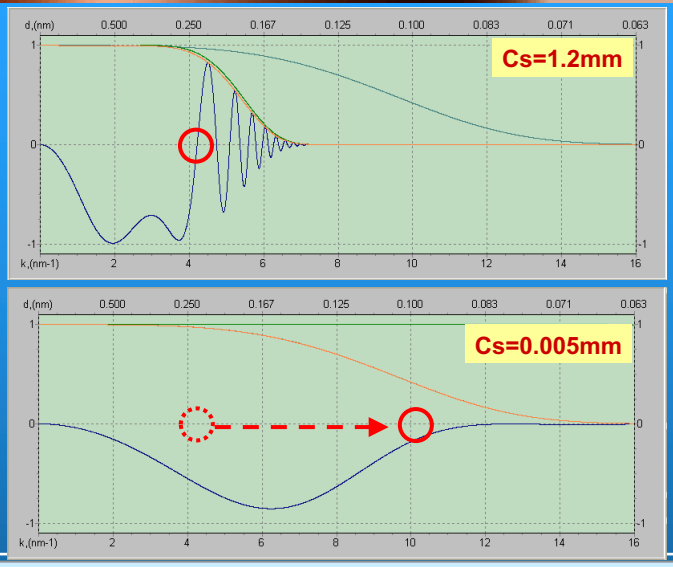
CTFs for a Cs-corrected microscope

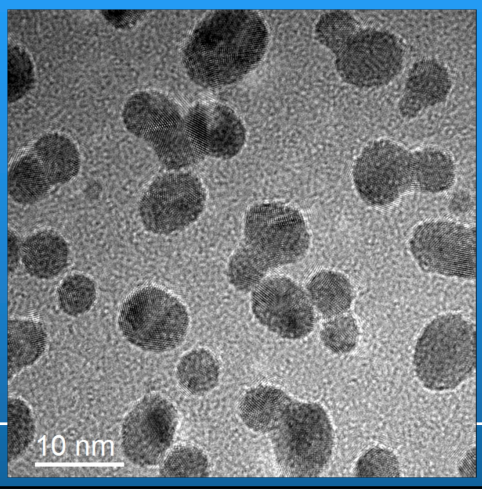


Cs corrector pushes point resolution to the information limit.

17

Applications: *Cs-corrected TEM image of Au particles*

An HRTEM image of Au nanoparticles taken with a non-corrected microscope at 300kV



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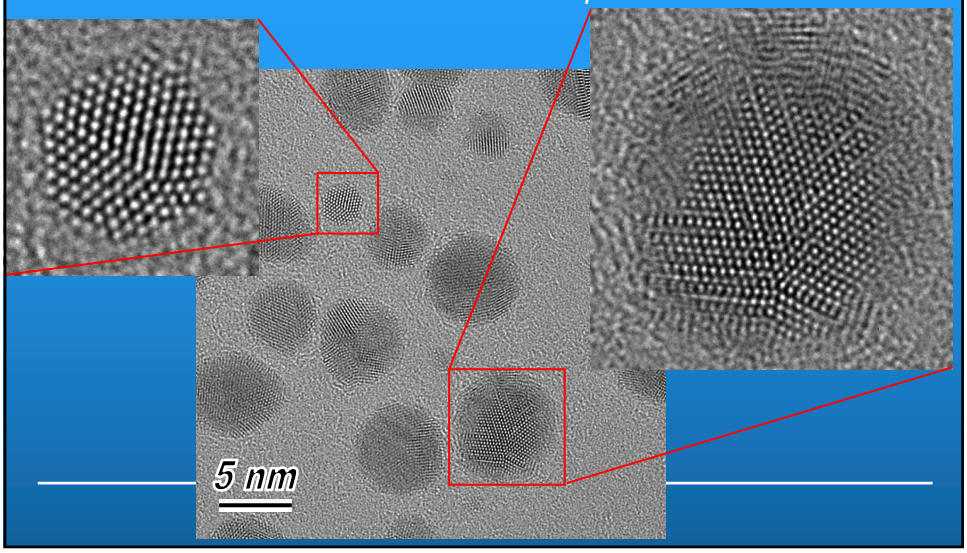
Applications: *Cs-corrected TEM image of Au particles*

An HRTEM image of Au nanoparticles taken with an aberration-corrected microscope at 200 kV.



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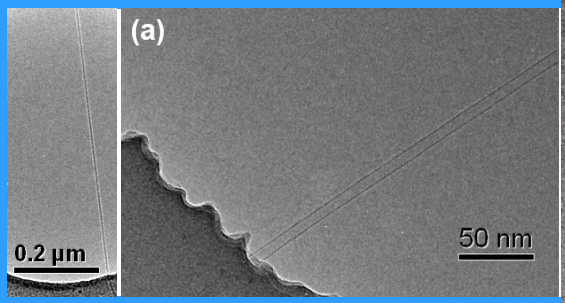
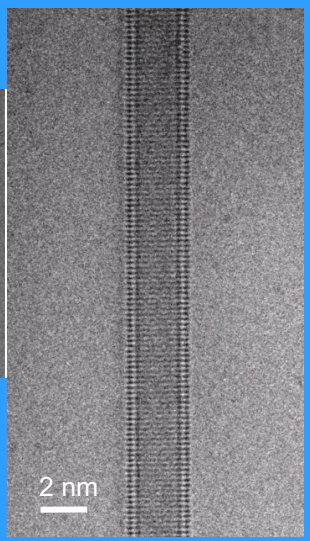
An image may mislead us …

What's more to see ?





The resolution is essential !

And, TEM is our choice !!

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TEM imaging: *things to remember*

1. Various imaging modes are possible in TEM by using an aperture to select different portions of the diffraction to form images.
2. "Contrast" is the appearance of brightness difference in your image. To understand the cause of the contrast is crucial for interpreting your image. What you see in an image is not always what it actually is.
3. "Resolution" defines the smallest features in the object that can be resolved in the image. Resolution is not only determined by the electron wavelength but also by the lens performance.
4. The contrast of a HRTEM Image for a thin sample can be tuned by adjusing the focusing condition.
5. Aberration correction is nowadays possible and has been put into practice. A new era of sub-Å electron microscopy is coming.

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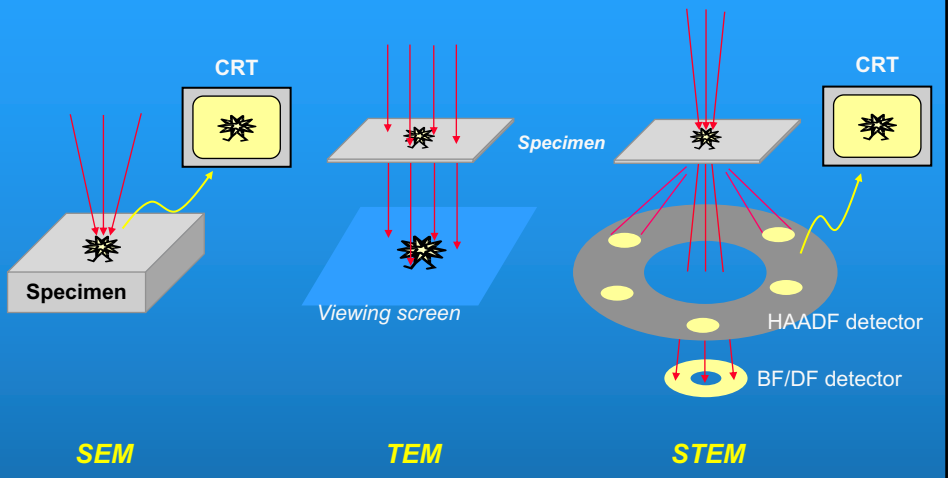
Scanning Transmission Electron Microscopy



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STEM imaging techniques

- STEM bright-field (BF)
- STEM annual dark-field (ADF)
- STEM high-angle annual DF (HAADF)

STEM:

Scanning Transmission Electron Microscopy

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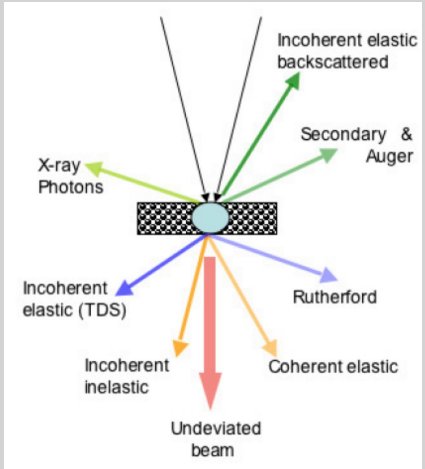
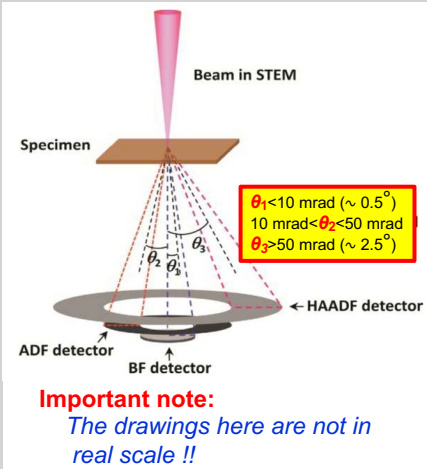
STEM: "electron scattering" vs "detectors"





Important note:

The drawings here are not in real scale !!

