

Atom Probe Tomography (APT) combined with Focused Ion Beam (FIB-SEM)

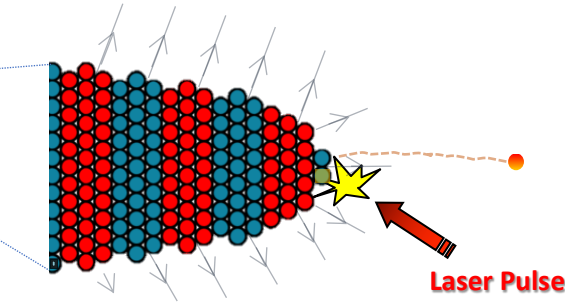
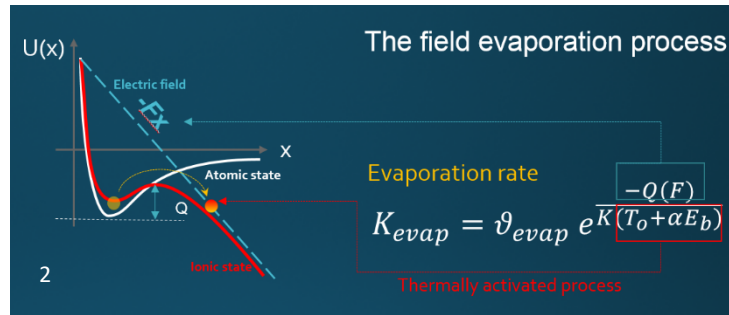
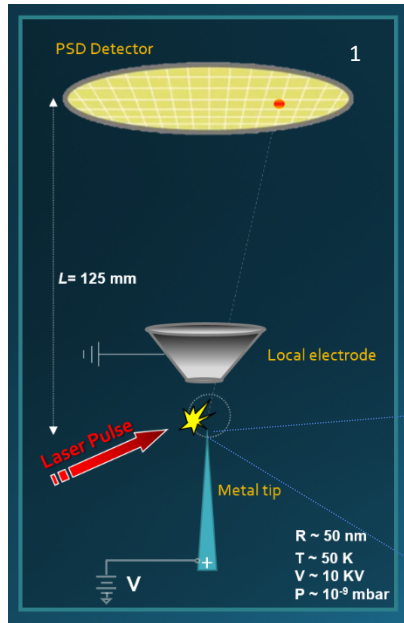
Atom Probe Tomography (APT) is a powerful high-resolution characterization method that provides three-dimensional mapping of individual chemical species with sub-nanometer spatial resolution and single-atom sensitivity.



Principle of (APT):

The Atom probe is combination of Field Ion Microscope (FIM) with Time-of-Flight (ToF) mass spectroscopy. In FIM, the sharp needle shaped sample with end radius of about 50-100 nm is placed in ultra-high vacuum conditions ($\sim 10^{-9}$ mbar) at cryogenic temperature (10 – 80 K). The electric field is applied to the needle specimen and is of the order of 10^{10} V/m. An image gas (He, Ne, Ar) is introduced in the vicinity of the positively charged needle. Gas atoms are ionized close to the needle surface and then accelerated away by the intense electric field. The impact of accelerated gas ions forms an image onto a phosphor screen which is related to the local topography of the specimen. Resolution of the order 1 Å can be achieved by FIM.

In Atom Probe Tomography, ToF mass spectroscopy is introduced to find the chemical identity of the ions evaporated from the tip surface. A detector with single ion sensitivity is used in APT and it is placed in front of the specimen which will determine the spatial (X,Y) positions of the detected ions. The theoretical background of the APT is illustrated in Figures 1 and 2.



The term of field evaporation is used to describe the APT method. It involves a combination of atom ionization and atom desorption from the surface that is exposed to a very intense electric field. When the surface electric field is sufficiently intense, the surface atoms can be removed from the surface while the electrons are drained into the surface, inducing the ionization of the atom. The ionized atom is then accelerated by the surrounding field away from the surface. The process of field evaporation is schematically shown in fig.2 along with atomic and ionic potential energy diagrams in presence and absence of the external electric field.

