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2 mm in diameter is used or when the specimen edges are masked with the holder. The disc specimens can be profiled on both surfaces or one surface can be left flat. A flat surface is preferable for electron-diffraction analysis as well as for secondary electron imaging.

The mechanical preparation of specimens has been greatly simplified by the development of two instruments by Gatan Inc. (6678 Owens Drive, Pleasanton, CA 94566, USA) (Alani & Swann, 1990). The first is a holder for disc samples that is used on a polishing wheel to grind and polish discs to a specific thickness. This holder has a height adjustment for the specimen, which can be ground and polished to a thickness of 50 μm by the use of various grades of abrasive. With the second instrument, called a 'dimpler™', the polished disc is profiled or dimpled on one side. This dimple is ground and polished with a sensitivity of 1 μm. The dimpled disc is then ready to be thinned in an ion-bombardment instrument.

3.5.1.3. *Final thinning by argon-ion etching*

Argon-ion bombardment or sputter etching is the simplest method for the final thinning of electron-microscope specimens. The application of the technique to ceramics and minerals was demonstrated in the early and mid-1960's with an apparatus commercialized by Paulus & Reverchon (1961; Tighe & Hyman, 1968) or similar designs (Bach, 1964; Drum, 1965). Since that time, numerous commercial instruments have been developed and are available in most electron-microscope laboratories.

The schematics in Fig. 3.5.1.1 show two types of arrangement of the instruments. There are two ion sources for etching from both sides of a specimen, a specimen holder that can be rotated, a viewing port, and a vacuum system. In the instrument in Fig. 3.5.1.1(*b*), the ion sources tilt instead of the specimen holder and an airlock system is used for sample exchange and for monitoring the sample during thinning. The new instruments are relatively trouble free and simple to use compared with the first-generation instruments. The ion sources operate at 4 to 10 kV with variable current to control desired thinning rate and the amount of specimen damage. Thinning rates of 1 $\mu m\,h^{-1}$ per ion source are average for normal specimens. The sputtering rates depend also on the angle of tilt (Fig 3.5.1.2) with respect to the ion beam. Faster rates cause more specimen heating and greater ion damage.

The Dual Ion Mill system has two chambers such as the one shown in Fig. 3.5.1.1(*b*) (Gatan Inc.). The chambers function independently, so that two specimens can be thinned simultaneously. The sample holder is raised through an airlock to the observation window at intervals in order to monitor the thinning process. A special beam detector can be used to stop the operation when the specimen perforates.

The specially designed Precision Ion Polishing System 'PIPS™' provides precise control over the specimen thinning area and is a dedicated low-angle instrument with a high thinning rate (Alani & Swann, 1992). The ion beams can be adjusted individually to specific angles, and can be switched on and off regularly during the thinning process. Additionally, the beams can be oriented with respect to specific line features of the sample to preserve edge detail, for example, in a stacked sample (Alani, Harper & Swann, 1992). Gases other than argon can be used for special etching conditions.

Ionic bombardment produces uniquely etched surfaces that are easily recognized in light and electron micrographs. With stationary specimens, closely spaced grooves and ridges are etched parallel to the direction of beam impingement. When the specimen is rotated slowly, these ridges are smoothed and an undulating orange-peel surface is produced. The severity of etching decreases when the angle of incidence to the ion beam is decreased to near grazing angles but uneven etching is never eliminated. The orange-peel texture is randomly located with

