

# Specimen Preparation

## CHAPTER PREVIEW

Specimen preparation is a very broad subject; there are books devoted to this topic alone. The intention here is to summarize the techniques, suggest routes that you might follow, and above all to emphasize that there are many ways to produce a TEM specimen; the one you choose will depend on the information you need, time constraints, availability of equipment, your skill, and the material. So we'll concentrate on the 'principles of cooking,' but won't try to list all the possible 'recipes.' One important point to bear in mind is that your technique must not affect what you see or measure, or if it does, then you must know how. Specimen preparation artifacts may be interesting but they are not usually what you want to study. Incidentally, we'll make 'specimens' from the 'sample' we're investigating so we'll look at 'TEM specimens,' but sometimes we, and everyone else, will interchange the two words.

The TEM specimen, when you've made it, must be electron transparent (usually) and representative of the material you want to study. In most cases (but not all) you would like your specimen to be uniformly thin, stable under the electron beam and in the laboratory environment, conducting, and non-magnetic (we'll discuss some exceptions as we proceed). Few specimens approach the ideal and usually you have to compromise. In general we can divide specimens into two groups: self-supporting specimens and specimens resting on a support grid or thin washer; the grid or washer is usually Cu but could be Au, Ni, Be, C, Pt, etc. Before discussing these two groups we will briefly review the most important part of specimen preparation, namely, safety. You may damage the microscope later, but this is the stage where you could do much worse to yourself and your colleagues.

It is often assumed that preparation of the TEM specimen will take several hours. Actually this time could be as short as 5 minutes or as long as 2 days even for the same material. For example, as you'll see, if you want to examine a piece of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ , the high-temperature superconductor, you could crush the sample in a pestle and mortar using a nonaqueous solvent, catch the small particles on a carbon film, and put the specimen in the TEM; time required is about 10 minutes. Alternatively, you might cut the sample into thin slices using a diamond saw, cut 3-mm-diameter disks from the slice, thin the disk on a grinding wheel, dimple the thinned disk, then ion mill to electron transparency at liquid-nitrogen temperatures, carefully warm the specimen to room temperature in a dry environment, and put it in the TEM; time required is 1 or 2 days. Which method you choose would depend on what you want to learn about your material.

### 10.1 SAFETY

Either the specimen itself or the best method for preparing it for viewing in the TEM may require extreme care. Even materials which are safe and relatively inert in bulk form may be hazardous in powder form. Four favorite (because they work so well) liquids for polishing solutions are hydrogen cyanide, hydrofluoric acid, nitric acid,

and perchloric acid. These liquids may be poisonous, corrosive (HF quickly penetrates the body and then dissolves the bone), or explosive (perchloric acid and nitric acid when mixed with certain organic solvents). It is clearly essential that you check with your laboratory manager, the reference texts, and the appropriate materials safety data sheets (MSDS) before you begin specimen preparation. This checking might also save a lot of time.

## SAFETY FIRST

This whole section should, of course, be in a big red box. Some of the chemicals we use are really dangerous. We remember HF, perchloric acid, and HCN all being used concurrently in one small specimen-prep room.

In spite of these restrictions you may still need/want to use these acids and acid/solvent mixtures. The ion thinner may not be available or you may not be able to accept the damage that ions produce. In this event there are five brief points that you should bear in mind.

- Be sure that you can safely dispose of the waste product *before* you start.
- Be sure you have the ‘antidote’ at hand.
- Never work alone in the specimen-preparation laboratory. Always wear safety glasses when preparing specimens and/or full protective clothing, including face masks and gloves, if so advised by the safety manual.
- Only make up enough of the solution for the one polishing session. Never use a mouth pipette for measuring any component of the solution. Dispose of the solution after use.
- Always work in a fume hood when using chemicals. Check that the extraction rate of the hood is sufficient for the chemical used.

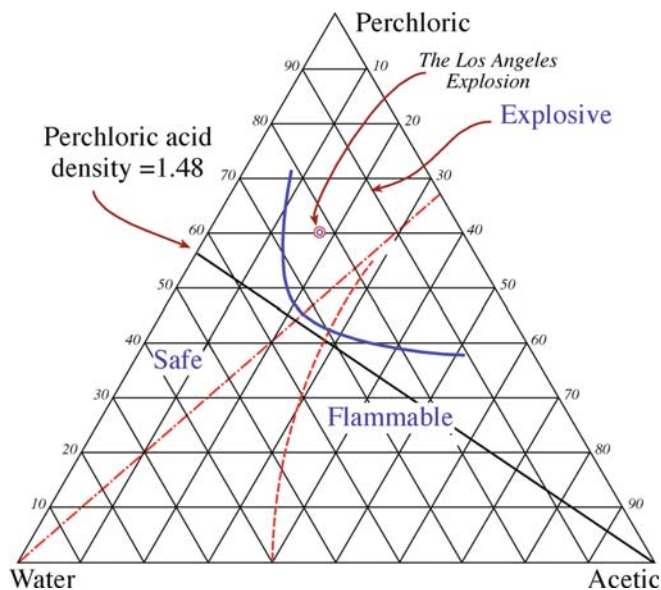
Since these four acids can be so dangerous, we’ll mention them specifically, but remember—always seek advice before chemically preparing specimens.

*Cyanide solutions:* If possible, avoid this solution even though you may see it in the textbooks. The only metal where it really excels is gold and you can thin this by very careful ion milling.

*Perchloric acid in ethanol or methanol:* If you have to use this ‘universal polish’ you should be aware that many laboratories require that you use a special dedicated hood which can be completely washed down since crystallized perchloric acid is explosive. The phase diagram in Figure 10.1 for the perchloric-acetic (acid)-water system makes the message clear. If you have to use perchloric-acetic acid mixtures or indeed when using any perchloric-containing mixtures, keep the density below 1.48. If you are very careful, if you *always* add the acid to the solvent, and you make sure that the liquid *never* becomes warm, then perchloric acid solutions can be used to produce excellent TEM specimens of Al, stainless steel, and many other metals and alloys.

*Nitric acid:* In combination with ethanol, this acid can produce explosive mixtures, especially if left for long periods of time and exposed to sunlight. It is preferable to use methanol rather than ethanol, but in either case, keep the mixture cool and dispose of it properly.

*HF:* This acid is widely used in the semiconductor industry and in ‘frosting’ light bulbs; the reason in both



**FIGURE 10.1.** Perchloric-acetic-water phase diagram showing the hazardous regions and the recommended density line for safe use of all perchloric solutions. Always operate to the left of this line.

cases is that it dissolves  $\text{SiO}_2$  leaving no residue. Careful use of dilute solutions can produce specimens that have large thin areas. Remember: if you use HF, completely cover any exposed skin; HF rapidly penetrates the flesh and dissolves bone and you won’t even feel it!

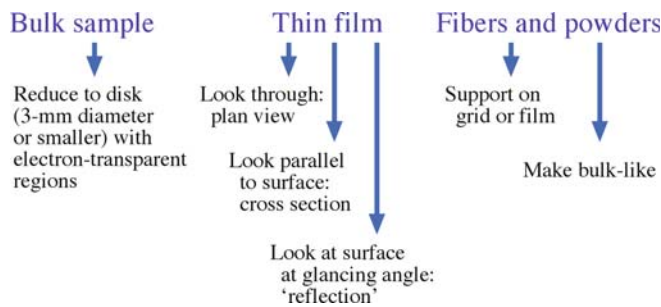
## 10.2 SELF-SUPPORTING DISK OR USE A GRID?

The type of TEM specimen you prepare depends on what you are looking for so you need to think about the experiment that you are going to do *before* you start thinning. For example, is mechanical damage to be avoided at all costs, or can it be tolerated so long as chemical changes don’t occur—or vice versa? Is the specimen at all susceptible to heat or radiation? Depending on the answers to these questions, some of the following methods will be inappropriate. A flow diagram summarizing the different preparation philosophies is shown in Figure 10.2.

## NANOMATERIALS

Think about your choice of material for the supporting grid.

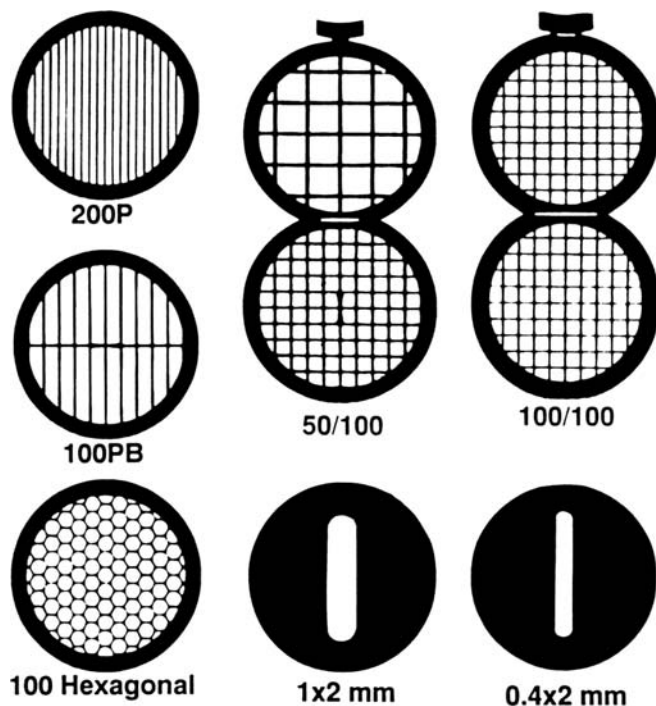
A self-supporting specimen is one where the whole specimen consists of one material (which may be a composite). Other specimens are supported on a grid or on a Cu washer with a single slot. Several grids are



**FIGURE 10.2.** Flow chart summarizing the different sample geometries you may encounter.

shown in Figure 10.3. Usually the specimen or grid will be 3 mm in diameter.

Both approaches have advantages and disadvantages. Both offer you a convenient way of handling the thin specimen, since either the edge of the self-supporting disk or the grid will be thick enough to pick up with tweezers. If possible, never touch your specimen when it is thin. We recommend vacuum tweezers, but you'll need to practice using them; you can quite easily vibrate the specimen and break the thin area. You can get round this by using mouth-vacuum tweezers but see the section on safety first. Mechanical stability is always crucial. For example, single crystals of GaAs or NiO break very easily, so it is usually an advantage to have your specimen mounted on a grid since you then 'handle' the grid. However, if you are performing X-ray analysis on



**FIGURE 10.3.** A variety of specimen support grids of different mesh size and shape. At top right is the oyster grid, useful for sandwiching small slivers of thin material.

a specimen the grid may contribute to the signal, because the X-rays can also arise from the grid. Thus you see a Cu peak in the X-ray spectrum where no Cu is present in the specimen. We'll talk in Chapter 33 about how to minimize this artifact. Of course, the self-supporting specimen essentially has the same problem—it's just not as obvious! In fact, the preferred geometry for such analysis is usually the one where the specimen is thinnest.

### THE DIAMETER OF TEM SPECIMENS

Why are the TEM specimens 3.05 mm in diameter? Because the manufacturers say so. Must this always be the case? Only if you need to double-tilt or tilt-rotate.

Why 3-mm disks? The disk diameter is usually a nominal 3.05 mm. We thus refer to the specimen as a 3-mm disk. Occasionally you will encounter a microscope which uses a 2.3-mm disk. The smaller diameter was used in earlier microscopes and has two important advantages, which are not fully exploited by modern machines. Ideally, the region of the specimen which you want to study will be located at the center of your disk, no matter how large the disk is. As we saw in Chapter 9, the reason is that, as you tilt the specimen in the microscope, the region of interest will then stay at the same position (height) above the objective lens and on the optic axis. Since, for a self-supporting disk, the rim of the specimen must be relatively thick and the total area of the material you'll study is small and confined to the center of the disk, you can make more 2.3-mm specimens from a given volume of material. This may be very important if the specimen is particularly special (expensive, rare) or if specimens break easily. A sample which is 5 mm × 5 mm will give one 3-mm disk or four 2.3-mm disks. The second advantage of such specimens relates to tilting; the smaller specimen holder can be manufactured to allow a greater tilt angle. Don't forget that if you need only one axis of tilt you may find the bulk holder useful. Then you can use a specimen which may be up to 10 mm long and 3 mm wide.

### 10.3 PREPARING A SELF-SUPPORTING DISK FOR FINAL THINNING

Preparation for final thinning involves three parts

- Initial thinning to make a slice of material between 100 and 200 μm thick.
- Cut the 3-mm disk from the slice.
- Prethin the central region from one or both faces of the disk to a few micrometers.