The field evaporation approach is considered as thermally activated process, where ions will leave the surface by crossing the lowered energy barrier due to the presence of the electric field. The applied laser pulse to the surface has a major influence on the field evaporation process, since the laser wave as an electromagnetic wave has an intrinsic electric field and the absorption of laser light in solids is known in heating the material. Therefore, the laser pulse causes field evaporation due to the temperature rise in the solid. The rise in temperature due to laser illumination is then proportional to the laser pulse energy (E_p), $T = T_0 + \alpha E_p$, where T_0 is the cryogenic temperature of the sample, and α is the absorption coefficient. The number of atoms evaporated per second (the evaporation rate) can be expressed by the following formula:

$$K_{evap} = \vartheta \exp \left(\frac{-Q(F)}{k(T_0 + \alpha E_p)} \right)$$

The identity of the detected ions is obtained from its mass-to-charge ratio (m/n). Where (m/n) is calculated from the equivalence between the potential energy of the atom at a certain applied voltage to the kinetic energy. This relation is given by,

$$\frac{m}{n} = 2eV \frac{t^2}{L^2}$$

APT instrument:

The APT machine consists of a transfer rod which enable to exchange the sample between the Air lock (Exchange chamber) and the measuring unit. The Air lock is equipped with a cooling finger to cool down some samples to the cryogenic temperatures. The measuring unit consists mainly of the sample shuttle and the detector. The laser unit is located directly under the measuring chamber (fig. 3). The wave length of the applied laser and the energy per laser pulse are well controlled via a special computer software.

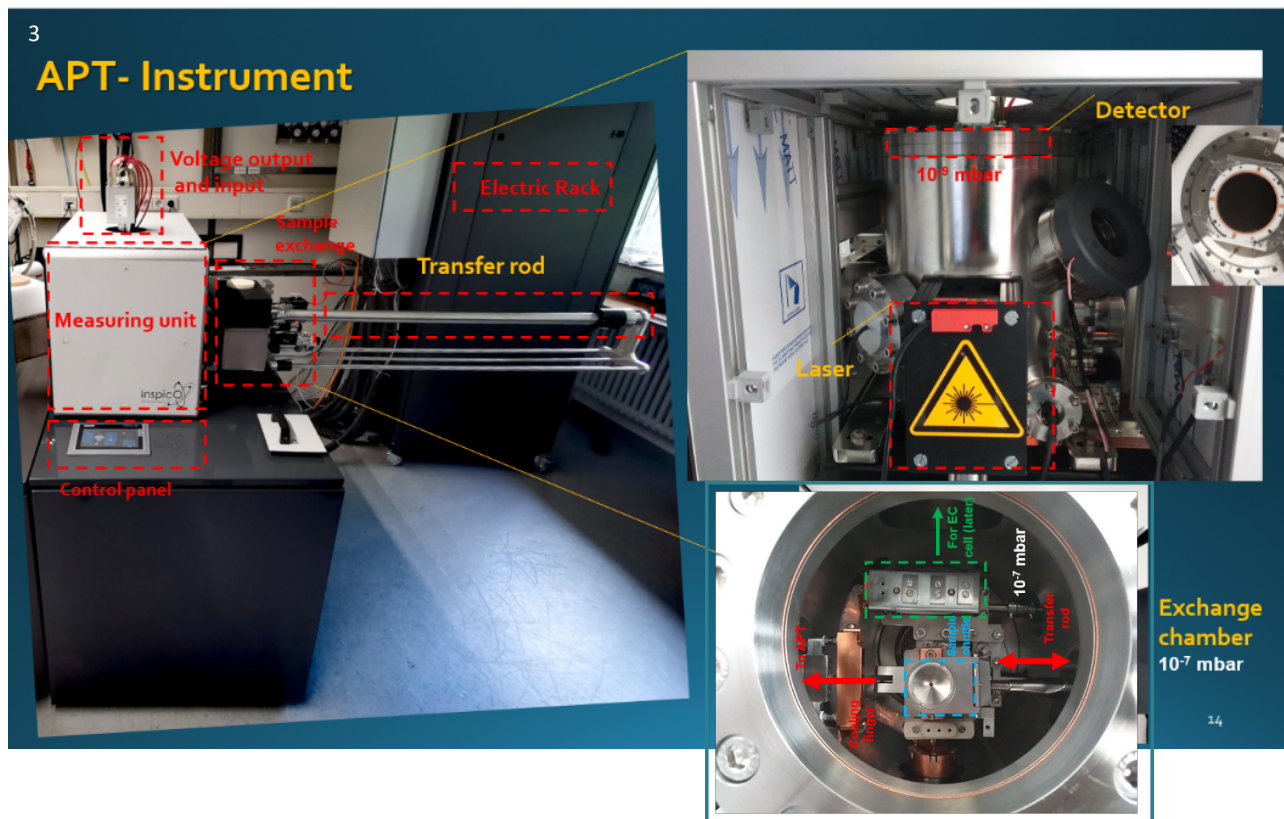
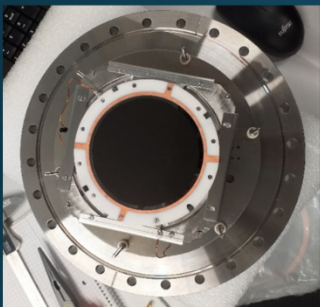
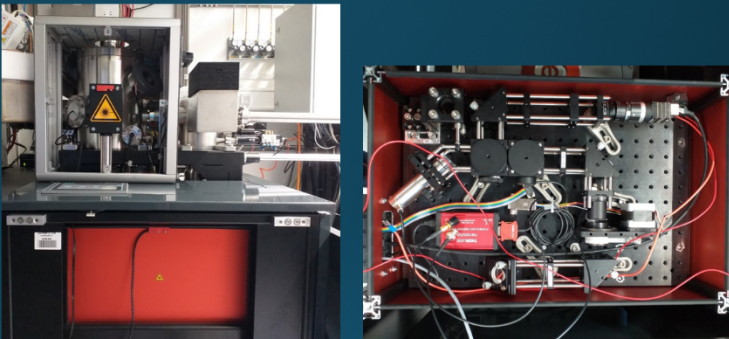


