Specimen preparation methods for the examination of surfaces and interfaces in the transmission electron microscope

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SUMMARY

Various techniques for the preparation of cross-sectional and plan view TEM specimens of surfaces and interfaces are described. Particular emphasis is given to preparative methods which are both generally applicable and which minimize differential thinning of the materials present on either side of the interface of interest, thereby improving the reliability of the approach.

1. INTRODUCTION

The general understanding of a variety of surface science problems has become increasingly dependent on gaining a knowledge of both the chemistry and structure of the interfaces involved. While a number of techniques can give averaged information over relatively large areas of a surface, few can compete with transmission electron microscopy (TEM) in its range and diversity of specialized approaches designed for the characterization of local structure variations down to resolutions on the atomic level. It is thus surprising that until recently few attempts have been made to characterize precisely located parts of a heterogeneous structure in the TEM. Increasingly, however, controllable methods are being developed for the preparation of samples containing specific surfaces or interfaces either in cross-section or in plan. Our aim here is both to draw together a description of the specific techniques currently available for making such specimens, and to explain how these techniques might be developed for a range of different types of problem.

In general the most useful form of ‘interface’ or ‘surface’ specimen contains the region of interest oriented in such a way that it can be viewed ‘edge-on’. In conventional plan-view specimens it is difficult to retain information on the height of a specific heterogeneity without the careful use of stereographic techniques which are inaccurate for height differences less than about $\xi_g/10$. The observation of an interface in cross-section overcomes the above projection problem. Specimens containing a surface in ‘plan view’ can, however, be useful if they are prepared at a fine angle to the surface of interest so that regions at different distances from that surface can be viewed separately. Diffraction information about different species, as a function of their distance from the boundary, can then be obtained by conventional methods, while moiré techniques provide accurate information on changes in lattice parameter across an interface. Such specimens do suffer from the disadvantage that it is difficult to determine the
precise depth of a structure beneath the original surface, so that the information obtained usually needs to be complemented by the examination of edge-on specimens.

A variety of methods have been reported for the preparation of edge-on TEM foils. These have varied from purely mechanical processes (see for example McCune & Plummer, 1982) to methods involving ion beam milling (see, for example, Bravman & Sinclair, 1984). The techniques are most commonly applied for semiconductor materials and are based on the approach first described by Abrahams & Buicocchi (1974) and developed by Sheng & Marcus (1980). Methods have also been described for making cross-sectional specimens of a metal/oxide interface but have generally involved either the adaptation of specimen holders for the microscope (Manning & Rowlands, 1980) or rather less generally applicable techniques such as ultramicrotomy (Akahori, 1961). At the same time developments in ion beam thinning techniques are facilitating the approach and many laboratories currently prepare interface specimens of a wide variety of materials for edge-on observation. We thus emphasize in our description of the methods which we have been applying, those aspects of the technique which are both readily generalizable for the preparation of this type of specimen and lend reliability to what can, without experience, be an extremely frustrating and time-consuming process.

2. THE METHODS

We describe below those methods which we are currently using for the preparation of both edge-on and plan view specimens of interfaces and surfaces in a very wide variety of materials. For clarity, specific details are given for a single example for each of the approaches described. Sufficient information is also provided of the ways we have applied and changed these methods in different applications to demonstrate the adaptability of the approach.

In section 2.1 we describe the different methods by which discs can be made containing an interface with its normal in the plane of the disc. In section 2.2 we discuss pre-ion beam thinning treatments while final thinning techniques are described in section 2.3. A method for the preparation of plan view specimens is presented in section 2.4.

2.1. Disc preparation for edge-on specimens

The primary problem in making a disc suitable for further thinning lies in making it sufficiently mechanically rigid. The most successful method we have found of achieving this is to surround the specimen area of interest in a ring. This can be done by two broadly applicable methods, as described separately below, the details of which change depending on the type of problem studied and the specimen materials involved.

Method 1. This method is used when the interface of interest can be formed on a pre-prepared and shaped specimen, as is the case when a solid state chemical reaction front in a metal is being examined. The technique is described as applied to the study of the high temperature oxidation of iron-based alloys (Newcomb & Stobbs, 1983). The outlines of the approach are shown schematically in Fig. 1.