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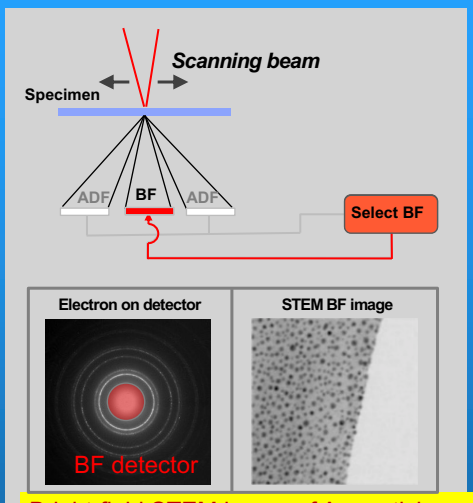
STEM: BF imaging modes



Bright-field STEM image of Au particles on a carbon film

BF – bright field

Collect those transmitted electrons that leave the sample at relatively low angles with respect to the optic axis

STEM-BF images are quite the same as conventional TEM images

Question: *Please tell the difference of TEM-BF and STEM-BF regarding their formations.*

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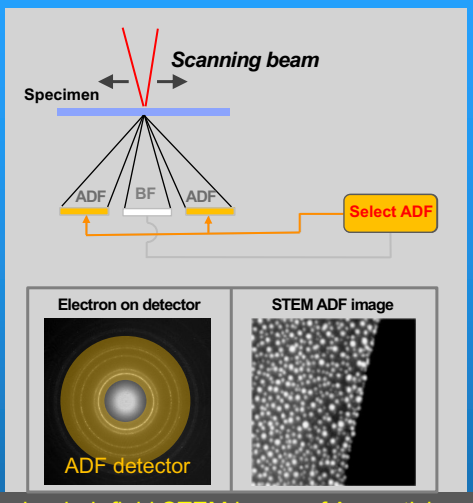
STEM: ADF imaging mode



Annular dark-field STEM image of Au particles on a carbon film

ADF – annular dark field

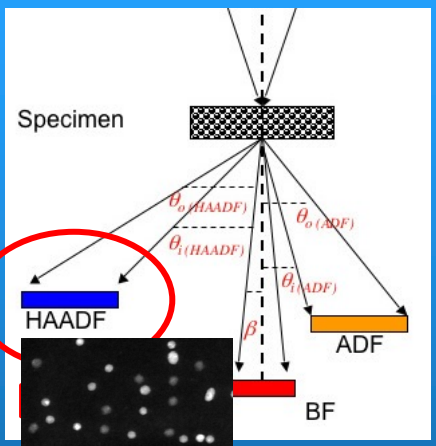
Electrons which have been scattered to relatively high angles are collected to form images.

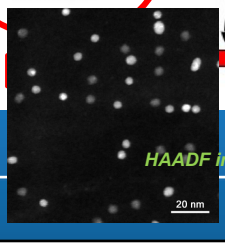
STEM-ADF images contain Bragg diffractions – coherent images

Question: *Please tell the difference of TEM-DF and STEM-ADF regarding their formations.*

26

Z-contrast in STEM: HAADF imaging mode





HAADF image of Au and Ag clusters

courtesy: Dr. N.P. Young, Oxford

HAADF – high angle annular dark field

The inner acceptance angle of the detector is made large enough (>50 mrad), to exclude all Bragg scattering.

Mostly TDS electrons are collected for imaging.

STEM-HAADF image is incoherent, and the contrast strongly depends on Z_{atom}.

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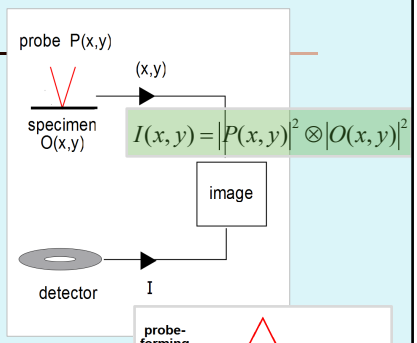
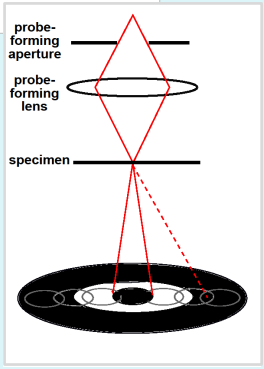
STEM- HAADF imaging

- A fine probe is scanned over the specimen point by point
- At each point (*x,y*) the signal is collected with an annular detector
  - The pixel intensity I(*x,y*) is a sum of all the signal falling on the detector
  - I(x,y) is correlated to the structure function O(*x, y*) which is convoluted with the probe function P(*x, y*).
- At high scattering angles, most of the signal is **Thermal Diffuse Scattering** (TDS)
  - **Incoherent**
  - Scattering localized on atomic columns
  - Scattering power proportional to Z^{α}



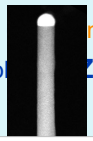


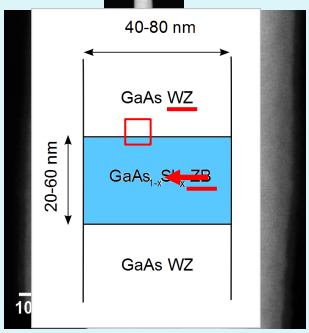
A directly interpretable image of the structure, with intensities related to the composition. **And, the probe shape and size determine the image resolution!!**

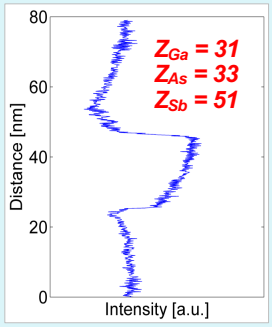
28

Heterostructured GaAs nanowires

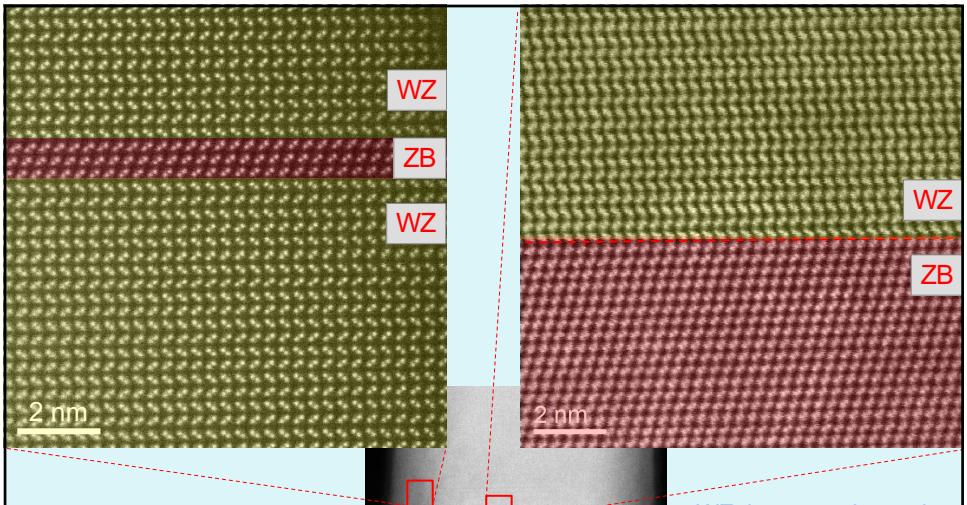
- GaAs nanowires (NWs) (Gallium arsenide)
- Molecular beam epitaxial (MBE) growth
- Pure GaAs NWs: Wurtzite (**WZ**) structure (纤锌矿结构，六方相)
- Partially alloyed with Sb (any):
  $GaAs_{1-x}Sb_x$ insert : Zinc bl**ZB**) structure (闪锌矿结构, 立方相)







