

Project for a Surface diffraction beamline at SOLEIL

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I- Introduction

Surface X-ray diffraction under grazing incidence (GIXD) is nowadays well established in the panel of surfaces and interfaces structural probes. Following the pioneering experiments of Marra and Eisenberger¹, dedicated surface diffraction beamlines have been built in almost all synchrotron radiation facilities. Indeed the structural information is a key step for a complete understanding of the physical and chemical properties of ultra thin heterostructures involved in modern materials science and technology.

The reduced dimension of artificial structures, thin films, wires or dots, induces new physical properties associated with the confinement. These effects, first observed in semiconductor quantum wells many years ago, are still the object of intense research in systems like self-assembled quantum dots for optoelectronics issues. A major effort is also dedicated nowadays to the understanding and design of metal/metal, metal/insulator or metal/semiconductor nanostructures where the magnetic and transport properties can be tailored by selecting the size of the individual objects.

The study of nano-objects has thus become very important not only for fundamental issues but also for its broad technological impact. Nanostructured systems concern physics, chemistry and also biology communities, interested in their optical, magnetic, electrical and catalytic properties. Heteroepitaxy, faceting, grafting are elemental processes leading to spontaneous nanopatterning and a detailed knowledge of the atomic structure of the initial substrate surface together with a continuous control of the structural and morphological evolution of all the components during the material processing is mandatory.

If many studies can be performed by laboratory UHV techniques like LEED, RHEED, STM, RBS..., directly coupled to the growth chamber, they are now very often complemented by GIXD experiments at different synchrotron radiation facilities. Moreover, for whole classes of materials and systems like the solid-liquid or solid-gas interfaces at high pressure, the "standard" UHV techniques cannot be used. It should be emphasized that such systems are at the core of several subjects of growing importance like the reactivity of metal catalysers, the study of glass-metal interfaces or the electrochemical interfaces among many others. These studies requiring brilliant hard X-ray sources, are being developed at third generation synchrotron facilities like ESRF and APS-Argonne. Indeed, more than simply bringing a

higher precision with respect to the standard UHV structural techniques, GIXD offers a unique tool to control easily the penetration of X-rays in the material from the very first atomic planes to several micrometers simply by tuning the incidence angle. This allows to study buried interfaces, to evaluate distortions induced by the surface structure deep inside the crystal or to probe the strain distribution across a thin film.

Nevertheless, the main specificity of GIXD is still to allow atomic structure determinations in surface science in the framework of the Born approximation of single scattering, which greatly simplifies the data treatment. To be reliable, these structure determinations imply a careful control of the surface and therefore ultra high vacuum conditions together with preparation and characterisation tools interconnected with the diffractometer. Moreover the high counting rate obtained with third generation synchrotron sources allows to perform studies *in-situ*, in real time and in extremely stringent experimental conditions (high temperature, magnetic field, gas atmosphere...), enabling to follow growth kinetics and surface structure transitions.

The importance of the sample preparation facilities associated with the GIXD experimental station has been clearly demonstrated by the studies performed on the GIXD beamline at LURE where a MBE facility is directly coupled to the UHV diffractometer. This original idea allowed studying surfaces and interfaces of technological interest like the III-V and II-VI materials. Among the many successful studies achieved on this beamline from the early days until recently, one can underline the surface structure of important GaAs(001) surfaces like the $c(4 \times 4)^2$, $(2 \times 4)^3$, $c(8 \times 2)^4$, the $c(2 \times 2)$ surface of CdTe⁵, the heteroepitaxy of ZnTe on GaAs⁶, among many others. The studies realised at LURE have evolved towards more complicated surface structures like those of ternary III-V compounds, bringing in the issues related with segregation and chemical ordering⁷. Indeed, these studies have introduced the diffuse scattering analysis, which opened new perspectives for addressing the mesoscopic ordering of materials and constitute a major research axis of the present proposal.

Another exciting domain that must to be covered by SOLEIL is the magnetic diffraction applied to surfaces and thin films. This new domain has become accessible thanks to the high flux delivered by 3rd generation synchrotron sources and the SOLEIL X-ray diffraction beamline should take benefit from the experience that has been acquired there. The scientific and technical achievements in this domain should guide the conception of the polarized sources and the design of end-stations optimized with respect to the magnetic sample environment, with a particular attention to the polarization analysis of the diffracted beam. The set-up of such a station would allow the investigation of the antiferromagnetic order in

the surface region which could almost not be studied up to now. The method could also find applications in chemistry and biology since adsorbed chiral molecules may also modify the polarization of the scattered light.

Other GIXD experimental set-ups working in UHV have been developed in France at the ESRF, on two different beamlines. The first one concerns the European open beam line ID3, which presents two very innovating and promising issues like the resonant surface magnetic diffraction and the high pressure gas reacted surfaces. The second set-up, operated on the French CRG beam-line BM32, has innovated by coupling the GIXD technique with the grazing incidence small angle X-ray scattering (GISAXS). This approach is important to obtain information on the very beginning of growth and particularly on the study of nanostructures (dots, wires, etc).

The present document is a foundation for the construction of a surface diffraction beam-line at SOLEIL with a particular attention paid to the control of the sample environment and the sample elaboration. All the examples developed in this document clearly show the importance of this coupling between the control of the external parameters (incoming species fluxes, high and low temperature, pressure, magnetic field, aqueous environment...) and the GIXD experimental set-up. Even if projections for the pertinent surface science to be developed in 5 to 7 years from now are somewhat speculative, it is an important task in order to define and optimise the new set-up. It will be the starting point for the definition of the beamline source and optics and for the preliminary design of the experimental station layout. The work presented in this manuscript emerges from a broad discussion within the French community where the new promising scientific domains were identified, which could be boosted by the construction of such a beam line at SOLEIL. The present project fully takes into account the existing set-ups and projected developments on other synchrotron radiation centers to propose complementary equipment that will enable the investigation of new scientific issues.

II- Scientific case

The following sections have been elaborated with the help of teams working in different laboratories whose research activities belong to a variety of scientific domains like optoelectronics, magnetism, spin electronics, catalysis, thermodynamics of surfaces and alloys, electrochemistry, transport properties. They are presently users of several techniques at the existing synchrotron radiation facilities while pursuing complementary researches with laboratory tools. It must be outlined that diffraction data analysis, relying in most cases on a large set of parameters, needs input from both theoretical and experimental complementary results on a mutual cross fertilization basis.