Fig (4.) shows some important specifications about the installed detector and the laser used in our laboratory.

APT- Instrument



- **Detector:** 75 mm diameter / Delay Line anode /Chevron MCP
 - 12 μm pore size
 - rate of analysis: 3×10^6 atoms/h
- flight length 125 mm,



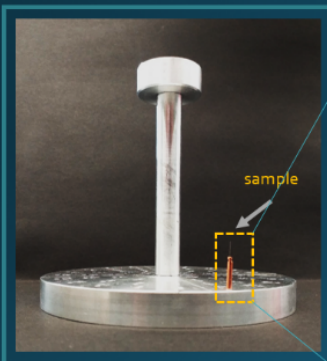
Laser Pulsed

- IR Laser, 1030 nm, (1.2 eV), Average Power: 5 W
@ pulses are generated at 500 KHz
- Energy/pulse up to 10 μJ
- Pulse duration <350 fs to 10 ps
- SHG: 515 nm, (2.4 eV) :Green
- THG: 248 nm, (5 eV) : UV

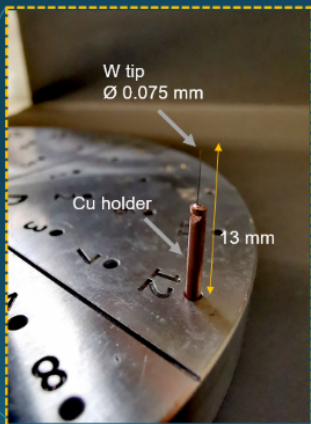
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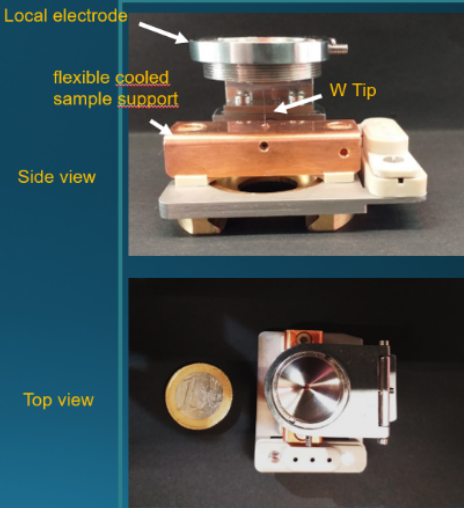
Figure (5) shows the sample shuttle outside the APT chamber. The sample is prepared very carefully for the APT measurements, since the curvature radius of the top most end of the sample should be around 20 nm in order to establish the field of evaporation. Therefore, the samples are etched electrochemically, and also shaped (if necessary) by Focused ion beam (FIB).