29



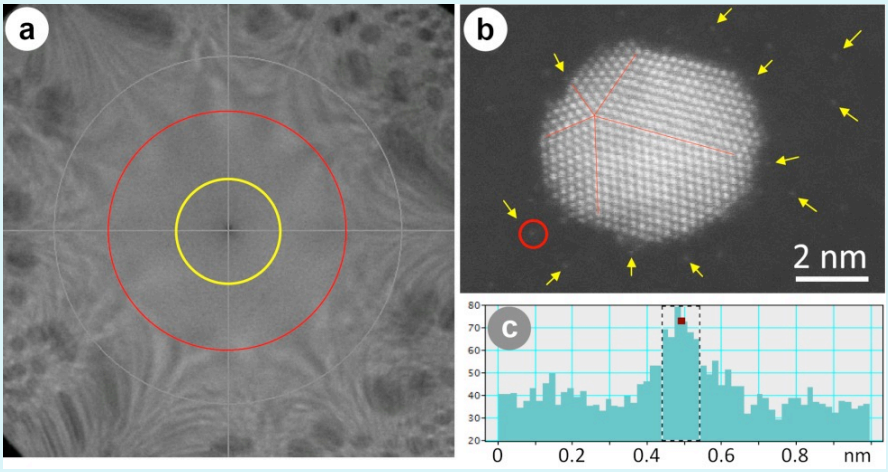
- WZ and ZB coexist;
- Ga and As columns well separated, 1.55 Å;
- Ga and As columns has different intensities.

- WZ: hexagonal wurtzite [11-20] orientation
- ZB: cubic zinc blende [110] orientation

30

STEM HAADF image: Single Au atoms detection (80kV)

--- H Jiang et al, Micron 43 (2012), 545



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STEM imaging: *things to remember*

1. In STEM, small size e-beam probe is formed and scanned cross a thin TEM sample, generating scattering electrons along a wide range of directions.
2. Various electron detectors with different acceptance angles are used to collect electrons with different scattering angles, forming BF, ADF and HAADF images accordingly.
3. For comparision, in conventional parallel TEM imaging, (TEM-) BF and DF images are formed by using the objective aperture to select a certain fraction of scattered electrons, which gives rise to a fundamental difference between the TEM and STEM modes.
4. STEM-BF and -ADF images are coherent images, while STEM-HAADF images are incoherent images.
5. The contrast of incoherent HAADF imaging strongly depends on atomic number Z, so-called Z-contrast imaging.
6. The resolution of HAADA imaging strongly depends on the probe size and shape, though the system instabilities and specimen drift in practice limit the achievable resolution.

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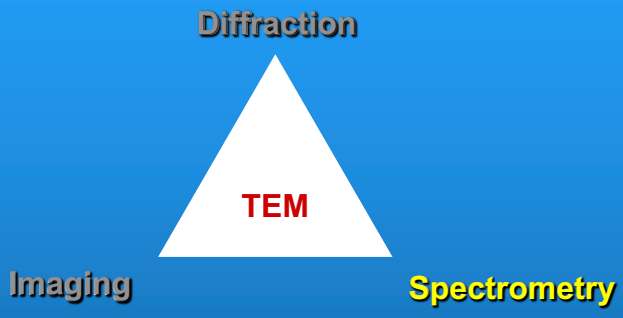
Three cornors

around Electron Microscopy



Spectroscopy is an option to a TEM !

33

Part IV

"Spectroscopy" in TEM

- EDS: X-ray energy dispersive spectroscopy
- EELS: electron energy loss spectroscopy

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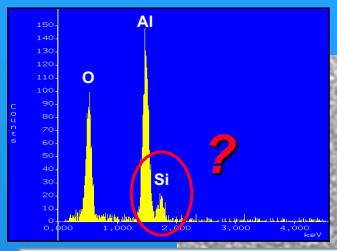
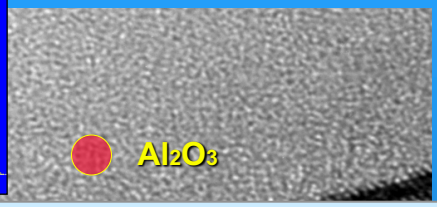
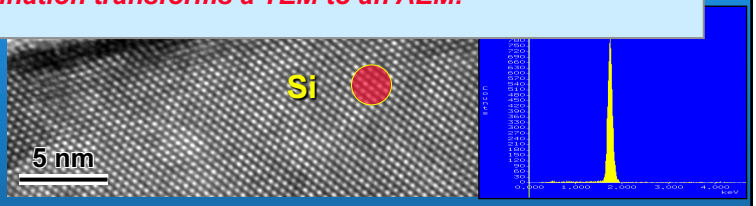
Can you tell what the materials are they in the image?



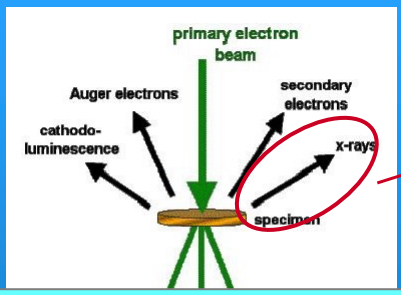


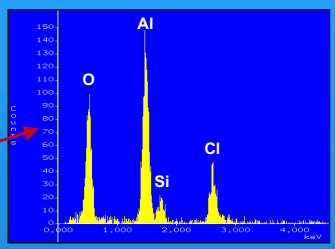
The combination of imaging and spectrometry is most powerful. This combination transforms a TEM to an AEM.



35

X-ray --- characteristic of elements





EDS picks up signals of X-rays for analysis. X-rays are emitted from the specimen by excitation of high-energy electron beam.

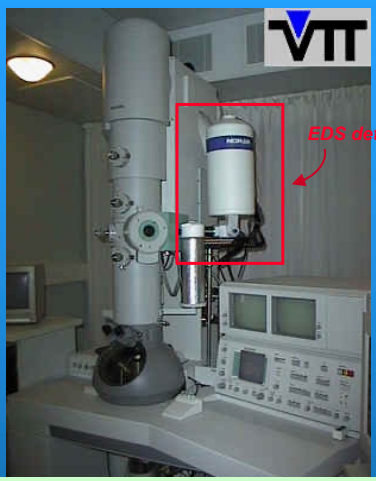
The spectrum is a plot of X-ray counts ("intensity") versus X-ray energy.

EDS:

*X-ray **E**nergy **D**ispersive **S**pectroscopy*

36

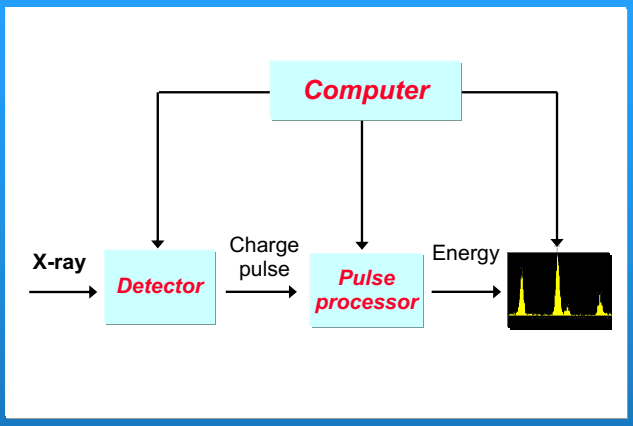
Device --- an optional tool attached to TEM



Usually, EDS is an option to a TEM (or SEM). No all TEM can do EDS.

37

Device --- an optional tool attached to TEM

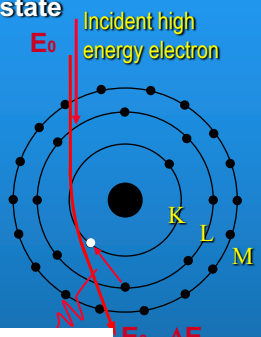


- **Detector**: generates a charge pulse proportional to X-ray energy, and then converted to a voltage.
- **Electronic device**: amplifying and processing weak signal
- **Analyzer**: data analysis and display

38

Generation of Characteristic X-ray

- **Ionisation**
  - The incident electron transfers its energy to a shell electron – *energy loss in incident electrons*
  - If the shell electron accepts an energy higher than its binding energy it is ionised
  - A vacancy in the shell produced– an excited state
- **Relaxation**
  - Electrons in higher energy shells will fill the vacancy
  - Relaxation of the ionised state occurs through emission of an Auger electron or an X-ray photon
  - Both are "characteristic" radiation as they reflect the shell energy structure



The energy loss in incident electrons give rise to ionization;
Relaxation of the ionization produces characteristic x-ray.

