
RISK OF YOUR RESEARCH BEING USED BY A SUPERVILLAIN FOR WORLD DOMINATION
HIGH
ROBOTICS
GENETIC ENGINEERING
PROSTHETICS
NEUROSCIENCE
MICROBIOLOGY
LASER OPTICS
PHARMACOLOGY
CHEMISTRY
MATERIALS SCIENCE
RISK OF THE THING YOU'RE STUDYING BREAKING FREE FROM YOUR FACILITY AND THREATENING THE LOCAL POPULATION
SOCIOLOGY
HISTORY
PSYCHOLOGY
LOW
HIGH
BOTANY
ENTOMOLOGY
GEOLOGY
MYCOLOGY
LINGUISTICS
MARINE BIOLOGY
PALEONTOLOGY
ORNITHOLOGY
ASTRONOMY
MOLASSES STORAGE
DENTISTRY
LOW

Sample Preparation

MSE 360

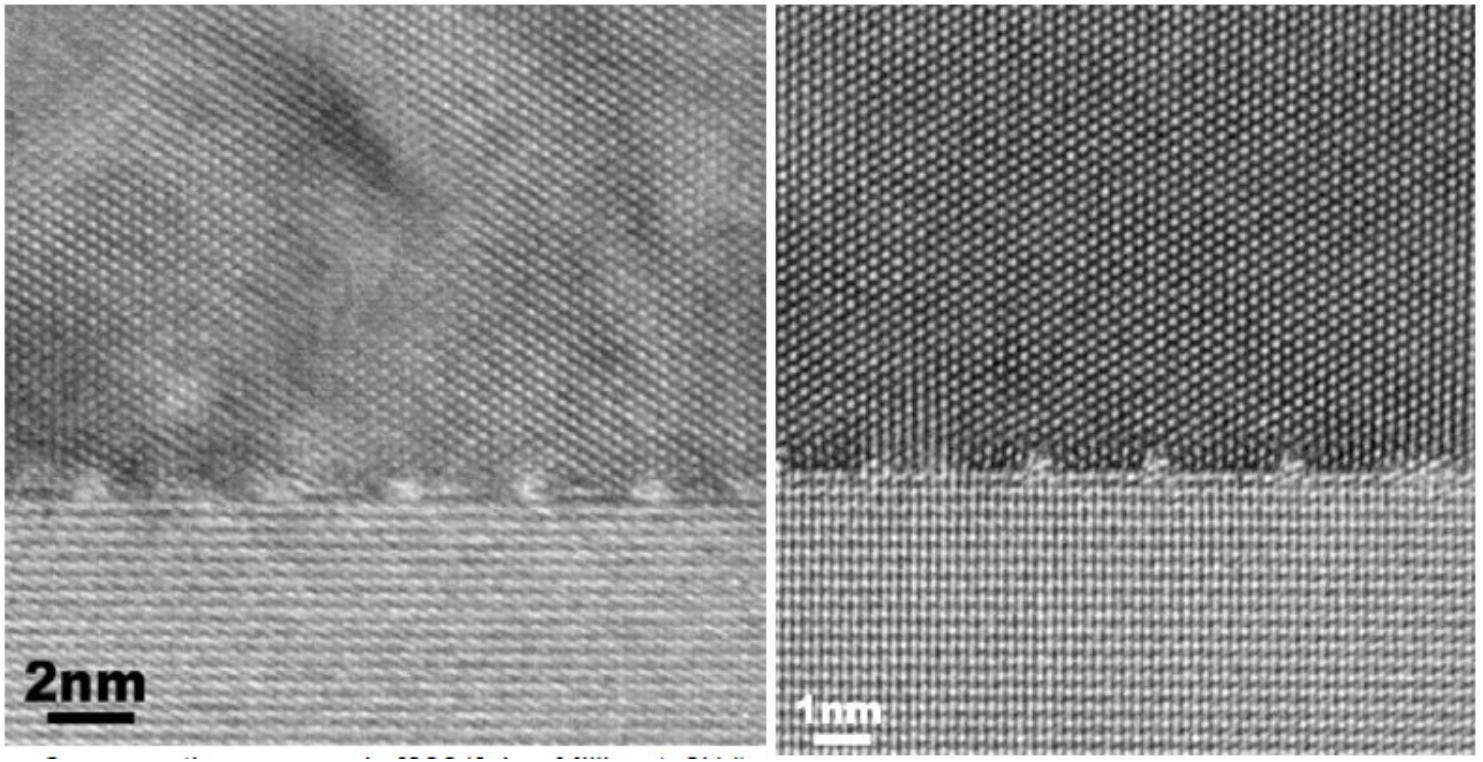
Spring 2022

5/10/22

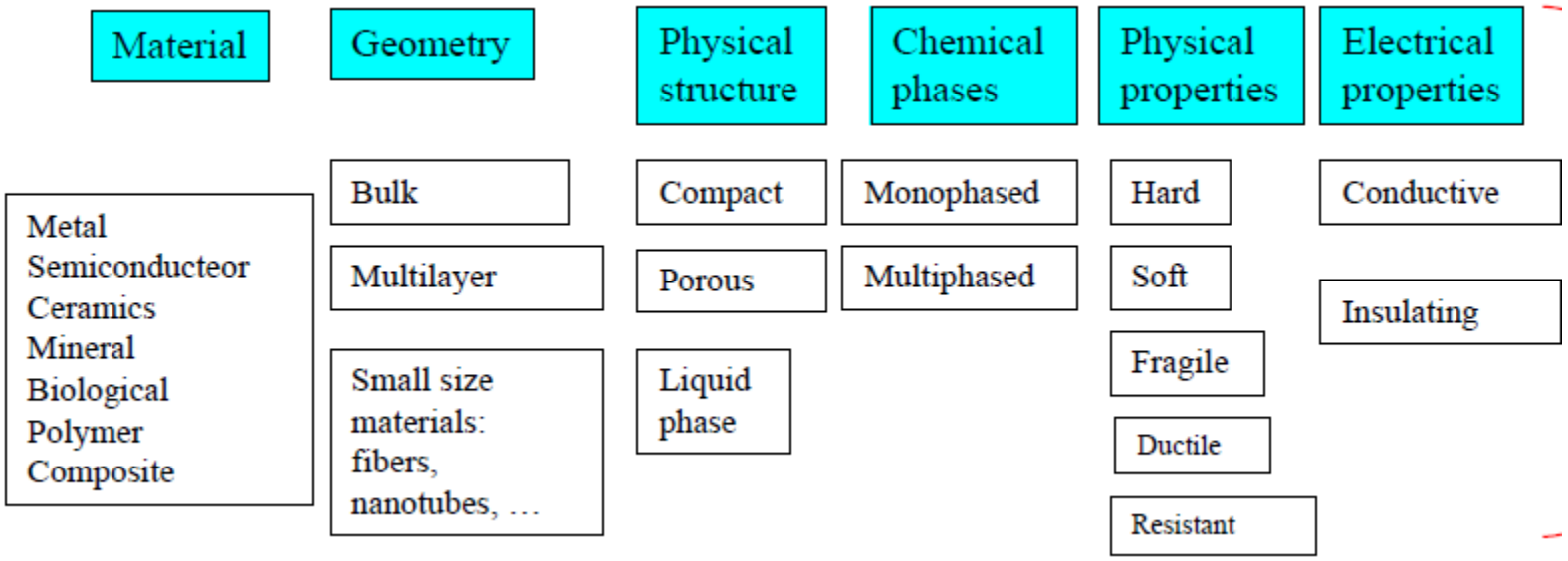
Why is Sample Preparation Important?

- Specimens need to have several properties:
  - Electron transparent (thinner is better!)
  - Flat
  - Electrically conductive
  - Representative of true nature of material
- Choose a technique that fits your experiment to make it easier
- Sample prep can make alignment easier (e.g. amorphous area, specimen orientation)

Sample Thickness



Factors to Consider

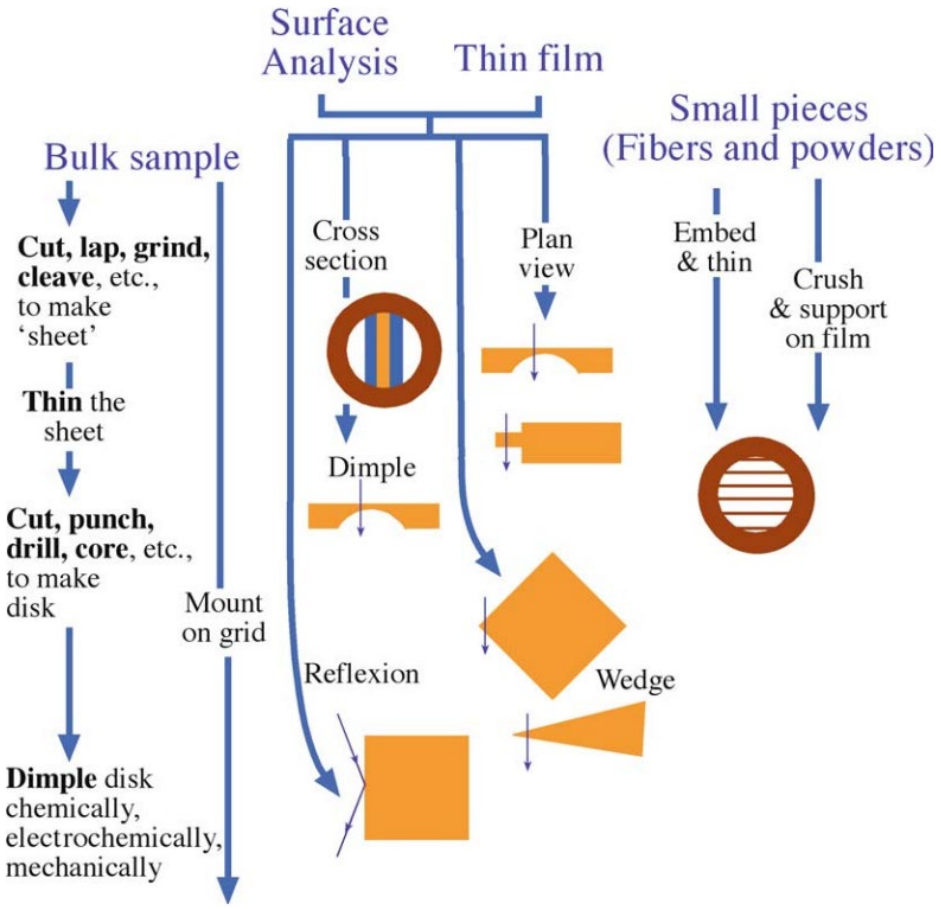


What information are you looking for?

- Morphology
- Composition
- Defects
- Atomic structure

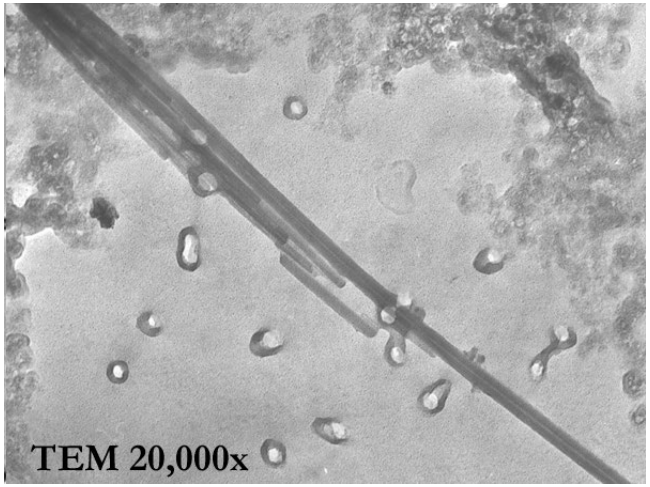
Techniques (not exhaustive)

- **Mechanical**:
  polishing, cleavage, crushing, ultramicrotomy
- **Mechanical + ionic**:
  grinding, dimpling, ion milling
- **Ionic**:
  focused ion beam (FIB)
- **Chemical**:
  electro-polishing
- **Physical**:
  thin film deposition
- **Brains**:
  have the sample make itself



“Brains” Methods

- MgO smoke particles
- Asbestos concentrations
- Scrape relevant material off (tribolayer)

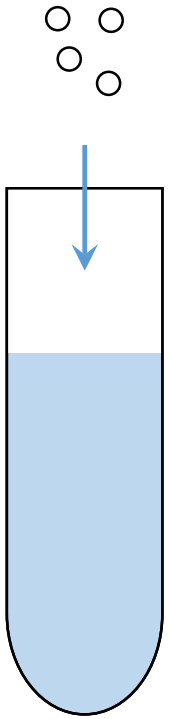


Powder Methods

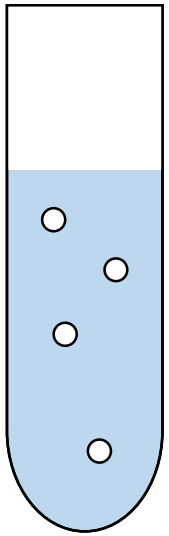
- Dip TEM grid into powder
- Drop cast from a solution or suspension (e.g. nanoparticles)
- Crush a brittle sample and disperse in a solution for drop casting
  - Be careful!
  - Won't work for metals
  - May cause deformation (e.g. fracture)
- Disadvantages:
  - Can't control orientation of sample

If you can avoid something, then avoid it.

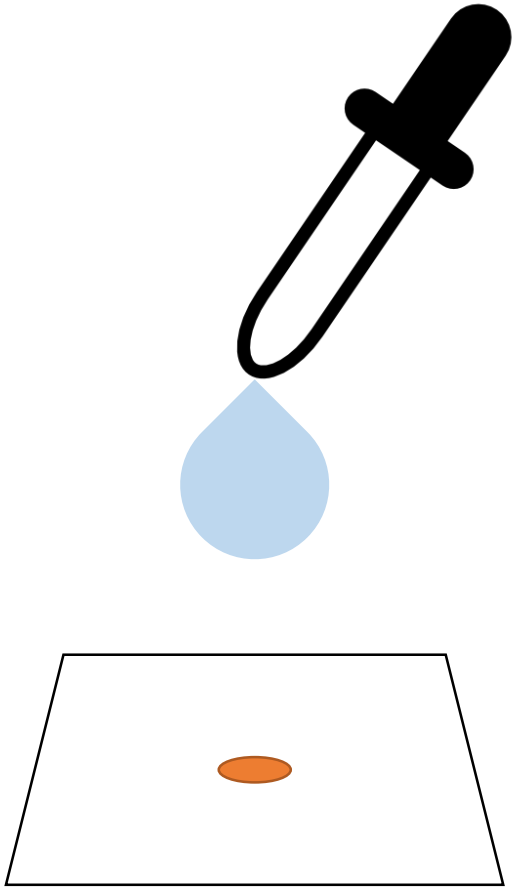
Drop Casting



Add very little amount of powder to a solvent (e.g. ethanol, isopropanol, etc.)