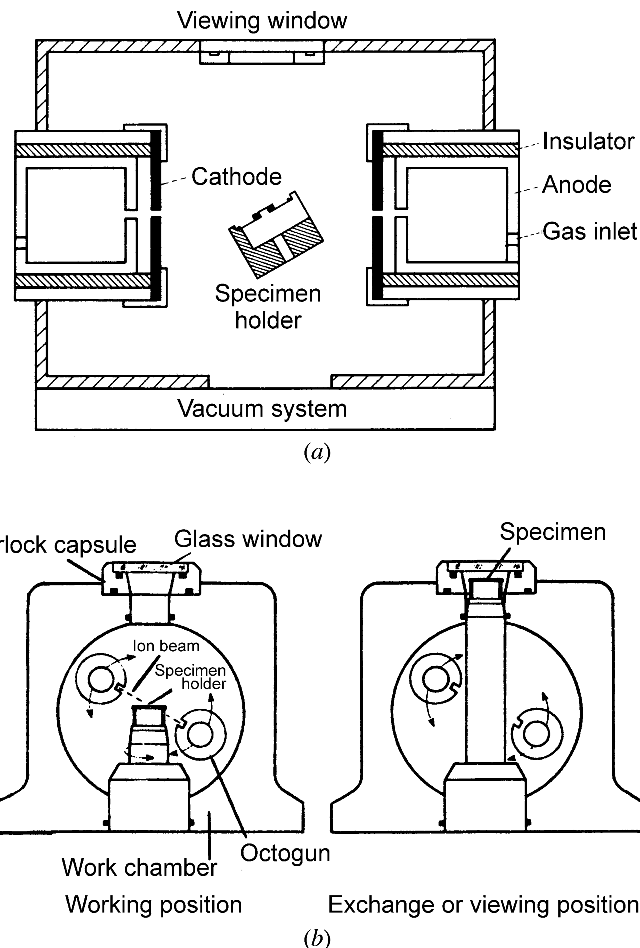

Fig. 3.5.1.1. The two types of arrangement for final thinning by argon-ion etching. (*a*) The system of Paulus & Reverchon (1961) with fixed ion sources, made by Alba. (*b*) The system of Swann with movable ion sources and an airlock for specimen viewing (drawing courtesy of Gatan, Inc.).

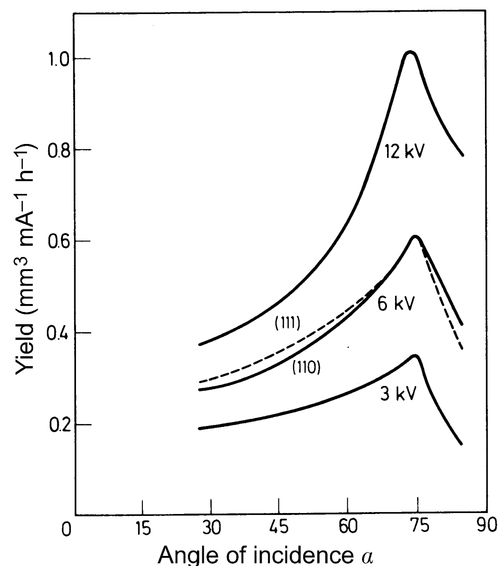

Fig. 3.5.1.2. Dependence of sputtering rate on the angle of tilt.

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Table 3.5.1.1. *Chemical etchants used for preparing thin foils from single-crystal ceramic materials; symbols: I immersion method; SFJ separatory funnel jet; CJ convection jet; BJ boiling jet*

Material	Etchant		References
Al_2O_3	85% H_3PO_4, 723–733 K	*I*, BJ	Tighe (1964)
$BaTiO_3$	H_2SO_4	CJ	Kirkpatrick & Amelinckx (1962)
$CaCO_3$	$C_6H_8O_7$ (dilute)	*I*	Braillon *et al.* (1974)
CoO	85% H_3PO_4	CJ	Remaut *et al.* (1964)
$LiNbO_3$	KOH, 623–673 K	*I*	Wicks & Lewis (1968)
MgO	85% H_3PO_4, 373 K	*I*, SFJ	Washburn *et al.* (1960)
$MgAl_2O_4$	85% H_3PO_4, 523–723 K	*I*	Lewis (1966)
MnO	HCl + NO_3		Barber & Evans (1970)
SiO_2	$NH_4F{\cdot}HF$, 453–473 K	*I*	Tighe (unpublished)
	HF, 373 K	*I*	
TiO_2	NaOH, 823 K	*I*	Barber & Farabaugh (1965)
$ZrSiO_4$	$NH_4F{\cdot}HF$ + KF (1:1), 693–703 K	*I*	Tighe (unpublished)
$Y_3Al_5O_{12}$	85% H_3PO_4, 573 K	*I*	Keast (1967)

respect to grain boundaries, dislocations, and other types of interfaces found in the thin foils. The severity of the orange-peel texture increases with bombardment time.

