M5052

Characterization of Materials and Nanomaterials

Graduate Program in Nanotechnology

Introduction to Electron Microscopy

Scanning Electron Microscopy

& EDS: Energy Dispersive X-ray Spectroscopy

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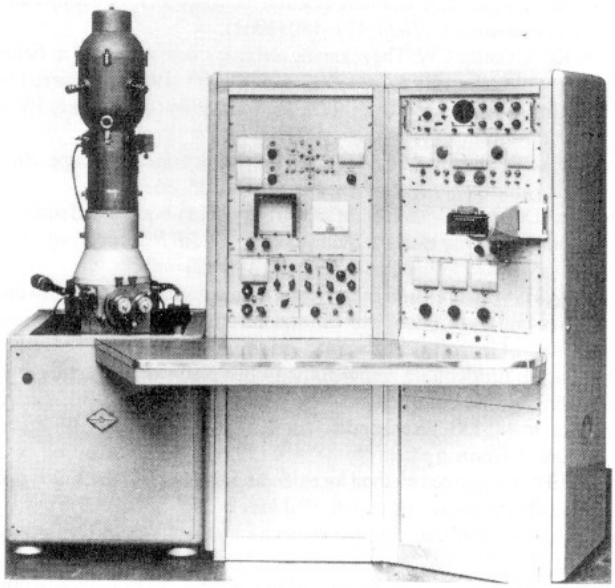
Electron Microscopy

The First Commercial Electron Microscope (TEM)



Cambridge Instruments Stereoscan

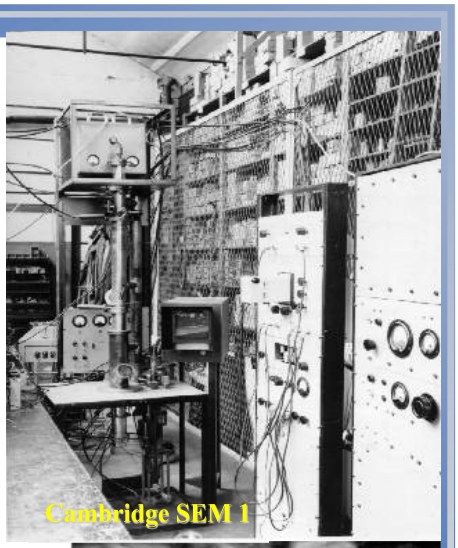
(First Commercial SEM)

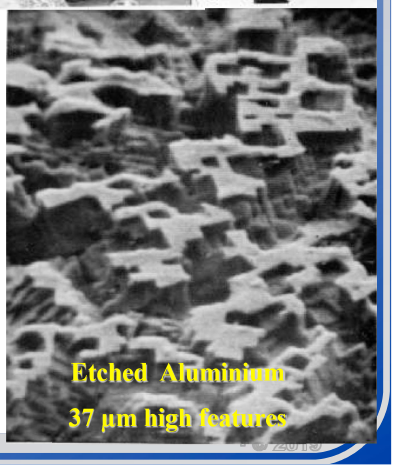
Brief History of Electron Microscopy

- 1931: Ernst Ruska and Max Knoll create the first Transmission Electron Microscope (TEM), in Germany
  - Magnification of only 14.4 X
  - Ernst Ruska received the Nobel in Physics in 1986
    - "for his fundamental work in electron optics, and for the design of the first electron microscope"
  - In 1932 they propose that TEM can have a resolution down to 2.2 Å
- 1933: E. Ruska and Bodo von Borries build the first electron microscope with greater magnification than an optical microscope (12,000X)
- 1935: Knoll first proposes the idea of the Scanning Electron Microscope (SEM)
- Ruska and von Borries develop the first commercial TEM for the Siemens company
  - 30,000 X magnification, commercial fabrication started in 1939
- 1938: First SEM by Manfred von Ardenne
  - TEM modified to work as a STEM
  - Limited to use of photographic film as detector
  - von Ardenne writes the first major papers on the principles of SEM in 1938 and 1940
  - World War II stopped von Ardenne's work on electron microscopy after his lab was destroyed in 1944
- 1942: V. Zworykin et al., from RCA Laboratories in the USA, report the first true SEM
  - Development discontinued due to technical problems and resolution of "only" 50 nm
  - TEM had better resolution so attention focused on that technique

Brief History of SEM

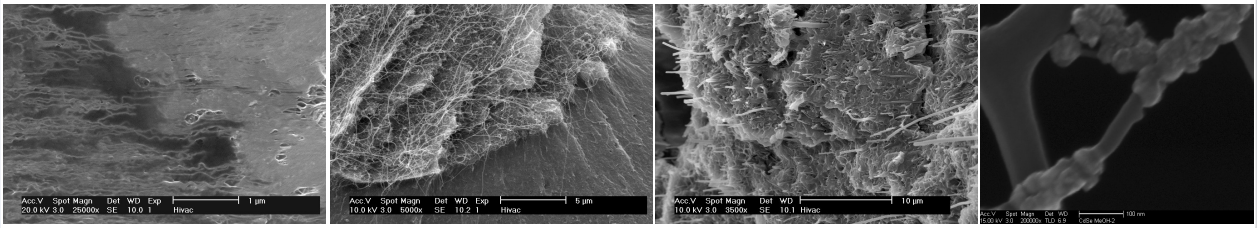
- Charles Oatley and his research group in Cambridge University (England) developed SEM
  - 1948: Oatley and Dennis McMullan build their first SEM
  - 1952: 50 nm resolution achieved
  - 1955: Oatley and Ken Smith publish the first article that clearly defines applications of SEM
  - 1955-1957: Everhart and Thornley develop an improved detector
  - 1960: Pease achieves 10 nm resolution
  - 1965: Cambridge Instruments produces the first five commercial SEM, under the name Stereoscan
- Commercial production of SEM by other companies starts soon after
  - JEOL in Japan was the second company to sell an SEM (also sells TEM)
- Currently the maximum resolution is ≤1 nm


Cambridge SEM 1


Etched Aluminium
37 µm high features

Scanning Electron Microscopy: Basic Principles

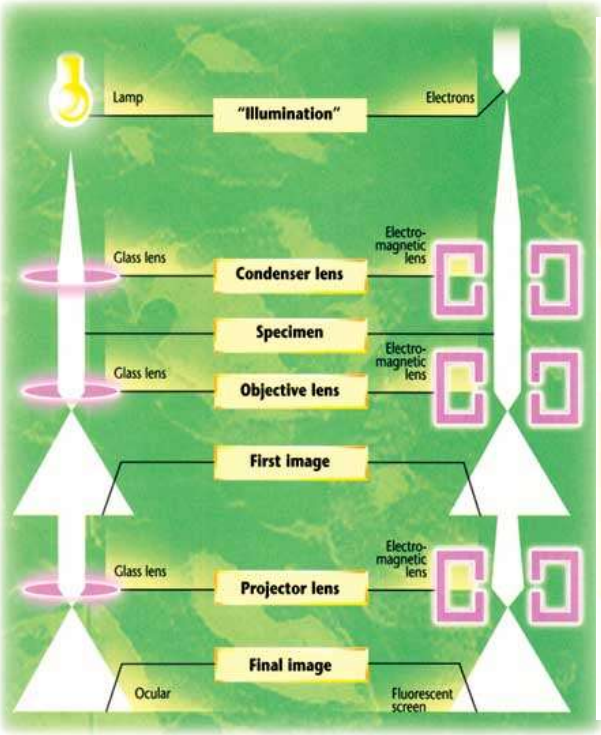
- Electron beam is accelerated by a difference in electric potential
  - 0.1 kV – 50 kV
- Electron lenses system focuses e-beam over the sample
  - Electromagnetic lenses
  - Beam diameter 1-10 nm
  - Current: 10^{-9} – 10^{-12} A
- Beam scanned as a pattern of lines over the sample
- Electron collisions with sample generate secondary electrons
  - Emission intensity depends mostly on sample topography
  - Other processes also occur
- A detector collects secondary electrons and forms an image
- Typical Resolution 1.5 - 3.0 nm
  - Two orders of magnitude better than optical microscopy, about an order of magnitude lower than transmission electron microscopy
  - Resolution < 1 nm is possible

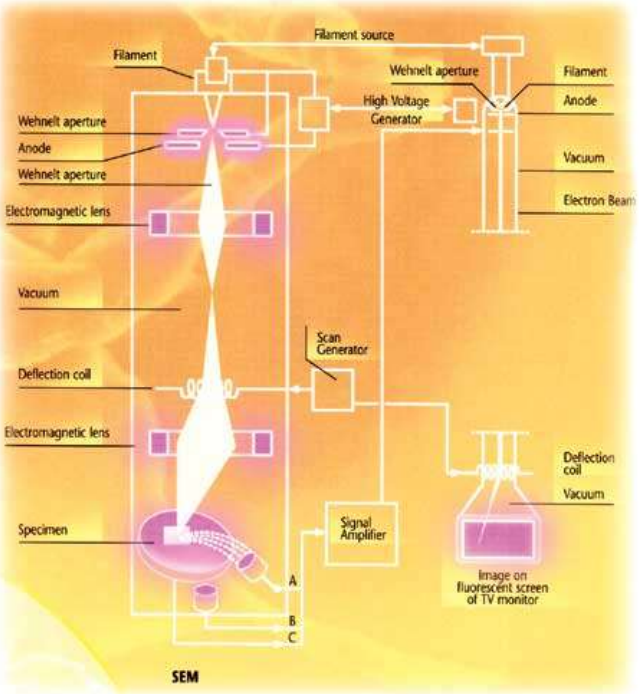


SEM images of carbon-nanotube polymer composites, Fernando J. Rodríguez-Macías, ©Fernando JRM, CC-BY-NC-ND

Comparison of Microscopy Techniques

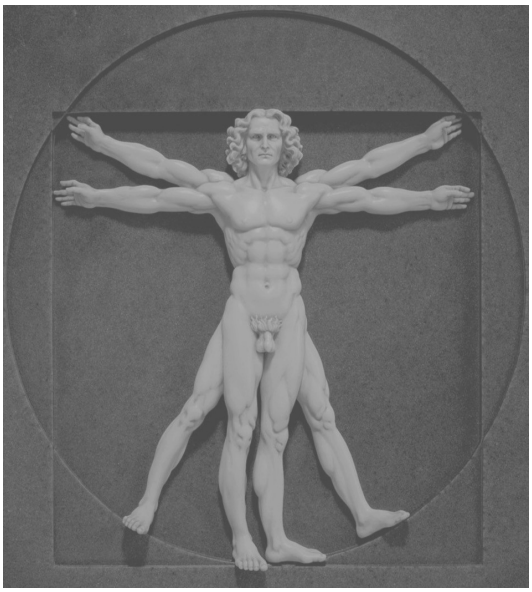
- Optical
- TEM
- SEM

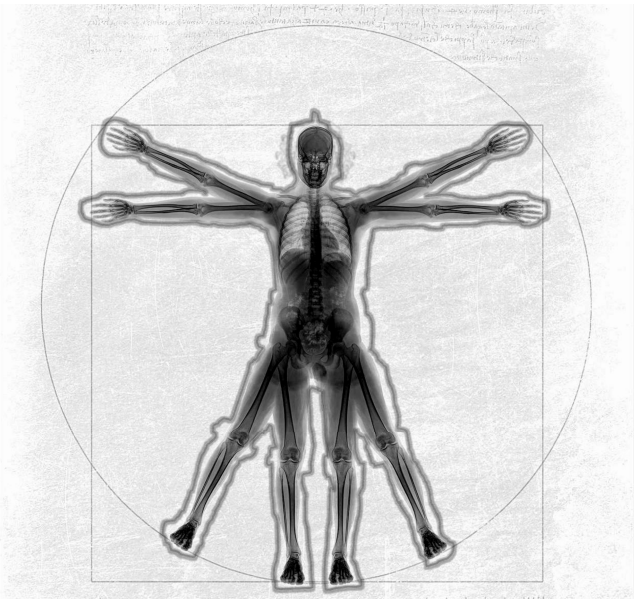




SEM vs TEM

- Scanning Electron Microscopy captures images with electrons that come from the surface
  - Equivalent to a photograph
- Transmission Electron Microscopy captures images with electrons that go through a thin sample
  - Equivalent to a radiography





SEM vs. TEM

- Image contrast depends on intensity of secondary electrons emitted, which depends (mostly) on sample topography
- Typical maximum resolution: 1.5–3 nm
  - Resolution < 1nm is possible
- Relatively simple sample preparation (surface observation)
  - Sample almost always has to be conducting
- Large field of view at low magnification
- Operates in high vacuum
  - Low pressure operation options exist

- Image contrast depends on the intensity of electrons that go through the sample
  - Function of atomic number, density, atomic order (e.g. crystallinity), sample thickness
- Typical maximum resolution: 0.1 nm
  - 0.05 nm resolution is possible in special cases
- Sample must be thin enough (<100 nm) to allow transmission
  - Sample preparation can be complicated
- Very small field of view
- High vacuum operation

- Phenom ProX benchtop electron microscope at the Chemistry and Nanotechnology Laboratories, School of Engineering and Science, Tecnológico de Monterrey, Campus Monterrey

Photo © Fernando JRM, released under a CC-BY-NC-SA license

- Carl Zeiss EVO MA25 VPSEM at the CETEC annex, Monterrey Campus of Tecnológico de Monterrey

SEM is placed inside a frame with a sensor to actively compensate for stray magnetic fields

- Necessary since it is not in a room with a Faraday cage, magnetic fields can deviate trajectory of electrons

SEM is placed over an active vibration isolation platform

- Necessary since it is not over a floor designed to minimize vibrations

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Electron-Specimen Interactions

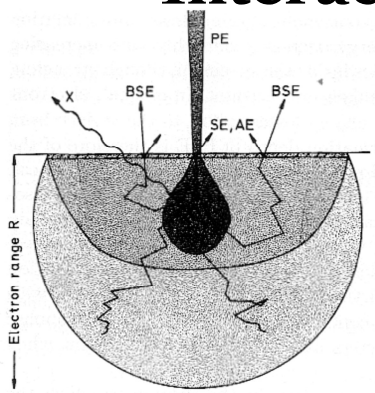


Fig. 1.4. Origin and information depth of secondary electrons (SE), backscattered electrons (BSE), Auger electrons (AE) and x-ray quanta (X) in the diffusion cloud of electron range R for normal incidence of the primary electrons (PE)

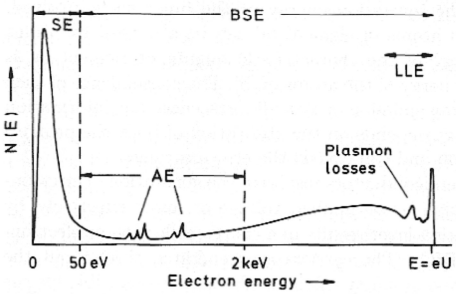
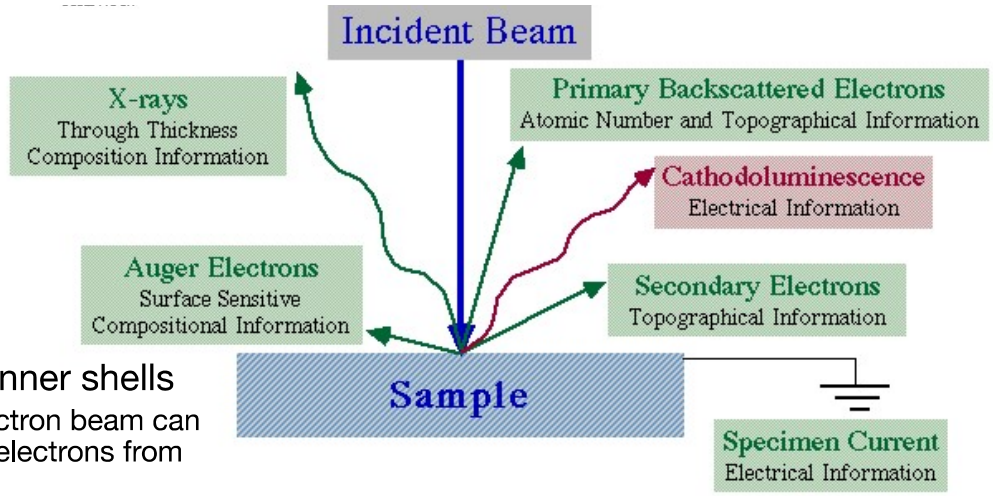


Fig. 1.5 Schematic energy spectrum of electrons emitted consisting of secondary electrons (SE) with $E_{SE} \leq 50$ eV, low-loss electrons (LLE) with energy losses of a few hundreds of eV, backscattered electrons (BSE) with $E_{SE} >$ 50 eV and peaks of Auger electrons (AE)

Figures taken from: L. Reimer, "Scanning Electron Microscopy: Physics of Image Formation and Microanalysis" 2nd. ed. Springer-Verlag, Berlin, (1998)

- Electron beam (primary electrons, PE) generates Secondary and Backscattered Electrons
- **Secondary Electrons (SE)**
  - Most commonly used to form SEM images
  - 2-5 eV energies
  - Generated by inelastic collisions
  - Easily collected by a positively charged grid
  - SE exit the surface from a thin layer of a few nanometers
- **Backscattered Electrons (BSE)**
  - By convention the limit between SE and BSE energy is defined as 50 eV
  - Inelastic scattering
    - Multiple collisions, with dispersion at large angles
    - Multiple energy losses
  - Backscattering coefficient is a function of atomic number, Z
  - BSE allows differentiating phases with different composition

