Optimisation of the wire-shadow TEM cross-section preparation technique

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Abstract

The wire-shadow technique is a simple and easy-to-use preparation method of cross-section specimens for TEM investigations. The method has been optimised for thin films on silicon and oxide (sapphire, MgO) substrates. A wire is glued onto the film. During thinning in a modified commercial ion-milling sample holder the shadow of the small wire protects part of the film. Non-shadowed areas of film and substrate are removed by ion sputtering. During ion thinning a sharp edge evolves in the wire shadow. As a consequence, the interface between film and substrate becomes transparent to electrons just at the point at which the wire is eroded away. Different wire materials (tungsten, Al₂O₃, carbon, nicalon (SiC) and nylon) and thinning geometries were tested. The best results were achieved using an amorphous carbon fibre with a diameter of 7 μm.

1. Introduction

Information about the structure of thin films on single-crystal substrates can be obtained by viewing cross-sectional specimens under a transmission electron microscope. The standard cross-section preparation techniques [1, 2] were developed for high-resolution TEM (HRTEM) where flat and very thin (< 10 nm) specimens are needed.

These methods for cross-section preparation are elaborate and need a considerable amount of time for the mechanical thinning and polishing of the specimen. Traeholt et al. [3] have proposed mechanical thinning down to 5–10 μm, while Helmersson et al. [4] and Strecker et al. [5] have used a many-step sequence to obtain a mechanically stable sample with a thickness of less than 30 μm. Due to the fragile nature of such samples, considerable care must be exercised during their preparation. After mechanical thinning, final thinning to electron transparency is made with an Ar ion and fast neutral beam. Typical final thinning times for oxide films and substrates are 10–30 h in our thinning equipment (Gatan Duo mill).

Another technique for preparing a cross-section specimen was reported by Bartsch et al. in 1987.
A selected part of the sample is protected by a tungsten wire. During ion-beam thinning the wire and the non-protected part of the sample are removed simultaneously, whereas the protected part of the sample is preserved. A thin, sharp wedge is formed in the wire shadow. The ion beam thinning is stopped just after the wire is eroded away near the centre of the specimen. The wedge is now transparent to electrons. A schematic drawing of the procedure is shown in Fig. 1. The thinning time is determined exclusively by the properties of the wire and the ion-beam parameters. Using a wire with a good homogeneity, the once optimised time can be used for every preparation. A typical time needed for thinning through a carbon wire (diameter 7 µm) was 2 h. The resulting specimen has a high mechanical stability compared to those obtained by the usual thinning procedures.

We optimised the wire-shadow technique described by Bartsch et al. for investigating a large number of specimens, to get a fast overview about parameters like film thickness, orientation, grain size and the evolution of a reaction layer between substrate and film. In the mean time a greater variety of potentially useful wires of different materials with diameters in the range of about 10 µm are available. Furthermore, the ion-milling system used in the earlier work has been replaced by machines allowing more flexibility in choosing the thinning parameters.

2. Experimental

2.1. Preparation of the specimen

Our samples were single-crystal substrates of Si, Al₂O₃ and MgO with dimensions of 10 × 10 × 0.5 mm³ covered by different thin films. Rectangular bars with a length of 2–3 mm, a thickness equal to the substrate thickness and a width of 200–300 µm were cut from the samples with a diamond saw. During sawing, the exposed surface of the film was protected by a thin glass slide secured to it with thermoplastic glue. Depending on the desired maximum tilting angle in the TEM, the width of the bars was reduced by grinding to a value of about 100 µm. A copper or molybdenum supporting ring (outer diameter 3.05 mm, hole diameter 1 mm, thickness 50 µm) was cut into two parts. The bar was glued onto one-half of the ring (Fig. 2) with a two-component epoxy glue. The surface covered by the thin-film points towards the middle of the supporting half-ring. During this step any excessive glue covering the front side of the bar has to be avoided. The last step is the most critical and needs some training. The ring is mounted in

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Fig. 1. Schematic diagram of the wire-shadow preparation technique.