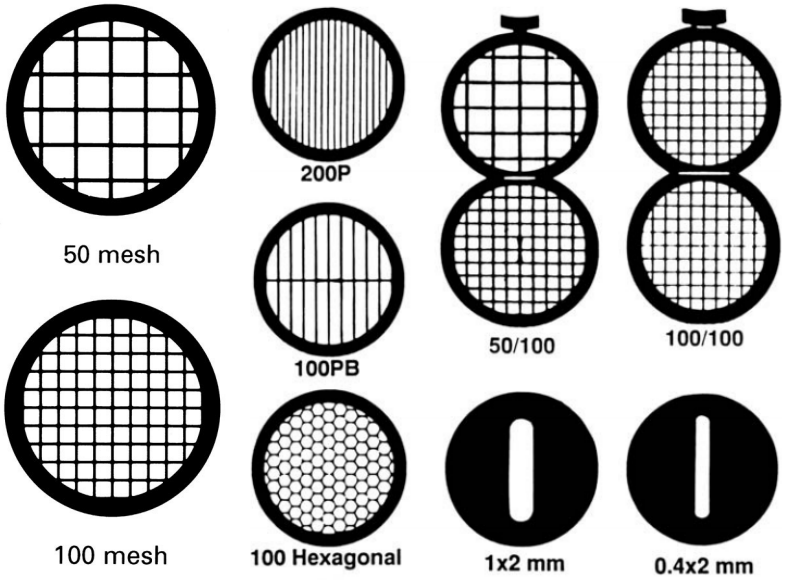


Sonicate until well dispersed

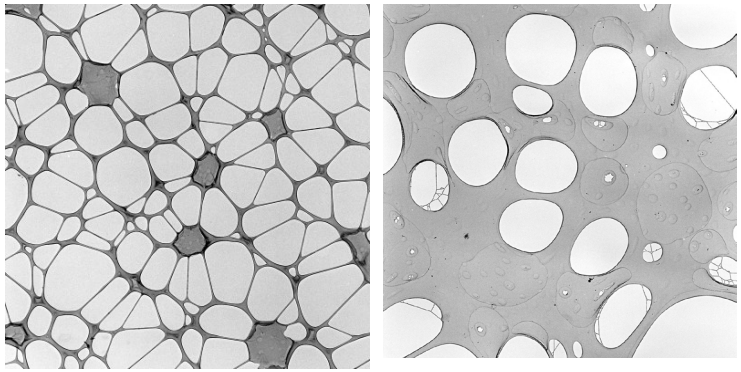


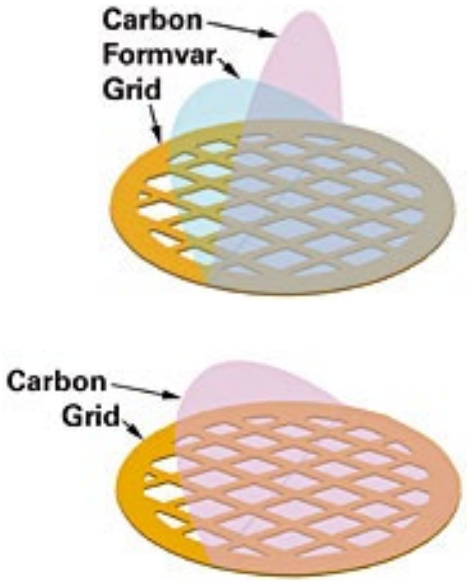
Drop cast onto a TEM grid over a Kimwipe (to surface tension of the solvent)

TEM Grids



- Many different grid types and shapes
- Film materials
  - Carbon – conductive, transparent
  - Formvar – adds support, but decreases resolution (interferes with signal)
  - Silicon nitride – stable at high temperatures
- Film shapes
  - Film
  - Lacey carbon
  - Holey carbon

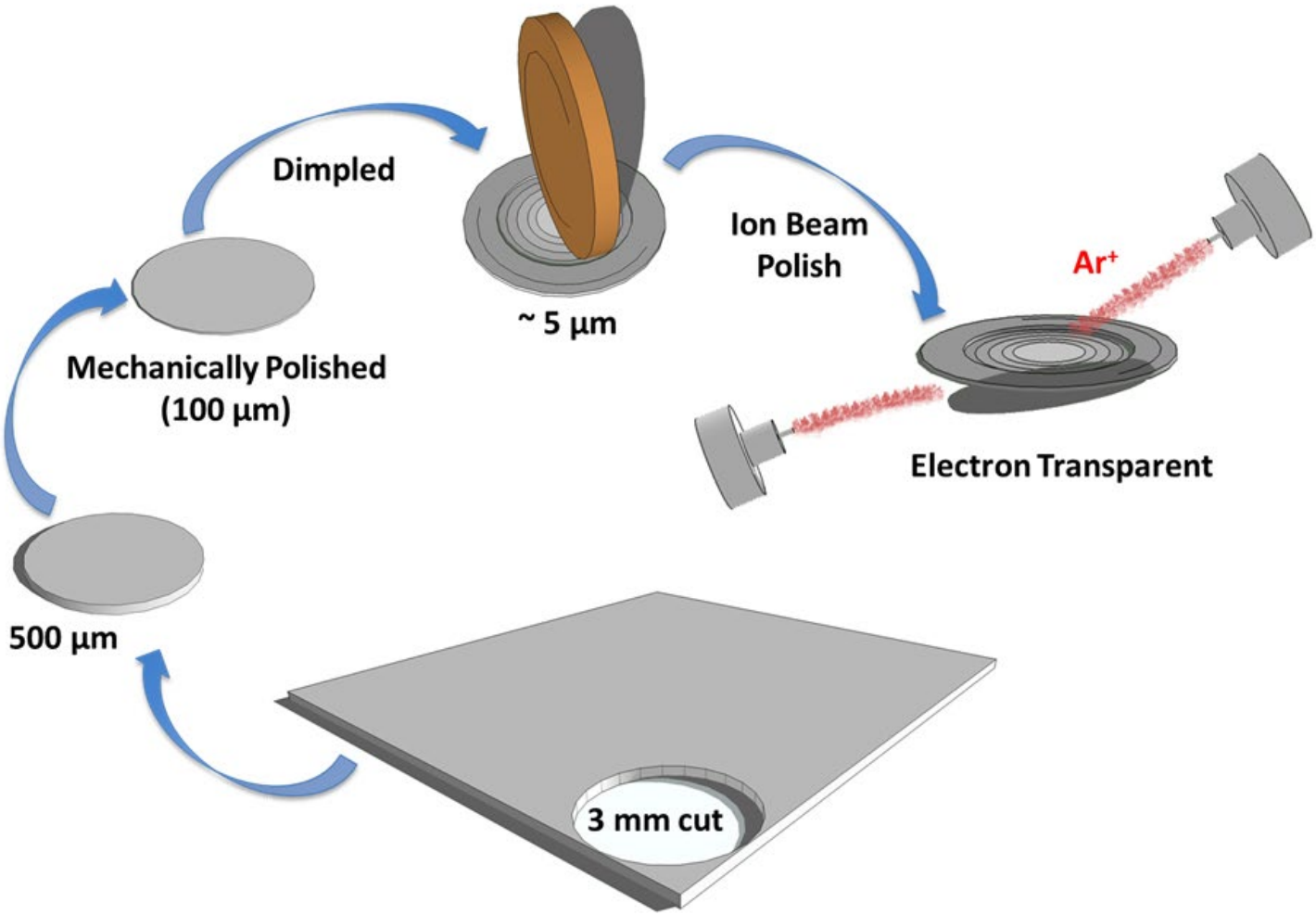




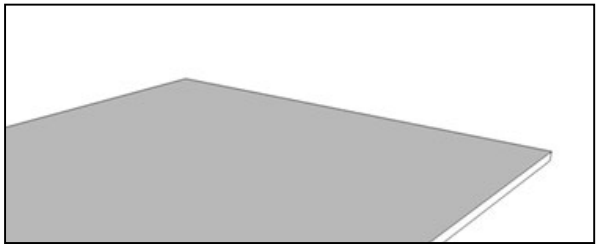
Bulk Materials

	Electropolishing	Ion milling	Focused Ion Beam
Metal and alloys	Yes	Yes	Yes
Ceramics	No	Yes	Yes
Polymer	No	Yes	Yes
Solid thin film	Not common	Yes	Yes

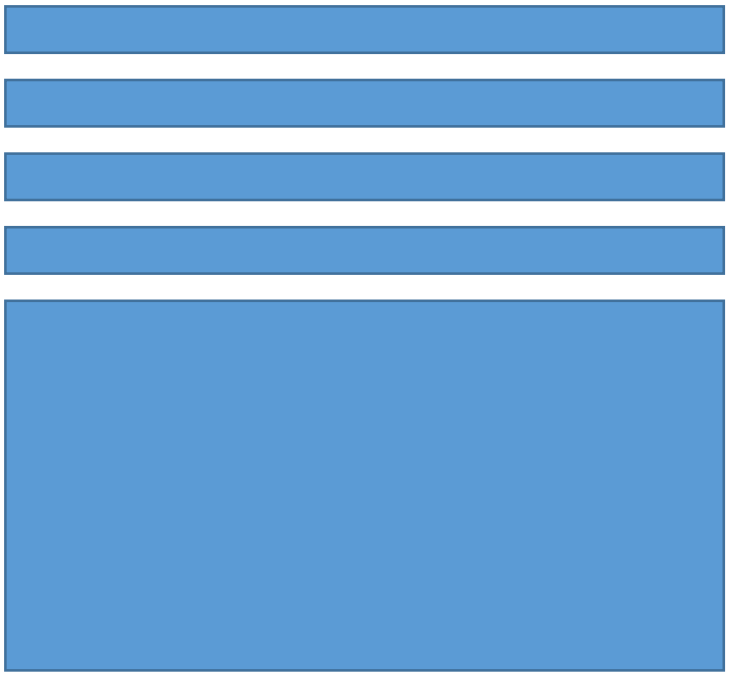
Ion Milling Procedures

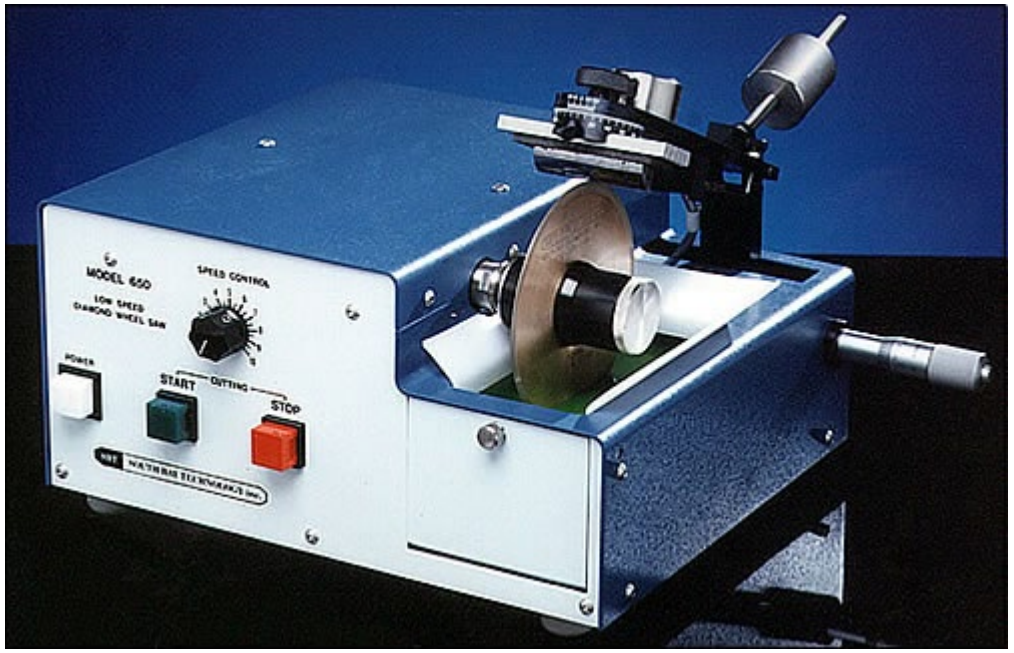


Cutting



~500 µm

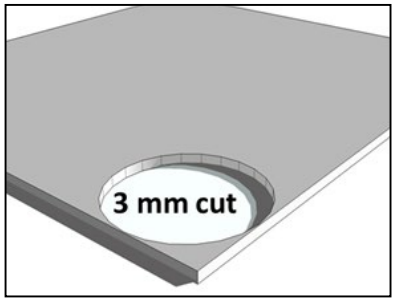




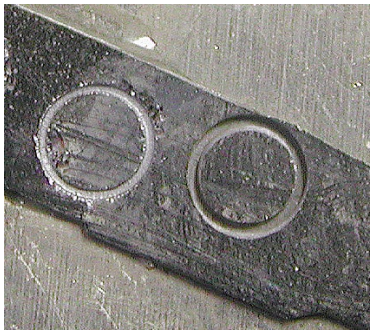
Low Speed Diamond Wheel Saw

- Alternatively, grow or buy a thin sample

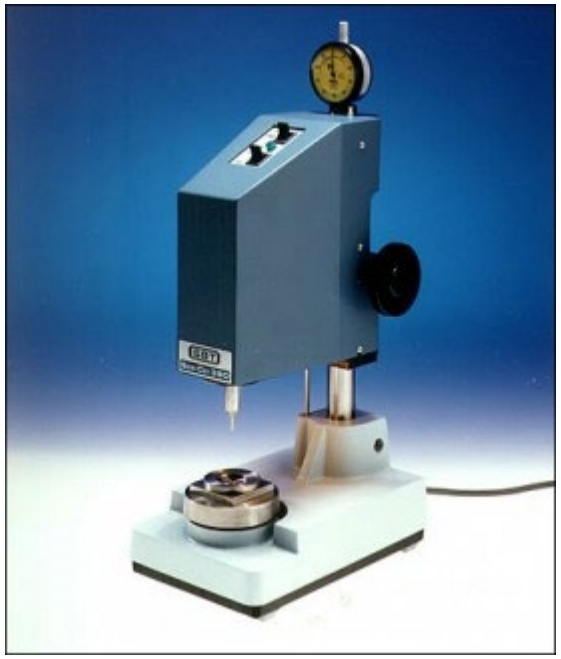
Disk Cutting



- Starting about 500 µm in thickness
- Cut into 3 mm disks using disc punch or ultrasonic cutter

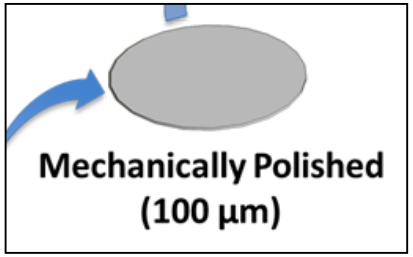


Disk punch (ductile)

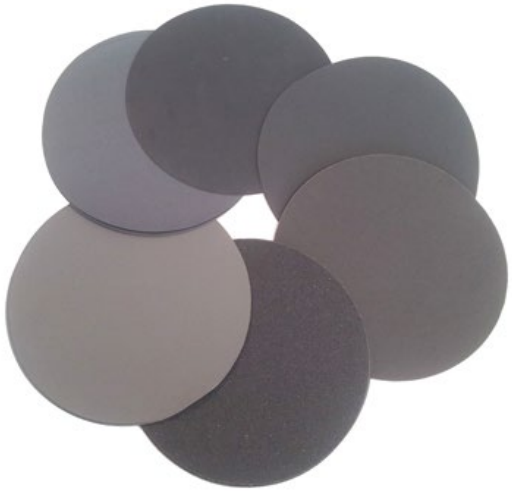


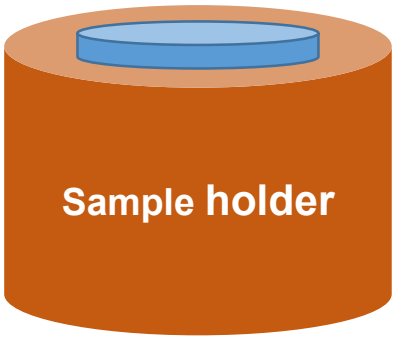
Ultrasonic disk cutter (brittle)

Mechanical Pre-Thinning



- Grind with SiC sandpaper
- Polish with Al_2O_3 or diamond suspension
- Thin until ~70-100 µm

