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!!!

The specimen preparation for transmission electron microscopy (TEM) should be as fast as possible and the specimen should contain few or no artifacts induced by the preparation process. It should also be adapted to the specific analysis or to the specific area that has to be observed. Therefore, it is crucial for any microscopist to know firstly the properties of the material to be analyzed and secondly the appropriate technique and the artifacts induced by the preparation, in order to be able to recognize these artifacts during TEM observation. Therefore, the main preparation techniques (mechanical, ionic, electrolytic, mechanical-physical) and their applications are discussed.

WHY IS THE SAMPLE PREPARATION SO IMPORTANT?

Mica sample (mineral)

Cross section, zone axis [0001], Ion Milling (>2kV)

Cross section, zone axis [0001], Ion Milling (down to 100V)
**INTRODUCTION**

Size and thickness of the sample

Diameter: 2.3 or 3 mm

1) Reduce size of large sample
2) Use 2.3 or 3 mm grid support for small sample

**Thickness: between 10 et 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

Sample as also to be:

- electrically conductive
- stable under vacum
- free of hydrocarbures contamination
- should not contain artefacts that could conduct to wrong analyse

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

It will be impossible to prepare a sample without any artefact, so the good method as to be chosen depending on the type of analyse needed and the type of artefacts induced by one or the other technique
**ARTEFACTS**

Ru/Zr/SrTiO₃
Preparation: tripod planar polish followed by Ion milling

Diamond grains used for grinding penetrate into the sample.
How to observe the true structure of a material?

Pas de dommages thermiques!
No thermal damages!

Mechanical - physical

INTRODUCTION

DIFFERENT TYPES OF PREPARATIONS:
- Mechanical polishing down to electron transparency
- Clivage
- Ultramicrotomy
- Crushing

Mechanical + ionic
- Grinding, (dimpling), ion milling
- FIB

Ionic

Chemical
- Electro-chemical polishing
- Chemical polishing or etching

Mechanical-physical
- Replica (direct or double)
- Thin film deposition
- ...

TYPE OF MATERIALS
- Semiconductors
- Metals and alloys
- Polymers
- Minerals
- Cements
- Ceramics
- Wood (paper)
- Etc.

THE OBSERVATION DIRECTIONS
- Planar view
- Transversal view (cross section)
- Anisotropes materials = planar or tranversal view

The 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.

ARTIFACTS:
- Surface roughness
- Creation of amorphous layer on both surfaces
- Ions implantation
- Creation of dislocations
- Modification of stoichiometry
- Differential thinning rates on different compounds or phases
- Heating

PZT
Pt
SiO
Si
THE PLANAR 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
- Précipitation
- ...

Advantage: large thin area
Drawback: no information about different positions along the observation axis

Materials:
- All kind

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

Method:

Scenario with various defect analysis techniques and images.
**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:**
- Heterogeneity along preferential axis
- Caractérisation of multilayers materials
- Layers thickness measurement
- Layers and interfaces structure analysis

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**THE TRIPOD METHOD**

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

**Direction of motion**

TiO2/Si Planar view

TiO2 / Silicon. Optical microscope, reflected light
Preparation for the first side polishing

First trick: choose good diamond lapping films

Deepness of abrasion depending on grain size

<table>
<thead>
<tr>
<th>Grain size (µm)</th>
<th>True rotation speed °/min</th>
<th>Minimal depth of abrasion (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>50-75</td>
<td>Until the sample is ground on the whole surface</td>
</tr>
<tr>
<td>15</td>
<td>20-30</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>10-12</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td>Minimum speed</td>
<td>18</td>
</tr>
<tr>
<td>1</td>
<td>Minimum speed</td>
<td>9</td>
</tr>
</tbody>
</table>

Defects can be introduced to a depth corresponding to three times the grain size used previously

Checking the sample under optical microscope

If no inverted microscope available, a modified microscope table can be used

Careful removal of the colloidal silica

Use hand to remove silica suspension from the pad

Wear gloves

Soft felt OP or DP type
Surface after final polishing

Optical microscope, bright field image

Dark field will show the best information about surface quality

Second side polishing

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

Tripod method

How to choose the wedge orientation?