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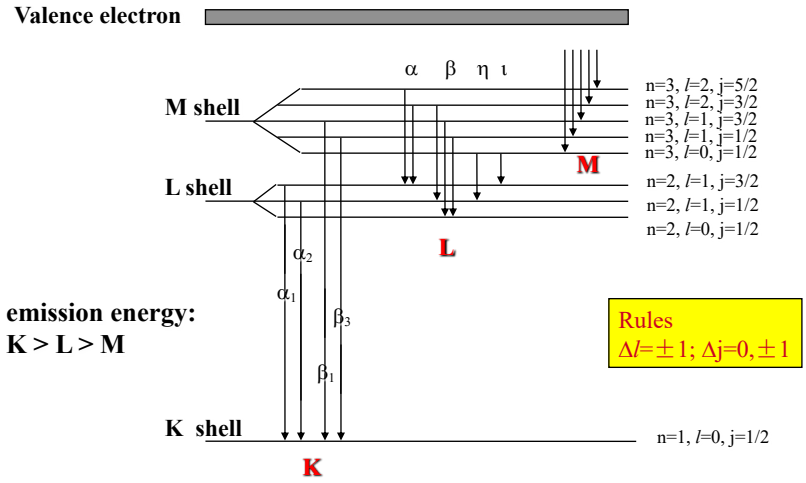
Characteristic X-ray -- Chemical Signals



Characteristic X-ray depends on only the energy difference between shells;
The energy of incident electrons must be high enough to generate X-rays.

40

Characteristic X-ray -- Chemical Signals

- **Examples of characteristic radiation (keV)**

	C	Si	Cu	Ba
K_α	0.277	1.739	8.040	32.188
K_β		1.836	8.904	36.373
L_α			0.930	4.469
M_γ				0.974

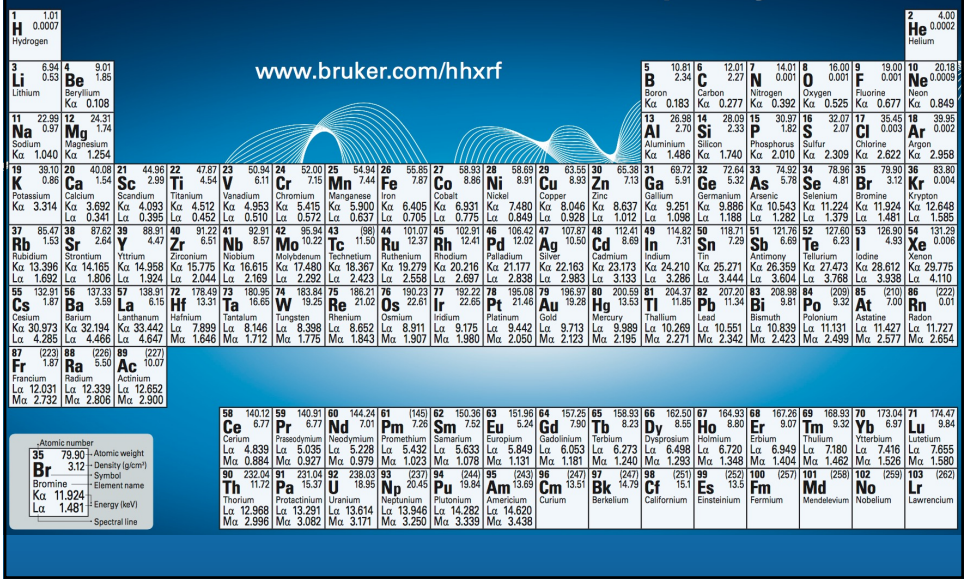
The characteristic energies of main elements have been tabulated, and can be easily found out in literature.
Actually modern computer system will identified the peaks automatically.

The detectable elements are from boron (5) to uranium (92)

41

Characteristic X-ray Energies

- **Periodic Table of Elements and X-ray Energies**



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Chemical analysis by X-ray

- Qualitative analysis
  - By the energy or wavelength, we can identify each peaks in the spectrum. EDS or WDS
  - Qualitative analysis is sometime enough if you simply wants to identify your sample.
  - Line profile and X-ray mapping
  - It is always necessary to do qualitative analysis first before doing quantitative analysis.
- Quantitative analysis
  - By the relative intensity of characteristic X-ray, we determine the concentration of the element in the sample.
  - The analysis accuracy depends much on the measurement and correction of the X-ray intensities.
  - Great efforts have been made to correct the intensity in many ways. We give only general principles.

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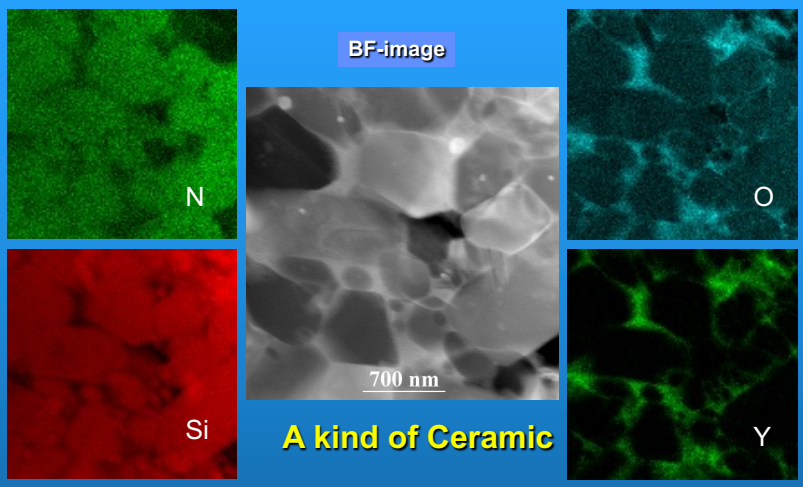
Mapping Elements by EDS



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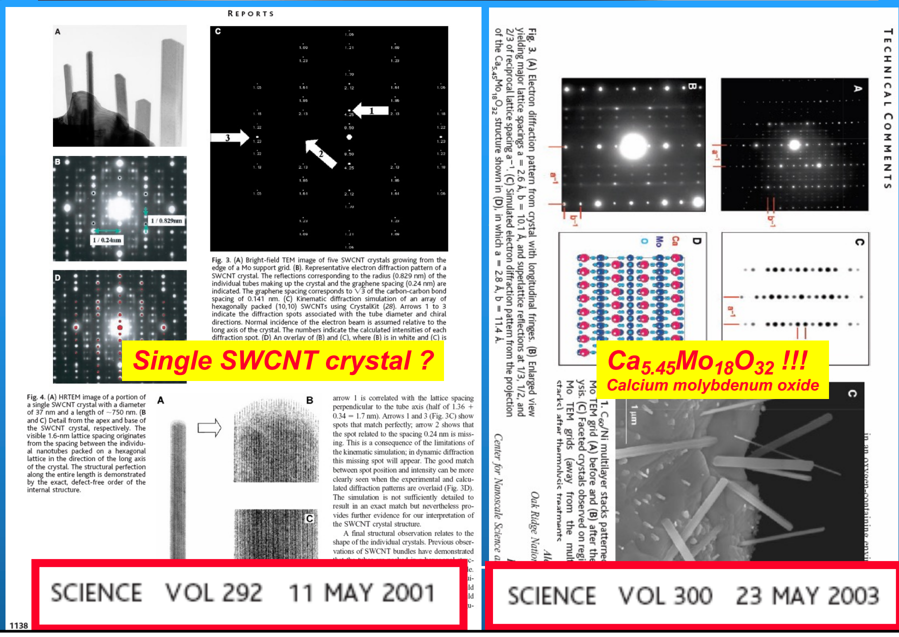
Why NOT EDS ? !



