esteem3

Enabling Science through European Electron Microscopy

Report on protocols for sample preparation techniques of ICT materials

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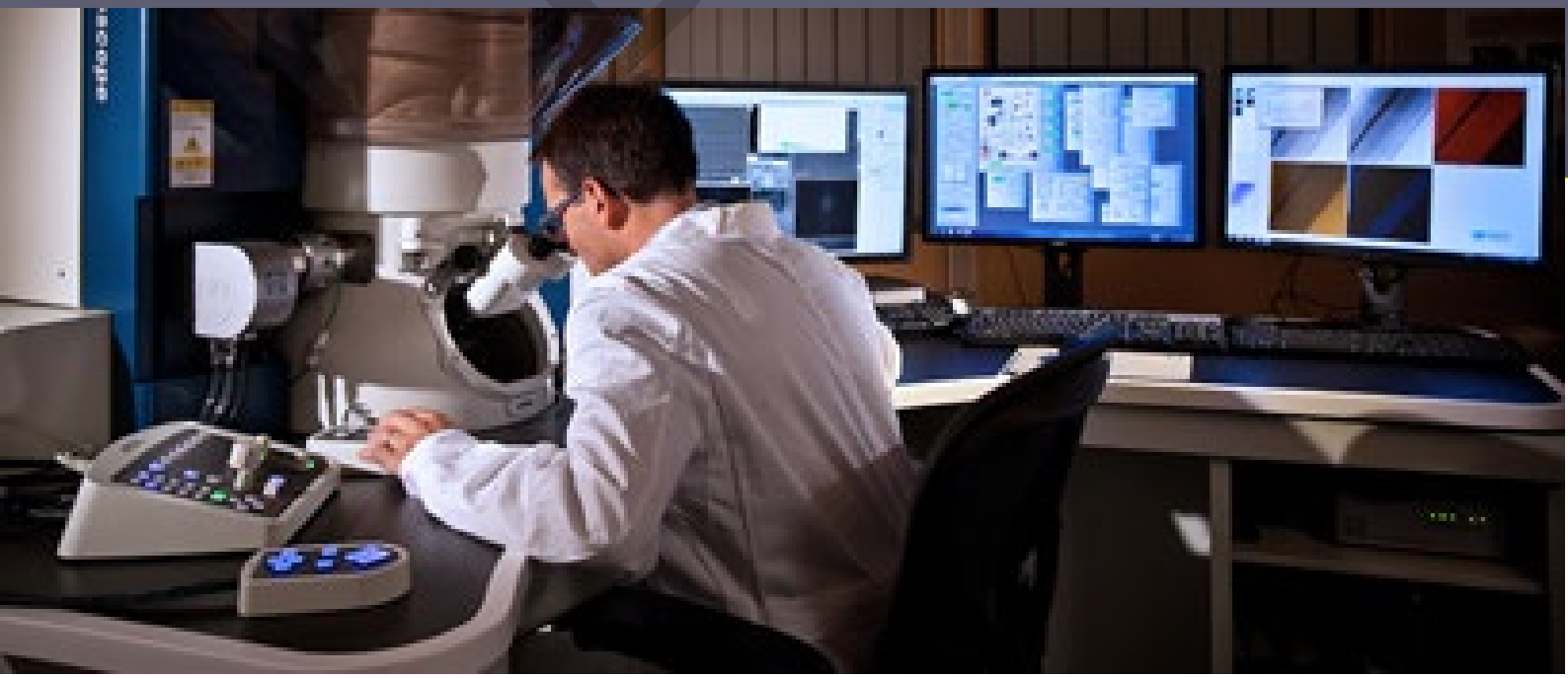

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Introduction

The quality of TEM samples that are to be studied by advanced TEM is crucial for what information that can be obtained, the spatial resolution that can be reached and also for avoiding misinterpretation of the collected data. Important aspects area avoidance of preparation artifacts, site specificity, micromanipulation, nanostructuting and speed.

Different specimen geomtries, for example, thin films, nanowires quantum dots and 2D materials pose different challenges, when it comes to providing access to the information that is to be extracted. The sample preparation is therefore a critical step in the procedure of advanced transmission electron microscopy. The preparation involves often several steps in the procedure and the work of developing a sample preparation method is promoted by experience from previously established techniques. It is therefore most valuable to have protocols and publications of already existing methods. This report summarises the sample preparation techniques that has been developed in WP7 for ICT materials.