The sample shuttle is equipped with flexible cooled sample support to cool down the samples to the cryogenic temperatures. A cone shaped local electrode is also installed to the shuttle in order to enhance the electric field at the sample.

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sample holder





Sample shuttle

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FIB-SEM instrument:

Our laboratory is equipped with a scanning electron microscope (SEM) with a focused ion-beam (FIB) facility. This technique combines a focus ion beam milling with high resolution scanning electron microscopy. The FIB-SEM technique offers high resolution SEM imaging and detection capabilities (1.4 – 0.7 nm) on a wide range of different samples. Thanks for the variety of integrated in-column and below the lens detectors (Trinity in-lens detection system). The FIB technique provides fast and easy preparation of high quality samples for the APT measurements. The FIB-SEM system is equipped with EDS and EBSD detectors for chemical and crystallography analysis. Figure (6) shows the commercial **Scios2 LoVac**® (Thermofischer) microscope.

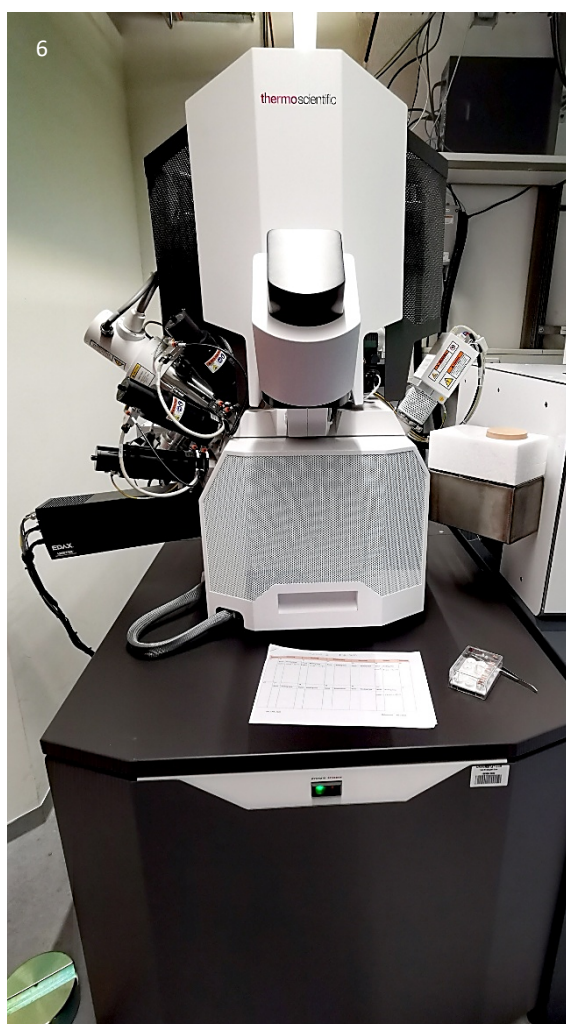
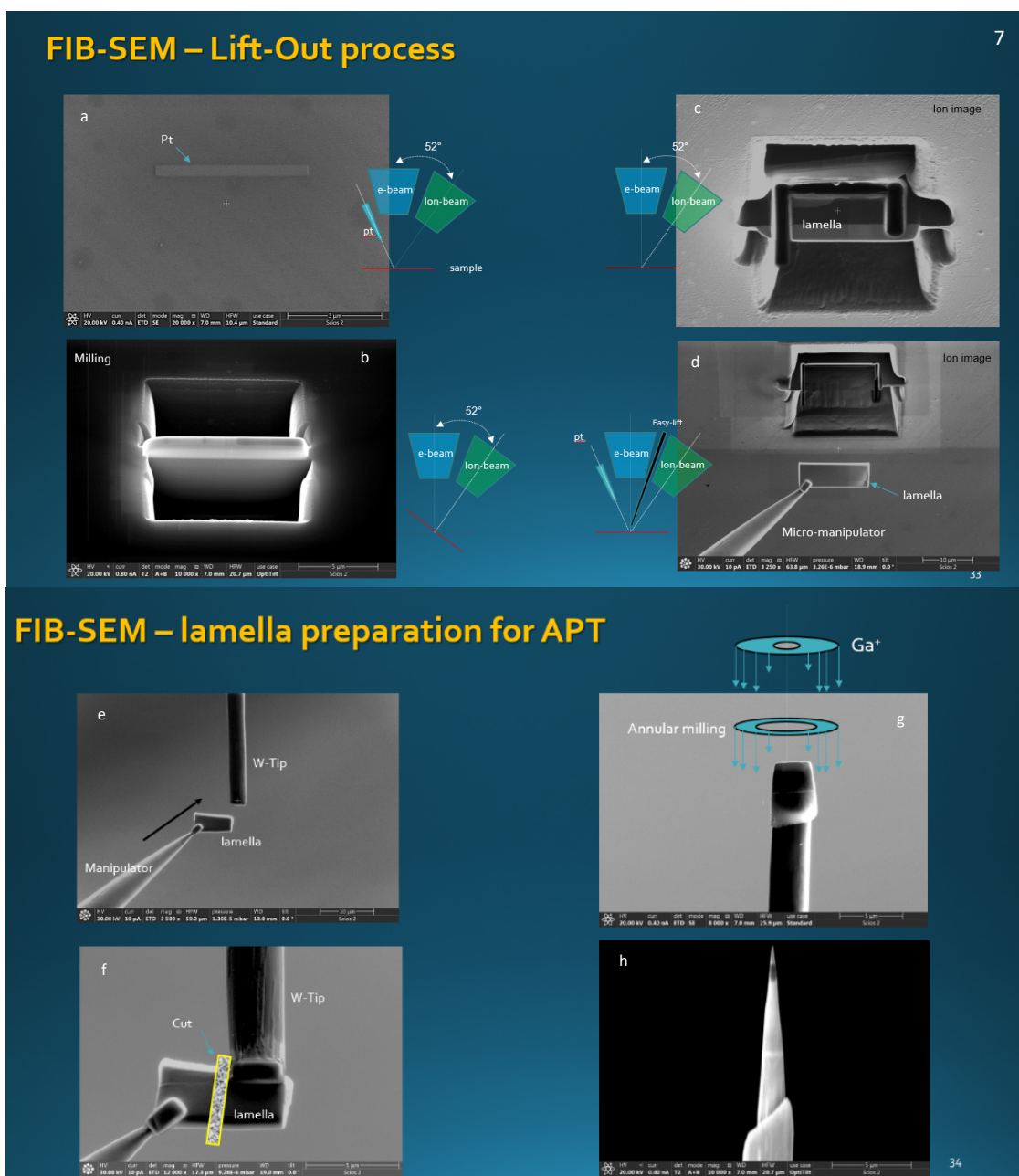