EDS: *things to remember*

1. EDS picks up X-rays that are emitted from the sample by high-energy electrons.

2. EDS can tell you in one minute what elements you have in your sample: It is fast and sensitive!

3. Both qualitative and quantitative analysis as well as elemental mapping are possible with EDS.

4. Do not forget about the possibility of artifacts in EDS which may affect the validity of quantitative analysis.

"Spectrometry" in TEM

- EDS: X-ray energy dispersive spectroscopy

- EELS: electron energy loss spectroscopy

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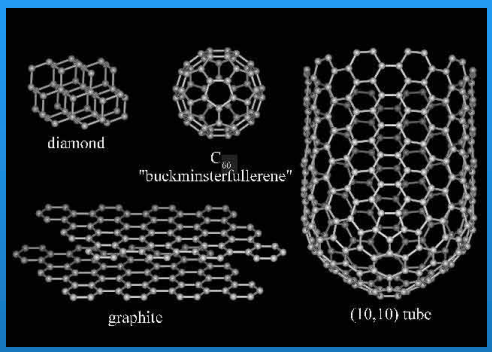
A pre-topic quiz: Does EDS work all time?

*Suppose that you are now given a sample which is believed to contain different forms of carbon-based materials, including **diamond**, **graphite** and **fullerens**. They are all made of carbon atoms, but of different structure as shown in the following picture:*



Variable forms of carbon

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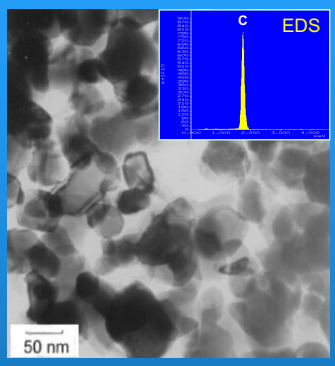
A pre-topic quiz: Can EDS always work?

In TEM, you have seen a typical bright-field (BF) image as below.

With EDS analysis, you see everywhere only one peak at energy 0.277 keV for carbon.

So, how would you like detect all different forms of the carbon in your specimen, by any possible analytical technique in TEM ?

EELS comes to help!



A bight-field TEM iamge

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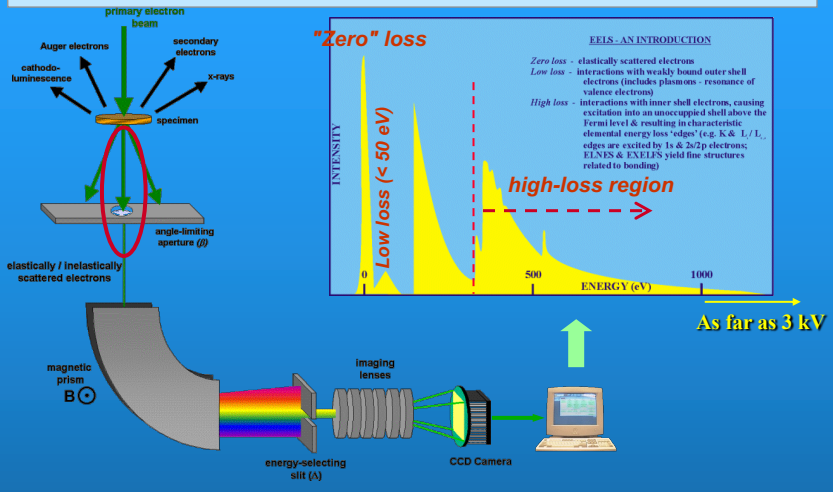
What is *EELS* ?

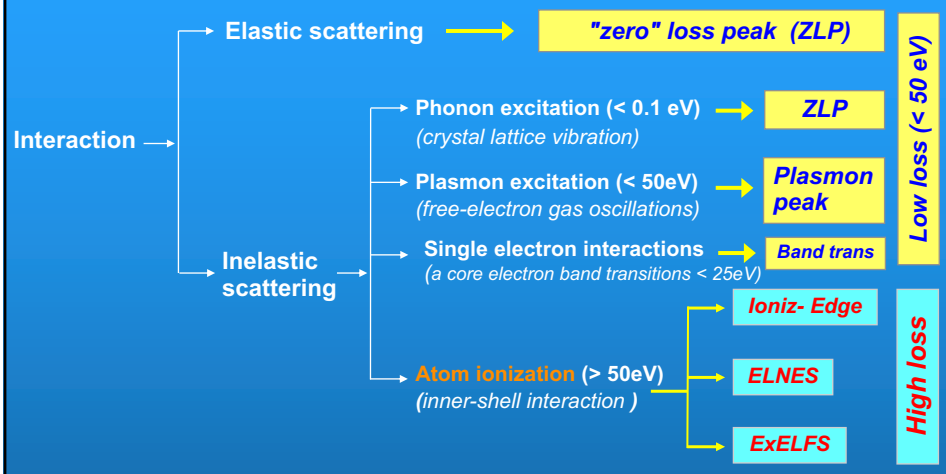
EELS: ***E****lectron* ***E****nergy* ***L****oss* ***S****pectroscopy*



EELS collects electrons that experience energy losses after ***"inelastic"*** *interaction with the specimen, then display their energy distribution.*

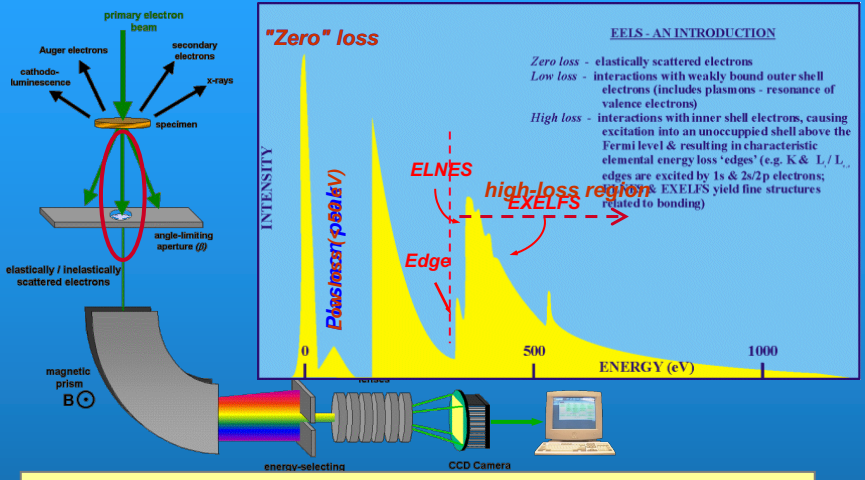
50

Energy loss by a variety of mechanisms



51

To explore the energy-loss spectrum



*EELS collects electrons that experience energy losses after "**inelastic**" interaction with the specimen, then display their energy distribution.*

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Device --- another optional tool to TEM

Notes:

The spectrometer can be mounted in principle all kind of TEM as a post-column attachment.

EELS spectrometer

Post-column GIF system

Like EDS, EELS is also an opition on a TEM.
Only those equipped with EELS can do.

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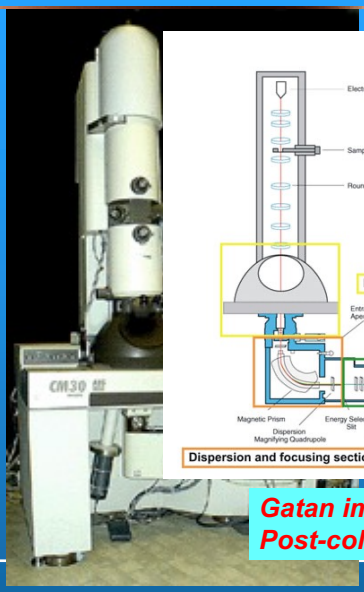
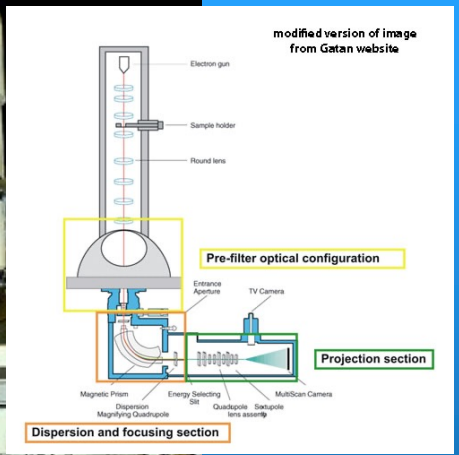
Device --- another optional tool to TEM





