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Sample Preparation for SEM

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Why sample preparation?

- The basic step for having good microscopy is having a proper specimen

- Using different methods for sample prep, we should think about their possible effect and influence in our materials and analysis.

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Think about your sample…

- Is it a conductor or insulator?
- Do you need a plane view or cross section sample?
- Is your material brittle, ductile or soft?
- Is it a multilayered or composite type of material?
- Is it a hydrated material?
- Is it to small to handle manually?
- Is it sensitive to vacuum?
- At what stage you are investigating the material? Raw material, prototype or product?
- Any other issues!

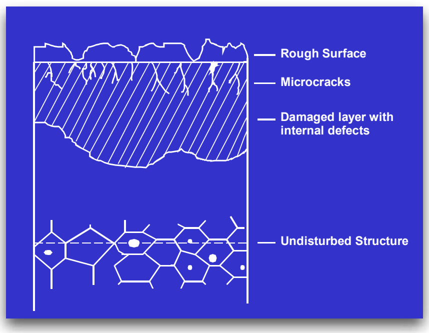
Common prep methods

Standard Materials (i.e. metals, ceramics)	Soft Materials (i.e. polymers, bio-materials)
Crushing	Dehydration
Cutting	Fixiation
Embedding (sometimes)	Staining
Mechanical polishing	Labeling
Ion milling	Freeze fracturing
Coating	Cutting (microtome, ion milling)
Cleaning	Coating
	Cleaning

Embedding & Polishing

Polishing wit

Damage from cutting & Polishing!



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Ion Milling

- Traditional mechanical polishing or cutting techniques apply significant lateral sheer forces to the sample and often result in surface artefacts such as scratches, smearing, delimitation and other damage at soft and composite materials.
- High resolution imaging, X-ray analysis and EBSD data can be compromised if the surface is rough or damaged.
- Ion milling techniques will remove artefacts resulting in a smooth, polished surface.
- Eliminates the requirement for a dedicated FIB for many applications.

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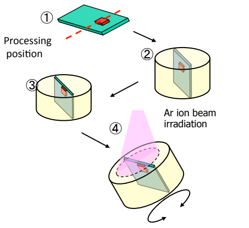
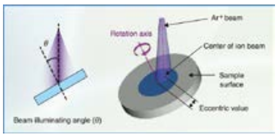
Ion milling – Flat surfaces





The flat milling method shifts the beam centre with its highest ion density away from the sample rotation centre, so that a wide region around the sample rotation centre is uniformly sputter-etched.

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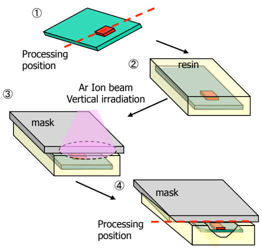
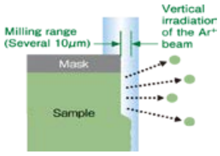
Ion milling – Cross sections

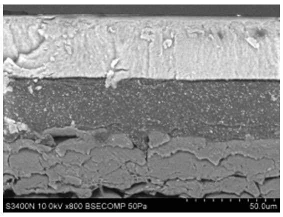




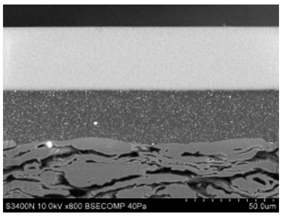
The intended cross sectional cutting edge is defined by the sharp edge of a mask accurately placed onto the surface of the sample. That part of the sample that extends out from the edge of the mask (shielding plate) will then be subjected to be sputter/etched by the incident Ar ions. Gradually a flat cross sectional surface is generated vertically below the mask edge. This method provides the highest precision for milling and ideal for high resolution imaging/analysis

Ion milling – Cross sections

Coated printing paper cut with razor



Before ion-milling



After ion-milling

Supporting

Solid Supports

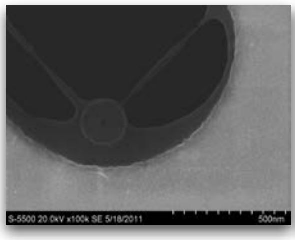
- Smooth conductive surfaces are ideal for deposition of materials/particles/fibers...
  - Si-wafers
  - Polished Al etc (not a stub, that has structure)
  - Al-foil
  - Freshly cleaved mica (for super smoothness)
  - Several commercial options are available.