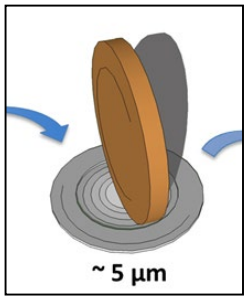


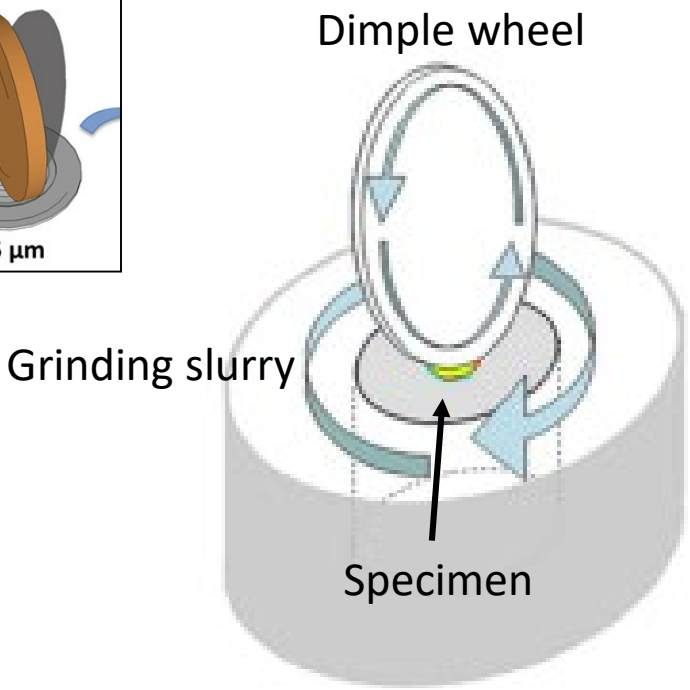


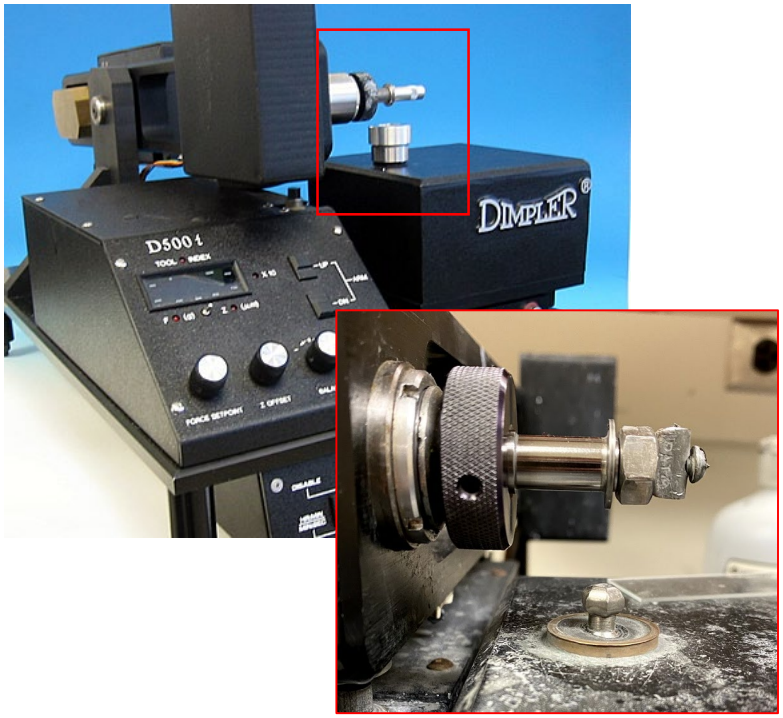
crystal bond wax

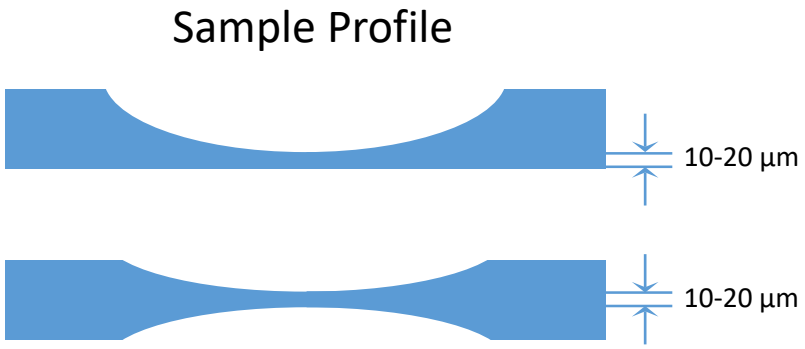
Dimpling

- Dimple down to ~10-20 µm
- Less time for ion-milling
- Large thin area for TEM

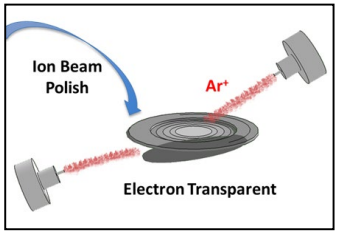


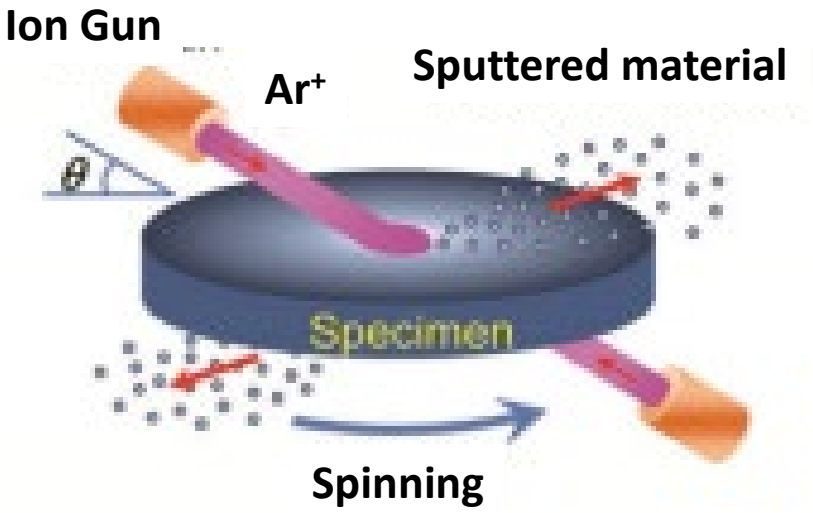


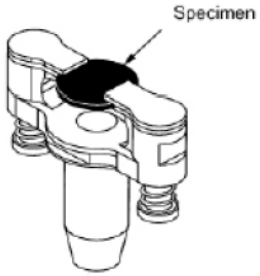




Ion Milling

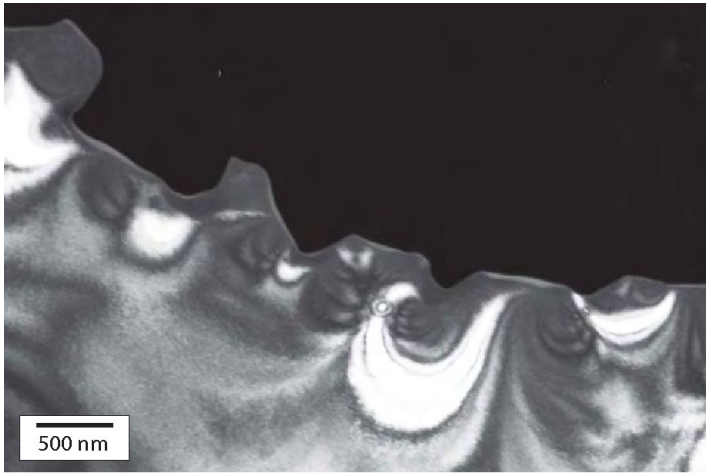






Precision Ion Polishing System (PIPS)

- Ar^+
- 0-10 kV
- 6^o – 12^o



Remove Amorphous Layer

NanoMill® TEM specimen preparation system

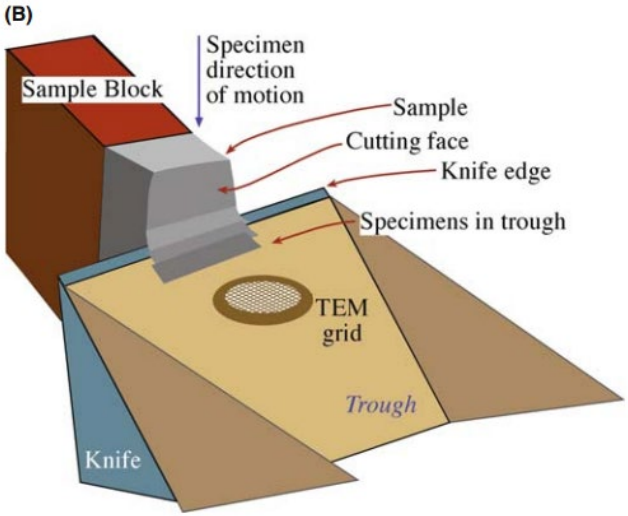
- Ultra-low energy ion source
- Concentrated ion beam
- Removes amorphous and implanted layers
- Ideal for post-focused ion beam processing and milling of conventionally prepared specimens
- Liquid nitrogen-cooled specimen stage

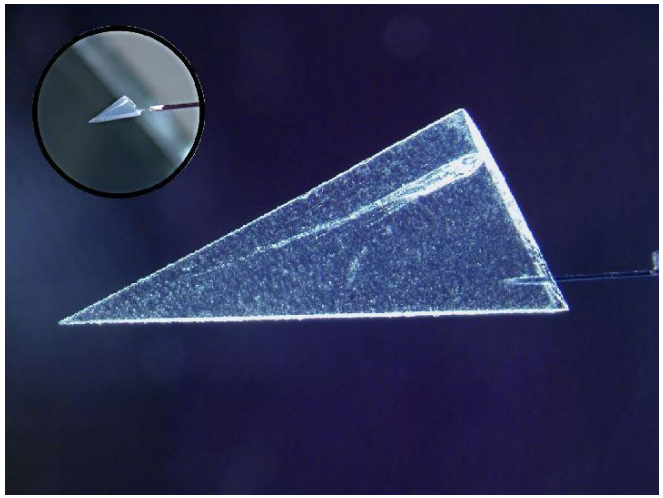
Fischione's Model 1040

Grinding + Ion Milling

- Pros:
  - Thin area for HREM
  - Most versatile thinning process, excellent for metal/oxide
- Cons:
  - Mechanical deformation
  - Amorphous layer
  - Radiation damage (and implantation)

Ultramicrotome

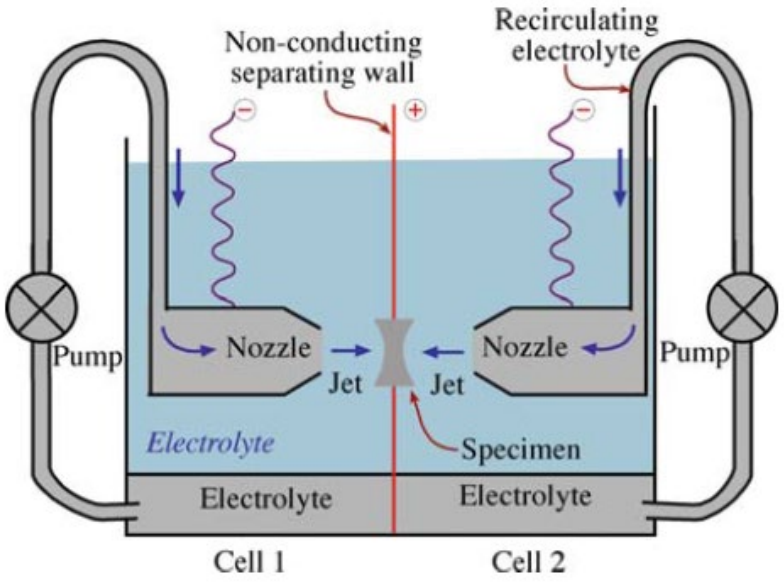




- Often used for sectioning biological samples or polymers (soft materials)
- Good for embedded samples
- Pros:
  - Leaves chemistry unchanged
  - Very thin samples
- Cons:
  - Fractures or deforms samples

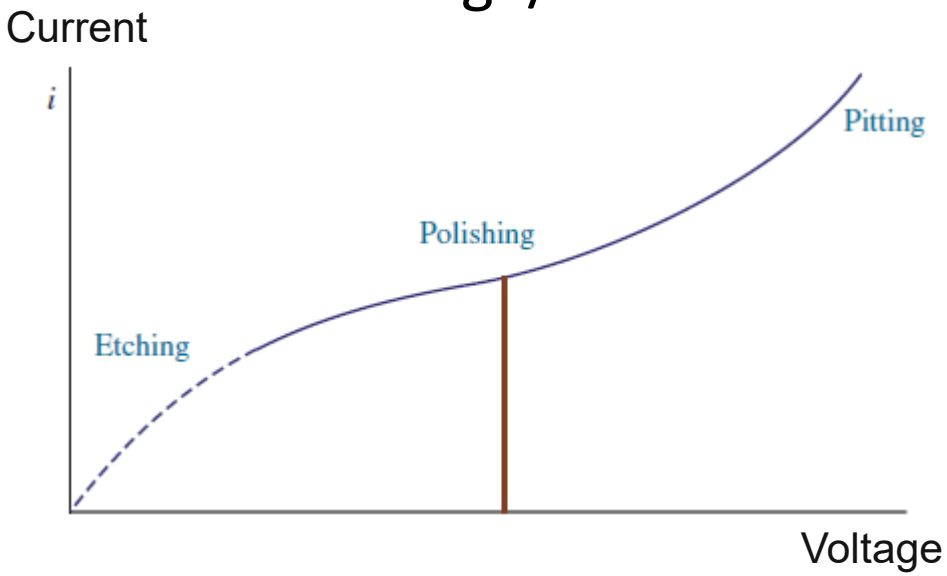
https://stardust.jpl.nasa.gov/news/status/2006_aaas.html

Twin-Jet Electropolishing



Schematic of a twin-jet electropolishing apparatus. The positively charged specimen is held in a Teflon holder between the jets.

- Electrolyte
- Temperature
- Jet speed
- Voltage/current

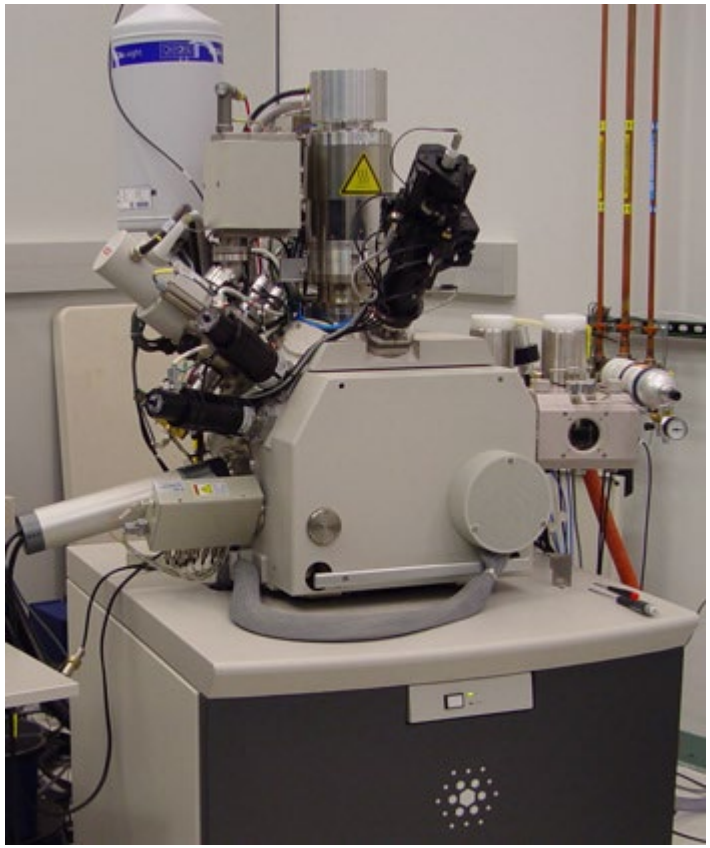


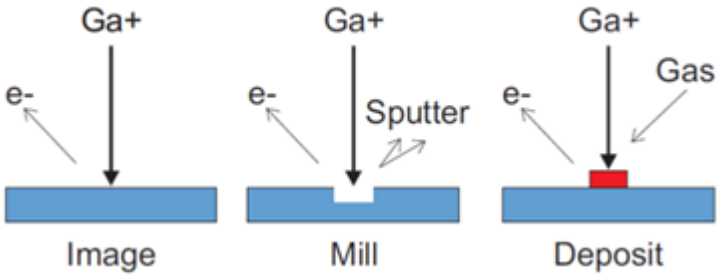
Electropolishing curve showing the increase in current between the anode and the cathode as the applied voltage is increased.