Electron-Specimen Interactions (2)



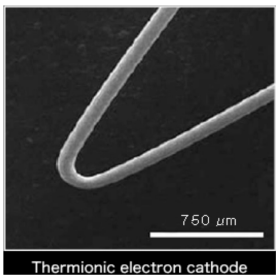
- Ionization of inner shells
  - High energy electron beam can knock out core electrons from atoms
    - Valence electrons fill the core shells of the atom and X-rays are emitted
    - X-ray emission from a volume
    - Photons created by this process can eject another valence electron: Auger electrons
      - Auger electron emission occurs only on the surface
- Electron Beam Induced Current (EBIC)
  - In semiconductors electron-hole pairs are formed due to inelastic dispersion. Applying a voltage or electric field results in a current by separation of charge carriers
- Cathodoluminescence
  - Photon emission due to recombination of electron-hole pairs

SEM & TEM: Components

- Similar elements used in both types of electron microscopes
  - Electron source, electromagnetic lenses, electron detectors
- High power sources (for the beam and the lenses)
- Vacuum environment for the electron beam
  - Rotary vacuum pumps (commonly used in laboratories) do not provide the high vacuum and ultra high vacuum levels necessary
    - Used only as "roughing pumps" to rapidly lower pressure to levels where a more efficient pump can be used
  - For high vacuum in the SEM chamber oil diffusion pumps or turbomolecular pumps are used
  - For ultrahigh vacuum in the electron beam column in SEM and TEM ion getter pumps are commonly used
    - TEM also uses "cryo-pumps": liquid nitrogen cooled surfaces where any volatiles condense and freeze
- Different configuration due to where the sample is placed
  - After the final lens in the SEM
  - Between the condenser and objective lenses in the TEM
- Different detectors used given the difference on the signals that are detected
  - In both some optional attachments are common, such as EDS detectors for elemental analysis
- In both instruments a STEM mode (scanning transmission electron microscopy) may be possible with optional attachments or configurations

Electron Microscope Components: Electron "Guns"

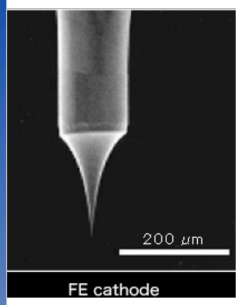
- Electron gun is the source of electrons
- Thermionic Electron Guns
  - Heated cathode under an electric potential
    - 1 kV - 50 kV potential between cathode and anode accelerates electrons
  - Emission current density (j_c) depends on work function (ϕ_w) of cathode material, cathode temperature (T_c)
    - Tungsten wire: T_c=2500-3000 K (T_m=3650 K), $j_c \approx 3$ A·cm^{-2}
    - LaB_6: T_c=1400-2000 K (T_m=2480 K), jc: 20-50 A·cm^{-2}
    - High vacuum is required
    - Wehnelt Cup below filament, with a negative potential, concentrates electron emission in a small area



Thermionic electron cathode

- Schottky (Field) Emission Guns (SFEG)
  - Schottky Effect: an increase in force of field E in cathode reduces the work function
  - ZrO/W(100), coating of ZrO reduces ϕw from 4.5 to 2.7 eV
    - Tc=1800 K, jc ≈ 500 A·cm-2
  - Extraction electrode at 4-8 kV
  - Emission depends on thermal energy, not properly field emission

Electron Microscope Components: Electron "Guns"



- Field Emission Guns (FEG)
  - Typically tungsten tips
  - Potential gradient ($\boldsymbol{E} \geq 10^7$ V·cm^{-1}) reduces band gap in front of the cathode
    - Electrons in the Fermi level only have to tunnel a few nanometers across the potential barrier
  - Two anodes:
    - One regulates field strength on tip (emission current control)
    - The other accelerates electrons (acceleration voltage control)
  - Requires Ultra High Vacuum (any ionized gas residue would destroy the tip)
  - It can work at room temperature (cold cathode field emission "CFE")
    - Commonly operated at Tc=1000-1500 K to avoid gas adsorption on tip

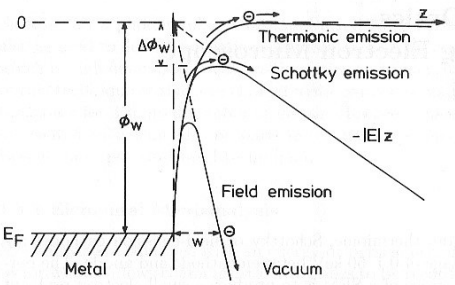


Fig. 2.1. Potential barrier (work function ϕ_w) at the metal–vacuum boundary and decrease of potential energy $V(z)$ with increasing external field $\boldsymbol{E}$ for thermionic, Schottky and field emission

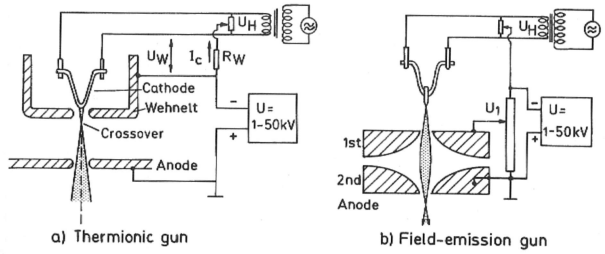


Fig. 2.2. (a) Thermionic electron gun consisting of cathode, Wehnelt cup and anode. The Wehnelt bias U_W is provided by the voltage drop of the emission current I_c across R_W. (b) Field-emission gun of the Butler type

Electron gun SEM images in previous and this page from: http://www.hitachi-hitec.com/ieee/en/fe.html
Figures in this page taken from: L. Reimer, "Scanning Electron Microscopy: Physics of Image Formation and Microanalysis" 2nd. ed. Springer-Verlag, Berlin, (1998)

- In an electron microscope, how many electrons reach the sample in one second?
  - Beam current in TEM is typically 1 pA; 1 A is 1 C/s
  - 1 Faraday is one mole of electrons and has a charge of 96 485.332 C
  - Alternate estimation: the charge of one electron is ~1.6×10^{-19} C/e

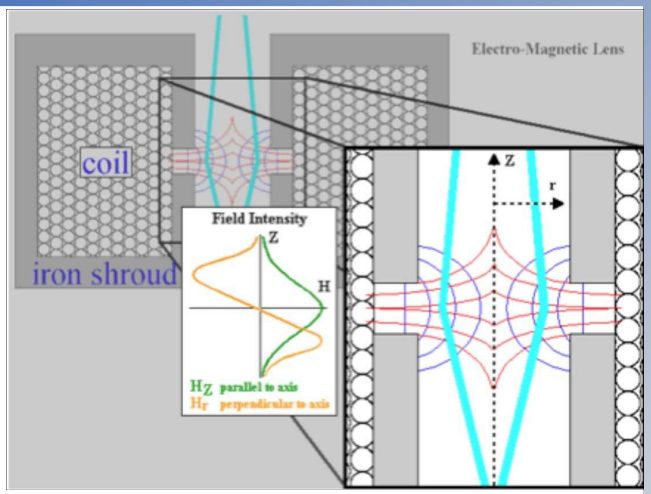
(Estimates are easy to calculate, as shown in class)

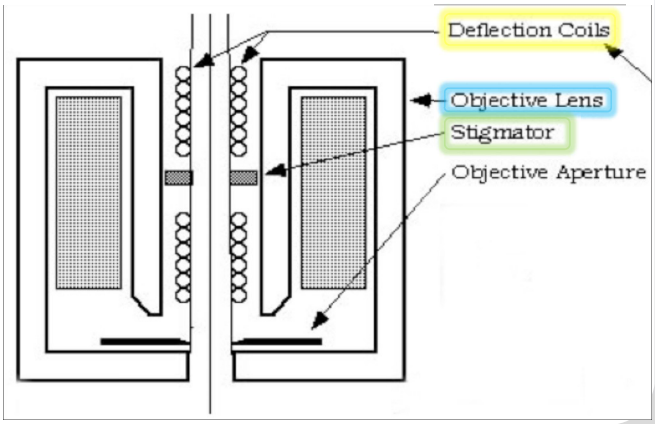
The electron gun in an electron microscope shoots millions of electrons per second!

- Or even thousands of millions:
  - Typical range for beam current is pA to nA
- NOTE: Since electrons repeal each other beam spot size increases with beam current (intensity)

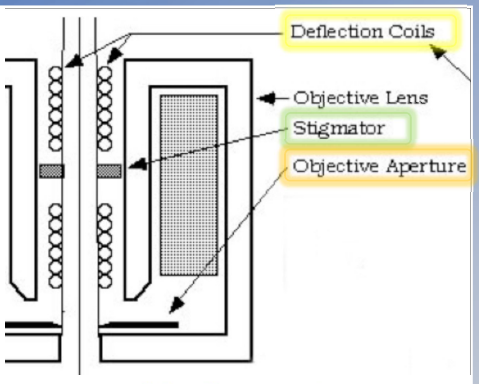
SEM Components: Lenses

- Electron trajectories modified by magnetic fields
- Electromagnetic lenses are essentially a wire spiral around a metallic cylinder (a solenoid)
- Condenser Lenses
  - Converges electron beam and passes it through a focal point
  - Focal point displaced up and down by magnetic field
  - Controls beam intensity
- Objective Lens (Final Lens)
  - Focuses electron beam over the sample
  - Short focal length, *f* (aberrations are proportional to *f*)
  - Must be large enough to include other elements (scanning coils, stigmator)





SEM Components



- **Scanning coils**
  - Deflection coils move the electron beam over the sample
  - A coil set for the *x* axis, another for the *y* axis
  - Synchronized with the monitor that displays image
- **Final Aperture**
  - Reduces or exclude extraneous electrons
    - Electrons with trajectories diverging from beam intercepted by objective aperture
  - Reduces some aberrations (improves focusing and sharpness)
  - Small aperture reduces brightness (beam intensity) but increases depth of field
- **Stigmator** compensates astigmatism
  - Equivalent to a lens rotated 90° with respect to the distortion that induces astigmatism

Lens Aberrations

- Similar to those from optical microscopy
- Axial Astigmatism
  - Asymmetric focus due to small mechanical imperfections
  - Electrons from perpendicular places focused at different distances from the lens

Lens Aberrations
in Electron Microscopy

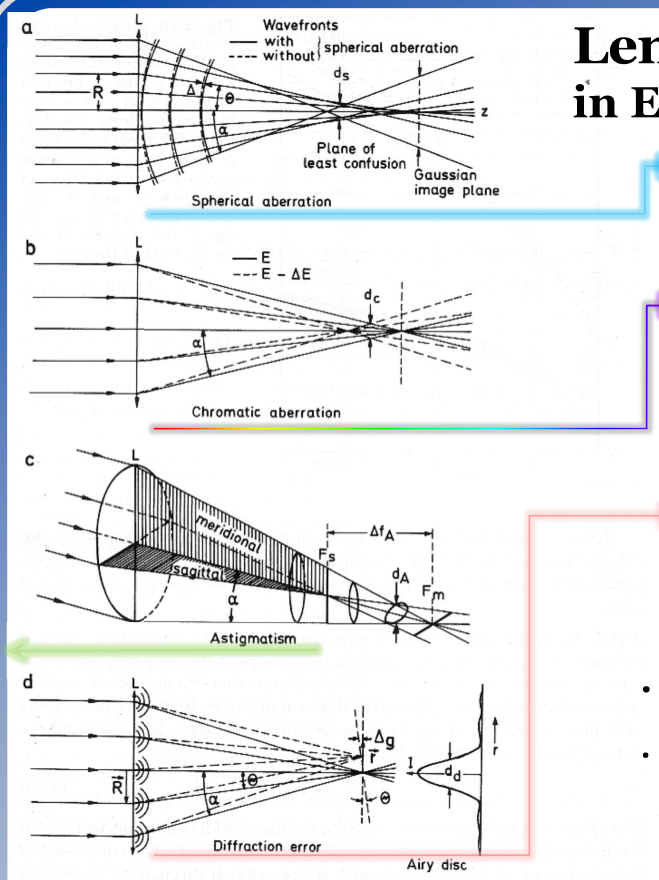


Fig. 2.9. Lens aberrations of an electron lens: (**a**) spherical and (**b**) chromatic aberration, (**c**) axial astigmatism and (**d**) diffraction error disc

- Spherical Aberration
  - Electrons at edge of beam, farther from optical axis, focused closer to the lens
- Chromatic Aberration
  - Electron guns naturally produce a small interval of electron energies
  - Focal length depends on electron energy (i.e. their acceleration voltage)
- Difraction Error
  - Final aperture may form a difraction pattern (Airy disc)
    - Minimized by proper aperture alignment

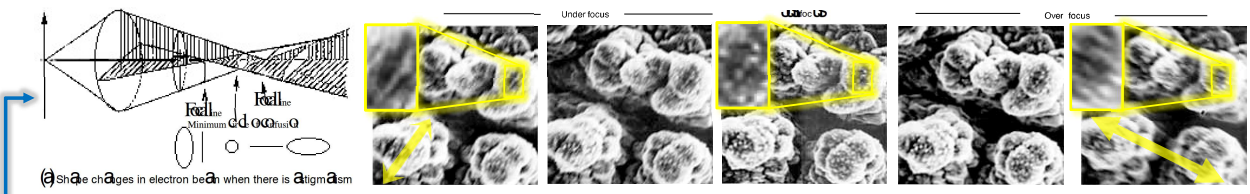
- **Final aperture helps reduce spherical and chromatic aberrations**
- ***Multipole lens correction of spherical and chromatic aberrations can increase resolution further***
- ***Highest Resolution in TEM requires aberration correction***

Figure from: L. Reimer, "Scanning Electron Microscopy: Physics of Image Formation and Microanalysis" 2nd. ed. Springer-Verlag, Berlin, (1998)

Astigmatism and the Stigmator in SEM

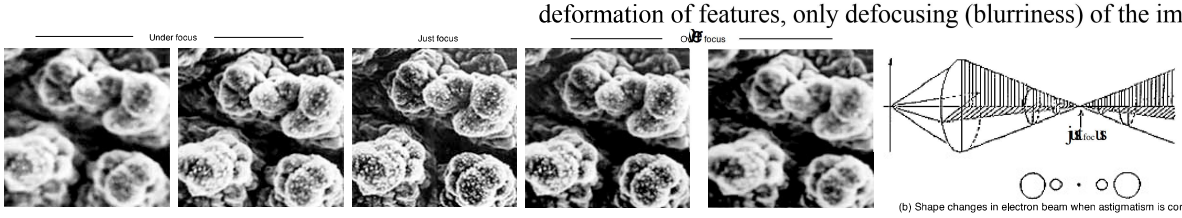
- Electron lenses always show astigmatism
- Stigmator compensates for the defects in beam focusing and makes images sharper
  - Proper adjustment of the stigmator at the beginning of an SEM session is a requirement for obtaining the best resolution

- Re-adjustment of the stigmator may be necessary during the session (e.g. if working distance changes, or it has been too much time since the start of the session)
- If there is a change in acceleration voltage, the stigmator would likely need to be readjusted



Before astigmatism correction circular features get deformed into ellipses in perpendicular directions for the underfocus and overfocus planes

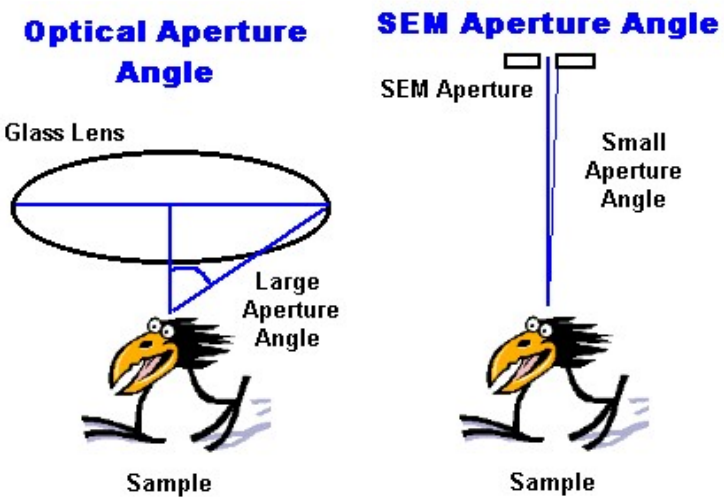
After astigmatism correction there is no elliptical deformation of features, only defocusing (blurriness) of the image

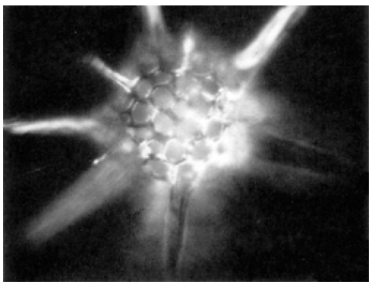


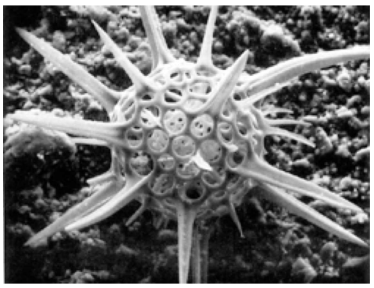
Images ©JEOL taken from: "A Guide to Scanning Microscope Observation" JEOL Ltd. [PDF downloaded in 2005 from wwww.jeol.com, no longer available online]

