5.2 The In situ Nanostructures and Surfaces (INS2) endstation

The INS station is devoted to studies of surfaces, interfaces, nanostructures and thin films in Ultra High Vacuum, in particular during their growth, by means of three techniques using hard X-rays: Grazing Incidence X-ray Scattering (GIXS, which here is generic for SXRD, GID, GIXRD etc…), Grazing Incidence Small Angle X-Ray Scattering (GISAXS), and X-ray Reflectivity (XR). In the recent years, a gas injector allowing for the injection of dangerous gases (silane, germane, H2S …) has been added to the existing MBE (up to seven sources) possibilities. The core diffractometer and UHV chamber has been completely renewed during the last years, thanks to a French Equipex.

These “Equipexs” were about 250 projects funded by the French government within its “Investments of Excellence” initiative, to develop or renew research platforms opened to the French research community. Basically the INS2 project, launched in 2012, consisted in completely rebuilding the instrument with a new faster and heavy-duty diffractometer coupled to a new larger UHV chamber equipped with Be windows (Fig. 5). It became operational during the year 2016, and was opened to external users for the two remaining years (2017 and 2018) before the ESRF shutdown.

Like the previous instrument, the new INS2 one is dedicated to *in situ* studies of the growth and structure of nanometric films, particles, nanowires or new 2D material, possibly *operando* and in real time, using diffusion/diffraction of hard X-rays. The growth is achieved using a combination of techniques including molecular beam epitaxy (MBE) and chemical vapor deposition (CVD). X-ray measurements allow, among other things, structural studies on the atomic scale by grazing incidence scattering at large angles (GIXS/GIXD/SXRD/XRR) and morphological studies on the scale of a few nanometers or tens of nanometers, by scattering at small angles in grazing incidence (GISAXS). The GIXS and GISAXS techniques can be used simultaneously in real time.

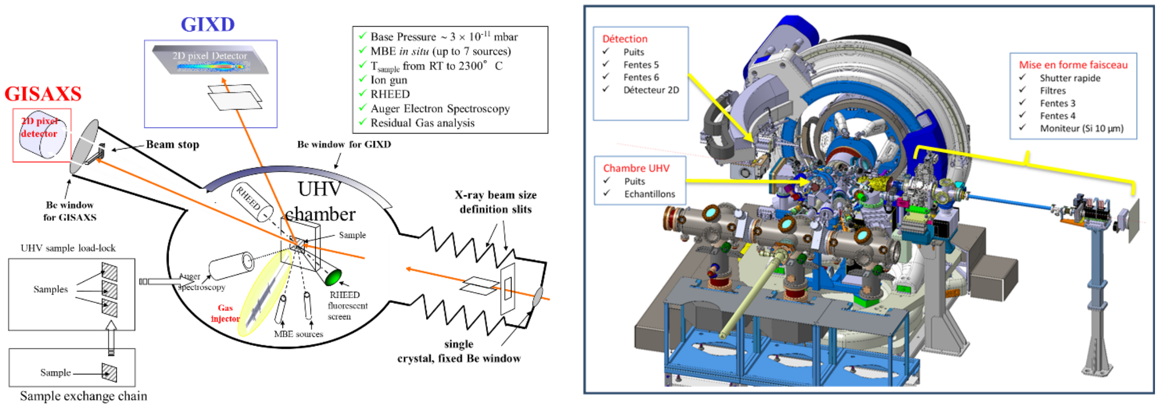


Fig. 5. Left: Schematic drawing of the principles of the INS2 setup, see text. Right: The CAD representation of the whole setup; see text for description

Compared to the previous instrument, INS2 can move the sample or the detectors 10 to 100 times faster, making it possible to study the nucleation/growth processes of quantum dots or 2D films or nanowires on a more relevant time scale. It also allows more structural and / or morphological information to be collected simultaneously by recording maps of the reciprocal space using fast 2D detectors. Finally, all these studies can be carried out under much better and more complex conditions.

