CHAPTER

9

SAMPLE PREPARATION FOR MICROSCOPIC AND SPECTROSCOPIC CHARACTERIZATION OF SOLID SURFACES AND FILMS

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9.1. INTRODUCTION

Characterization of materials in the solid state, often loosely referred to as *materials characterization*, can be a vast and diverse field encompassing many techniques [1–3]. In the last few decades, revolutionary changes in electronic instrumentation have increased the use of highly effective automated instruments for obtaining analytical information on the composition, chemistry, surface, and internal structures of solids at micrometer and nanometer scales. These techniques are based on various underlying principles and cannot be put under one discipline or umbrella. Therefore, it is important first to define the scope of techniques that can be covered in one chapter.

In this chapter we are concerned with the two common categories of materials characterization: microscopy and spectroscopy. Microscopy implies obtaining magnified images to study the morphology, structure, and shape of various features, including grains, phases, embedded phases, embedded particles, and so on. Spectroscopy implies investigation of chemical composition and chemistry of the solid. Within spectroscopy, bulk techniques such as infrared, Raman, and Rutherford backscattering require minimal sample preparation and are not touched upon. Emphasis is placed on the spectroscopy of the outer atomic layers where sample preparation and handling become important.

Within each category, different techniques may have their own restrictions, requirements, and concerns. As the analytical instruments become

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Table 9.1. Common Microscopic Techniques and Sample Preparation Concerns

Technique	Description
Optical microscopy (OM) Reflection Transmission Phase contrast Polarized light	Surface and internal microscopy, crystallographic information identification of particulates. Maximum magnification ~1000×. Final sample preparation: Polish and etch one side for reflection modes (Fig. 9.1). Some thinning for transmission mode.
Scanning electron microscopy (SEM)	Surface and internal morphology with 1000 Å or better resolution. Special techniques to characterize semiconductor and magnetic devices. Final sample preparation: Polish and etch (apply coating if required) one side (Fig. 9.1).
Transmission electron microscope (TEM) Scanning transmission electron microscope High-resolution electron microscope Analytical electron microscope	Internal nanostructure. Some case of surface structure if using replicas. Spatial resolution 2–5 Å. Phase determination (often with stained specimens) capability. Crystallographic information from ~4000 $Å^2$ area. Sample preparation: Very critical. Ultrathin specimens needed (Section 9.3 Table 9.4).

more sophisticated, robust, and user friendly, some stringency of sample specifications can be relaxed, but those fundamental to the analytical process remain. In this chapter, we provide a brief introduction to those sample preparation concerns that every user should be aware of. Tables 9.1 and 9.2 provide a brief summary of the analytical techniques whose sample preparation concerns are covered in this chapter.

9.1.1. Microscopy of Solids

The oldest microscopy technique for materials analysis was optical microscopy. Even to this day, for feature sizes above 1 μm, this is one of the most popular tools. For smaller features, electron microscopy techniques such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are the tools of choice. A third family of microscopy includes scanning probe tools such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM). In these relatively recent techniques, sample preparation concerns are of minor importance compared to other problems, such as vibration isolation and processing of atomically sharp probes. Therefore, the latter techniques are not discussed here. This chapter is aimed at introducing the user to general specimen preparation steps involved in optical and electron microscopy [3–7], which to date are the most common

Table 9.2. Common Surface Spectroscopic Techniques and Sample Preparation Concerns

Technique	Description
Auger electron spectroscopy (AES)	Elemental analysis of surfaces and films, high resolution (ca. 500 Å) from top ~1- to 20-Å layer. Limited valence-state information. Depth profiling. Sample preparation: Surface cleaning or in situ surface creation.
X-ray photoelectron spectroscopy (XPS)	Elemental analysis of surfaces and films, depth profiling (slow). Reveals detailed chemical state of elements; molecular composition can be deduced from peak sizes and shapes. Sample preparation: Surface cleaning or in situ surface creation.
Secondary-ion mass spectroscopy (SIMS)	Ultrahigh sensitivity in qualitative elemental and molecular compound analysis, isotope analysis, rapid depth profiling of composition, but no chemical information. Spectra interpretation and quantitation difficult. Sample preparation: Minimal (included here for comparison only).
Ion scattering spectroscopy (ISS)	Monolayer or less contaminant can be analyzed in the ppm range. Elemental information. Sample preparation: Surface cleaning or in situ surface creation.
Energy dispersive spectroscopy (EDS)	Qualitative and quantitative elemental analysis and elemental maps inside electron microscope. With Be window detector Na $\rightarrow$ U, with thin window detector C $\rightarrow$ U analyzed. Detection limit ~0.1%. Sample preparation: Same as SEM or TEM (wherever attached).
Wavelength dispersive spectroscopy (WDS)	Qualitative and quantitative elemental analysis inside electron microscope, no elemental mapping. Sharper peaks compared to EDS and no peak overlaps. Detectable elements C $\rightarrow$ U, detection limit ~0.2%. Sample preparation: Same as SEM or TEM (wherever attached).

microscopic techniques used by the scientific community. If one had to identify which technique is most heavily dependent on sample preparation methods (and related facilities and skill), the unanimous answer would be transmission electron microscopy. It is therefore reasonable that the longest section of this chapter is devoted to that technique.

For both optical and electron microscopy, specimen preparation is crucial, the basic concern being that the specimen prepared be a true represen-

tative of the sample. The first step obviously is to cut the specimen to size and to grind and polish the surface to expose the feature(s) of interest. These steps are commonly referred to as *metallography* even though they are applicable to all materials, and are discussed in Section 9.2.1. For reflection modes of microscopy, optical and SEM, polishing may need to be followed by etching, as discussed in Section 9.2.2.

In optical microscopy, the probing (or illuminating) beam is light that is either reflected off or transmitted through a specimen before forming its image. The image is formed by contrast between different features of the sample (brightness, phase, color, polarization, fluorescence, etc.) depending on the illuminating source. Magnification is controlled by a system of optical lenses. The limit of resolution (or the maximum magnification that will provide any meaningful contrast) is normally limited by the wavelength of the light used and not by the lens. According to diffraction theory, the closest distance between two points that can be resolved in an image is proportional to the wavelength λ.

The primary difference between optical and electron microscopy is that the latter uses an electron beam as the probe. Since 10- to 500-keV electron beams have much lower wavelengths than light, the resolution is greater. At the same time, the electron beam requires completely different instrumentation (source, collimator, detector, magnification control, etc.). Moreover, electrons are very readily absorbed by matter. Therefore, the entire path of the beam, from source to specimen to detector, has to be in vacuum. From the sample preparation point of view, this is of major significance. For specimens that may change in vacuum, biological tissues, for instance, this can be a major concern, and newly developed accessories such as environmental cells [8] need to be added to the microscope.

For scanning electron microscopy of electrically insulating materials, the surface of the specimen may be electrically isolated when bombarded with electrons. This leads to charge buildup on the specimens that makes imaging or other analysis difficult. To address this issue, special sample coating steps are often required and have been discussed in Section 9.2.3.

When transmission electron microscopy is used, the specimen has to be extremely thin (on the order of 0.1 to 10 μm) for the highly absorbable electrons to penetrate the solid and form an image. Preparing such a thin solid specimen with minimal artifacts is a very complicated problem that makes sample preparation a crucial step in the use of this technique. Therefore, a substantial part of this chapter (Section 9.3) is devoted to specimen thinning issues in TEM.

As the title suggests, in this chapter we stress solid materials and films. Therefore, special concerns related to fluids or biological specimens are not addressed [9]. We cover the most commonly applicable methods that the

user can employ in most laboratories with commercially available instrumentation. Also discussed are possible artifacts arising from each preparation step and ways of minimizing or countering them. In addition to the most widely used sample preparation techniques, some newer developments have been touched upon, but these are by no means exhaustive. It must be stressed that despite this being a mature field, many new techniques and variations are being introduced regularly [10] and it is not possible to explain or even list them all. So, some omissions are inevitable.

9.1.2. Spectroscopic Techniques for Solids

Bulk spectroscopic techniques such as x-ray fluorescence and optical and infrared spectroscopies involve minimal sample preparation beyond cutting and mounting the sample. These are discussed in Section 9.2.1. Spectroscopic techniques such as wavelength dispersive spectroscopy (WDS) and energy dispersive spectroscopy (EDS) are performed inside the SEM and TEM during microscopic analysis. Therefore, the sample preparation concerns there are identical to those for SEM and TEM sample preparation as covered in Section 9.3. Some special requirements are to be met for surface spectroscopic techniques because of the vulnerability of this region. These are outlined in Section 9.5.

In recent decades we have seen an explosion of various spectroscopic techniques for analyzing the elemental composition and chemical states of solid surfaces and films. This explosion has stemmed in part from the large number of surface- or interface-related problems seen in integrated-circuit performance, composite reliability, corrosion, nanostructured components, and so on. Instruments themselves can range from stand-alone units to attachments in national synchrotron facilities or multitechnique systems built around special fabrication sites. However, the basic principle of the technique, and therefore the basic concerns with sample preparation, stay the same.

The most commonly used surface spectroscopy techniques for analyzing the composition and chemistry of solid surfaces are x-ray photoelectron spectroscopy (XPS), auger electron spectroscopy (AES), secondary-ion mass spectroscopy (SIMS) and ion scattering spectroscopy (ISS). Of these, the first two are the most popular for quantitative analysis of the outer surface (10 to 20 Å). All of these involve bombarding the surface with a particle probe (electron, photon, or ion) and analyzing the energy of an outgoing particle. In XPS, the probe is an x-ray photon and the detected particle is the photoelectron emitted by it. In AES, the probe is an electron and the signature particle is a lower-energy electron. In SIMS and ISS, both are ions. The relative advantages and disadvantages of these techniques are tabulated

in Table 9.3. Most of the sample preparation concerns we discuss in this chapter are pertinent to AES, XPS, and ISS. Since SIMS is a completely destructive technique involving postmortem analysis, sample preparation does not require as much care.