The method you use will depend on what you want to study and the physical characteristics of the material (whether it is soft or hard, ductile or brittle, delicate or robust, single phase or a composite, etc.).

### 10.3.A Forming a Thin Slice from the Bulk Sample

The materials you may need to thin can vary enormously. Clearly, we have to treat ductile and brittle materials differently.

(a) *Ductile materials such as metals.* Usually you don't want to introduce mechanical damage. For example, you may want to study the defect structure or the density of defects in processed materials. The ideal method is to use a chemical wire/string saw, a wafering saw (not diamond—the soft metal will dull the blade), or spark erosion (electro-discharge machining) to get a thin slice  $< 200 \mu\text{m}$ . (A string saw works by passing the string through an acid or solvent and then across the sample until the string 'cuts' through the sample; for example, you can use dilute acid to cut copper.) You could also roll the material to, very thin sheet, then anneal it to remove the defects introduced by rolling but that's a different material-processing route.

(b) *Brittle materials such as ceramics.* Here there are two cases: (i) where you must not introduce mechanical damage, (ii) where you don't mind introducing mechanical damage or the material won't damage. You have several options depending on the material. Some materials (Si, GaAs, NaCl, MgO) can be cleaved with a razor blade; these are materials with a well-defined cleavage plane and it is possible to carry out repeated cleavage to electron transparency (see Section 10.6.E). The ultramicrotome (see Section 10.6.B) allows you to cut very thin slices for immediate examination. If you don't want to cleave the specimen or you want to prepare a specimen parallel to a plane that doesn't cleave, you will need to use a diamond wafering saw. There are special techniques for some materials: you can, for example, use water as the solvent on a string saw to cut rock salt. One of the main limitations with sawing is that the process destroys some of your sample.

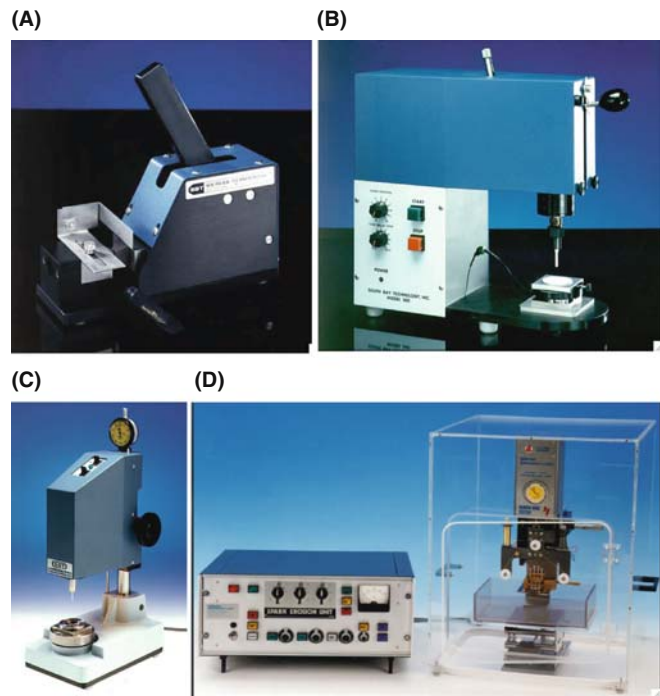
### 10.3.B Cutting the Disk

The same constraints hold for the coring process as for cutting slices: if the material is reasonably ductile and mechanical damage is not crucial, then the disks can be cut using a mechanical punch. A well-designed punch can cut disks with only minimal damage around the perimeter, but the shock can induce shear transformations in some materials. For more brittle materials the three principal methods are spark erosion (also essential when you need to avoid damage in a metal), ultrasonic drilling, and using a grinding drill. In each case the cutting

tool is a hollow tube with an inner diameter of 3 mm. Again, you want the wall of the tube to be thin to minimize the amount of material that is wasted. Spark erosion is used for conducting samples and introduces the least amount of mechanical damage. The choice between an ultrasonic drill (vibrating in  $\text{H}_2\text{O}$ ) and a grinding (or slurry) drill is often a matter of personal preference or availability. Both remove material mechanically and are widely used for ceramics and semiconductors. The drill may leave small particles in the specimen, and *all* mechanical thinning methods leave some surface damage. As a rule of thumb, abrasives produce damage to  $3\times$  their grit size. So a  $1\text{-}\mu\text{m}$  abrasive will cause damage to  $3 \mu\text{m}$  below the surface of each side of the specimen. Hence the final disk must be thicker than the  $2\times$  the damage depth or else mechanical damage will always be visible in the final specimen. Four different coring instruments from one manufacturer are shown in Figure 10.4.

#### CORING

Like extracting the core of an apple or a rock sample from the earth.



**FIGURE 10.4.** Four different coring tools from South Bay Technology. (A) A mechanical punch for stamping disks from thin sheets of ductile materials. A sheet sample is placed in the punch and the handle on the right is pushed down, ejecting a 3-mm-diameter disk suitable for thinning. (B) An abrasive-slurry disc cutter uses a rotary motion of the coring tube to drill round the disk. (C) An ultrasonic cutter. (D) A spark-erosion cutter; the erosion takes place under a solvent and behind a safety shield.

Note that there are variations for all these techniques: e.g., for Si, GaAs, and some other materials, you can glue the sample to a support, coat it with a protective layer, and cut circles through the film—then chemically etch the desired region. You need to experiment but the method should introduce no mechanical damage.

### 10.3.C Prethinning the Disk

The aim of this process is to thin the center of the disk while minimizing damage to the surface of the sample. In general we will refer to this stage as ‘dimpling’ no matter how the thinning is achieved. Any damage you create at this stage will have to be removed during the final thinning process (if you’re interested in defects or if the damage changes your chemistry).

Most commercial mechanical dimplers use a small-radius tool to grind and polish the disk to a fixed radius of curvature in the center. Although the first instruments for dimpling were ‘home built’ the commercial models (see Figure 10.5) are now well developed. You can control the load, precisely determine the thickness of removed material (the depth of the dimple), quickly change the polishing tool, and interrupt the process to remove the sample for closer examination before continuing. The investment is well justified for materials laboratories. One alternative that has been used successfully is a (recycled) dentist’s drill and some imagination. Typically dimpling can be carried out to produce regions  $\sim 10\ \mu\text{m}$  thick although, in principle, precision dimpling with microprocessor control can sometimes produce electron-transparent specimens which are  $< 1\ \mu\text{m}$  thick.

For mechanical dimpling, as a general rule, the same guidelines apply as to all mechanical polishing; always gradually decrease the ‘grit’ size and conclude with the finest available, again ensuring that the final specimen thinness is  $> 2\times$  the damage depth of the smallest grit dimension. The better the polished surface, the better the final specimen. If both sides of a disk are dimpled the chances of final perforation occurring in the center are substantially increased, but in some cases you may wish to preserve one side of the specimen and thin from the other side only. One-sided dimpling is then essential prior to thinning to perforation.

Dimpling can also be performed chemically. Often in the case of Si this is achieved by allowing a jet of HF and  $\text{HNO}_3$  to impinge (from below as shown in Figure 10.6) on the Si disk which has the edges lacquered to produce a supporting rim. The  $\text{HNO}_3$  oxidizes the Si and the HF removes the  $\text{SiO}_2$ . Similar approaches use Br and methanol for thinning GaAs. This dimpling method uses dangerous chemicals, but it is very efficient. It can even be carried to final perforation with care.

(A)



(B)

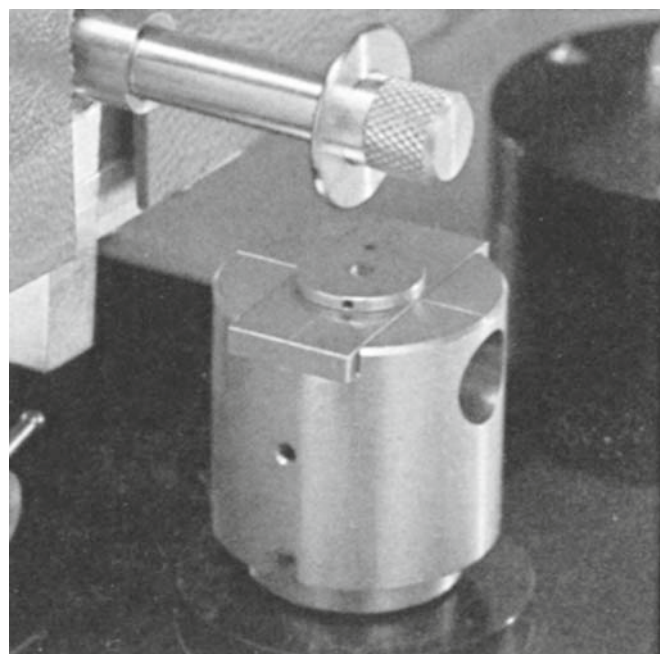
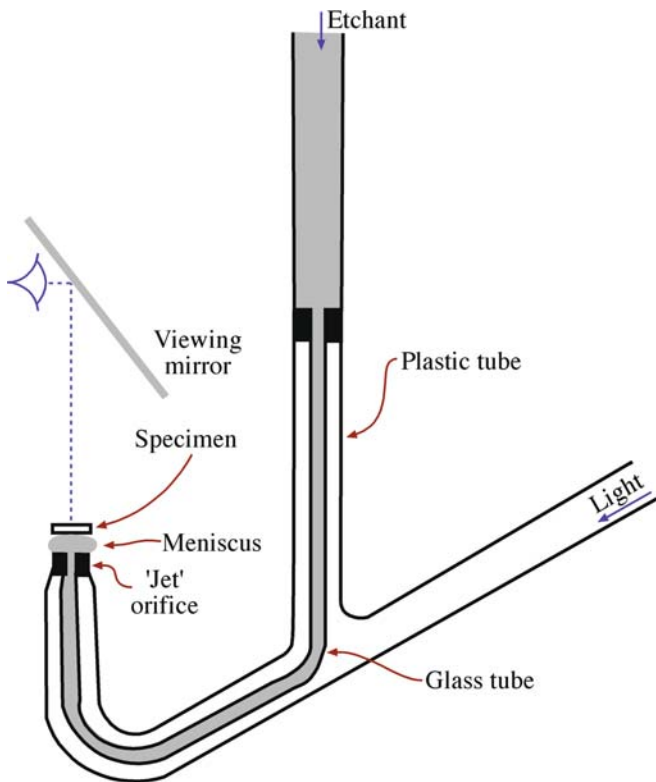


FIGURE 10.5. (A) Dimpling apparatus; (B) the grinding tool and specimen support block.

TEM specimen preparation has been revolutionized through the development of the tripod polisher; this tool can help you to thin your sample mechanically to less than  $1\ \mu\text{m}$ . You must consult the general references at the end of the chapter before using this tool. The tripod polisher, so called because it has three feet, is simply a device to hold your specimen while you mechanically thin it on a polishing wheel. You can purchase a tripod polisher commercially or build your own.



**FIGURE 10.6.** Surface dimpling using a chemical solution, e.g., to remove Si from one side of a disk. The light pipe permits visual detection of perforation using the mirror.

### TRIPOD POLISHER

The tripod polisher has been used for many decades in the gem industry. It just looked different.

For some materials, such as Si, you can use this polisher to thin the specimen to electron transparency.

There are, however, several secrets in using the tripod polisher.

- You must use a very flat polishing wheel; the recommended approach is to use a glass platen. Take the greatest care in adjusting the micrometer to level the tripod.
- You need a supply of fine diamond lapping films; these are not inexpensive but it is a false economy to use them after they are worn. Always use a new sheet for polishing the second side of your sample since it is then particularly vulnerable.
- The diamond lapping films must not have an adhesive backing; you 'fix' them to the glass platen using the surface tension of the water and ensure that they are flat using a wiper blade. Bumps under the films will destroy your specimen.
- Any debris on the film will reduce its useful life; if the pad dries with polishing paste still present you should discard it.

- Minimize the effect of debris, which you produce on the polishing film as you thin your sample, by paying careful attention to where you place the specimen on the polishing wheel; orient interfaces in cross section samples normal to the radius and don't cross the debris trail.

With practice, tripod polishing can dramatically reduce the time required for the final thinning step. This tool has had a major impact on making TEM a quality-control instrument, particularly in the semiconductor industry.

## 10.4 FINAL THINNING OF THE DISKS

### 10.4.A Electropolishing

Electropolishing can only be used for electrically conducting samples such as metals and alloys. The method can be relatively quick (a few minutes to an hour or so) and it can produce foils with no mechanical damage. But it can change the surface chemistry of the specimen and it can be hazardous to your health as you can see from the safety section at the start of the chapter.

