Preparation of nanotubes for cross-sectional TEM/STEM observations

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Modern wet chemical synthesis methods, such as sol-gel, coprecipitation, electrophoretic deposition (EPD) etc., enable preparation and processing of nano-sized powders, nanorods and nanotubes. The most common sample preparation technique for TEM/STEM observations of these nano-sized materials is to disperse them on a holey and/or lacy carbon coated grids. This simple method proves to be quite suitable for observation of isotropic nano-sized powders while for anisotropically shaped nanostructures (nanorods and nanotubes) one can only observe these 1D nanostructures along their length since they deposit flat on the carbon film due to their large aspect ratio. However, for more complete structural and chemical characterization one has to be able to prepare and analyze cross-section thin slices of these 1D nanostructures as well. This is why in our work we present the following two approaches to prepare cross-section thin slices of nanotubes: *ion-milling and ultramicrotomy*. As a model material we used $SrTiO_3$ nanotubes that were prepared by electrophoretic deposition of the $SrTiO_3$ sol into anodic aluminum oxide templates (AAO) [1]. A typical polycrystalline $SrTiO_3$ nanotube obtained by the EPD process is shown in figure 1. For TEM observation the specimen was prepared by dispersing $SrTiO_3$ nanotubes in ethanol by ultrasonic agitations and dropping the suspension onto the lacey carbon coated nickel grids.

For preparation of $SrTiO_3$ nanotubes cross-section thin films by ion-milling, an epoxy resin and $SrTiO_3$ nanotubes were mixed together and the mixture was deposited between two silicon substrates which were subsequently prepared as a cross-section. After mechanical preparation the specimen was ion-milled at 4 keV and 10^o incident angle (Bal-Tec RES 010) [2]. Due to random orientation of $SrTiO_3$ nanotubes embedded into the epoxy resin the regions showing cross-sections of the nanotubes can be readily found (Fig. 2). However, ion-milling produced amorphisation of the nanotubes and the regions of interest mostly remain embedded in the resin which makes detailed HRTEM studies not possible.

For preparation of $SrTiO_3$ nanotubes cross-sections by ultramicrotomy [3, 4] the nanotubes were embedded in an epoxy resin. Unclosed flat embedding moulds were used. After hardening the resins in the moulds, the hardened resin blocks were removed and were trimmed in the high-speed milling system Leica EM-TRIM2. Then they were transferred to the ultramicrotom Leica EM-UC6. The face to be sectioned was aligned perpendicular to the axis of the specimen holder. The rough surface after the trimming was removed by a 35^o diamond blade. After that 40 to 70 nm thick sections were cut with a knife speed of 1 mm/s at the cleavage angle of 6^o. Finally, the cut sections were picked up on a lacey carbon coated cooper grids an examined in a TEM. Figure 3 shows two different regions form the thin slice obtained by ultramicrotomy. A large number of cross-sections with different orientations through $SrTiO_3$ nanotubes were found. A radial (Fig. 3a) and an axial cross-section (Fig. 3b) are shown. Since the slices are cut from both sides it is reasonably to assume that the epoxy resin does not cover the material on any side of the slice and that the $SrTiO_3$ material is fully

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exposed for either imaging (TEM, HRTEM, STEM) or spectroscopy analysis (EDXS, EELS). Also ultramicrotomy introduces no artifacts unlike ion-milling (beam damage, sputtering, etc.). The results of our work clearly show that this technique is superior to methods involving ion-milling for preparing cross-sectional specimens of 1D nanostructures, such as nanotubes and/or nanorods.

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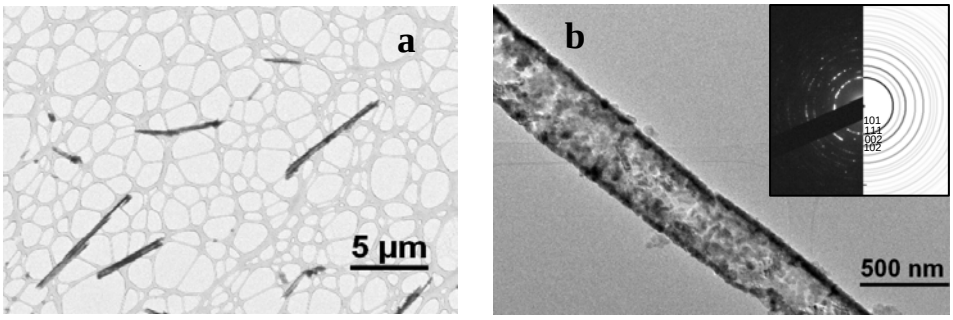

Figure 1: BF-TEM images of $SrTiO_3$ nanotubes obtained by EPD method. TEM specimen was prepared by ultrasonic deposition of nanotubes onto lacey carbon coated nickel grid. (a) Low magnification image showing distribution of nanotubes. (b) Higher magnification BF image showing the polycrystalline nature of a nanotube.

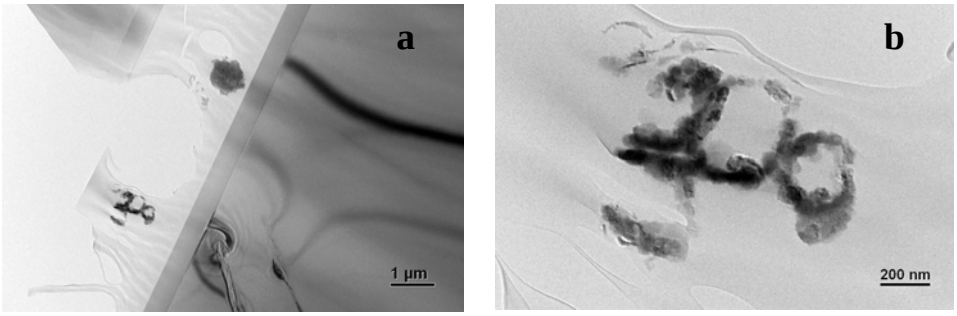

Figure 2: BF-TEM images of ion-milled $SrTiO_3$ nanotubes. Images (a) and (b) show the nanotubes which are embedded in the resin.

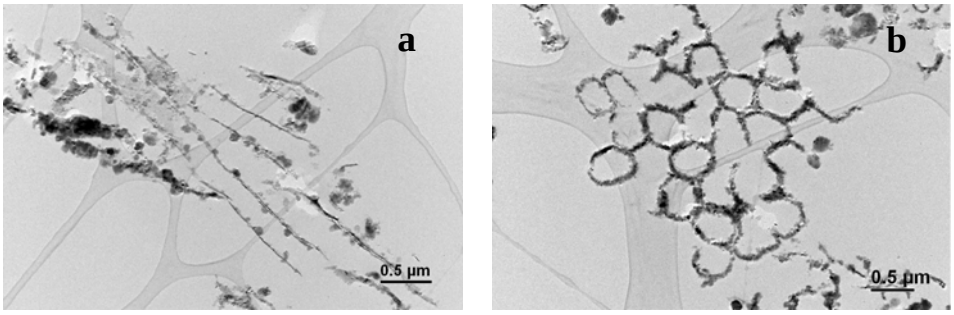

Figure 3: BF-TEM images of (a) radial and (b) axial cross-sections of $SrTiO_3$ nanotubes obtained by ultramicrotomy.

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