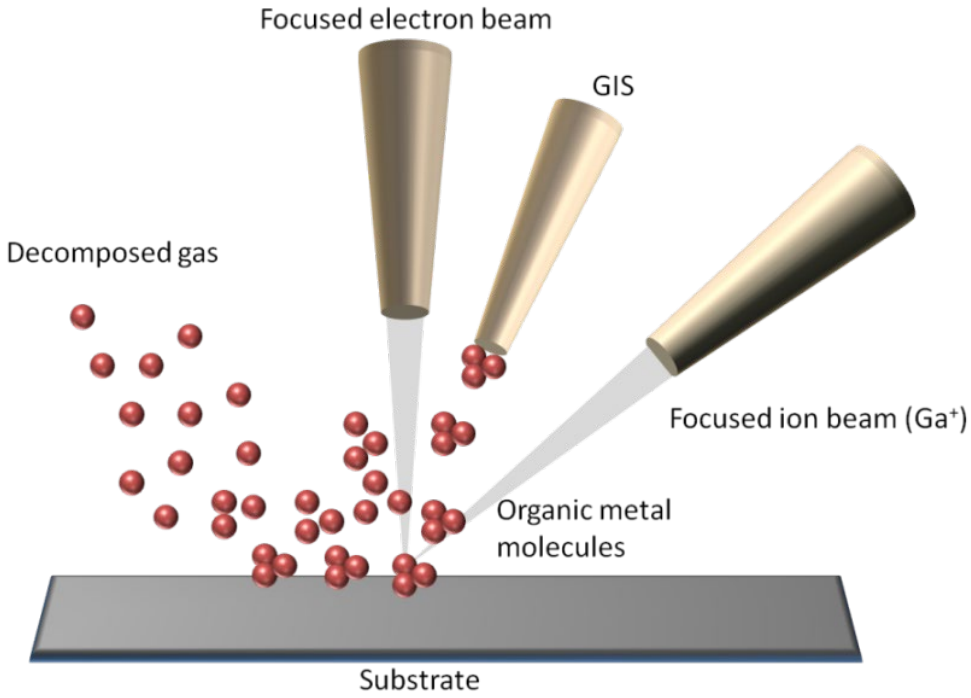
Twin-Jet Electropolishing

- Pros
  - No mechanical damage
  - Free of surface roughness
  - Free of strain hardening
- Cons
  - Preferential etching of multiphase material
  - For conductive materials
  - May change surface chemistry

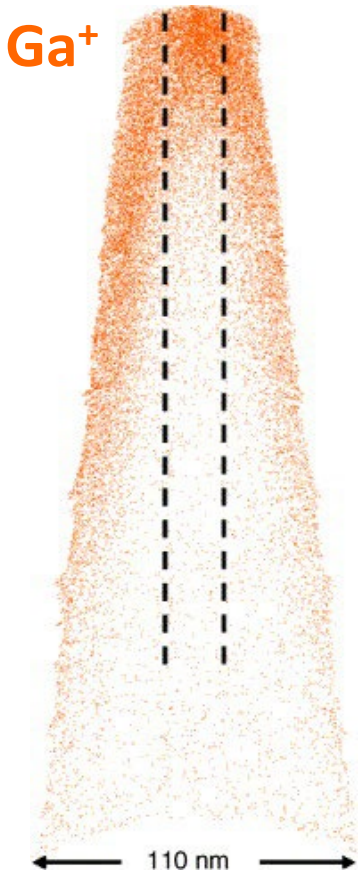
Focused Ion Beam



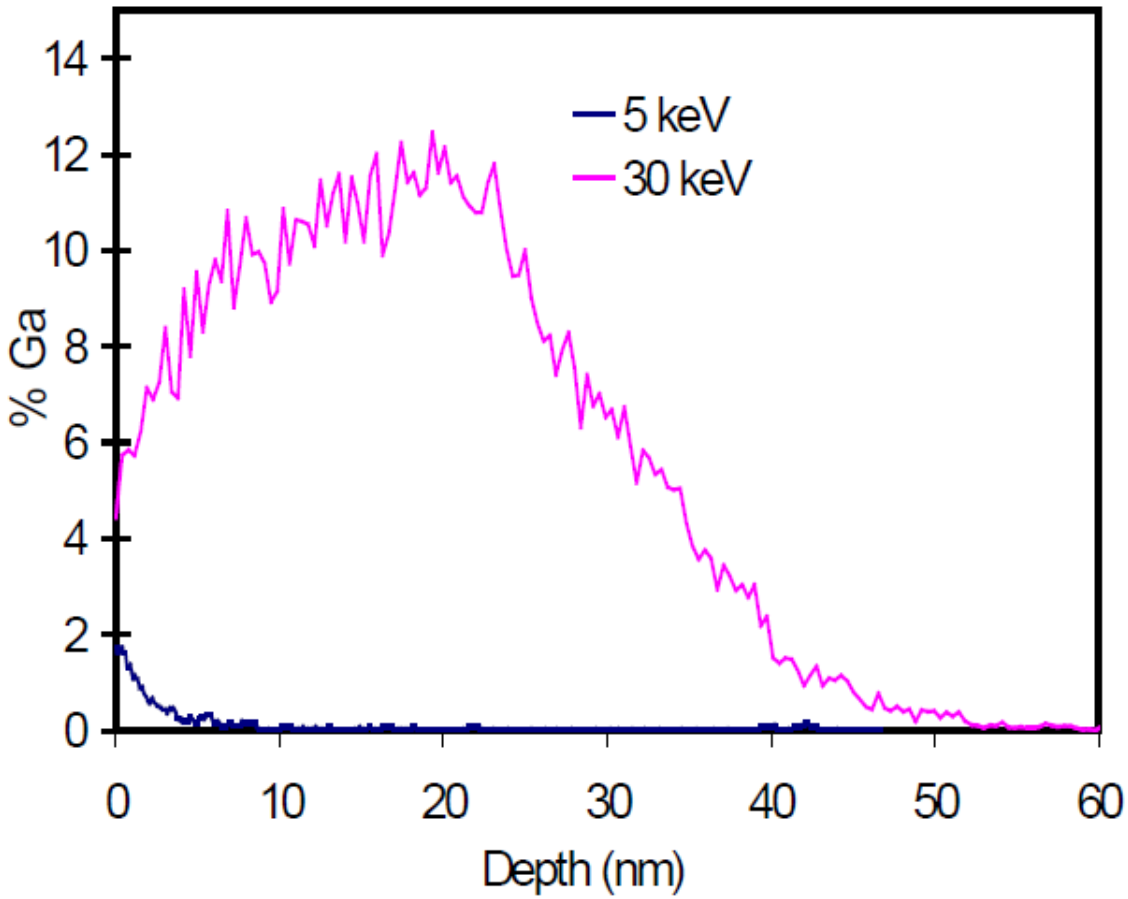




Ga^+ Implantation



Atomic-map of a Si specimen sharpened in a FIB with 30 keV Ga ions

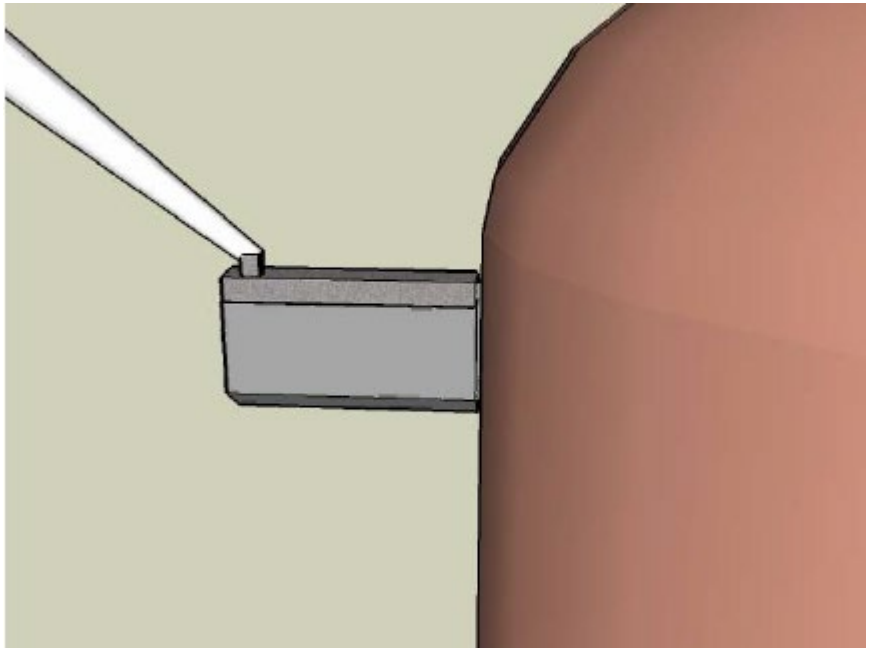


Ga^+ implantation profile in Si for 30 keV and 5 keV accelerating energies.

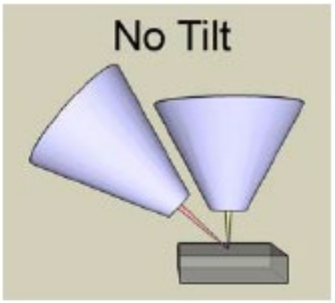
Thompson K, Lawrence D, Larson D J, et al. *Ultramicroscopy* 107 (2007) 131-139

TEM Sample Prep with FIB

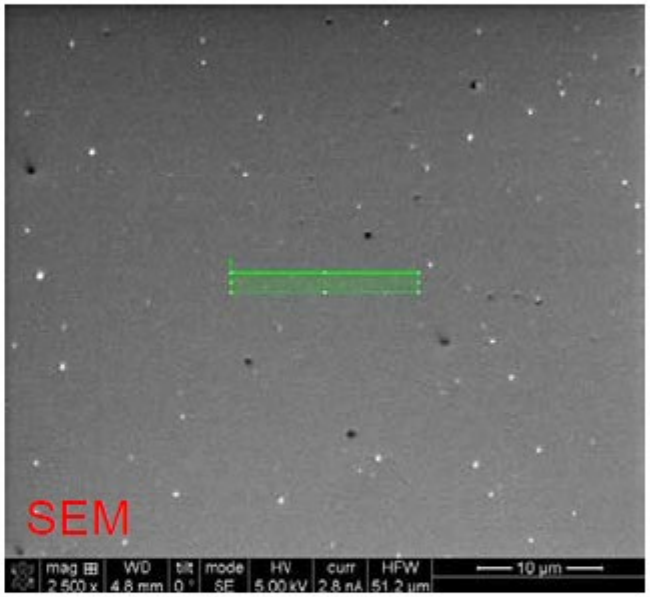
1. Pt Deposition
2. Bulk-Out
3. U-Cut
4. Lift Out
5. Mounting
6. Thinning
7. Cleaning

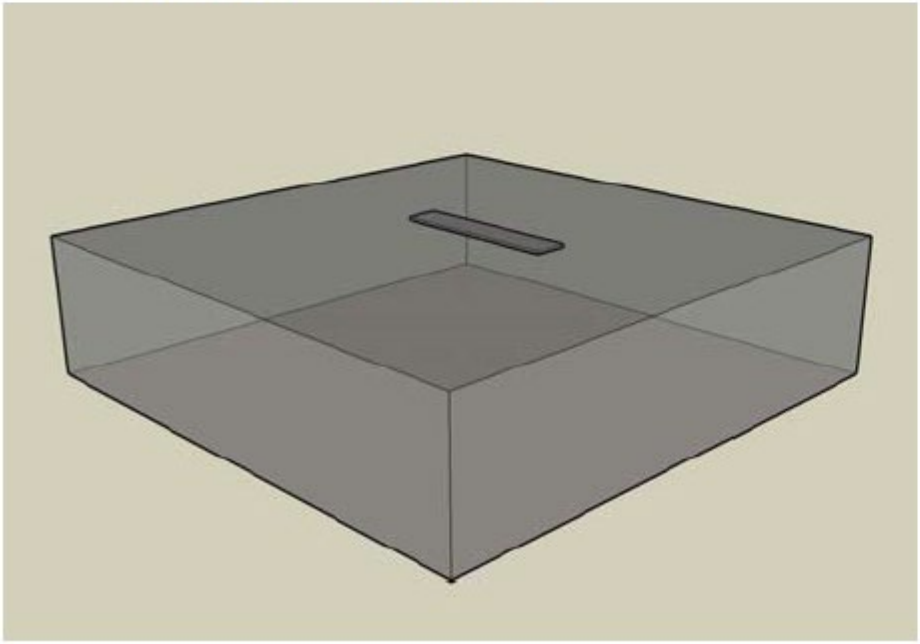


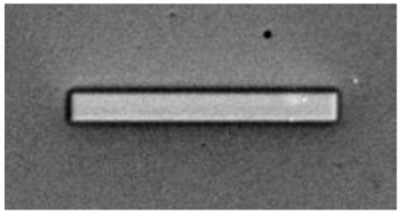
E-beam Pt



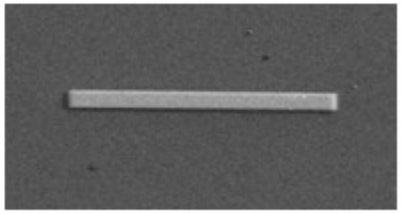
- 0° Tilt
- Application: Pt e-Dep
- Shape: Rectangle
- 15μm (X) x 1.5μm (Y) x 200nm (Z)
- 2-5kV, >1.4nA







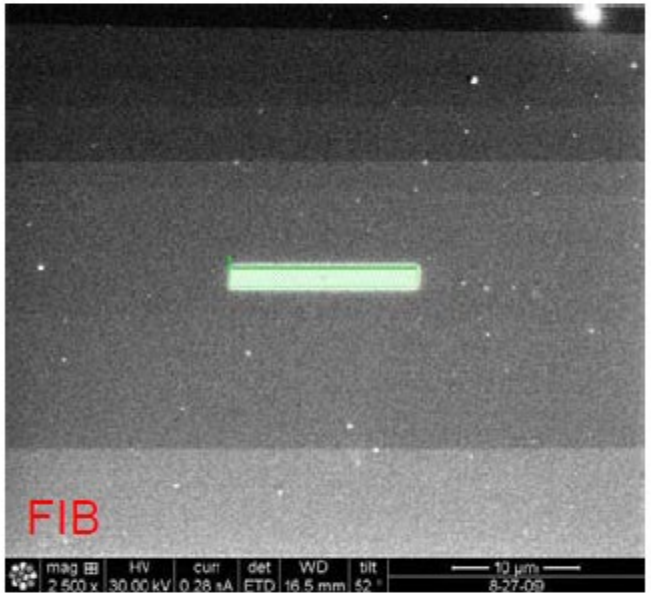
E-beam dep at 0° Tilt (SEM)

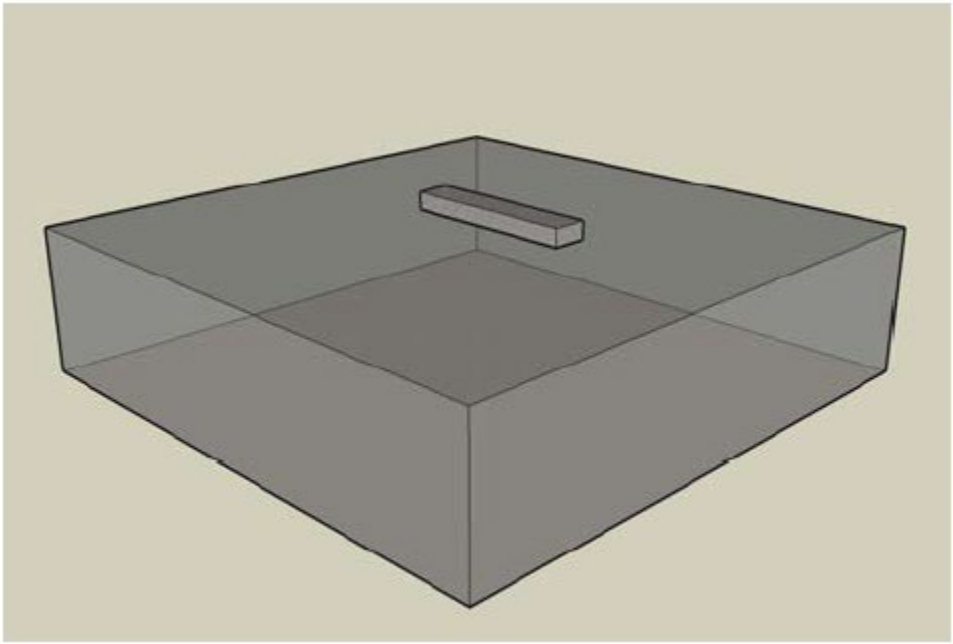


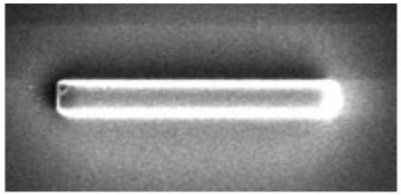
E-beam dep at 52° Tilt (SEM)