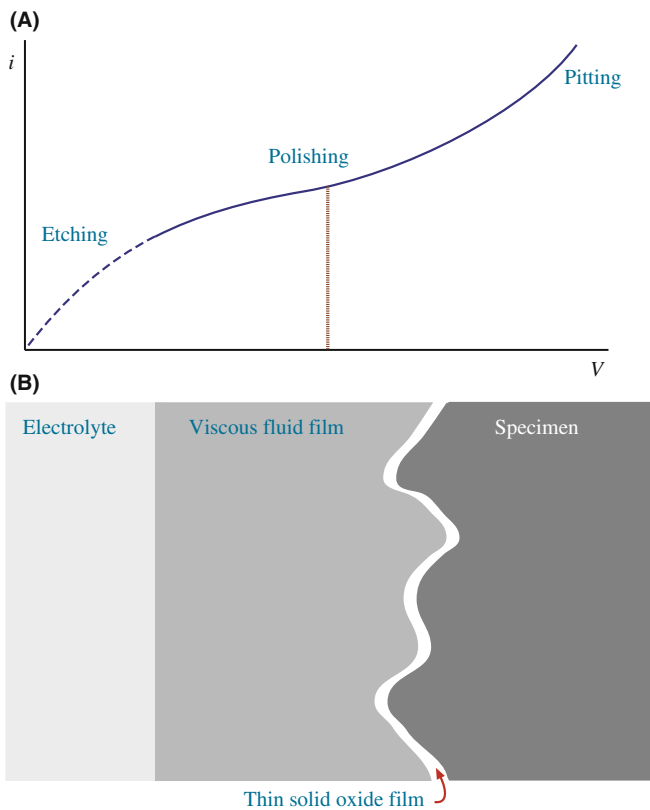
The basic premise is that there is a certain applied voltage at which the current due to anodic dissolution of the specimen creates a polished surface rather than etching or pitting, as shown in Figure 10.7. The classical jet polish is shown in Figure 10.8A. By keeping the volume of the reservoir constant, the jet falls under constant pressure. The voltage is applied between the tip of the pipette and the specimen. A twin-jet apparatus can be used to pump a jet of electrolyte onto both sides of the dimpled disk, as shown schematically in Figure 10.8B. A laser beam or light sensor detects transparency and a warning sound is given. At the warning, the electrolyte flow must be cut off immediately to prevent loss of thin area and the disk must be rapidly extracted from the electrolyte and washed in solvent to remove any residual film of electrolyte which may etch the surface.

Undoubtedly you get better at electropolishing with practice, but reproducing the correct conditions of temperature, electrolyte solution chemistry, stirring rate, applied voltage, polishing current, etc., can only be achieved through trial and error.

### 10.4.B Ion Milling

Ion milling involves bombarding your delicate thin TEM specimen with energetic ions or neutral atoms and sputtering material from your film until it is thin enough to be studied in the TEM. A schematic diagram and a commercial model are shown in Figure 10.9. The variables which you control include the voltage,





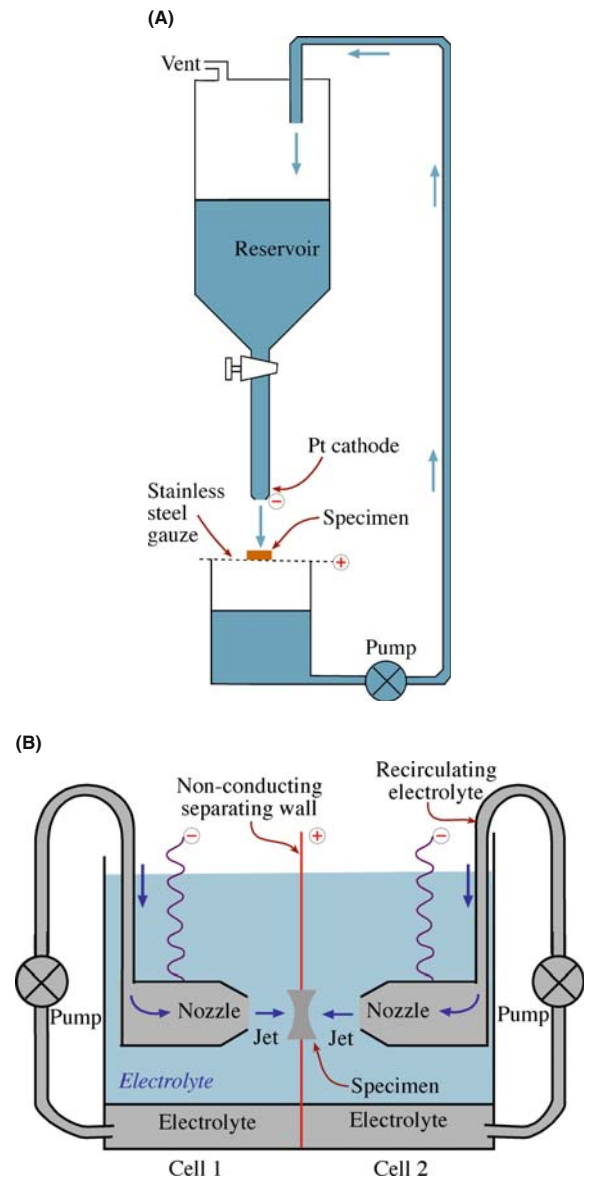
**FIGURE 10.7.** (A) Electropolishing curve showing the increase in current between the anode and the cathode as the applied voltage is increased. Polishing occurs on the plateau, etching at low voltages, and pitting at high voltages. (B) The ideal conditions for obtaining a polished surface require the formation of a viscous film between the electrolyte and the specimen surface.

temperature of the specimen (e.g., cold milling (liquid N<sub>2</sub>)), the nature of the ion (Ar, He, or a reactive ion (iodine)) and the geometry (the angle of incidence).

### ION THINNING

Variables are ion energy, angle of incidence, vacuum, initial surface topology, initial chemistry, initial orientation, initial crystallography of the surface, beam energy, and beam profile. Note the word *initial*.

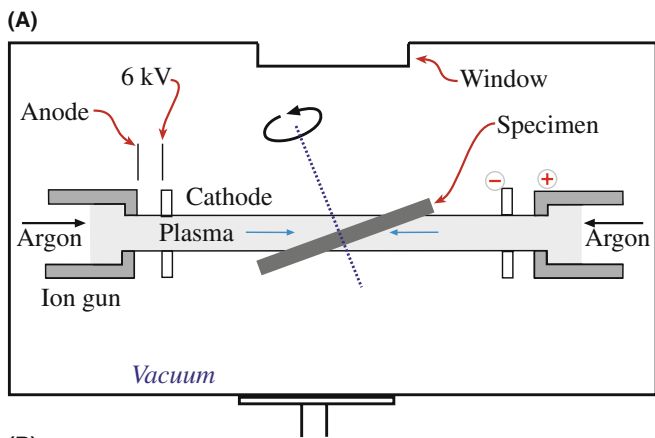
An accelerating voltage of 4–6 keV is usually used. The ion beam will always penetrate the specimen to some extent, so we minimize this by inclining the incident ion beam to the surface of the specimen. In the past, we often aligned the ion beam at an angle of 15–25° to the surface. However, Barna has shown that this angle of incidence should be avoided in many cases since it leads to compositional thinning; use an inclination of <math>\leq 5^\circ</math> to avoid preferential thinning and minimize ion implantation. Some implantation will occur so that the chemistry of the near-surface region is changed and the



**FIGURE 10.8.** (A) Jet electropolishing by allowing a single jet of gravity-fed electrolyte to thin a disk supported on a positively charged gauze. The disk has to be rotated periodically. (B) Schematic of a twin-jet electropolishing apparatus. The positively charged specimen is held in a Teflon holder between the jets. A light pipe (not shown) detects perforation and terminates the polishing.

material is physically damaged (the top layer is often amorphized). If you use a low angle of incidence (<math>< 5^\circ</math>), you'll deposit the energy of the ion beam in a region close to the surface of the specimen. A lower beam energy or a lower  $Z$  ion will also do less damage, but in both cases milling time will increase (Figure 10.10). In principle, you could also control the vacuum around the sample.

One thing you must remember is that ion thinning is closely related to ion-beam deposition. One manufacturer uses a similar arrangement to coat samples for SEM. The result is that material removed from one



**FIGURE 10.9.** (A) Schematic diagram of an ion-beam thinning device: Ar gas bleeds into an ionization chamber where a potential up to 6 keV creates a beam of Ar ions that impinge on a rotating specimen. Although not shown, the whole apparatus is under vacuum. The specimen may be cooled to liquid-N<sub>2</sub> temperatures and perforation is detected by the penetration of ions through the specimen. (B) Typical ion mill.

part of the sample can easily be redeposited elsewhere on the sample.

The theory of ion milling is complex. We can define the sputtering yield to be the number of atoms ejected per incident ion; the yield depends on the mass of the incoming ion. The yield also depends on the ion used and the sample being milled. The principal variables are

- *The ion:* mass, energy, charge, and angle of incidence
- *The 'target':* mass density, atomic mass, crystallinity, crystal structure, and orientation

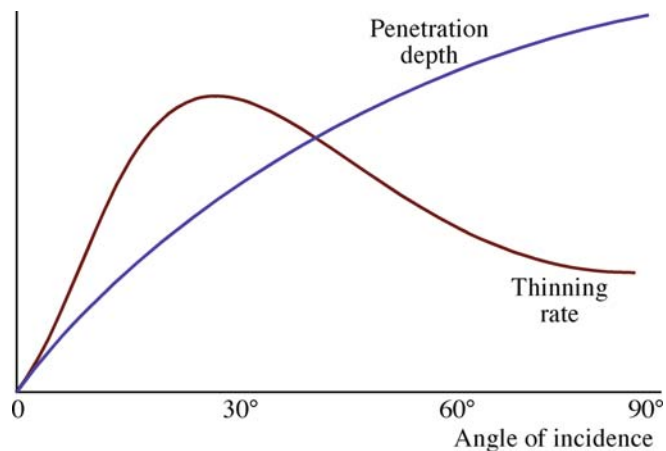
Ar is used because it is inert, heavy, and not naturally present in most samples. Special applications may use reactive iodine, or add oxygen, etc.; this idea of reactive-ion etching is commonly used in semiconductor processing. The problem is that the reactive ion may contaminate or corrode your thinning device, the diffusion pumps, etc. Heavy ions give less penetration, but create more damage.

Most of the thinning parameters are generally fixed except the ion energy, the angle of incidence and any rotation, and the temperature of the specimen. A typical approach is to start with rapid thinning conditions (heavy ions, high incidence angle) and slow the thinning rate as perforation approaches. The effect of incidence angle on the thinning process is shown in Figure 10.10. Cooling the specimen is recommended for almost all materials; otherwise, it is possible that the ion beam might heat it to 200°C or higher. Even in metals which have good thermal conductivity, the creation of vacancies through ion damage can cause diffusional changes equivalent to heat treatment at such temperatures.

You may encounter discussions of whether to use ions or neutral atoms; one idea is that neutralized ions should not be affected by charging of a non-conducting specimen. It is not clear that neutral atoms remain neutral throughout the thinning process so this may be a moot point.

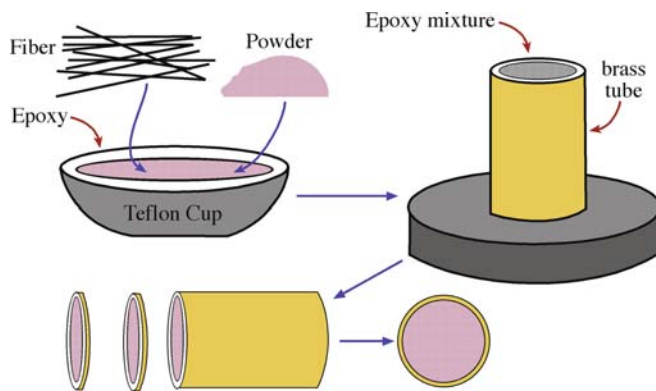
Ion milling is the most versatile thinning process, being used for ceramics, composites, polyphase semiconductors and alloys, and many cross section specimens. In addition, fibers and powders, which constitute a wide range of important materials, can also be thinned by ion milling. To do this, you have to first embed the particles or fibers in epoxy and transfer the mixture into a 3-mm brass tube for strength. The next step is to saw the tube/epoxy mixture into 3-mm disks and finally dimple and ion mill to electron transparency, as shown in Figure 10.11. A similar method (but without the brass tube) can be used prior to ultramicrotomy of powders and fibers (see Section 10.6.B).