Assessment of sample quality

Within the scope of a master thesis at GRA, a combination of different mechanical and ion thinning methods was explored to achieve comparable or even better results compared to traditional FIB preparation. Samples of silicon, silicon germanium, germanium and gallium nitride are prepared both in plan view and in cross-sectional view. The quality of each prepared sample is assessed based on visible defects and artefacts, the sample thickness and the processing time.

Bright-field TEM imaging was combined with t/λ maps, which were obtained via EFTEM imaging, providing information about the sample thickness in units of the inelastic electron mean-free path λ. Based on this information, the preparation procedures were optimized and documented in detail, with the aim to reproduce them as closely as possible. Figure 1 exemplary shows t/λ maps of GaN samples prepared with two different thinning techniques in comparison.

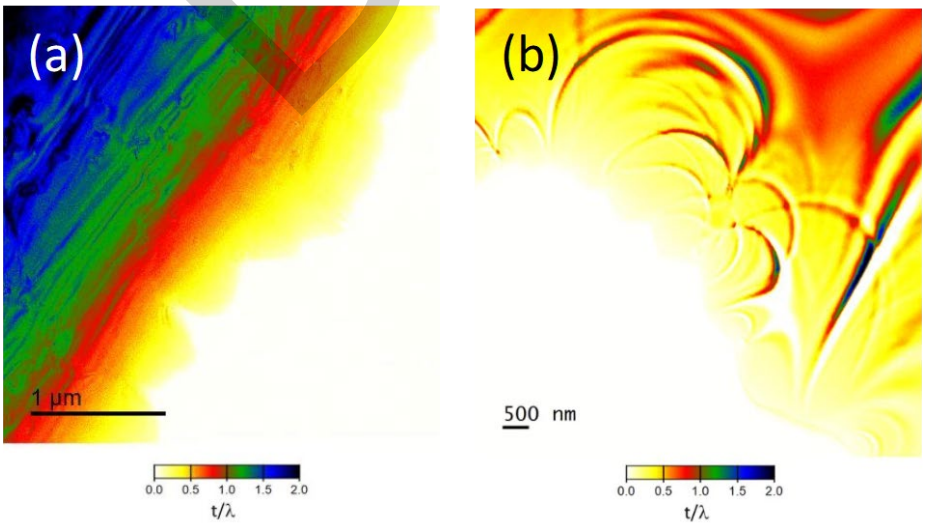

Figure 1. t/λ thickness maps of two GaN samples prepared with an optimized wedge polishing procedure followed by Ar ion milling in (a) and mechanical dimpling followed by ion milling in (b).

Wedge polishing

Doping elements have a tremendous impact on the properties of functional materials. Therefore, their distribution and characterization are of high importance for manifold applications. The change in physical properties of a doped material can reach from optical characteristics up to modified electrical or magnetic properties. In particular, the properties of photocatalytic oxide materials, such as $SrTiO_3$, can be dramatically improved by integrating foreign atoms like Nb, Ta or Rh in trace concentrations. Improved techniques for the preparation using wedge polishing and characterisation of such samples were developed (GRA, STU) in order to localize single dopant atoms within the crystal by quantitative HAADF imaging supported by quantitative multi-slice simulations. Our results for Ta (0.01 wt.%) doped $SrTiO_3$ (STO) are shown in Figure 2. Ta preferentially occupies the Ti positions within the perovskite structure. A sample thickness of less than 5 nm was measured via position-averaged CBED (PACBED). Under such conditions, we were able to localize Ta dopants on the TiO column positions of STO in [100] orientation. Furthermore, a drop in intensity within certain Sr columns is detected, which is likely caused by the presence of Sr vacancies within such columns.