Gatan image filter (GIF)
Post-column type

http://iubemcenter.indiana.edu/3200FS.html

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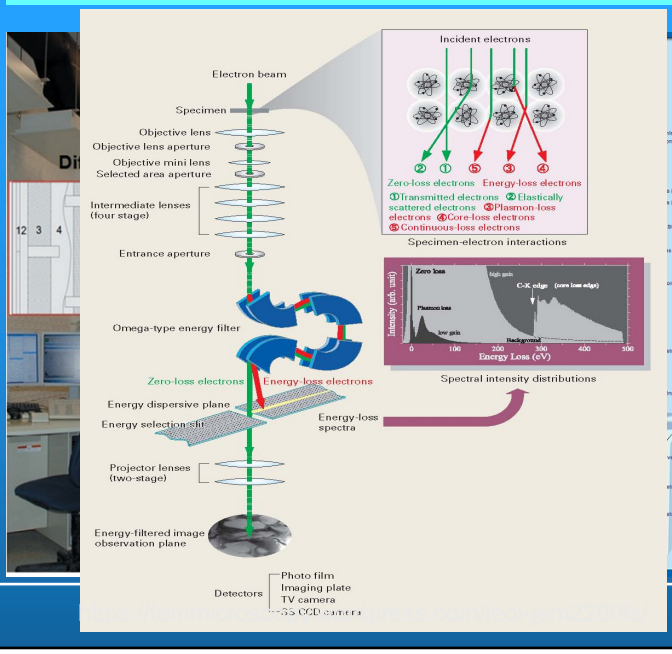
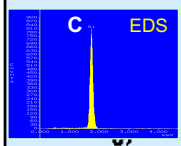
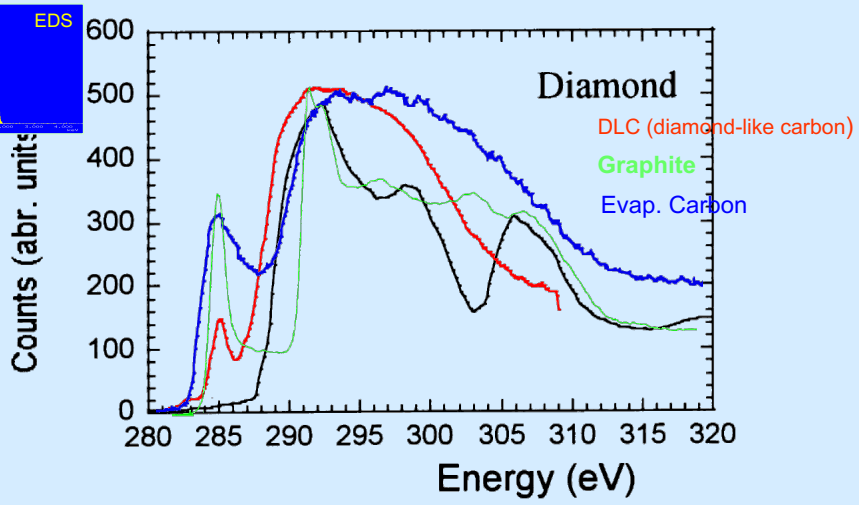
In-column Ω - filter (Aalto NMC: JEOL-2200FS microscope)



55

EELS --- more than compositional analysis





sp^2/sp^3 obtained from peak intensity

J. Yuan, Micron 515 (2000)

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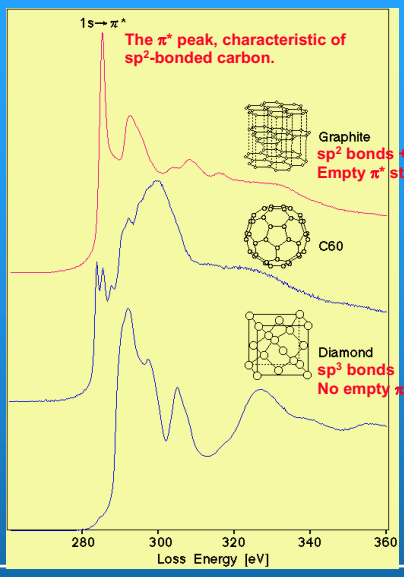
EEL spectra of CARBON family members



From the fine structure of the absorption peak, the difference in bonding state and local electronic state can be detected.

Diamond, graphite and fullerene are the matters which consists of only carbon, so that, all of these specimens have absorption peaks around 285 eV in EELS corresponding to the existence of carbon atom.

However, The strong and sharp peak at the absorption edge identifies the empty π^* states, into which the 1s electrons are transferred in graphite, while the diamond K edge has no such peak.

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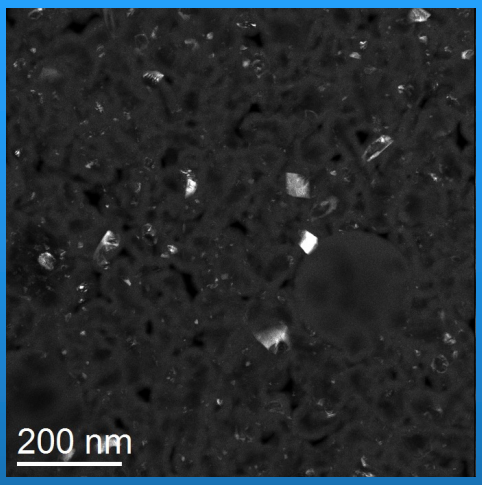
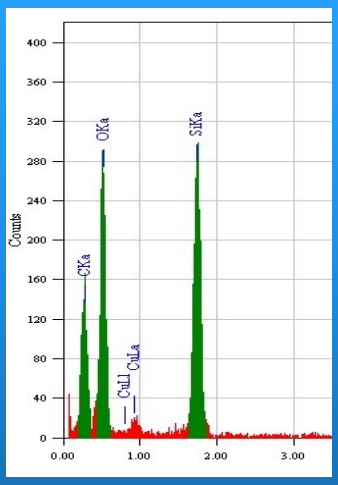
Nano-diamond particles coated with silica





In collaboration with Dr. Jessica Rosenholm
Åbo Akademi University, Turku

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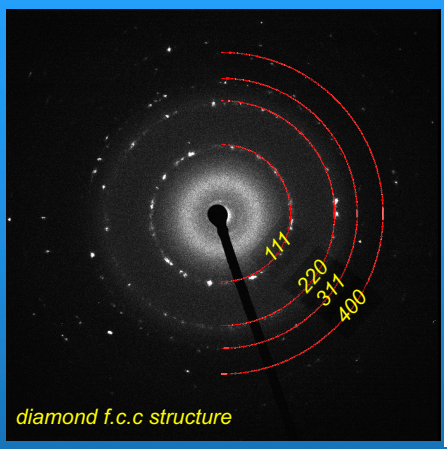
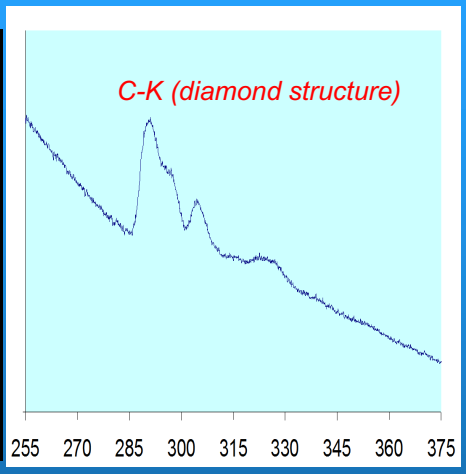
Nano-diamond particles coated with silica





In collaboration with Dr. Jessica Rosenholm
Åbo Akademi University, Turku

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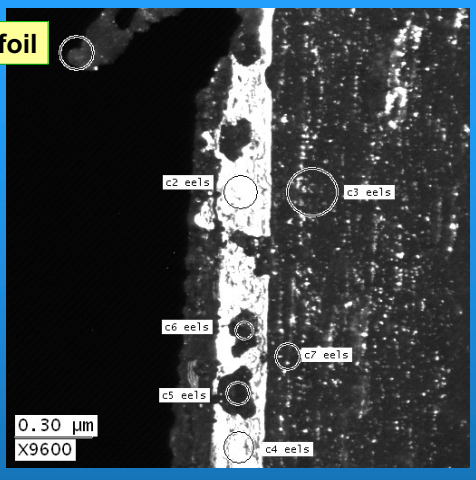
Another example: Cu oxidation

Samples from:
Tampere Univ. Tech.

