

Chapter 2

Experimental Techniques

In this chapter we present the experimental techniques used in the development of this thesis, for the fabrication of samples and for subsequent characterization. The sample fabrication was carried out in three “Dual Beam” (SEM/FIB) systems with similar characteristics: Nova 200 NanoLab and Helios NanoLab 600 stationed in the Advanced Microscopy Laboratory, Institute of Nanoscience of Aragon (INA-LMA), University of Zaragoza, and the Nova 600 NanoLab installed at the Eindhoven University of Technology (TU/e). The characterization of the samples was performed in situ (SEM, EDS, electrical transport measurements) and ex situ (AFM, PPMS, HRTEM, STEM/EELS,...) in the Advanced Microscopy Laboratory, Institute of Nanoscience of Aragon (LMA-INA) and the Physical Measurements Service of the University of Zaragoza.

2.1 Nanolithography by “Dual Beam”

2.1.1 Description of a “Dual Beam”

In Chap. 1 we provided an overview of a “Dual Beam” system, detailing the fundamental parts that make it up and its wide range of applications. Owing to the important role that this tool has played in the development of our research, including the fabrication of samples, we definitely consider it “the heart” of this thesis. Figure 2.1 shows a photograph of the Helios NanoLab 600 instrument, one of the “Dual Beams” used for fabrication of nanostructures.

In Fig. 2.2 we can see inside the process chamber of the Nova 200 NanoLab (left; another “Dual Beam” widely used for the growth of nanostructures in the development of this thesis) and the Helios NanoLab 600 (right). Given the importance of these systems in the development of this thesis, we now indicate which aspects of the equipment or tools have been used specifically.

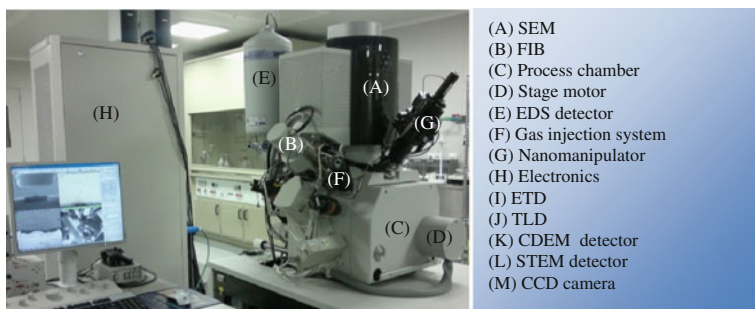


Fig. 2.1 Photograph of the Helios NanoLab 600 “Dual Beam” system installed in the clean room of the LMA-INA. (ETD Everhart–Thornley detector, TLD through-the-lens detector, CDEM continuous-dynode electron multiplier)

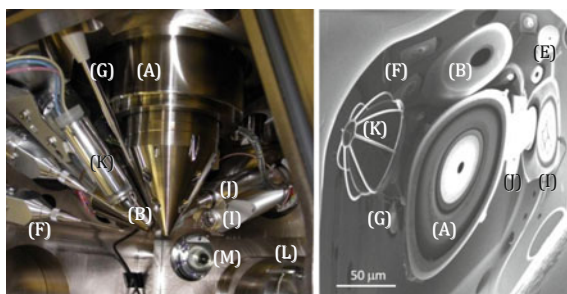


Fig. 2.2 Inside the process chamber of two Dual Beams. *Left* Photograph of the Nova 200 NanoLab installed at the LMA-INA. *Right* SEM image. An insulating material to be charged by the FEB irradiation acts as an “electronic mirror” and allows us to get a fascinating picture of some pieces of the Helios NanoLab 600 from the perspective of the sample

1. Acquisition of high resolution images using the appropriate SEM, STEM and FIB detectors
2. Milling by FIB: cross sections, etc.
3. Nanofabrication by SEM: growth of Co, Fe and Pt nanodeposits
4. Nanofabrication by FIB: growth of W and Pt nanodeposits
5. Compositional analysis of nanodeposits by the EDS technique
6. Electrical characterization of the fabricated nanodeposits by the four-probe technique
7. Manipulation of micro and nanostructures using a nanomanipulator
8. TEM sample preparation.

