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Enabling Science through European Electron Microscopy

Report on protocols for advanced sample preparation of devices for in-situ experiments

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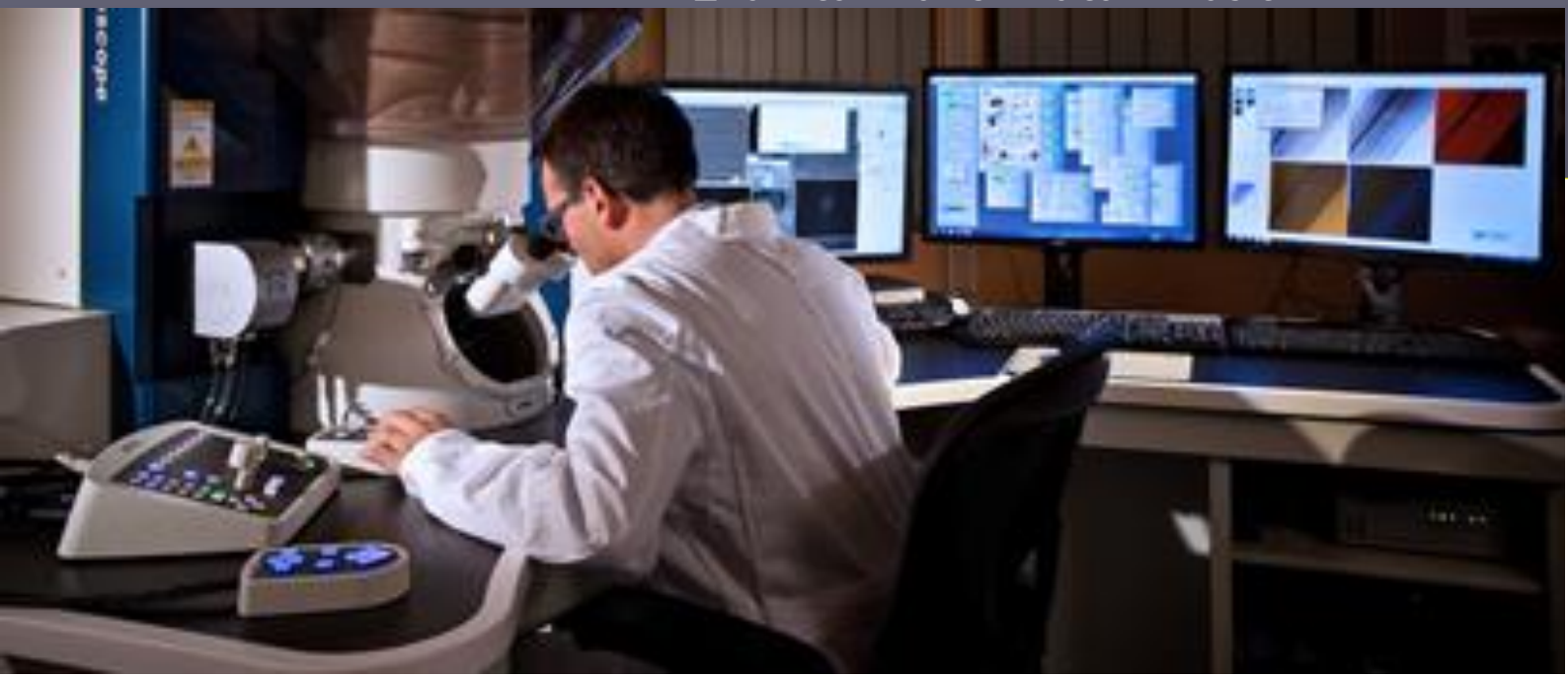

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V0.1		César Magén, Martin Hytch	First draft of deliverable
V0.2		César Magén	Feedback from partners
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Introduction

In-situ TEM experiments require often specific sample preparation protocols to produce viable specimens for the application of external stimuli. The procedures to be followed are as rich and varied as the nature of the material to be studied and the type of in-situ experiment that can be designed. Some examples include the extraction of specimens from a single device, special lift-off procedures to place the specimen in electron-transparent windows or pre-patterned chips, the use of special supports for temperature-dependent, liquid or gas environment, smart protocols for electrical contacting or local biasing, or adapted strategies for beam sensitive materials, among others. Most of these methods rely on the use of Focused Ion Beam (FIB) milling and lift-off techniques to extract, transfer and attach/contact electron-transparent specimens into the in-situ holder or set-up. Next, we summarize the main ESTEEM3 developments in this field carried out until now.