  Glass is not a good idea as it's an insulator.

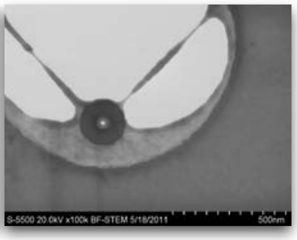
  But your can still end up with charging of the specimen and artefacts due to adhesive glues...
- Customised grips, clamps, cross section holders

Film Supports

Looking at really small particles, it's sometimes better to mount them on a grid with C-support film. Even if you are not using a TEM!



SE



BF

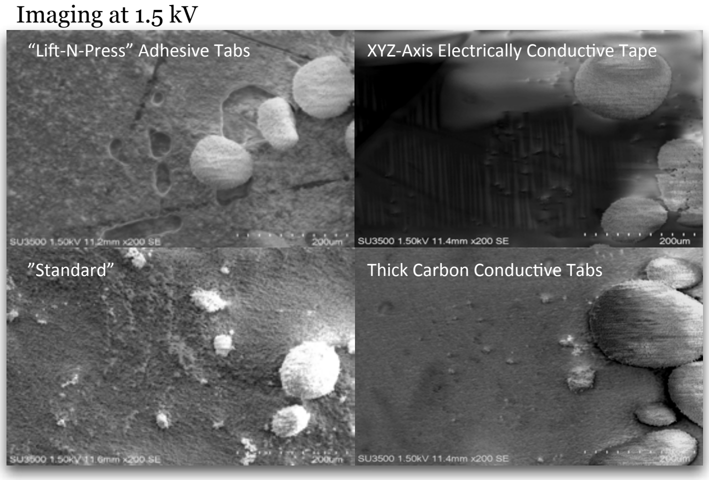
No charging effects in SE-mode @ 20 kV!

Mounting

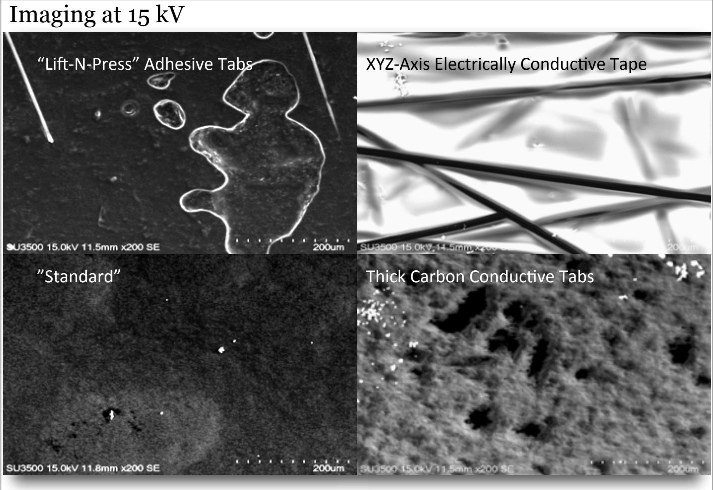
Adhesives

- Sticky carbon tape
  - Contain A LOT of low molecular and volatile adhesives, mobile COH, and it's elastic!
  - Porous!
- Colloidal graphite
  - Available with and without adhesives, water or solvent based (excellent for powders!)
  - Possible to dilute
- Silver paint/glue/epoxy
- Epoxies
- Waxes
  - Underestimated, great for fixation. Use a wax with suitable Tm, for instance CrystalBond 509
- Polyelectrolytes (large macromolecular polymers with inherent charge)
  - KVPS (-) or PEI (+)
  - Bonds nano/microscaled materials of opposite charge nicely to a smooth surface like Si or a TEM-grid.

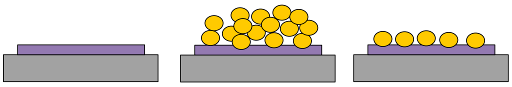
Imaging at 1.5 kV



Imaging at 15 kV



Colloidal graphite or silver



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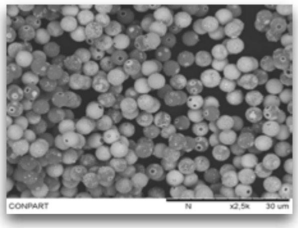
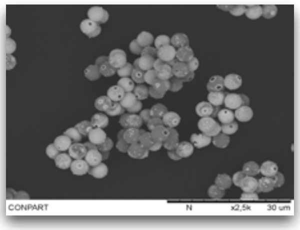
Colloidal graphite or silver





“Nano”-particles glued with colloidal graphite (isopropanol based).