The UHV chamber is designed as a hybrid system. First, it allows “classic” ultra-vacuum studies including heating up to high temperatures (1500°C standard; up to 2350°C with a special, non-transferable sample mount), ion bombardments, Auger electron spectroscopy and Reflection High Energy Electron Diffraction measurements, as well as measure of partial pressures of residual gases or of gases injected into the chamber. Second, it also accepts samples that are transferred from other processing chambers equipped with 1-inch Moly-block, thanks to two specific UHV transfer suitcases. Third it can be used to grow different nanomaterials by MBE or by CVD or by combining the two growth methods. A large number of evaporation sources are available, either of the "Knudsen" type or of the electron bombardment type. More than 8 can be simultaneously mounted on the chamber. A very specific injector associated with a versatile and secure gas distribution system is available for the CVD. Nitrogen and hydrogen plasma sources as well as a large source of silicon are also available. This chamber is fitted with a large number of flanges of different diameters and easily accessible, making it possible to envisage very varied configurations, rarely available on similar instruments.

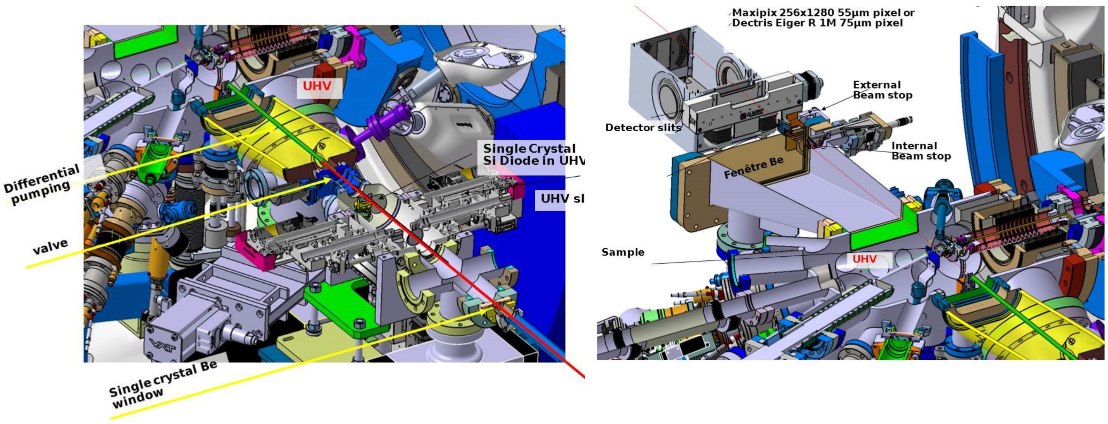
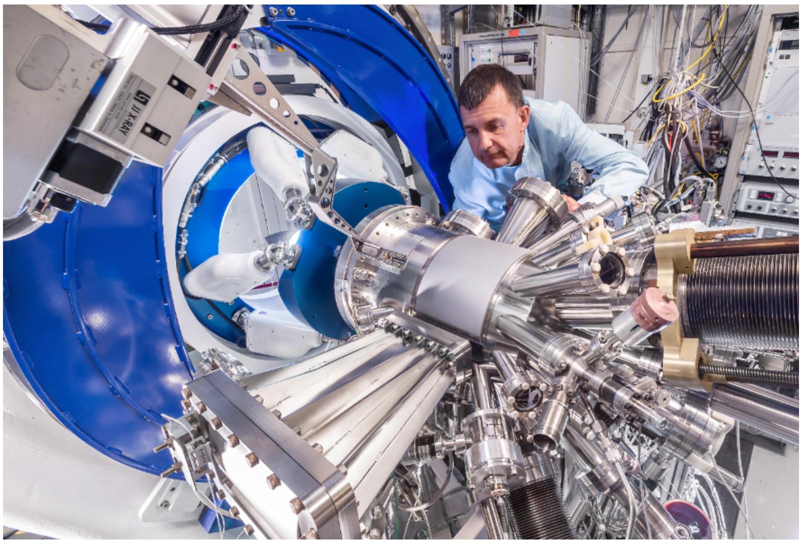


Fig. 6: Inside of the UHV chamber detailing the sample, sample holder, furnace, and inside slits and beam-stops, together with the wide rectangular exit Be window for low delta angles

The goniometer and the chamber were designed entirely in 3D CAD (Fig. 5) and are therefore perfectly integrated. The goniometer was produced by the *Symétrie* company. It comprises a basic rotation around a vertical axis making it possible to define the angle between the beam and the surface of the sample, kept vertical. This rotation moves the entire diffractometer. In addition to this, the detector can be positioned on a portion of a sphere by two other rotations, and the sample can rotate around the perpendicular to its surface, after it has been aligned using a hexapod. All these movements are very fast (up to 20 °/s), precise (better than 0.0005 °) and controlled by encoders. The detectors use hybrid pixel technology: Maxipix 5x1 for diffraction and Eiger 1M for GISAXS. The circle supporting the hexapod is mounted on a large vertical axis that allows removing it from the inside of the circle in order to easily access the chamber *via* its large flange for instrument mounting and maintenance.