*Remember:* Always beware of artifacts: some stories best illustrate this. Goodhew reports that Ar bubbles



**FIGURE 10.10.** Variation in penetration depth and thinning rate with the angle of incidence. High-incidence angles promote implantation, which is undesirable. The rate of thinning reaches a maximum at ~20° incidence, after which the beam penetrates rather than sputters the sample surface. Initial thinning should start at 20–30° reducing to <10° as perforation approaches.





**FIGURE 10.11.** Sequence of steps for thinning particles and fibers by first embedding them in epoxy and forcing the epoxy into a 3-mm (outside) diameter brass tube prior to curing the epoxy. The tube and epoxy are then sectioned into disks with a diamond saw, dimpled, and ion milled to transparency.

form in silicon at a depth of  $\sim 10$  nm after 5-keV thinning. Elemental analysis (XEDS) of some  $\beta$ -aluminas which had the correct structure by HRTEM (composition  $K_2O \cdot 11Al_2O_3$ ) gave a composition with the K completely replaced by Ar. Glasses and zeolites can also accommodate large amounts of Ar. Cooling the specimen can often reduce contamination and surface damage. It is best to use two ions guns. If this is not acceptable, because you want to study the surface region, then you may want to coat one side with a polymer-protective lacquer and then dissolve this coating after thinning to remove sputtered material.

**Why Rotate and Cool the Specimen?** The specimen is usually rotated (at a few rpm) during thinning, otherwise you tend to get surface structure—grooves which run in certain directions; if you see these, check to see that the rotation has not stopped. In the preparation of cross-section specimens, you may use beam blockers and rotation control. In the first, you physically block the sample to shield it in certain directions from the ion beam so that it cannot thin, say an interface, preferentially. In the second, you vary the rate at which you rotate the sample to achieve the same effect. The latter is preferred if it is available since the time spent thinning the specimen is maximized.

**Why cool the specimen?** You can minimize atom migration in or on the specimen. We noted above that the specimen might be heated to  $>200^\circ\text{C}$  otherwise. An additional advantage is that the cooling system also cools the surroundings to give a contribution of cryopumping and simple cryotrapping. However, you have to give the specimen time to warm up after milling which can increase preparation times.

**Tilting the Specimen** This depends on your ion miller but if you're choosing a new machine there may be an advantage in tilting the gun rather than the specimen. If

the specimen is inclined, then you need a clamping ring and you may sputter this when you thin the specimen. This has led to the development of ion polishing instruments (see later) where the ion thinner has been optimized to provide a low angle without a retaining clamp. The specimen rests on a support and can be thinned at an angle of  $4\text{--}5^\circ$ .

**Practical Design of the Ion Miller** The schematic diagram in Figure 10.9 doesn't do justice to a modern ion miller which is a highly sophisticated piece of equipment. Two ion guns are available to thin from each side. The operating vacuum is  $< 10^{-3}$  Pa without Ar and  $10\text{--}10^{-1}$  Pa when Ar is bled into the gun. The ion guns are basically hollow chambers into which the Ar is introduced; then it is ionized and accelerated through a hole in the cathode. The hole gradually enlarges due to ion sputtering and cathodes need replacing after some time to maintain a high-intensity ion beam. More advanced gun designs incorporate saddle fields to focus the ion beam at the specimen and increase the thinning rate. The beam can be neutralized in some systems if the charged ions cause too much damage.

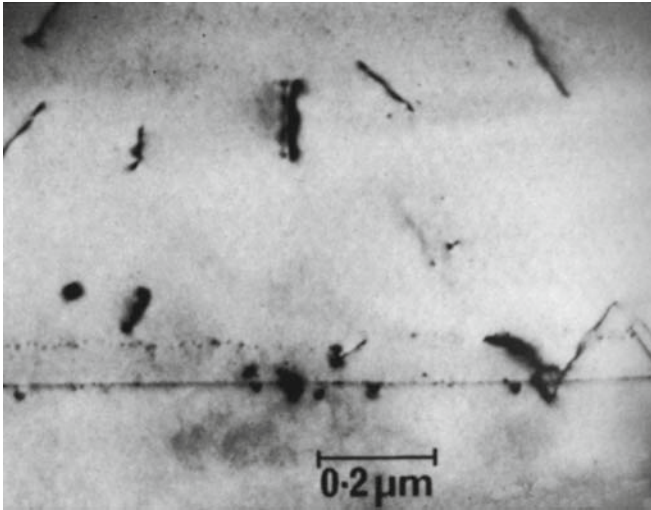
Some special phrases you'll encounter

- **Reactive ion milling.** The classic example is the use of iodine in the work described by Cullis and Chew. Iodine has a clear advantage for InP where the formation of In islands under Ar thinning is suppressed. In CdTe only growth defects were observed in iodine-thinned specimens, but many other defects were found in the same material thinned using Ar ions (Figure 10.12).
- **Beam blockers and variable rotation speeds.** Often the epoxy in a cross-section specimen thins faster than the specimen. Therefore we want to direct the ion beam at the different materials for different amounts of time. The two approaches used are blocking the beam geometrically using 'beam blockers' or varying the rotation velocity; e.g., you don't want the beam to thin along the interface. The latter approach can be extended further to oscillate the specimen, always keeping the ion beam at the same angle of incidence, so that it is never parallel to the interface.
- **Low-angle, low-energy ion mills.** Examples include the PIPS (Gatan's precision ion polishing system) and Baltec's Gentle Mill. These ion mills combine high-powered ion guns and a low angle of incidence ( $4^\circ$ ) to thin one side of a specimen with minimum surface damage and heating. The low incidence angle removes any surface roughness and differential thinning problems, while the high-power guns ensure reasonable thinning rates. The Gentle Mill can even be used to thin FIBbed specimens (when not on a C foil) (see Section 10.7).

(A)



(B)



**FIGURE 10.12.** BF images of CdTe showing (A) defects (dark spots) in Ar-thinned specimen and (B) undamaged crystal thinned by reactive-iodine ion milling. The residual defects in (B) were formed during CdTe crystal growth.

Some final points to remember

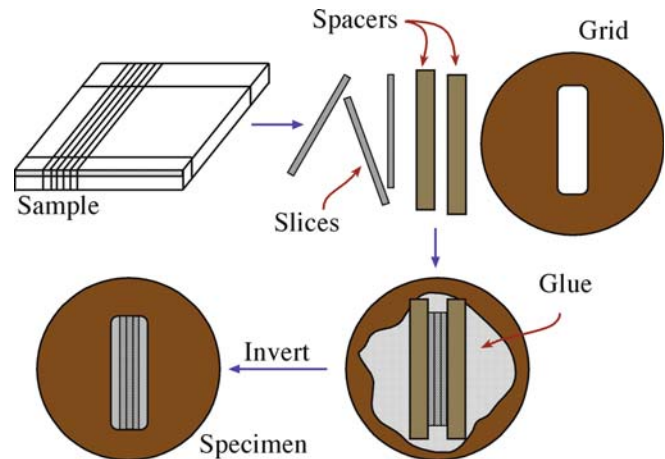
- Materials thin at different rates. It's a good idea for the person responsible for the ion millers to run a test specimen periodically with nominally the same conditions, to be sure that the machine is still working optimally.
- Don't start with a thick sample. Always make the surface as smooth as possible before beginning to ion thin.
- Keep a record of what conditions you use: record the beam current, angle of incidence, rotation rate, and kV.
- Ion milling will form a layer on one surface or both which will probably be a combination of amorphous, highly damaged, and implanted material! The chemistry of the layer will differ from the rest of the specimen. The thickness of crystalline material will thus be less than the total thickness.

## 10.5 CROSS-SECTION SPECIMENS

The cross-section specimen is a special type of self-supporting disk. You must master this preparation technique if you are studying interfaces. We have often stressed that one of the principal limitations of the TEM is its insensitivity to variations in the structure and chemistry of the specimen in the direction of the electron beam. Therefore, if we are to look at structural and chemical variations close to an interface we have to prepare specimens in which the interface is parallel to the electron beam and this involves cross sectioning the sample. The most widely studied cross-section samples are semiconductor devices which often have multiple layers and therefore have multiple interfaces. But any composite materials, samples with surface layers (e.g., oxide-metal interfaces), MBE specimens, quantum-well heterostructures, etc., are candidates for this type of preparation.

There are numerous techniques for preparing cross-section specimens. Many details are reported in four MRS proceedings so we'll only describe a few basic principles. First, rather than trying to thin one interface only, the sample can be cut and glued together to produce several layers, rather like a club sandwich. Then the sandwich is sectioned such that we can see the layers, as shown schematically in Figure 10.13. In this process, a critical step is the gluing of the sections to form the sandwich. Several epoxies are available that cure at low temperatures, so that you won't heat treat the specimen inadvertently. The thickness of the epoxy layer must be such that it is thick enough for good adhesion, but not so thick that it is completely thinned away during final ion milling.

You can then cut the glued sections into 3-mm rods using an ultrasonic drill. Alternatively, you can cut the



**FIGURE 10.13.** Schematic sequence for cross-section specimen preparation: the sample is cut into thin slices normal to the interfaces which are glued together between spacers which could be Si, glass, or some other inexpensive material so that they are wider than the slot in the grid. The 'club' sandwich is then itself glued to the grid (over the slot) and ion milled to perforation.

samples smaller and encase them in a 3-mm thin-walled tube. Section the filled tube into disks which you can then ion thin. The advantage of this method is that the final specimen has a thick ring of the tube metal around it, which gives it mechanical stability. With multiple interfaces the final thinning is almost always guaranteed to produce electron transparency at a useful region.

## 10.6 SPECIMENS ON GRIDS/WASHERS

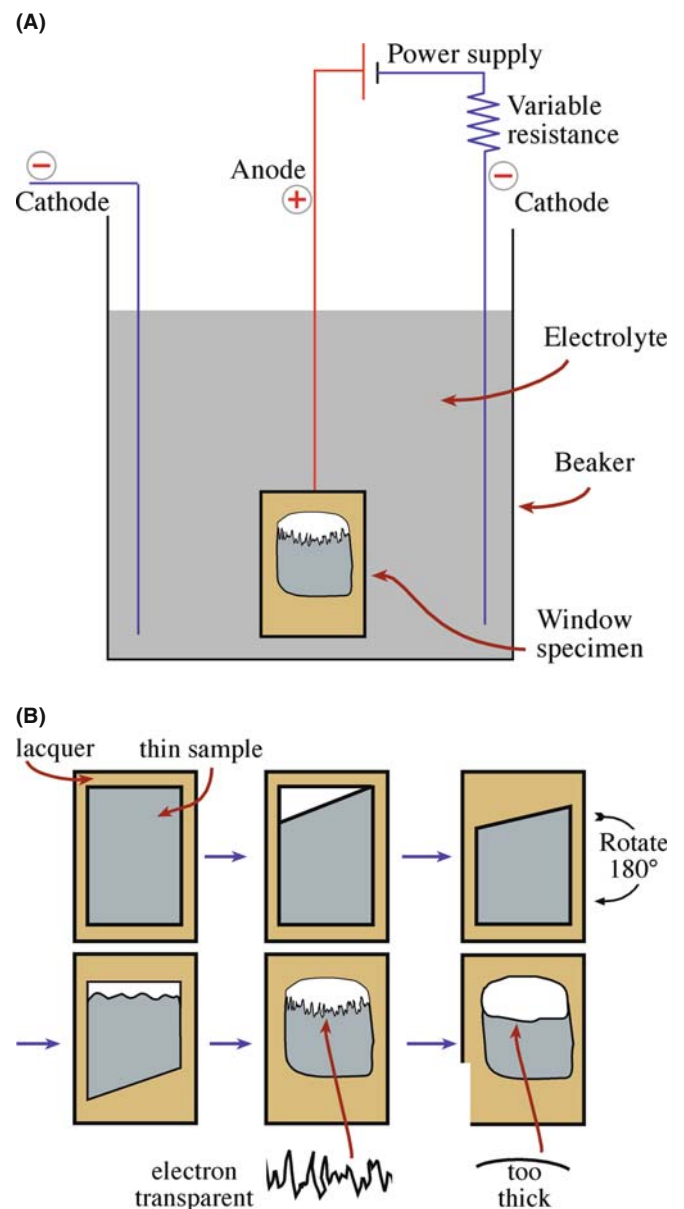
The alternative to self-supporting disks is to make small electron-transparent portions of the specimen or create particles and support them on a thin film on a grid or washer. We can deposit these small particles on amorphous or crystalline films. The classic example is the amorphous carbon film (the holey carbon film), but this is not always the best choice. Some of the particles of the material of interest will be located partially over a hole so that they do not overlap anything else.