An oxidized Cu foil



Note: The dark-field image of *fcc* Cu (111) gives more details about the surface structure. A strip of Cu_2O is clearly shown by dark-field TEM image.

EELS analysis was done in the marked areas, and indicated that the white strip in the image is copper oxide.

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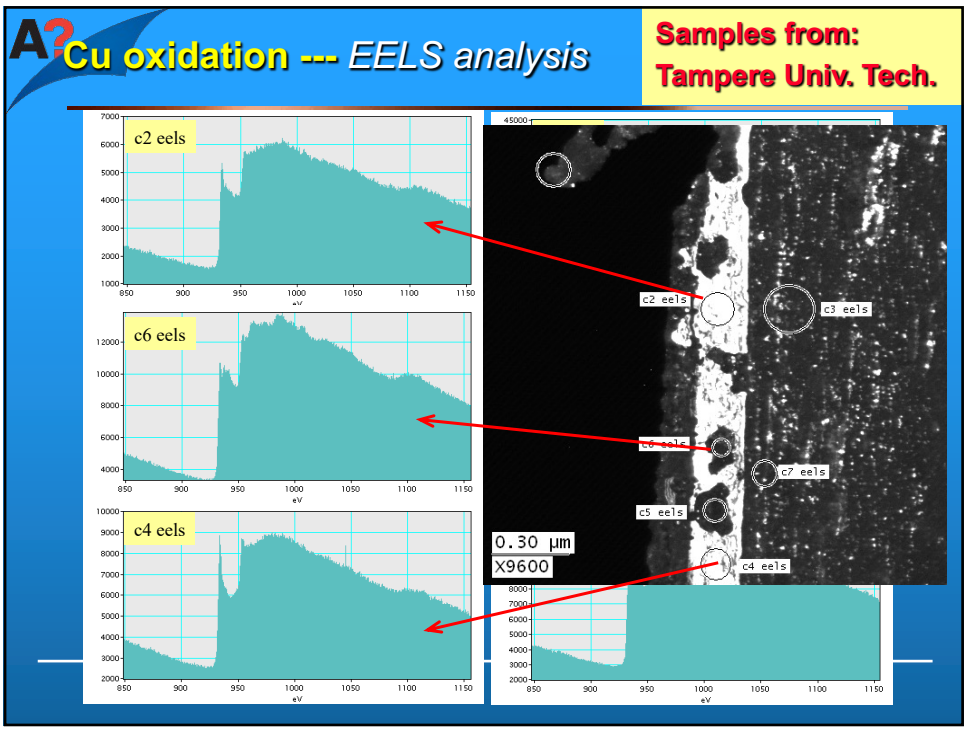
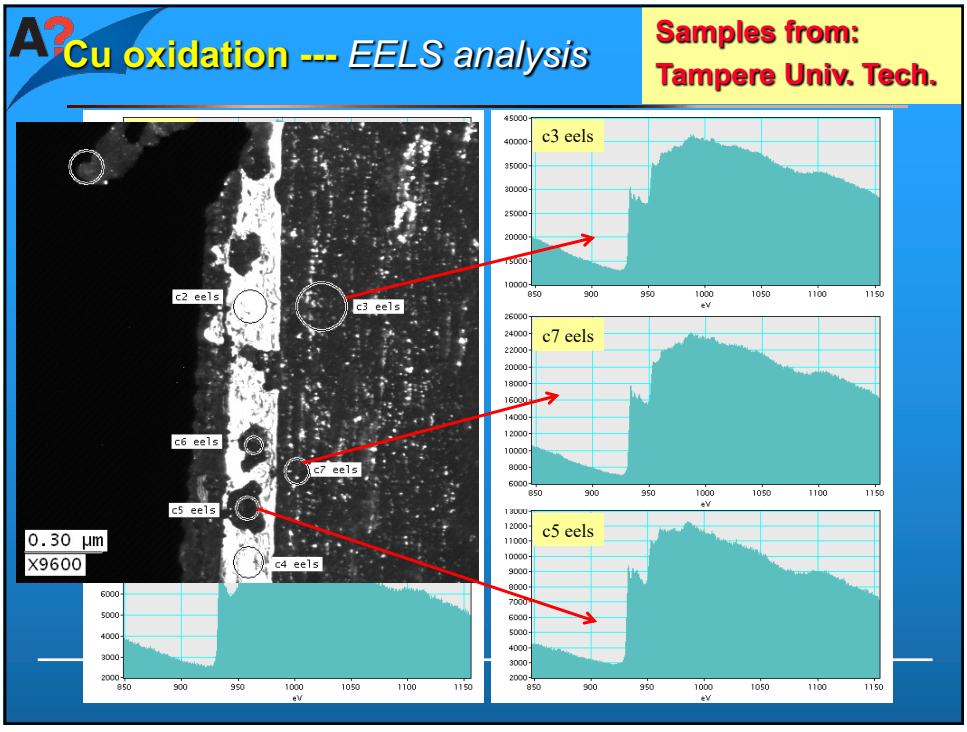

Cu oxidation --- EELS analysis
Samples from:
Tampere Univ. Tech.
c2 eels
c6 eels
c4 eels
c3 eels
c7 eels
c5 eels
0.30 µm
X9600

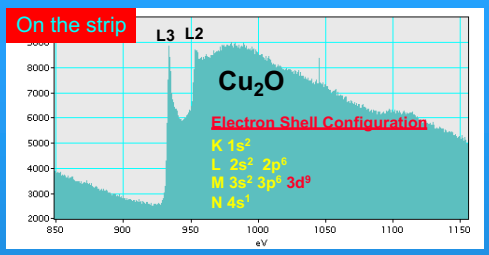
61


Cu oxidation --- EELS analysis
Samples from:
Tampere Univ. Tech.
c2 eels
c3 eels
c6 eels
c7 eels
c5 eels
c4 eels
0.30 µm
X9600

62

Two types of Cu spectrum: Pure Cu and Copper oxid

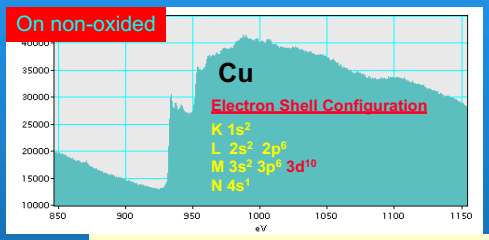
On the strip



Note: Electron energy loss spectrum (EELS) from the fresh Cu foil.

Since Cu metal has all its 3d states filled so there is no "white line" in spectrum while typically the L edges of other transition metals show such intense sharp lines.

On non-oxided



Upon oxidation, some 3d electrons in Cu are transferred to the oxygen, leaving unfilled states, and the white line appears in the oxide spectrum.

Note: **the L-edges of the transition metals show intense sharp "white lines". These sharp lines arise because the ejected L shell electrons don't entirely escape from the atom and have a very high probability of ending up in unfilled d band states. If the d band is full, like in pure Cu, the L2,3 edge does not show these intense lines.**

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EELS: *things to remember*

1. **EELS collects primary electrons that suffer energy losses after inelastic interaction with the specimen.**

2. **Electrons may lose energies by a variety of mechanisms, hence, EELS provides a wide range of structure information of your sample about:**

   Elemental composition (identification)
   Chemical bonding
   Band structure (unoccupied states)

   Valence and conduction electron density
   Polarization response (complex dielectric function)
   Sample thickness
   … …

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EELS vs. EDS --- *too many differences*

EDS	EELS
• X-rays provide elemental information only	• Elemental, Chemical, & Dielectric information
• Inefficient signal generation, collection &detection inefficient x-ray mapping	• Very efficient in every respect => higher sensitivity to most elements very efficient mapping technique
• Slow technique (hours)	• Fast technique (seconds to minutes)
• X-ray spectra can contain information from column and other parts of sample	• EELS spectra have no such artifacts
• High detection efficiency for high Z elements	• High detection efficiency for low Z elements
• Energy resolution > 100eV causes frequent overlaps	• Energy resolution 0.3-2eV gives far fewer overlaps
• Only simple processing required	• More complex processing required => *Needs more hardware & software automation*