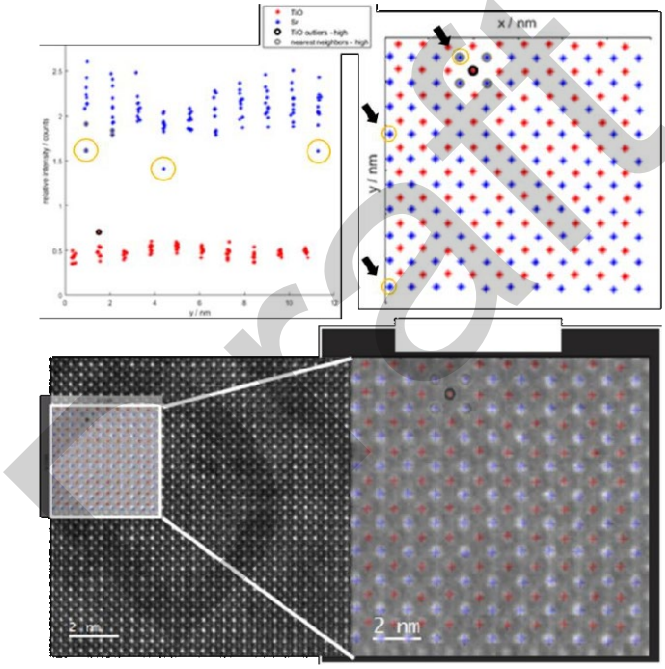

Figure 2. Analysis of a HAADF image section with side view (top left) and top view (top right) as well as overlay results. Ta dopant position marked with black circle and with nearest Sr neighbours in grey, Sr vacancies in orange.

Quantum dots

By combining tripod polishing followed by Ar+ ion milling (Figure 3) with focused ion beam cutting with subsequent low-energy milling and cleaning (Figure 4), high quality TEM samples of quantum dot structures were reproducibly prepared [1].

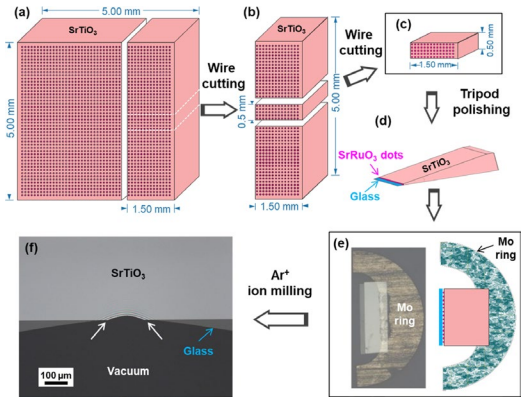

Figure 3. Schematic diagram of TEM sample preparation by tripod polishing followed by Ar^+ ion milling (TP&IM). (a–c) Cutting slabs of 1.5 mm width and 0.5 mm thickness using a wire saw. (d) Preparation of wedge-shaped specimen by tripod polishing. (e) Attaching a tripod-polished sample to a molybdenum half ring. (f) Milling the central region of the thin part of the wedge by Ar^+ ion milling to obtain the finalized TEM specimen. The white arrows mark the areas of interest; the blue arrow marks the glass layer. [1]