A cylinder of alloy under investigation is first machined to the dimensions shown in Fig. 1(a), and is then cut down the middle using a 200 μm thick SiC wheel. This procedure allows any prior oxidation treatment such as abrasion or electropolishing to be given to the surfaces of both semicylinders (Fig. 1b). After oxidation, each half of the oxidized specimen is electrochemically plated (Fig. 1c) in order to protect the extremely friable outer oxides during later grinding and polishing. Nickel is a suitable electrodeposit because its rate of ion beam thinning has been found to match that of most of the oxides formed on the iron-based alloys which we have studied. Typically 50–100 μm of plate is deposited which both protects the surface layer and allows its unambiguous identification during subsequent electron microscopy. A Watts plating solution can be used to give a deposition rate of ∼50 μm h⁻¹. If the material under examination, together with its reaction products, ion beam thin at an appreciably different rate from nickel alternative plating materials are available (see, for example, Field & Weill, 1961).

A general problem which frequently arises, as when chromium oxide is formed on stainless
steels, is that the outermost oxidation reaction product is a poor conductor. Under these circumstances the electrodeposition process can be improved by coating the surface prior to plating with either gold or carbon.

Now that the surfaces of interest are protected, the semicylindrical specimens are clamped together at each end and the plating continued while rotating the specimen on its axis, so as to improve the uniformity of the deposit. Plating to a thickness of approximately 250 μm provides the essential supporting ring which is so important for the handling of the specimens. Discs approximately 300 μm in thickness can now be cut from the composite cylinder using a SiC slitting wheel. The optical micrograph in Fig. 2(a) shows a specimen prepared in the manner described: the two protected oxide layers, sandwiched between the alloy substrates and nickel deposits, may be observed lying across the centre of the 3 mm diameter disc. Further processing of such a disc is carried out as described in section 2.2. It should be noted that in our experience the use of variations in the above technique involving glueing methods to bond the two specimens face to face are very unreliable when the oxides, or other compounds at the surface, are either rough or at all fragile.

Simple adaptations of the plating technique for the production of the bulk specimen, from which discs are then cut, have been applied to the preparation of edge-on specimens for the examination of melt spun ribbons (Rout & Donovan, 1984), ultramicrotomed metal chips (Stobbs et al., 1976) and thin multilayers of, for example, Au/Ag (Baxter & Stobbs, 1984). In the latter two cases copper proved to be a more suitable plating material than nickel. The method has also been modified successfully to allow the examination of dislocation microstructure variations in regions ahead of the tip of a fatigue crack. The approach taken in this instance
Fig. 3. Schematic diagram of the preparation of TEM foils for cross-sectional observation of fatigue crack tips. Discs are cut from bulk (a) and electropolished nickel deposited on individual specimens (b). Nickel plate is then removed from both surfaces of the disc using simple grinding techniques, the thickness of the pre-ion milled specimen being simultaneously reduced to ~ 50 μm. The nickel in the fatigue crack is retained (c). Specimens are thinned off-set in the ion miller (d) to ensure that areas ahead of the crack tip are preferentially milled (e). Further milling can then be performed in order to sequentially examine different regions of the same specimen.

is shown in Fig. 3, and it should be noted that the confined and field sensitive regions of a crack tip make it desirable to use an electropolishing method. The quantity of material deposited in the crack tip may be optimized by plating after ‘discs’ have been cut from the bulk (Fig. 3c).

Method 2. This method has more general application than that described above and is used when the surface layer or interface of interest has to be cut from a bulk sample. The technique has been adopted for cross-sectional studies of melt spun ribbons (Newcomb et al., 1984), anodized aluminium (Newcomb, 1984) and diffusion barriers on semiconductors (Boothroyd & Stobbs, 1984). The basic approach, as used when the surface, substrate and supporting material beam thin at similar rates, may be understood with reference to Fig. 4. Essentially the cross-sectional specimen is supported in a slotted rod which is itself then encapsulated in a tube of 3 mm outer diameter.