2.1.2 SEM

The electron column is based on a field emission electron source, with a W filament. The optics of the column focuses the electron beam to obtain the best resolution: 0.9 nm operating at 15 kV, 11 pA.

2.1.3 FIB

The ion column can focus the ion beam down to 5 nm in diameter using the smallest aperture of the system (~ 1 pA), which gives us the ability to mill or grow ultranarrow structures on the order of a few nanometers. The maximum aperture of the Magnum column in the Nova 200 NanoLab and Helios NanoLab 600 allows us to operate with a current of ~ 21 nA (beam diameter ~ 411 nm), very useful for milling large areas or trenches, as in TEM sample preparation.

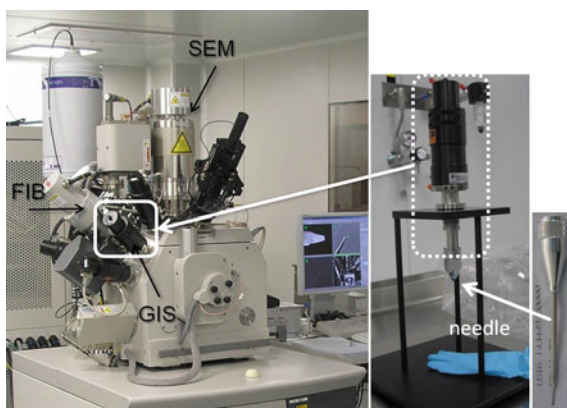
2.1.4 Gas Injection System and Precursor Materials

2.1.4.1 Gas Injection System

The gas injection system (GIS) is compact and individual for each precursor material, as seen in Fig. 2.3. Both insertion and retraction of the GIS and the opening of the valve that allows the gas precursor to enter the process chamber are very fast.

The temperature of the crucible, where the precursor material is stored, and the needle, which is screwed to it, is homogeneous and controlled. Therefore, the pressure in the crucible is constant and, as a consequence, the flow of molecules that is released through the needle is only related to the saturation vapor pressure

Fig. 2.3 Photograph of a “Dual Beam” in which the port where the GIS is installed is indicated. In the smaller photographs we see the needle through which the precursor gas leaves (*right*) and the GIS on a platform (*center*)



and the resistance to the gas flow caused by the needle. The vapor pressure of a precursor material is given by the Clausius–Clapeyron equation, where $\log(P) \propto 1/T$. Given this equation, a change of ± 0.1 °C of the crucible temperature would result in a variation in pressure of about 1 %. The GIS allows the temperature to be controlled within that range of values, so that the flow delivered by the needle may have a variation of ± 1 %. The valve is opened automatically in the GIS, except in the case of Co and Fe precursors, when it is opened manually to avoid an abrupt rise in the chamber pressure. Moreover, the precursor temperature should not be too high to prevent the precursor chemistry being modified by natural thermal decomposition [1]. The temperatures of the precursor materials used in the development of this thesis were between 22 and 55 °C.

In addition to the gas flow exiting the GIS needle, it is important to know the sample area that is covered by precursor gas molecules. This area depends on several factors, such as the incidence angle of the needle, the separation of the needle from the substrate surface, the distance from the needle tip to the area of interest on the sample, and the shadow effect [2].

2.1.4.2 Precursor Materials

Most of the precursor materials used in FEBID and FIBID are organometallics that are widely known and implemented in other growth techniques such as CVD. For a simple implementation and installation in the “Dual Beam” is preferable that they are solid or liquid at room temperature (with exceptions such as xenon difluoride,