Depth of Field

- Distance above and below focal plane that appears in focus
  - Typically 10-60% of the width of the field of view
  - Inversely proportional to electron beam angle (aperture angle α)
- Depth of field of SEM is 100 to 500 times better than optical microscopy
  - Optical microscopy requires large apertures to increase resolution (in the focal plane), but that limits depth of field (height of focal plane that is in focus)
  - Example: radiolarian skeleton



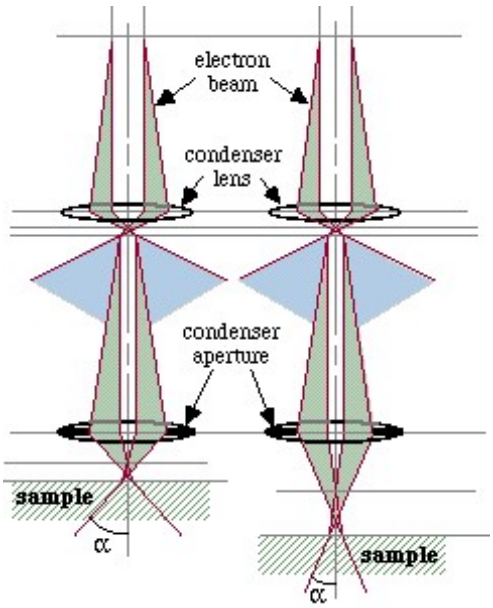




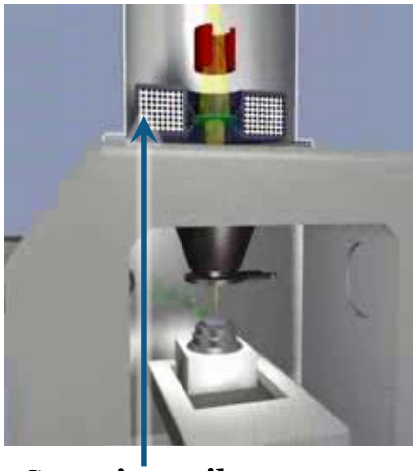
Working Distance

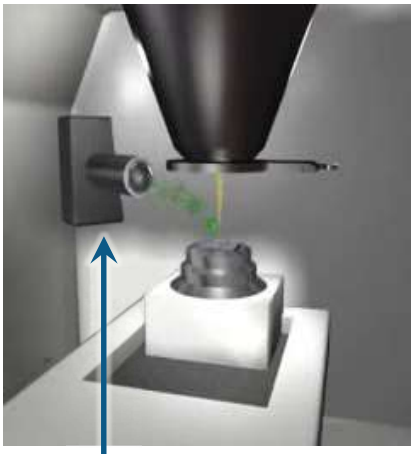
- Distance from final lens to optimal focus point of the electron beam
  - When operating an SEM linking Z (physical distance on the motorized stage and sample holder) to WD is usually one of the first things to do

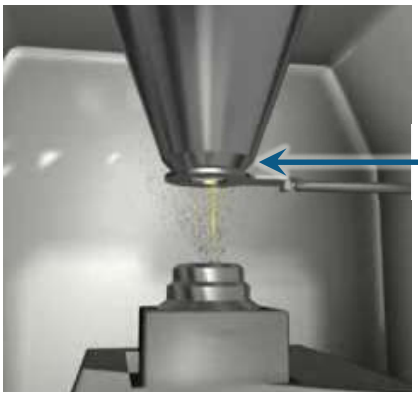
By moving sample away from lens
- Working Distance increases
- Demagnification decreases
  - Lens current is reduced
  - Increased Focal Length
- Spot Size increases
  - Lower resolution
- Divergence angle (α) decreases
  - Larger depth of field



	Small WD	Large WD
Spot Size	Smaller	Bigger
α	Bigger	Smaller
Depth of Field	Smaller	Bigger
Resolution	Higher	Lower







Scanning coils raster the electron beam over the sample

Everhart-Thornley secondary electron (SE) detector has a charged grid (usually ~200 V) to attract low energy electrons

Backscattered Electron (BSE) detector is a ring around the final aperture over the sample

Everhart-Thornley Secondary Electron Detector

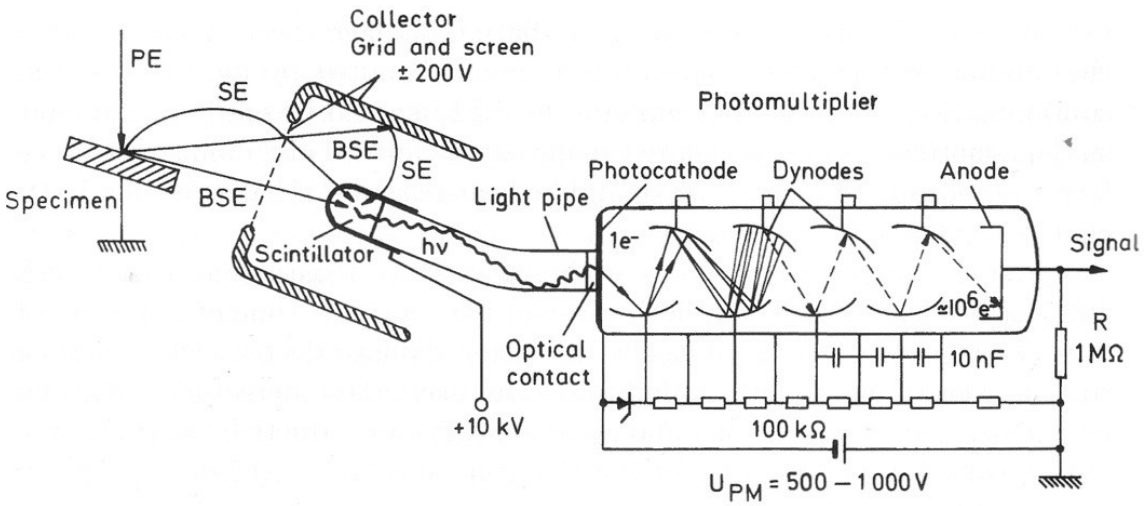


Fig. 5.1. Scintillator–photomultiplier combination (Everhart–Thornley detector) for recording secondary electrons

- Note: if the collector grid is negatively biased, low energy electrons (SE) are repelled and the E-T detector can be used as a BSE detector

Figure from: L. Reimer, "Scanning Electron Microscopy: Physics of Image Formation and Microanalysis" 2nd. ed. Springer-Verlag, Berlin, (1998)

Contrast in a SE Detector

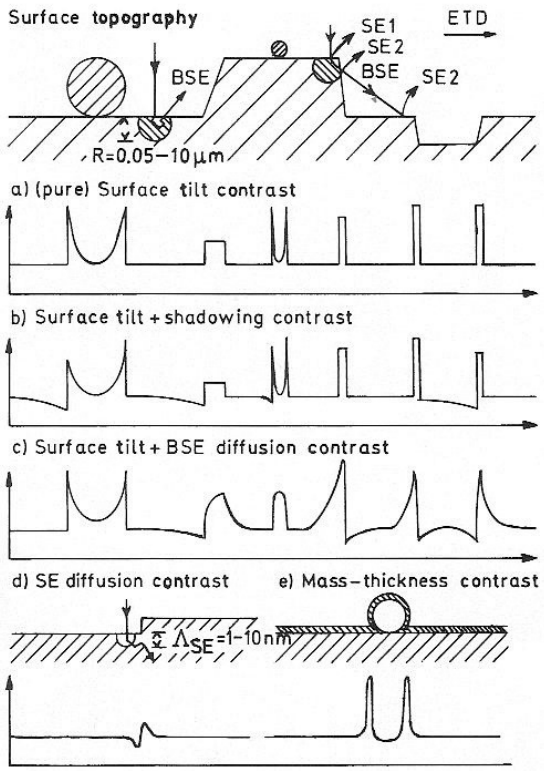


Figure from: L. Reimer, "Scanning Electron Microscopy: Physics of Image Formation and Microanalysis" 2nd. ed. Springer-Verlag, Berlin, (1998)

- Most of the contrast is due to topography
- Other factors affect image appearance

a) Surface tilt contrast
- SE yield depends on tilt angle of local surface perpendicular to incident ray

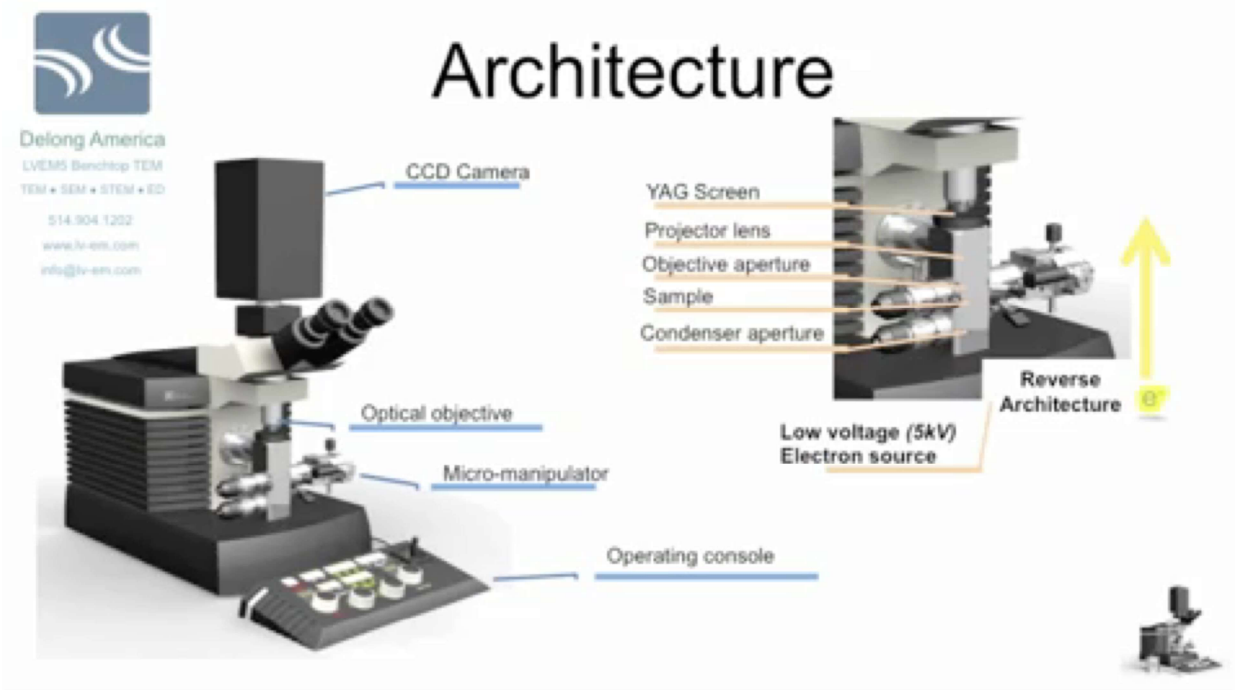
b) Shadowing Contrast
- Detector (to the right) can not collect all SE, normal surfaces in the opposite direction to detector appear darker

c) BSE Diffusion Contrast
- Near borders exiting BSE excite more SE

d) SE Diffusion Contrast
- Occurs when distance to a border is on the order of SE exit depth (~0.5-20 nm)

e) Mass Thickness Contrast
- Number of SE produced by metallization coating is approximately proportional to the mass thickness that the primary electrons have to penetrate

Video showing operation of a compact SEM + TEM



Video taken from: https://youtu.be/DVEYdXw687E

Magnification

- Magnification is the ratio between the area in which the image is projected (of width $\boldsymbol{B}$) and the observed area (of width $\boldsymbol{b}$)
- $\boldsymbol{M = B/b}$
  - The area of the projected image is fixed in an electron microscope (fixed width of viewing screen)
- Scanning a smaller area: larger magnification
  - Scan area controlled by scanning coils in SEM
  - In TEM beam width, controlled with condenser lens, determines magnification
- Low magnification: large deflection angles
  - Lens aberrations may have larger effects: lower resolution
- Magnification is not a constant of the image
  - An image projected at twice the size shows twice the original magnification
- Magnification is not the same as resolution
  - Magnification refers to the size of the image
  - Resolution refers to the ability to resolve detail

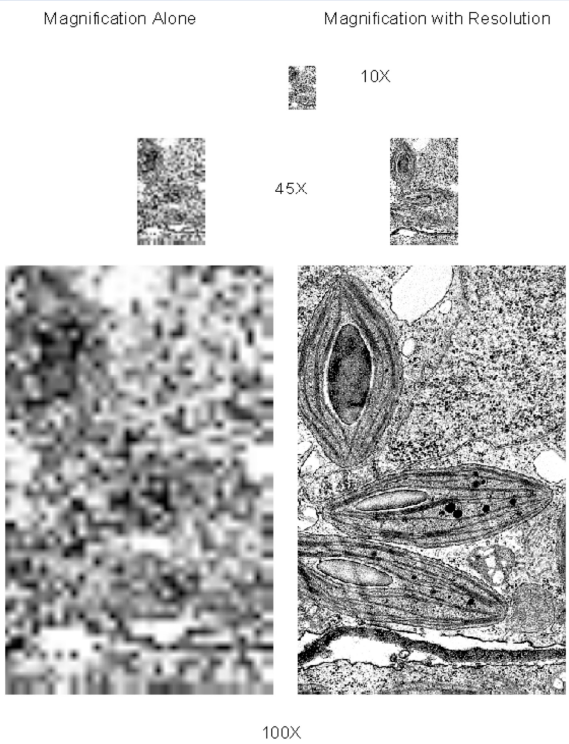


Image (optical microscopy, used as example only) taken from: W.H. Heidcamp, Cell Biology Laboratory Manual; Chapter 1: The Microscope
http://homepages.gac.edu/~cellab/contents.html
© Dr. William H. Heidcamp

Resolution

- Resolution is not the same as magnification
  - But without high resolution high magnification is useless
    - Images taken at the highest magnification will not show details if the instrument does not have the resolution to show it
- Resolution: the ability to resolve (distinguish) two points separated by a distance
  - Can not be smaller than electron beam diameter (probe size or spot size)
- Resolution depends on sampling volume (the part of the sample where the detected signal originates)
  - Sampling volume is a function of the electron beam energy and diameter
  - Sampling volume is a function of the sample composition and other factors

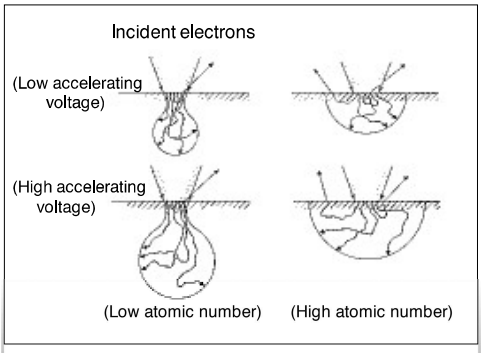
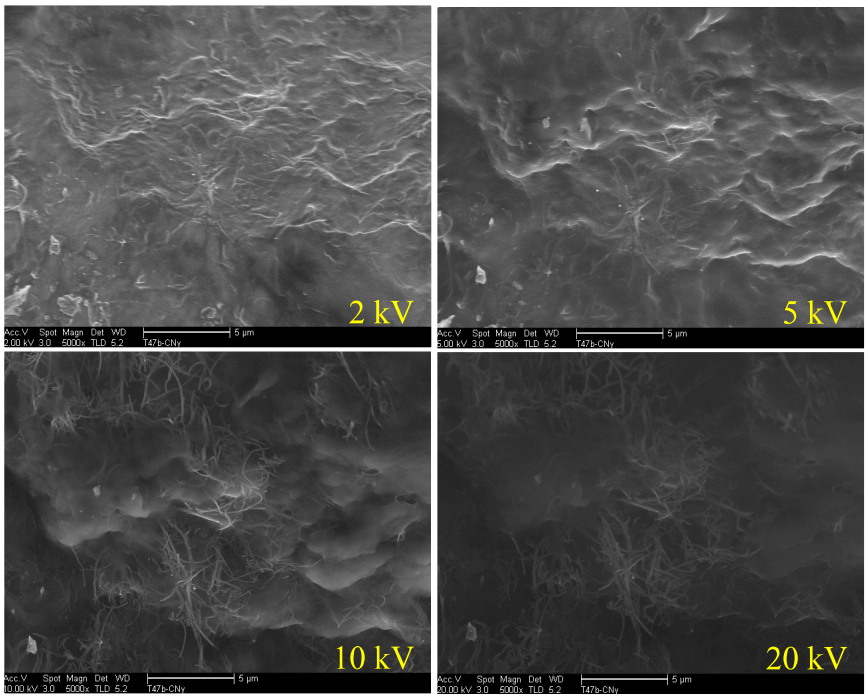


Figure showing electron diffusion volume (related to sampling volume) changing with sample atomic number and acceleration voltage

- Maximum resolution is not an instrument constant: it depends on the application
  - Resolution values specified by manufacturer are determined under ideal conditions with a specimen designed to evaluate high resolution
- Obtaining the maximum resolution depends on the electron microscope operator

Electron-Specimen Interactions:
Acceleration Voltage and Imaging in SEM



SEM images of composite of carbon nanotubes and polyamide-6,6
(Taken by Fernando J. Rodríguez-Macías, in an FEI XL-30 SEM at IPICYT, around 2006)