A- Self-organised Surfaces

There is a great interest, nowadays, in the surface community and in industry for the self-organised surfaces (in the following, self-organised systems should be understood as systems exhibiting **at equilibrium** a long range order with a period in the supra-atomic range (i.e. a period greater than a few nanometers). This interest is mainly due to the potentiality of such systems to be used as templates for further growth of nanoclusters. The template should provide a good periodicity in the position of the clusters, furthermore it should lead to a cluster size distribution narrower than the distribution obtained by free growth⁸. The spatial periodicity is believed to lead to cooperative properties as collective plasmons or superparamagnetism with a possible transition to a "super" ferromagnetic phase. The control of the size distribution is especially useful for two applications. First, concerning the magnetic clusters, one can guarantee a common easy axis of magnetisation for all clusters and square shaped hysteresis cycle. Second, in an approach of catalysis model, the role played by the size and shape in the cluster reactivity could be systematically studied, offering an alternative route to the techniques using soft landing of cluster beam.

To obtain optimised series of templates, it is important to understand the phenomenon of self-organisation itself. While the elastic relaxation of the substrate is widely considered as the self-organisation driving force, several questions are still open: which part does the thermal disorder play? What are the mechanisms controlling the kinetics of self-ordering?

Moreover, in spite of their practical interest, both the period control and the ability to predict which systems self-organise, are far to be reached.

For these studies on self-organised surfaces and on clusters grown on templates, GIXD is complementary to near-field microscopy (AFM or STM) as demonstrated by two experiments recently performed at LURE.

In the study of the faceting behaviour of gold (111) vicinal surfaces⁹, X-ray diffraction evidenced the existence of a stacking-fault in the wider terraces appearing in this self-organised faceting. The discovery of this stacking-fault played a major role in the understanding of self-organisation of gold vicinal faces and allowed a thorough explanation of the observed features which takes into account both the long range elastic interactions due to the bulk relaxation (Marchenko-Vanderbilt mechanism)¹⁰ and a local optimisation of a surface coincidence cell (Frenkel-Kontorova mechanism). In the study of the N/Cu(100) square patterned system¹¹, the periodic relaxation of the substrate was shown to be the main contribution to the intensity of the diffraction satellites associated with self-organisation (Fig. 1); by measuring elastic forces at a microscopic scale, GIXD led to the first proof that bulk elastic relaxation is the driving force for self-organisation.

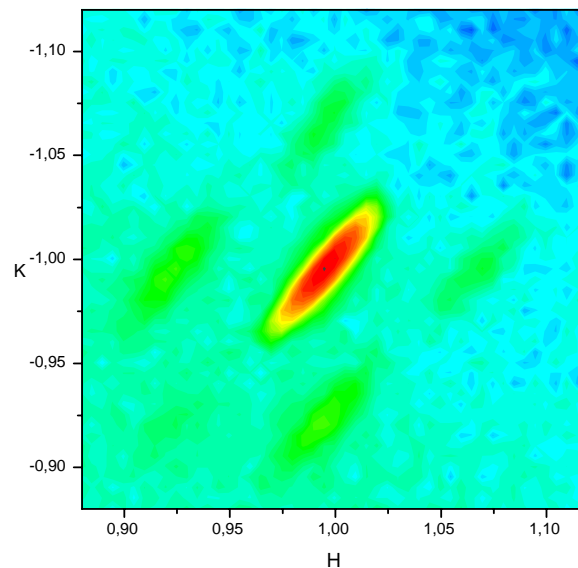


Figure 1: Intensity map around (1,1,1.3) for 0.8 ML of N on Cu (100). The diffraction satellites associated with the self-organisation can be seen on the reciprocal space map, exhibiting the same elongated shape (controlled by the resolution function of the diffractometer) as the crystal truncation rod.

It is worth noting that these two experiments have been performed on a first generation synchrotron source, therefore using a third generation source and an optimised end station (2D detector), the integrated intensity of the weak diffraction satellites, their position and moreover their shape should be measurable in a wide range of external parameters (temperature, time, exposure pressure...). Such experiments should enable to access to the physical properties of self-organization, thermal disorder or kinetics for instance, for which there exist no theoretical predictions and very few experimental results.

GIXD thus clearly appears as a very powerful technique to address the following issues: mechanisms and control of self-organization, cluster growth on self-organized templates, physical properties of self-organized clusters.

B- Surface magnetic X-ray diffraction

The first experimental results on the magnetic X-ray diffraction were obtained by de Bergevin and Brunel¹², who measured the weak specular magnetic reflections of the NiO cubic antiferromagnet. An X-ray tube was used at that time, delivering a count rate of about two photons per minute superimposed to a background eight times bigger. The magnetic reflections could nevertheless be resolved after accumulating over a period of several days!

A substantial progress has been accomplished today mainly thanks to the high photon flux now available at third generation synchrotrons like the ESRF (European Synchrotron Radiation Facility, Grenoble, France). The polarization analysis has become essential for hard X-rays magnetic diffraction since only the photon interaction with the magnetic moment of the sample can change the polarization of the light. In summary, charge scattering has no effect on the polarization of light whereas magnetic scattering induces a rotation on the original X-ray beam polarization. The use of horizontal and vertical linearly polarized light coupled with a polarization sensitive analyser is thus mandatory for an experiment to be carried out efficiently on magnetic scattering.

As an example, the angular dependence of the intensity of the specular reflections of NiO(111) was studied¹³. When the polarization is considered, the intensity modulation is directly related to the magnetic domain structure of the antiferromagnet. The analysis of the shape of the resonance for $\sigma\sigma$ and $\sigma\pi$ polarization channels allows determining the spin polarization of the involved electrons. One major remaining problem is that a large volume of the sample is necessarily integrated in the specular geometry.