9.2. SAMPLE PREPARATION FOR MICROSCOPIC EVALUATION

See Figure 9.1 for the basic steps in microscopic evaluation.

9.2.1. Sectioning and Polishing

The most obvious requirement, of course, is that the specimen be cut to size. The size depends on the microscope and could range from a few centimeters in a normal SEM to a few inches in a specially designed SEM. In TEM, of course, since the thickness is extremely low and the sample needs to be on a grid or support, the specimen is normally a few millimeters in size. Ductile metals are sometimes rolled into sheets before cutting into the desired size. It needs to be kept in mind that this process itself will lead to defect creation and microstructural changes that need to be annealed out [11]. Some polymers and composites are easily available as sheets anyway, so this step is not of any concern. In the large variety of bulk materials that it is not possible to form into sheets, sectioning the sample to a thin slice is the only way to start.

Sectioning is generally done by saw or cutting wheel. With a regular saw, surface damage can extend 200 μm or more into the sample. This damage depth can be reduced considerably if fine cutting tools are used. This is where a rotating saw with fine blades can help. Diamond-impregnated blades as thin as 10 μm are readily available for this purpose. These wheels have counterbalanced loading to avoid excessive pressure on the sample. Simultaneous lubrication and cooling with water, oil, or alcohol is desirable, and by proper selection of rotational speed, cutting pressure, and saw size, it is possible to get thin (perhaps 100 μm) slices of even the hardest materials, with surface damage extending to less than 1 μm [12].

A still narrower and more precise cut is possible with a wire saw, whose cutting surface is a fine wire wetted with an abrasive-containing liquid. The wire can be made to form a loop running over pulleys or can be a single length running back and forth on an autoreversal system. The main drawback with either of these designs is that the wire gets thin with cutting and might break before the specimen is complete. This is especially true when cutting hard samples. Replacing a broken wire halfway through a cut may make it difficult to resume cutting at exactly the same place.

Table 9.3. Capability Comparison of Common Surface Spectroscopic Techniques That Involve Electron or Ion Detection

Technique	Information Obtained	Elements Detected	Analysis Volume	
			Depth	Width
Auger electron spectroscopy (AES)	Elemental surface composition, lateral mapping	Li-U	0.5–10 nm	50 nm–30 μm
X-ray photoelectron spectroscopy (XPS)	Elemental surface composition, chemical states and bonding, lateral mapping	Li-U	0.5–10 nm	10 μm–1 mm
Ion scattering spectroscopy (ISS)	Atoms exclusively at outermost monolayer	Li-U	One monolayer	1 mm
Secondary-ion mass spectroscopy (SIMS)	Elemental composition profile, isotope identification	H-U	0.5–500 nm	1 μm–1 mm

Technique	Advantages and Limitations	Sensitivity	Probing Particle	Analyzed Particle
Auger electron spectroscopy (AES)	Fast, semi-quantitative, possible beam damage, very limited chemical information	10^{-3}	1- to 10-keV electrons	1- to 2000-eV electrons
X-ray photoelectron spectroscopy (XPS)	Minimal damage, very sensitive to chemical states, quantitative, depth profiling slow	10^{-3}	X-rays	1- to 1500-eV electrons
Ion scattering spectroscopy (ISS)	Exclusively top monolayer, charging effects and contamination extremely critical	Varies, higher for heavy elements	He^{+} ion	He^{+} ion
Secondary ion mass spectroscopy (SIMS)	H–He detection, very high sensitivity, quantification unreliable, destructive	10^{-4}–10^{-8}	0.5- to 10-keV ions (Ar^{+}, O^{+}, etc.)	Secondary ions

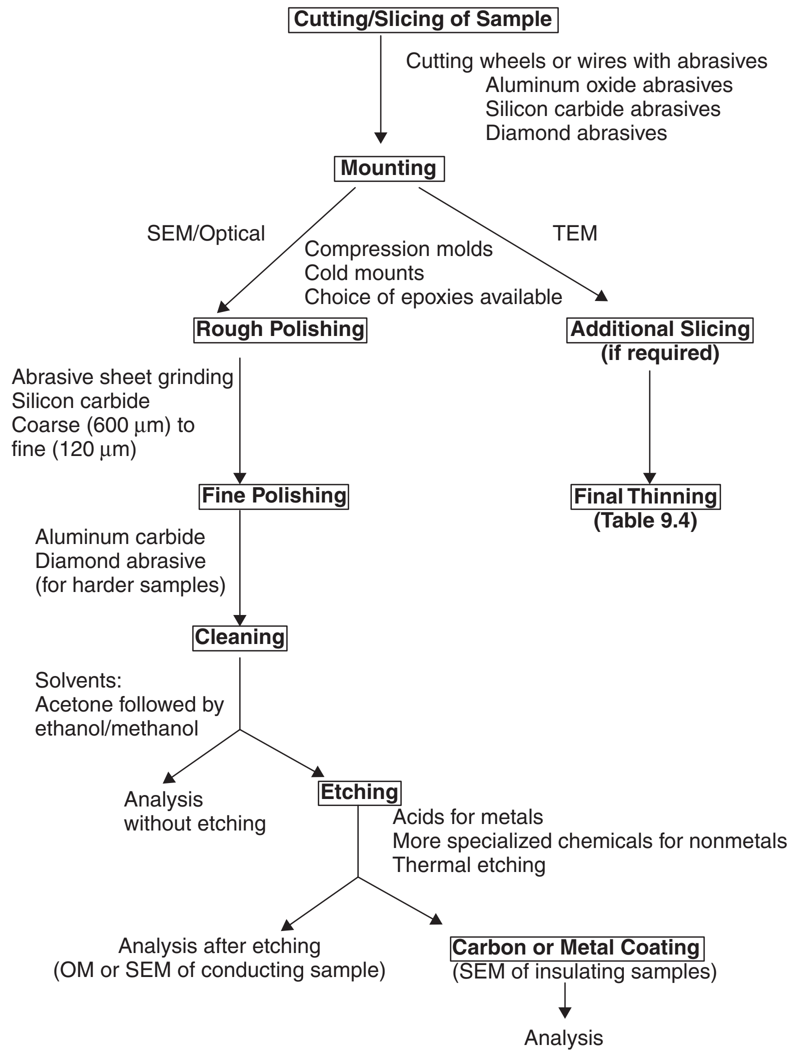


Figure 9.1. Basic steps for specimen preparation-microscopy.

A variation of the wire saw that can cut some specimens without deformation or mechanical damage is the acid string saw [13]. This is a wire saw where the abrasive is replaced by an etching agent and the cut occurs from a chemical reaction rather than mechanical abrasion. This is suitable for metals or other reactive solids that have effective etching solutions. Of

course, for chemically inert samples such as some ceramics, this is not an option and slicing has to done mechanically.

After the sample has been sliced, the surface needs to be ground and polished to get a flat face with uniform analysis conditions across the region of interest. This procedure can be tedious and, in some cases, challenging. In most cases, the cut specimen is either compression-molded or cold-mounted in a polymer mold. If this is not possible, the specimen can be glued externally on a metallic mount. The mold (or mount) makes it easy to hold the specimen by hand or machine during polishing. When the specimen is set inside the plastic mold, the edges are protected during polishing. When externally glued on the mount, the edges can be rounded during polishing.

The next step is to grind the surface on abrasive paper or cloth, starting from course grit and using progressively finer and finer grit sizes. A general guideline for simple materials is to start with 50-grit SiC paper and go through three or four levels, finishing with 600 grit. This is followed by finer polish, Al_2O_3 suspension is recommended for most except for very hard surfaces, where diamond paste can be used. These suspensions and pastes are available with abrasives as fine as 0.05-μm particle size [14]. At each step of polishing, deformations introduced during the previous step need to be removed [15]. Since very little material is removed at the finer steps, the preceding step has to be thorough. Polishing wheels on which the abrasive is placed can be rotated at different speeds and the sample (mounted or molded) can be held on it with moderate pressure, either manually or on an automatic arm. Automatic polishers often offer better reproducibility [16]. After the final grinding step, no scratches should be visible on the surface.

9.2.2. Chemical and Thermal Etching

Polished unetched samples can show macroscopic cracks, pits, and so on, but no microstructural details because there is not yet any contrast-producing feature on the surface. These will be revealed by the etching process. The term *etching* is generally used to mean physical or chemical peeling of atomic layers. However, in the context of surface etching for microstructural evaluation, the idea is to expose the lowest-energy surface by chemical or thermal means. This will expose defects such as grain boundaries and bring out the contrast between different phases or different crystallographic orientations that etch at different rates. Specimen etching is a vast and matured area in itself, and several handbooks are available that describe and tabulate recipes for final polishing and etching of specific materials [6,17–19].

A simple example of the importance of the etching process is illustrated in Figure 9.2. The freshly polished surface prior to etching will have no varia-

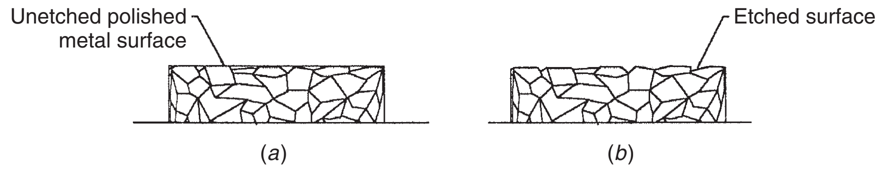


Figure 9.2. Effect of etching on surface profile; the polished unetched surface (*a*) is completely flat with no features to show, whereas the etched surface (*b*) shows the microstructural profile.

tion in contrast across the grain boundary because it is completely flat. But during chemical attack on the surface, the grain boundary region will be eroded faster than the rest of the grain and therefore there will be very fine grooves along the boundary that will be visible under the microscope.