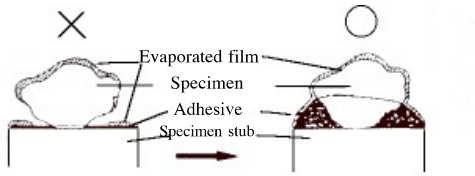
- With Lower Acceleration Voltage
  - Image shows only the actual surface
  - Resolution of some features may be lower
- With Higher Acceleration Voltage:
  - E-beam penetrates further in the sample
  - Higher Resolution for many features
    - But sharpness of surface features may be reduced
  - Features or components below the surface may appear in the image
- *User must beware of image artifacts when interpreting images*

Some Applications of SEM in Materials Science and Nanotechnology

- Examine natural surface of materials
- Observe internal features exposed by fractures or by cutting
- Fractography: Analysis of fracture surfaces
  - Aspects related to materials failure or mechanical properties
- Observe transformations due to a variety of treatments
  - Chemical, thermal and other treatments
- Composite Materials Analysis
  - Observation of the dispersion of the reinforcement
  - Observing interface between matrix and reinforcement (adhesion and wetting)
  - Visual determination of porosity
- Nanomaterials
  - Characterize shape and size distribution of nanostructures and nanoparticles
  - Additional analysis with SEM accessories (EDX, etc.) are also very useful
- *Et cetera, etc.*

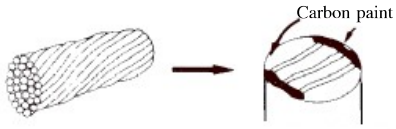
Sample Preparation for SEM

- Almost any solid specimen can be examined
  - Vacuum chamber size may be the only limitation for sample size
- Conducting samples can be observed directly
- Non-conducting samples may require thin conducting coating to prevent charging during observation
  - Coating must make electrical contact to ground via stage
  - Gold coating may increase emission of SE and thus increase resolution for some features
    - But resolution is lost for features that are smaller than the thickness of the coating
  - If sample has irregular shape use of conducting carbon paint is recommended
    - Tip: if you don't have conducting paint a thin strip of conducting tape for sample mounting can be used to make electrical contact
- Samples must be dry and/or not contain any volatile components
  - Organic molecule impurities can contaminate sample chamber
    - Solvent evaporation step required if conducting paint is used



(b) Insufficient adhesive (a) Insufficient adhesive

Fixing of a bulk specimen

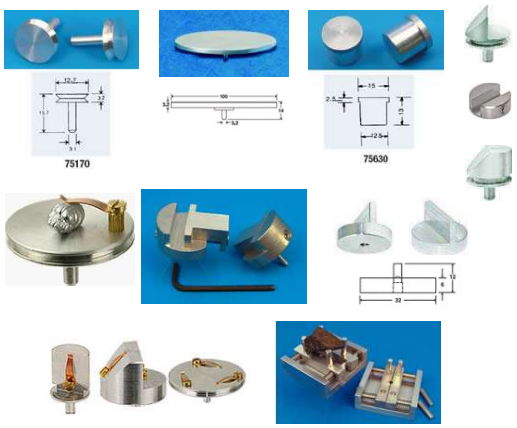


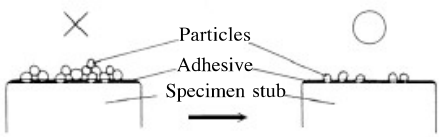
Fixing of fiber

Sample preparation diagram ©JEOL taken from: "A Guide to Scanning Microscope Observation" JEOL Ltd. [PDF downloaded in 2005 from wwww.jeol.com, no longer available online]

Sample Preparation for SEM

- Samples must be firmly mounted and affixed to sample holder
  - Carbon tape or copper tape
    - Very low vapor pressure conductive adhesive. NOT regular office double sided tape
  - Graphite or silver paste as adhesive
    - Requires a solvent evaporation step
  - In some cases sample can be be deposited over a substrate or sample holder
    - For example, nanoparticles from suspension, over a well polished Al surface or another flat conducting surface
  - A variety of sample holders is available from several suppliers
  - Mechanical clamping is an option for some samples
- No loose powders should be introduced
  - Even less so if they are non-conducting
  - Blowing compressed air over sample is recommended to remove loose particles





Remove excessive particles

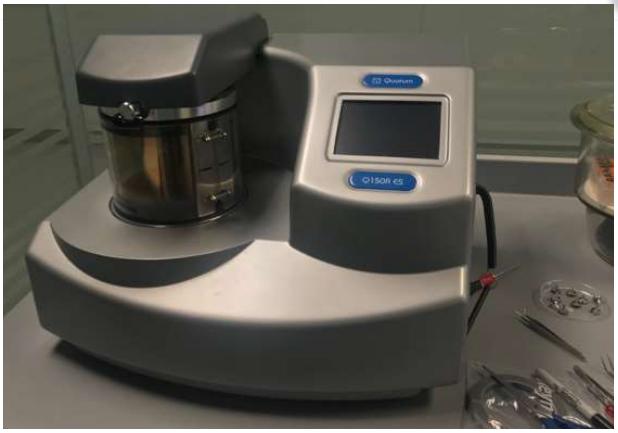
Photos and schematics of SEM samples holders taken from: < https://www.emsdiasum.com/microscopy/products/sem/mounts.aspx > < https://ravescientific.com/sem-sample-holders/s-clip-sample-holders >. Particle sample preparation diagram ©JEOL taken from: "A Guide to Scanning Microscope Observation" JEOL Ltd. [PDF downloaded in 2005 from wwww.jeol.com, no longer available online]

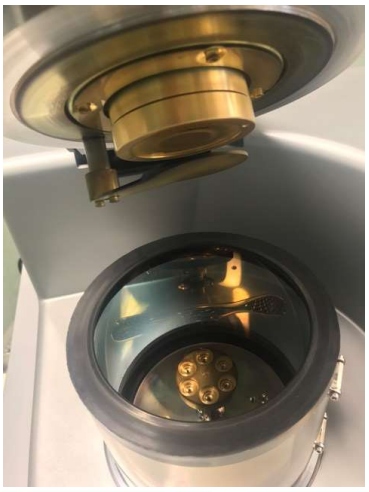
Sample Coating for SEM: Sputtering

- Positive inert gas ions bombard the target material (cathode *)
  - Sputtering dislodges atoms from target, which can then deposit on the substrate
  - Sputtering typically uses argon to create the glow discharge
  - Pressures: 20–150 mTorr

    * In Spanish the technique is sometimes called "*pulverización catódica*"

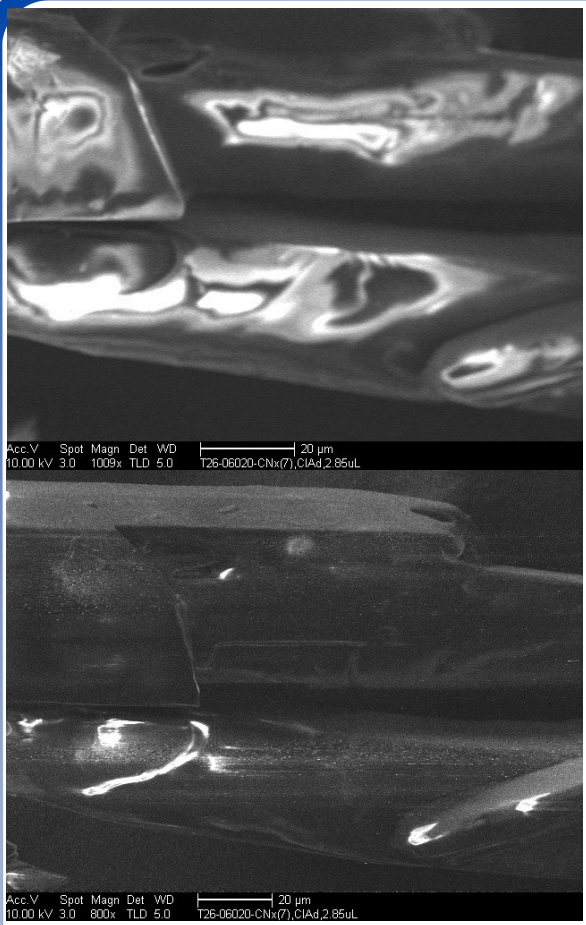
- Sputtering targets for SEM are usually made of gold
  - Other metals may be used too
  - Carbon coating is another option





Sputter Coater at the SEM imaging facilities of the CETEX Annex of Campus Monterrey.

Photos © Fernando JRM, released under a CC-BY-NC-SA license



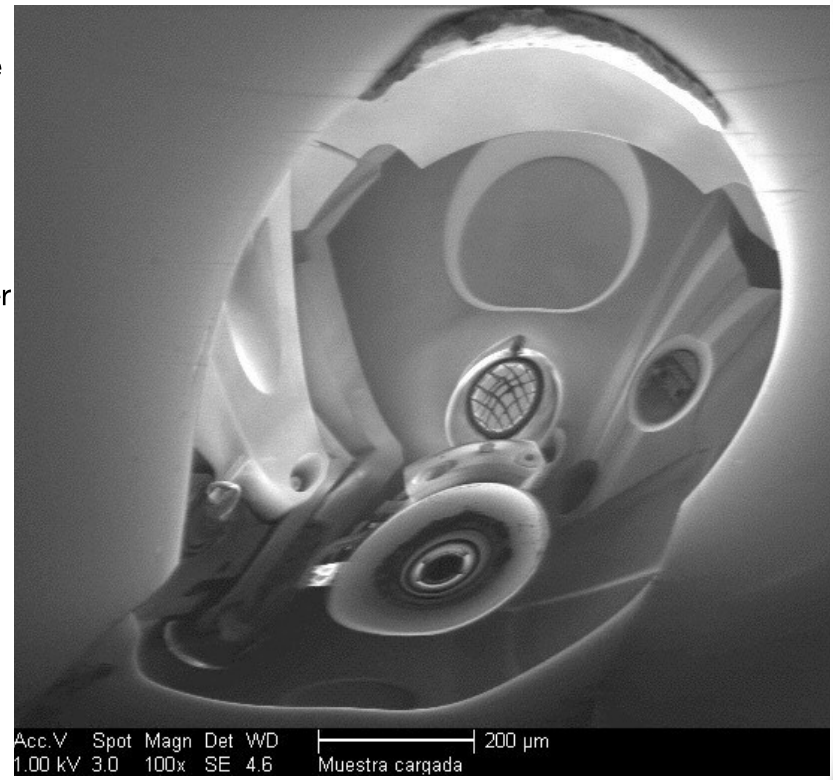
Charged Sample Artifacts

- Charged zones look extremely bright due to deflection of electrons
  - Adjacent zones may look darker
- Image artifacts can be produced in the detector
- Adjusting contrast and brightness is difficult
- Acquiring images may be impossible
- **Avoid sample charging!!!**
  - Use lower acceleration voltage
  - Use sputter coating for low conductivity samples

SEM images of composite of carbon nanotubes and polyamide-6,6, due to deficient dispersion of nanotubes the polymer charges (in a composite with good CNT dispersion no charging would usually be observed).
(Taken by Fernando J. Rodríguez-Macías, in an FEI XL-30 SEM at IPICYT, around 2006)

Extreme Example of Charged Sample

- Non-Conducting sample acting as electron mirror
  - Secondary electrons are generated from impact of electrons from the reflected beams with the walls of the SEM chamber
  - The wire grid seen on the center is the grid of the Everhart-Thornley detector
  - The conical feature is called the polepiece, is part of the final lens
    - The opening of the beam column looks dark since only primary electrons come from that spot



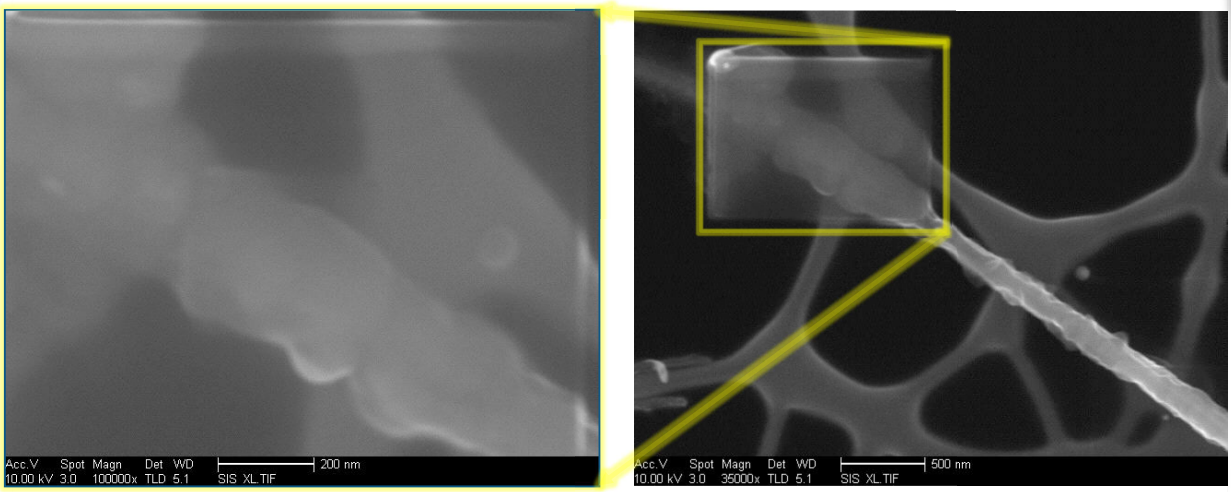
SEM image courtesy of Daniel Ramírez-González, taken in an FEI XL-30 SEM at IPICYT, around 2007)

Carbon Contamination

- Presence of hydrocarbons is almost unavoidable
  - Silicone or hydrocarbon oils from vacuum pumps, vacuum grease on seal, *fingerprints*
- Organic molecules deposited on the sample decompose under electron irradiation
  - They usually polymerize and cross-link
  - Carbon rich contamination film (or *even a column under a static beam)*
    - Observed as a darker area usually (but in some cases it can look brighter)

- **Minimize Contamination**
  - Always use gloves when handling and preparing samples
  - Rotary pump should not be used as the only pump for long periods
    - Pump oil has a very low vapor pressure but it does evaporate slowly
    - Switch to high vacuum pump at pressures of 0.1-0.2 mbar
  - Use only high vacuum grease (e.g. Apiezon) for O-ring seal lubrication and fluorocarbon seals (Viton)
  - Use of turbomolecular pump for high vacuum instead of oil diffusion pump
  - Fill chamber with dry nitrogen
  - Use low temperatures
    - Cold traps to condense volatiles, or cool sample to prevent evaporation
  - Clean sample with solvents when appropriate
    - But after a day exposed to the environment it will again be contaminated

Example of carbon contamination deposit



- Rectangular feature highlighted on image to the right is the area shown on left image
- This was not part of the sample: a carbon film formed as the beam was scanned
  - This is an extreme case, usually only a thin carbon coating will be seen over scanned areas
- Resolution is lowered, and surface features seen are not representative of sample morphology

SEM images of composite of carbon nanotubes and polyamide-6,6.
(Taken by Fernando J. Rodríguez-Macías, in an FEI XL-30 SEM at IPICYT, around 2006, © Fernando JRM, under a CC-BY-NC-SA license)

Some Advantages of SEM

- Relatively easy to use
- High resolution
  - Even ≤ 1 nm for FEG-SEM
    - Hitachi claims 0.4 nm (at 30 kV) for their Ultra High Resolution SEMs (1.6 nm resolution at 1 kV)
- Large interval of magnifications
  - From tens to hundreds of thousands
- Large Depth of Field
  - 300 times better than in optical microscopy
  - "tri-dimensional" appearance of images
- Wide field of view
- Less sample preparation than TEM
- Direct Imaging of the Surface
  - Image formation is relatively simple
- Can be combined with elemental analyses (EDX, BSE, Auger)
- For thin samples it can be combined with TEM
  - if STEM detector is available
    - NOTE: STEM resolution in SEM is lower than in a "real" TEM/STEM

Disadvantages and Limitations of SEM

- Operating in high vacuum (10^{-5} torr) limits use for wet or biological samples
  - Sample prep for drying without any deformation can be labor intensive
  - Low Vacuum or "high pressure" SEMs are an alternative
- Lower resolution than TEM
- Only the surface is observed
- Bi-dimensional images of tridimensional surfaces
  - Stereoscopic pairs can be created
- Charge accumulation in insulating samples
- For organic, biological and polymeric samples there can be thermal decomposition
  - Metallic coating of a few nm can protect against this
  - But coating process may also result in thermal damage
- Radiation induced decomposition of organic materials
  - Radiation induced decomposition of inorganic materials is very rare
    - Radiolysis: decomposition due to ionization
    - High mobility ions can migrate due to charge in insulating materials

Variations of SEM

Some related techniques, optional modes, or accessories can extend the usefulness of SEM, among them: ESEM/LVEM, STEM, FIB

Low Vacuum / Environmental SEM

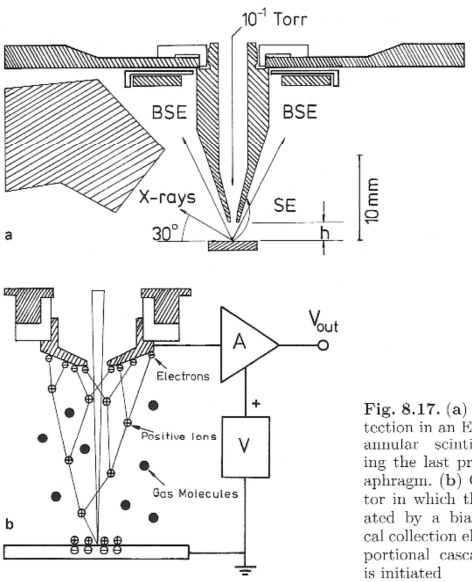


Fig. 8.17. (a) BSE and x-ray detection in an ESEM by two semi-annular scintillators surrounding the last pressure-limiting diaphragm. (b) Gaseous SE detector in which the SE are accelerated by a bias V on the conical collection electrode and a proportional cascade multiplication is initiated