In another recent experiment on ID20¹⁴, it has been shown the possibility to use a surface geometry together with the dynamical polarization analysis (figure 2). The penetration of X-rays can be reduced in this case. For NiO (111) the antiferromagnetic Bragg peaks have been studied with respect to the incidence angle, which allowed selecting the penetration depth of X-rays down to 2 nm in both resonant and non resonant conditions, thanks to the use of the polarization analysis. When the incidence angle reaches the critical angle for total external reflection (incidence smaller than one degree), the counting rate was still of about 50 counts/s. The surface magnetic signal has all the features of surface diffraction (refraction at the critical angle of total external reflection, large extension perpendicularly to the surface, i.e. scattering rods, ...). In resonant conditions, X-ray magnetic scattering is increased by an edge dependent factor (factor 3 at K edge, 100 at L edge)¹⁵. However the ESRF setup on ID20 remains a feasibility facility for surface studies, excluding sample preparation since a UHV chamber cannot be implemented on the diffractometer because of geometric limitations.

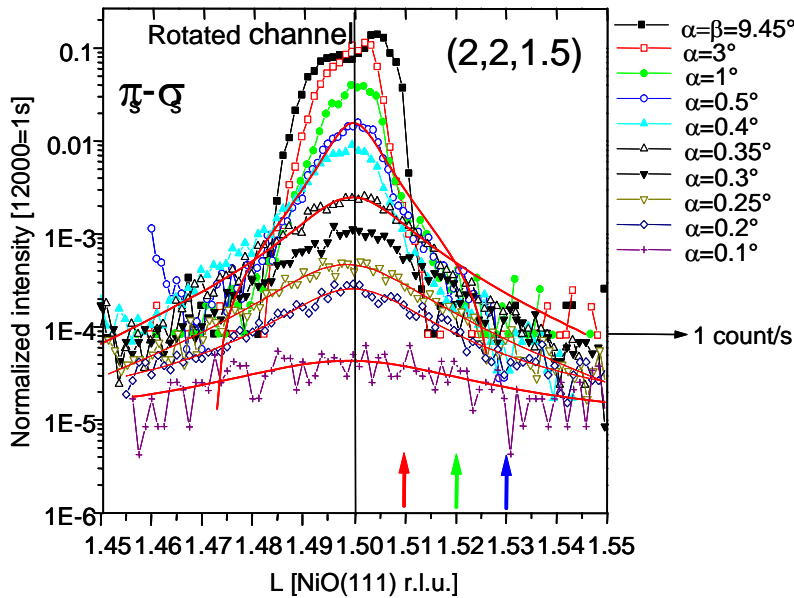


Figure 2: Scan across the asymmetric (2,2,1.5) NiO(111) antiferromagnetic peak, in the rotated polarization channel, with respect to the incidence angle in non-resonant experimental conditions at $\lambda=1.583\text{\AA}$. The polarization analysis efficiency was 99.98% at the Brewster angle of the analyzer crystal.

The understanding of the magnetic and antiferromagnetic domain structure in the surface region, the Néel transition as well as the interaction with other materials are almost unexplored topics. They became recently very important to understand the operation of new devices based on the magnetic exchange coupling, extensively used in GMR (Giant Magneto-Resistance) spin valve sensors. Such sensors that should lead to the MRAMs (Magnetic

Random Access Memories) are currently under intense investigation at the SP2M laboratory (CEA/Grenoble). One way to better understand the fundamental mechanisms related with these devices is to be able to perform in situ studies. The experimental station which would allow this type of studies does not yet exist.

It can be imagined if we combine the set-ups of ID-03 with the polarization analysis of ID-20 beam-line at ESRF. It should be stressed that both beam lines are oversubscribed (1 proposal over 3 accepted on ID20 and 2 over 3 on ID03¹⁶). Implementing the polarization analysis on a surface diffractometer is reasonable if included from the design stage. In this case, it consists simply in several circles that are conjugated in the detector arm.

Another important development concerns an internal magnetic field surrounding the sample, allowing switching the magnetic field from parallel to perpendicular with respect to the surface plane. This is not trivial but its implementation can open the way for resonant magnetic surface diffraction experiments, thanks to the asymmetry ratio of the surface scattering¹⁷ both for in-plane and out-of-plane magnetization.

Working at high X-ray energies has another important advantage: the surface atomic structure as well as its magnetic properties can be both determined. The structural determination is often lacking when soft X-ray magnetic scattering is performed. Within the framework of magnetic diffraction at SOLEIL we wish to build a transfer system that allows the transfer under vacuum from samples from the soft X-ray beam-lines to the hard X-rays ones.

In summary, a high energy surface magnetic scattering beam line at SOLEIL would help the understanding of the magnetism and antiferromagnetism of surfaces and interfaces. Several studies can be predicted like the magnetic and structural determinations, the access at the electronic structure and at the electron spin polarization state, to separate the orbital and the spin contributions etc...

C- Study of the initial stage of the epitaxial growth by in-situ X-rays diffraction

GISAXS Technique

The elaboration of well-defined nano-organised objects demands a precise control of the growth parameters which requires by the way, the understanding of the processes related with nucleation and growth in terms of size, shape and correlation distance between islands.

The equilibrium morphology of such objects can be visualized by scanning probe microscopy (SPM) or studied by x-ray scattering. However, several phenomena on these systems show fast evolution under UHV, even at room temperature, thus demanding in-situ and in real time studies. GISAXS is complementary to SPM techniques since it provides an overall information on the sample, combining the potentiality of small angle X-ray scattering (SAXS) with the surface sensitivity of grazing off-specular reflectivity.

In fact, SAXS is sensitive to heterogeneities in the electron density on a mesoscopic scale ($10\text{-}10^3 \text{ \AA}$) so well adapted to study the particles distribution. Like grazing incidence X-ray Diffraction (GIXD), SAXS experiments can be carried out at or near total external reflection of the material¹⁸. It is possible to study nanostructures deposited on a flat surface or even embedded in the matrix of a thin layer and it does not even require the matrix sample and/or the deposit to be crystalline. The scattered signal is collected under grazing exit angles, in the forward direction, using a 1D or a two-dimensional position sensitive detector placed perpendicular to the incident beam path. The 2-D detector has the advantage to reveal directly a possible anisotropic shape of the scattering pattern which is normally related with an anisotropic spatial distribution and shape of nano-objects¹⁹. The Born approximation (kinematic approximation) can be used to extract the morphology and electron density of small scattering objects which greatly simplifies the GISAXS interpretation. For large scattering objects (very small angles) and high specular substrate reflectivity (very smooth surface) however, it becomes necessary to introduce the distorted-wave Born approximation (DWBA) to take into account reflections and eventually multiple scattering effects²⁰. GISAXS can be used to determine *in situ* and *in real time* the morphology of small islands (1nm-10nm) during growth at different temperatures, under ultra high vacuum (UHV), from the very beginning of the growth. The 2D scattering pattern gives access to the average lateral size, height and separation between islands (island density), and even statistic distribution of these parameters. Fig. 3 presents recent results obtained using a UHV-GISAXS set-up²¹. The growth of metallic Ag clusters has been studied as a function of coverage and temperature and it can be seen that structural parameters related with the clusters can be directly accessed.