Pt Dep (Ion Beam)

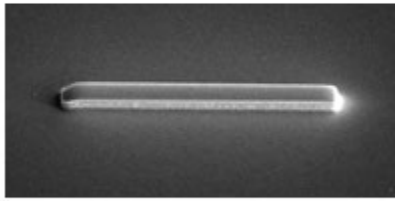
- 52° Tilt
- Application: Pt Dep
- Shape: Rectangle
- 15μm (X) x 1.5μm (Y) x 1.5μm (Z)
- 30kV, 93pA-0.28nA







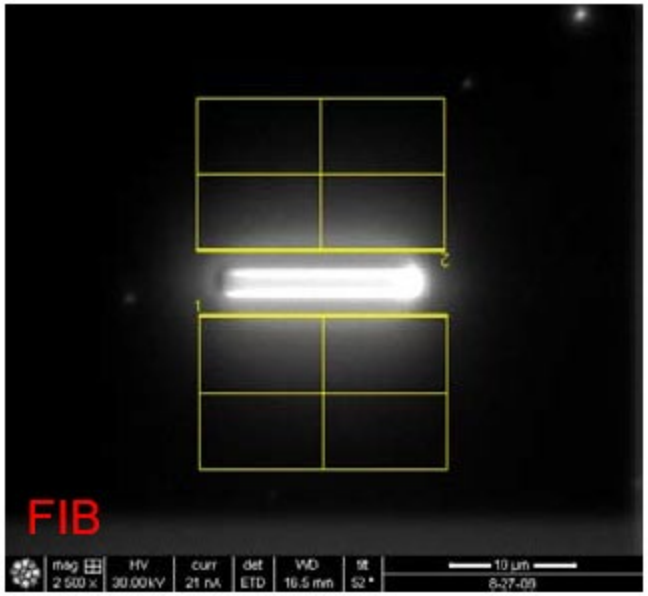
I-beam dep at 52° Tilt (FIB)

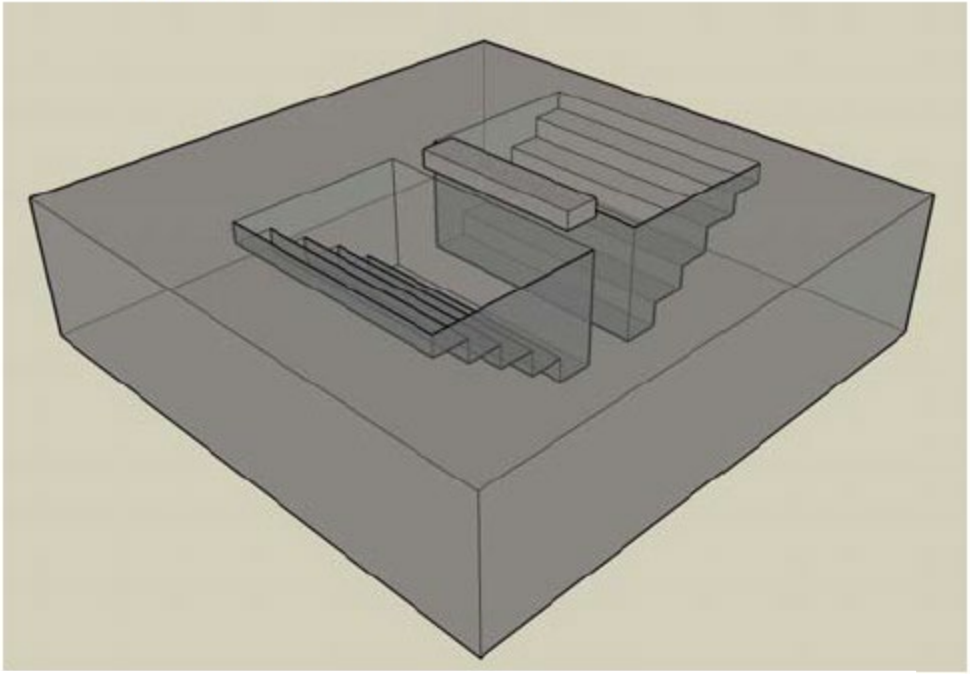


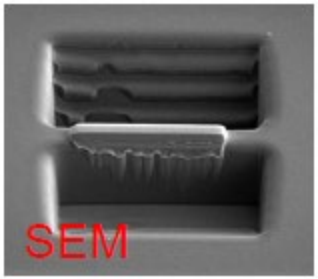
I-beam dep at 52° Tilt (SEM)

Bulk-Out

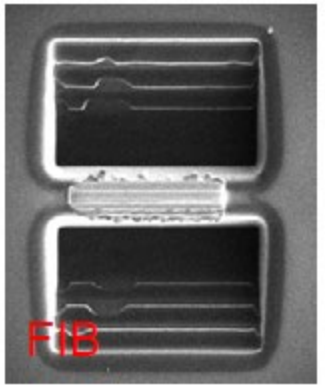
- 52° Tilt
- Application: Si
- Shape: Regular Cross Section
- 20μm (X) x 12μm (Y) x 6μm* (Z)
- 30kV, 6.5-21nA



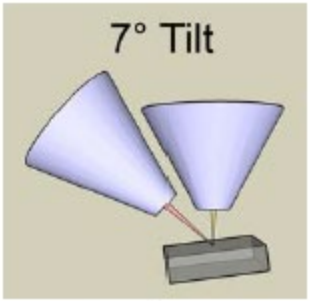




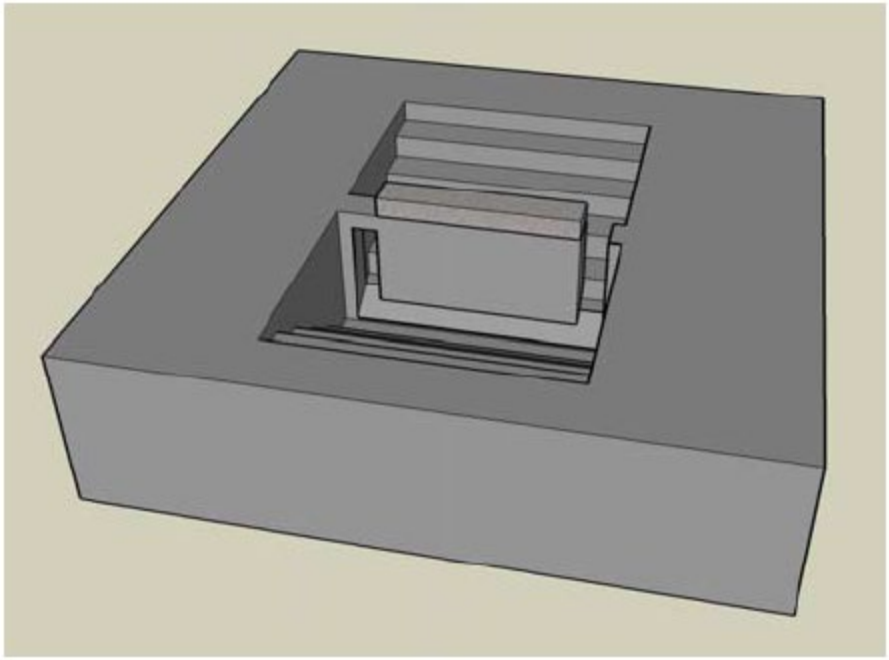
Bulk-Out (1/2)
at 52° Tilt

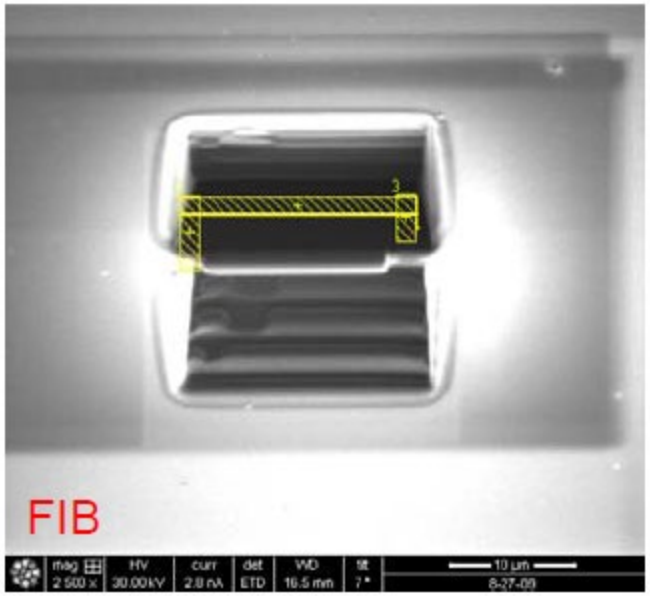


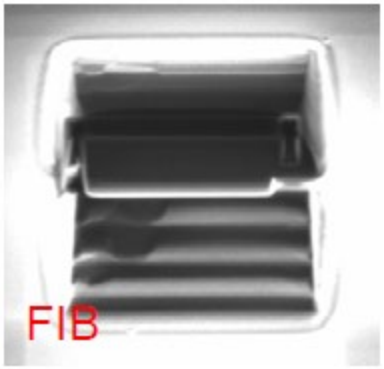
U-Cut



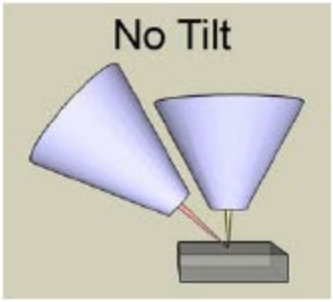
- 7° Tilt
- Application: Si
- Shape: Rectangles
- 1.5μm wide, overlapping
- 30kV, 0.92-6.5nA



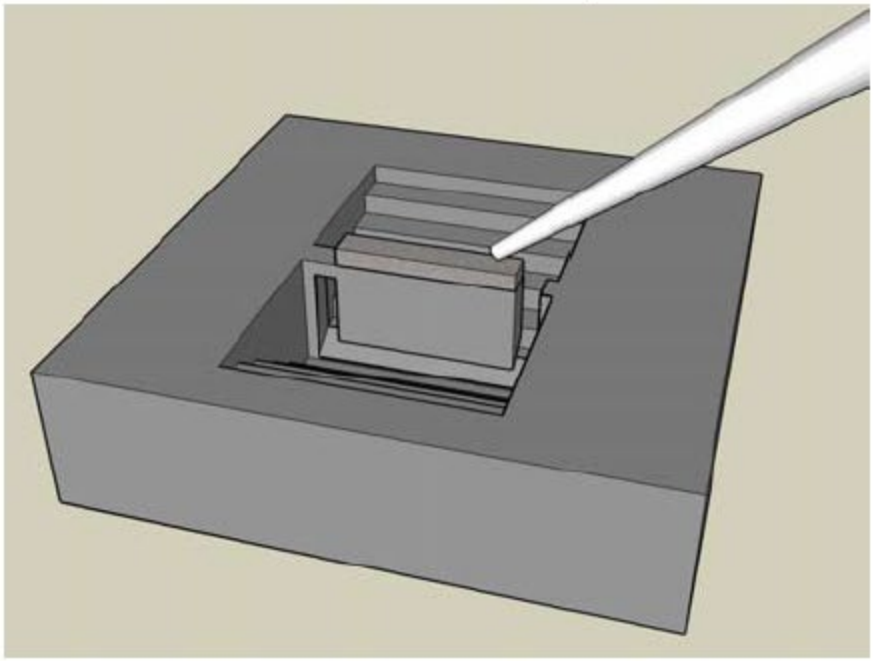


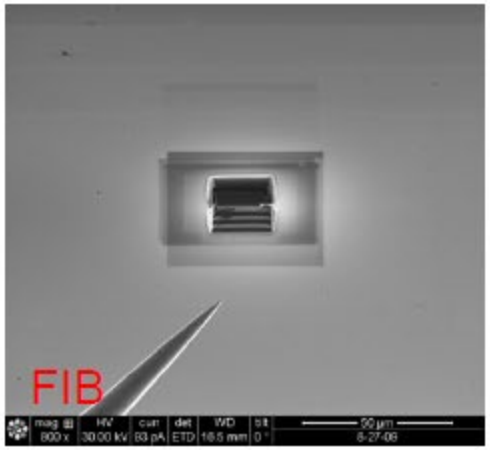


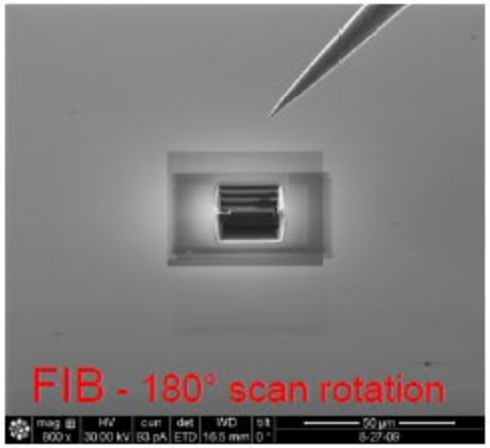
Lift-Out

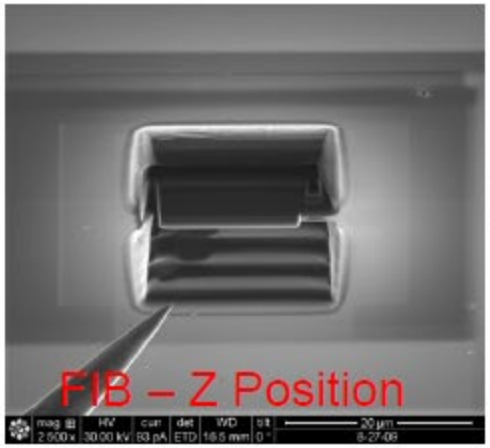


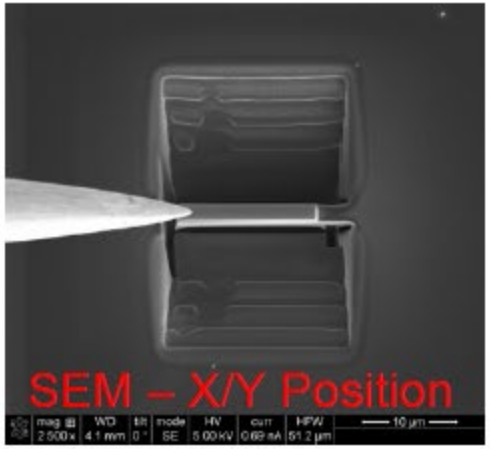
- 0° Tilt
- Insert Omniprobe at Park
- Drive to Eucentric High
- Lower to ~10μm from sample
- Insert Pt GIS needle
- Position tip within ~200nm of sample
- 180° scan rotation is helpful