- Gas ionization used to amplify SE signal
  - Ionization "cascade" by collision of SE with gas molecules
  - Voltage between GSED (gaseous secondary electron detector) and sample mount can amplify signal

- LVEM: Low Vacuum SEM
  - "LVEM" sometimes used to indicate an instrument that can also operate at Low Voltage
- VP-SEM: Variable Pressure SEM
- ESEM: Environmental SEM
  - Sometimes the term ESEM is used to denote that a specific environment (atmosphere) is used
- Sample chamber pressures of a few torr (on the order of $10 - 10^2$ Pa) in environmental mode
- Differential Pumping used to keep beam column at ultra high vacuum (~10^{-9} torr) and allow low vacuum (a few torr) in the chamber
- Inside chamber primary electron beam spreads
  - Electron "skirt" has lowered intensity and only contributes to background noise
  - Secondary cations neutralize charge in sample
  - Can image non-conducting samples
- Chamber atmosphere can be chosen
  - Water vapor is most common
  - Allows imaging of wet and biological samples

STEM: Scanning Transmission Electron Microscopy

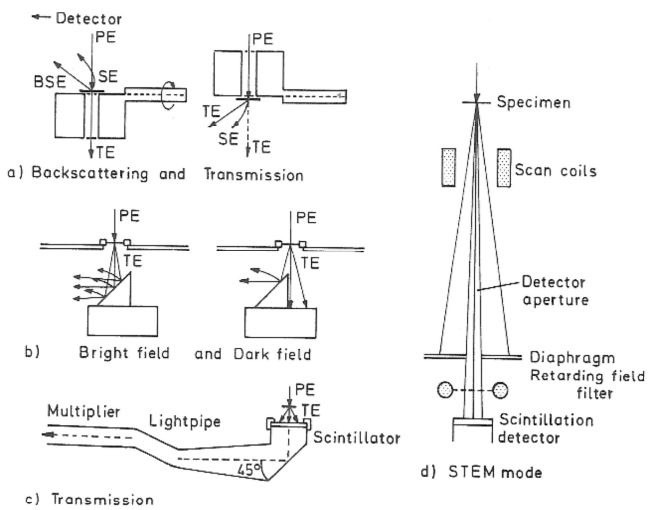
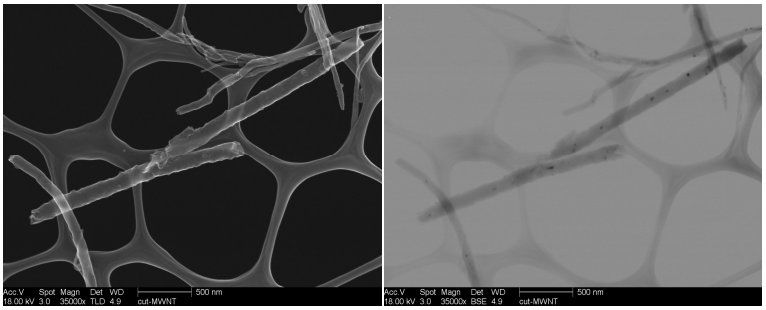


Fig. 8.14. Different specimen stubs and detector arrangements used for recording transmitted electrons in a SEM: (a) specimen stub for backscattered and transmitted electrons, (b) TE/SE conversion for bright- and dark-field images, (c) scintillator and light-pipe below a transparent specimen, (d) STEM mode for recording diffraction patterns and electron energy filtering

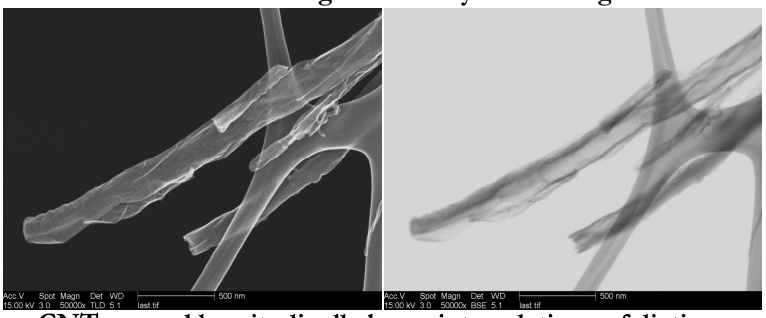
- Additional detector in the SEM can be used to measure transmitted electrons on thin samples
  - Transmitted electrons: bright field
  - Can detect also diffracted electrons: dark field
- Can give additional information on thin samples
- STEM in SEM is limited to the same resolution as the SEM mode
  - STEM in TEM gives atomic resolution, given that TEM by nature can achieve higher resolutions than SEM

SEM+STEM Example: Chemical Modification of Carbon Nanotubes

- CNT functionalized by the "nanotube salts" method
  - Method can be used for *in situ* polymerization with several polymers
- Electron microscopy showed indications of partial opening as a "side effect"
  - Opening increased by exfoliation processes after intercalation
  - Under optimized conditions there is full opening ("unzipping") of carbon nanotubes to form graphitic nanoribbons
- STEM allowed to distinguish clearly between surface damage (observed by SEM) and nanotube "unzipping"
- First report that showed that carbon nanotubes could be "unrolled" into nanoribbons



CNT with surface damage due to oxyacid cutting treatment



CNT opened longitudinally by an intercalation-exfoliation process ("exMWNT")

A.G. Cano-Márquez; F.J. Rodríguez-Macías; J. Campos-Delgado; C.G. Espinosa-González; F. Tristán-López; D. Ramírez-González; D.A. Cullen; D.J. Smith; Mauricio Terrones; Y.I. Vega-Cantú; "Ex-MWNTs: Graphene Sheets and Ribbons Produced by Lithium Intercalation and Exfoliation of Carbon Nanotubes", *Nano Letters,* 9(4), 1527-1533 (2009). DOI: 10.1021/nl803585s

Focused Ion Beam

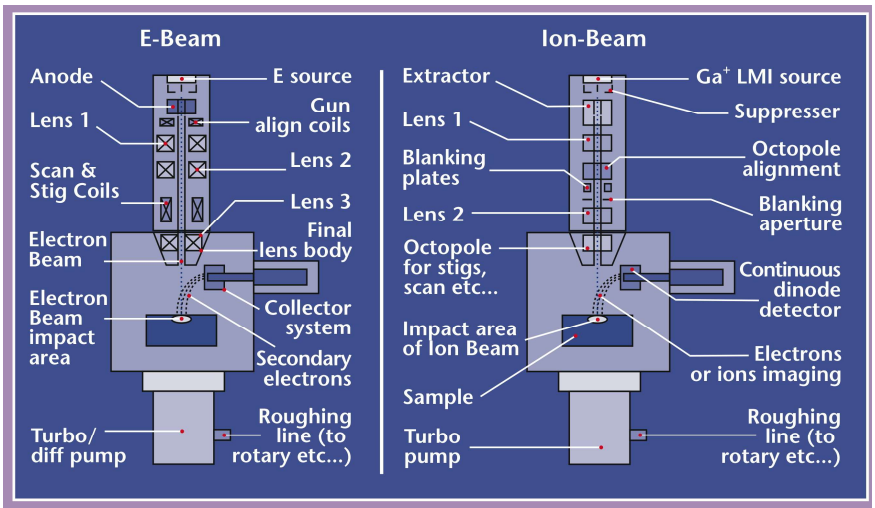


Figure 8: Schematic presentation of SEM and FIB and the many similarities of the instruments.

- Ion beam focused by electromagnetic lenses over the surface generates secondary electrons, which can be used for imaging
- Ion beam also causes sputtering, which can be used to etch and pattern the sample
  - Ion Beam Lithography

Image taken from: "Focused Ion Beam Technology, Capabilities and Applications", PDF brochure, © 2005 FEI Company downloaded in 2012 from www.feicompany.com. No longer available online, FEI is now part of Thermo Fisher Scientific

Focused Ion Beam (FIB)

- Related to SEM, and uses similar instrumentation
- Instead of e-beam a beam of Ga^+
  - Impact of gallium ions generates secondary electrons
    - Imaging with the ion beam
  - Impact of Ga+ atoms erodes surface (sputtering)
    - Can etch the sample ("milling")
    - Secondary ions from specimen atoms can provide compositional information and also be used for imaging
  - Ga+ ions can also react with some chemical substances
    - Useful to deposit metals, for example
  - Lithography via a combination of etching by ion beam and masking through metal deposition
    - Can be used to create device prototypes, or to fix lithography masks
- Dual Beam Systems
  - Electron beam and FIB in the same instrument

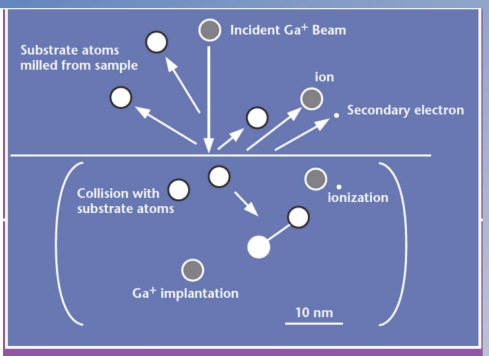


Figure 5: Interactions of the ion beam with the sample surface. The unique control offered by beam currents and spot sizes allow use of the FIB for both nano engineering as well as for high resolution imaging using secondary electrons as well as ions.

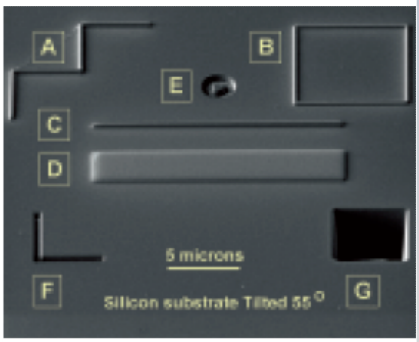


Figure 15: Silicon surface showing both milling and deposition capabilities as examples of the creation of local structures. A, B, C and D are micro-depositions, whereas E, F and G are structures milled into the sample.

Images taken from: "Focused Ion Beam Technology, Capabilities and Applications", PDF brochure, © 2005 FEI Company downloaded in 2012 from www.feicompany.com. No longer available online, FEI is now part of Thermo Fisher Scientific

FIB

- Useful for observation of materials and device failures at the nanoscale
- Useful for special TEM sample preparation
  - Cut thin slice with FIB: less distortion than ultramicrotomy

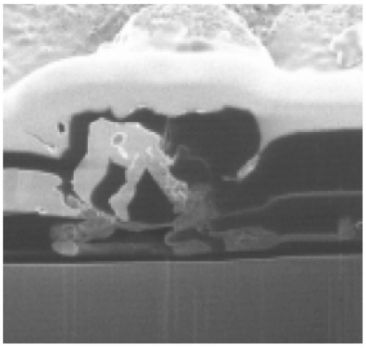


Figure 14: Example of a cross-section imaged and made by the FIB. The cross-section shows an insulation defect on a semi-conductor device.

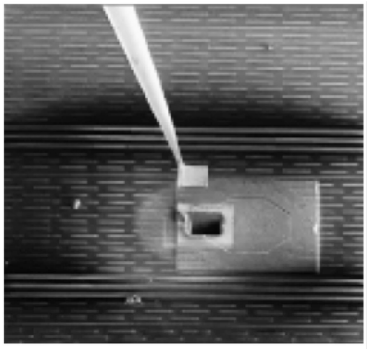
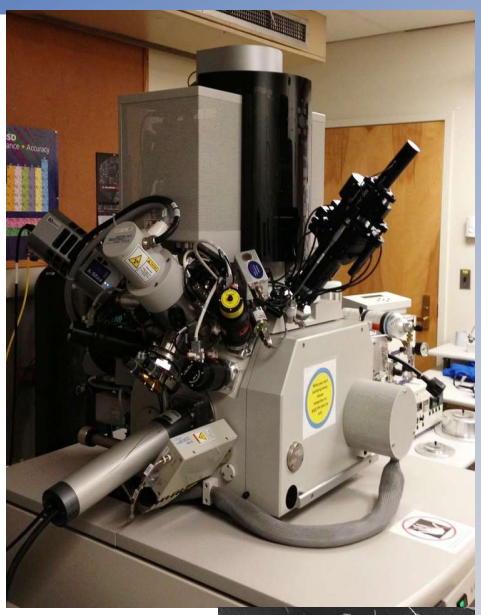
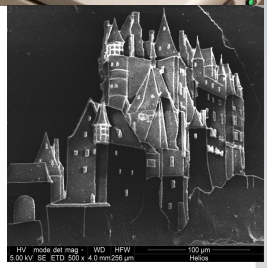


Figure 16: In-situ foil extraction using micro-manipulators in the chamber. The next stage is that the TEM lamella shown on the tip is deposited on a TEM grid, or "micro-welded" onto a support ring that fits in the TEM.

Figures taken from: "Focused Ion Beam Technology, Capabilities and Applications", PDF brochure, © 2005 FEI Company downloaded in 2012 from www.feicompany.com.



Arbitrary patterns can be etched



Sandcastle etched in a grain of sand from: http://www.cmarcelo.com/#/sandcastles/

Some Focused Ion Beam (FIB) Applications

- Deposition of metals can be used to make electrical circuits for testing nanostructures and for device prototypes
  - Can also be used in the semiconductor industry to fix lithography masks or to edit circuits in prototypes

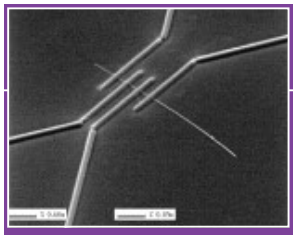


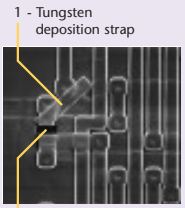
Figure 39: Ion beam deposited tungsten nano-wires for direct electrical measurements (4 point probe) of nano structures, in this case a carbon nanotube.

On-Chip Circuit Editing

Precision focused ion beam (FIB) milling and deposition enable the editing of existing circuits to shortcut the debug and test cycle. Advanced FIB techniques facilitate the editing of deep sub-micron technologies, planarized devices and flip chip packaged parts. FIB circuit changes are done by opening circuit nodes from the top, then connecting these nodes together by depositing metal over the top insulator into these new vias, and finally cutting unwanted tracks.

FIB Metal Deposition

New connections are added using FIB deposition (1), and the original path of the circuitry is cut (2). The new circuit design is now ready for testing/debug.



- Etching with the FIB can be used to look at cross-sections of materials or for patterning

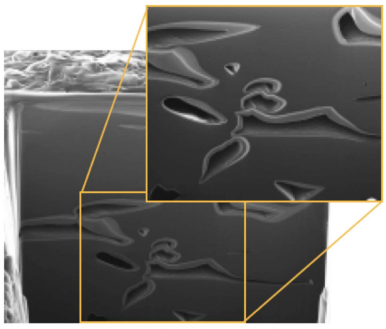


Figure 48: FIB cross-section through an uncoated bi-phase polymer. This shows a mixing process failure in the molded polymer product. Insert: detailed view showing separation of polymer phases around air pockets.

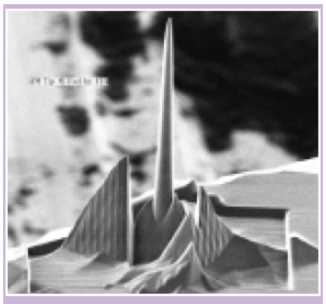
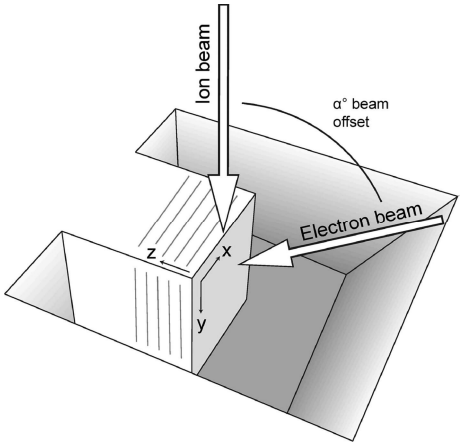


Figure 44: SE image made with FIB showing a silicon AFM tip machined to be a super-tip, with very small radius for high resolution AFM imaging.