The choice of a chemical etchant is, of course, very dependent on the sample that needs to be etched. As mentioned earlier, a large number of compilations are available in the literature and this is an ever-expanding field in an age of ever-increasing use of new materials. The common thread among all these recipes is that the surface material needs to be chemically attacked so that fresh surface is exposed underneath. For metallic elements and alloys, these are predominantly acid- or peroxide-containing solutions. Aqueous nitric acid (hot or cold) is often the first solution tried. A stronger etchant could be a mixture of nitric, hydrofluoric, and hydrochloric acids. In some cases, methanol is used as a solvent instead of water. Hot orthophosphoric acid can be used in the case of inert oxides. Many electronic materials such as GaAs and recently, superconductors [20] can use halogen in ethanol. The extent of etching needs to be monitored carefully. After sufficient contrast is brought out, the specimen should be rinsed thoroughly in a nonreactive solvent (e.g., acetone, alcohol) to prevent further corrosion. It must be noted that the same ingredient that is used for limited surface etching in optical microscopy or SEM is often used in a different consistency and potency for sample thinning that is crucial for transmission electron microscopy. Therefore, more details of chemical etching and polishing are given in Section 9.3.3.

If the material is so inert chemically that no corrosive etchant is available, allowing the surface to relax at a high-enough temperature (in the range where substantial diffusion is possible) will have a similar effect. Diffusion of atoms will tend to bring the surface to its equilibrium or quasi-equilibrium state [21,22], which often leads to phenomena such as faceting of certain planes and grain boundary grooving. These processes will lead to contrast between different areas of the sample.

9.2.3. Sample Coating Techniques

In the SEM, electrically nonconducting specimens can absorb electrons and accumulate a net negative charge that repels the following electron beam, thereby degrading the image [21]. To a certain extent, lowering the accelerating voltage or reducing the spot size can reduce this artifact, but that would limit the instrument capability considerably. The best way to counter this is to coat the specimen with a thin conducting film. In the past, organic antistatic agents have been tried, but the best method is to deposit a thin film (tens of nanometers) of a metal or carbon [6]. This step, although not mandatory, is also used in some TEM studies to enhance electronic contrast.

It needs to be pointed out that inside most electron microscopes, spectroscopy is also performed. The electron beam used for imaging can excite x-ray fluorescence, especially in the heavy elements of the sample, and the energies of these photons can be analyzed to identify these elements. For this type of analysis (energy dispersive spectroscopy being the most common configuration), the x-ray signal from the coating element needs to be kept in mind. Carbon is the most benign because it gives an almost undetectable signal. Metal coatings such as gold will give their characteristic signal and the investigator needs to check in advance whether this will interfere with any peaks from the specimen. The most common techniques of sample coating are thermal evaporation and sputter coating.

Thermal Evaporation

Thermal evaporation involves passing a current through a refractory filament that holds the evaporation source. This source can be a metal such as gold or palladium, or pure carbon. The assembly is placed in an evacuated chamber containing the sample (Figure 9.3). The filament is resistively heated by passing high current through it, and this in turn heats the evaporation source. As the vaporization temperature of this source is reached, a stream of atoms is released in the chamber. This stream of metal or carbon atoms will coat every object in its line of sight, including the sample. A common step used to ensure uniform coating is to rotate and tilt the sample stage during evaporation. This technique is sometimes called *rotary evaporation*. The reverse trick can be used in special circumstances to create the opposite effect: nonuniform coating for shadowing purposes. If this is desired, the sample is held stationary at an oblique angle to the evaporation beam so that surface features sticking out produce shadows on the deposited coating. This artifact would highlight such features.

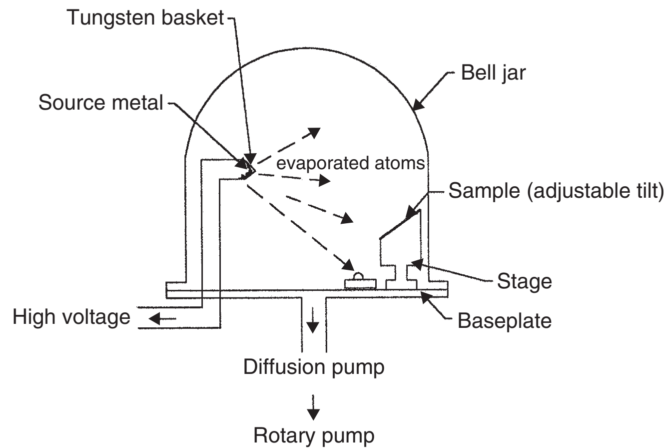


Figure 9.3. Simple thermal evaporation system.

Sputter Coating

Sputter coating involves erosion of atoms from a suitable target by energetic particles and subsequent deposition of these atoms on the sample. It requires lower vacuum than thermal evaporation coaters and does not depend on line-of-sight phenomena to coat the target. Sputter coaters are classified into five types depending on how the energetic particles are produced: plasma, ion beams, radio frequency, penning, and magnetron sputtering. Detailed designs and principles of each type are available in several books and monographs [24]. At this time, the use of sputter deposition is not confined to basic metal/carbon coating for microscopic purposes. Sputter technique is used today to deposit complex compounds in electronic devices, and many sophisticated sputtering systems and targets are available commercially. The most basic type that can commonly be used for SEM (Figure 9.4) consists of an evacuated bell jar containing a cathode made of the target material (the material with which the sample needs to be coated), an anode, and the sample stage. Inert gas (Ar, N) is bled into the chamber and energized by the creation of glow discharge. This kicks off target atoms which are deflected in all directions by collision with the gas atoms and are eventually deposited on cold surfaces, including the sample. The overall drift is toward the anode, but the random motion of individual metal atoms makes the deposition multidirectional in the surface scale, and even rough surfaces can be uniformly coated.

Artifacts of Coating

Some artifacts may be caused by surface deposition of which the user should be aware. One possible problem that can arise in either of the two techniques

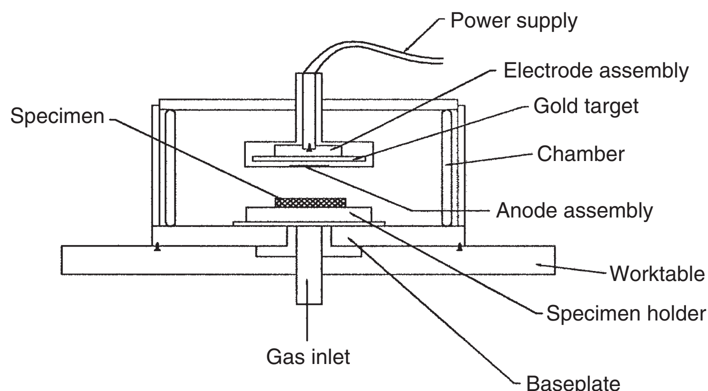


Figure 9.4. Commonly used sputter-coating arrangement.

is hydrocarbon contamination. Vacuum pump oils and improperly cleaned starting sample are common sources. This may produce uneven coating or, in extreme cases, cracks or discontinuities in the coating. Another artifact is thermal damage, which sometimes manifests as pitting or local melting of the film. This can be avoided by increasing the source–sample distance in thermal evaporators or by using lower plasma currents and voltages in sputter systems. Modern deposition chamber designs have reduced this problem to a great extent, and only very sensitive samples require cooling stages. An artifact that may be quite pronounced in thermal evaporators and much less troublesome in sputter coaters is distortion of a rough surface profile. Features that rise above the surface shadow the region behind it and can be exaggerated, whereas pits or grooves that are below the surface level are shielded and do not obtain a coating. This can be avoided by rotating and tilting during the deposition process. A problem that can arise in poorly designed sputter coating systems, but not in a thermal evaporator, is surface etching of the specimen itself. Sometimes a material from a chamber component other than the target material may be sputtered onto the sample. But these problems can easily be recognized and corrected by chamber modifications.

9.3. SPECIMEN THINNING FOR TEM ANALYSIS

As mentioned earlier, once a TEM sample is cut into a thin roughly uniform slice, it needs to be thinned extensively in regions where it will be electron transparent. In extremely rare cases of synthetic materials, the specimen itself can be prepared as a thin film. This is often the technique used to make

test specimens for calibrating the instrument [7]. In such specimens, sample thinning is not an issue. But in the vast majority of TEM studies, the starting material is much larger and a slice from it is cut out which eventually needs to be thinned down to an acceptable thickness.

The maximum thickness allowable depends on the electron scattering factor of the material. A general rule of thumb is that the higher the atomic number of the elements in the sample, the greater the electron scattering factor and the thinner the specimen needs to be. Therefore, under identical conditions, an aluminum (Al) sample could be more than 10 times thicker than a uranium (U) sample to provide the same TEM picture quality. For amorphous samples under 100-kV electrons, a few hundred nanometers of Al and a few tens of nanometers of U are often the limits for regular TEM analysis. Higher accelerating voltages can tolerate thicker specimens. When the sample is crystalline, the thickness requirement need not be as stringent. Bragg reflection at certain orientations allows an anomalous thickness of the material to be penetrated [7,11]. So a curved specimen can have certain regions with enhanced transparency (regions that have the correct orientation for Bragg's diffraction condition). The alternative approach used in all TEM systems today is to have a tilting stage. Here, the specimen can be tilted so that any particular area can be put in a Bragg's or anomalous absorption condition. Modern TEMs also have image-intensifying devices for low-intensity operation which can "see through" slightly thicker samples.