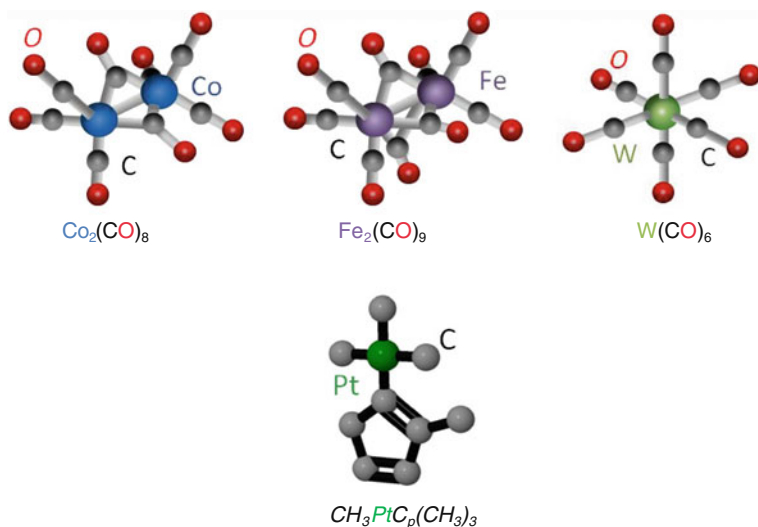


Fig. 2.4 Precursor materials used in this work for nanostructure growth

XeF_2) and their sublimation temperature is close to room temperature. Other considerations to take into account in the selection of precursor materials suitable for FEBID and FIBID are based on toxicity and health risks.

The following precursor materials were used in this work (see Fig. 2.4):

1. Dicobalt octacarbonyl, $\text{Co}_2(\text{CO})_8$, GIS temperature = 27 °C
2. Diiron nonacarbonyl, $\text{Fe}_2(\text{CO})_9$, GIS temperature = 28 °C
3. Tungsten hexacarbonyl, $\text{W}(\text{CO})_6$, GIS temperature = 55 °C
4. Methylcyclopentadienyl (trimethyl) platinum, $(\text{CH}_3)_3(\text{CH}_3\text{CpPt})$, GIS temperature = 45 °C

The different nature of each precursor material influences the decomposition under the FEB or FIB. Therefore, the nanostructures grown with each precursor exhibit different composition, microstructure and physical properties as detailed in the following chapters.

2.2 Micro-Hotplate

In this section we briefly explain the experimental setup we used to study the influence of substrate temperature on the decomposition of the precursor material $\text{Co}_2(\text{CO})_8$ during nanostructure growth. The results are given in Sect. 3.4 (Chap. 3).

The main element of the experimental setup is a micro-hotplate based on a Pt layer, which uses the Joule effect to convert electrical power into heating power to introduce a current by a DC voltage or current source. Thus, the temperature could be increased up to ~650 °C.

For electrical access from outside the microscope to micro-hotplate, we designed and fabricated some connection pieces, which are essential elements of the experimental setup. We list the most important elements here:

1. Commercial micro-hotplate KMHP-100 (Kebaili Corporation) based on a Pt film (~400 nm thick) embedded in a suspended membrane type of sandwich of SiO_2 (~500 nm thick)/ Si_3N_4 (~1.5 μm thick)/ SiO_2 (~400 nm thick), with a working area of about $250 \times 150 \mu\text{m}$ (see Fig. 2.5d).
2. Support plate with four terminals to fit the micro-hotplate to the four metal contacts which are bonded to the four wires (see Fig. 2.5c).
3. Sample holder in which is installed the support plate mentioned previously, indicated by a green rectangle in Fig. 2.5a, which is fully engaged in the process chamber (see Fig. 2.5b).
4. Connector to the port of the door of the process chamber, indicated by a white rectangle in Fig. 2.5a.
5. Connector from the door of the process chamber to a connection box, marked by a blue square in Fig. 2.5a.
6. DC voltage source.
7. Connection box.