Fig. 2. Fe–9Cr–1Mo oxidized at 600°C in 1%CO–CO₂ for 1000 h showing a pre-ion milled disc and electron transparent regions of the duplex and metal/oxide interfaces. Cross-sectional optical micrographs showing (a) a 3 mm disc where a two-layered oxide sandwiched between the metal substrate and supportive nickel plate may be observed and (b) the duplex oxide scale at higher magnification. It should be noted that the nickel plate and oxide are adherent and the latter is thereby protected during ion beam milling. Bright field TEM micrographs demonstrating different oxide morphologies through the depth of the scale at (c) the duplex oxide interface (as at A in (b)) and (d) the metal–oxide interface (as at B in (b)). M₃C₆ precipitates may be observed in the alloy beneath the fine grained and inward grown spinel oxide (Newcomb & Stobbs, 1983).
The sample must first be reduced to the dimensions shown in Fig. 4(a) and this can be done in a variety of ways depending on the nature of the specimen. A slitting wheel or even a fine hacksaw can often be used for this purpose as when examining the hardened surface of a metal. This was the method used in a recent study of white layer formation on the running surface of a railway line (Newcomb & Stobbs, 1984), images of which are shown in Fig. 5. Alternatively, spark machining can be used when softer microstructures are being studied and would be required, for example, to prepare specimens for the edge-on examination of the dislocation microstructure where a persistent slip band in a fatigued single crystal reached the surface of a specimen. Semiconductor substrates may of course be cleaved, though in cases where a specimen has to be examined in a number of different directions, suitable wire cutting methods may be applied: ternary III–V compounds, for example, are often viewed at 45° to their cleaving direction.

For most applications of the technique the relevant surface is coated, both to protect it during later stages of the process and to facilitate the recognition of the true ‘geography’ of the specimen’s upper surface in the ion beam thinned foil. It is important, however, as noted in section 2.1, to select a coating which, though different from the substrate, matches its ion beam thinning rate. Typically, it is sufficient to protect edge-on semiconductor specimens, which ion beam thin at relatively high rates, with ~50 nm of gold sputtered onto the surface using for example an Emscope SC5000 sputter coater. Cross-sectional specimens which ion mill at much
lower rates may be electroplated with either copper or nickel, the later material matching the thinning characteristics of most iron-based specimens.

The cross-sectioned specimen must now be supported in a slotted rod as shown in Fig. 4(b). Again it is important to choose a material for this rod which ion beam thins at approximately the same rate as the specimen which it is supporting since the use of a low thinning rate material can lead to adverse sputtering and shadowing during ion beam milling. Typically, we use Type 316 stainless steel as a support for iron-based materials and brass for most semiconductor applications. The ion beam thinning characteristics of the material used for the support tube, into which the slotted rod and specimen are eventually fitted, are not important since this part of the milled disc is normally protected by tantalum support plates during the thinning process. The tube material, however, should preferably be plastically softer than the rod since this facilitates fitting the rod tightly into it, without any danger of damaging the specimen.

The geometry and thickness of the slot cut in the rods (typically 30 mm in length), which are machined to fit the 3 mm brass tubes, can be important. We therefore tend to stock a variety so that we can choose the most appropriate for a given specimen. In general the surface to be examined should be at the centre of the disc to be milled so the slot needs to be cut (using a slitting wheel) off centre in the rod. Symmetric and rather broader slots can, however, be used when two specimens are to be inserted face to face. Occasionally, as when examining the cross
section of thin (≤100 \(\mu m\)) specimens such as a melt spun ribbon, it is convenient to pack several specimens into a single slot. In general, however, the slot width should be kept to less than about 20% of the rod diameter, and is chosen to ensure a tight fit of the specimen.

When single specimens are inserted into the rod it is preferable to bond the specimen into the rod and the rod into the tube in a single process. However, when two specimens are inserted into a rod it is advantageous to bond the specimens together first. This procedure ensures that the important bond width between the two surfaces of the specimens is minimized, and can equally allow coarse grinding of the back surfaces of a paired specimen to improve its fits into the slot. While a variety of bonding materials have been tried we find that standard twin pack Araldite (cured for 3 days at room temperature) is adequate, and that discs may be cut from such specimens as described above with no specific precautions.

The difficulty in applying the method successfully increases considerably when the specimen to be examined consists of a surface and substrate which have very different thinning rates. The usual situation, as when examining silicides on silicon or niobium-based Josephson junctions, is that the surface layer has a lower thinning rate than the substrate. Now the double specimen technique described above can help considerably. Equally if the double specimen, bonded face to face, is back ground to fit the slot with a slight wedge angle then the shadowing effect of the rods during ion beam thinning has different effects at different stages of the milling process after perforation. The optimum thinning stage for observation of the perforated disc can be judged optically. In general it is best to minimize the slot width of the rod for this type of specimen though it can sometimes be helpful to position it well off centre, which further exaggerates shadowing effects by using the changes in natural thinning contour across the disc. Other ‘double polishing’ approaches can however be used as will be discussed in sections 2.2 and 2.3.

