High-Quality Sample Preparation by Low kV FIB Thinning for Analytical TEM Measurements

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Abstract: Focused ion beam specimen preparation has been used for NiTi samples and SrTiO3/SrRuO3 multilayers with prevention of surface amorphization and Ga implantation by a 2-kV cleaning procedure. Transmission electron microscopy techniques show that the samples are of high quality with a controlled thickness over large scales. Furthermore, preferential thinning effects in multicomponents are avoided, which is important when analytical transmission electron microscopy measurements need to be interpreted in a quantitative manner. The results are compared to similar measurements acquired for samples obtained using conventional preparation techniques such as electropolishing for alloys and ion milling for oxides.

Key words: low kV thinning, FIB, NiTi, multilayer oxides, TEM, sample preparation

INTRODUCTION

Sample preparation is a crucial step in the investigation of solid-state materials using transmission electron microscopy (TEM). The sample should be electron transparent, but without being damaged or altered by the specimen preparation. Depending on the material, one has to choose the most suitable thinning technique; whereas bulk materials can often be crushed, multilayer thin films or coatings should be prepared as a cross section or a plan view using mechanical polishing and ion milling. Electropolishing is another well-known technique, mostly used to prepare (inter)metallic samples, because these materials are conducting, too soft for crushing, and easily damaged by ion milling. The techniques mentioned above result in samples that are of sufficient quality for standard TEM work such as, for example, electron diffraction and conventional HRTEM. However, recent advances in TEM techniques impose higher demands on sample preparation. For quantitative composition analysis of electron energy loss spectroscopy (EELS) measurements, energy filtered TEM (EFTEM) images, and high angle annular dark field scanning TEM (HAADF-STEM) images, a uniform or exactly known sample thickness is preferable because the recorded signal intensity depends on both sample thickness and sample composition. Samples prepared by the conventional techniques mostly have a severe wedge shape and often preferential thinning occurs in multicomponent samples. Focused ion beam (FIB) preparation of TEM samples may overcome these problems.

Sample preparation by FIB has been extensively used for semiconductor materials and devices. In the present work, the technique is applied to a NiTi bulk and a SrTiO3/SrRuO3 multilayer (ML) sample. Moreover, rather than focusing on short preparation times (as often demanded by the semiconductor industry), the main goal is to prepare high-quality samples with a controlled sample thickness. It is known that FIB samples can be prepared with parallel sidewalls, but a major disadvantage is that due to the heavy Ga⁺ ions used for thinning, an amorphous layer may be created at the surface of the sidewalls. For Si, this layer can be up to 20 nm or more, depending on the conditions used (Holland et al., 1983; Cairney & Munroe, 2002). Obviously, this surface amorphization will complicate quantiative TEM measurements. The thickness of this layer can be reduced by low kV Ga⁺ polishing when the sample is already sufficiently thin. However, lowering the energy of the ion beam leads to a significant loss in lateral resolution of the thinning process. Moreover, until recently low kV cleaning was restricted to 5 kV, but it has been shown by Giannuzzi et al. (2005) that, for Si, cleaning at 2 kV can be done and results in high quality samples. In the present study, the low kV method is applied to NiTi and SrTiO3/SrRuO3. Furthermore, special attention will be paid to sample thickness and preferential thinning.

The quality of the samples is investigated by HRTEM, energy dispersive X-ray spectroscopy (EDX), EFTEM, and HAADF-STEM. The results are compared to measurements obtained for samples that have been prepared using the conventional preparation techniques.
FIB sample preparations are performed using FEI Strata 400 STEM and Nova 600 FIB-SEM systems, both equipped with a sidewinder column, in which thinning is carried out by a focused Ga\(^+\) ion beam. Live imaging can be performed by the ion beam as well as the electron beam. In both instruments the two columns are positioned under an angle of 52° with respect to each other.

Conventional TEM images and EDX patterns are recorded using a LaB\(_6\) Philips CM20 operated at 200 kV and equipped with a LINK analytical QX 200 system. EFTEM and HRTEM measurements are obtained on a Philips CM30 FEG (operated at 300 kV), equipped with a GIF200 post column energy filter. For the HAADF-STEM images, a JEOL 3000F is used.