Images taken from: "Focused Ion Beam Technology, Capabilities and Applications", PDF brochure, © 2005 FEI Company downloaded in 2012 from www.feicompany.com. No longer available online, FEI is now part of Thermo Fisher Scientific

FIB-nt: Nanotomography with a FIB/SEM

- Acquisition of three dimensional information by recording a sequence of images at different depths
- Typical process exposes a defined volume within trenches defined with the FIB
- A slice is then removed with the FIB and an SEM image of the layer is acquired
  - Optional: acquire compositional information with EDS or other techniques
- The milling is repeated and a new image is recorded
- This process is repeated several times
  - Automated software typically used
- Specialized software is used to build a 3D model from the series of 2D images

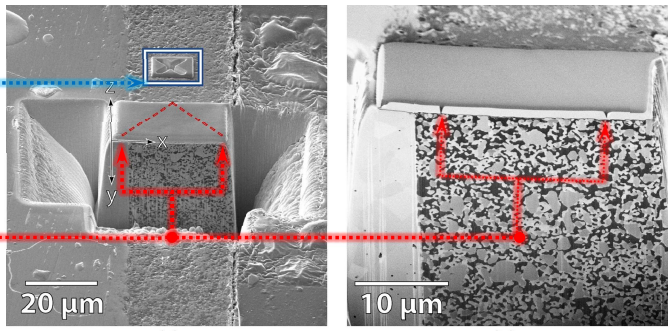


Schematic of FIB-*nt* experimental geometry. The sample is positioned at the intersection of the electron and ion beams for simultaneous imaging and milling. α is typically in the range of [50–55]°

Image taken from: J.A. Taillon, C. Pellegrinelli, Y.-L. Huang, E.D. Wachsman, L.G. Salamanca-Riba, *"Improving microstructural quantification in FIB/SEM nanotomograph"* Ultramicroscopy 184 (2018) 24–38. DOI: 10.1016/j.ultramic.2017.07.017

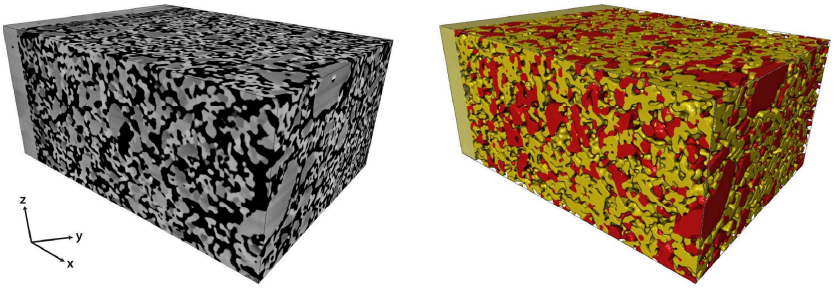
FIB-nt: Nanotomography with a FIB/SEM

- Marks are made in the sample for alignment during automated data acquisition and to calibrate depth
  - Note: a protecting Pt layer is added on the edge to make slice milling more uniform



(a) (b)

- Example of FIB-nt of a porous cathode for a Solid Oxide Fuel Cell (SOFC)
  - Dimensions of the volume are (26.4, 19.9, 12.1) µm.
  - LSM: $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3+\delta}$
  - YSZ : $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$



(a) (b)

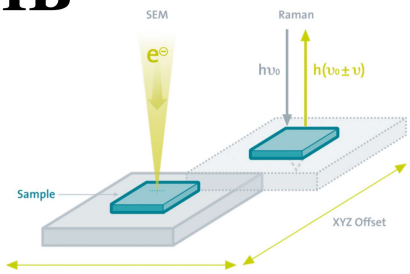
(a) Three-dimensional view of the acquired SEM images (Pore – black, LSM – mid-gray, YSZ – bright gray)

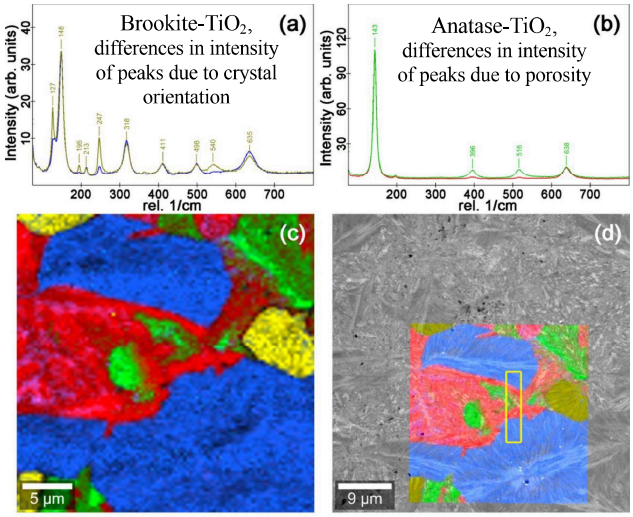
(b) reconstruction into a 3D volume model after image preprocessing and segmentation (Pore – not shown, LSM – red, YSZ – yellow).

Images taken from: Ultramicroscopy 184 (2018) 24–38

Example: SEM+Raman+FIB

- Correlative Raman Imaging and Scanning Electron Microscopy
  - RISE: Raman Imaging Scanning Electron Microscopy "introduced by TESCAN and WITec in 2014"
  - Confocal Raman spectroscope integrated with SEM
  - Instrument automatically moves sample between Raman microscope and SEM



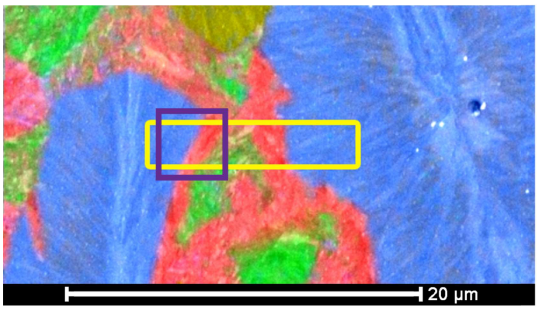


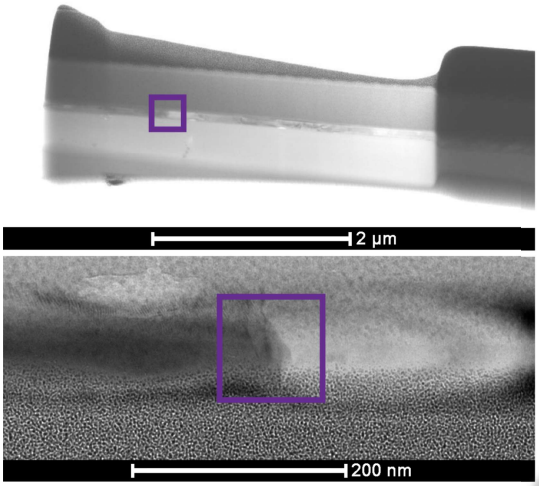
Color coded Raman Mapping RISE (Raman+SEM) image

- Raman+SEM used to identify regions with different crystal structures and the phase boundary, in a TiO_2 sample
  - J.S. Mangum, L.H. Chan, U. Schmidt, L.M. Garten, D.S. Ginley, B.P. Gorman *"Correlative Raman spectroscopy and focused ion beam for targeted phase boundary analysis of titania polymorphs"* Ultramicroscopy **188** (2018) 48–51, DOI: 10.1016/j.ultramic.2018.02.007
- FIB used to cut specimen for TEM

Example: SEM+Raman+FIB

- Specimen of area of interest cut with a Focused Ion Beam and observed in TEM
  - Ultramicroscopy **188** (2018) 48–51, DOI: 10.1016/j.ultramic.2018.02.007
- FIB cut sample thinned down to ca. 80 nm by Ion Milling
  - Ion milling: sputtering by Ar ions (or other inert gas)
  - This removes areas with damage due to the Ga ion beam





EDS:
Energy Dispersive (X-ray) Spectroscopy

🇪🇸 Espectroscopía por Dispersión de Energía de rayos-X

The interaction of high energy electron beams with samples results in the production of X-rays

A special attachment can be used *in both SEM and TEM* to measure those X-rays

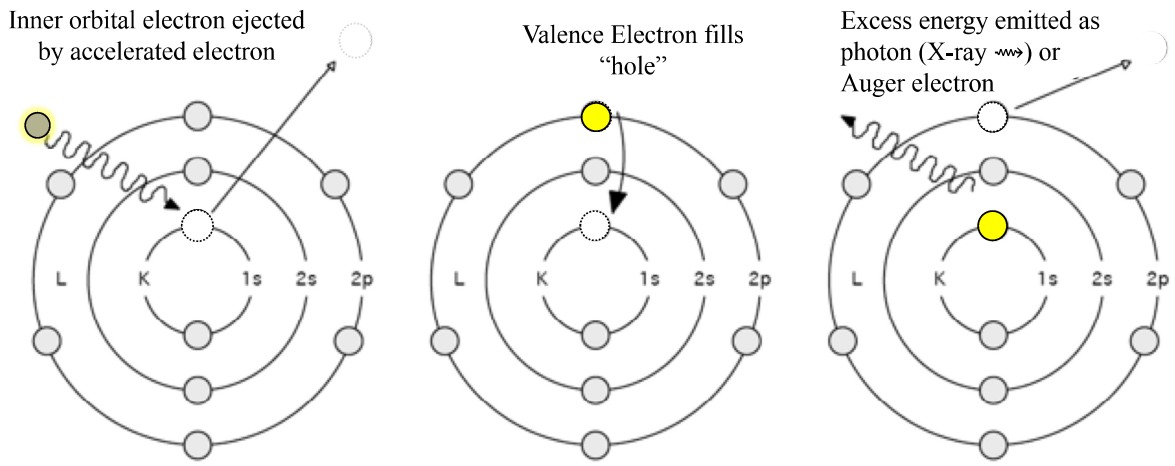
EDS is an elemental analysis technique: the energy of the X-rays emitted is characteristic of the elements that produce them

Sometimes called EDX, or XEDS

Electron Probe Micro Analyzer (EPMA): a dedicated instrument that used the EDS principle for elemental analysis of materials

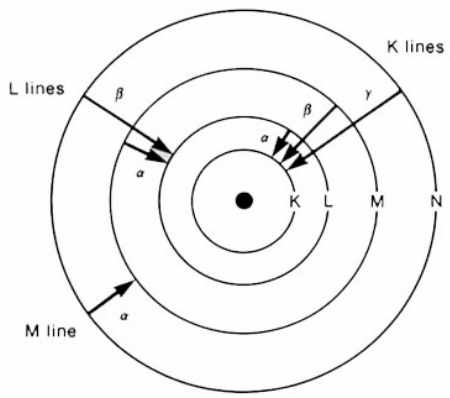
EDS Principle

- Electrons in primary beam have enough energy to eject electrons from the inner orbitals of sample atoms
- Valence electron fills the hole and emits excess energy as an X-ray photon
  - Energy of the photon is measured by a specialized detector
- Auger Electrons: when excess energy from electron transition ejects an outer shell electron instead of emitting an X-ray
  - Auger electron spectra can be used for analysis, but is not a common analytical technique

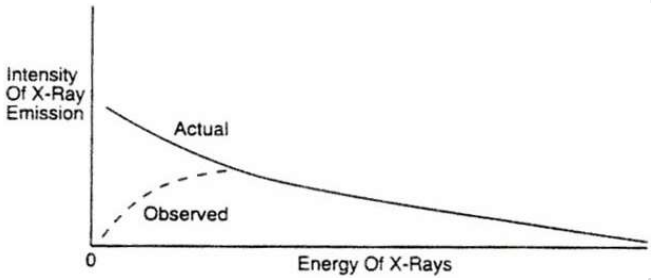


X-ray Signals in EDS

- EDS lines are called K, L, M, depending on the level from which the electron was ejected
  - EDS lines also designated according to from which level an electron "falls" to fill the hole
  - Electron comes from one level up: α
  - Two levels up: β (e.g. K_β line if e^- drops from M to K)
  - Three levels up: γ
- In addition to characteristic X-rays a continuum X-ray background signal is produced due to interaction of electrons with the nuclei of the atoms



- Bremsstrahlung (from German: bremsen 'to brake' + Strahlung 'radiation') X-rays are produced when the electrons lose energy by interaction with the positive nucleus and emit that energy as photons
  - Part of this energy is filtered by a window in the EDS detector
- Intensity of x-ray background increases with probe current (beam diameter), acceleration voltage and atomic number of elements in the sample
- Peak/background intensity ratio is very important when quantifying by EDS

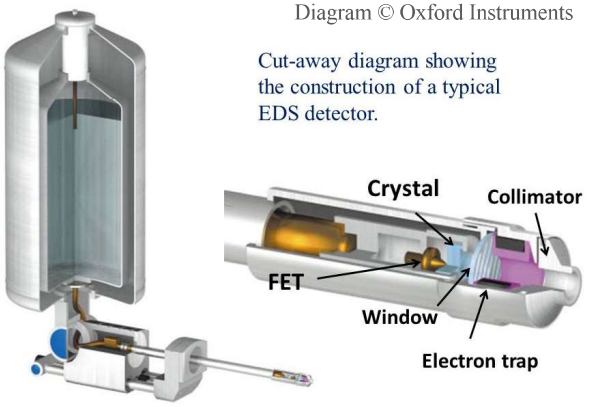


EDS detectors

- Energy is measured by how much ionization X-rays produce in a semiconductor crystal
  - Older detectors required liquid nitrogen cooling
- Newer models (silicon drift detectors) use Peltier cooling and usually offer better sensitivity and energy resolution
  - Peltier effect: use of electric current to carry heat away from a junction between two conductors
- Detector is placed at the angle and the position where X-ray emission is largest
- X-rays can also be measured by wavelength dispersion
  - ***WDS**: Wavelength Dispersive X-ray spectroscopy*

Diagram © Oxford Instruments

Cut-away diagram showing the construction of a typical EDS detector.

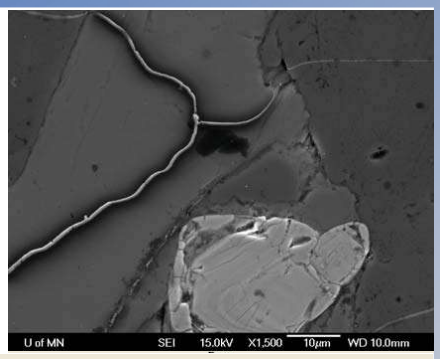


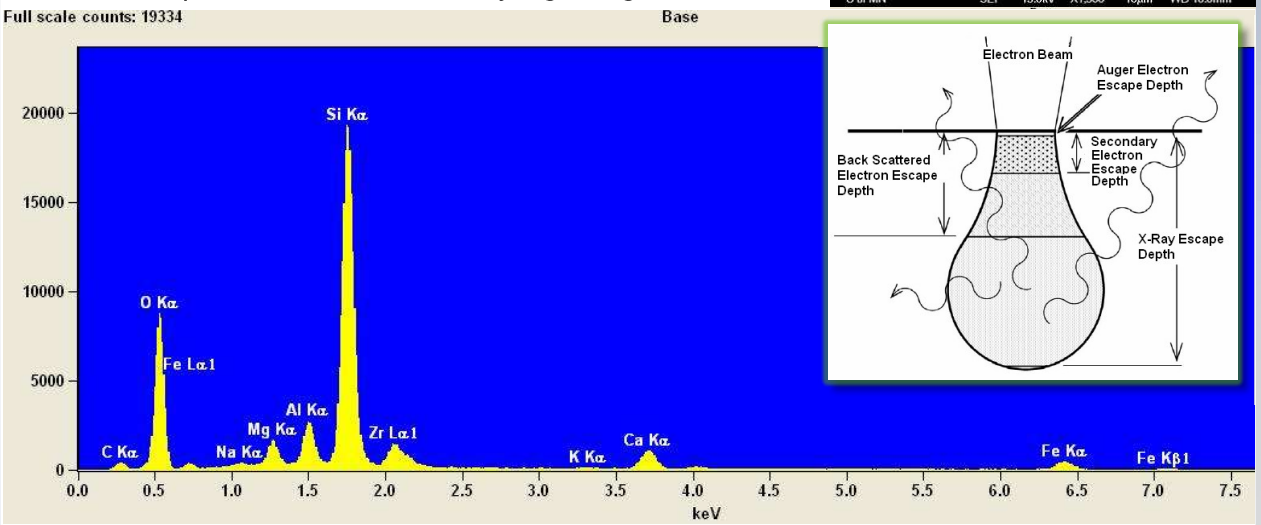
EDS detector of the Carl Zeiss SEM at Campus Monterrey

Photo © Fernando JRM, under a CC-BY-NC-SA license

EDS Characterization

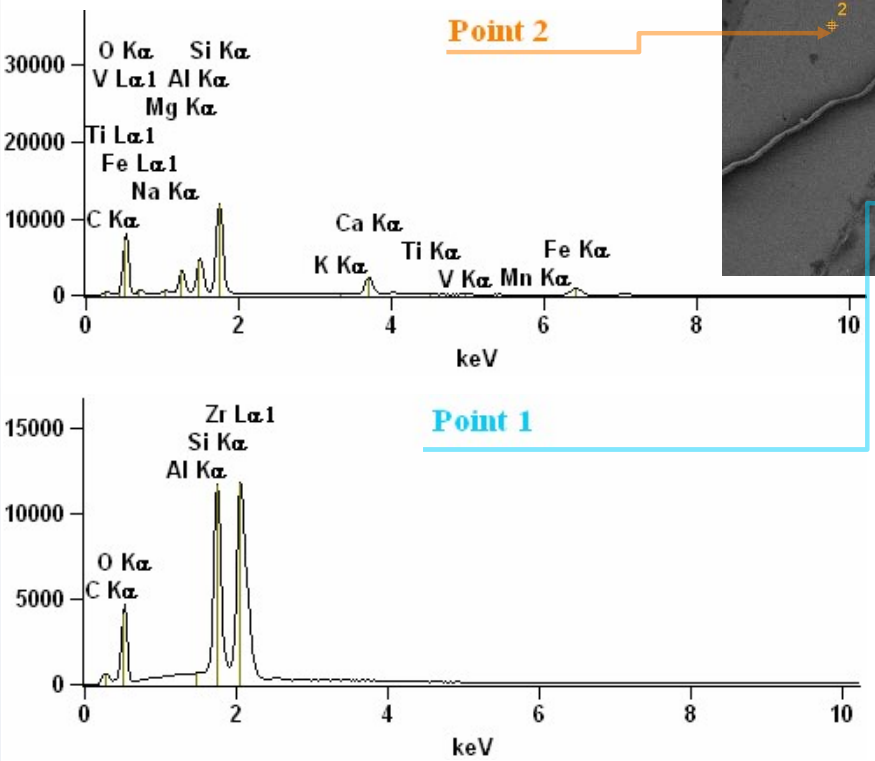
- When there is no prior information, or to confirm the expected composition, an spectrum can be acquired from the whole area observed under SEM
- This spectrum will show the characteristic X-rays of all elements *under* the observed area
  - Some of the detected elements could literally be *under* the surface due to the interaction volumes between the electron probe and the secondary signals generated