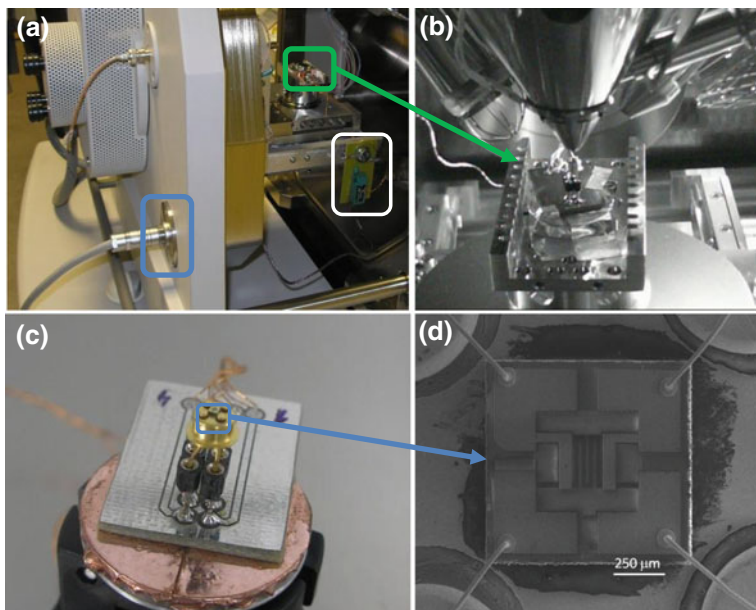
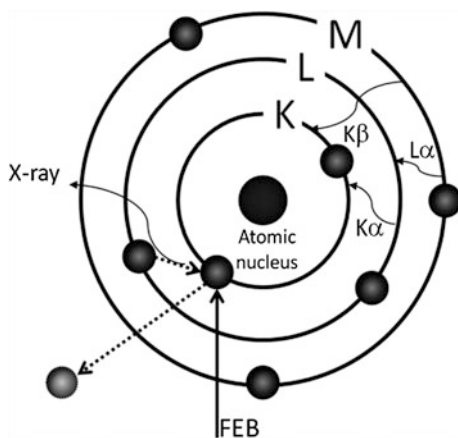


Fig. 2.5 **a** Photograph of the open door of the process chamber of the “Dual Beam”. The *blue rectangle* on the *left* indicates the connection from the computer. On the *right* we can see the platform where the micro-heater is installed (indicated by the *green rectangle*). The *white rectangle* marks the connection to the port in the door of the process chamber. **b** Photograph of the inside of the process chamber of the “Dual Beam”, where we can observe the micro-hotplate. **c** Photograph of the micro-hotplate inserted in the sample holder, which is installed in the process chamber. **d** SEM image of the micro-hotplate connected to four terminals

Fig. 2.6 Schematic representation of the physical basis of the EDS technique



2.3 Energy Dispersive X-Ray Spectroscopy

Compositional analysis of nanostructures grown by FIBID and FEBID was carried out in situ inside the “Dual Beam” by the energy dispersive X-ray spectroscopy detector (Oxford Instruments) (see Figs. 2.1 and 2.2), which collects the X-ray signal generated when the FEB scans the sample.

The incident electrons produce excited atomic states and the photon energy of X-rays emitted in the de-excitation is specific to each element, which allows semi-quantitative determination of the sample composition using the ZAF [3] method (see Fig. 2.6). This technique is simple to use and particularly sensitive to heavier elements.

The FEB interaction volume depends primarily on FEB acceleration voltage, FEB incidence angle with the substrate and the nature of the substrate. The energy resolution is on the order of ~ 125 eV and the spatial resolution depends on the interaction volume and FEB probe used (see Fig. 2.7). Thus, in the analysis of nanostructures as in our case we take special care in selecting the parameters to obtain the most representative spectrum of the nanostructure fabricated. As nanodeposits from different precursors have a completely different composition, we must select the best conditions for collection of individual spectra.

Just to find a starting point for all of them, if we analyze nanowires with lateral size and thickness below 100 nm, we should use a low FEB accelerating voltage to decrease the interaction volume, and a probe or FEB diameter < 100 nm whenever we want to analyze elements that have atomic transitions below the voltage chosen. Thus, we try to avoid atomic transitions of the substrate in the spectrum, which we should eliminate in the data processing.