All things considered, specimen thickness is still a crucial issue in TEM, and all thinning techniques are geared toward creating foils or regions in foils that are 0.1 to 10 μm in thickness. Often, it is convenient to keep thinning a region until the sample is perforated near the center, with a ring of thicker specimen outside to provide support. The edge of the perforation will probably have thin regions suitable for analysis. This can be accomplished by starting with a "dimpled" sample. This means that the sample is cut such that a small region near the center has a smaller cross section that its surrounding (Figure 9.5*a*). Dimpling can be accomplished by any of the modern machining and micromachining tools, such as spark machining, ultrasonic drilling, photolithography, and jet drilling. The most common route is to use a mechanical dimpler, which could be as simple as a 1-mm rod tool. A second option is to start with a wedge-shaped sample (Figure 9.5*b*) supported at the thick end. After final thinning, the tip of the wedge will have thin regions of acceptable transparency. A third approach, more commonly used in conjunction with chemical or electropolishing, is the window technique. Here, the specimen is protected on the outer edges by a chemically inert lacquer that can be painted on to form a frame. Subsequent thinning will allow only the unprotected window to be thinned down (Figure

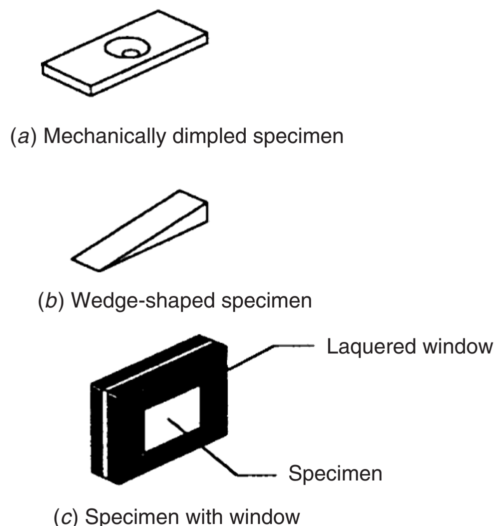


Figure 9.5. Specimen geometries prior to the final thinning step: (*a*) dimpled specimen; (*b*) wedge sample; (*c*) lacquered window for chemical or electropolishing.

9.5*c*). A specimen that is cut into one of the shapes above can subsequently be thinned down to electron transparencies. The most commonly used methods for final thinning can be categorized as described below.

9.3.1. Ion Milling

Ion milling involves bombarding the specimen at an oblique angle with a beam of inert gas ions (such as Ar) so that surface atoms are stripped off. The scientific principle behind ion-beam thinning and semiquantitative treatments of the thinning process are available in many books [25]. In general, ion bombardment is a very versatile process that can be used in several ways. When low-energy (1 to 5 keV) ions are used at oblique incidence to the surface, the erosion or sputtering rate can be very slow. This layer-by-layer erosion at the atomic scale, used extensively for cleaning and contamination removal of surfaces, is discussed in Section 1.5. At higher voltages and medium beam currents (typically, 5 to 10 keV voltage and 200 $\mu A/cm^2$ current density of Ar^+ beams), ion bombardment can be used for macroscopic thinning of TEM specimens at a reasonable rate.

A schematic of the experimental setup is shown in Figure 9.6. (This particular apparatus has two chambers, so that two samples can be thinned simultaneously, but it is also common to have a single-chamber ion mill.)

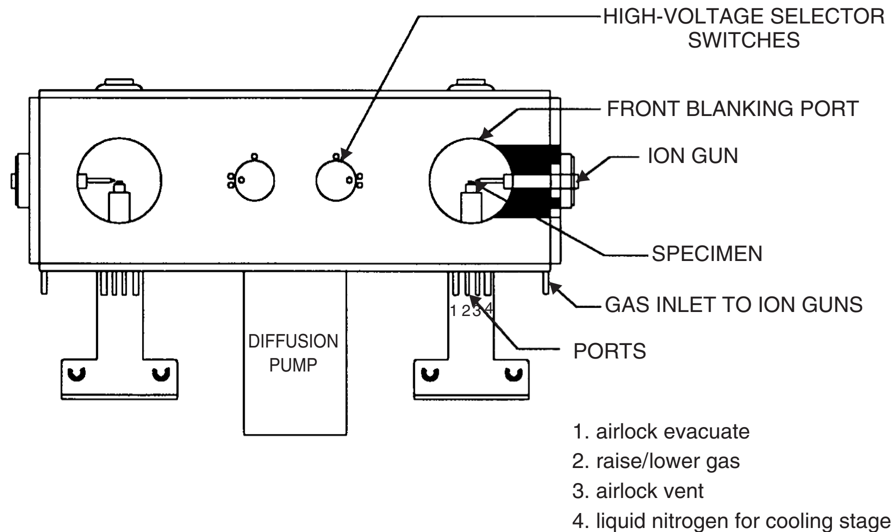


Figure 9.6. Ion milling apparatus.

The basic requirement is a diffusion-pumped chamber attached to an ion gun. The ion gun is filled with high-purity inert gas such as Ar. This gas is accelerated between two electrodes with a high potential difference. This ionizes the gas and a beam of focused and collimated gas particles is aimed at the specimen surface. Modern electronics allows very precise manipulation of the ion beam in several ways. Most ion milling machines are single-beam systems where one surface of the specimen is thinned. Alternatively, double-sided machines are also available where there are two ion beams focused on either side of the same specimen that is milled from both the top and bottom surfaces.

The primary advantage of ion milling is that it is universally applicable to any solid material. The major possible artifact that needs to be understood and monitored by the investigator is beam-induced damage [10,26–28]. There are many aspects to changes in the near-surface region caused by ion beams. Some changes are related to very superficial surface bonding and compositional changes that may not be of much concern in TEM. But other "deeper" changes that can influence TEM studies are structural and compositional alterations. Figure 9.7 shows a ripple pattern on a carbon fiber that has been ion milled for TEM observation. The exact mechanisms that lead to such an alteration are not always clear, but beam-induced roughness is often to blame.

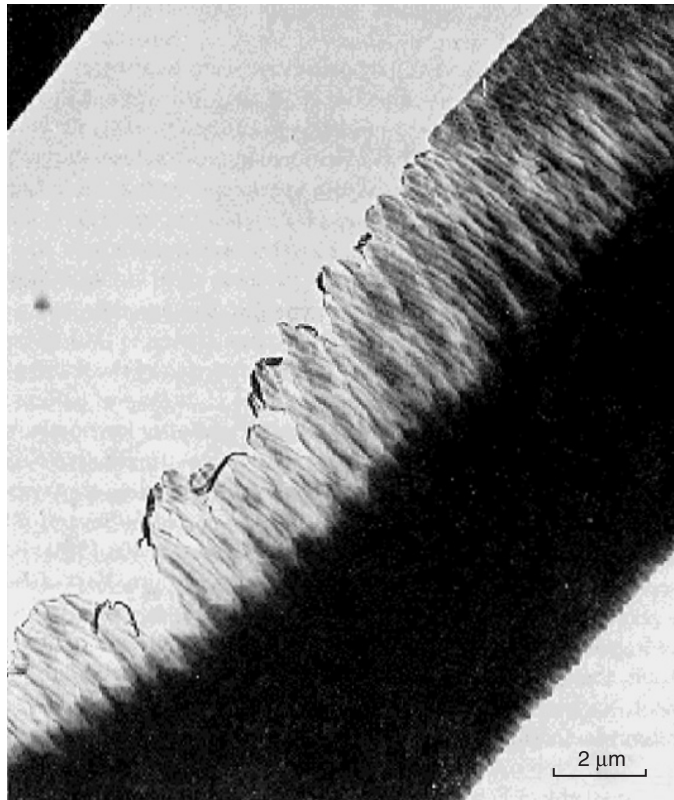


Figure 9.7. Carbon fiber ion-milled for TEM analysis; the ripple pattern is a common observation attributed to the ion milling process. (Adapted from Ref. 11.)

Many artifacts are further aggravated by sample heating because the ion milling process can cause a substantial increase in temperature in some materials. As an example, temperature increases of 100 to 370°C have been reported for semiconductor materials under normal conditions [26]. These effects can be minimized by (1) keeping the ion current density low, (2) using a lower incident angle, or (3) using a heat sink. The latter option is available in most new machines where the specimen can be mounted on a ''cold stage'' that has liquid nitrogen circulating through it.

9.3.2. Reactive Ion Techniques

Reactive ion techniques are relatively recent and popular modifications of the traditional ion milling technique described earlier. Here, a reactive gas is

used to supplement or replace the inert-gas ions. This approach is becoming widely available because reactive ions (mainly halogen-containing gases) are being used extensively by the semiconductor industry for cleaning and patterning very large scale integrated (VLSI) device materials.

In reactive ion-beam etching (RIBE), the inert gas is replaced completely by a chemically reactive gas, so the sample is bombarded with a stream of ions that have a strong interaction with the substrate, and material removal can be very rapid. However, instrument corrosion can be a major concern. The ion gun, milling chamber, and pumping system are all exposed to large quantities of reactive gases and are prone to degradation.

This problem is reduced in the chemically assisted ion-beam etching (CAIBE) approach, which is a compromise between RIBE and inert ion milling. In this technique, a reactive gas is kept in contact with the area as it is being milled with inert Ar ions. For several compounds that produce undesirable artifacts with inert ion milling, RIBE or the gentler CAIBE can be useful alternative [30] dry milling procedures. Figure 9.8 shows such an example in a compound semiconductor (InP). Regular ion milling produces islands of metallic indium due to preferential sputtering of P. This artifact is eliminated completely when iodine-assisted CAIBE is used.

9.3.3. Chemical Polishing and Electropolishing

Chemical polishing and electropolishing were the most commonly used techniques in the past when metals were the materials most commonly studied in TEM [11]. The idea is to corrode the material rapidly and wash away the corrosion products so that it keeps getting thinner. The main difference between these polishing steps and the surface etching step discussed in Section 9.2 is that here, rapid and uniform material removal is the prime concern, whereas in chemical etching case, the goal was to expose low-energy surface configurations in order to enhance contrast.