**FIB Sample Preparation**

Both specimens are essentially prepared in a similar way using the wedge cut followed by an *in situ* welding lift-out technique with only minor differences in the applied parameters. This method has several advantages such as, for example, the minimization of redeposition of sputtered material and the possibility to return to the FIB instrument for further thinning after investigation in the TEM. The basic principles of this technique have been documented before (Langford & Petford-Long, 2001; Giannuzzi & Stevie, 2005) and include the deposition of a central protective Pt strip and staircase thinning at 7 nA at both sides of the region of interest until a specimen with a thickness of approximately 1 \(\mu\)m is obtained. Directly after this step the specimen is tilted away over 7° with respect to the ion beam and an undercut is made to release the sample by a needle (Fig 1a). Next, the specimen is welded to the needle and lifted out of the substrate; the stage is then moved to a different holder that contains the final grid onto which the specimen is welded (Fig 1b). After attaching using *in situ* Pt deposition, the needle is separated from the specimen. In the following step, the specimen is thinned until it becomes electro-transparent (~100 nm) using the 30-kV ion beam and a current of 30 pA for NiTi and 100 pA for the ML sample. During this process the stage is tilted 1.2° positive and negative with respect to the direction of the ion beam to prepare parallel sidewalls (Young et al., 1998). The incident angle of the ion beam while thinning determines how parallel the sidewalls of the specimen will be. The angle required depends on the ion–solid interactions of the specimen. For slower sputtering materials, a 1.2° incidence angle is often used, whereas faster sputtering requires higher angles (Prenitzer et al., 1998). At 100 nm thickness, thinning at 30 kV accelerating voltage is stopped to prevent the formation of an amorphous layer on both sidewalls of the specimen.

Finally, low kV cleaning is carried out at 5 kV and 2 kV for the NiTi (Fig. 1c,d) and 8 kV and 2 kV for the ML sample (Fig. 1e) on both sides of the sample. For the ML sample at 8 kV a so-called cleaning cross-section pattern under a 2° incidence angle is used. This pattern approaches the area of interest line by line, which minimizes redeposition effects onto the sample sidewalls. For the NiTi sample, which is a much harder material, a regular box thinning at 5° stage tilt must be used. During thinning, the sample thickness is observed by live SEM imaging at low kilovolts. At 5 or 8 kV the sample is thinned to a sample thickness below 70 nm. As soon as the Pt top layer starts to disappear and the sample becomes electro-transparent the thinning process is stopped. For the final low kV cleaning 2 kV and 10 pA with an incidence angle of 5° is used. The area of interest is exposed to the ion beam using box thinning for 10–20 s per side for the ML sample and up to 10 min for the NiTi material. The thinning process can again be monitored using SEM.

**RESULTS**

**Multilayer Sample**

The SrTiO\(_3\)/SrRuO\(_3\) multilayer sample consists of a repetitive sequence of 10 unit cells of SrTiO\(_3\) and 10 unit cells of SrRuO\(_3\) deposited onto a DyScO\(_3\) substrate. Ga\(^+\) ion implantation at the sidewalls is studied using EDX: The results indicate a Ga\(^+\) content of less than 1%, independent of sample thickness, which is, in fact, the detection limit of the present EDX system.

In Figure 2a, a HAADF-STEM image of the sample is shown. In this image, the intensity scales with the atomic number Z of the compound and therefore, the bright layers correspond to SrRuO\(_3\), whereas the darker layers consist of SrTiO\(_3\). In Figure 2b a HAADF-STEM image is presented of a similar sample prepared by mechanical polishing and Ar\(^+\) ion milling at 5 kV under an angle of 8° followed by a gentle milling at 0.8 kV for 30 min. For both images, intensity profiles are made in which the peaks correspond to the SrRuO\(_3\) layers. The background intensity is an indication of the sample thickness, and by comparing both profiles, it can be concluded that the thickness of the sample prepared by FIB is almost constant over the complete multilayer, whereas the thickness of the sample prepared by ion milling shows a nonlinear decrease of approximately 7%. It must be noted that the thickness of the two top layers of the FIB prepared sample is lower as well, meaning that the sidewalls at the tip of the FIB sample are not perfectly parallel either.