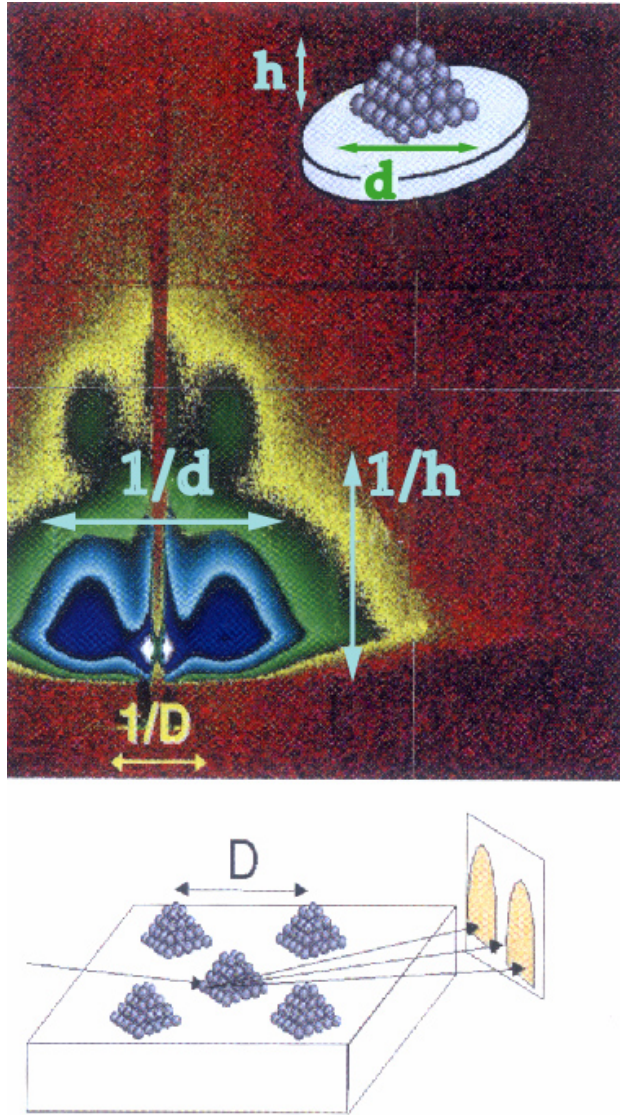


Figure 3: Two dimensional CCD image of the diffraction intensity in GISAXS geometry, after21.

GISAXS technique needs a bright synchrotron radiation source (flux, collimation) with tuneable photon energy in order to perform anomalous scattering measurements. In this case, anomalous dispersion near absorption edges enables to obtain information on the chemical composition of islands, and study segregation effects like those observed in bimetallic islanding¹⁹.

A particularly interesting field of study is the formation of exotic particles or clusters (non-equilibrium shape, imperfect structure, nanosegregation) by ion assisted atomic deposition on amorphous substrate¹⁹. A precise control of the growth parameters can lead to the formation of well-defined nano-organized systems. But, to obtain the control and

understanding of the process, it is necessary to follow, the cluster formation mechanisms in terms of structure, shape, size and in-plane distribution, by GISAXS and GIXD.

In another field, self-organized islands (like quantum dots) obtained by heteroepitaxial growth (strain effect) can be studied also by coupling GISAXS and GIXD on the same x-ray scattering apparatus²². As in the previous case, the structural information, obtained by GIXD can be complemented with respect to the ordering effects (lateral and vertical) induced by strain field, by GISAXS (shape, size and orientation symmetry). In summary, an experimental end-station allowing in-situ (UHV, temperature or gas pressure) and in-real-time (growth or reaction kinetic) grazing incidence X-ray scattering (GISAXS and GIXD) will open brand new opportunities to nanostructured surfaces studies and/or nano-objets dispersed on a surface.

Growth by Laser Ablation Technique

The discovery of the high T_c cuprate superconductors in the late eighties was the starting point for major efforts in the epitaxial growth of oxide thin films (cuprates, manganites with mixed valence, ferromagnetic and ferro-electric oxides, compounds with spin ordering..). Many groups have tried to implement the existing techniques in view of growing thin films of these new materials: reactive evaporation, ionic and cathodic sputtering, laser ablation, molecular beam epitaxy and more recently epitaxy in vapour phase by pyrolysis of organometallic precursors. The major difficulty was to supply the oxygen needed for the structural equilibrium of these materials, in techniques directly derived from ultra-high vacuum technology. For cuprates, this difficulty is well illustrated by the equilibrium thermodynamic diagram of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ system²³. To supply the oxygen pressure required, it was mandatory to use chemical species more reactive than simple molecular oxygen: atomic oxygen, ozone, oxides of nitrogen²⁴. In the end, only two techniques working at relative high oxygen pressures (0.1 -> 1 Torr) were able to produce good results in reasonable time: cathodic sputtering and pulsed laser ablation.

The reliability of these techniques is still questioned mainly due to the lack of accurate knowledge on the basic mechanisms governing the growth, in particular during the initial growth stages and on the substrate-epilayer interactions. Unfortunately, the elevated pressures preclude in-situ and real time control of the growth by most surface techniques commonly used in UHV. A recent example of major interest deals with the ferromagnetic perovskites

(LaSrMnO₃, LaCaMnO₃,...) usually grown on substrates like SrTiO₃, so with an important heteroepitaxial misfit which induces strong lattice deformations. This has a dramatic effect on the double exchange as well as on the magnetic properties. The relaxation mechanisms for these systems cannot be described by simple models based on the energetics, and GIXD and GISAXS techniques are well adapted to address such kind of problems. A laser ablation experimental set-up enabling *in-situ* GIXD data collection has been developed at the APS: the kinetics of the homoepitaxial growth of SrTiO₃ has been reported (Fig. 4)²⁵, opening new exciting possibilities to investigate the diffusion and re-crystallisation of arriving species at the substrate surface.