The key again is selection of the proper chemicals. Here, three functions are required of the polishing chemical: an oxidizing (corroding) agent, a depassivator that constantly dissolves the stable or passivating layer formed near the surface, and a viscous component that lingers near the surface to provide macroscopic polishing. For standard metals (and recently, for other materials) tabulated recipes are available in the literature [11]. The easiest method of chemical polishing would be to dip the sample in the chemical using tweezers or a clamp. Slight heat may be applied if required. Since the goal of a final thinning step is to cause perforation, a weak zone may be created by using a dimpled specimen or a window sample and dipping it halfway into the reactive chemical. Attack occurs most rapidly at the solution surface, starting the perforation at the center in that level. Since chemi-

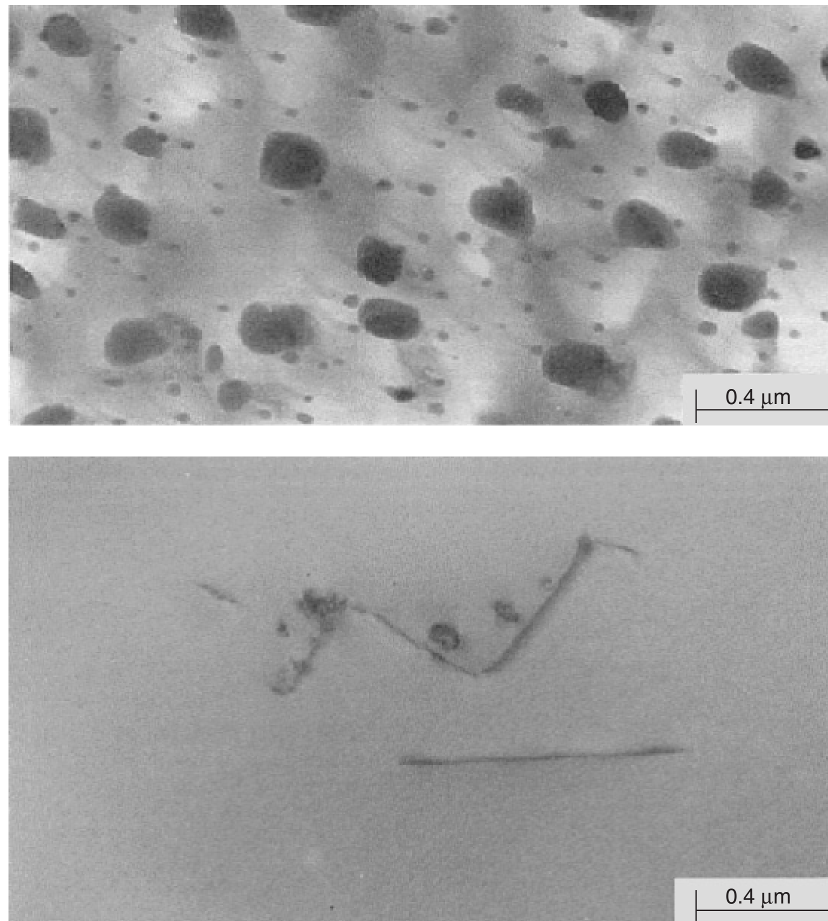


Figure 9.8. Influence of reactive gases on ion milling of delicate materials. The top figure shows an InP specimen after regular Ar-ion etching. Islands of metallic indium are formed by this process. The bottom figure shows same material thinned by iodine-jet-assisted ion etching (CAIBE). The islands are not formed and actual nanostructural features can now be studied. (Adapted from Ref. 30.)

cal polishing uses primarily strong corrosives at high temperatures, it is difficult to control the final stages of thinning once perforation begins. This can be eased in case of conductive specimens by using an electric field to control the potency of the chemical (electroplishing).

The term *electropolishing* is used when an electric potential is applied through the chemical solution using the specimen as the anode. A simple

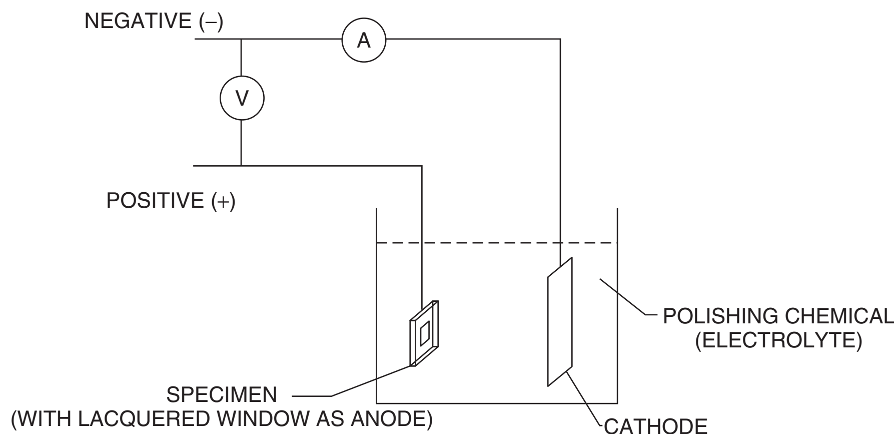


Figure 9.9. Schematic of an electropolishing unit.

schematic is shown in Figure 9.9. At low voltages, current through the electrolytic cell increases linearly with voltage and slow surface etching occurs. At higher voltages, where the current–voltage plot indicates uniform current, steady removal of material occurs at the anode. This voltage range is preferred for thinning purposes. Each sample–electrolyte system is calibrated for optimum conditions, and a large number of studies are summarized in handbooks and textbooks [11].

An important variation of electropolishing is the jet polishing technique. In this method, the electrolyte is introduced as a jet through a nozzle. The jet can be directed parallel or perpendicular to the sample, depending on what flow pattern is desired. Parameters such as sample visibility and thinning geometry are taken into consideration in different designs for commercial jet polishing systems.

Needless to say, all wet chemical techniques should be followed by thorough and repeated washing and drying after processing. Residues from insufficient cleaning can be a major problem not only for surface spectroscopy techniques (discussed later), but also for TEM analysis, where every "speck" of solvent residue is considerably magnified (Figure 9.10).

9.3.4. Tripod Polishing

It is possible to prepare thin foils from hard materials by mechanical methods alone. This is especially useful for modern nonmetallic electronic materials such as compound semiconductors and multication oxides. These materials are not easily polished chemically, and ion beams can cause unequal

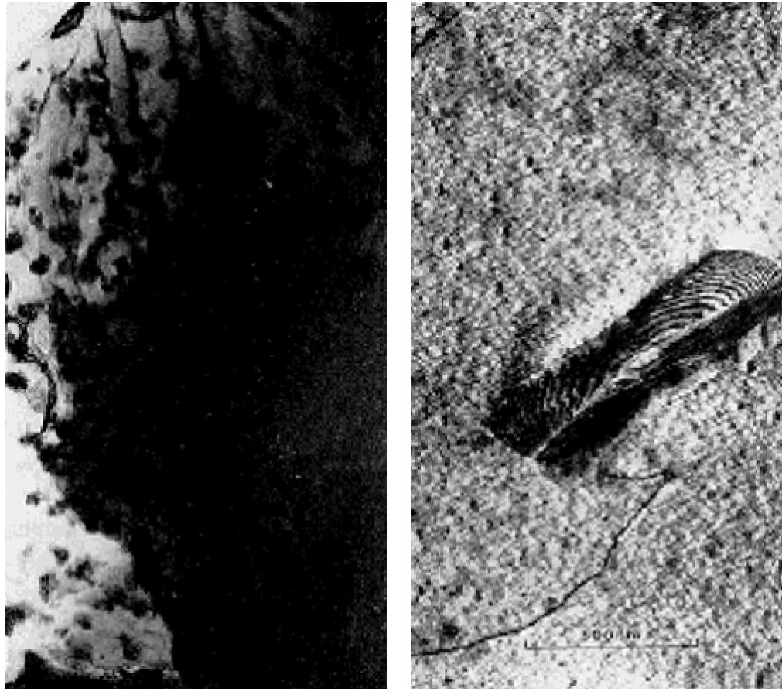


Figure 9.10. Importance of specimen cleaning after chemical or electrochemical processing: The image on the left was inadequately washed, and the image on the right was taken after thorough washing. (Adapted from Ref. 11.)

sputtering of different elements, thereby changing the material [10,28,29]. Modern mechanical polishing setups such as the tripod polisher [31] can be especially useful for these samples. This setup (Figure 9.11) allows lapping of the material with a progressively increasing wedge angle so that the final specimen is thin enough for electron transmission at one end. One side of the sample is polished by a conventional technique to the finest final polish available (0.05-μm alumina, if possible). The specimen is then glued on the polished side to a platform that is held by three micrometers (forming a tripod). The micrometer heights can be adjusted individually so that the exposed side of the specimen faces the polishing wheel at any desired angle. The idea is to keep lapping off this side with a gradually increasing angle with respect to the other side so that the final shape is a wedge. This is a delicate operation, especially in the final stages when the sample is very small and fragile. But with some experience, this often becomes the quickest and least damaging thinning route for complex compounds.