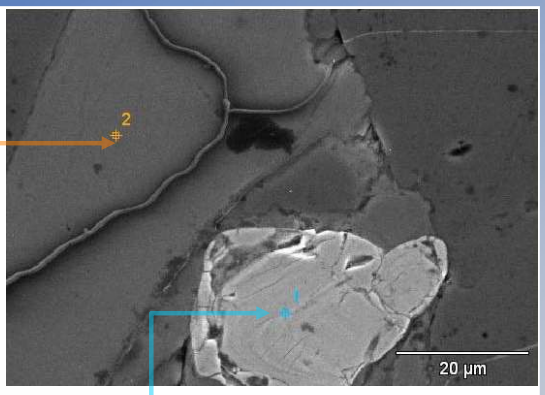




Images taken from: Bob Hafner "Energy Dispersive Spectroscopy on the SEM: A Primer"
Downloaded from < http://www.charfac.umn.edu/instruments/eds_on_sem_primer.pdf > accessed: November 2016

EDS point spectra

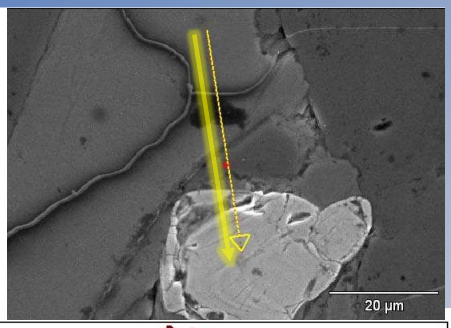




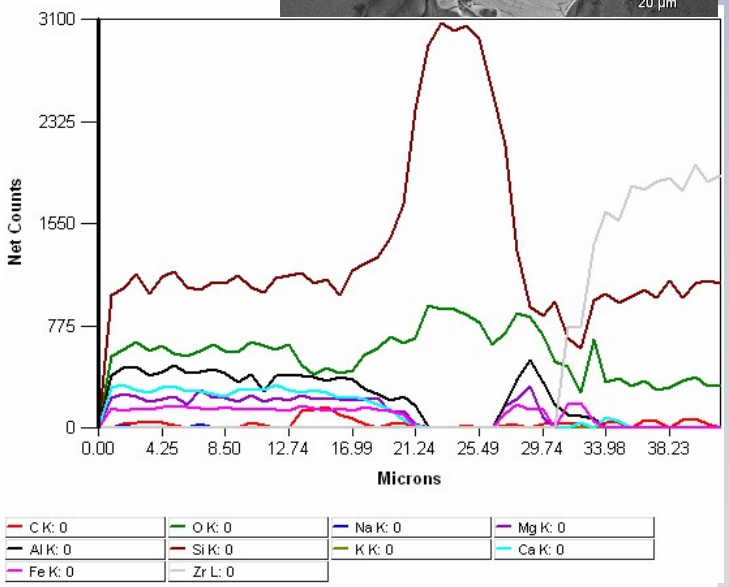
- Spot spectra can be acquired, to analyze if different regions have the same or different composition
  - Electron beam is left stationary over point of interest for a time long enough to acquire a good spectrum

Images taken and slightly modified from: Bob Hafner "Energy Dispersive Spectroscopy on the SEM: A Primer". Downloaded Nov. 2016 from < http://www.charfac.umn.edu/instruments/eds_on_sem_primer.pdf >

EDS line spectra



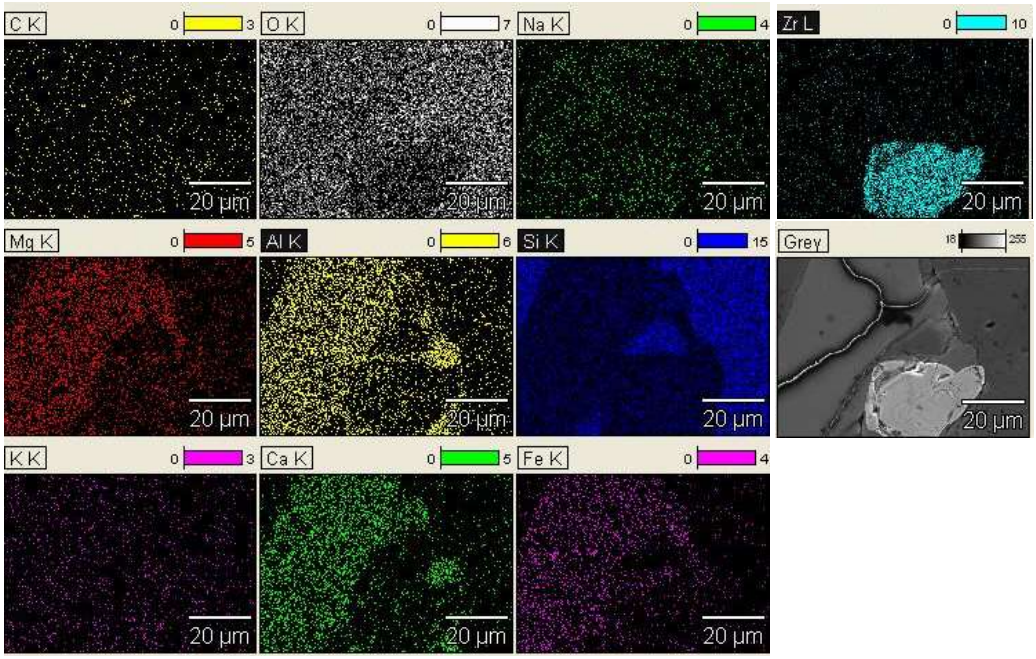
- Spectra acquired along a line to see if there are concentration gradients, or different phases
  - Plot represents intensity of X-ray signal vs. distance for one peak of each element of interest
  - Peak selected depends on whether it can be resolved and the peak/background ratio
    - E.g. in example Fe K_β line is not as useful, it is very low in intensity compared to K_α
- Line direction is arbitrary and set with the SEM/EDS scan software
  - In most cases the SEM control software communicates directly with the EDS software
- Line is formed acquiring EDS spectra sequentially on different points along the line
  - Increased acquisition time for each point can increase spatial resolution



Images taken and slightly modified from: B. Hafner "Energy Dispersive Spectroscopy on the SEM: A Primer". Downloaded Nov. 2016 from < http://www.charfac.umn.edu/instruments/eds_on_sem_primer.pdf >

EDS mapping

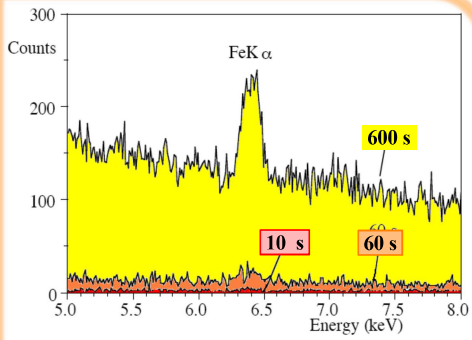
- Full scan over the observation area can be used to map composition and the existence of different phases
  - These may require minutes or even hours, depending on area size and map resolution desired



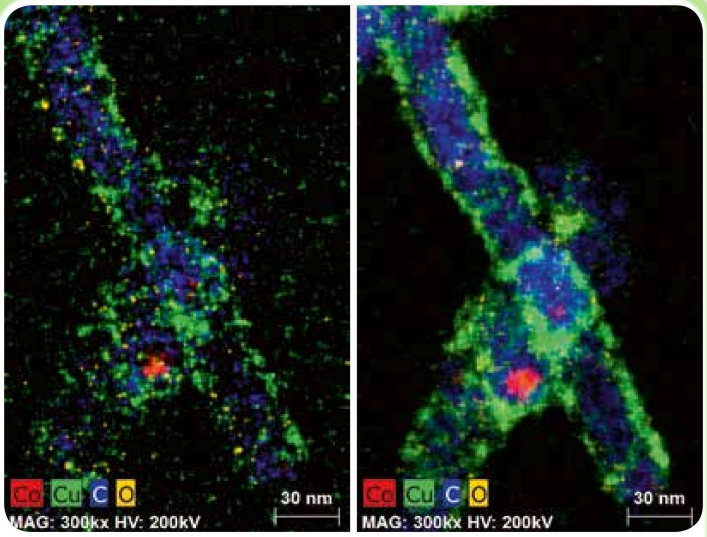
Images taken from: B. Hafner "Energy Dispersive Spectroscopy on the SEM: A Primer". Downloaded Nov. 2016 from < http://www.charfac.umn.edu/instruments/eds_on_sem_primer.pdf >

EDS Mapping

- Longer acquisition time improves map resolution and may help reveal low intensity peaks
  - Different EDS equipment models may have faster acquisition times



Example of how a longer acquisition time can help a peak stand out from the background noise



CuO-coated multi wall carbon nanotubes with Co-catalyst particles analyzed with the XFlash® 6T | 30, spot size 1.5 nm, 400 pA beam current. The measurement was performed with two different acquisition times: 3 min. (left) and 47 min. (right). It can be seen that the 3 min. measurement already shows almost all relevant structures, while the longer acquisition time adds detail. Sample courtesy: S. Herrmann, T. Wächtler, Chemnitz University of Technology

Image from a promotional brochure from Bruker showing how mapping resolution increases with a longer acquisition time (EDS in TEM)

EDS constraints and limitations

- Typical values for EDS detectors are:
- Spatial resolution: micrometer scale
  - Can not be better due to the very way the signal is generated)
  - Low atomic number (Z): 1–5 μm^3
  - High Z: 0.2–1 μm^3
  - Spatial Resolution:
- Energy resolution: 130 eV (Full Width Half Max) at Mn K_α
  - Newer instruments may have better resolution, about 121 eV
- Limit of detection: 1000 – 3000 ppm; >10% wt%
- Can identify only elements heavier than Beryllium

- Precision: about ±0.1%
- Accuracy (95% analysis).
  - ±1% when calibrated with pure standards on site
  - ±2% when calibration is not on site and making corrections for geometry and settings of the microscope used
  - ±5% for particles and rough surfaces "without standards"

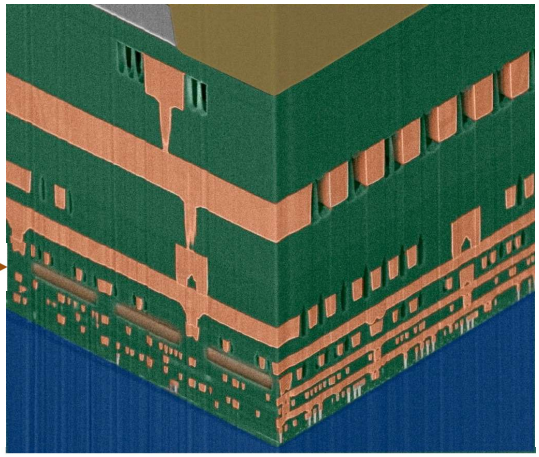
- *Note:* ***WDS***, Wavelength Dispersive Spectroscopy has better energy resolution, especially for low Z elements (e.g. 10 eV at Mn K_α), and can detect lower concentrations (~1 wt%)

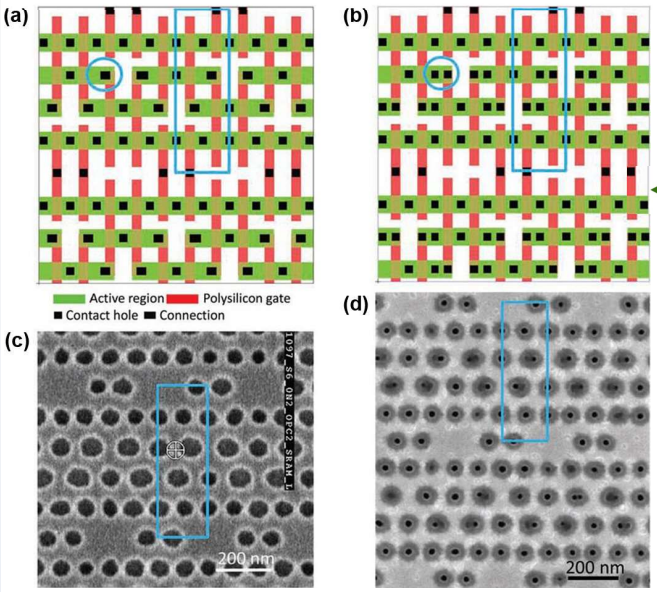
Some Examples of SEM characterization

Example: Lithography Nanostructures from Block Copolymers

- False color SEM image showing IBM "air gap" porous insulation channels between copper interconnects in an integrated circuit
  - False colors are added to grayscale SEM images to highlight specific features
  - The "air-gap" holes are patterned using self-assembled nanostructures from block copolymers

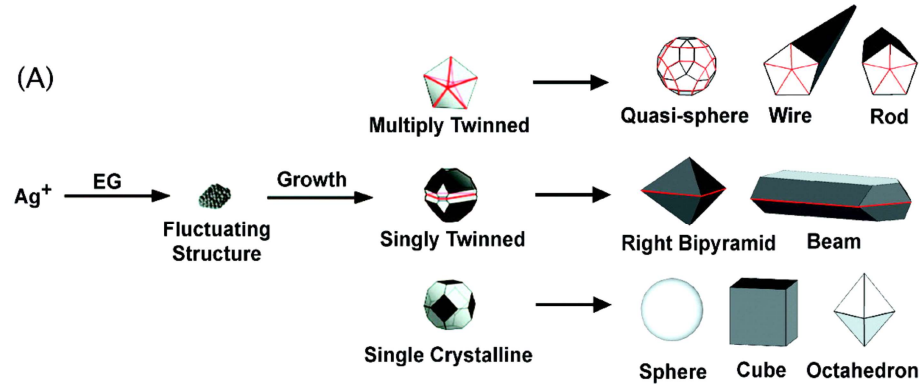
Image downloaded in 2013 from http://www03.ibm.com/press/us/en/presskit/21463.wss

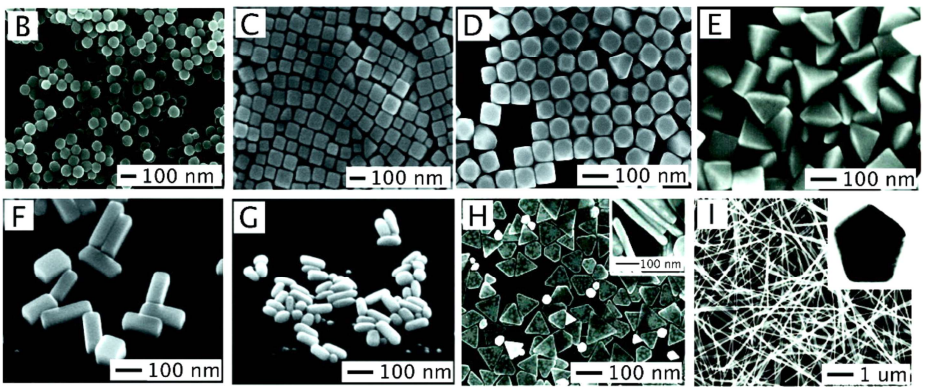




- Block copolymers used as mask to shrink dimensions of holes for connection to transistors in circuit. SEM shows that diameter is reduced from 100 nm to 15 nm
- (a) Contact hole layout of the IBM 22 nm 6T-SRAM circuit. (b) Modified layout by replacing the rectangular connections with square holes and one of the modification (highlighted by blue circles) [66]. SEM images of (c) Si contact holes fabricated with ArF immersion photolithography and (d) corresponding contact hole shrinkage result for IBM 22 nm 6T-SRAM circuit layout
- Taken from: S.-J. Jeong, J.Y. Kim, B.H. Kim, H.-S- Moon, S.O. Kim, *"Directed self-assembly of block copolymers for next generation nanolithography"* Materials Today **16** (2013) 468