The thin supporting film should have a uniform thickness; the idea is that you are not actually interested in this material and therefore want to minimize its effect on the image of the material you are interested in.

The particles may stick to the film or may have to be clamped between two grids. Special hinged ‘oyster’ grids (see Figure 10.3) are available which make this very easy. Some of the processes we’ve already discussed can be used to make these specimens.

### 10.6.A Electropolishing—The Window Method for Metals and Alloys

Electropolishing is an application of electrochemistry and is regarded by many as a ‘black art’: a recipe which works one day but might not work the next. We can electropolish a thin sheet of metal. First cut the sheet into a square  $\sim 10$  mm on the side, then seal the edges with a polymer lacquer to prevent preferential attack. The ‘window’ of exposed metal is immersed in electrolyte (usually cooled to slow the rate of dissolution), surrounded by a cathode and a voltage is applied, as in Figure 10.14A. The solution may or may not be stirred. The correct voltage will ensure that a viscous layer of electrolyte builds up at the surface of the specimen which results in uniform controlled thinning without pitting or corrosion. After some time, which you have to determine experimentally, the sheet is removed, cleaned, and turned through  $180^\circ$  and replaced in the bath as shown schematically in Figure 10.14B. If this procedure is done correctly (and this might require several rotations) the sheet will finally thin in the center. If final thinning occurs too near the top of the sheet, the edge of the perforation is smooth and relatively thick. After perforation, remove the sheet and cut off slivers of material from around the



**FIGURE 10.14.** Window polishing. (A) A sheet of the metal  $\sim 100$  mm<sup>2</sup> is lacquered around the edges and made the anode of an electrolytic cell. (B) Progress during thinning: the initial perforation usually occurs at the top of the sheet; lacquer is used to cover the initial perforation and the sheet is rotated  $180^\circ$  and thinning continues to ensure that final thinning occurs near the center of the sheet; if the final edge is smooth rather than jagged it is probably too thick.

perforation using a scalpel under an inert solvent such as ethanol. Catch the floating slivers on oyster grids, dry them and they are ready for viewing.

### 10.6.B Ultramicrotomy

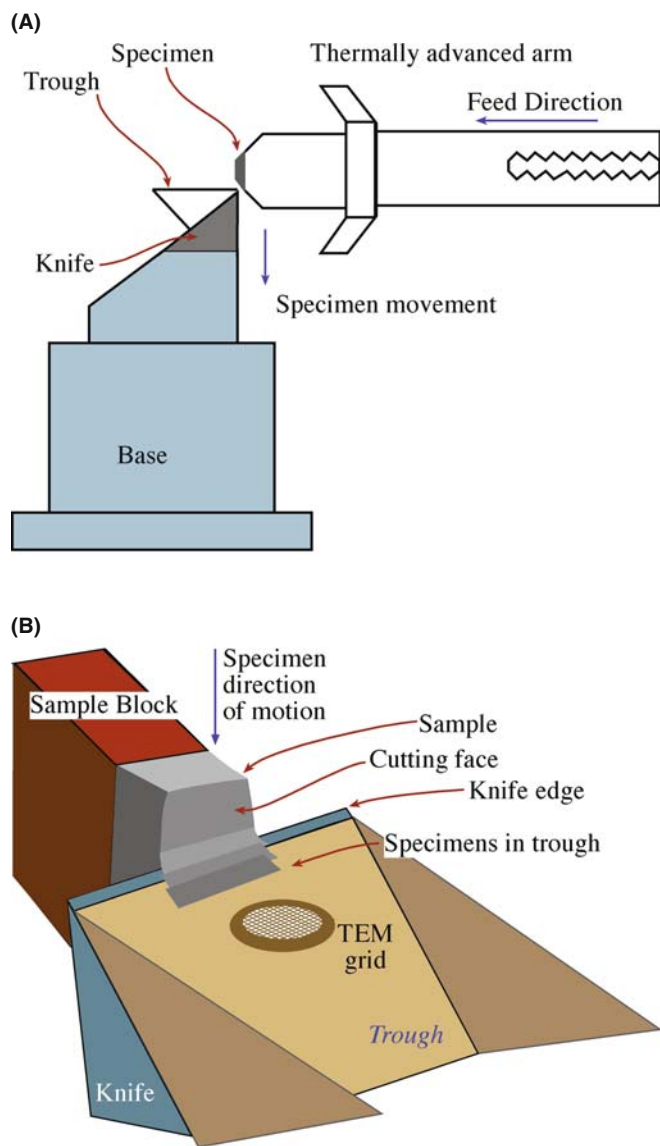
The microtome has long been used for sectioning biological materials. A tome is a ‘piece cut off’ so a microtome refers to the instrument used to cut a very thin tome (not like the one you’re reading). With care and



much practice the biologist can reconstruct a 3D picture of the specimen. For visible-light microscopy the specimens are usually  $<0.1$  mm thick; for the TEM the slices may be  $<100$  nm thick and the instrument is known as an ultramicrotome. These instruments are routinely used for biological samples or for polymers where the samples tend to be quite soft. More recently, they have been used for many studies of crystalline materials. The principal advantages of the technique are that it leaves the chemistry unchanged and is thus ideal for AEM specimens, and you can use it to create uniform thin films of multiphase material. The main disadvantage, of course, is that it fractures and/or deforms the samples and therefore is most useful in cases where the defect structure is of secondary (i.e., zero) importance.

The ultramicrotome operates by moving the specimen past a knife blade. The blade can be glass (cheap) for soft materials but will be diamond for harder ones. Since there are so many possible applications, we will describe a few and refer to the references at the end of the chapter for more details. Two processes can occur in principle: the knife can cut a soft sample or it can cause a partly controlled fracture in a hard/brittle sample. In either case the limiting process is usually plastic deformation of the sample. The principles of this technique are shown in Figure 10.15.

You may also find ultramicrotomy useful if you want to study particles or fibers which are too small to thin individually but are too large to be electron transparent. You can embed the sample as we saw for the ion-thinned particles but without using the metal sheath (see Figure 10.11). We also use epoxy if the sample contains so many interconnected pores that it cannot be thinned mechanically. For porous materials, place the sample in a vacuum chamber, pump out the chamber, and coat the sample with epoxy using a dropper in the chamber. When the sample is fully encapsulated, admit air to the chamber so as to push the epoxy into the pores. After curing, you can ultramicrotome the sample in the usual way.



**FIGURE 10.15.** Ultramicrotomy. (A) The sample is first embedded in epoxy or some other medium or the whole sample is clamped and moved across a knife edge. (B) The thin flakes float off onto water or an appropriate inert medium, from where they are collected on grids.

### 10.6.C Grinding and Crushing

Many brittle materials such as ceramics and minerals are most easily prepared by crushing in a clean pestle and mortar (preferably in an inert liquid). The liquid containing the particles can then be ultrasonically stirred and allowed to settle. Particles suitable for TEM are too small to be seen by eye and the supernatant liquid in which they remain should appear clear. A drop of this liquid, if placed on a holey carbon film on a grid, will evaporate in a dry environment, leaving a distribution of the particles on the support film. If the particles have to be crushed dry, then agglomeration can be a problem. Electrostatic forces sometimes cause small particles to clump together and distributing them on a

grid can be very difficult. In these cases, it sometimes pays to mix up the crushed material in an epoxy, then ultramicrotome the epoxy, as we just described in the previous section.

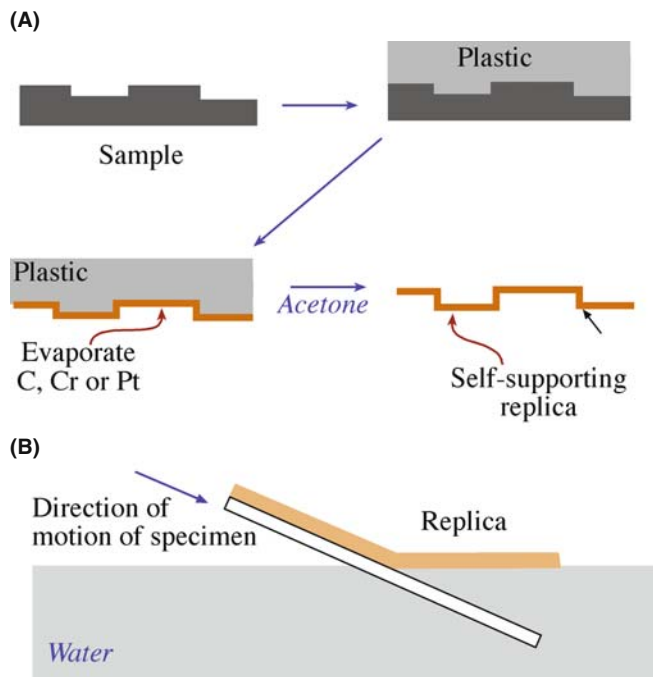
We can collect dust particles found in airborne pollution by simply exposing a support film (on a grid) to the atmosphere for a period of time. Interstellar dust can be sampled from a spacecraft or a high-flying plane.

### 10.6.D Replication and Extraction

These methods are among the oldest TEM specimen-preparation techniques. We use direct replication to

study fracture surfaces or surface topography in general. Evaporate a carbon film on the surface of interest, then etch away the underlying surface with an acid so that the carbon film floats off. If you coat this film with a heavy metal at an oblique angle, you will thus produce a sample that shows enhanced mass-thickness contrast (see Chapter 22); support the film on a grid for observation. As an alternative (Figure 10.16A) you can first replicate the surface by softening a plastic, pressing it on the surface, and allowing it to harden. Pull off the plastic replica, coat it with carbon, then dissolve the plastic with a suitable solvent, and pick up the carbon replica on a support grid. If the carbon replica is produced directly from a metal surface, it may be necessary to dissolve some of the metal with acid then float off the carbon onto distilled water before picking up on a grid, as shown in Figure 10.16B. After picking up on a grid it may be useful to coat the replica obliquely with a heavy metal to enhance any topographic (thickness) contrast.

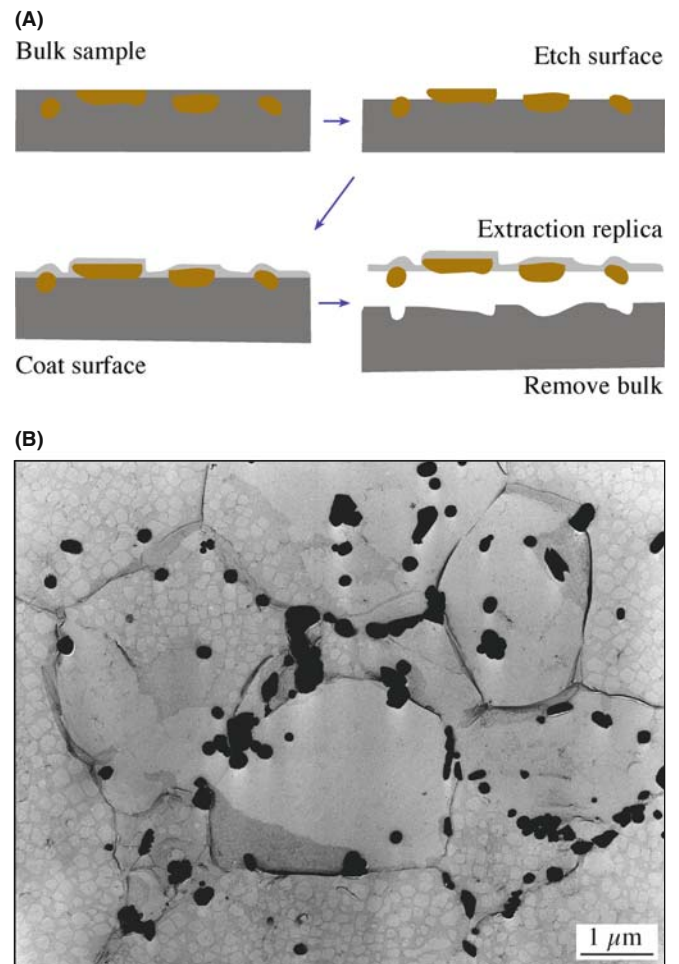
Extraction replication has seen a resurgence of interest since AEM techniques appeared, because we can extract a particle from its surrounding matrix, thus



**FIGURE 10.16.** (A) Replication of a surface by the two-step method: spray acetone on the surface to be replicated before pressing a plastic (usually cellulose acetate) onto the surface which softens in contact with the acetone; the plastic is removed from the surface when it has hardened and a C, Cr, or Pt film is evaporated onto the replicated plastic surface; the plastic is then dissolved with acetone and the evaporated film retains the original topography. (B) Alternatively, the direct carbon replica of a metal surface may be floated off on distilled water after scratching the carbon and etching to free the film, which may subsequently be shadowed obliquely to enhance the topography.

allowing us to analyze that phase alone without interference from electron scattering into the matrix.