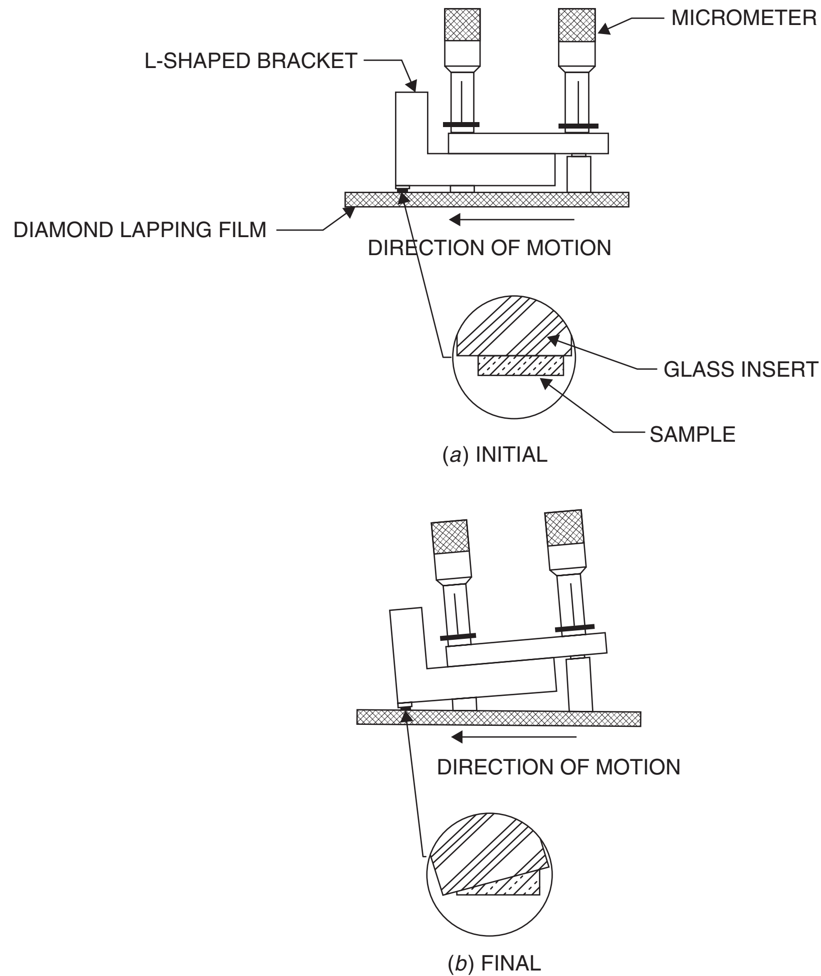


Figure 9.11. Modern tripod polisher.

9.3.5. Ultramicrotomy

Ultramicrotomy was one of the oldest sample preparation techniques used for soft biological specimens. With the improvement in instrumentation capabilities, this approach is making a comeback into the mainstream engineering materials, especially polymers. It involves directly sectioning an extremely thin sample using an ultramicrotome and dropping it in a liquid, where it will float and can latter be retrieved. A schematic of the ultra-

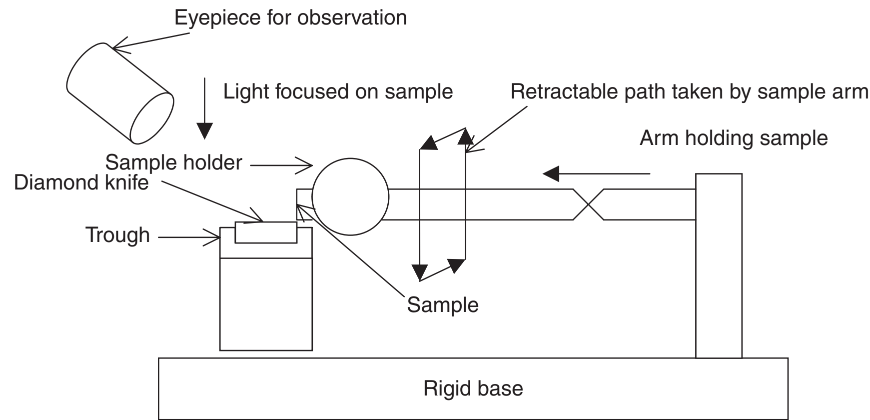


Figure 9.12. Schematic of a modern ultramicrotome.

microtome is shown in Figure 9.12. Samples processed in this way are different from those obtained by other techniques discussed so far. The earlier techniques resulted in thin wedges or perforated foils that were supported by thicker parts of the specimen. Here, the entire sample is a thin piece that has to be self-supporting and also retrievable from the liquid into which it is dropped. It must be noted that except for strong bulk materials strong enough to withstand the cutting force and remain rigid, most samples require embedding, special trimming, and specimen holding arrangements. It is therefore a slightly more complicated method of sample preparation, but works very well in some cases. Some recent articles [32] give detailed description of accessories and recent variations used by investigators. Figure 9.13 is an example of how an ultramicrotome section can reveal features distributed over a large area.

9.3.6. Special Techniques and Variations

Since the consumers of the TEM technique come from a wide variety of backgrounds, interesting variations of sample preparation are introduced all the time. Some examples of unusual approaches are as follows [8]:

- Modern lithography techniques can be used to make many submicrometer windows on the sample. The sample can then be thinned to obtain many small transparent regions. The advantage is that if lithography facilities are available, several regions of the specimen can be analyzed simultaneously for statistical sampling.

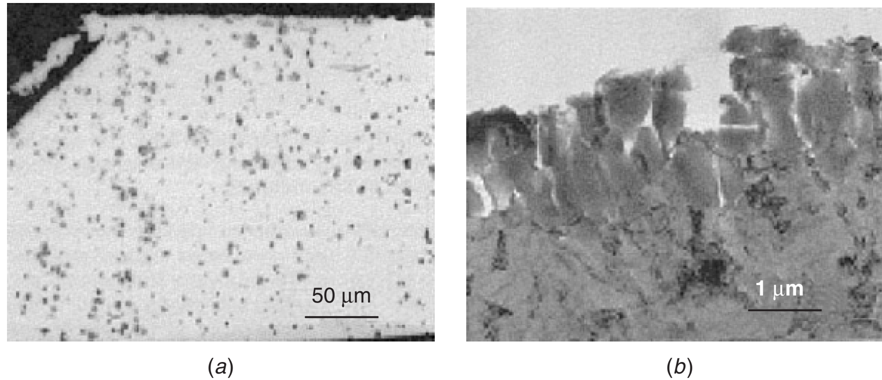


Figure 9.13. Correlation of ultramicrotome specimens with more traditional images. Image (*a*) is from a routinely sectioned and polished specimen and image (*b*) is from an ultramicrotomed specimen of the same sample. This provides a relatively large area of electron-transparent region so that details of the grains can be studied. (Adapted from Ref. 32.)

- The conventional dimpling machine has recently been modified to perform chemical polishing with a reactive etchant [33].
- Some crystalline materials can have two cleavage planes that form a thin wedge. They can therefore be fractured along these planes to form wedges with electron-transparent regions. This technique, called *wedge cleaving*, can only be applied to specific crystals.
- A focused ion beam (FIB) can be used instead of a conventional ion mill to mill a sample. In such cases, especially targeted regions of a sample can be thinned for observation in the TEM. This technique requires expensive instrumentation but is becoming extremely popular in the age of VLSI devices and nanostructured components, where precise thinning of specific areas is necessary.

9.4. SUMMARY: SAMPLE PREPARATION FOR MICROSCOPY

In summary, sample preparation is an essential part of microscopy and there are many techniques (and variations) that can be used. The approaches very commonly used to prepare specimens for analysis are as follows: The sample needs to be cut to size using one of the slicing methods outlined. The cut sample is either set in a mold or mounted externally on a polishing mount. This step is followed by a series of coarser to finer grinding on SiC grit

paper. For optical microscopy and SEM, subsequent fine polish is done using diamond-abrasive paste or alumina suspension. Polished samples are then cleaned thoroughly and etched chemically or thermally to reveal surface contrast.

For TEM analysis, the cutting and grinding steps are similar except that samples are cut as small as one can handle. Subsequently, the ground sample is dimpled, wedged, or lacquered to provide a thin region supported by a thicker rim. It is then processed further using one of the final thinning techniques until some electron transparent regions are obtained. Table 9.4 summarizes some options, and provides guidelines for the new user. After this step, the very delicate sample is retrieved, cleaned, and placed in the grid or glued to the special holder suitable for TEM.

Table 9.4. Summary of Some Final Thinning Techniques for TEM[a]

Technique	Advantages	Disadvantages
Ion-beam thinning	Universally applicable; good for two-phase materials and chemically resistant materials; large thin areas; reproducible	Slow, ion-beam damage and structural alterations often possible
Chemical thinning	Quick	Not easy to control; chemical recipes for new materials often not available
Electropolishing	Quick and controllable	Applicable to electrical conductors only
Mechanical polishing (tripod technique or similar setup)	Fairly simple; no chemical or ion-beam concerns	Only for very hard materials or too much damage; slow and tedious; needs practice
Ultramicrotomy	Large thin areas that may not require additional thinning	High amount of deformation; not suitable for hard materials; slow; often irreproducible; needs practice
Special method: cleavage	Quick and easy	Very limited applicability (only materials that have clear cleavage planes); may introduce damage

[a] It must be noted that this is a very vast field, and many techniques, patents, and variations are used for specific applications.

9.5. SAMPLE PREPARATION FOR SURFACE SPECTROSCOPY

See Figure 9.14 for the basic steps in surface spectroscopy.

Special Constraints for Surface Spectroscopy

As discussed earlier, bulk spectroscopic techniques do not require much sample preparation and are not included here. Surface spectroscopic techniques have special concerns. Since the surface is the outer skin of the solid, it is the most dynamic and sensitive region. It can change constantly by two types of mechanisms: (1) exchanging atoms, ions, or molecules with the environment: (2) restructuring and redistributing atoms with the bulk. The first mechanism (exchange with environment) results in impurity adsorption, vaporization, and corrosion. The second process results in segregation, relaxation, and restructuring of the surface. Because of the evolutionary nature of this region, the major sample preparation concern is to make sure that the required surface (and not a contaminated or altered one) is the one that is exposed to the probe and getting analyzed. In other words, preserving the test surface or cleaning it with minimal alterations is the major sample preparation challenge.