In Figure 3, both samples are again imaged by HAADF-STEM, but now at a higher magnification. The quality of both images (Fig. 3a obtained for the FIB prepared sample and Figure 3b obtained for the ion milled sample) is comparable. Clearly, the amorphous layer, if existing, related to specimen preparation by FIB is not hampering the quality of the image in comparison to the ion milled prepared sample.
Figure 1. **a:** Lifting out of the NiTi sample. **b:** Welding of the sample to the TEM grid. **c, d:** Sample shape after 5-kV cleaning (c) and after 2-kV cleaning (d). **e:** Sample shape of the multilayer sample. (a and b are ion beam images; c, d, and e are SEM images.)
NiTi Sample

The NiTi sample has an overall composition of Ni$_{52}$Ti$_{48}$ and contains (semi)coherent Ni$_4$Ti$_3$ precipitates. These lens-shaped precipitates appear as the elliptical features in Figure 4a. In diffraction patterns (inset) obtained from regions at the edge of the sample (encircled) an amorphous ring is present indicating the presence of some amorphization.

One of the issues when preparing the NiTi samples in the conventional way (electropolishing) is preferential milling of the precipitates. It is therefore not straightforward to obtain samples that are sufficiently thin for HRTEM and show proper polishing for the precipitate as well as the matrix. However, the high-resolution image of the matrix–precipitate interface shown in Figure 4b, demonstrates that this problem can be overcome by FIB. Furthermore, the

Figure 2. HAADF-STEM images of the ML sample for the FIB prepared sample (a) and ion milled sample (b). The intensity profiles, obtained along the direction indicated by the white rectangle, show that the thickness of the FIB prepared sample is more uniform.

Figure 3. Comparison of the quality of a high-resolution HAADF-STEM image for the FIB prepared sample (a) with the ion milled sample (b). This indicates that the effect of a possible amorphous layer introduced by FIB is negligible.
superstructure, which can be observed in this figure, indicates that the ordered structure of the precipitate is maintained during the FIB preparation process. The lack of gallium implantation by Ga\(^+\) is confirmed by EDX measurements, showing that the percentage of Ga\(^+\) ions is again lower than the detection limit of the system (~1%).

To investigate the presence of preferential thinning, EFTEM thickness maps are obtained using the log-ratio method (Egerton, 1996). In this procedure, two intensity maps are acquired; one is formed by all transmitted electrons \(I_t\), unfiltered image, the other one by selecting only those electrons that did not lose any energy \(I_0\), filtered image. The relative drift between the unfiltered and filtered images was corrected by a standard cross-correlation technique when computing the ratio map \(I_t/I_0\). The sample thickness \(t\) is given by

\[
\frac{t}{\lambda} = \ln \left( \frac{I_t}{I_0} \right),
\]

with \(\lambda\) being the mean free path for all inelastic scattering, which is about 100 nm for NiTi alloys.

A global thickness profile presented in Figure 5 as obtained from the encircled area in Figure 4a shows that the sample thickness starts at about 20 nm and increases to about 40 nm over a lateral distance of 0.45 \(\mu\)m. Although this means that the sidewalls are not completely parallel, a slow and linear increase in thickness is found, which allows one to exactly determine the sample thickness based on the lateral distance from the edge of the sample.