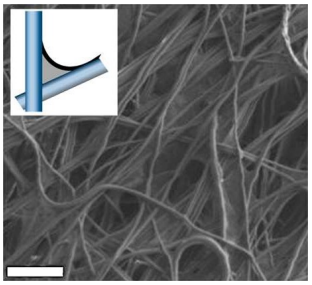
SEM of Silver Nanoparticles



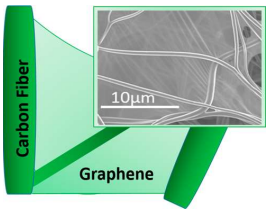


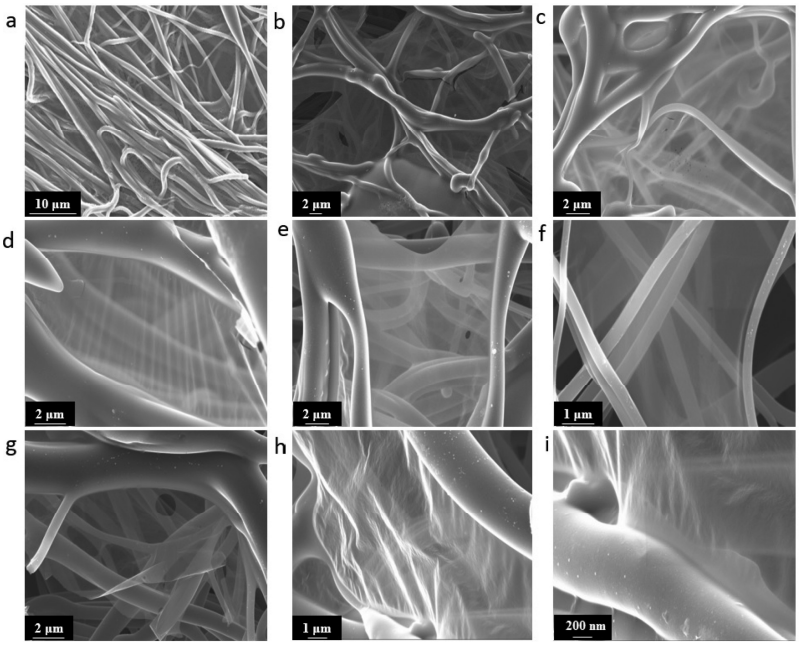
- Silver nanoparticles synthesized by the polyol method (reduction with ethylenglycol) can grow in a large variety of shapes depending on growth conditions, as shown by SEM
- Figure taken from: M. Rycenga, C.M. Cobley, J. Zeng, W. Li, C.H. Moran, Q. Zhang, D. Qin, Y. Xia *"Controlling the Synthesis and Assembly of Silver Nanostructures for Plasmonic Applications"* Chem. Rev. **111** (2011) 3669 // DOI: 10.1021/cr100275d

Example: SEM of Graphene-Carbon Nanofiber Hybrids



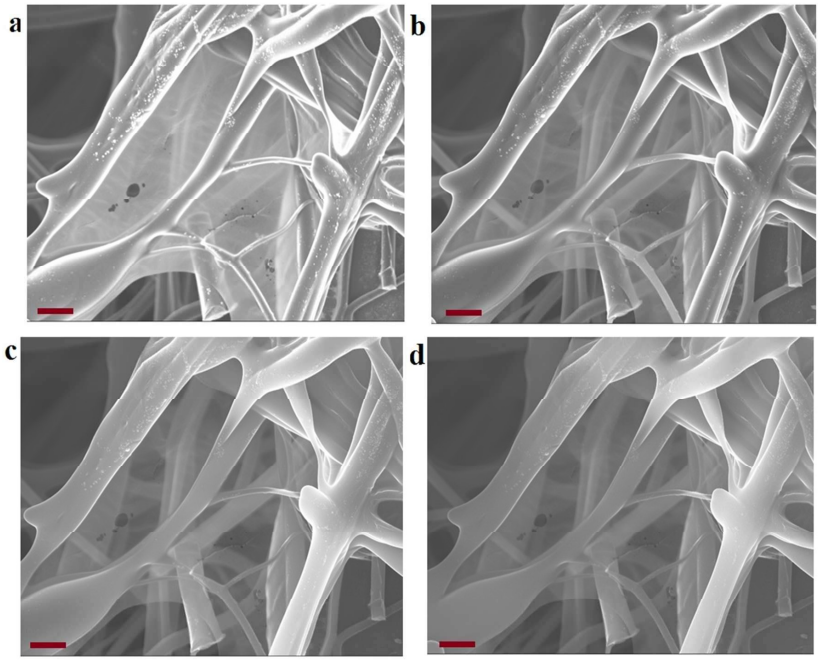
- Polymer fibers made by ForceSpinning can be made with polymer membranes in between fibers
  - Use of salt in the spinning solution, and acid vapor dehydration treatment, with high relative humidity
- Pyrolysis treatment transforms those "veils" into graphene sheets





Taken from M. Akia, L. Cremar, M. Chipara, E. Munoz, H. Cortez, H. De Santiago, F.J. Rodríguez-Macías, Y.I. Vega-Cantú, H. Arandiyan, H. Sun, T.P. Lodge, Y. Mao, K. Lozano, "In Situ Production of Graphene-Fiber Hybrid Structures." ACS Applied Materials and Interfaces, 9(30), 25474-25480 (2017) DOI: 10.1021/acsami.7b07509 // © American Chemical Society

SEM of Graphene-Carbon Nanofiber Hybrids



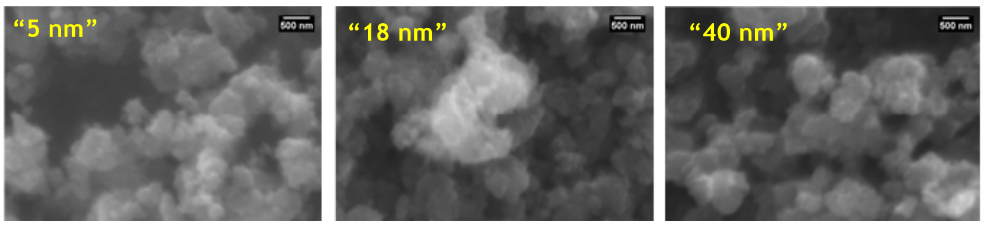
- Figure S1. Graphene sheets, imaged in SEM at different acceleration voltages a) 3 kV, b) 7 kV, c) 15 kV, and d) 19 kV (scale bars: 2 µm).
- The contrast between the fibers and film decreases at higher voltage, which indicates the ultrathin nature of the graphene nanosheets. As the acceleration voltage is increased the penetration depth of the electron probe increases and the extremely thin graphene sheets become more transparent, with secondary electrons from the fibers below contributing more to the final image, until at 19 kV the graphene film almost seems to disappear.

M. Akia, L. Cremar, M. Chipara, E. Munoz, H. Cortez, H. De Santiago, F.J. Rodríguez-Macías, Y.I. Vega-Cantú, H. Arandiyan, H. Sun, T.P. Lodge, Y. Mao, K. Lozano, "In Situ Production of Graphene-Fiber Hybrid Structures." ACS Applied Materials and Interfaces, 9(30), 25474-25480 (2017) DOI: 10.1021/acsami.7b07509

Example: Wear Reduction with Nanolubricants

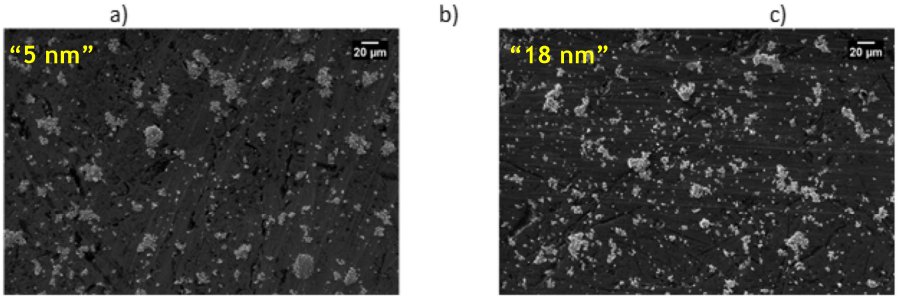
- Nanoparticles can reduce wear when added to lubricants
  - Thesis project of Marcelo R. Martínez-Gamero (B.S. Chemistry and Nanoscience May 2019)
- Use of different surfactants to stabilize a suspension of TiO_2 nanoparticles of different nominal sizes
- SEM showed that as-received NP are extremely agglomerated
  - This made the dispersion in lubricant (PAO4, polyalphaolefin) more difficult

As-received TiO_2 NP over carbon tape



a) b) c)

TiO_2 NP deposited from water suspension (made by sonication) over the aluminum pin. Sonication broke some agglomerates but micrometer sized particles remain

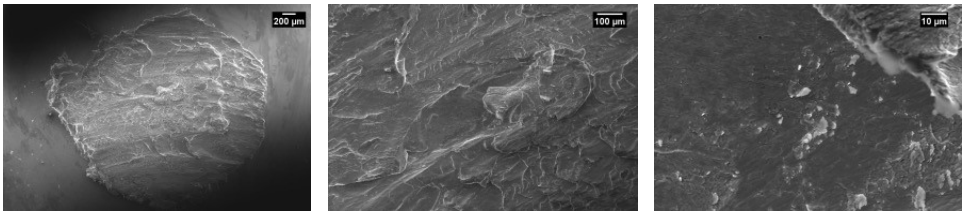


e) f)

Example: Wear Reduction with Nanolubricants

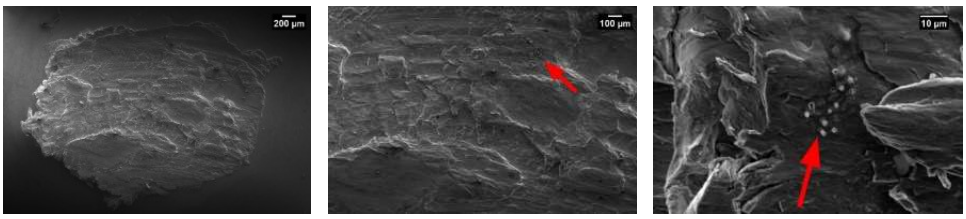
- Use of different surfactants and nanoparticle sizes showed different levels of wear reduction
- SEM showed that wear patterns were different for different formulations and that in some cases titania deposited over the steel ball bearing

Ball bearing wear after pressure loss limit test of nanolubricant with "5nm" TiO_2 NP in PAO4 lubricant with stearic acid as surfactant



a) b) c)

Ball bearing wear after pressure loss limit test of nanolubricant with "5nm" TiO_2 NP in PAO4 lubricant with CTAB as surfactant



d) e) f)

Images from thesis byMarcelo R. Martínez-Gamero (B.S. Chemistry and Nanoscience May 2019), advisors: Fernando J. Rodríguez-Macías, Laura Peña-Parás (UDEM)

NOTE: these samples were rinsed with hexanes before observation to remove lubricant and avoid carbon contamination of SEM chamber!

Example: Fluorination of Nitrile Rubber

Yadira Vega-Cantú, Robert Hauge, Lewis Norman, W. E. Billups "*Enhancement of the chemical resistance of nitrile rubber by direct fluorination*" Journal of Applied Polymer Science. 2003; **89**(4) :971 - 979

- Problem: mechanical failure of poly(acrilonitrile-*co*-butadiene) in petroleum extraction (rubber in contact with $ZnBr_2$ brines at high pressure and temperature)
  - $ZnBr_2$ induces chemical degradation of polymer
  - Fluoropolymers: more expensive not the same mechanical properties
- Solution: Surface fluorination
  - $ZnBr_2$ diffusion is limited and surface becomes less reactive
- Study of surface fluorination conditions
  - Different surface changes depending on experimental conditions

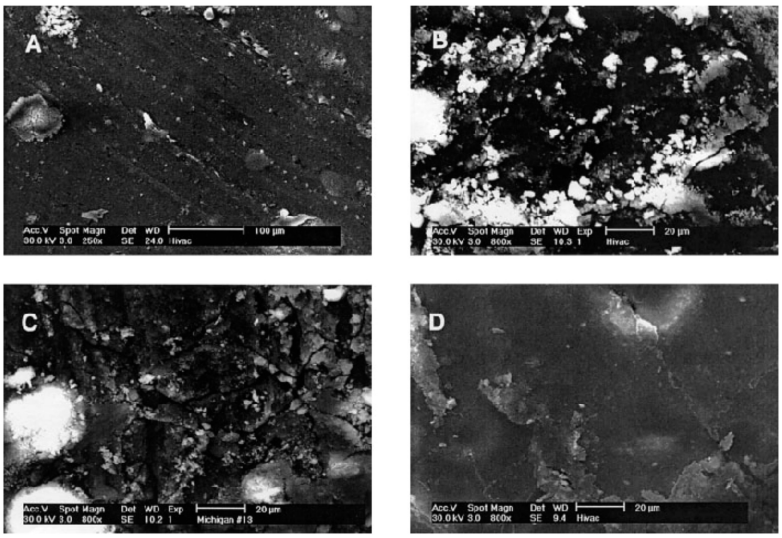


Figure 2 SEM images of NBR samples fluorinated under diverse conditions with fluorine in helium: (A) untreated NBR, (B) NBR fluorinated at room temperature for 24 h, (C) NBR fluorinated at 50°C for 5 h, and (D) NBR fluorinated at 100°C for 5 h.

Example: Fluorination of Nitrile Rubber (2)

- SEM study allowed to choose the fluorination parameters that produced less surface damage

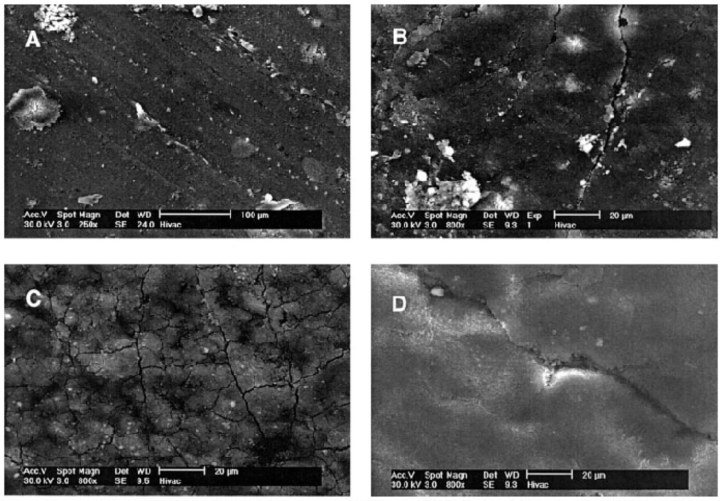


Figure 3 SEM images of NBR fluorinated with 50% F2/HF (1:1) in helium: (A) untreated NBR, (B) NBR fluorinated at room temperature for 24 h, (C) NBR fluorinated at 50°C for 5 h, and (D) NBR fluorinated at 100°C for 5 h.

- Diffusion of zinc bromide
  - Use of EDS in the microscope to quantify bromine concentration at a distance from a cross-section border (depth)
    - Spectra acquired from center points of imaging areas at different distances from edge
  - This proves that surface fluorination reduces diffusion
  - Depth of fluorination was studied the same way

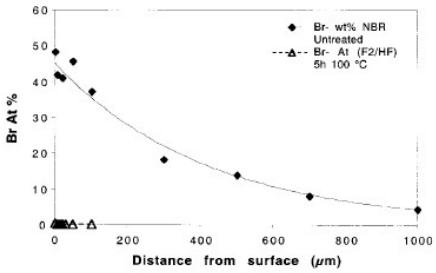


Figure 5 Bromine diffusion in NBR fluorinated at 100°C and treated with zinc bromide completion fluid at 85–90°C for 72 h. At, Atomic.

Example: Fluorination of Nitrile Rubber (3)

- Fractography:
  - NBR under tension undergoes homogeneous fracture, after exposure to $ZnBr_2$ it has brittle fracture
  - Does fluorination modify type of fracture?
    - Brittle fracture is more evident with the treatment that least reduces $ZnBr_2$ diffusion (fig. 12 A)
  - Surface fluorination helped preserve the viscoelasticity of the rubber

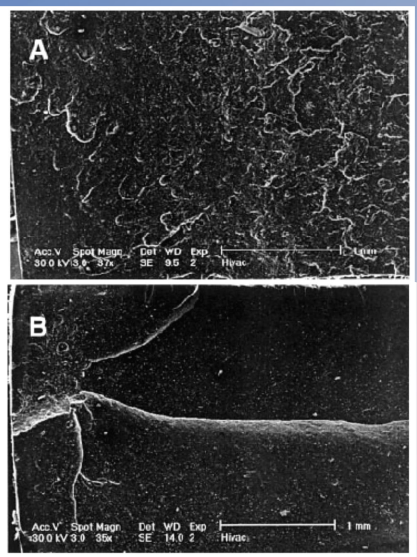


Figure 11 SEM images of the tensile fracture surfaces of NBR: (A) original and (B) after exposure to zinc bromide fluid.

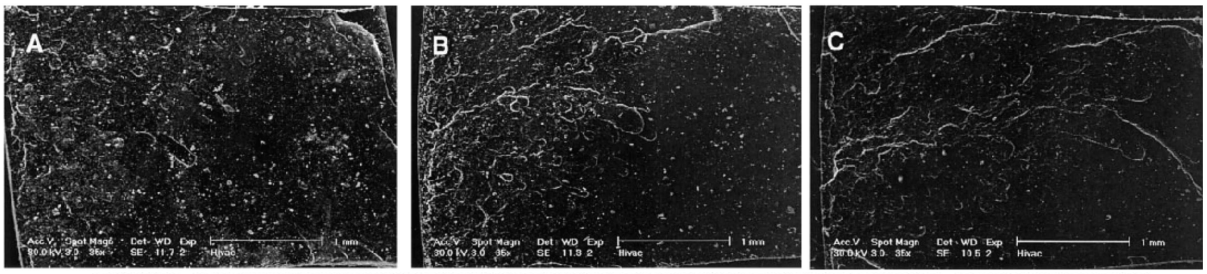


Figure 12 SEM images of the tensile fracture surfaces of fluorinated NBR at (A) room temperature, (B) 50°C, and (C) 100°C after exposure to zinc bromide fluid.