6.1.1 Advanced sample preparation for in-situ biasing (TOU)

TEM is the most appropriate tool to analyse in-situ local changes in electromagnetic fields, crystalline structure and chemical composition of working devices. Apart from nanometre spatial resolution, TEM allows the study of individual devices, thus providing crucial information to microelectronics manufacturers for the development and optimization of (future) devices in terms of reliability, speed and power consumption. However, few investigations on real devices in operation have been performed using electron microscopy. The main limitation is the preparation of suitable samples for operando experiments that allow reliable comparisons with conventional electrical characterisation of the on-chip devices.

In this task, we have developed a robust protocol to extract TEM lamellae containing a device from a chip using FIB and mount it in a biasing TEM holder in such a way that the active area remains operational. In this way, electron holography (EH) experiments can be performed to measure the electric field within and around the device whilst functioning. Care is taken to minimising artefacts due to the ion-beam thinning process, in particular surfaces effects, and to maintain the quality of the electrical contacts. These samples are extremely fragile, both electrically and mechanically, and different steps were required to optimise the success rate of experiments.

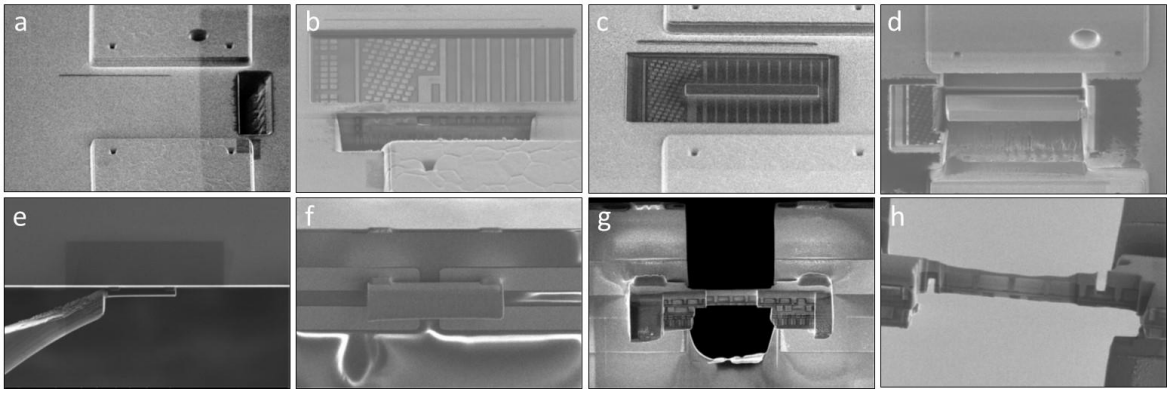

Figure 1. FIB preparation of specimen-device for in-situ biasing and operando experiments: (a) sample grounding & electrode connections; (b) Cu connects visible after FIB processing; (c) protective Pt layer; (d) sample pre lift-out; (e) sample welding to dedicated TEM grid; (f) chunk welded on TEM grid; (g) TEM grid membrane milling and vacuum area for EH reference wave; (h) final thinning and electrodes separation.

Figure 1 shows the preparation protocol applied to a commercial nanocapacitor device from STMicroelectronics [1]. A thin conductive layer (gold-palladium alloy) is first deposited on the wafer's surface to ensure charge evacuation. The sample is then grounded by opening the pad (Fig. 1a) and connecting the top surface to the grounded Si substrate; the charge from scanning electron beam (SEM) will be drained off to the ground during sample preparation. The sample is then top-down processed using FIB until the layer of interest is reached. Cu lines, which connect the nanocapacitors, are now exposed (Fig. 1b) and top and bottom electrodes are electrically connected by depositing a Pt layer (Fig. 1c).