Subsurface ion damage occurs and is imaged as spotty black-dot contrast that is typical of point-defect clusters. The presence of the ion damage affects experiments that involve heating of the thin foil but is otherwise accepted as an artefact of the process. In materials such as silicon, the ion damage is sufficient to cause vitrification of the specimen at or near the surface. The argon that is implanted in specimens can be detected with the element-analysis systems.

One troublesome artefact of the ion-thinning process is the surface contamination that is produced by sputtering from tantalum or molybdenum or stainless steel parts of the specimen holder and the cathode. Debris may interfere with the analysis. The sputter debris is frequently located along interfaces of cracks and pores and adds to the contrast effects. Additional contamination occurs during one-sided thinning. The sputter debris adheres to the non-thinning side and must be removed by light-ion etching at the end of the thinning process.

3.5.1.4. *Final thinning by chemical etching*

Chemical dissolution methods for preparing electron-transparent specimens were developed before ion thinning was perfected. These methods are not used extensively, but they have some advantages particularly where ion thinning may disturb the surface composition or structure of a particular material. It is advantageous to use chemical dissolution in some stages of specimen preparation, for example to relate etch pits to dislocations, to prepare a defect-free surface, and to remove the ion-damaged surface from thin disc specimens (Barber & Tighe, 1965). The thinning conditions must be chosen carefully to avoid artefacts such as preferential dissolution at grain boundaries, precipitates, and dislocations, or surface precipitates produced by a supersaturated solution.

Suitable solvents and dissolution conditions must be found for each new material. Some of the chemical etchants used for thin-section preparation are listed in Table 3.5.1.1.

Devices that squirt a jet of chemical solvent at the disc or slab specimen are used to obtain careful control over the final thinning to electron transparency (Kirkpatrick & Amelinckx, 1962; Tighe, 1964; Washburn, Groves, Kelly & Williamson, 1960).

Predictable dissolution rates are obtained by varying the concentration and temperature of the etchant. Solutions can be found that will produce a smooth surface polish or an etch-pitted surface. For example, corundum is etched in boiling phosphoric acid at a temperature approximately 50 K lower than the temperature used for polishing. Surfaces with different crystallographic orientations have different dissolution rates. Useful sources of information about possible etchants are mineralogical and chemical handbooks that discuss production of etch figures and crystallographic facets (Dana & Ford, 1922; Honess, 1927).

3.5.1.5. *Evaporated and sputtered thin films*

Thin nonmetallic films are prepared by electron-beam heating and by plasma sputtering for direct applications such as optical and dielectric films and for standard samples for calibration of the X-ray and electron-energy-loss element-analysis spectrometers on the electron microscopes. The thickness, crystallinity, and composition of the evaporated films are determined by the method of deposition. Co-evaporation from several electron-beam sources is used to produce films of different composition. Reproducible polycrystalline as well as amorphous microstructures are produced using heated and unheated substrates of glass, mica, metal, carbon. The crystalline electron-beam-evaporated films are used for diffraction standards and have been used to observe line broadening and lattice-spacing shifts that result from strain and compositional differences in the films.

Glasses with known compositions are used as sources for plasma sputtering to make thin-film composition standards. Such standards are required for quantitative analysis of ceramic transmission-electron-microscope specimens.

3.5.2. Metals

The aim of the specimen preparation is to obtain a sample (thin foil) of adequate electron transparency to permit the acquisition of images and diffraction patterns of the internal microstructure that is unaltered by the preparation method from that existing in the bulk material. When transmission electron microscopy is carried out at 100 to 200 keV, the sample thickness must lie in the range 0–1000 nm. The useable thickness decreases with increasing mean atomic number and with the requirement for ultra-high (atomic) resolution or for *in situ* chemical analysis by electron-energy-loss spectroscopy (Penneycook, 1981, 1982). In metallic systems, which can undergo plastic (permanent)

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