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Fig. 2. Schematic diagram of the specimen glued to a supporting ring and definition of the angles α and β. For reference purposes, e⁻ indicates the direction of the electron beam in the TEM relative to the sample.
a holder with the bar facing upward. At the two ends of the top surface of the bar, a small amount of two-component epoxy glue is placed using the end of a single strand of hair. A piece of the wire with a length of a few millimetres is centred at the middle of the bar. Since the glue has a high viscosity, the wire is fixed. A thin film of glue between the bar (thin film) surface and the wire is obtained by heating the specimen under reproducible conditions to a maximum temperature of 100°C. During heating, the viscosity of the glue is reduced such that it creeps by capillary forces into the space between the bar and the wire. As this step determines the glue thickness between bar and wire, it has a significant influence on the quality of the thinned specimen.

2.2. Thinning

Thinning was performed in a Gatan Duo Mill with a beam consisting of Ar ions and fast neutrons (here called "ion beam"). Gun voltage and current were 5 kV and 0.25 mA per gun. One-half of a standard Gatan copper specimen holder was cut away to fit to the half ring. Different combinations of (i) the angle \( \alpha \) between wire and beam and (ii) the rotation regime of the specimen holder (angle \( \beta \)) were tested. Fig. 2 shows the geometry used. The ion sources can be tilted up to \( \pm 40^\circ \) out of the specimen holder surface plane (angle \( \alpha \)). A second angle \( \beta \) between wire axis and beam direction can be changed by rotating the specimen holder. The thinning morphology resulting from a fixed beam (\( \alpha = 0^\circ, \beta = 90^\circ \)) was found to be quite wavy. Another problem was the formation of thinned wedges at different heights. The electron beam in the TEM has to penetrate two or more of these wedges, blurring the picture. A single wedge can be formed using simultaneously two beams with negative (\( \alpha = -7^\circ \)) and positive (\( \alpha = +7^\circ \)) tilting. The original thinning equipment provides for continuous specimen rotation, and also sector speed modes, by which the rotation speed for defined angle intervals is decreased (high speed 10 rpm, low speed 2 rpm). The motor controller was modified to reduce the speed in the low-speed angle segments to 1 rpm. A further reduction of the rotation speed was not possible, due to the friction resistance the motor has to overcome.

The sharpness of the wedge depends on the thinning coefficient ratio of film/substrate and wire. For our samples of slowly thinning oxide thin films, the sharpness of the wedge was sufficient for the examination of films with a thickness up to 100 nm in a 200 kV microscope (Philips CM20 Twin).

The ion beam is focused to the specimen centre using an aperture in the cathode. As thinning proceeds, the edge of the aperture is sputtered away. Thus, the diameter of the ion beam increases. With a new aperture, the thinning time for a 7 \( \mu \)m diameter carbon fibre was 1 h 50 min. After 80 h of aperture usage the thinning time increased to 3 h. Stopping the thinning just after the glue and a part of the film are removed in the middle of the specimen was found to give the best results. A slight long-scale variation in the wire diameter leads to the development of a wavy thinning profile. While some portions of the film are thinned away, there exist typically three to five positions with a useful slow transition from parts with remaining glue covering the film surface to the interface between film and substrate. If the optimum thinning time is exceeded, the film at the centre of the specimen is lost. The time period for a complete removal of the film is about half an hour.

2.3. The wires

For obtaining a good protection of the shadowed film the wire should have a low sputtering coefficient. It is well known that the sputtering coefficient for crystalline materials depends strongly on the crystal orientation [8]. Known materials of low sputtering yield are refractory metals like tungsten, oxides like aluminium oxide and amorphous carbon. We have tested such wires with diameters ranging from 6 to 25 \( \mu \)m.

The polycrystalline tungsten wire had a mean diameter 10 \( \mu \)m with a deviation of \( \pm 20\% \). The grain size varied between 2 and 10 \( \mu \)m, the largest grains occupied the whole diameter of the wire. The ratio in the sputter coefficients of a silicon substrate and the tungsten wire is about 1 : 3 [9]. The aluminium oxide wire was also polycrystalline with a diameter of 25 \( \mu \)m. The thickness was quite uniform along the wire with a variation of \( \pm 5\% \) and some roughness due to the polycrystallinity. The grain
size ranged from a few hundred nanometers and up to 2 μm. The best wire material tested was amorphous carbon with a diameter of 6–15 μm.