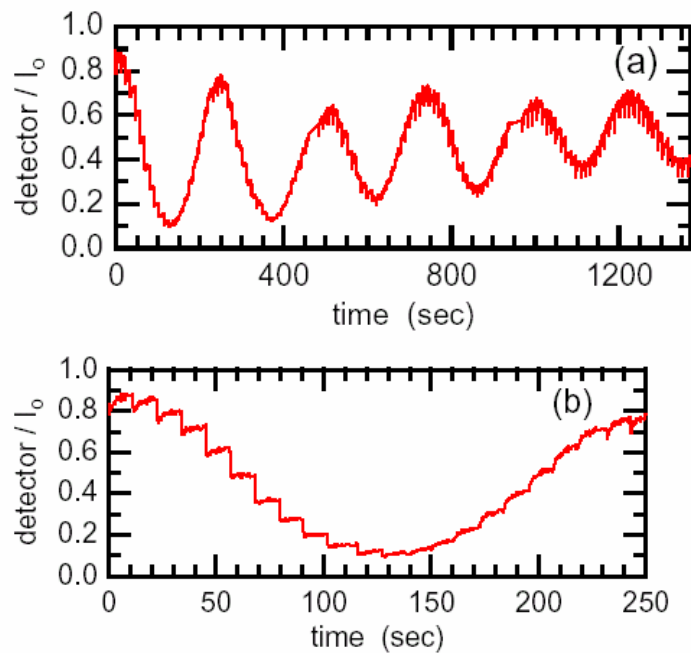


Figure 4: Time-resolved diffraction for SrTiO₃ homoepitaxy at $(0\ 0\ \bar{1}2)$ anti-Bragg position. (a) Oscillations from layer-by-layer growth, and (b) expanded view of individual pulse reflectivity transients for the first oscillation period

No such set-up is available yet as a user's facility and it would be very interesting to develop at SOLEIL a chamber dedicated to oxide film growth, allowing real time studies by X-ray diffraction. This would certainly produce invaluable information about the initial growth steps on these important materials.

The experimental set-up will thus allow to follow *in-situ* the hetero-epitaxial strain variation, a phenomenon which has been very little studied up to now, in spite of the major importance of the strain state on the properties of many oxides (magnetic perovskites for example²⁶). The knowledge of such mechanisms is a key point to further improve the

crystalline quality of thin films and thus to develop the potential applications of these materials (memories, magnetic sensors...).

D- Solid-gas interfaces in catalytic environment

To understand the microscopic mechanism involved in heterogeneous catalysis, one needs to precisely determine the reactive site and the reaction pathway thus identifying the intermediary steps of reaction. Surface studies help to characterize the chemically adsorbed species participating in the surface reaction. These studies required however techniques adapted to ultra high vacuum or at least to very low pressures(low energy electron diffraction-LEED, near field microscopies-STM, electron spectroscopies-XPS/AES., vibrational spectroscopies like HREELS, infra-red-IRRAS), which are far from the real conditions of a catalytic reaction. The results obtained under these extreme conditions can hardly be extrapolated to the real conditions of reactions, which occur in ranges of pressures 8 to 10 orders of magnitude higher. Indeed the reorganisation of a surface in the presence of a gas and the real nature of the intermediate phases produced during the catalytic reaction can be very different from those observed in ultra-high vacuum or at low pressures. Only the most strongly bonded species are expected to remain under ultra-high vacuum whereas the weakly bonded states may desorb very quickly. We know that these weakly interacting species referred to as precursors, are precisely the ones supposed to guide the reaction towards its final product. The identification of these species as well as the characterization of the active sites are thus essential for a further comprehension of the reaction mechanisms. The development of new techniques to study the surfaces in reactive environment is thus an essential point to attain such information.

The major difficulty remains in combining the constraints for the ultra-high vacuum environment, where the surfaces are first prepared and characterized with the high pressure controlled atmosphere of reactive gases. This last phase excludes all the techniques using the electrons. The results obtained by the group of Somorjai at Berkeley demonstrate the interest of such studies for the catalysis. As an example, their study by STM on Pt(111) indicated the presence of dense layers of CO in equilibrium with the gas phase forming a new structure incommensurate with the Pt(111) lattice, and completely different from the structures formed under low pressures²⁷.

A different approach has been recently developed at ESRF by Peters et al. who built a UHV chamber equally compatible with high-pressure studies and adapted to a heavy-duty X-ray diffractometer. As a first example, they followed the structural evolution induced by CO adsorbed on the (110) surface of Ni from 10^{-10} mBar to 3 Bars. At 130°C, a high CO pressure produces the reorganization of the surface of the Nickel substrate in microfacets of index (111)²⁸. Such structural information is essential in order to determine the active sites in catalysis and opens also the possibility to detect if the molecules on the surface present a long range order. X-ray diffraction is non-destructive and can be used to probe any type of gas environment in a large range of pressure, from the ultra-high vacuum up to very high pressures. With the high brilliance of the new synchrotrons, it becomes also possible to study these reactions in real time.

For SOLEIL, it would be interesting to use the facilities of the standard UHV surface diffraction beam-line, offering the traditional tools of surface science to prepare and to characterize the surfaces in ultra-high vacuum. After this step, we propose to develop a new chamber dedicated to X-rays diffraction and allowing experiments from UHV up to the real working pressures of different gases.

E- The study of electrified interfaces in liquid environment

A second example involving "real interfaces" is represented by electrochemical interfaces which are important for catalysis, energy production, chemical synthesis, corrosion or even for crystal growth. Electrochemistry strongly contributes to new nanotechnologies in different domains like nanomagnetism. The chemical properties and the reactivity of the electrochemical interface strongly depends on the atomic surface structure of the electrode. Among the various surface sensitive techniques, surface X-ray diffraction provides an in-situ probe for the atomic arrangement of the electrode surface but also for the interfacial ordered layers surrounding it. The weak interaction between X-rays and matter means that only a small fraction of the incoming beam is diffracted by the surface and the interfacial region. This can be overcome if one takes the advantage of bright synchrotron radiation sources.