The extracted sample is directly welded to an electron- transparent grid with Au pre-patterned tracks (Fig. 1e,f). Tungsten depositions are used to ensure electrical connection between the sample and grid. To meet electron holography criteria, the region of interest (here, thin high-K dielectric Ta_2O_5 layer sandwiched between two metal electrodes) must be no more than 500 nm away from the vacuum region (Fig. 1g), where the reference wave passes the sample. The next preparation step consists of separating the top electrode from the bottom one to create two distinct electrical connections for in-situ biasing. Two separation cuts (bottom left and top right) are visible on Fig. 1h. A final thinning of the lamella with a low energy ion beam (8 or 16 kV) for minimizing surface damage is performed, until a uniform thickness below 100 nm is reached for electron transparency.

The results from the operando electron holography experiment are summarised in Figure 2 [1]. A sequence of electrical biases was applied to the device mounted in-situ (Figure 2a) and holograms recorded, including a reference hologram with both electrodes grounded. The phase due to the electrical biasing (Fig. 2b) represents the distribution of the electrical potential in and around the device. Quantitative results can be obtained by comparing the experiments with modelling (Fig. 2c) to determine the effects of the stray fields and surface layers [2]. The excellent agreement is a gauge of the reliability of the sample preparation protocol.

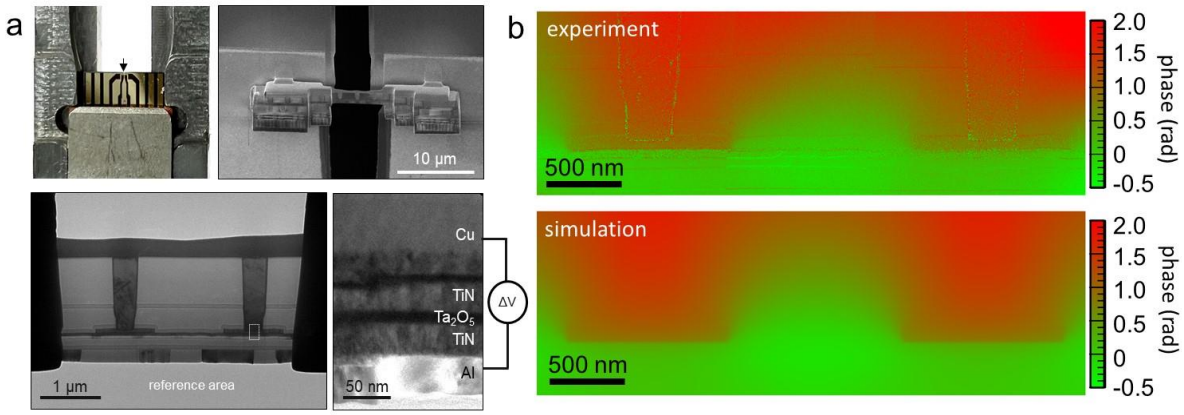

Figure 2. Operando electron holography on working nanocapacitor device: (a) sample-device on chip inserted in in-situ biasing holder (Hummingbird) and progressive enlargements showing active area; (b) experimental electron hologram phase map due to biasing; (c) corresponding simulated phase map from finite-element modelling.

This sample preparation protocol is not limited to devices but can be applied to thin-layer samples by depositing surface electrodes.

6.1.2 Advanced sample preparation in cryogenic conditions for in-situ experiments (ZAR)

In-situ experiments on beam sensitive materials is a remarkable challenge in many aspects. In addition to the damage introduced by the TEM experiment itself, specimen preparation without any significant modification of the original physical properties of the material or devices becomes additionally complex due to the special geometry and restricted dimensions. Indeed, the use of Ga^+ FIB lamella preparation is usually mandatory, instead of gentler, less invasive preparation approaches.

An example of these difficulties is the specimen preparation of high ion (oxygen) mobility thin film oxides, which might be in non-volatile memories based on resistive switching or solid oxide fuel cells. In this type of materials, both electron irradiation and specimen preparation can induce unwanted oxygen diffusion, which causes a drastic transformation of the crystal structure of the thin film oxide and, consequently, of their functional properties.