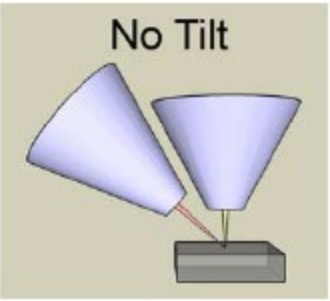




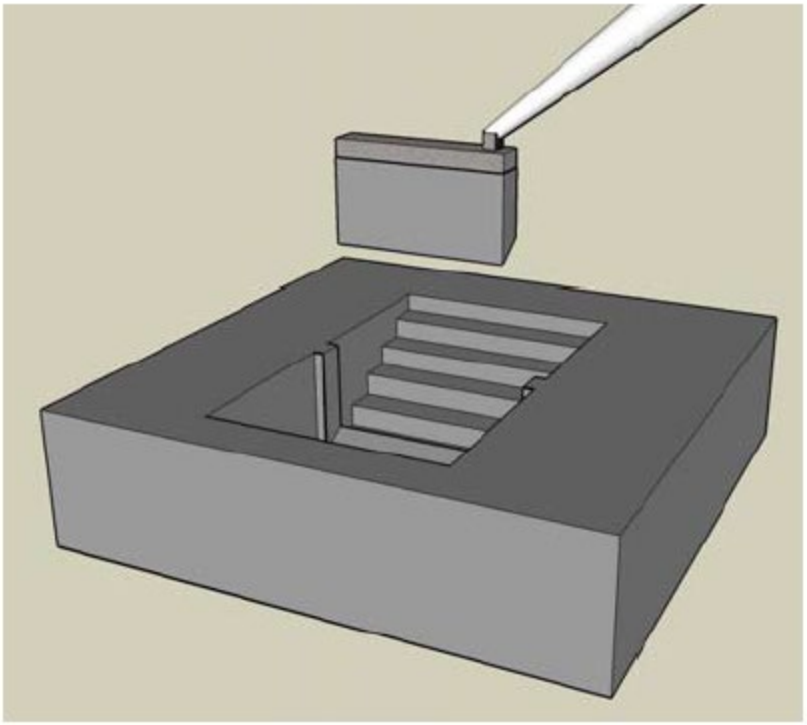


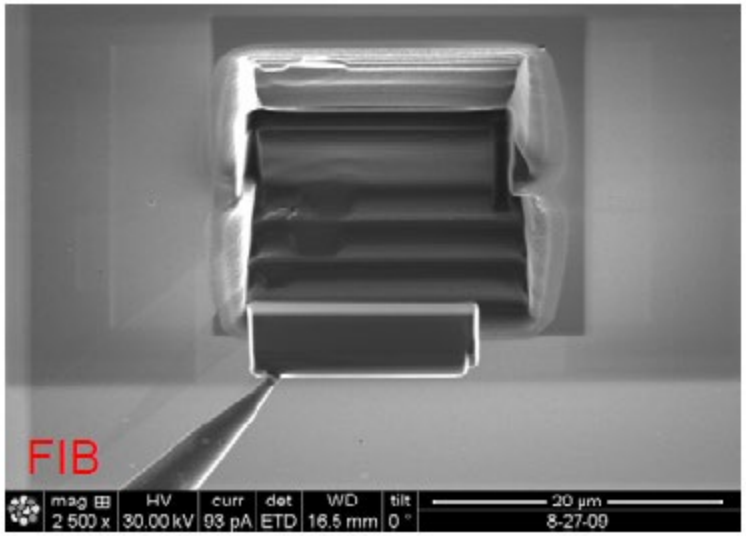


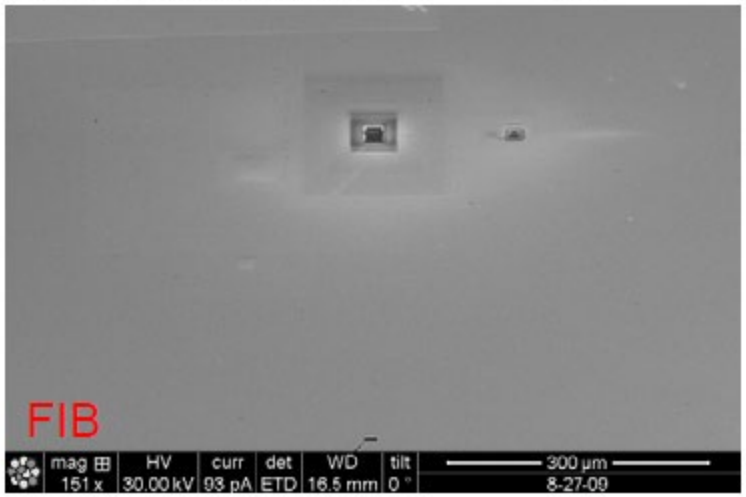
Lift-Out



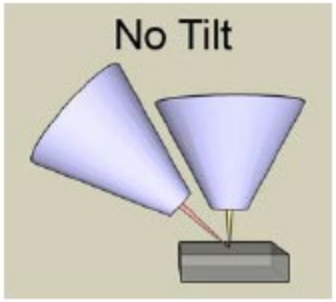
- 0° Tilt
- Raise Omniprobe ~10μm
- Retract Pt GIS needle
- Send Omniprobe to Eucentric High
- Retract Omniprobe



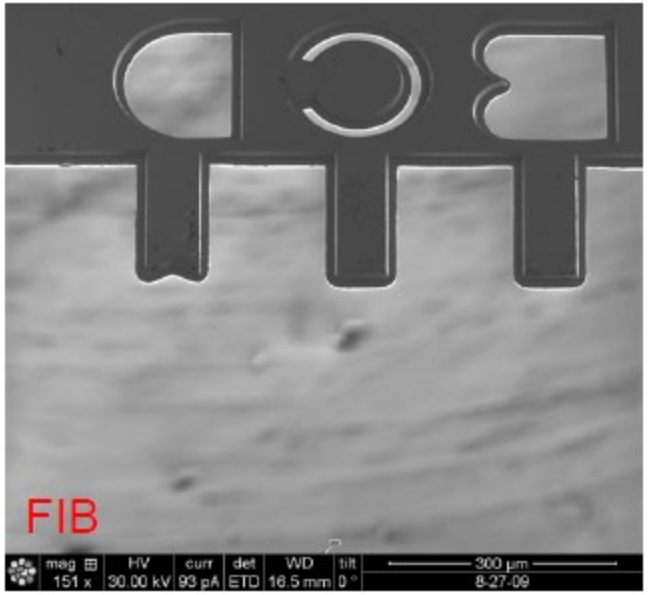


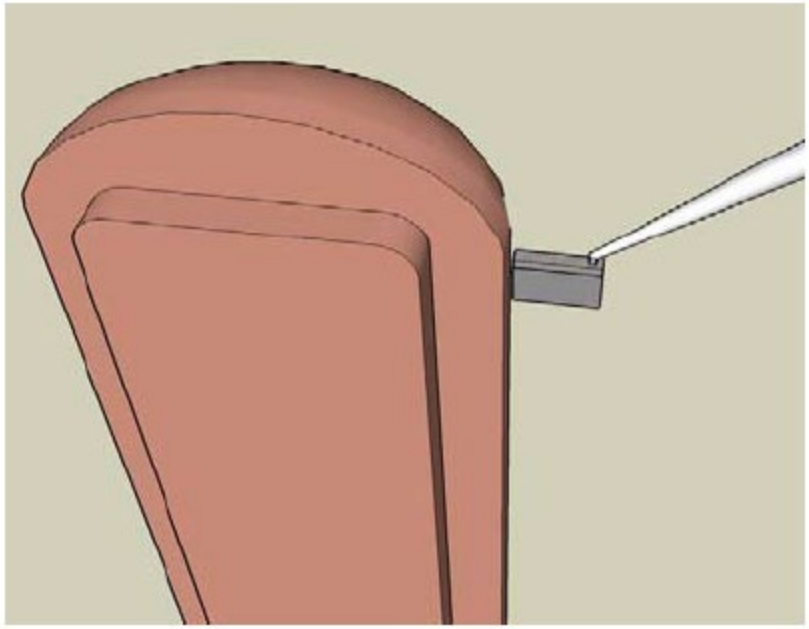


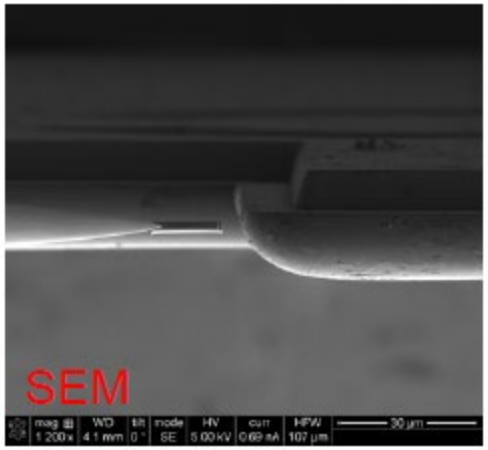
Mounting

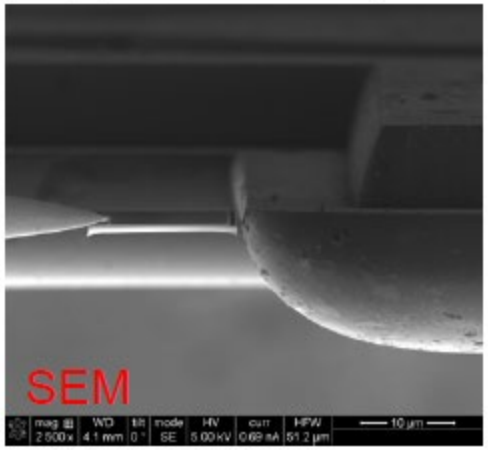


- 0° Tilt
- Reset eucentric height on grid
- Insert Omniprobe at Eucentric High
- Lower to within ~10μm of grid
- Insert GIS
- Position sample within ~200nm of grid

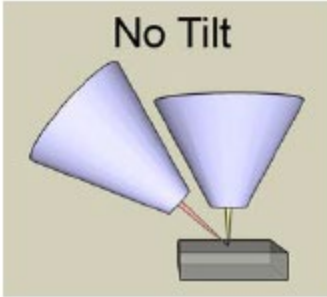




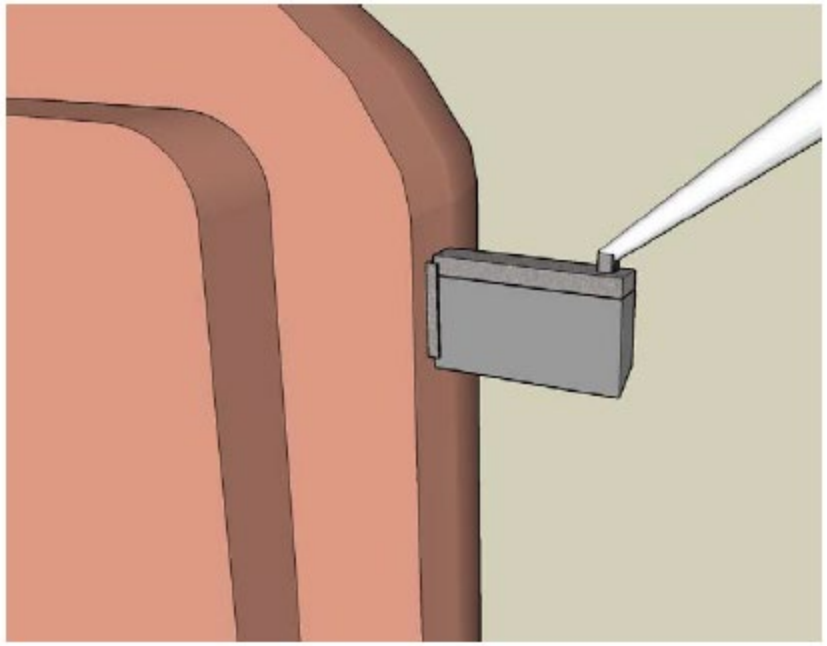


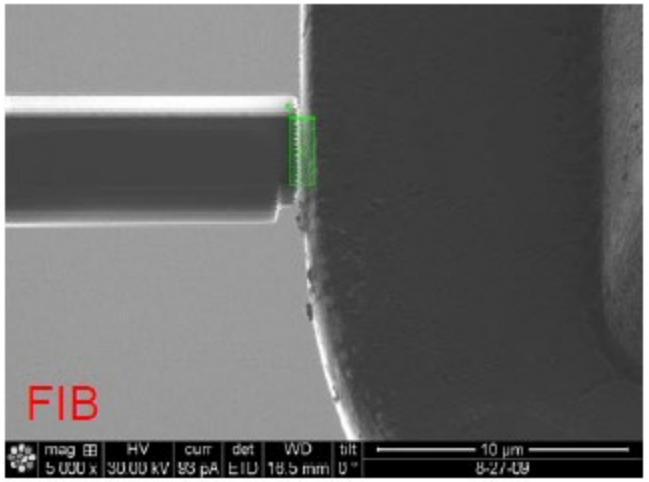


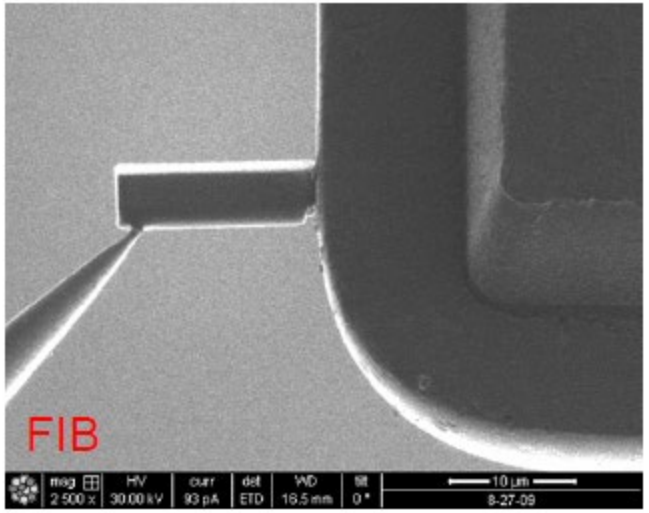
Mounting



- 0° Tilt
- Application: Pt Dep
- Shape: Rectangle
- Size: ~1μm (X) x 3-5μm (Y) x 0.5μm (Z)
- 30kV, 28-93pA

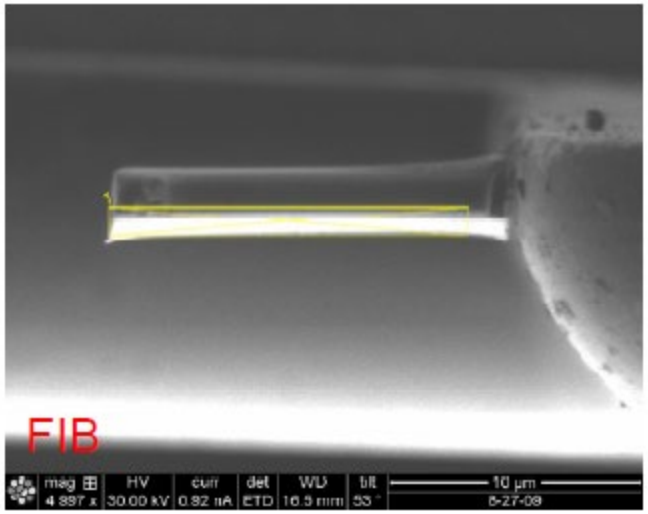


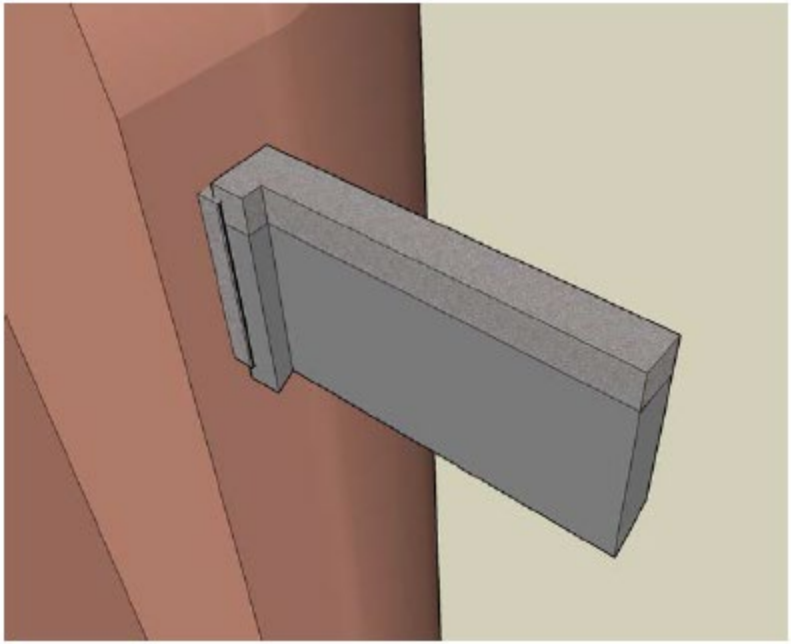


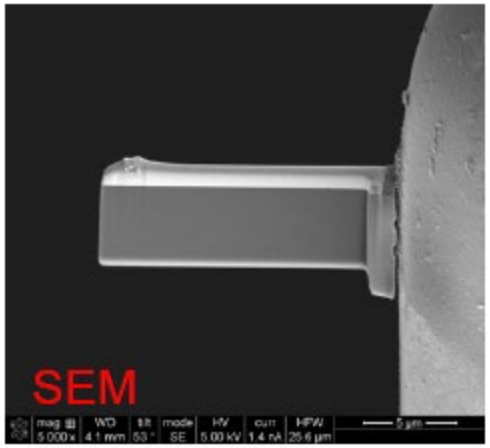


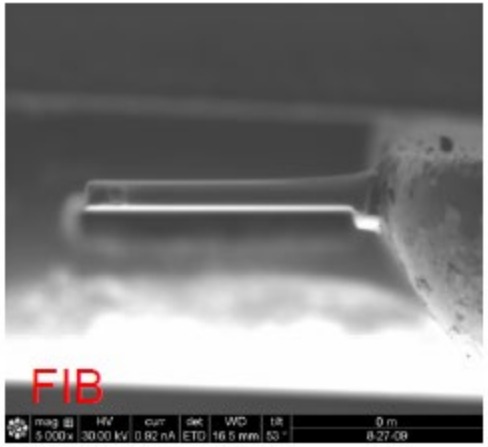
Thinning

- 53-54° Tilt
- Tilt into sample 1-2°
- Application: Si
- Shape: Cleaning Cross Section
- Size: ~10μm (X) x ~500nm (Y) x ~3μm (Z)
- 30kV, 0.46-2.8nA