Figure (7) shows the FIB-based lift-out process and annular milling for needle shape sample preparation together with geometry of the sample holder during the procedure. The process

shows firstly a selection of a specific site for lift-out sample preparation and Pt coating (a). Trenching on either side of the surface to get a triangular wedge shape (b). The area of interest is then determined and milled (c). A special nanomanipulator is used to detach the prepared lamella (lift-out) from the surface (d). Then, the prepared lamella is attached on the microtip post (e, f). The annular milling is then applied to reshape the microtip to the desired radius (g). The final needle shape specimen with <50 nm end diameter is shown in (h).



3D reconstruction and mass spectrum of W microtip:

The APT system has been calibrated by measuring different materials such as tungsten. Figure (8) represents the 3D reconstruction of W microtip. The number of the evaporated species is around 1.8 M atoms. A 3D computer model of the evaporated ions is reconstructed by processing the recorded ion hits taking into account the sequence of detection events and evaluating the trajectories by the help of the point projection law.

Each point in the reconstructed model corresponds to an ion. As seen in Figure (8) the individual atomic planes in the [100] crystallographic direction is perfectly detected. The measured distance between the atomic planes in [100] direction is 2.22 Å which is in a good agreement with the theoretical value.

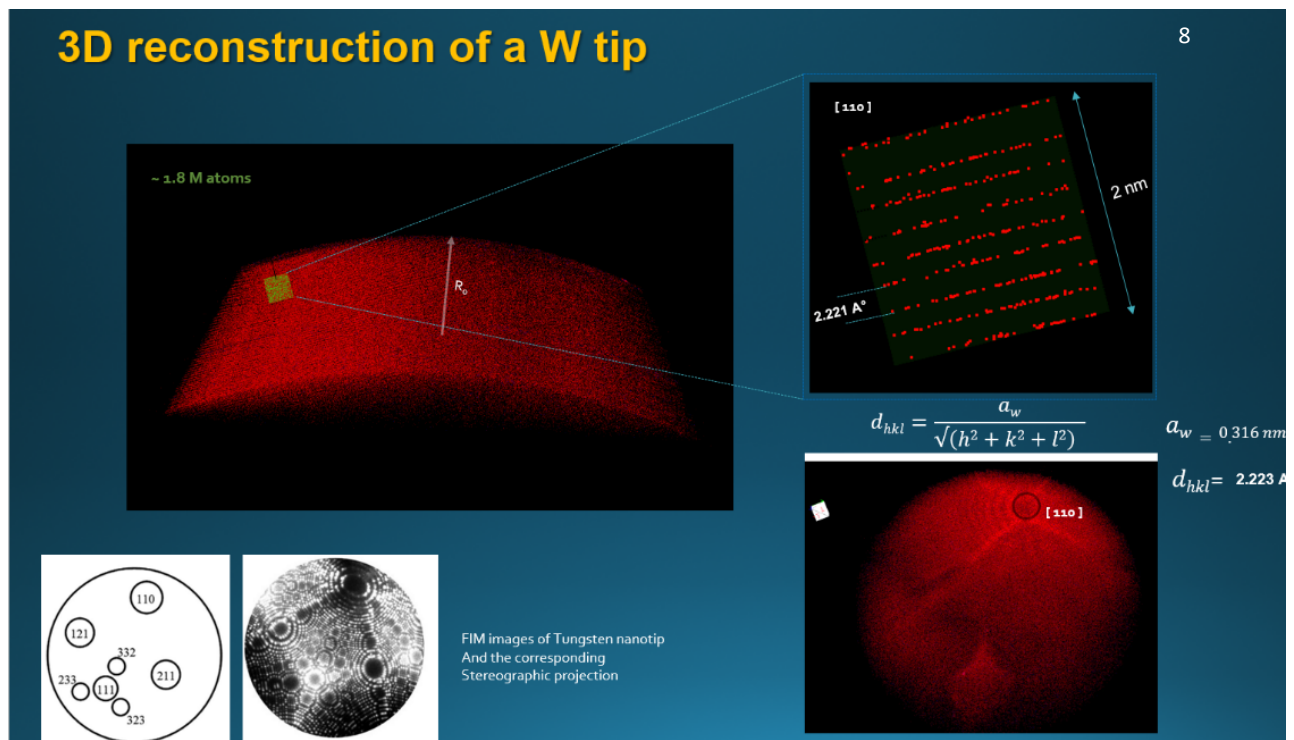
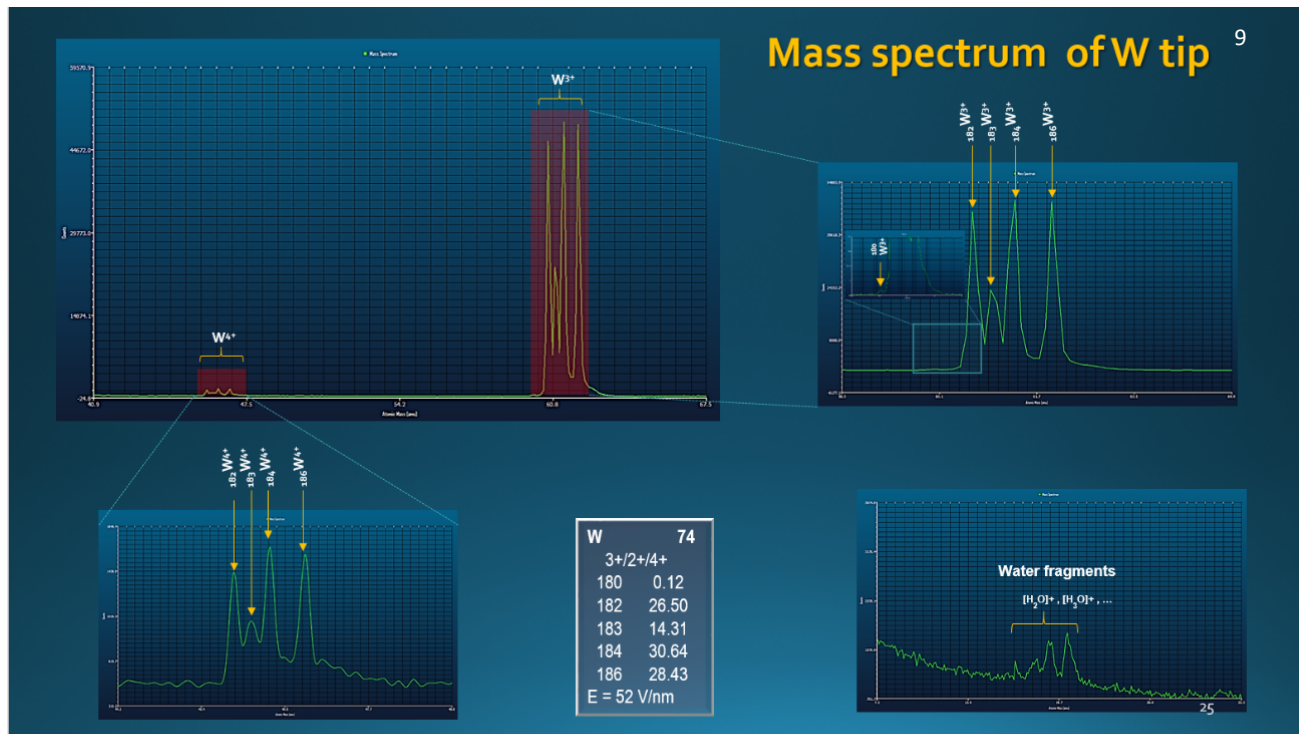
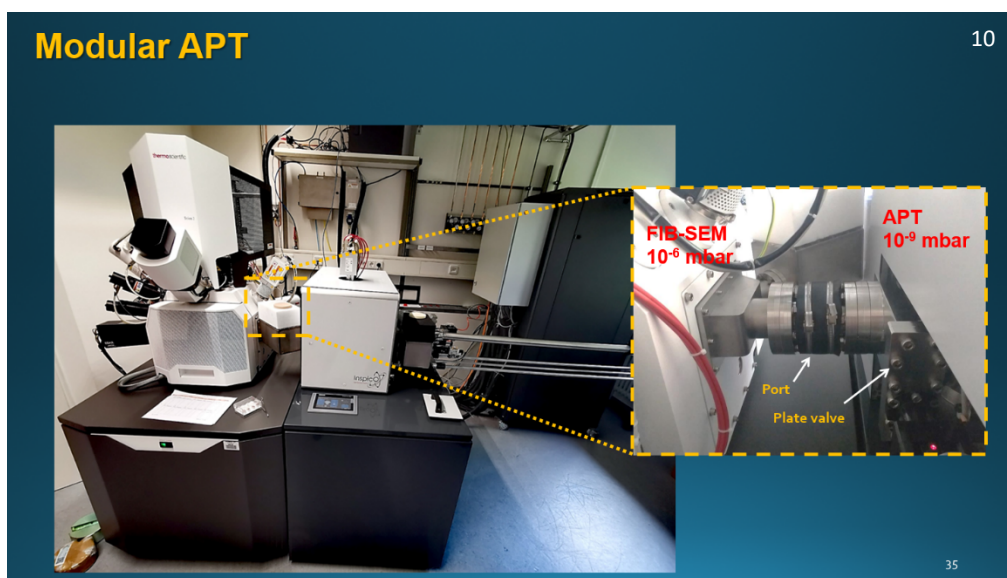


Figure (9) show the measured mass spectra for W microtip. In this spectra several peaks related to the ionic species of W are observed. The spectrum shows the well-known five isotopes of W: W^{180} , W^{182} , W^{183} , W^{184} and W^{186} for ionic W^{3+} and W^{4+} species. Some residual water fragments were detected. The field of evaporation during the measurements was monitored as a function of the sample depth, and it was almost stable at 52 V/nm.



Machine development:

Currently the APT machine has been developed to overcome the problems which might occur during the sample transfer process between the APT and the FIB-SEM chambers. Therefore, both machines have been connected together via a special connection port as shown in figure (10).



In this case, it is not necessary to break the vacuum to transfer samples between both chambers, as result, unwanted reactions and sample damage can be avoided during several transfer processes.

Further developments are in progress right now to analyze the samples prepared by electrochemical methods by APT technique. An extra chamber which will represent the electrochemical cell will be installed and attached to the APT system. The attached EC cell will offer in-situ electrochemical measurements and more detailed insights about the structure of the solid / liquid interface will be performed.

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