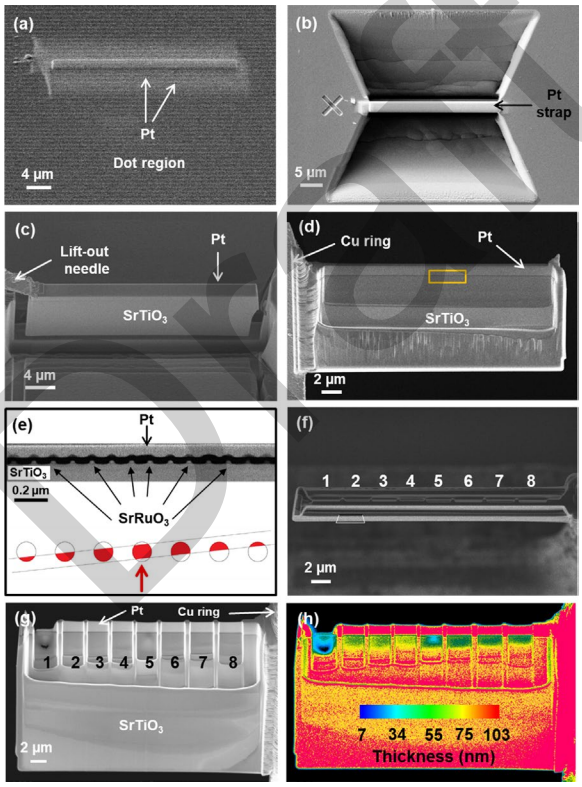

Figure 4. TEM sample preparation with a focused ion beam (FIB). (a) Deposition of a Pt protective layer on the bulk surface via electron-beam and ion-beam induced deposition. The straight Pt strap is deposited at an angle of 5° with respect to the QD rows. (b) Cutting of two trenches on both sides of the Pt strap with a Ga^+ ion beam leaving a thin section of material isolated at the center. (c) Separation of the lamella from the bulk with an U-shaped undercut by an in-situ lift-out of the specimen with a micromanipu- lator (Kleindiek MM3A). (d) Attaching of the FIB lamella to a half-moon-shaped copper (Cu) grid (Omniprobe 3 post lift-out grid) using Pt. (e) Upper part: Imaging of the QDs by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of the yellow box region marked in (d). Bottom part: A sketch of the cutting geometry of QDs at different positions. (f) Thinning of the FIB lamella from two sides (top view). Eight regions of interest were set for fine thinning. (g) Back-scattered electron image of the final FIB lamella, that was thinned from both sides. 8 regions are separated by thicker walls. (h) Thickness map of the lamella based on the backscattered electron signal, where the STO substrate was used as a reference for the thickness evaluation. [1]

In situ electrical measurements on individual semiconductor nanowires

In situ TEM is a powerful technique for directly correlating properties and structures of nanomaterials. *In situ* TEM measurements on semiconductor nanowires often require directly contacting and manipulating individual nanowires for electrical and mechanical measurements in TEM. Sample preparation for such measurements is challenging due to the nanoscale dimension and 1 dimensional (1D) morphology of the nanowires. In this protocol, we describe a procedure for transferring individual GaAs nanowires from growth substrate to TEM sample grid with minimum artifacts, as well as means by which electrical contacts on the nanowires can be established and improved, using focus ion beam - scanning electron microscope (FIB-SEM) [2, Protocol on ESTEEM3 website].

The GaAs nanowires were grown on Si substrate using a self-catalyzed method. The length of the nanowires is ~ 15 µm. The diameter of the nanowires is ~ 150 nm. The FIB-SEM instrument used in this protocol was a FEI Versa 3D FIB-SEM. A Cu half grid from Omniprobe was used as sample support for the transferred nanowires. The in situ TEM sample was mounted in a Nanofactory scanning tunneling microscopy (STM) – TEM sample holder for in situ straining and electrical measurements.

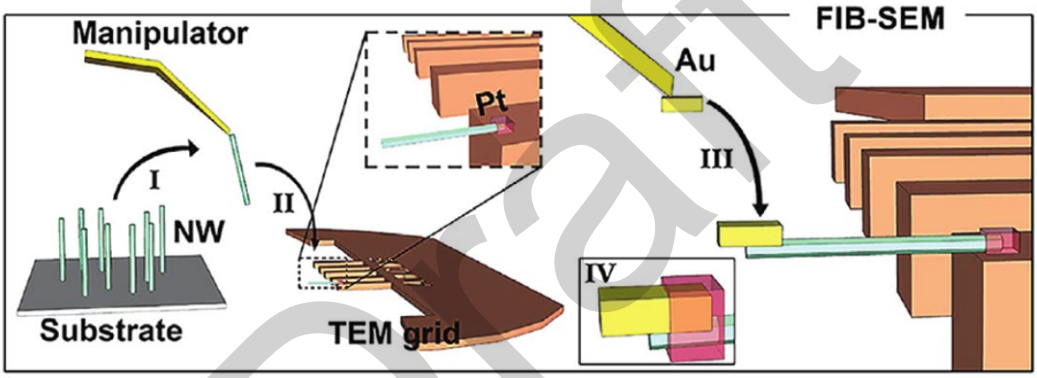

Figure 5. Schematic of the FIB sample preparation procedure for in situ TEM measurements on semiconductor nanowires. In step I, a micromanipulator in FIB-SEM was used to scratch the Si substrate surface. A nanowire was attached to the manipulator due to Van der Waals force. Then, the nanowire attached on the manipulator was transferred to the TEM half grid (II). One end of the nanowire was placed on the grid and the contact was fixed by EBID of Pt. Afterwards, a small piece of Au was transferred and attached onto the free end of the nanowire using the manipulator (III). The Au piece was welded on the nanowire using EBID of Pt (IV). [2]