Substantial progress has been made in the determination of the structure of the electrochemical interface at an atomic level²⁹. By combining several surface and interface sensitive techniques such as Scanning Tunnelling (STM) and Atomic Force (AFM) Microscopy³⁰, X-ray Absorption³¹ and Grazing Incidence X-ray Diffraction (GIXD)³² it is

now possible to access, under controlled potential, to the atomic arrangement of surface electrodes in both direct and reciprocal space. This allows quantitative studies on several fundamental interfacial phenomena, such as the reconstruction at the electrochemical interface, the underpotential deposition (UPD) of metal monolayers on foreign substrate, the phase transitions in adsorbed films...

The strong absorption of X-rays by the electrolyte implies severe experimental constraints. In fact, a thin electrolyte layer spectro-electrochemical cell was often used to improve the signal to noise ratio. Such thin layer cell geometry may however disturb drastically the electric field distribution across the interface as well as the control of the electrode potential, being in many ways incompatible with rigorous electrochemical requirements. As a compromise, many cells were designed so that electrochemistry was performed with a thick layer of the electrolyte covering the electrode to decrease the large potential drop associated with the thin layer configuration. After scanning to the desired electrode potential, the cells were then set in the thin layer geometry for x-ray diffraction measurements. Such procedure limits the studies to static or quasi-static regimes, preventing any kinetics investigation of the electrochemical interface.

The new generation of high energy synchrotron sources allows to work at high X-ray energy (around 20keV) with a very high photon flux on the sample. Taking this advantage, new spectro-electrochemical cells have been designed fulfilling rigorously the electrochemical requirements (Fig. 5) (3 electrodes configuration, very low potential drop, semi infinite diffusion limit...) and allowing GIXD experiments in both static and kinetic regimes³³.

The potentialities of this new concept of electrochemical cell to study surfaces in real electrochemical conditions have been demonstrated in following the kinetics of the gold reconstruction and the copper hetero-epitaxial growth on gold. Fig. 6 presents the evolution of the surface morphology and reconstruction diffracted peak as function of the electrode applied potential. It can be seen that this type of cell allows a fast cycling of the potential, mandatory for kinetic studies. By studying the metal growth on noble substrates like Pt or Au one can obtain very important information on the microscopic growth mechanisms involved in electrochemistry.

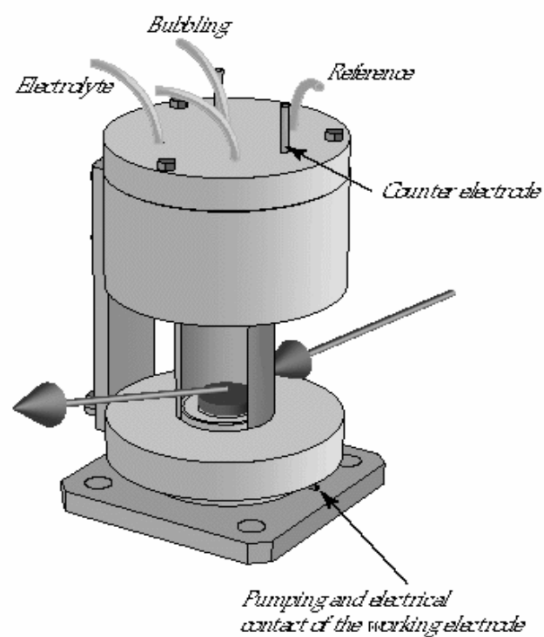


Figure 5 - Spectro-electrochemical cell based on the three electrodes standard cell for X-ray diffraction experiments:

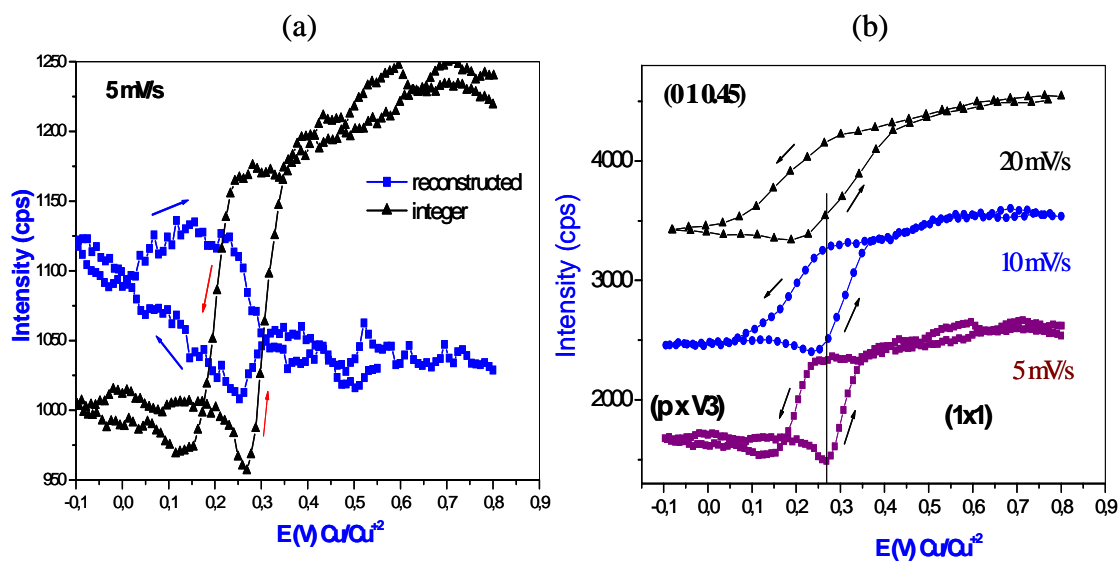


Figure 6 - (a) Evolution of the diffracted intensity from the satellites as compared to the integer order (0 1 0.45) peak. (b) Diffracted intensity from the (0 1 0.45) reflection during voltammetric cycles at different scan rates.