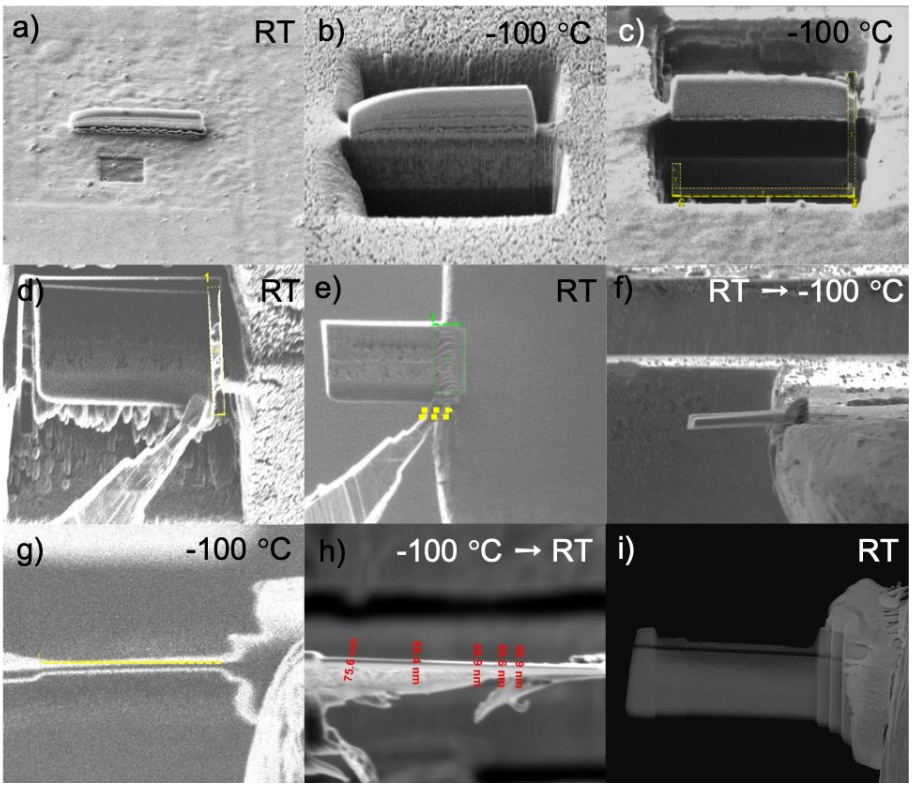

Figure 3. Cryogenic preparation of TEM lamella of beam sensitive $SrFeO_{3-\delta}$. a) Pt-FEBID & Pt-FIBID protection of the area of interest at RT; b) trenches milling at -100 °C and 30kV Ga FIB*; c) first step of lift-off at* -100 °C*; d) lamella attached to the micromanipulator and final lift-off; e) welding of the lamella to the TEM grid; f) cooling to* -100 °C *for final thinning; g) final thinning at low voltage (8-15 kV Ga FIB); h) profile of the final specimen; i) general view of the finished lamella at RT.*

In this task, we have endeavored the investigation of the kinetics and morphology of the physico-chemical transformation of $SrFeO_{3-\delta}$ thin films by the in-situ application of electric fields with a STM metallic tip. An external electric field can induce a topotactic transformation between a conducting perovskite-type structure with randomly oriented vacancies, which transforms into an insulating brownmillerite $SrFeO_{2.5}$ phase [10]. This transformation has been analyzed ex-situ and specimen preparation for TEM experiment has proven to be challenging, being the perovskite phase metastable

and prone to transform into the brownmillerite phase by ion irradiation [11]. Due to these difficulties, cryogenic FIB sample preparation has been attempted.

