OVERVIEW OF SAMPLE PREPARATION TECHNIQUES FOR
TRANSmission ELECTRON MICROSCOPY IN MATERIALS SCIENCE

Why is the specimen preparation so important?

Because no good sample preparation, no good TEM observation!!!
Why is the sample preparation so important?

Because no good sample preparation, no good TEM observation!!!
INTRODUCTION

Size and thickness of the sample

Diameter: 3 mm

1) Reduce size of large sample
2) Use 3 mm grid support for small sample

Thickness: between 10 and 200 nm depending on the material and the kind of observation to be done

1) depend on chemical composition
2) high resolution observation, EELS analysis or not

Electrons transparent area, yes, but how, where ???
INTRODUCTION

Sample has to be:

♣ electrically conductive
♣ stable under vacum
♣ free of hydrocarbures contamination
♣ should not contain artefacts that could lead to a wrong analyse

The sample for TEM observation must be representative of the true nature and morphology of the material

It would be impossible to prepare a sample without any artefact, so the best method has to be choosen depending on the type of analyse needed and the type of artefacts induced by one or the other technique

TEM Samples preparation_D.Laub_2014
INTRODUCTION

DIFFERENT TYPES OF PREPARATIONS:
- Mechanical polishing down to electron transparency
- Cleavage
- Ultramicrotomy
- Crushing
- Nanoparticles dispersion
- Grinding, (dimpling), ion milling
- FIB
- Electro-chemical polishing
- Chemical polishing or etching
- Replica (direct or double)
- Thin film deposition
- ...

TECHNIQUES

Dispersing Electron transparent Nanoparticles for TEM

Observation: random direction

Observations:
- Particles size and shape
- HRTEM
- Diffraction
- EDX analysis
- ...

TEM Samples preparation_D.Laub_2014
Working with nanoparticles or nanofibers

Safety rule n° 1: preparation under fume hood!

Absolutely not needed

Not needed but up to you!

Absolutely needed

Choice of solvent to disperse particles

Polar, non-polar or does not matter?

Ethanol: polar

Toluene: non polar

Polar solvents have large dipole moments (aka "partial charges"): they contain bonds between atoms with very different electronegativities, such as oxygen - hydrogen.

Non polar solvents have low dielectric constants (<5) and are not good solvents for charged species such as anions.
Dispersion

Concentration

Dilution

Ultrasound

Dispersion time needed: from 1 minute to several hours

Ready to pick up the droplet

Ultrasonic Device to Disperse Nanomaterial

One droplet on the grid: 3 ways

With the perfect loop

Dry under infra-red or standard desk lamp

TEM Samples preparation_D.Laub_2014
Selection of suitable support grid

- Standard carbon coated grid (C thickness 25–40 nm) 1
- Ultrathin carbon film (4–5 nm) 2
- Holey carbon film with ultrathin carbon windows (5 nm) 3
- Holey carbon film 4
- Lacey carbon film 5
- ...

Depends on the analysis to be done and the particles size

A few examples of dispersion

Before TEM observation

At least 1 hour under infra-red or standard desk lamp = removal of some hydrocarbons

SiO₂-Fe particles

Au particles

C nanotubes
**Ion Milling**

Using electric discharge, Ar\(^+\) ions of some kV are generated and focused on the sample. The goal is the crystal lattice destruction at the surface followed by ejection of superficial atoms.

**DRAWBACK and ARTEFACT:**
- Surface roughness
- Creation of amorphous layer on both surfaces
- Ion implantation
- Creation of dislocations
- Modification of stoichiometry
- Differential thinning rates on different compounds or phases
- Heating

**TECHNIQUES**

**THE PLAN VIEW**

*Observation parallel to the growing axis or to the preferential axis of the material*

**Observations:**

- Crystalline defects
- Linear defects (dislocations, ...)
- Planar defects (twins, ...)
- Study of structure and granular interfaces
- Precipitation
- ...
Super conducting wire
Preparation: wedge mechanical polishing + ion milling 20 min

Sample + TEM observation: N. Merck

Planar view of a super-conducting wire
TEM image, bright field

SrTiO₃, Grains boundary
(J. Ayache)