Next, preferential thinning at the precipitates is investigated. Figure 6a shows an unfiltered image of the FIB prepared sample from within the encircled area in Figure 4a, and precipitates (indicated on the figure) can be observed due to the presence of diffraction contrast. The thickness map shown in Figure 6b and displaying the value for \(t\) in each pixel as obtained by formula (1) does not show any clear variations in thickness, indicating that preferential thinning of the precipitate is absent. This is confirmed by the intensity profile in Figure 6c, which was obtained along the direction indicated by the white rectangle. It must be noted that similar results are found in thicker regions of the specimen. The results are compared with the thickness variations for a precipitate in an electropolished sample. Such a sample is prepared by mechanical grinding up to 120 \(\mu\)m of thickness followed by electropolishing until the specimen is perforated and electron transparency is obtained surrounding the small hole. This is performed with a twin jet device (Tenupol-3) and an electrolyte consisting of 80% methanol and 20% sulphuric acid at a temperature of 280 K and a potential of 20 V. In Figure 6d the unfiltered image is presented and the filtered image or thickness map is shown in Figure 6e. In this figure, a darker contrast can be observed in the precipitate, and this corresponds to the dip that is present in the intensity profile (Fig. 6f). Clearly, in this case, the precipitate is thinner compared to the matrix and thus preferentially etched.

**DISCUSSION**

It was already shown in the past that the FIB is an excellent tool to prepare TEM samples. Until now, most of the dedicated and quantified work has been done for semicon-
ducting compounds. For those compounds, chemical wet polishing is often used to remove amorphization damage caused during the FIB preparation (Jinschek et al., 2004). This method however, cannot be applied for all solid-state materials. In the present study, high-quality samples of NiTi and SrTiO$_3$/SrRuO$_3$ multilayers are prepared by wedge lift out, followed by a 5-kV and 2-kV Ga$^+$ cleaning procedure. From TEM measurements it is shown that this results in high-quality samples. For NiTi, HRTEM images show that FIB thinning has not damaged the superstructure of the precipitates. For SrTiO$_3$/SrRuO$_3$, it is possible to obtain HAADF-STEM images with atomic resolution. In both cases Ga$^+$ implantation was found to be below the EDX detection limit. These results indicate that amorphization and/or surface damage can be significantly reduced by the low kV cleaning procedure applied in this study. Indeed, samples that have not been subjected to the final stage of 2-kV cleaning for the indicated periods of time reveal Ga concentrations up to 25% for the NiTi and 15% for the ML and strong diffuse intensity rings in diffraction patterns obtained from the thinnest areas. Furthermore, we have investigated the use of FIB prepared samples for advanced TEM methods such as EFTEM and HAADF-STEM. All these techniques require samples with a uniform or known thickness, because quantitative interpretation of chemical profiles is only possible if the sample thickness is exactly known or known to be uniform. A HAADF-STEM comparison between an ion milled sample and a FIB prepared sample of SrTiO$_3$/SrRuO$_3$ shows the advantage of using FIB for thin films and multilayer samples: Samples with a uniform thickness are obtained, whereas the ion milled sample shows a strong nonlinear increase in sample thickness. For electro-polishing of NiTi samples that include precipitates with a slightly different composition, the situation may be even worse: The precipitates are thinned at a different speed and may even be completely removed before the matrix reaches a thickness that is sufficiently thin for (HR)TEM. This will obviously complicate the quantitative interpretation of analytical measurements as well (Tirry & Schryvers, 2005; Yang et al., 2005). However, the EFTEM results presented in this study show that, using FIB, samples in which the precipitates and the surrounding matrix have the same thickness can be obtained successfully. The method presented here can be expected to be extended for a broad range of systems for which conventional TEM sample preparation or FIB preparation without low kV cleaning does not yield the required sample quality.

**Conclusions**

FIB specimen preparation with 5-kV and 2-kV cleaning has been applied to NiTi and SrTiO$_3$/SrRuO$_3$ multilayers. By HRTEM, HAADF-STEM, and EDX it is demonstrated that the cleaning process yields samples in which the amorphiza-
tion as well as Ga⁺ damage is significantly reduced when compared with samples that have not been subjected to the low kV cleaning. The sample thickness is investigated by EFTEM and HAADF-STEM and it is shown that FIB results in samples with controlled thickness over lateral distances as large as 0.5 μm. Furthermore preferential thinning effects for multicomponent samples are avoided.

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