We have employed a FEI Dual Beam Nova Nanolab 200 equipped with a cryo-transfer system from Quorum Technologies to obtain lamellas in cryo conditions by putting the sample stage in contact with a flux of cryogenic vapor of liquid nitrogen. The process begins with the room-temperature deposition of a protective layer of Pt grown successively by focused electron beam induced deposition (FEBID) and focused ion beam induced deposition (FIBID) on the surface of the area of interest (Fig. 3a). This step could be performed at cryogenic temperatures, in which a condensation of the Pt precursor takes place in the region of interest, but afterwards it would be required to develop the condensate layer by heating up at room temperature. The next step implies the cooling of the sample stage at approximately < -100 °C, where the standard lamella preparation procedure continues with the rough ion milling of the specimen. Trenches are dug at both sides of the region of interest to produce a thick lamella of approximately 1-1.5 μm thick (Fig. 3b). Next, lift-off process begins by performing a U-shaped ion beam pattern on the inclined object to detach the specimen from the bulk sample except from all sides except one (Fig. 3c). Then, the stage is heated up to room temperature to enable the welding of the specimen to the micromanipulator, complete detachment of the lamella, and welding of the object to the TEM grid (Fig. 3d-e). For the final ion beam thinning at lower voltages (from 15 to 8 kV), the stage is cooled again to -100 °C (Fig. 3f) to complete the preparation of an electron transparent lamella with a thickness of around 50 nm (Fig. 3g-i). This is the critical step due to the combination of poor ion beam resolution and mechanical instabilities due to thermal drift and vibrations at low temperatures. Figure 4 shows the differences between room temperature specimen preparation of $SrFeO_{3-\delta}$ and cryogenic specimen preparation.

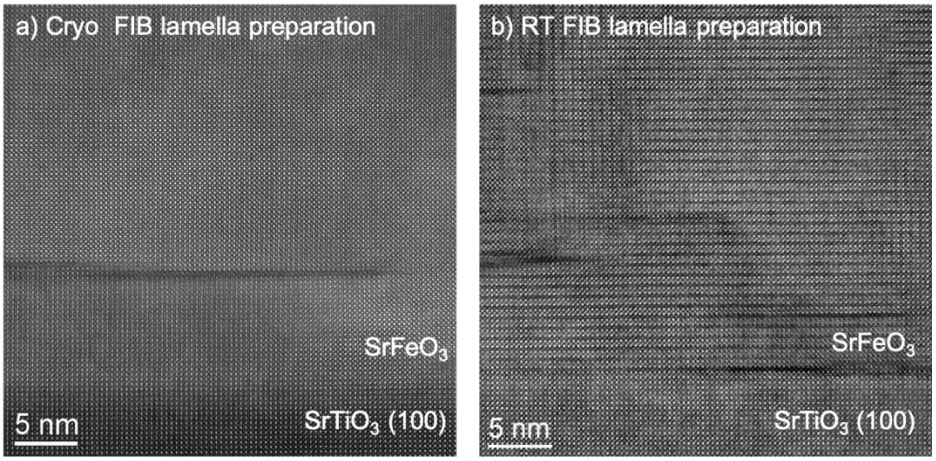

Figure 4. Cryogenic preparation of TEM lamella of beam sensitive $SrFeO_{3-\delta}$. a) HAADF-STEM image of a cross-sectional TEM lamella of a $SrFeO_3$ thin film prepared using the protocol described in this report. b) HAADF-STEM image of the same system prepared by standard RT Ga FIB.

The optimization of this procedure to allow the full exposure of the $SrFeO_{3-\delta}$ thin film to the conductive STEM tip is required to allow the application of local electric field (with lateral resolution comparable to the radius of the tip, of several tens of nanometers). For this purpose, the Pt layer has to be removed without damaging the $SrFeO_{3-\delta}$ thin film. This is being attempted by the deposition of a thick carbon layer prior to the Pt FEBID deposit. This would enable the later removal of the Pt layer, and subsequent cleaning of the carbon layer by plasma cleaning. The test of this approach is currently underway.