The various steps for extraction are shown in Figure 10.17A. The sample is polished metallographically to expose the particles on the surface. An appropriate etching process is used to remove the matrix such that the particles stand proud of the surface. A carbon film is evaporated onto the surface and scored into  $\sim 2$  mm squares. Then the etching is continued. As the matrix is dissolved, the squares of carbon film float to the surface carrying the particles with them. Catch one of these squares on a grid and you have your specimen ready for the TEM as shown in Figure 10.17B. Again, oblique shadowing may be useful to enhance image contrast, but not if you plan to use AEM.



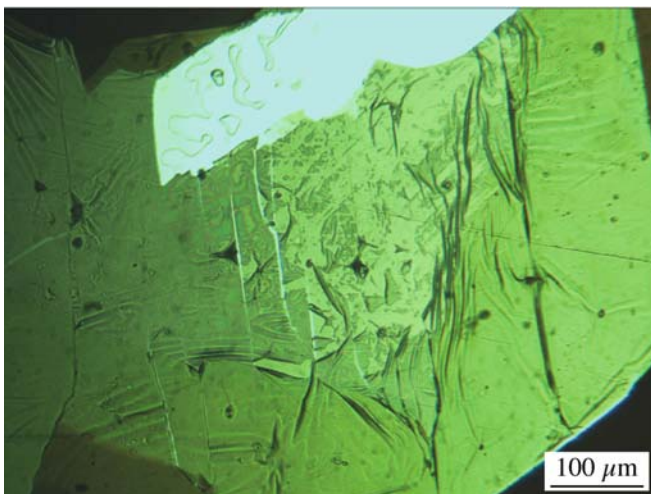
**FIGURE 10.17.** (A) Making the extraction replication: particles embedded in a matrix are revealed by etching the matrix, which leaves the particles standing proud of the surface; a thin amorphous carbon film is evaporated over the particles, then the rest of the matrix is etched away leaving the particles adhering to the carbon film. (B) Example from a  $\gamma/\gamma'$  alloy showing not only that the particles are mainly located at the grain boundaries but also the different contrast from  $\gamma'$  grains and two-phase  $\gamma/\gamma'$  grains.

### 10.6.E Cleaving and the SACT

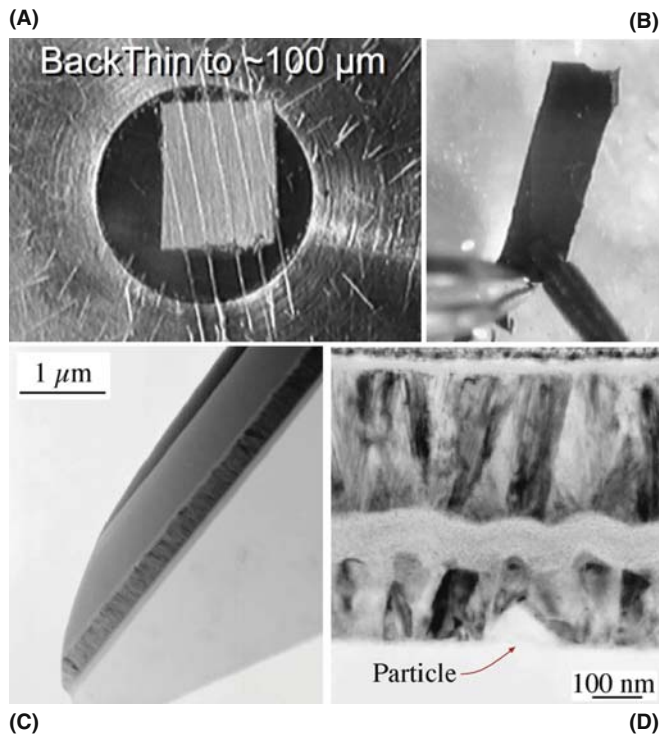
Cleaving is one of the oldest techniques and has been used to make thin specimens of graphite, mica, and other layer materials that are weakly bonded along one plane. The classical idea is to attach adhesive tape to both sides of the sample and then pull the two pieces of tape apart. This process is repeated until the specimen is thin enough for TEM. You can really only tell this by experience: as it becomes thinner, graphite becomes a lighter shade of gray in transmitted visible light. Molybdenite ( $\text{MoS}_2$ ) becomes a lighter shade of green as illustrated in Figure 10.18. Place the tape with the thin flake of material in a solvent to dissolve the glue (all traces of glue *must* be removed). This technique is not as easy as it once was. The glues used to be readily soluble in trichloroethylene which is now a known carcinogen.

A special variation on cleaving, known as the small-angle cleaving technique (SACT), is illustrated in Figure 10.19. The idea is to propagate a crack through the sample along a plane that is not a natural (crystallographic) fracture plane and then create another crack that is shallowly inclined to the first fracture surface. The technique can be applied to crystalline samples such as Si coated with thin films or to coated glass samples (as shown in Figure 10.19) that have no preferred fracture plane. In the case of glass, this is particularly attractive since the only alternative is ion milling which tends to implant argon into the open structure of the glass and is thus not suitable for AEM specimens.

Figure 10.19A shows a sample that has been scribed with several parallel lines. Each of the rectangular samples can then be fractured again by pressing on it with a stylus to produce a sharply wedged specimen. With luck, the resulting sample is electron transparent as seen in Figure 10.19D where a small particle of NaCl is imaged



**FIGURE 10.18.** Image of cleaved  $\text{MoS}_2$  showing regions of different shades of green, which correspond to different thicknesses.



**FIGURE 10.19.** SACT of a coating on glass. (A) Scratch the sample; (B) cleaving along the scratch; (C, D) TEM images.

between a glass substrate and a coating layer. Although it is a hit-and-miss technique, you can make so many specimens in one sitting that a hit is assured (with lots of practice). You can then put this sample into the FIB and produce an even better sample without spending too much FIB time (money).

#### SACT

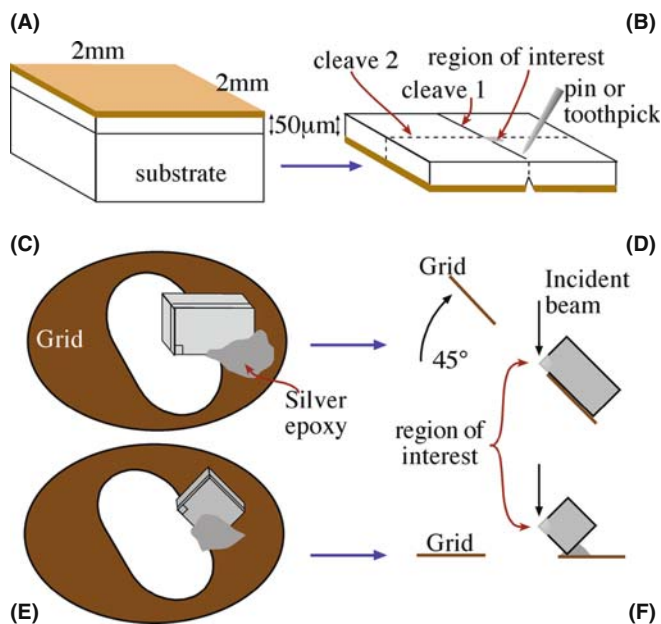
The small-angle cleaving technique is invaluable for films on Si or glass where there is no crystal structure; making the  $90^\circ$  wedge would be a LACT!

### 10.6.F The $90^\circ$ Wedge

The  $90^\circ$ -wedge specimen was developed because many compound semiconductors such as GaAs are grown with a (001) surface and can be easily cleaved on the (110) and ( $1\bar{1}0$ ) planes that are perpendicular to this growth surface. When you are practiced at cleaving the sample as shown in Figure 10.20, you can examine a specimen in the TEM within 30 minutes of completing the growth.

Mount the specimen as shown in the figure, preferably so that you won't need to tilt it in the microscope. Although the specimen is only transparent close to the edge of the 'hole,' you will have a long strip of material suitable for viewing. As always, beware of artifacts. If your specimen is perfect, you will know exactly how





**FIGURE 10.20.** The 90°-wedge specimen: (A) prethin to create a 2-mm square of the multilayers on a Si substrate; (B) scribe the Si through the surface layers, turn over, and cleave; inspect to make sure the cleavage is clean, giving a sharp 90° edge; reject if not; (C, E) mount the 90° corner over the edge of a hole in a Cu grid; (D, F) then insert in the TEM; note that two different orientations are available from a single cleavage operation.

thick it is at the position you choose for study. We will find this wedge useful when we discuss image contrast in Part 3.

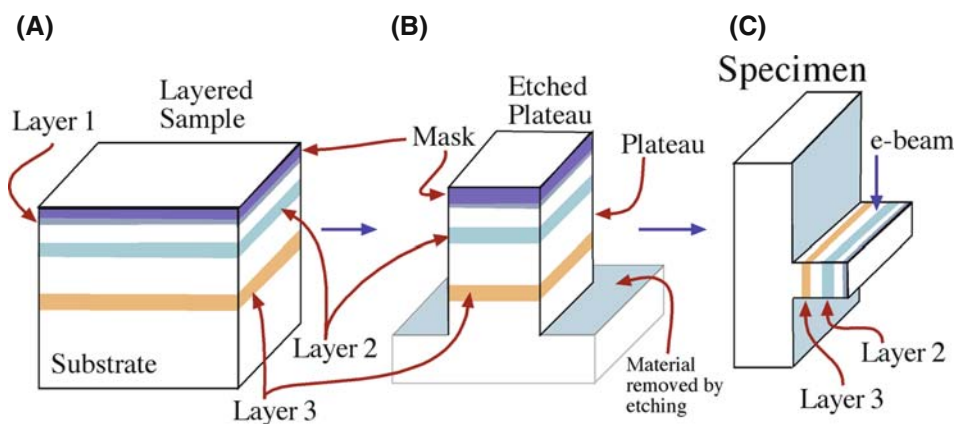
### 10.6.G Lithography

Here we use a technique developed for advanced engineering applications. Lithography is used in the microelectronics industry to define fine lines of width down to 100 nm. An illustration of how lithography can be used specifically to prepare TEM specimens (as opposed to

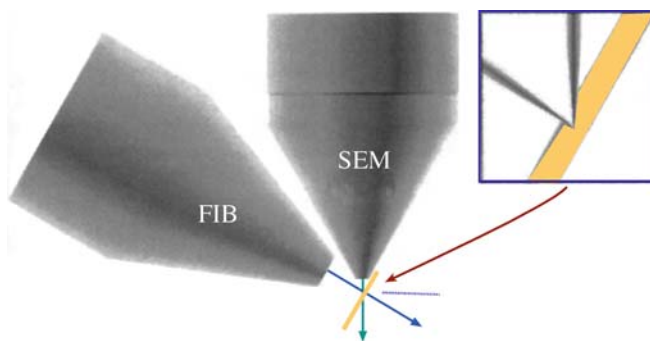
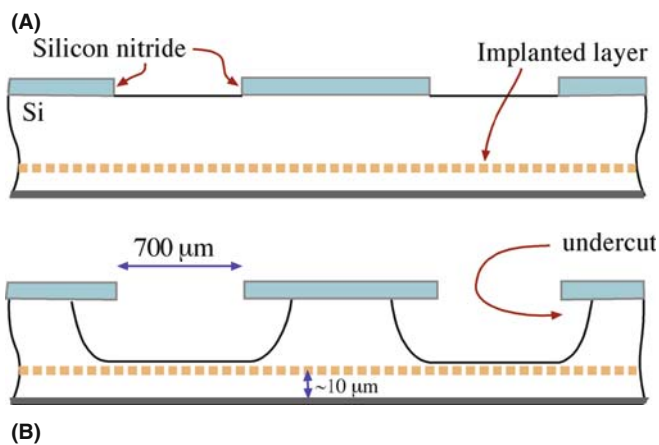
generating a structure which might best be characterized by TEM) is shown in Figure 10.21. We can draw lines on the layered material using standard lithographic techniques. Material on either side of the lines is then removed by etching (chemical or ion) to give a plateau which is thin in one direction. We then remove most of the remaining substrate and attach the specimen to a support washer. We can then observe the specimen directly in the TEM. Although the width (formerly height) of the electron-transparent region is narrow it can extend across the entire hole in the 3-mm disk. The major disadvantages or limitations of the technique are (i) the dimension in the direction of the electron beam is fixed by the lithographic capabilities and (ii) tilting the specimen may quickly cause the thicker region to block the electron beam.