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Coating

Why coating?

- Coating makes the sample surface conductive and easier to image and analyse in requested voltages and beam currents as it eliminates charge build up, a phenomenon that disrupts generation of SEs and excitation of X-rays. Coating also reduces thermal damage.
- The resolution of the SEM in SE mode is limited by the diffusion range of secondary electrons, especially in low Z materials, adding a conductive layers improves the range.
- Improving SEM resolution therefore requires two steps:
  - minimising or eliminating the spread of secondary electrons
  - improving the signal to noise ratio so that more detail can be seen

The solution can be to coat the specimen.
(Or to clean the surface and work at low kVs!)

Different types of coating

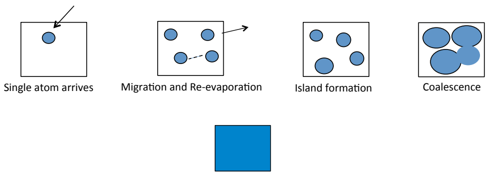
- Metal Coatings
  - Thick coatings
  - Medium resolution or standard coatings
  - High resolution coatings (mainly for FE-SEMs)
  - Metal Particulate Coatings

- Carbon Coatings
  - Suitable for EDS/EBSD-analysis

- Relief and/or "Double" coatings
  - Au + C or similar to enhance contrast and reveal surface details/structures

Coating theory

Evaporation (carbon) is a straight-line process, while sputtering (metals) is a random one in which deposition occurs from many directions



Film formation (in best case)

In general, the better the vacuum, the better the coating.

Metal Coatings

- Metals are generally deposited via sputter-coating, a physical vapor deposition process (PVD) generated by ionising a low pressure inert gas (usually argon) with a target of noble metal.

- Certain metals require e- or ion beam coating systems (really reverse process from ion milling, remember?) due to low sputtering yields and high melting points.

- Results are a function of several factors:
  - Gas type and pressure
  - Potential between target and work piece
  - Current density
  - Distance from target to work piece
  - Time (thickness is linear to time, however, evenness might not be...

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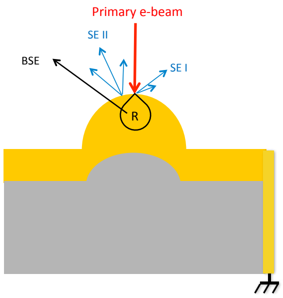
Traditional “thick” coating



THICK (20 nm) metal or C layer

Examples: Cr, Ta, W, Pt, Au or C
R: mainly within coating Layer

SE I/II escape depth 1-3 nm
BSE escape depth 10-100 nm

Topographic resolution limited by thickness of the metal coat and the SE II range

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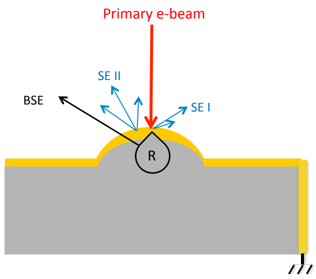
Medium res. or standard coating



THIN (5-10 nm) metal or C layer

Examples: Cr, Ta, W, Pt, Au or C
R: mainly in sample

Standard coating, suitable for conventional field emission SEMs

SE-signal: SE I and converted BSE (=SE II) from the metal layer. Both depend on F. Mainly SE II.
Little signal contribution from specimen

Topographic resolution limited by thickness of the metal coat.

SE resolution ≈ BSE resolution

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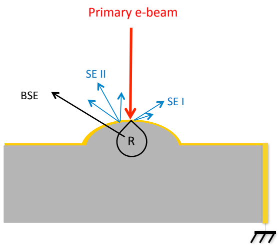
High resolution coating (for FE-SEMs)



VERY THIN (1 nm) metal Layer

Examples: high Z, Cr, Ta, W,
R: in sample

SE-signal: SE I and very little SE II from the metal layer.
Little signal contribution from specimen

SE produced beneath the metal layer cannot leave the specimen

Topographic resolution limited by thickness of the metal coat and the diameter of the electron beam.