2.2. Pre-ion beam milling treatments

If ion beam milling is to be used, discs prepared by either method 1 or method 2 must first be reduced to \(~50\ \mu m\) in thickness by mechanical grinding and polishing, though for some applications the whole surface or interface region in metals may be electropolished.

Single discs approximately 300 \(\mu m\) in thickness are mounted on a steel block using a low melting point (\(\sim 75^\circ C\)) wax. This provides a rigid and adherent support for the specimens while they are ground on a rotating 1200 grit SiC wheel to a thickness of \(~100\ \mu m\). The discs may then be further polished on standard metallographic wheels, though in our experience it is rarely necessary to take final lapping beyond 6 \(\mu m\) diamond paste. A relatively scratch-free surface for ion beam thinning is, however, important since the ion erosion of rough surfaces generally encourages differential etching and the formation of ridges. Optical examination of discs at this stage should reveal a near mirror finish and specimens which show evidence of cracking either in the bulk (as in semiconductors) or at interfaces (as for example between metal and oxide) should be discarded. The thickness of the specimen disc can now be measured with a micrometer and, after a remount on the metal block, the back surface is ground and polished as described above to a final thickness of between 30 and 50 \(\mu m\). If discs in this thickness range fail when demounted, because the rod was either too tightly or too loosely fitted into the tube, it is usually adequate to slightly increase the disc thickness at the end of the grinding process, though this of course increases the final ion beam thinning time. It should be noted that it is sometimes useful to give the discs a slightly wedged section to facilitate the progressive thinning of a region of interest in the interface along the length of the slot.

Many edge-on metal specimen discs may be given pre-ion beam milling electropolishing treatments using an accurately alignable gravity feed system. This can be done simply to reduce the disc thickness or to thin a region preferentially which will subsequently ion beam mill slowly. We have frequently applied this approach successfully in the preparation of edge-on specimens of oxides on metals: excessive grinding can damage the very friable and often porous oxides which also ion mill faster than the metal substrate.
2.3. Ion beam milling

By comparison with chemical or electrochemical polishing techniques, ion beam milling is an extremely unsatisfactory method of producing an electron transparent TEM foil. The main disadvantages of the technique are the way the surface region of the thinned specimen is both damaged by the incorporation of small dislocation loops and distorted because of the way it is dilated. Equally the process leaves the surface chemically active so that even a cooled specimen, thinned using 99-998% argon, will often oxidize during the milling process unless extreme precautions are taken to purify the gas used. In principle a light final chemical or electrochemical polish can be used to remove such damage, although if a polish is known for the different materials in the interface region of interest it is arguable that such a thinning should have been used in the first place. However, a situation in which a post ion beam milling chemical polish is of particular use is exemplified by the problem of how to study the annealing characteristics of ion beam implanted dopants in a semiconductor. It is not essential to remove the thinning damage, but this is fortunately relatively easy in this case since most semiconductors have well-controllable chemical polishes.

When applying ion beam milling methods there is a general tendency to use both too high an accelerating voltage and too high an erosion angle. The characteristics of ion erosion are well documented (see, for example, Barber, 1970) and the optimum accelerating voltage for a given specimen and ion at incident angles of between 15° and 20° is below 1 kV. Such calculations do not, however, take account of the fact that most commercial systems operate at a reduced efficiency at low voltages, while the presence of a reactive gas will often dominate the milling process at low erosion rates. Edge-on specimens of niobium-based Josephson junctions are particularly difficult to thin and in this case it may be advantageous to improve the base pressure of the ion beam miller and try alternative bleed gases. In general, of course, the early stages of milling can be carried out at fairly high incident beam angles (25–30°), but both the edge contour and the damage depth are markedly improved by reducing the erosion angle to about 12° while simultaneously reducing the accelerating voltage. During this stage of the thinning process it is particularly important to maintain the beam current.