However, the carbon quality and its thickness uniformity depends on the manufacturing process used by the supplier. In one case the carbon wire was made by heating a nylon fibre in vacuum. The resulting wire was porous and the thinning coefficient was comparatively high. Light microscopy of carbon wires from other suppliers with a nominal diameter between 10 and 15 μm revealed marked fluctuations in their diameter. A carbon wire with 7 μm diameter and a uniformity of better than 5% (supplier: Goodfellow, Cambridge, Great Britain, order number 005712) provided the best results. In the electron diffraction image some smeared out rings were observed, indicating the material to be either amorphous or crystalline with very small grain size.

Additionally, a polymer fibre “Nylon 66” and a “Nicalon” wire which contained SiC as its main component were tested. The polymer wire was not sufficiently resistant against the ion beam to be useful. The SiC wire with a diameter of 15 μm also showed a too fast thinning behaviour considering the large diameter, which was identical to the one for a carbon wire with only 7 μm diameter.

3. Results

The uniformity of the wire thickness depends on the state of crystallinity and also on the manufacturer. Polycrystalline wires with grain sizes above 100 nm always possessed a rough surface. The ion beam thinning rate of crystals depends on the relative orientation of beam and low-index planes. For the tungsten wires we observed a strong influence of this effect. While some grains were thinned away quite fast, others remained. The polycrystalline aluminium oxide wires also resulted in a variation of the thinning speed over small distances along the wedge with the consequence of a wavy thinning morphology. One advantage of the amorphous carbon fibres was a homogenous thinning independent of the position along the wire.

A critical parameter is the thickness of the glue between specimen surface and wire. The two-component epoxy glue showed strong capillary forces only for amorphous carbon wires with low and homogeneous diameter. The glue thickness between film surface and wire was a few hundred nanometers for the optimum carbon fibres with a diameter of 7 μm. The sharpness of the wedge thinned in the shadow of the wire deteriorates if the thickness of the intermediate glue layer is higher.

Different combinations of angles between ion beam and specimen during thinning were tested. The wedge sharpness and the flatness of the thinned specimen depend on the two angles α and β. A sharp wedge can be obtained for a number of thinning parameters, like a stationary beam perpendicular to the wire (α = 0° and β = 90°), a stationary beam nearly parallel to the wire (α = 0°, β = 20°) and also if the sample is rotated during thinning.

Different rotation regimes were compared (two ion sources operating with α = ± 7°: rotation with constant speed and sector control with low rotation speed if the beam is either nearly perpendicular (β from 70° to 110°) or parallel (β from − 20° to 20° and 160° to 200°) to the wire. If the ion beam is in an orientation nearly perpendicular to the wire for a long time, a wavy thinning morphology is obtained. This thinning profile contains a large number of narrow transitions from parts where the film is too thick to be penetrated by the electron beam in the TEM to positions where the film is completely removed. The flatness of the thinned specimen is better for a thinning with the ion beam nearly parallel to the wire. The best reproducibility of a steady thinning morphology was obtained using simultaneously two ion beams with a tilt angle α of ± 7° and a sector control of the sample rotation with the beam remaining for half of the time nearly parallel to the wire (β from − 20° to 20° and 160° to 200°). Fig. 3 shows an example of a flat and steady thinning morphology achieved with these parameters (microscope Philips CM20 Twin with an acceleration voltage U = 200 kV). A stationary beam nearly parallel to the wire (one ion source, β fixed at 20°) can give even better results (see Fig. 4; microscope JEOL 4000EX with U = 400 kV), but the reproducibility was found to be not as good. If film and substrate consist of a material with a high thinning coefficient compared to the
carbon wire, a sharper wedge is formed. Fig. 5 shows a bright-field image of a Si–Si/Ge quantum wire structure on a silicon substrate (microscope JEM 1000 with $U = 1$ MV).

4. Summary

The wire-shadow technique was optimised for TEM cross-section preparation of thin oxide films. Best thinning results were achieved with an amorphous carbon wire. A commercial ion milling system was modified to maximise the reproducibility. Advantages of this method are its reliability, low consumption of material from the original sample and a short and well-defined time for ion thinning of the sample. Placing the wire on top of an interesting sample detail gives the possibility of selective thinning.

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