6.1.3 Sample Preparation of Graphene Oxide Films for the Study of their Thermal Reduction via In-situ Joule Heating Effect (ZAR)

The reduction of graphene oxide (GO) is a very important point for the application of this nanomaterial. As already reported, **ZAR** has carried out an in-depth investigation of the thermal reduction of GO via *in-situ* TEM studies [5, 6]. For performing such studies, a critical aspect, in particular for the thermal reduction via the Joule heating effect and the simultaneous measurement of the conductivity of such GO films during the whole process of their reduction and graphitization [5], is the films' preparation. A focused-ion beam (FIB) instrument was used to cut and transfer a piece of the GO film to the DENSsolutions nanochip assisted by micro-needles and a gas injection system (GIS). Several approaches have been employed and the best result was obtained by the application of two micro-needles used for GO transport and electrostatic discharging of the metal contacts, combined with focused-electron and focused-ion beam induced deposition (FEBID/FIBID) of C (precursor gas $C_{10}H_6$) for electrical contacting and fixation of the film to the chip.

Figure 5 shows four images acquired during the FIB-based preparation of the sample. First, a piece of the GO film suspended on a Cu grid is cut and taken out using a micro-needle (Fig. 5a). The piece is transferred to the in-situ chip while a second micro-needle touches one of the contacts to avoid electrostatic charging (Fig. 5b). The piece is then connected to the two contacts of the chip using FIB induced deposition of C guaranteeing good mechanical fixation and electrical contact without introducing heavy metal contamination (Fig. 5b). Although the time of electron and ion beam irradiation is kept to a minimum, a modification of the film cannot be completely inhibited. A comparison of EEL spectra and diffraction patterns before and after the FIB transfer is displayed in Fig. 6. The alteration is mainly given by the deposition of an additional contamination layer containing C (C absolute content increased by 24%), a small amount of O (increased by 5%) and probably Ga resulting in a slightly lowered overall O content (24% decreased to 21%) and an increased thickness of the transferred piece in comparison to the original GO sample. The actual sample may thus be seen as a GO core wrapped in amorphous carbonaceous contamination.

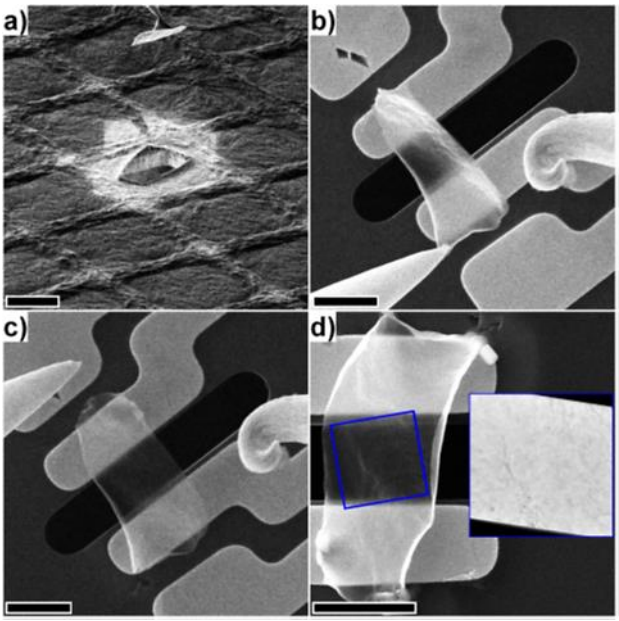

Figure 5. FIB-assisted GO sample preparation. (a) FIB image of a GO piece taken out with a micro-needle from a continuous film on a Cu grid. SEM image of (b) approaching and (c) connected GO piece while

grounding the Pt contact pad with the second micro-needle. (d) SEM image of electrically connected GO piece and a TEM image of the film as inset. Scale bars are (a) 10 and (b-d) 5 μm.