III - Potential users

The following list presents, together with the contributors to the present APS, the *leaders* of research proposals accepted on the DW12 LURE surface diffraction beamline, in the last years and new potential users

Semiconductor Surfaces and Interfaces

V.H. Etgens, *M. Marangolo* (Lab. Minéralogie-Cristallographie, Paris)
D. Paget, LPMC (Ecole Polytechnique)
P. Chiaradia, Univ Tor-Vergata (Rome, Italie)
F. Solal, PALMS (Université de Rennes)
A. Barski (CEN-Grenoble)
J. Massies (CRHEA, Sophia-Antipolis)
T. Argunova (Ioffe Institute-Saint-Petersbourg)
J.M. Themlin (GPEC-Marseille)
M.G. Betti, *C. Mariani* (Univ. La Sapienza, Rome, Italie)
V. Corradini (Univ. Modena, Italie)
F. Le Normand (IPCMS, Strasbourg)

Surfaces and Interfaces of Metals and Metallic Alloys

Y. Garreau, *A. Coati* (LURE)
S. Rousset, B. Croset, *G. Prévot*, *Y. Girard* (GPS-Jussieu)
L. Barbier (CEN-Saclay)
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IV-Beam line description

A-Source

Our choice concerning the source is oriented towards an undulator delivering a high photon flux at medium to high energy which is necessary to ensure that a good signal can be extracted from a surface (small quantity of matter) especially in the case of diffuse scattering studies. Moreover, the low horizontal divergence of this type of insertion device provides a good definition of the incident angle on the surface. The precise control of this angle is mandatory for both the control of the probed depth on the sample as well as to reduce the background level coming from the underlying volume. The optimal size of the beam on the sample should be around one millimeter vertically and 50 μm horizontally. The energy will range from 4 to 20keV with the low energies being needed to study resonant magnetic diffraction at the K edges of the elements such as Cr, Fe, Co or Ni (6-9 keV) and high energies essential for surfaces studies in a liquid environment (strong absorption). Actually, the U20 undulator, installed on a short section (1.8 m) seems to fulfil our requirements with the additional condition of placing a tilted mirror at 45° in front of the experimental set-up in order to exchange vertical and horizontal dimensions of the beam (see page 23).

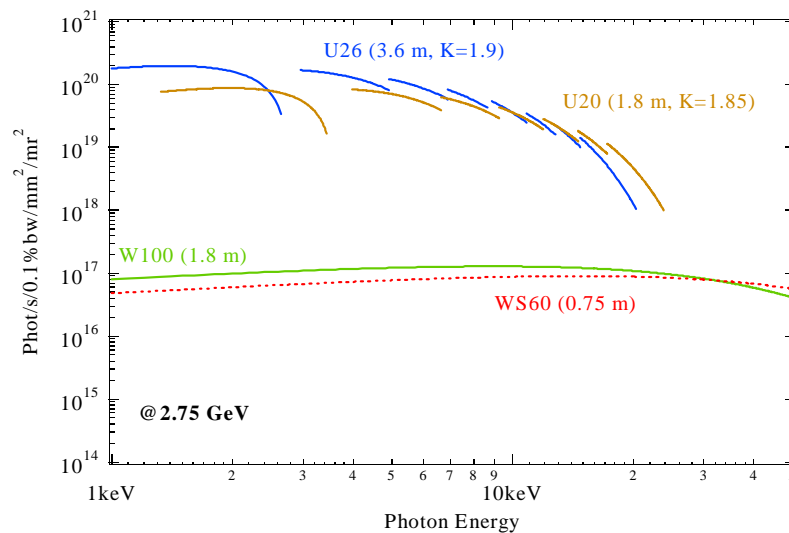


Figure 1 :

No adjustable polarisation can be envisaged on this type of insertion device. We plan to use one or two $\frac{1}{4}$ wave plates to obtain circular and vertical linear polarisation in the range from 6 to 10keV.

	$\sigma_{ex}(\mu\text{m})$	$\sigma'_{ex}(\mu\text{rad})$	$\sigma_{ez}(\mu\text{m})$	$\sigma'_{ez}(\mu\text{rad})$
Short Section (L=1.8 m)	388	14.5	8.08	4.61

Table I : Electrons source parameters on short straight section.

B - Optics

First Mirror

One option which is being studied is the vertical focusing. If this is needed, the first mirror M1 will be bendable (elliptical or parabolic shape) at 18 m from the point source. This mirror, which in any case enables to make the beam parallel, will be made of silicon with part of it coated with a 50 nm layer of heavy element (e.g. Rh, Ir or Pd). Figure 2 displays the reflectivity versus energy diagram for a beam incidence angle of 0.175° (3 mrad). For an energy range from 4 to 10 keV, the uncoated part of the Si mirror can be used while for energies between 10 to 20 keV, the metal coated stripe is more appropriate. The mirror acts also as an harmonics rejector preventing high order reflections from the monochromator.

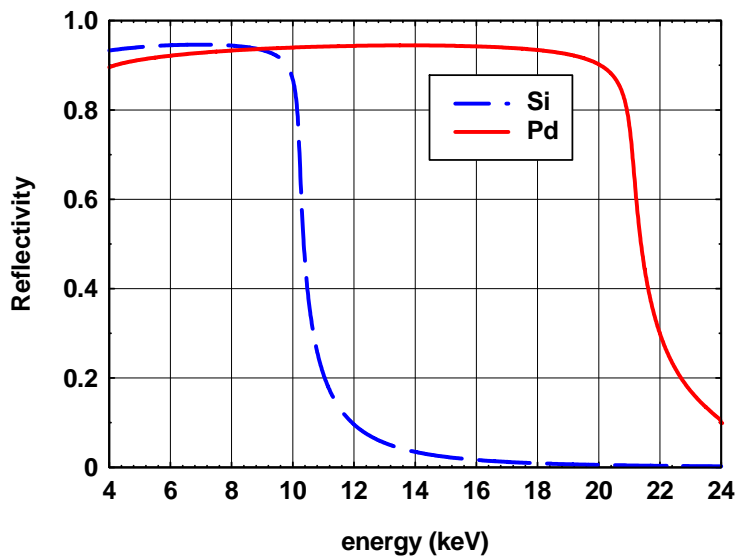


Figure 2 : Reflectivity versus energy for different mirror coating at 0.175° incidence angle.

Monochromator

The wavelength selection will be made by a double-crystal monochromator, located at 22.5 m from the point source, with a fixed-exit.

The optical system is designed to be tuneable from 4 to 20 keV using two sets of crystals, Si(111) and Si(311) in the monochromator, with the angular accessible range of the double crystal monochromator from 5 to 30°. Even if the beam line is conceived to operate in UHV without Be windows, one thin removable Be window can be installed near the front end of the beam line for safety purpose. Figure 4 shows the transmission of different Be filters versus energy. From this calculations, we can see that at 4 keV, a 100 µm Be filter gives only 85 % of transmission, showing the necessity to correctly optimise this component.