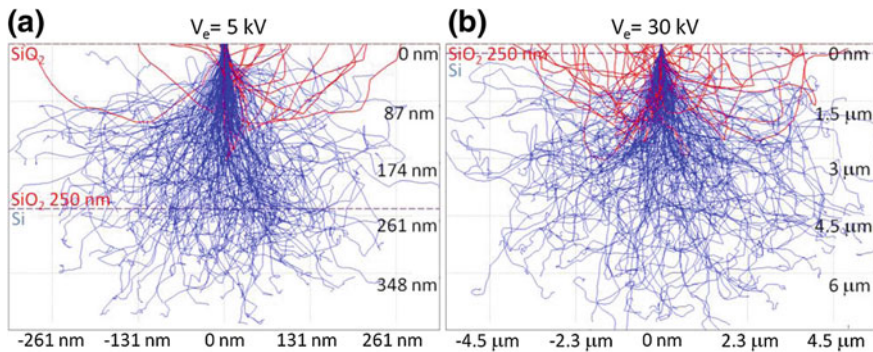


Fig. 2.7 Simulation of the FEB interaction volume on a thermally oxidized silicon substrate by the program CASINO (“*monte CARlo Simulation of electroN trajectory in sOlids*”) [4] at (a) 5 kV and (b) 30 kV

2.4 Structural and Compositional Characterization at the Nanoscale

2.4.1 TEM Sample Preparation by “Dual Beam”

The recent technological advances in transmission electron microscopy, which allow us to study individual atoms, mean that for these studies an appropriate sample preparation has become the cornerstone of a successful subsequent analysis. The thickness of these samples should be less than 100 nm, allowing the FEB to pass through the sample and the transmitted electrons to be collected. For the acquisition of high-resolution images samples should be even thinner, ~ 50 nm thick.

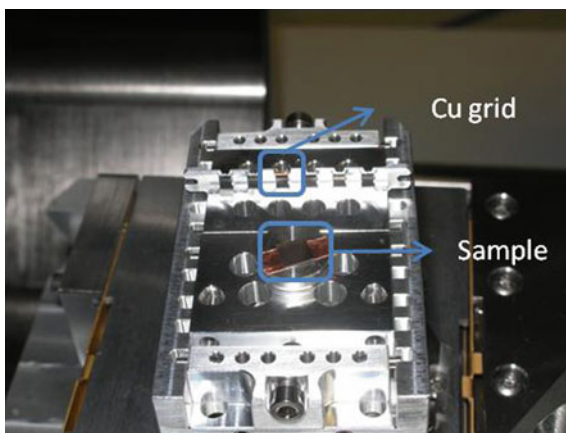
The continued development of techniques based on the use of a “Dual Beam” has reduced the time for and complexity of the TEM sample preparation process. As example of this is the use of a specific holder for the whole process of the lamellae preparation for a cross-sectional view without breaking the vacuum in the chamber. In Fig. 2.8, we show a photograph of this specimen holder installed on the stage of the microscope, indicating the sample from which we will take one slice and the standard Cu grid used as a support, where the lamella will be welded for further manipulation and TEM study.

In the preparation process, we combine several techniques available on the “Dual Beam”, such as deposition by FEBID and FIBID, milling by FIB, and nanomanipulator control. Moreover, as we work on an area of only about $50 \mu\text{m}^2$, the rest of the sample is preserved for other types of studies.

Next, we detail the following steps in the lamella preparation [5–8]:

1. Pt FEBID. The Pt layer protects the area of interest during sputtering by the FIB (see Fig. 2.9a). Thus Pt FEBID prevents the damage or amorphization that can occur in the first nanometers of the surface of a Pt layer grown by FIBID. Deposit dimensions: $15 \times 2 \times 0.1 \mu\text{m}$ (length $\times$ width $\times$ thickness).