### 10.6.H Preferential Chemical Etching

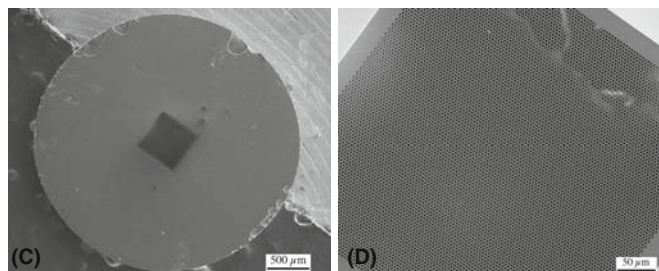
The principle behind this technique is the same as for lithography: we remove part of the sample to leave an area which is electron transparent. The trick is to keep part of the final specimen thick enough for handling, or ideally for supporting, the specimen. Naturally, this approach only works with certain materials although the principle might be extended to other thin films. The technique has been used for III–V compounds where  $\text{Al}_{1-x}\text{Ga}_x\text{As}$  acts as an etch stop for GaAs and for Si where an etch stop can be produced by implanting with boron (Figure 10.22). In both cases, the resulting thin layers may be used as substrate materials for thin-film studies rather than as the subject of study in their own right. An extreme example of this approach is the use of thin films of  $\text{Si}_3\text{N}_4$  as an ‘etch stop’ so that a uniform layer of amorphous  $\text{Si}_3\text{N}_4$  remains across the window. Such specimen supports are commercially available; diamond films can be made in a similar way.



**FIGURE 10.21.** Etching of a multilayer sample (A). Etch away most of the sample, leaving a small etched plateau (B); mask a region < 50 nm across and etch away the majority of the surrounding plateau. If this thin region is turned 90° and mounted in a specimen holder (C), the interfaces are now parallel to the electron beam.



**FIGURE 10.23.** Schematic of a two-beam (electron and ion) FIB instrument.

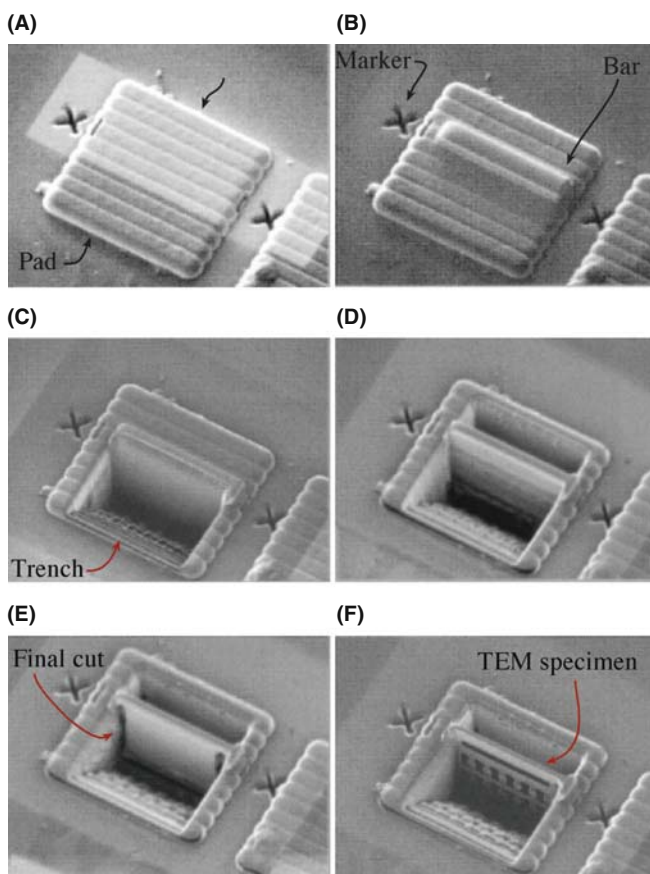


**FIGURE 10.22.** Lithographic techniques applied to thinning a multilayer specimen: (A) the unthinned sample is shown with a grid of  $\text{Si}_3\text{N}_4$  barrier layers evident. Etching between the barrier layers, shown in (B), produces an undercutting down to the implanted layer which acts as an etch stop, producing a uniform layer  $\sim 10 \mu\text{m}$  thick. Further thinning with a different solution produces large areas of uniformly thin material (not shown) supported by the  $\text{Si}_3\text{N}_4$  grid and the remaining unthinned regions. (C, D) A commercial  $\text{Si}_3\text{N}_4$  thin films support disk; (D) is the enlarged view.

## 10.7 FIB

The focused-ion beam (FIB) instrument is becoming much more readily available as prices moderate and their value is realized; however, a FEG-equipped FIB can still cost more than your TEM. We deal with FIB more extensively in the companion text but include a summary here because you must know about it even if you can't get access to one yet.

When preparing TEM specimens we can think of the FIB essentially as an SEM with a built-in ion mill. (Sometimes it's an ion gun with an SEM attachment.) The single ion gun produces a well-controlled beam of Ga ions (rather than Ar used in the ion mill). In the simplest (cheaper) design the ion beam also acts as the electron beam of the SEM with the secondary electrons being used to form the 'SEM' image of the sample. A schematic of the FIB is given in Figure 10.23. The various stages in the preparation process are shown in Figure 10.24. The pad in (A) is the coating of Pt. The two Xs, to mark the region of interest, have been drawn on the sample using the ion beam, and another Pt strap



**FIGURE 10.24.** Stages in making TEM samples using a FIB instrument. (A) The area of interest has been marked. (B) A Pt bar is deposited to protect this area from the Ga beam. (C, D) The two trenches are cut. (E) The bottom and sides of the slice are (final) cut. (F) The TEM specimen is polished in place before extracting it.

is deposited between them (B). Next, two staircases are cut out on either side to leave the thin wall shown in (C) and (D). In (E) the 'wall' has been trimmed away at the sides so that it is only supported at the top. The last step

(F) is to ion-polish the thin wall until it is really a thin TEM specimen and finally attach it to a probe for lift out or use static electricity to lift it out and place it on a supporting (usually C) film. Attaching the FIBbed specimen to a probe is becoming the norm since it allows the FIBbed specimen to be further cleaned to remove Ga contamination and/or reduce the thickness further. An FEI version of the instrument is shown in Figure 10.25. We'll discuss the details of FIB in the companion text because not everyone can afford

to buy a FIB or can afford to use one even if it is 'available'!

## 10.8 STORING SPECIMENS

The best advice is to look at your specimen as soon as possible after preparation. If that is not possible, then keep your specimens under optimum conditions. Usually this means keeping them dry (water vapor affects the surface region of most materials), perhaps in an inert atmosphere (dry nitrogen works well, or a dry-pumped, oil-free vacuum desiccator) and in an inert container (a glass petri dish with filter paper).

The next problem is long-term storage; for periods up to 1 month, you can use the above procedure. If you want to keep the specimen longer, your choices can be more difficult. Don't use gelatin capsules for anything resembling 'delicate' material. Don't use slotted grid-holders for anything which might deform (break or bend) during handling; that rules out self-supporting ceramics, metals, and semiconductors. Always use vacuum tweezers to manipulate delicate specimens (remember safety when using mouth-vacuum tweezers). Remember, your most important specimen is the one most likely to break, bend, interact with sharp tweezers, or jump onto the floor.

Last, old specimens can be cleaned by ion polishing or chemical cleaning. This process does thin the specimen further so you may lose the area you originally studied. Ion polishing can also be useful for 'sectioning' specimens. The 'safer' re-cleaning (or refreshing) method is to use a plasma cleaner but this can change your sample.

If your specimen is a collection of nanoparticles, you will realize that such particles can be so reactive that they may have changed before they reach the TEM even for the first time. You may then have to use techniques that are more familiar to cryo-transfer users, such as transferring the specimen from the preparation chamber to the TEM in a controlled environment. Such a procedure is not routine using conventional holders.

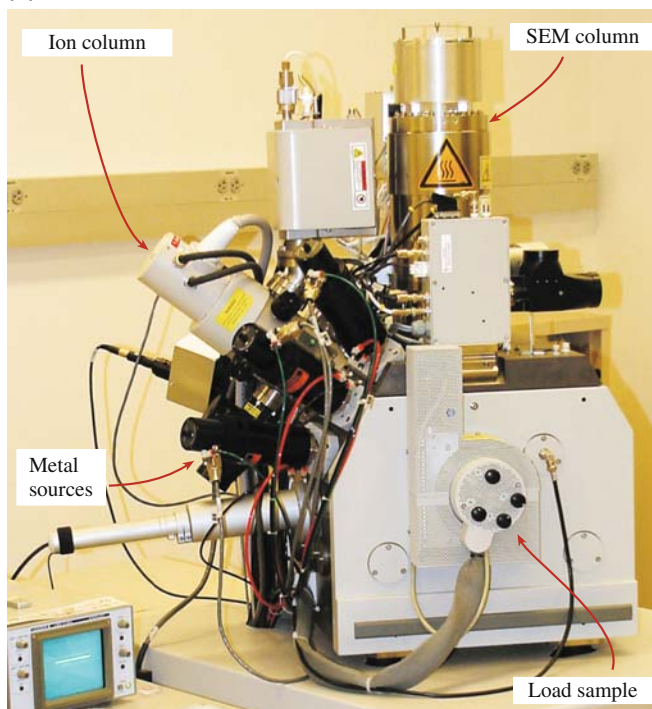
## 10.9 SOME RULES

We stress once again that you must know what you want to study in your specimen before you begin specimen preparation. Figure 10.26 is a second flow chart to summarize the various possible options. Be aware of the limitations of the method you choose, particularly the artifacts introduced. Table 10.1 summarizes the artifacts introduced by various methods.

(A)



(B)



**FIGURE 10.25.** A dual-beam FIB instrument. (A) Overview; (B) enlarged view to compare with Figure 10.23.



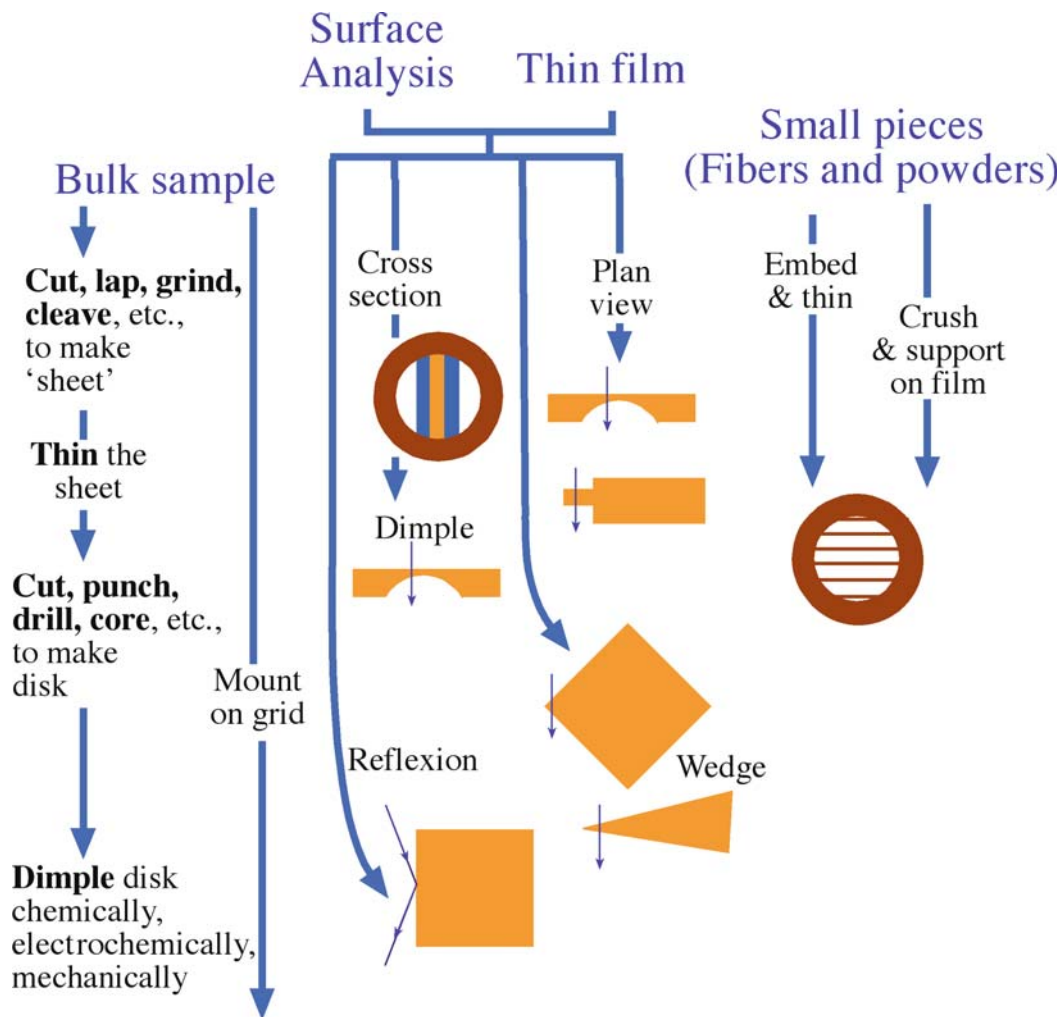


FIGURE 10.26. Summary flow chart for specimen preparation.