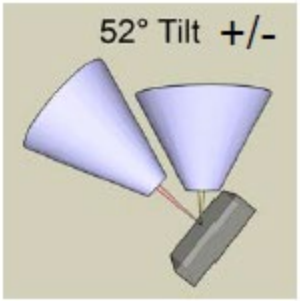




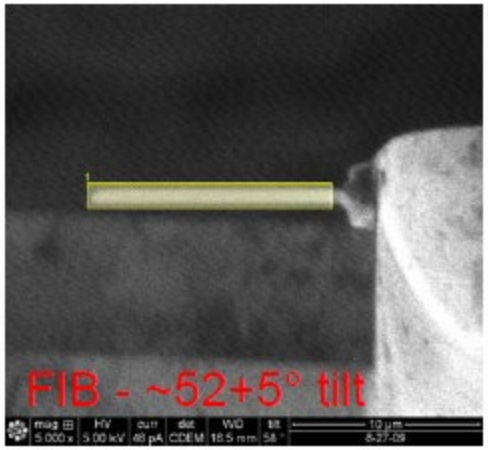


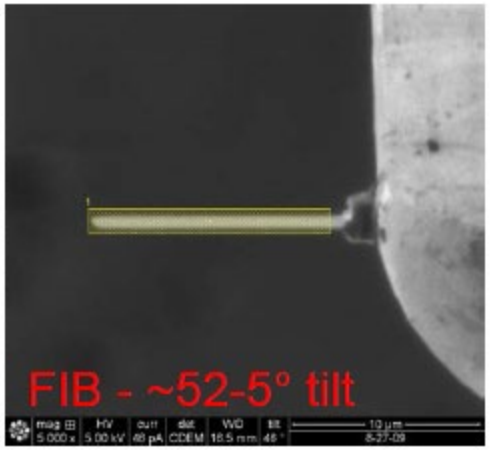


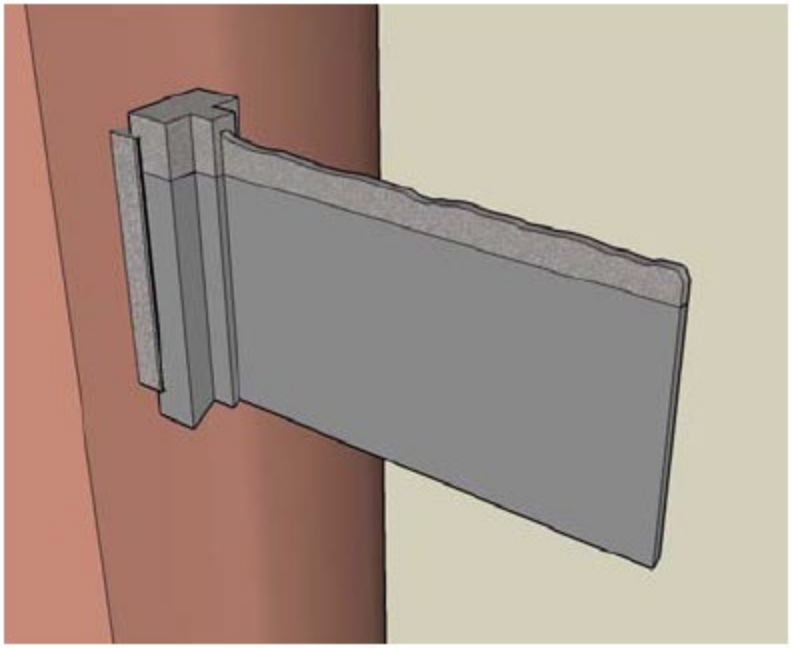
Cleaning

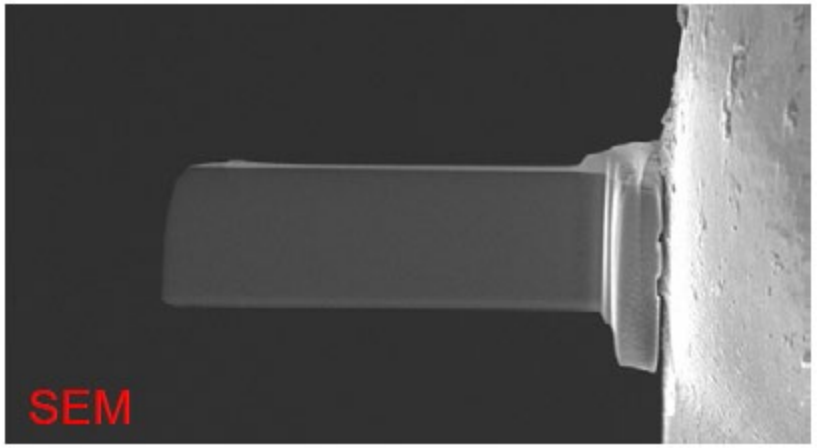


- Tilt into sample +/- 3-5°
- Application: Si
- Shape: Rectangle
- Size: ~10μm (X) x ~2μm (Y)
- 5kV, ~46pA
- ~2-5min per side



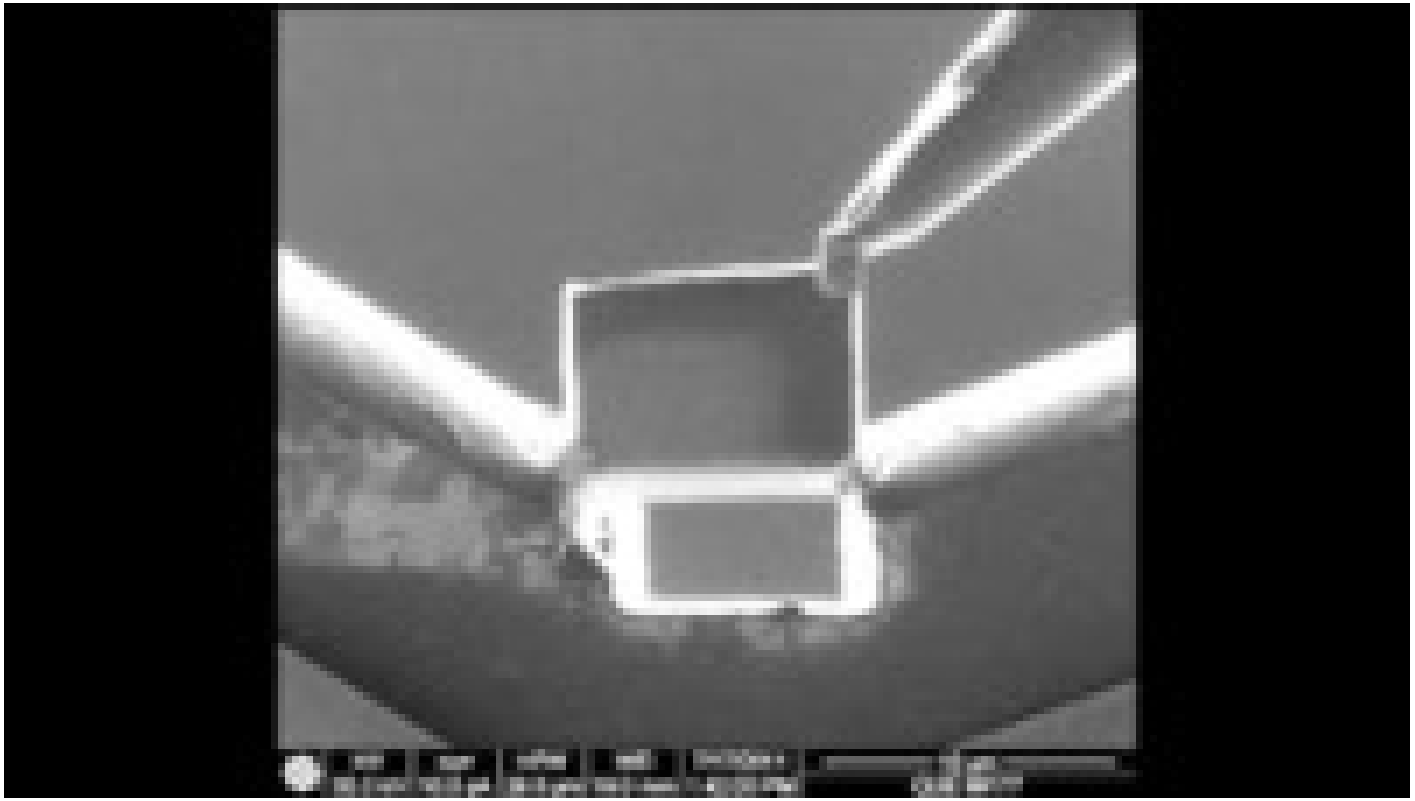




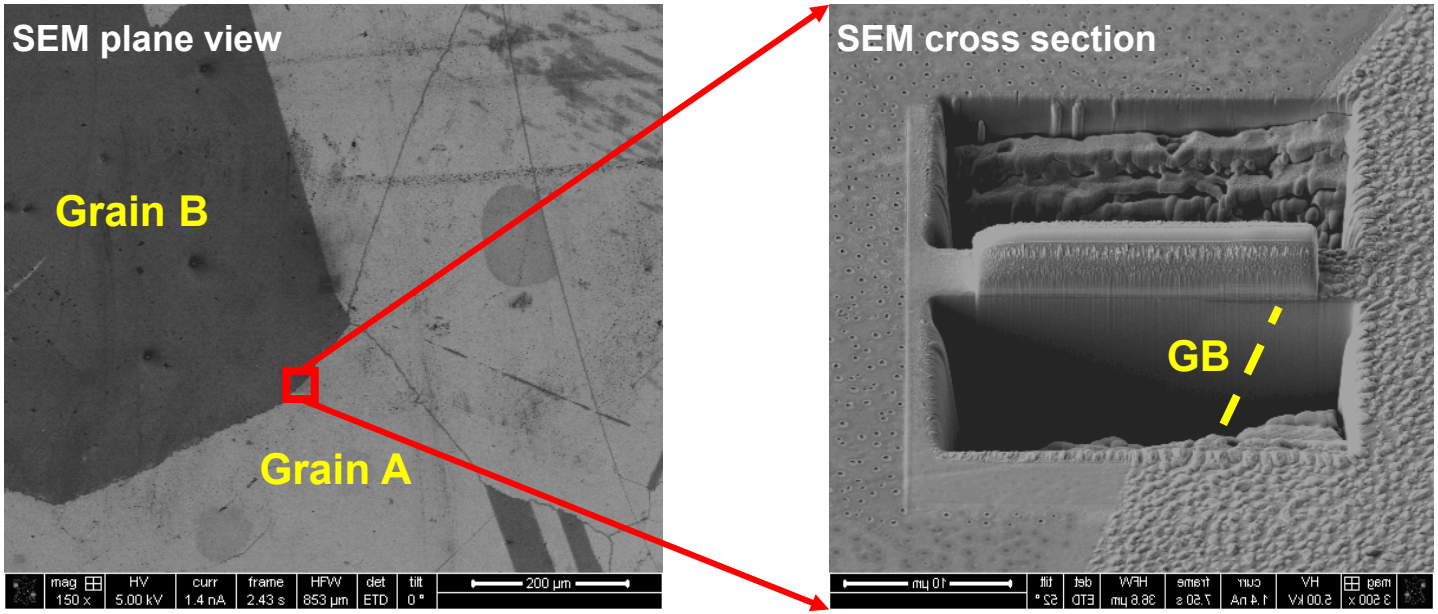


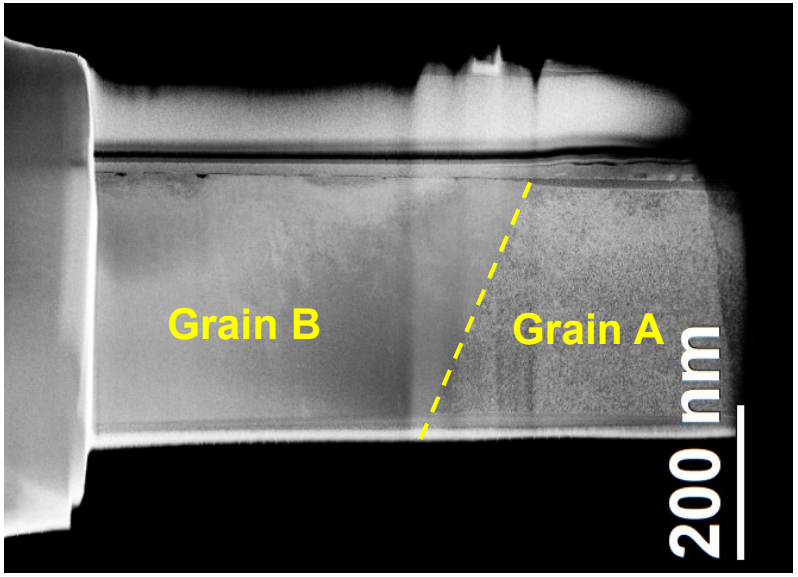
FIB Lift-Out Process

https://www.youtube.com/watch?v=vNOpzDViAhE



Site-Specific TEM Specimen



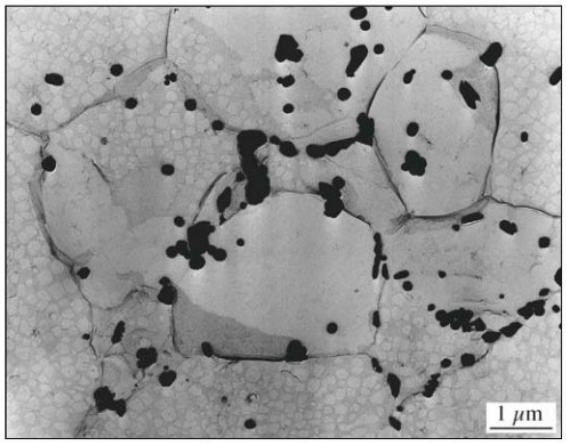


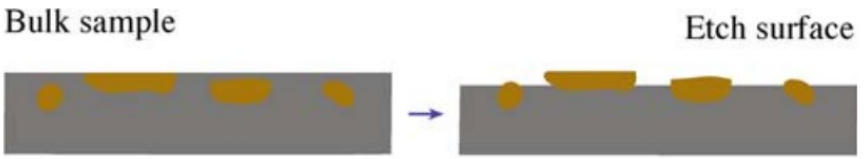
Sample Prep Artifacts (1)

- Variable thickness VS uniform thickness
  - Difficult to image and understand
  - Limited area for EELS and chemical analysis
  - May not see low density features (defects, precipitates)
  - Poor statistics
- Surface films
  - Contamination (Left over residue from sample prep method)
  - Surface oxides
  - Irregular topography
  - Contamination buildup
  - Amorphization