Fig. 2.8 Photograph of a specific sample holder for TEM sample preparation



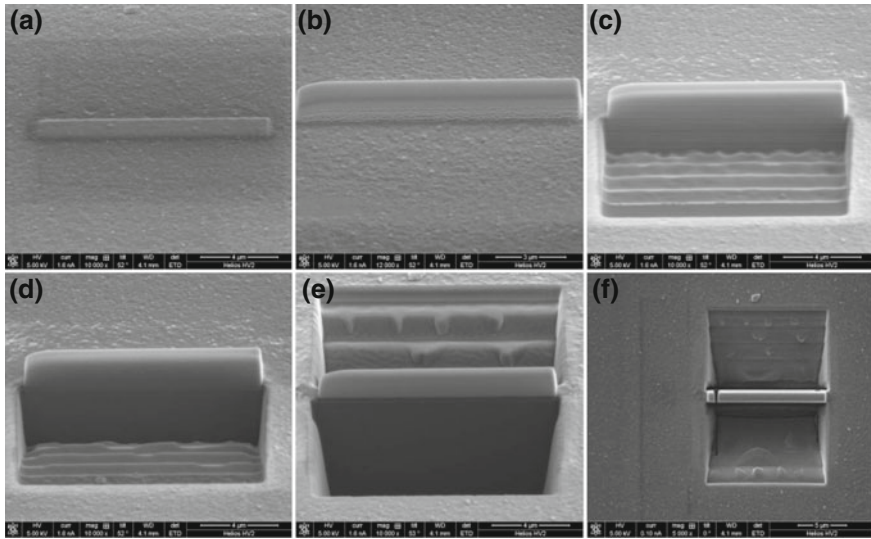


Fig. 2.9 SEM images illustrating stages of the TEM sample preparation, excluding the lift-out and final thinning and polishing

2. Pt FIBID. A film is deposited on top of that previously grown by FEBID to protect the area of interest during the following stages of milling (see Fig. 2.9b). Deposit dimensions: $15 \times 2 \times 1 \mu\text{m}$ (length $\times$ width $\times$ thickness).
3. Rough milling by FIB. Material on both sides of the area covered with Pt is removed by FIB (see Fig. 2.9c–e). Trench dimensions: $18 \times 9 \times 4 \mu\text{m}$ (length $\times$ width $\times$ depth). Lamella thickness after this stage is $\sim 1 \mu\text{m}$.
4. Fine milling by FIB. Material on both sides of the area covered with Pt is removed by FIB. Trench dimensions: $18 \times 1 \times 4 \mu\text{m}$ (length $\times$ width $\times$ depth). Lamella thickness after this stage is $\sim 0.5 \mu\text{m}$.
5. FIB cutting with an inverted U-shape. This does not completely release the lamella from the substrate (see Fig. 2.9f).
6. A film is deposited on that previously grown by FEBID to protect the area of interest during the following stages of grinding (see Fig. 2.9b).
7. Lift-out by an Omniprobe nanomanipulator, model 200. The nanomanipulator is a sharp tungsten tip of $1 \mu\text{m}$ diameter. It is inserted into the process chamber and its movements are motorized in the plane and on the z -axis with nanometer precision (maximum resolution of 10 nm). Thus, the nanomanipulator approaches the interest area until almost touching the lamella (see Fig. 2.10a). Then, we “weld” the nanomanipulator to the lamella by a Pt FIBID deposit and release the lamella from the substrate by three FIB cuts, with inverted U-shape (see Fig. 2.10b). Once the lamella has been released from the substrate and attached to the nanomanipulator (see Fig. 2.10c), we move the nanomanipulator towards the TEM grid (see Figs. 2.10c and (d)) and grow