The other feature specific to surface spectroscopy techniques is that they require ultrahigh vacuum (10^{-8} to 10^{-11} torr) since they involve detection of charged particles (Table 9.3). Therefore, the investigator needs to be aware if their sample is prone to degradation or alteration in vacuum. This is especially true of biosolids that prefer a liquid environment or even complex compounds that may have volatile components. In some cases, surface spectroscopy is still performed on such solids taking the vacuum-related artifacts into account. In other cases, differentially pumped sample holders might be designed which can keep the test surface at somewhat higher pressure than ultrahigh vacuum, but the range of allowable environments is not very large. Owing to the extremely low penetration depth of low-energy electrons, the extent of pressure and atmospheric manipulation possible for successful electron spectroscopy of vacuum-sensitive samples is extremely limited, even to this day.

From a sample preparation point of view, it must be remembered that several of the methods may require processing in vacuum, which implies remote sample handling and manipulation from outside the test chamber. There is a wide variety of intricate commercial instrumentation available for this step, and most designs allow additional customization, depending on vacuum chamber configuration.

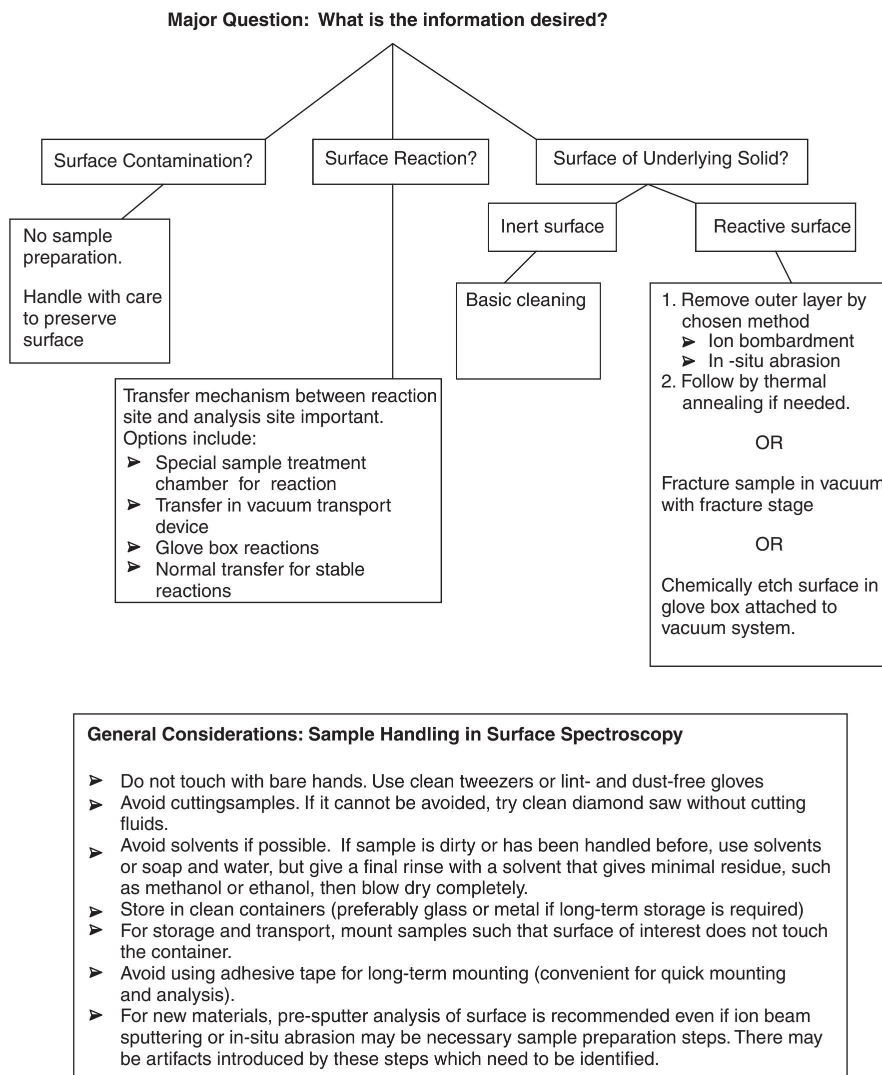


Figure 9.14. Specimen preparation/handling for surface spectroscopy.

Sample Handling and Storage Requirements

It cannot be overemphasized that these techniques study the top 1 to 20 nm of the surface, which is extremely prone to contamination. Therefore, sample handling and storage become serious concerns for these techniques,

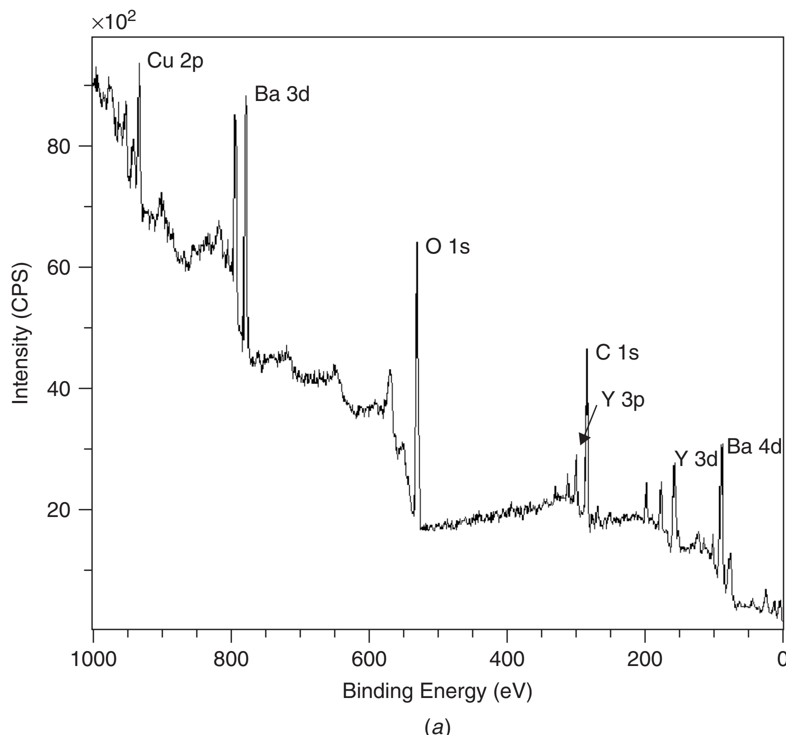
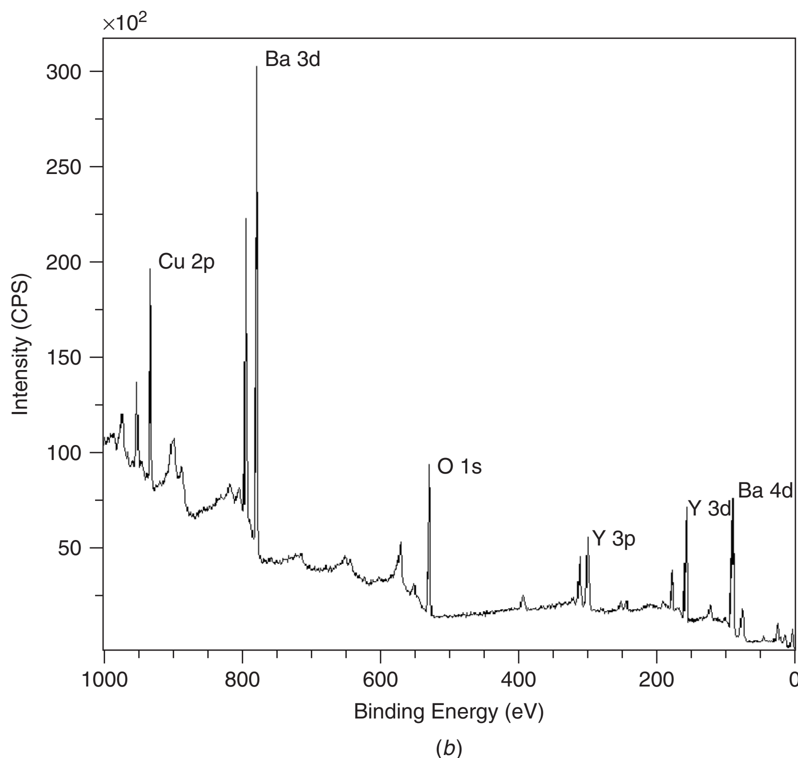


Figure 9.15. Influence of sample cleaning on XPS scans taken on a thin-film superconductor. (*a*) Survey scan from an as-received surface. (*b*) Survey scan from surface after ion-beam (sputter) cleaning. Note the reduction in the C1s peak after cleaning. (*c*) Comparative Ba3d scans from both cases. Note the change in shape and size as the surface contaminant layers (probably containing carbonates and hydroxides of Ba in addition to other components) are removed. The peak shapes and intensities of other cations change, too. Initial data represent the composition and chemistry of the contaminant layer, whereas that from sputtered sample represents those of the pure underlying superconductor (possibly with sputter-induced changes that need to be accounted for).

more so in some samples than others. The general rule of thumb is that high-surface-energy materials (such as metals, especially the reactive ones) are always coated with atmospheric reaction products, whereas low-energy surfaces (such as Teflon) are relatively stable. The stable group can be analyzed directly on introduction into the vacuum chamber. But a vast majority of solids fall under the former group and need to be treated in vacuum by one of the in situ methods outlined below (unless, of course, one is interested in the analysis of the atmospheric contaminant itself).