Advantage: large thin area

Drawback: no information about different positions along the observation axis

Materials:
- All kind

Method:
- Diamond saw
- Spark machining
- Slicing
- Mechanical pre-polishing

Thickness +/- 500 μm

Thickness 1 +/- 20 μm
- Non metallic
- Metallic
- Electrolytic dissolution

Possible defects
- Dislocations
- Irradiation
- Amorphisation of surface layers
- Modification of chemical composition

TEM Samples preparation, D. Laub, 2014
**CROSS-SECTION**

Observation perpendicular to the growing axis or to the preferential axis of the material

**Advantage:** observation of anisotropy along the growing axis

**Drawback:** small thin area

**Observations:**
- characterization of multilayer materials
- layers thickness measurement
- layers and interfaces structure analysis

TEM Samples preparation_D.Laub_2014

**Method**
THE TRIPOD METHOD

Mechanical thinning, in a wedge configuration, down to electron transparency or to a thickness that requires very short ion milling time.

The Tripod tool

TEM Samples preparation_D.Laub_2014
Preparation for the first side polishing

Polishing with diamond-impregnated lapping films; Finish with colloidal silica

Second side polishing

Polishing from back side
Result after final polishing for a Si substrate sample

Si$_3$N$_4$/ Si optical microscope, transmitted light

TiO$_2$/ Si, optical microscope, reflected light

Planar polishing using Tripod polisher

- 4 areas to observe
- Easy to manipulate
- Needs longer ion milling time
Example 1: InP/GaAs cross-section

After final polishing.
The arrow shows the glue line.

InP/GaAs interface: TEM, bright field
Image L. Sagalowicz, EPFL.

Same sample after ion milling: 1h at 5 keV, 10 min at 2 keV, 16° angle, 2 guns.

Experimental conditions
TEM Samples preparation, D. Laub, 2014

GaN on sapphire substrate

AlInN/GaN Bragg mirror multilayers
GaN
sapphire
1 μm
dislocations

TEM image, dark field

TEM image, bright field

Additional ion milling: 15 minute, 3 and 2kV, 2 guns, sectorial rotation, 5° angle
TEM observation
Thin PbLaTiO\textsubscript{3} ferroelectric film on SrTiO\textsubscript{3} substrate

J. Ayache, CSNSM-CNRS-IN2P3, 91405 Orsay
TEM Samples preparation_D.Laub_2014

THE FOCUSED ION BEAM (FIB) METHOD
Gaz: usually Galium
The FIB (Focused Ion Beam)

For:
- Planar view
- Cross-section
- Any orientation

H-Bar method

TEM Samples preparation_D.Laub_2014

The FIB (Focused Ion Beam)

Preparation of lamella H-bar method

FIB prép.: F. Bobard  Images MET: M. Cantoni, CIME-EPFL

TEM Samples preparation_D.Laub_2014
### Comparison between techniques: Tripod and FIB

<table>
<thead>
<tr>
<th>Nb$_3$Sn filament in a bronze matrix. Tripod method + Ion milling low angle (5°). Only the filaments edges and the matrix are electrons transparent</th>
<th>Same sample prepared by FIB. The lamella has a constant thickness and the entire filaments + matrix are electrons transparent</th>
</tr>
</thead>
<tbody>
<tr>
<td>M.Cantoni, EPFL-Lausanne</td>
<td>M.Cantoni, EPFL-Lausanne</td>
</tr>
</tbody>
</table>

*TEM Samples preparation D.Laub 2014*

### FIB (Focused Ion Beam)

« Internal Lift out »

*F. Bobard, M. Cantoni, CIME-EPFL*

*TEM Samples preparation D.Laub 2014*
THE CLEAVED WEDGE METHOD

The cleaved wedge is a monocrystalline substrate (+ layers), dimension about 0.6/0.6 mm, obtained by 2 or 3 cleavages along designed atomic planes that give a perfect edge.

Cleavage: make use of the fact that crystals may be split along planes which are weakly bonded.

GaAs wafer e.g.

Origin of the contrast:

- The observed contrast is linked to the sample thickness and its chemical composition.
- As for a cleaved wedge, the sample thickness is accurately known, the chemical composition can be deduced from the thickness fringes profile.
- The electron beam is parallel to the layer interfaces.
- The layer interfaces are put forward by a discontinuity of the fringes (perpendicularly to the wedge edge).

P.A. Buffat, J.D. Ganière, EPFL.
Chemical composition measurements for AlGaAs/GaAs interfaces can be done to interpret the thickness fringes profile in a semi-quantitative way.