Sample transfer for studies with *in situ* MEMS devices

In situ TEM using MEMS devices have enabled a large variety of *in situ* TEM measurements with high stability, controllability, and versality, such as in situ heating, mechanical stressing, electrical biasing, liquid and gas environment experiments. In practice, the use of the MEMS devices for *in situ* measurements is not always straightforward. Especially, preparation and transfer of samples onto the MEMS devices can be challenging, due to several factors. First, the size of the area on the MEMS device, where it is suitable for placing the samples, is small. The TEM samples often need to be mounted in a designated area on the devices with a precision at the µm scale or higher to be able to, for example, connect the samples to the pre-fabricated electrodes on the MEMS devices. The size of the MEMS devices is usually tens of mm^2. Second, MEMS devices normally have a flat surface, which is necessary for fabricating functional circuits, connections, channels for enabling in situ stimuli or environment. But it can be difficult to transfer a TEM sample onto such a surface while minimizing misalignment,

contamination, mechanical stress and damage. Focus ion beam – scanning electron microscope (FIB-SEM) is a widely used tool for transferring TEM structures onto *in situ* MEMS devices because its ability of high resolution imaging, electron or ion beam induced deposition, ion milling and in situ manipulation. Normally, the manipulator in a FIB-SEM is utilized to contact the TEM sample from a substrate or sample support, after which electron/ion beam induced deposition is used to weld the sample on the manipulator for lift-out. The sample attached to the manipulator is then moved to be close to and aligned with the surface of the MEMS device. Electron/ion beam induced deposition is again used to weld the sample onto the MEMS surface. Finally, often Ga ion beam is used to cut the sample free from the manipulator. In such a process, the use of a Ga ion beam seems to be inevitable, though it can cause amorphization and ion implantation, changing the inherent structure in the sample. It is thus important to find a way to reduce or avoid the use of ion beam in the transfer process.

In this protocol, a procedure is described for transferring individual nanostructures or TEM lamella onto MEMS devices while avoiding ion beam induced artifacts in the transfer process, using FIB-SEM [3, Protocol on ESTEEM3 website]. The main idea is to use a dummy nanowire as the transfer probe instead of using the manipulator in the FIB-SEM. The nanowires used in this protocol are GaAs nanowires with a length of ~ 15 µm and diameter of ~ 100 nm. The advantages of using these nanowires are that they are thin (~ 100 nm), relatively long and flexible. Other nanowires with similar dimensions and properties can also be used. A FEI Versa 3D FIB-SEM was used for sample transfer. The MEMS device used is a Hysitron electrical push-to-pull (EPTP) device for simultaneous *in situ* mechanical and electrical measurements, see Figure 6. In this example, individual nanowires lying on a substrate were used as the TEM sample that needed to be transferred onto the MEMS device, but the same transfer procedure can be applied to TEM lamella as well.

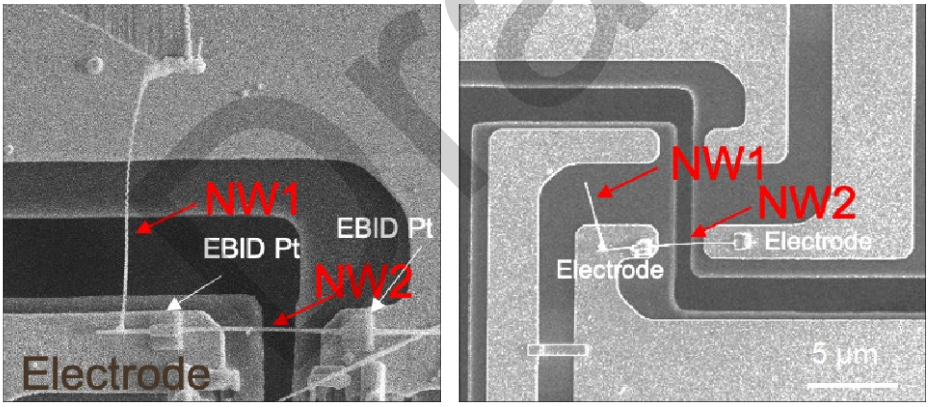

Figure 6. Transferring the nanowire sample onto the MEMS device. Left: the nanowire sample was moved to contact the MEMES surface in the designated area where there are two electrodes separated by a ~ 3µm gap. The two ends of the nanowire were contacting the two electrodes and fixed on the electrodes by EBID Pt. Right: the manipulator was gradually retracted until the dummy nanowire broke from the manipulator. Though the dummy nanowire was still attached to the nanowire sample, it did not affect in situ TEM measurements. [Protocol on ESTEEM3 website].

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