Figure 9.15 illustrates this point from XPS data taken on a complex oxide

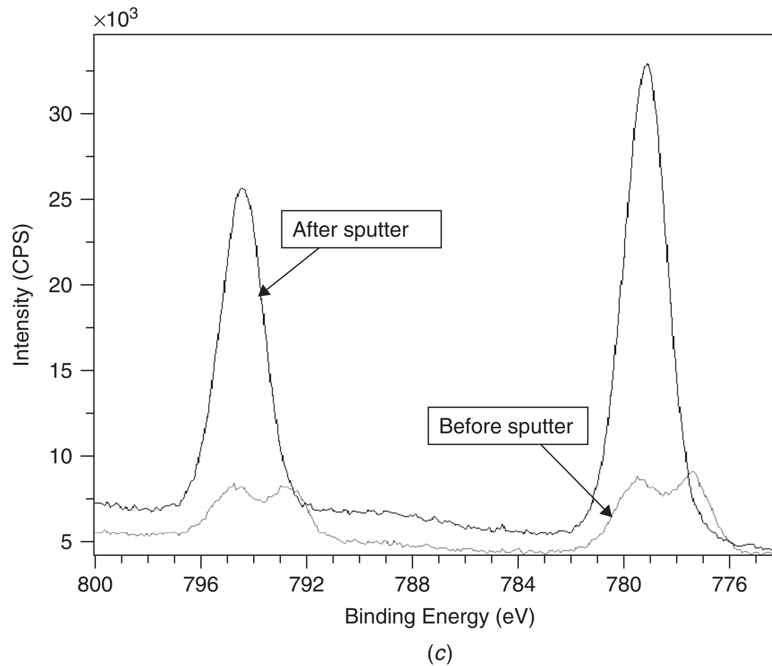


(*b*)

Figure 9.15. *(Continued)*

(thin-film superconductor). Figure 9.13*a* was taken on the as-received sample that was carefully handled and stored in a desiccator immediately after fabrication. Figure 9.15*b* was taken from the same sample after it was sputter cleaned as described in Section 9.5.1. Carbon is detected in Figure 9.15*a* as indicated by the C1s photoelectron peak. In addition, the shapes and sizes of component peaks can be substantially different, as is apparent in Figure 9.15*c*, which is the Ba3d peak. The shape change indicates that the binding environment of the detected atom is different in the as-received surface and the cleaned surface. Therefore, data prior to sample processing would be useful in identifying initial surface contaminants, whereas the data after sputter cleaning would be required for the actual composition and chemistry of the solid. Therefore, the investigator should be clear about what information is needed before processing the sample for analysis.

In all situations, grease-free, powder-free gloves and/or clean dry tweezers are essential for handling. Any grease or oil from human skin and other



(*c*)

Figure 9.15. *(Continued)*

sources can vaporize in the chamber and degrade the vacuum in addition to contaminating the test surface. In general, storage in a desiccator or a partially evacuated chamber is recommended. It is sometimes necessary to leave the sample in a vacuum chamber overnight to desorb atmospheric contaminants. If the sample is mounted with adhesive tape or silver paint for analysis, care must be taken to check the vacuum compatibility of the adhesive as well as the solvent/sample compatibility. Some solvents can diffuse along the sides of the sample and leave a film of contaminant on the analysis surface.

If a surface-sensitive solid is processed in one site and needs to be transported to the analysis site without exposure to the atmosphere, a "vacuum briefcase" or special transportation module needs to be used. This would consist of a small portable vacuum chamber that is capable of attaching and transferring samples between processing and analysis stations. Understandably, designs of such instruments are system specific and often complicated. Most manufacturers of vacuum and surface analysis systems can offer customized options for specific systems.

9.5.1. Ion Bombardment

Ion bombardment is the most common treatment used for surface cleaning inside vacuum and almost a standard attachment in most surface analysis instruments. It requires a controlled gas inlet and an ion gun. The former requires a source of high-purity noble gas (normally Ar), a regulated line between a high-pressure gas container, and an ultrahigh-voltage (UHV) system followed by a precision leak valve that allows extremely controlled introduction of gas into the chamber. The ion gun ionizes the neutral gas atoms introduced and accelerates them to a specific energy. Several designs are available, some with additional capability that can focus, raster, and manipulate the outgoing beam in several ways. The basic principle is to shoot noble gas ions (normally, 0.5- to 5.0-keV Ar^+ ions) at the surface. This results in atoms from the surface being eroded away by energy exchange with this beam. It can be regarded as a slower and more controllable version of the ion milling process used for thinning TEM specimens (Section 9.3.1). In this process, also termed *sputtering*, the rate of material removal is determined by using standards having known thickness. Of course, the sputter rate of each solid will be different other factors remaining identical, but a commonly used standard is an epitaxially grown oxide film on Si. The parameters of the ion beam (beam voltage, gas flow rate, current densities, etc.) are adjusted in a given instrument to maintain a sputter rate of about 3 to 5 nm/min for SiO_2.

Ion bombardment is a relatively severe treatment and can introduce artifacts in terms of compositional, chemical, and topographic changes. Compositional changes can be caused in compounds where different elements are likely to have different sputtering rates [28,36]. Chemical states of elements can also change. For instance, several electronic oxides are known to show lower oxidation states of cations after sputtering [28]. Any initial irregularity or hard particle on the surface can result in increased roughness after sputtering. Chemical and compositional changes cannot be compensated for and therefore should be taken into account during data analysis. Physical roughness can sometimes be dealt with. In some cases, heating the surface after sputtering (annealing) can soothe out surface irregularities. However, all samples cannot tolerate high temperatures. In rare instances, the sample is rotated during sputtering or, alternatively, two or more guns are used to sputter at different angles. These options can reduce the extent of topographic roughness caused by sputtering but add substantially to the cost of the machine.

Despite these artifacts, sputtering is the most versatile, robust, and universal surface cleaning tool used in electron spectroscopy. It can also be used in conjunction with the analysis tool to perform what is commonly referred

to as *depth profiling* of the specimen. Depth profiling involves bombarding a specific area of the specimen surface with Ar^+ ions and analyzing the freshly exposed surface after each bombardment. This sputter analysis cycle is repeated several (10 to 100 is typical) times to obtain compositional and chemical information of the solid as a function of depth from the surface. This combination of sample preparation and analysis capabilities makes this tool very popular in surface spectroscopic systems.

9.5.2. Sample Heating

Some stable surfaces that tend to absorb only loosely bound surface contaminants can be cleaned by heating alone. Refractory metals and silicon surfaces can be cleaned sufficiently by *flash heating*, which implies heating them to a very high temperature for a very short time whereby surface oxides become unstable and vaporize in vacuum [34]. Heating of a specimen can be as simple as passing current through the sample holder (many labs build this in-house) to sophisticated heating/cooling stages available commercially that can have programmable heaters for heating and liquid nitrogen pumps for cooling on the same device. It must be noted that while heating alone can clean only few types of solid surfaces, heating in conjunction with ion beams can be adapted to preparing a wide variety of materials.

9.5.3. In Situ Abrasion and Scraping

In situ abrasion and scraping is a specialized method for cleaning relatively soft solid surfaces. A razor blade or a grinding tool (brush, abrasive grinder, etc.) is attached at an appropriate angle to rotating or sliding shafts inside the vacuum system. The surface can thus be scrubbed while inside the chamber prior to analysis. Several types of UHV abrading tools are available commercially, the choice depending on the sample to be cleaned. Needless to say, the cleanliness and purity of the scraping surface are important. Moreover, care should be taken not to use the same scraper on different surfaces without in-between cleaning, as this will result in cross-contamination between samples.

9.5.4. In Situ Cleavage or Fracture Stage

A specialized method for sample preparation is to fracture or cleave the sample inside the vacuum system, thus creating a fresh surface for immediate analysis. Some crystalline materials (semiconductors, anisotropic structures such as graphite, etc.) have preferred cleavage planes that can be sectioned inside the chamber using a blade or chisel (operated through bellows

from outside). Other materials can be introduced with a notch or weak spot in a specially designed fracture stage so that the sample is broken inside the chamber and the newly exposed surface placed in analysis position. This type of sample processing is especially useful in studies where one needs to investigate failure mechanisms (intergranular, intragranular, along specific phase boundaries, etc.). In situ fracture attachments can be obtained in several complicated designs and are beyond the scope of this chapter. Some specific examples can be seen in the references cited or manufacturer brochures [34,37].

9.5.5. Sample Preparation/Treatment Options for In Situ Reaction Studies

A large (and ever-expanding) field where surface spectroscopic techniques are used include in situ study of reaction chemistry, film growth, and so on. In these studies it is difficult to argue where sample preparation ends and sample treatment (a part of the actual experiment) starts. Such studies are almost always conducted in a system that has a sample preparation/treatment chamber attached to the analysis chamber. The initial steps, of course, would be to clean the surface by sputtering, heating, scraping, and so on. This can be followed by deposition of solids or exposure to gases/plasmas at specific temperatures and pressures. The former (deposition of solids) is in itself a large field of investigation and can be very simple or very complicated. A simple step may involve thermally heating a metal-coated filament, whereas a complex deposition may require a multimillion-dollar deposition system attached to the spectroscopic chamber. Exposure to gases is a relatively common surface preparation option that involves one or more high-purity gas containers, central manifold, and precision leak valve(s). In some ways, these requirements are similar to those for ion-beam sputtering and are often easy to install.

9.6. SUMMARY: SAMPLE PREPARATION FOR SURFACE SPECTROSCOPY

The major challenge of sample preparation for surface spectroscopy involves producing a clean, pristine surface that is well characterized and reproducible. The suitable cleaning technique will depend on several factors, such as chemical affinities, composition, geometry, vacuum tolerance, and so on. The most commonly used technique is ion-beam etching or sputtering. This step can be accompanied by or followed up with heat treatments in vacuum. Other special treatments include in-vacuum scraping, abrasion, and fracturing. Treatment with other gases can be used in rare occasions for specific

applications. Most sample preparation processes here involve specialized ultrahigh-vacuum instrumentations.

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