**ULTRAMICROTOMY**

Slicing of the sample to a constant thickness of 20-200 nm, using a diamond knife, carried out at room temperature

**CRYO-ULTRAMICROTOMY**

Slicing of the sample to a constant thickness of 50-200 nm, using a diamond knife, carried out at low temperature
ULTRAMICROTOMY, CRYO-ULTRAMICROTOMY

Observations
- Statistic of particles size
- EDX chemical analysis, EELS chemical analysis (needs thin constant thickness)
- Material microstructure
- Cross-section or plan view of materials that cannot be ion milled, mechanically or electrolytically thinned
- Heterogeneous materials, multilayer
- Small diameter fibres or tips
- Powders (metallic or not)

Materials
- Polymer /polymers with additional compounds
- Catalyst
- Geological
- Biomaterial
- Wood
- Metal

Drawback:
- Deformation of the sample due to compression or/and cracks
- Dislocations
- Shape modification
- ...

The ultramicrotome
- Cutting speed control
- Thickness selection

The knives
- ultra diamond knives 35° and 45° angles

PS spheres in Epon cuted with a 15° knife
- cut with a 45° knife

Courtesy Helmut Gnaegi, Diatome
Method

- Reduce the sample size if needed
- Embed the sample if needed

Important: the embedding resin should have the same hardness/softness as the sample

For porous material: embedding under vacuum or infiltration-embedding


**Cutting the sample to the desired (or possible) thickness**

- Section thickness 40 - 50nm
- Sectioning speed 0.2mm/sec

**Damage induced**

- region of intense shearing
- section compression
- sample compression expansion
- knife
- cracks
- Brittle Materials
- Ductile Materials

Diatome, Helmut Gnaegi presentation
Section collection - “fishing”!

Results

Optical microscope, transmitted light  TEM, bright field image

Diatome, Helmut Gnaegi presentation
TEM Samples preparation_D.Laub_2014
ELECTRO-CHEMICAL POLISHING (JET POLISHING)

Effect of electrolytical polishing is due to anodic dissolution of a pre-polished surface in an electrolyte bath

- A bath for the electrolyte
- A continuous current source
- An anode (the sample)
- A cathode

Observations:
- Dislocations (orientation)
- Twins (macles)
- Grain boundaries
- Precipitates and phases
- ....
Use highly acidic electropolishing solutions (e.g. 70% phosphoric acid for water) =>
- metal surface cannot passivate (no oxide layer)
- metal highly soluble, dissolves at high rate

Solution has high viscosity, therefore metal ions cannot diffuse quickly
- metal precipitates into salt (Jacquet layer)

Rate of dissolution controlled by diffusion of metal ions from surface;
Dissolution faster at peaks than troughs => polishing regime in which sample becomes flatter as it etches

Material must be an electrical conductor

- Metal and alloys, one or more phases
- Carbides
- Graphite
- Some oxides
- Some composite materials with metallic matrix and fine particles

**Advantage:** non destructive method

**Drawback:** may cause preferential etching, dissolution of interface or some phases

**Possible damages:** eventually residual oxidation layer at the sample surface
### CHEMICAL POLISHING

Same principle as electro-polishing but more difficult to control
The solutions are more reactive and used at higher temperature

- **Observations:**
  - Similar to the plan-view or cross-section

- **Materials:**
  - Metals
  - Semiconductors
  - Oxides
  - Glass
  - ...

- **Method:**
  - Cutting and/or cross section procedure
  - Polishing onto soft tissue, specific for chemical addition
  - Chemical thinning until hole

- **Advantage:** possible for non conductive materials

- **Drawback:** dislocations, etching (etch pits)

- **Possible damages:** residual oxidation layer at the sample surface

---

### THE REPLICA METHOD

The replica is the reproduction of the sample surface topography.
It is done by polymer, carbone or oxide film deposition onto the surface sample, which is then removed from the sample and observed into TEM.

**Observations**
- Multiphase materials
- Surface topography
- Second phase particles analysis obtained by the extraction replica method
- Radiation sensitive samples

**Method**
- Film deposition, either « soft » polymer or in a solvant solution
- Carbon film deposition for non conductive samples
- Pulling away the film from the sample by its immersion into solvant, by pulling out or by chemical etching of the sample.
- Mounting the replica onto a 2.3 mm or 3 mm support grid
Don't forget that sample preparation is also...

"...like cooking!!!..."