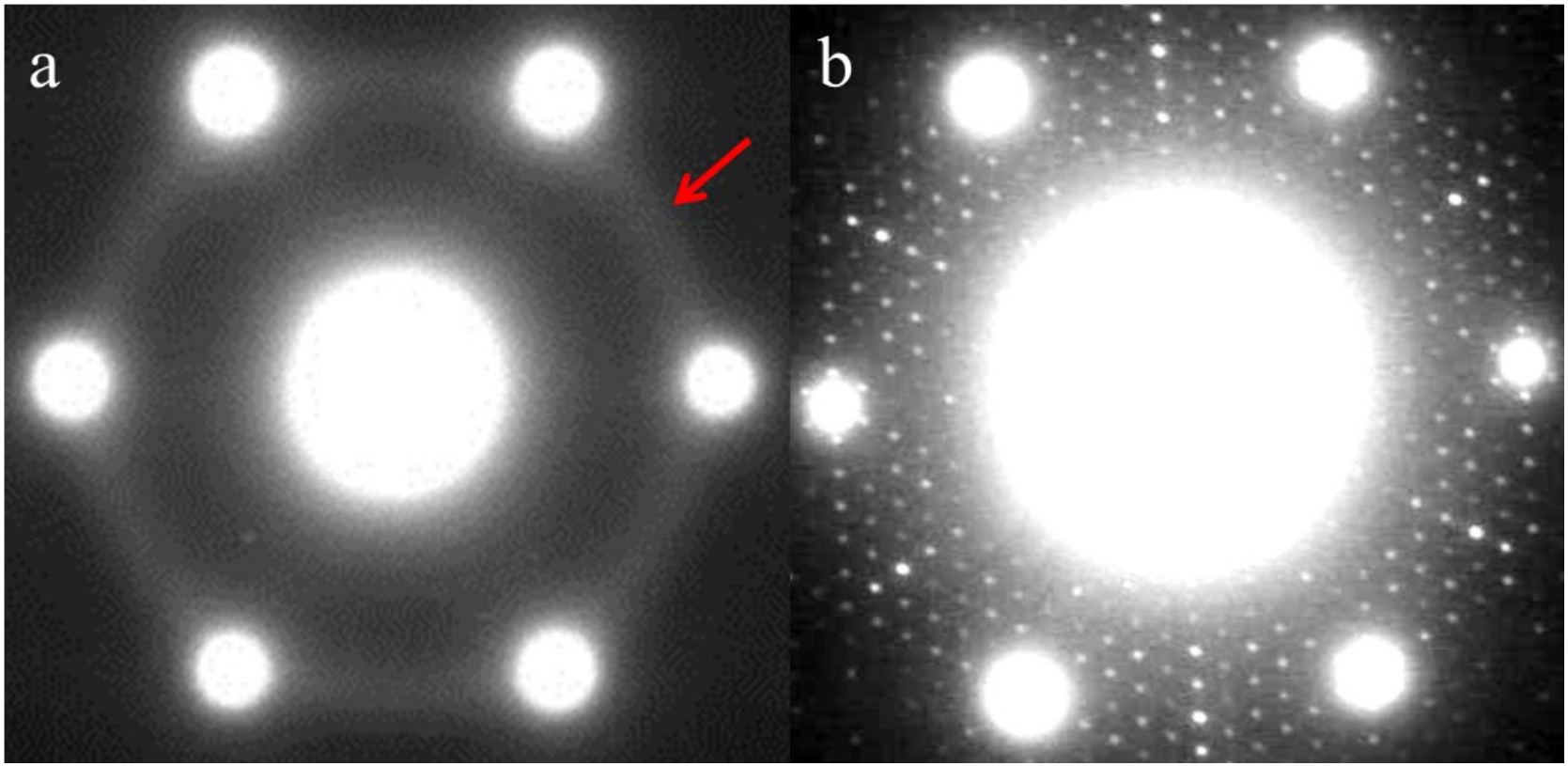
Sample Prep Artifacts (2)

- Differential thinning
  - Different phases or orientations thin at different rates
  - Grain or phase boundary grooving
- Selectivity
  - Not representative of full sample
  - If you crush a sample, you lose microstructure information
  - Debonded regions that fall off
- “False” defects
  - High defect density obscures microstructure
  - Deformation caused defects
  - Heating changes defects





Sample prep can affect experimental data



Case Studies: Sample Prep & General Electron Microscopy Techniques

Case Study I

You find an unlabeled single crystal sample in your lab. You believe it is some type of ceramic. Using electron microscopy, how would you determine what the sample is?

How would you determine its orientation?

Case Study II

A colleague comes to you with a sample. They claim they grew $SrTiO_3$ nanoparticles doped with 0.3 wt% La. How would you prepare a sample? What techniques would you use to characterize the nanoparticles?

Case Study III

Manufacturers often apply a coating to drill bits to increase their strength. You are contacted by a company interested in making a new coating, but they want to see what other manufacturers are using first. How would you prepare a sample to determine what the coating is?

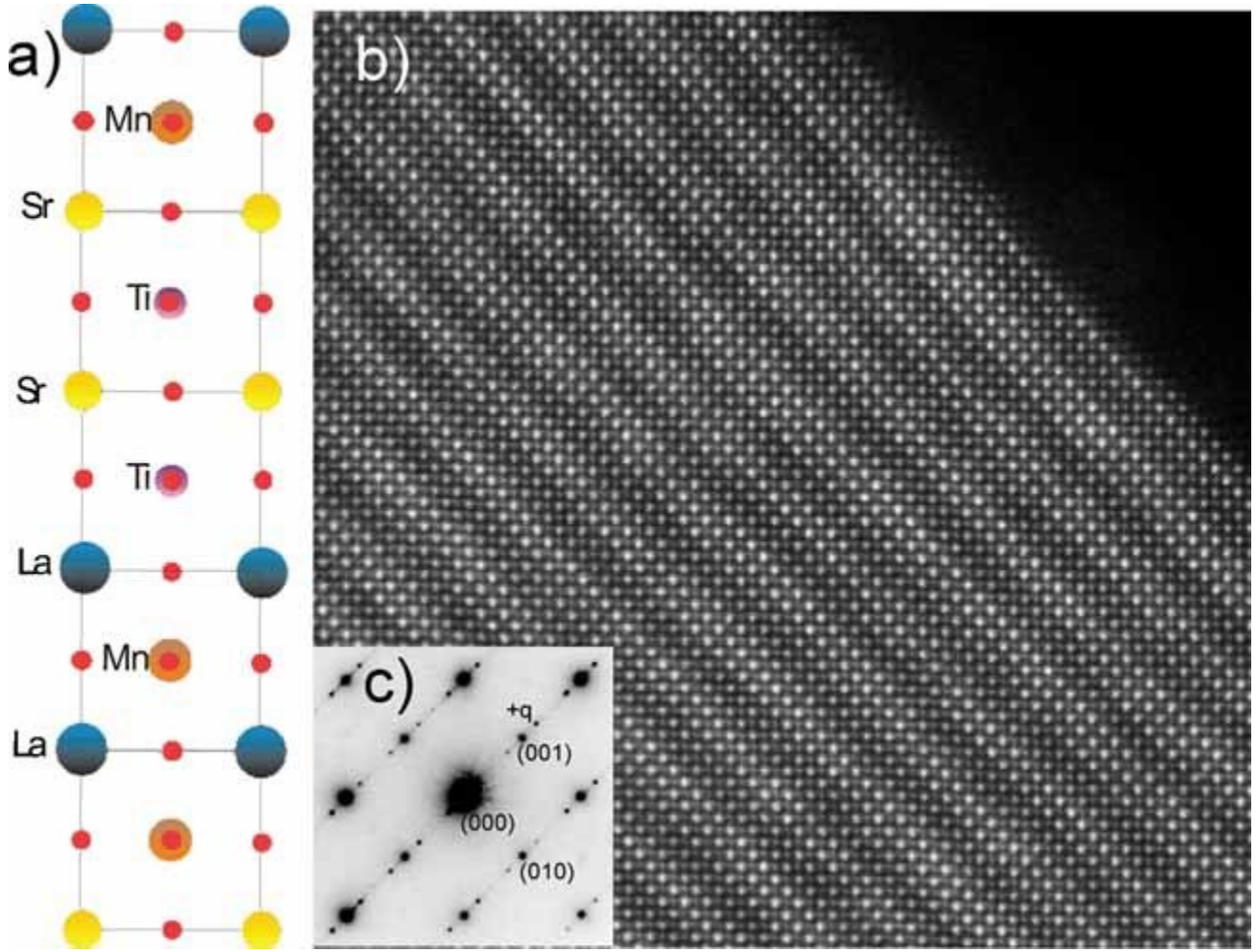
Case Study IV

Your customer has several alloyed samples of different compositions and is interested in their corrosion resistance, especially what is happening at grain boundaries. For instance, what is the grain boundary orientation and composition? How would you prepare samples and characterize the grain boundaries?

Case Study V

Your collaborator has grown a superlattice structure of *m* x ($LaMnO_3$)/*n* x ($SrTiO_3$) layers (*m* = *n* = 2). You are tasked with characterizing the quality of the growth (i.e. sharp interfaces, defect free, stoichiometry). How would you prepare a sample and what techniques would you use?

Case Study V



A. B. Shah *Adv. Mater.* 22 (2010) 1156-1160.

SEM Sample Prep

SEM Sample Preparation

1. Identify the needs of your specific sample.
   - Mechanical Stability
   - Vacuum Sensitivity
   - Beam Sensitivity
   - Conductivity
2. Determine which sample preparation techniques are appropriate.
   - Cutting
   - Polishing
   - Coating
   - Freezing
3. Determine what microscope conditions are necessary.
   - High Vacuum vs. Low Vacuum
   - Accelerating Voltage
   - Beam Current

Cutting, Grinding, Polishing

- The SEM sample stage is very large.
  - Up to tens of centimeters in diameter.
- Cutting may be required to isolate a small portion of a larger part.
- Cross-sectional analysis required cutting to expose interior of sample.
- Once cut, grinding and polishing may be used to smooth the surface and remove unwanted topological contrast.
- Grinding refers to using fixed abrasives such as sandpaper while polishing refers to the use of abrasives suspended in a liquid.

Automated Polishing

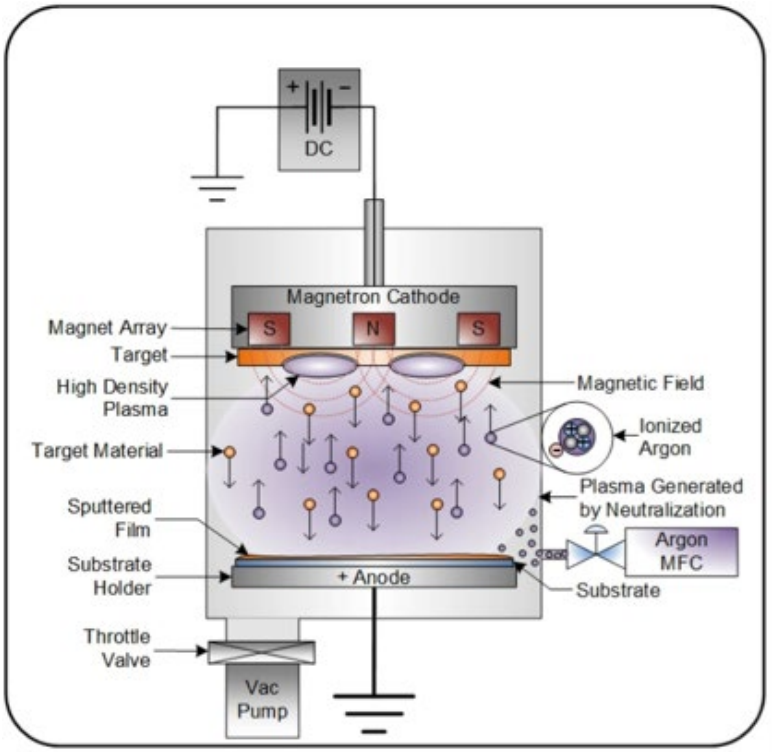
- Samples can be mechanically polished on a felt turn table saturated with abrasive colloidal suspensions.
  - Typical abrasives include diamond, silica, and alumina.
- Samples are implanted in resin or glued to a sample holder to produce samples of uniform size.

Imaging Non-Conducting Samples

- To perform SEM imaging, the sample must be conducting. Electrons accumulate on the surface of the sample and build up a charge.
- Surface charge will distort the image and create bright spots. Can also damage the sample due to localized heating.
- However, many materials are insulating or only partially conducting.
  - Ceramics
  - Semiconductors (undoped)
  - Biological Materials
- To image these materials, they must be coated with a thin conductive layer.

Plasma Coating

- Atoms of a conducting element such as platinum or gold are ionized by a plasma.
- The ionized atoms get deposited on the sample and create a thin, surface conforming layer.
- Ions can come from a sputter target or from a volatile chemical precursor such as osmium-tetroxide.
- An ideal film is only a few nanometers thick and uniform across the surface.



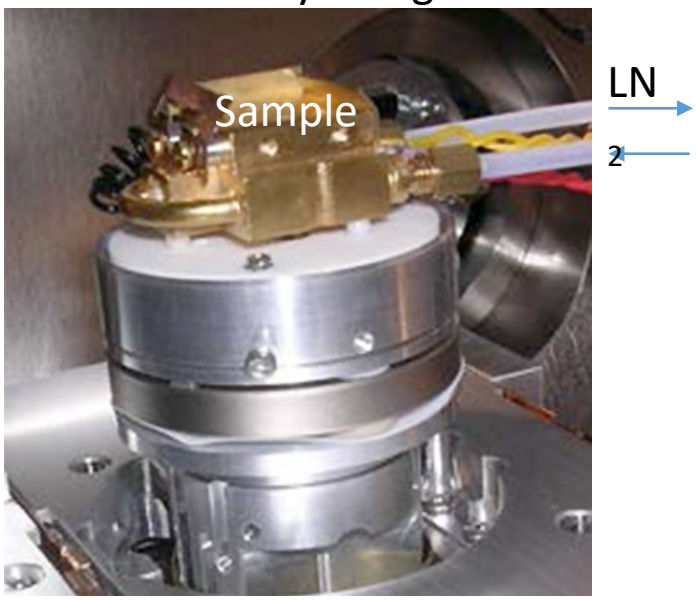
Imaging Wet or Dirty Samples

- Traditional SEM requires a high vacuum.
  - Electrons emitted from the sample ionize nearby atoms before they can reach the detector.
  - The atmosphere will scatter the electron beam and damage the electron gun.
- If a sample contains water or other high vapor pressure compounds, it will be destroyed by the vacuum or prevent the chamber from pumping down.
- There are several different methods to image these types of samples.
  - Sample Drying
  - Environmental SEM
  - Cryo-SEM

Cryogenic Freezing

- The rate of outgassing of many materials decreases dramatically when frozen.
- Wet samples can be dry frozen to remove water or cryogenically frozen to solidify the water into amorphous ice.
- Frozen samples are difficult to work with.
  - Exposure to atmosphere can cause condensation and rapid thawing.
  - Freezing may cause damage to delicate samples due to the expansion of water when frozen.
- Frozen samples must be prepared and transported in insulated vacuum containers and imaged in a microscope with a cryogenically cooled sample stage.

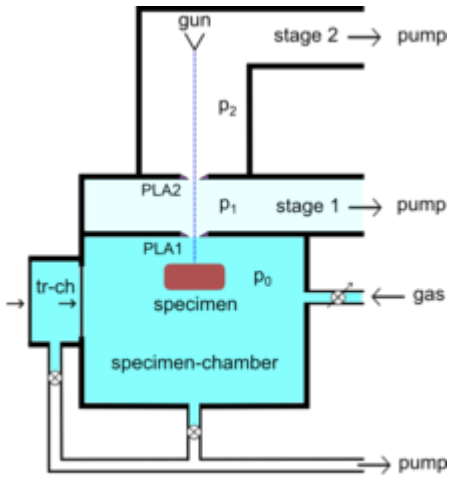
SEM Cryo-stage



Cryogenic Sample Transfer Suitcase

Environmental SEM (ESEM)

- ESEM uses a differential pumping mechanism to allow for a higher chamber pressure while maintaining a low electron gun pressure.
  - The path between the chamber and the gun is restricted by one or more small orifices which restrict the diffusion of atoms to the electron gun.
  - Pumps are actively running to keep the electron gun at a low pressure.
- Allows for imaging of wet samples without any drying or processing that could change the structure.
- Can also be used to image non-conducting samples without a conductive coating.
- Poor image quality due to attenuation of electron beam and electron signal.



Basic ESEM gas pressure stages

People in Science

	Undergraduate	PhD student	Postdoc	PI / Professor	Technician
seen by **Undergraduate**					
seen by **PhD student**					
seen by **Postdoc**					
seen by **PI / Professor**					
seen by **Technician**					

SKetching-Science