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Metal Coatings

Most commonly used metals are:	
Gold	Medium resolution, good sputtering yields, require only low partial pressure
Silver	
Platinum	
Palladium	High resolution, forms films, require very clean atmospheres due to affinity for oxidation
Chromium	
Aluminium	
Nickel	
Tantalum	Very very fine particles or films, require e- or ion beam coating due to low sputter yields and high Tm
Tungsten	
Iridium	

Often alloys are used in order to decrease particle size.
Typical Au/Pd 4:1 is preferable to pure gold.
As two different atom types start nucleation on a surface they limit epitaxial growth of each other and help form an almost uniform film.

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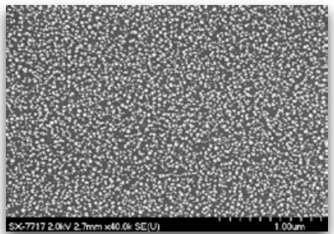
Metal Particle Coatings



3nm layer of Au/Pd

- Au produces very big particles (30nm), pure gold is not always suitable for coatings.
- Alloys, such as Au/Pd, make much smaller (1-3nm) particles
- These all have a very high SE yield and can be deposited in a regular, low cost, sputter coater
- Such coatings are stable and for long periods of time
- Particulate coatings are ideal below 100kx but they can be useful even at higher magnifications, sometime the particles help...

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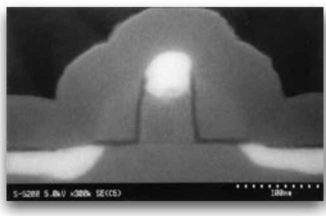
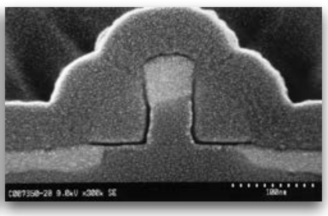
Metal Particulate Coatings

UHR SEM Coating results



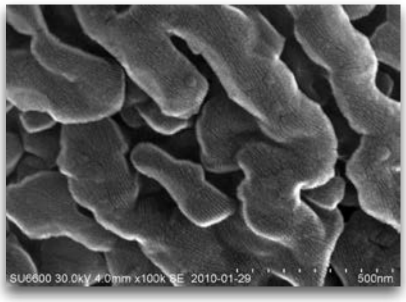
Uncoated



Platinum coated

Note the benefits of a reduction in charging and the gain in image contrast and detail.
The fine grain - while visible - permits accurate focus and image stigmation.

Metal Particulate Coatings
enhancing surface functionalities and structures



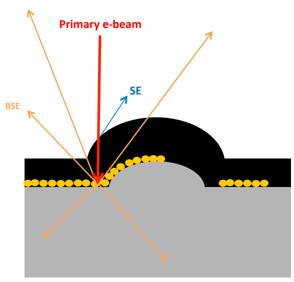
The coating enhances surface structure of chitin, here forming semicrystalline fibrils.

Carbon Coatings

- Usually the choice for EDS/EBSD-applications as it has excellent transparency (light element), is inert and electrically conductive.
- Carbon is evaporated via DC resistive heating, either from pure graphite materials such as rods or fibers.
- Carbon coating has mainly three features:

1. Virtually transparent at higher kVs because of low density and thickness
2. Amorphous, no structure
3. Low SE emission

Relief and/or “Double” coating
combining two different coating agents



Relief coating
Coating “from the side”

Double coating
First adding a very thin metal (1-3 nm) layer for contrast, then a thicker carbon film for conductivity

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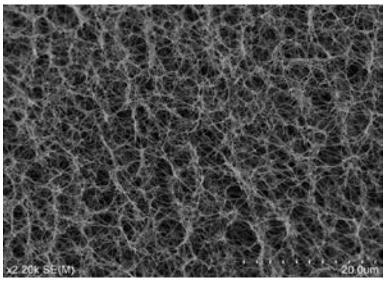
“Double” coating



Au + C coated critical point dried bacterial cellulose, a highly porous material (99,1%) with surface area ~100 m²/g.

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Keep in mind!

- Good coatings are an essential part of high resolution work
- Thin coatings are better than thick coatings – so do not make your sample into a piece of jewellery
- Below x100k magnification particulate coatings are superior to those of for instance Cr.
- Above x100k magnification one can use Cr or Ti continuous films to generate mass thickness contrast and enhance resolution, or use nano-granular Pt or W films
- Use the down-sides of coating to your advantage; relief-coat or enhance surface structures!