A specific feature of the INS instrument developed over the years were in-UHV slits, knife edge and beam stops that allowed minimizing the unwanted background scattered by all elements put in the beam prior to the sample. This was further developed in this new version (see Fig. 5 left) by using a fixed (as opposed to moving before) Be window about 3 meters before the sample. In addition, this Be windows is single-crystalline, and thus does not yield any background scattering (except for Bragg peaks that are out of the beam).

The use of two pairs of in vacuum slits before the monitor and of a single crystalline Si diode monitor (Fig. 5 right) help further minimizing the background. Finally, the large rotation of the whole instrument to define the incident angle chamber rotation over a wide range (-1 to 20°) is allowed by a large oval bellows. The remaining background is further suppressed thanks to slits, knife-edge and beam stops inside UHV that are precisely aligned thanks to UHV piezoelectric translation tables (Fig. 6). The large chamber beryllium window is made of a big cylindrical part as before, but, again, the background from the exit beam is suppressed by replacing the part of the Be window crossing the exit direct beam by a flat Be window that is 500 mm farther, just before the 2D detectors (for GIXD or for GISAXS). This has been developed at the expense of a complexification of the detector slits, since the anti-scattering slit is placed on a translation to move it out when measuring close to the direct beam. Altogether, these features provide really background free (except that coming from the sample) measurements, both at low and high angles, which is hard to achieve with this geometry except when using an extremely small beam such as from ID beamlines.



The sample holder is a long rod in UHV ended by the sample heater at one end, and by a CF63 mounting flange at the other end. This flange is connected to a differentially pumped rotary feedthrough, itself connected to a large, heavy duty hexapod in air for a 6-degrees of freedom sample alignment on the one end, and to a large bellows connected to the main chamber, that accommodate for these sample motions, on the other end. The hexapod allows for three perpendicular ±5° $_1$ and rotations of 0.001° accuracy and three X,Y,Z translations of m accuracy. All the other rotary motions have 0.005° absolute accuracy, lower than 0.001° resolution; axes parallel or perpendicular within 0.001°, and a sphere of confusion of 60 μm for the sample motions and

100 µm for the detector ones. The (±200°) sample rotation and the detector (-15°, +126°) rotation can reach speeds of 20°/s, and the out of plane detector rotation (-1, 45°) reaches 10°/s. The rotation defining the incident angle can be moved between -1 and 20°, without disconnecting the chamber from the Modutrack introduction system, thanks to a long bellows in between.

On the exit side, a large, rectangular flange mounted on the chamber let the beam travel toward a large, rectangular Be window placed 500 mm away from the sample. A T-shape beam stop is placed in UHV just before this exit Be windows (plus another one just after), allowing to stop the direct and reflected beams before they are scattered by the exit window. The low-angles lost in detector angle delta (from -1 to 12 degrees) because the hemispherical Be windows has to be discontinued to be allowed for this, is recovered on the negative side through the large rectangular Be window.

The detector arm holds a fully motorized slit placed just before the detector, which may be either a Maxipix 5x1 or an Eiger 1M R pixel detector, and a detector slit is placed as close as possible to the Be windows of the main chamber at large δ angles, and moved away for delta δ angles smaller than 12°. The slit opening is defined by the rotation of 2 parallel tungsten rolls around and axis perpendicular to the beam.

For its two years of use, the INS2 setup has proved to be perfectly adapted to a number of experiments performed either by the internal team or by external users. Among these studies, one may cite the growth of high quality oxide layers and their detailed quantitative structural determination by SXRD; the demonstration of organized growth of preformed FePt clusters when deposited on the moiré induced by the deposition of graphene on Ir(111) surfaces; the characterization of many different 2DMaterials like Te-based transition metals dichalcogenides like $MoTe_2$, $ZrTe_2$, $HfTe_2$,$TiTe_2$ etc…; the *in situ* growth of MoS_2 on Au111 using the injector to inject H_2S gas and the intercalation of Cs below it; the substitution of Se by S in $PtSe_2$ TMDCs leading to Janus type SPtSe etc.