- Large thin area
- Difficult to prepare
- 2 thin areas to observe
- More or less easy to make
- Relatively strong

Optical microscope, reflected light

TEM, bright field
Some examples

Powders, fibers, ...

Materials: all including powders

SiO2 powder embedded in Epoxy and glued on a silicon stripe

Planar polishing using Tripod polisher

• 4 areas to observe
• Easy to manipulate
• Needs longer ion milling time

SOME EXAMPLES

Example 1: InP/GaAs cross-section

InP/GaAs interface: TEM, bright field

Image: L. Sagalowicz, EPFL.

After final polishing.
The narrow shows the glue line.

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

Experimental conditions

TiOx/Si [100], planar view

ZnO/glass, cross-section

Interference fringes
Optical microscope, reflected light

Optical microscope, reflected light
Cu/SiO2/Si cross-section.

Artefact or not?

Thicker area

Sample preparation D. Laub, TEM analysis F. Cosandey, Rutgers University, USA

Near hole area.

TEM observation

GaN on sapphire substrate

Additional ion milling: 15 minutes, 3 and 2kV, 2 guns, sectorial rotation, 5° angle

Near hole area.

TEM observation

Au particles /TiO2, cross-section, planar grounded

Ion milled at low incidence angle, sectorial rotation for 15 minutes

TEM images F. Cosandey, Rutgers University

Si sample doped with He (cavity) TEM image, bright field

No ion milling

Bright field TEM images

High resolution TEM image

J. Werkmann, IPCMS, Strasbourg
**TEM observation**

**Au/SiO₂ layer on Si Substrate. No ion milling**

Optical microscope, reflected light, mag. 1000x

Artefact

**TEM bright field image**

A. Schüler, S. de Chambrier, EPFL, Lausanne

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**TEM observation**

**Thin PbLaTiO₃ ferroelectric film on SrTiO₃ substrate**

Tripod no ion milling

Dimpler+ions

J. Ayache, CSNSM-CNRS-IN2P3, 91405 Orsay

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**THE FOCUSED ION BEAM (FIB) METHOD**

Gaz: usually Galium

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

F. Bobard, M. Cantoni

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**The FIB (Focused Ion Beam)**

H-Bar method

F. Bobard, M. Cantons
The FIB (Focused Ion Beam)

Preparation of lamella H-bar method

Nb3Sn multifilaments /bronze matrix

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

Comparison between techniques: Tripod and FIB

FIB (Focused Ion Beam)

« Internal Lift out »

F. Bobard, M. Cantoni, CIME-EPFL

Comparison between techniques: FIB and Tripod

Low magnification picture of a Nb3Sn filament.

Same sample at higher magnification. Dark field image. This FIB lamella is not thin enough to allow HRTEM.

Some sample prepared with the Tripod technique. (the Ti substrate is not visible here) A part of the HA layer has been removed during grinding and polishing. Despite that and the irradiation defects, HRTEM observation is possible.
Comparison between techniques: FIB and Tripod

**Tripod + Ion milling**

**FIB thinning**

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**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.

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**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).

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**How to cleave?**

- Partially scribe the sample with a fine diamond scribe onto layers surface.
- Plastic rule.
- My fingers.
How to cleave?

- Turn it over, roll on the cylinder on the full sample
- Small samples must be turned over very carefully
- Select good wedges using optical microscope

Positioning the wedge cleaved sample on the grid support

Take care of:
1) Eucentricity
2) Left and right
3) Sample orientation should be about 45° with respect to the direction of the electron beam

Few examples

Chemical composition measurements for AlGaAs/GaAs interfaces

Calculations (TEM5) can be done to interpret the thickness fringes profile in a semi-quantitative way.
Quantum wells degradation in AlGaAs by Zinc diffusion from the surface
J.D. Ganière, EPFL

Comparison between a cleaved wedge and a “usual” cross-section of quantum wells AlGaAs/GaAs

P.A. Buffat, J.D. Ganière
EPFL

Si substrate

P.A. Buffat, EPFL-CIME, Lausanne

GRINSCH AlGaAs

 poly Si/SiO2/Si [111]