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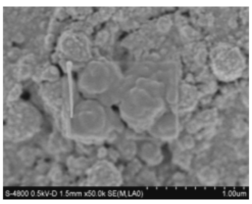
Cleaning

Contamination

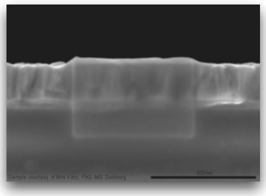
… mobile, often low M_w, hydrocarbons that will migrate across the surface to the e-beam, often hindering imaging at high magnifications and/or low acceleration voltages. Also, EBSD or EDS/WDS acquisitions can be affected if hydrocarbon deposition builds up over time.



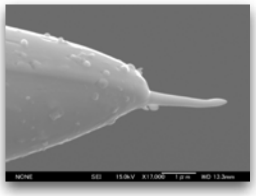
EBID and general contamination on “mesoporous” TiO

Contamination

Electron Beam Induced Deposition (EBID)



Forms "black squares" or lines....



...but can also be useful for making AFM-tips!

Contamination

Typical sources of contamination...

- Environmental Contamination
- Handling Contamination (plastic bags!)
- Dirty holders, carbon adhesives...

- Grinding Media and Lubricants
- Embedding and Mounting Compounds
- Re-deposition of Materials During Ion Milling

- Oil contamination from pumps in coating devices
- Oil contamination from pumps in microscope

- **How clean is really your lab? How clean are you?**

Cleaning Contamination

Always go for...

- Keeping all things clean: holders, tweezers, stubs... Clean often!
- For SEM: a suitable mounting agent without low M_w adhesives (for instance colliodal graphite without cellulose)
- Plasma clean the specimens before imaging

... and don't forget the microscope!

- A dry pumping system in your microscope, preferably a turbo molecular pump backed by scroll pump
- If possible, a plasma cleaner connected to EM-chamber for in-situ cleaning of stage etc.
- An anti-contaminator on your microscope, use a liquid nitrogen cold trap close to the sample if available

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Different approaches to cleaning

- Solvent cleaning
  - Solvent and Acid etch
    - Removes grease and other “fatty” compounds
    - Can and will leave a passive films behind
  - Distilled water
    - Can leave a passive film behind
- In-situ cleaning
  - Heating and/or Vacuum heating
    - Degasses specimen
    - Can damage specimen by thermal degradation
  - CO2 Snow gun
    - Removes most particles on surfaces
    - Can cause condensation on surface
  - Plasma cleaning
    - Removes hydrocarbons
    - Can make the surface hydrophilic (highly reactive)

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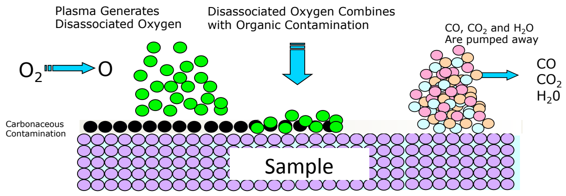
Plasma cleaning



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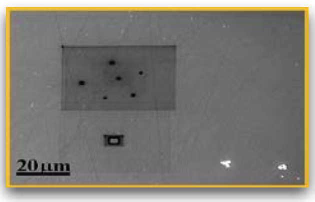
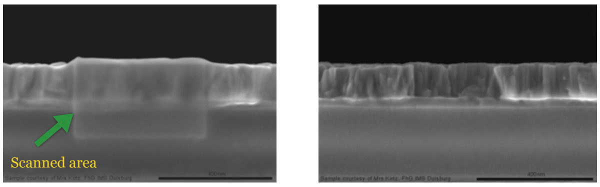
Example: Silicon



Before plasma cleaning

After 5 minutes of plasma cleaning.

Example: TiN-Si cross section



SE images at 3 kV, before and after 30s of plasma cleaning.

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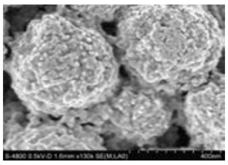
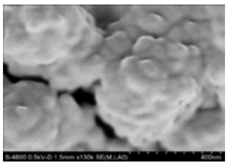
Keep in mind!





- A cleaned surface is highly reactive!
  Remember, negative surface charges.
- As soon as a cleaned specimen is taken into ambient environment it begins to get absorb contaminators again.
- Even storing the sample in vacuum desiccators will not prevent the growth of bacterial or microbial surface contaminant films because the source of the problem is often carried in by the specimen itself
- Repetitive action is therefore required!

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Questions?