Given that the precautions described in sections 2.1 and 2.2 are followed, specimens with

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**Fig. 6.** Schematic diagram of the shadowing method used to prevent differential ion beam thinning. It should be noted that erosion across an interface only takes place from the direction of the lower thinning rate material.
locally different thinning rates can be thinned with adequate uniformity using a double ion beam gun and a rotating specimen stage. If, however, the thinning rate changes markedly across the interface to be thinned we have found it useful to mask the specimen in the manner shown in Fig. 6 so that erosion across the interface takes place only from the direction of the low thinning rate material. The masking method used is based on an approach described by Manning & Rowlands (1980) and has the generally beneficial effect of reducing any local irregularities or bevelling left by the previous grinding or electropolishing treatments. While the use of a mask minimizes differential thinning effects it also tends to lead to sputter deposition of the masking material at the thinned edge of the specimen. This sputtered material

Fig. 8. The application of combined edge-on and plan view observation to the study of the high temperature characteristics of a PdEr contact layer on (100)Si (annealed at 350°C for 1 h). The PdEr/Si interface is shown edge-on in (a), where Pd, Si precipitates may be observed to have grown into the Si substrate. Different depths of the PdEr/Pd, Si layer are shown in plan view in (b) and (c) as indicated in (a). The uppermost region of the PdEr layer is shown in the dark field image in (b) where microcrystalline Pd, Er and surface Er, O₃ may be observed (see diffraction pattern). At the PdEr/Si interface (as at C in (a)) epitaxial growth of Pd, Si has occurred. The moiré fringes and diffraction pattern show that growth has occurred in [001]Pd, Si/[100], [010] Si orientations.
can be easily removed by a brief final erosion period with the masks removed but to facilitate its identification the masks should be made of a different material than the specimen: we use two brass half 6BA brass washers when thinning the interface between iron alloys and their oxides.

2.4. ‘Plan view’ specimens

There are two situations in which plan view specimens of an interface should be prepared in addition to those of edge-on geometry. The first of these arises when there are liable to be gross lateral irregularities (on the 10 μm scale or more) in and around the plane of the interface, as can occur in either surface wear or oxidation. In the latter case it may, for example, be important to determine the distribution and geometry of any pores in an outer scale, while in lubricated wear specimens local pockets of lubricant can sometimes become trapped in the deformed surface at lateral separations such that it would be difficult to determine their distribution using ‘edge-on’ samples alone. Perhaps more surprisingly, it is equally useful to prepare plan view specimens when the reaction products at an interface are three-dimensionally isolated and small (<50 nm). This is partially for convenience in that, although convergent beam diffraction patterns can easily be obtained from particles of well under 10 nm in size, it is often very useful to obtain in addition a conventional selected area diffraction pattern from a number of such particles. While this is often impossible if the particles occur in only a very narrow zone at the interface, plan view specimens enable this to be done very easily. At the same time the lateral morphology of such reaction products is also seen directly in plan view. Indeed, at the very early stages of a reaction, when the particles can be of near unit cell size as for example in some metal/silicon reactions (Stobbs, 1984), projection problems in an edge-on specimen would make it difficult to be sure that the reaction was in fact locally inhomogeneous without the use of dark field techniques on the plan view specimen.

Plan view specimens are in general much more easy to make than those of edge-on geometry. A near surface region can, for example, be readily protected using a substance such as Lacomit which can be later removed chemically, so that the specimen can then be milled further from the back. Alternatively, and by contrast with the way differential polishing characteristics across the interface are the main problem in preparing edge-on samples, such differences can be made use of when making a plan view specimen: for example, a specific chemical polish can often be used to thin the material on one side of the interface without affecting that on the other. This approach has been used successfully in the examination of both silicon oxide and silicides at a silicon interface.

A particularly useful approach when the reaction products extend over a reasonable range from the interface, allows different depths in the specimen to be viewed in a single plan view specimen. This can be achieved, as is shown schematically in Fig. 7, by off-centering the polish (whether electrochemical, chemical or ion beam) on either side of the specimen. In practice uncertainties in the height of the specific region examined from area to area in the plan view specimen make it essential to examine also an edge-on section. Examples of micrographs obtained from both types of specimen of the reaction zone between PdEr and silicon are shown in Fig. 8.

3. CONCLUSION

We have described above the principal ways in which the main problems associated with the preparation of edge-on samples can be overcome, the approaches given being, where possible, those which can be generally applied. The most important aspects of the technique ensure the rigidity of the specimen during thinning by encasing it securely and minimize differential thinning effects by the use of masks. It is emphasized that the use of plan view specimens in conjunction with those of edge-on geometry can often be particularly helpful.

In conclusion, it is significant that the most exciting images of a surface obtained in recent years (demonstrating reconstruction) were taken of a specimen which was essentially prepared in the microscope: the edge of a gold island was decontaminated by leaking water vapour into
the microscope column (Marks & Smith, 1983). Future developments in the methods of producing cross-sectional samples will centre around improvements in our understanding of the reactive ion beam thinning methods currently of considerable interest in the semiconductor industry.

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