TABLE 10.1 Artifacts Produced During Specimen Preparation (after T. Malis)

Artifact/problem	Consequence
<i>Variable thickness</i>	<ul style="list-style-type: none"> <li>▪ Limited local area for chemical mapping (EP, IT, C, CD)</li> <li>▪ Very limited area for EELS</li> <li>▪ Somewhat limited area for absorption-free XEDS</li> <li>▪ Omission of low-density defects</li> <li>▪ Distorted defect densities (EP, IT, TP)</li> </ul>
<i>Uniform thickness</i>	<ul style="list-style-type: none"> <li>▪ Limited diffraction information (UM)</li> <li>▪ Limited microstructure information (UM)</li> <li>▪ Handling difficulties (UM)</li> </ul>
<i>Surface films</i>	<ul style="list-style-type: none"> <li>▪ Bath residue, spec. dissolution and/or redeposition EP</li> <li>▪ Enhanced surface oxide (EP)</li> <li>▪ Extremely irregular topographies (IT)</li> <li>▪ Faster contamination buildup under beam (EP, R)</li> <li>▪ Retention of matrix on extracted particle</li> <li>▪ C-redeposition (UM—embedded, UM, C, R—support films)</li> </ul>

**Table 10.1**(continued)

Artifact/problem	Consequence
<i>Differential thinning</i>	<ul style="list-style-type: none"> <li>▪ Cu<sub>2</sub>O formation from Cu grids upon heating (R, UM, C)</li> <li>▪ Ion amorphization, diffusion-pump oil, redeposition (IT*)</li> </ul>
	<ul style="list-style-type: none"> <li>▪ Different phases thin at different rates (EP, IT)</li> <li>▪ Different orientations thin at different rates (IT)</li> <li>▪ Grain/phase boundary grooving (EP, IT)</li> <li>▪ Anodic attack of matrix/particle (UM)</li> </ul>
<i>'Selectivity'</i>	<ul style="list-style-type: none"> <li>▪ Perforation influenced by local defect structure (EP, IT)</li> <li>▪ Very limited or no microstructure information (C, R)</li> <li>▪ Weak local regions debond and fall out (all)</li> </ul>
<i>'False' defects</i>	<ul style="list-style-type: none"> <li>▪ Microstructure obscured by high defect density (UM, CD)</li> <li>▪ Deformation-induced defects (EP, TP)</li> <li>▪ Ion-induced loops, voids (IT)</li> <li>▪ Heat-altered defects (EP, IT)</li> </ul>

EP: electropolished; UM: ultramicrotomed; CD: controlled dimpling; R: extraction replication; IT: ion thinned; TP: tripod polish; C: cleavage (grinding, crushing).

## CHAPTER SUMMARY

Specimen preparation is a craft and there is no substitute for hard work, careful, detailed experimentation and lots of practice as you seek to master it. This is the most tedious aspect of all of TEM work but, if you invest the time, your reward will be the best of times on the TEM itself. The quality of your data is at least directly proportional to the quality of your specimen (and this relationship is often far stronger than the linear nature just implied). You simply have to find the method that works best for your particular material. While there are many cook-books available, the recipes are often too individualized and not to your specific taste.

There are few rules for specimen preparation except that thinner is usually better, although such specimens are more prone to artifacts. Think about each step and what it might do to change the microstructure or microchemistry of your material. Take care to avoid the physical dangers that are present whenever you use dangerous chemicals, ionizing radiation, or sharp knives. Be clean, use fresh materials, tidy up after yourself, and apply all the other lessons that you learned in kindergarten!

Although all the equipment mentioned here is available commercially, most were originally developed on a shoestring budget in someone's lab so you can always build your own electropolisher or even an ion mill. If you are working with brittle materials, buy or build a tripod polisher and learn how to use it.

A last reminder: The recipe books listed below are a great source of ideas. New recipes are appearing all the time. As is often the case in cooking it helps to see an expert chef in action to realize what is possible. In other words, when you have seen a really good TEM specimen, you'll know what yours should look like.

## REFERENCES

These references only give a sampling. More extensive lists, especially for the more specialized techniques like FIB, are given in the companion text.

## GENERAL TECHNIQUES

An extensive list of references is included in the chapter on specimen preparation in the companion text.

The first four references below are essential: from the MRS Proceedings.

- i. Bravman, JC, Anderson, RM and McDonald, ML (Eds.) 1988 *Specimen Preparation for Transmission Electron Microscopy of Materials Mater. Res. Soc. Symp. Proc. 115* MRS Pittsburgh PA. (Number I in

the series.) We've updated the flow chart in the article on p51 by Goodhew, PJ, The tripod polisher is described by Klepeis, SJ, Benedict, JP and Anderson, RM on p179. (Pictures of the gem variety are shown in Figure 36.3 of *Ceramic Materials* by Carter and Norton.) Brown, JM and Sheng, TJ describe the use of lithography on p229.

- ii. Anderson, RM (Ed.) 1990 *Specimen Preparation for Transmission Electron Microscopy of Materials, II* Mater. Res. Soc. Symp. Proc. **199** MRS Pittsburgh PA.
- iii. Anderson, RM, Tracy, B and Bravman, JC (Eds.) 1992 *Specimen Preparation for Transmission Electron Microscopy of Materials, III* Mater. Res. Soc. Symp. Proc. **254** MRS Pittsburgh PA. Alani, R and Swann, PR (1992) discuss ion milling on p43.
- iv. Anderson, RM and Walck, SD (Eds.) 1997 *Specimen Preparation for Transmission Electron Microscopy of Materials, IV* Mater. Res. Soc. Symp. Proc. **480** MRS Pittsburgh PA.

## CHEMICAL POLISHING

Thompson-Russell, KC and Edington, JW (1977) *Electron Microscope Specimen Preparation Techniques in Materials Science* Macmillan Philips Technical Library Eindhoven Netherlands. Many recipes.

## ION MILLING AND FIB

- Barber, DJ 1970 *Thin Foils of Non-metals Made for Electron Microscopy by Sputter-Etching* J. Mater. Sci. **5(1)** 1–8. First use of ion milling to make a ceramic TEM sample.
- Barna, A 1992 *Topographic Kinetics and Practice of Low Angle Ion Beam Thinning* in MRS Proc. **254** 3–22. An early advocate of using low-energy ion beams.
- Cullis, AG, Chew, NG and Hutchinson, JL 1985 *Formation and Elimination of Surface Ion Milling Defects in Cadmium Telluride, Zinc Sulphide and Zinc Selenide* Ultramicroscopy **17** 203–211. The paper on reactive-ion milling of TEM samples.
- Giannuzzi, LA and Stevie, FA 2004 *Introduction to Focused Ion Beams: Instrumentation, Theory, Techniques and Practice* Springer Verlag NY. The guide to FIB.
- Harriott, LR 1991 *The Technology of Finely Focused Ion Beams* Nucl. Instr. Meth. Phys. Res. Section B: Beam Interactions with Materials and Atoms **55B** (1–4) 802–810. One place to start if you're interested in 'Why Ga?'
- Medard, L, Jacquet, PA and Sartorius, R 1949 *Sur les dangers d'explosion des bains aceto-perchloriques de polissage électrolytique (Explosion Hazard of Acetic and Perchloric Acid Mixture Used as Solution in Electrolytic Polishing)* Rev. Metall. **46(8)** 549–560. Jacquet has many other papers on specimen preparation if your French is good.

## OTHER MATERIALS

- Carter, CB and Norton, MG 2007 give some illustrations of the tripod polisher used to facet diamond in *Ceramic Materials: Science and Engineering* Springer Verlag NY.
- Malis, TF 1989 *AEM Specimens: Staying One Step Ahead* in *Microbeam Analysis-1989* 487–490 Ed. P.E. Russell, San Francisco Press San Francisco gives a discussion of using the microtome for hard samples.
- Sawyer, LC, Grubb, DT and Meyers, GF 2008 *Polymer Microscopy* 3rd Ed. Springer Verlag NY gives the details for preparing polymer specimens.

## THE COMPANION TEXT

A complete chapter in the companion text not only discusses more specialized techniques but also extends this chapter's discussion.

## SELF-ASSESSMENT QUESTIONS

- Q10.1 Name two ways you can damage yourself more than your specimen while preparing it.
- Q10.2 What are the differences between self-supporting specimens and specimens resting on a grid or thin washer?
- Q10.3 What is the main problem associated with using a grid?
- Q10.4 What does dimpling mean?
- Q10.5 What should we keep in mind when using the tripod polisher to pre-thin the specimen?
- Q10.6 What is the difference in the use between electropolishing and ion milling?
- Q10.7 Why do we need to use a low angle of incidence in ion milling?
- Q10.8 Why do the specimens need to be rotated and cooled during the ion-thinning process?
- Q10.9 Why are various chemical etching techniques used in TEM specimen preparation?
- Q10.10 Why do you want the region of interest of your specimen to be in the center of the grid?
- Q10.11 What methods can be used for preparing thin specimens (initial thinning) of ductile materials?
- Q10.12 How is the thickness of your specimen affected by the damage done to the surface?



- Q10.13 Why might you need to cool the electrolyte during electropolishing?
- Q10.14 What are the advantages and disadvantages of ultramicrotomy?
- Q10.15 When is it reasonable to use a mechanical punch?
- Q10.16 As a 'rule of thumb,' how much damage does a typical abrasive cause to a specimen?
- Q10.17 How would you go about creating a GaAs cross-sectional TEM specimen? If the material is heat sensitive (i.e., it reacts) what can be done to minimize the heat load?
- Q10.18 If specimen preparation is so important, why do we spend relatively little time discussing this issue in the book, in class, and in our training?
- Q10.19 List the four most widely used polishing solvents.
- Q10.20 List at least three precautionary measures you should bear in mind while using hazardous chemicals.
- Q10.21 What precautions are necessary for short-term storing of specimen?

### TEXT-SPECIFIC QUESTIONS

- T10.1 When and why would you take the time to use the window method (Figure 10.14) to prepare thin foils of a metal sheet rather than dimpling and jet polishing (Figure 10.8)?
- T10.2 What TEM technique would benefit most from ultramicrotomed specimens and which technique would benefit least?
- T10.3 List five different particle samples that might be easily prepared for viewing in a TEM. Give a literature (research journal) reference for each one.
- T10.4 Nanotubes, nanowires, buckyballs, etc., are nano-scale specimens that have recently received significant attention. How would you prepare such specimens for examination in the TEM?
- T10.5 If you had a large piece of a weld from which you wanted to prepare a thin specimen of a very specific region (e.g., the heat-affected zone or a single-pass region) for chemical analysis, how would you go about preparing such a specific thin specimen?
- T10.6 List the advantages and disadvantages of making a replica of a specimen surface as in Figure 10.16 to view in the TEM rather than viewing the surface directly.
- T10.7 List the advantages and disadvantages of making an extraction replica of particles from a specimen surface as in Figure 10.17 to view in the TEM rather than viewing the particles within a thin foil.
- T10.8 What kinds of difficulties might arise when attempting to perform elemental analysis in the AEM when your specimen has been (a) electropolished or (b) ion milled? How might those difficulties be overcome?
- T10.9 Why might ultramicrotomy be the ideal specimen preparation method for AEM but totally unsuitable for routine TEM imaging and diffraction?
- T10.10 Why should your specimens remain isolated from you and other human beings after they are thinned?
- T10.11 Use Figure 10.26 where appropriate to propose a method for getting a TEM specimen from
- A. the join in a soldered copper alloy
  - B. catalyst particles on a substrate
  - C. a specific junction in a semiconductor device