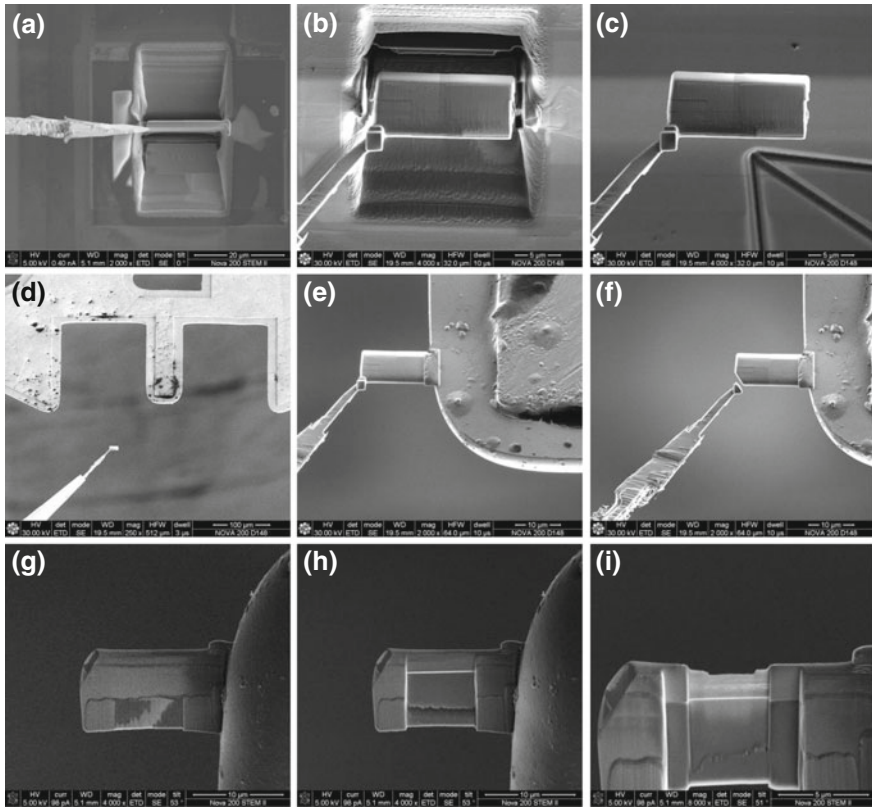


Fig. 2.10 SEM and FIB images illustrating the most delicate stages of the TEM sample preparation: the lift-out and the thinning and polishing

the Pt FIBID to weld the other end of the lamella to the grid (see Fig. 2.10e). Finally, we release the nanomanipulator from the grid by a FIB cut (see Fig. 2.10f). After the lift-out, we sharpen the nanomanipulator by FIB for the next use and retract it to its initial position.

8. Thinning. Fine milling by FIB. Material on both sides of the area covered with Pt is removed by FIB. Trench dimensions: $10 \times 0.1 \times 2 \mu\text{m}$ (length $\times$ width $\times$ depth) (see Fig. 2.10g). The process is repeated while the design length is reduced by about $\sim 4 \mu\text{m}$ until the lamella thickness is $\sim 50 \text{ nm}$ (see Fig. 2.10h).
9. Polishing by FIB at low voltage ($< 5 \text{ kV}$). Cut dimensions: $4 \times 0.01 \times 1 \mu\text{m}$ (length $\times$ width $\times$ depth). The process is repeated until the thickness of the lamella is $\sim 30 \text{ nm}$ (see Fig. 2.10i).
10. Transfer of the Cu grid and the welded lamella to a microscope (TEM/STEM) for imaging and analysis study.

Polishing is carried out at low FIB voltage because the thickness of the amorphization layer generated in the lamella depends on this voltage. It can reach around 20 nm below its surface when the FIB operates at 30 kV. However, if we reduce the voltage to 2 kV, the thickness of the damaged layer is reduced to ~ 2 nm.

The complete process of TEM cross-sectional sample preparation can take several hours, but it is still much faster and less destructive than manual sample preparation, which requires a large number of processes, such as successive cuts of the sample using a diamond saw, gluing the sample in the sandwich shape, curing of the glue in a furnace, mechanical polishing, ion polishing, ... This can take from several hours to a few days of work depending on the type of material being worked. Some examples of the results obtained thanks to excellent FIB lamella preparation at LMA-INA are reflected in the following references [9–15].

2.4.2 *Transmission Electron Microscopy*

Transmission electron microscopy (TEM) is a technique to obtain structural information from a very thin sample (thickness < 100 nm). The electron beam is relatively wide and simultaneously illuminates the entire working region through the sample thickness; its interaction is reflected in the transmitted electrons, from which the projected image is generated in real space and the corresponding diffraction diagram in reciprocal space. Normally, the beam accelerating voltage is from 100 to 300 kV. The TEM image can be generated from diffracted or scattered electrons using a variety of contrast mechanisms that provide information about the morphology, crystallography and composition of the sample, with a spatial resolution at the atomic scale of 0.1 nm. Do not forget that this provides a two-dimensional projection of three-dimensional objects.

The HRTEM images presented in Chaps. 3 and 4 were taken at the Advanced Microscopy Laboratory, Institute of Nanoscience of Aragon, University of Zaragoza, by Dr. César Magén using a Titan [3] High-base (FEI) at 300 kV with spherical aberration corrector, C_s (spherical aberration coefficient). The spherical aberration correction of the objective lens can achieve a spatial resolution of at least 0.1 nm.