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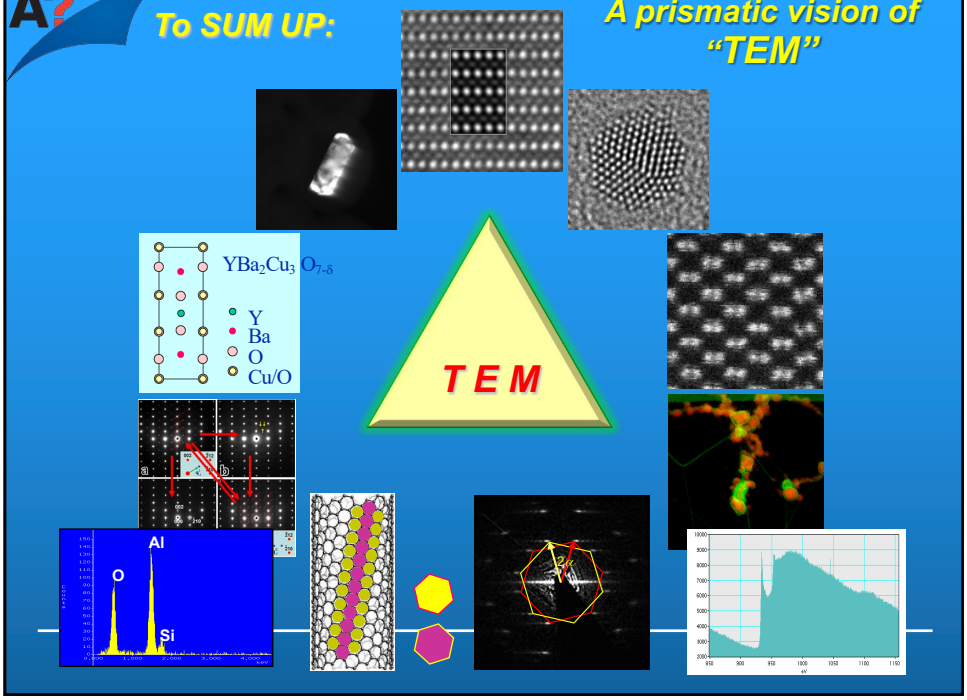
To SUM UP:

A prismatic vision of "TEM"



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a new trend in TEM

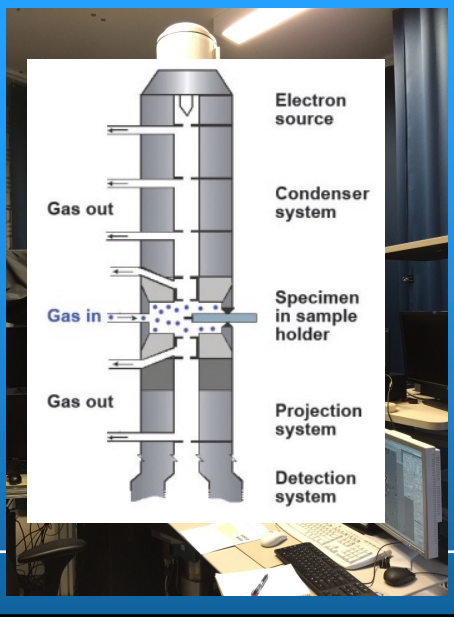
ETEM: *in-situ* studies in a TEM

ETEM:

***E**nvironmental **T**ransmission **E**lectron **M**icroscopy*

67

A versatile ETEM in NIST, USA



- *FEG 80 – 300 kV*
- *Cs-corrected, monochromated*
- *E-cell pressure (differential pumping) (up to 20 mbar for a variety of types of gases)*
- *Temperature up to 1200 ℃*
- *Dynamic at atomic resolution in real time (< 0.1nm)*
- *in-situ Raman measurements*

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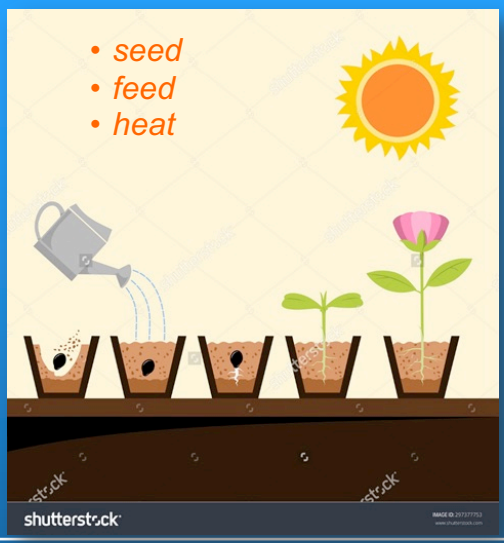
To investigate how CNTs grow ?



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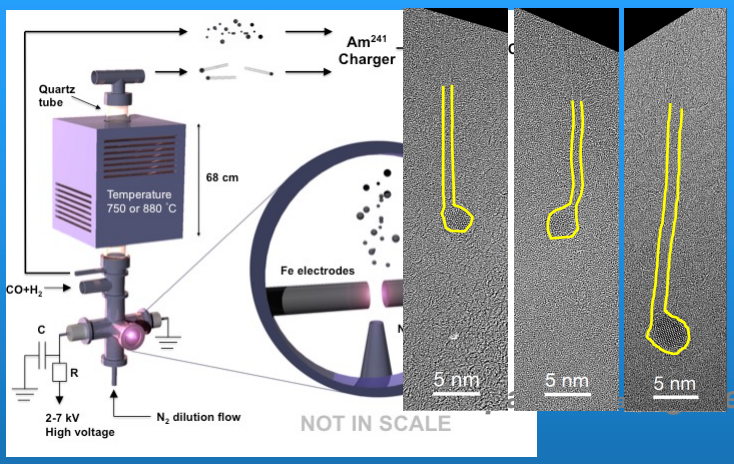
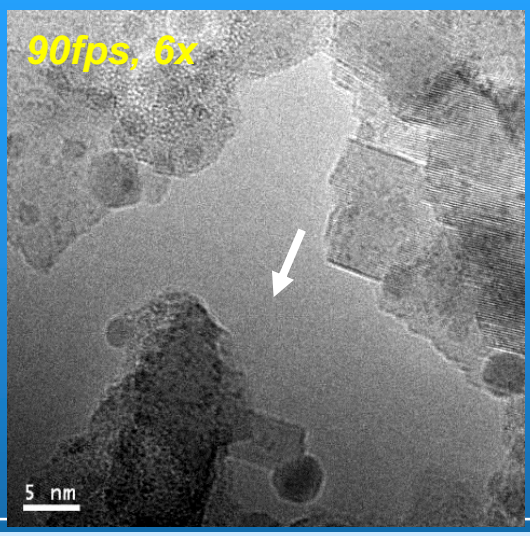
A CVD reactor for CNT growth



70

Seeing is believing: Real-time CNT growths

*Growing carbon nanotubes inside a TEM --- **an in-situ study***



Co(Mo)-MgO, C_2H_2 ~ 2.63 x10^{-4} mbar, 900℃, TEM at 80kV

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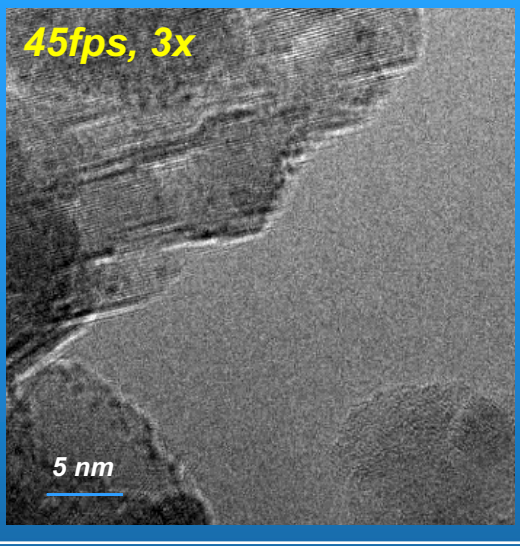
Real-time reaction: How a DWCNT grows?



Co(Mo)/MgO, C2H2 ≈ 1.37 x10-4 mbar, ≈ 900℃

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TEM resources

- Recommended TEM textbooks:
  - D. B. Williams und C. B. Carter: *Transmission Electron Microscopy*, New York: Plenum Press (1996).
  - L. Reimer: *Transmission Electron Microscopy*, Berlin: Springer (1997).
  - Z.P. Lu, A Practical Guide to Transmission Electron Microscopy --- *Fundamentals*, Copyright © Momentum Press® , LLC, 2016
- Electron microscopy journals:
  - *Micron*
  - *J. Electron Microscopy*
  - *Ultramicroscopy*

Thank you

for you attention !!