Cleaving planes are different from the one of GaAs
THE ULTRAMICROTOMY

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

THE CRYO-ULTRAMICROTOMY

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

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

Method

• Reduce the sample size if needed
• Embed the sample if needed

For porous material: embedding under vacuum or infiltration-embedding

Important: the embedding resin should have the same hardness/softness as the sample.
<table>
<thead>
<tr>
<th>Resin</th>
<th>Knife angle</th>
<th>Compression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lowicryl K4M</td>
<td>45°</td>
<td>24%</td>
</tr>
<tr>
<td></td>
<td>35°</td>
<td>12%</td>
</tr>
<tr>
<td>EM-Bed</td>
<td>45°</td>
<td>20%</td>
</tr>
<tr>
<td></td>
<td>35°</td>
<td>14%</td>
</tr>
<tr>
<td>Spurr's (hard grade)</td>
<td>45°</td>
<td>17%</td>
</tr>
<tr>
<td></td>
<td>35°</td>
<td>10%</td>
</tr>
<tr>
<td>LR White (hard grade)</td>
<td>45°</td>
<td>13%</td>
</tr>
<tr>
<td></td>
<td>35°</td>
<td>8%</td>
</tr>
<tr>
<td>Epofix</td>
<td>45°</td>
<td>11%</td>
</tr>
<tr>
<td></td>
<td>35°</td>
<td>6%</td>
</tr>
</tbody>
</table>

**Cutting and embedding semiconductors samples**

- Coatings
- Substrate
- Embedding
- Cardboard
- Cyanacrylate glue
- Flat embedding mold (no silicon !)

**Two step trimming**

First trimming step

Second trimming step by ultramicrotomy (500nm sections)

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

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

**Induced damages**

- Ductile Materials
- Brittle Materials
Thin slices are done!
Now we have to fish them!!

Nice weather
TEMP SUPEROS.

Sections collection
Diatome, Helmut Gnaegi presentation

Results
Optical microscope, transmitted light
TEM, bright field image
Some examples

Mica sample

Mechanical thinning followed by ion milling did not give a suitable result.

Final thinning by ion milling, optimized for high speed abrasion.

Same sample, prepared by ultramicrotomy.

2) Synthetic hydroxyapatite needle

Sectioned perpendicular to its length (C axis).

J. Hemmerlé, INSERM U 424, Strasbourg.

3) Amorphous Si/Si

Ion beam deposited amorphous Si film on a Si substrate.

Distome, Helmut Gnaegi presentation.

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
- ...

Si-Fe/SiO2 particles Embedded in epoxy.

TEM bright field image.

Si-Fe/SiO2 particles Embedded in epoxy.

TEM bright field image.

Si-Fe/SiO2 particles Embedded in epoxy.

TEM bright field image.

Si-Fe/SiO2 particles Embedded in epoxy.

TEM bright field image.

Si-Fe/SiO2 particles Embedded in epoxy.

TEM bright field image.

Carbon particles in epoxy resin.

TEM, bright field image.

J. Ayache, UMR-CNRS-IGR, Villejuif.

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J. Ayache, UMR-CNRS-IGR, Villejuif.

J. Ayache, UMR-CNRS-IGR, Villejuif.
Current density is proportional to the concentration gradient: lower in crevasses, stronger on projections = lavelling of surface roughness.

Principle

Electrolytic bath: - acid or alcaline solution - viscous solution - ionisable liquid

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

The plateau

Voltage Current Distribution

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 planar 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 solvent solution
- Carbon film deposition for non-conductive samples
- Pulling away the film from the sample by its immersion into solvent, by pulling out or by chemical etching of the sample
- Mounting the replica onto a 2.3 mm or 3 mm support grid

Comparison between techniques:
Fine particles dispersion- Cleaved wedge and Tripod method

Four techniques for one sample !!!!!!

Embedded with G1 (Epotek) resin
Tripod polished (wedge)
Glued on a grid
Embedded in Araldite Epoxy
Sliced with an Ultramicrotome
Don't forget that sample preparation is also...

...like cooking!!...

Thank you for your attention!