The HRTEM images of Pt deposits grown by FEBID and FIBID summarized in Appendix A and W deposits grown by FIBID summarized in Chap. 5 were taken at the Scientific-Technical Services of the University Barcelona by Dr. Jordi Arbiol, with a JEOL 2010F at 200 kV, 0.19 nm spatial resolution.

2.4.3 Scanning Transmission Electron Microscopy

A transmission electron microscope can be modified or converted to a scanning transmission electron microscope by adding a beam scanning system. Beam deflection is performed by scanning coils. In fact, you can carry out STEM using a SEM column at relatively low energies (30 kV) or, as mentioned before, by a high-voltage TEM column (100–300 kV). High voltages provide better resolution and the electrons are able to pass through thicker samples. The high-energy STEM resolutions achieved are close to those of TEM.

2.4.4 Electron Energy Loss Spectroscopy

In electron energy loss spectroscopy (EELS), the material to be tested is exposed to an electron beam known kinetic energy distribution in a small range. Some of the primary electrons undergo inelastic scattering, lose energy—which is transferred to the electrons or sample atoms—and are deviated randomly from their path. The amount of energy lost by the electrons can be measured by an electron spectrometer and interpreted in terms of the source of that energy loss. The main types of mechanisms of inelastic interactions include phonon excitation, plasmon excitation, electron excitation, and incident radiation loss.

This technique measures the composition, the chemical bond and the valence at the nanoscale. It usually works better for light elements of low atomic number and the energy resolution can be of the order of ~ 1 eV.

The fine structure analysis is performed by the ELNES (energy-loss near-edge structure) determination method, which gives details of the ionization structure and thus of the bond associated with each atomic species. The white lines are well-defined spectra, with very abrupt transitions due to narrow d or f bands.

The STEM images and EELS spectra in [Chap. 3](#) of this thesis were taken and analyzed by Dr. Rodrigo Fernández-Pacheco in the STEM Group, Laboratoire de Physique des Solides (CNRS-UMR 8502), Université Paris-Sud, using a STEM VG HB 501 at 100 kV and a Gatan 666 spectrometer, optically coupled to a CCD camera.

2.5 Ex Situ Electric Transport Characterization

The electrical characterization of our samples in a wide temperature range from 0.3 to 300 K and applied magnetic field perpendicular to the substrate from +9 to −9 T was performed using a commercial system, the “Physical Properties Measurements System” (PPMS), from Quantum Design at the Department of Scientific Instrumentation, Physical Measurement Area, University of Zaragoza

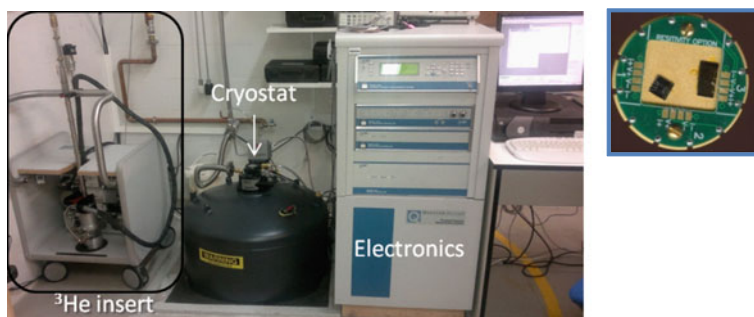


Fig. 2.11 Photograph of PPMS equipment (Quantum Design) installed in the Physical Measurements Service at the University of Zaragoza. In the inset, we show a photograph of the specimen holder provided with three independent measurement channels, each with four points, and used in the resistivity option

(see Fig. 2.11). In most cases, the option used for the characterization of our FIBID and FEBID deposits by four contacts was the resistivity in AC mode. In specific cases, as in Chap. 5, the resistivity in DC and AC mode with a ^3He cooling system was used. For measurements below 2 K, the PPMS system has the option to work with a ^3He refrigeration system that cools to 300 mK (see Fig. 2.11).

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Functional Nanostructures Fabricated by Focused
Electron/Ion Beam Induced Deposition

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2014, XVII, 143 p. 98 illus., 46 illus. in color., Hardcover

ISBN: 978-3-319-02080-8