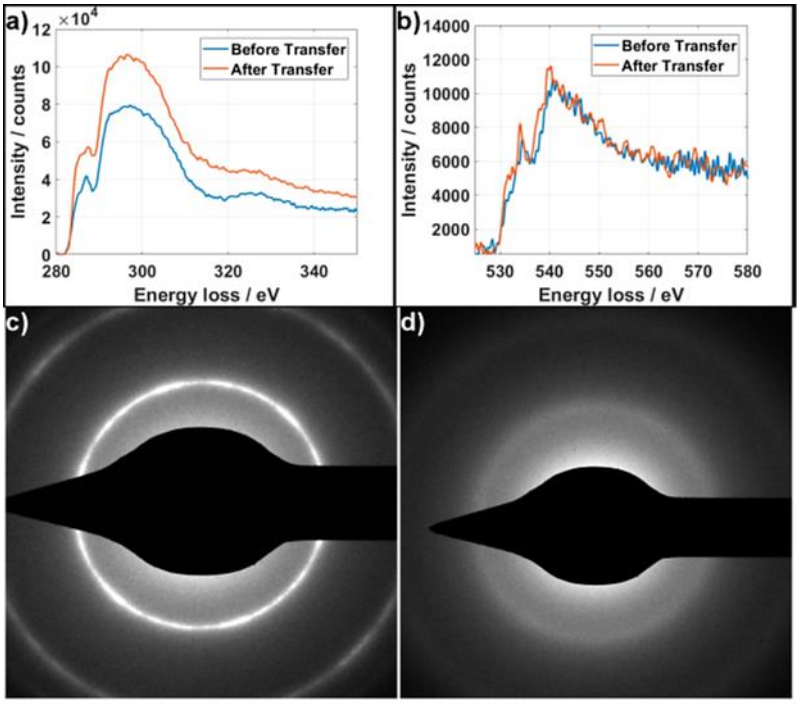

Figure 6. Sample modification during FIB transfer. Comparison of EEL spectra of (a) C-K edge and (b) O-K edge before (blue) and after (red) the FIB transfer. While the C signal is increased and modified due to the presence of deposited C contamination, the O signal is only marginally affected. The presence of amorphous contamination is also visible in the comparison of the diffraction pattern (c) before and (d) after the transfer. The amorphous layers introduce a stronger background signal leading to smeared out diffraction rings of the GO film. The texturing of the drop-casted GO film is not seen anymore after the transfer.

References

[1] M. Brodovoi, K. Gruel, L. Chapuis, A. Masseboeuf, C. Marcelot, M. J. Hÿtch, F. Lorut, and C. Gatel, Proc. 47th International Symposium for Testing and Failure Analysis Conference (ISTFA 2021) (ASM International) pp 190-195. *In-situ electrical biasing of electrically connected TEM lamellae with embedded nanodevices.* 10.31399/asm.cp.istfa2021p0190

[2] K. Gruel, R. Serra, A. Masseboeuf, C. Gatel, and M. J. Hÿtch, Proc. Colloque de la Société Française des Microscopies (SFmu 2021, Reims). *Modeling electric fields in nanocapacitors observed by operando electron holography*.

[3] Elías Ferreiro-Vila, Santiago Blanco-Canosa, Irene Lucas del Pozo, Hari Babu Vasili, César Magén, Alfonso Ibarra, Juan Rubio-Zuazo, Germán R. Castro, Luis Morellón, Francisco Rivadulla. Advanced Functional Materials 29 (2019) 1901984. *Room-Temperature AFM Electric-Field-Induced Topotactic Transformation between Perovskite and Brownmillerite $SrFeO_x$ with Sub-Micrometer Spatial Resolution*.

[4] E. Ferreiro-Vila, D. Bugallo, C. Magén, F. Rivadulla, and J. M. De Teresa. Applied Physics Letters 116, 163103 (2020). *Topotactic transformation in SrFeO3−δ triggered by low-dose Ga+ focused ion irradiation*

[5] Hettler, S.; Sebastian, D.; Pelaez-Fernandez, M.; Benito, A. M.; Maser, W. K.; Arenal, R. In-Situ Reduction by Joule Heating and Measurement of Electrical Conductivity of Graphene Oxide in a Transmission Electron Microscope. *2D Materials* **2021**, *8* (3). https://doi.org/10.1088/2053-1583/abedc9.

[6] Pelaez-Fernandez, M.; Bermejo, A.; Benito, A. M.; Maser, W. K.; Arenal, R. Detailed Thermal Reduction Analyses of Graphene Oxide via In-Situ TEM/EELS Studies. Carbon 2021, 178, 477–487. https://doi.org/10.1016/j.carbon.2021.03.018.