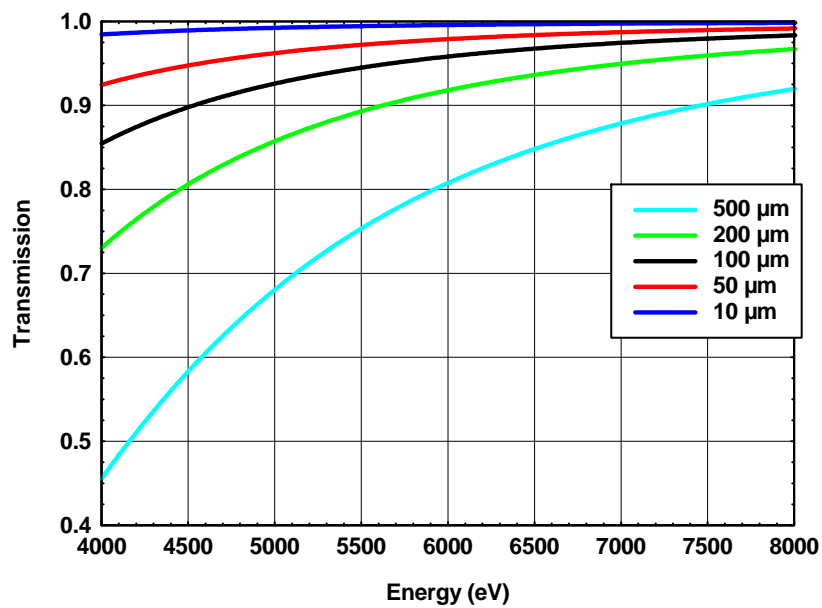


Figure 3 : Transmission of Be filters versus Energy

Polariser

The adjustable polarisation should be obtained through one or two $\frac{1}{4}$ wave plates according to the needs for circular or vertical linear polarization. The rate of vertical linear polarization obtained by two $\frac{1}{4}$ wave plates ($\sim 95\%$) may have to be improved. One possibility to increase this rate would be the use of a double (see quadruple) reflection channel-cut crystal diffracting in the horizontal plane. The reflection selected in this "front polariser" must be as close as possible to Brewster angle (the same condition holds for the choice of the reflection for polarisation analyser in front of the detector).

Tilted mirror at 45°

One recent idea is to introduce a tilted 45° mirror after the monochromator. In fact as it was developed inside the scientific part, surface X-ray diffraction requires small divergence **and** size of the beam in the horizontal plane. The problem is that the source delivers a beam with a small size/divergence in the vertical direction. Since the addition of any focusing element remains a complicated challenge especially when an energy scan is needed, we thought of using a tilted 45° mirror to exchange the source size/divergence between both directions (vertical-horizontal). The major consequence of this device is a physical displacement of the beam laterally as well as vertically. Even if these shift values are small, it is necessary to take them into account when positioning the experimental set-ups (see table II). The same incidence angle and the same coating as for the first mirror M1 will be used.

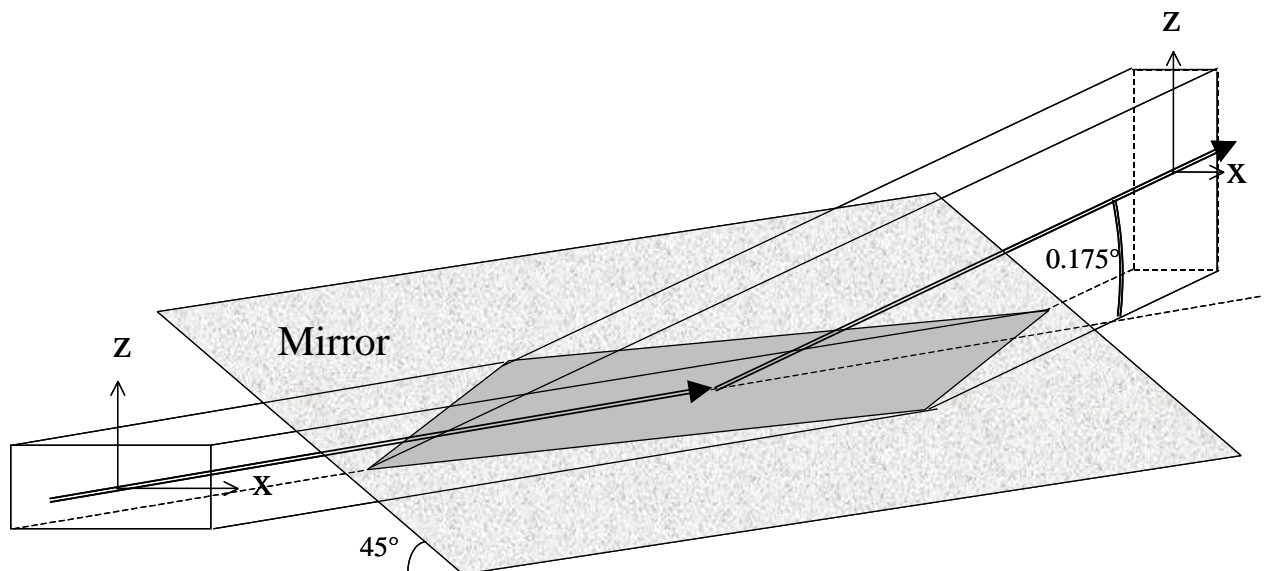


Figure 4 : Schematic view of a tilted 45° mirror

ray tracing

Ray tracing¹ calculations are in progress to characterize the flux and the shape of the beam at the sample location.

¹ The ray tracing calculation are performed with a code developed by the Caminotec Cie

C - Experimental set-up

Taking into account the diversity of sample environments required for many different experiments, the choice of a unique diffractometer seems compromised. The optimum solution would be to use two diffractometers on line, sharing the same detection equipments: the first one dedicated to UHV experiments, will be placed at the end of line. The second one, known as “ multi-purpose ” will be conceived to accommodate different chambers for high or low pressure (cf Study of the interfaces solid-gas in catalytic environment) or even cells for the studies in liquid environment. The two diffractometers must have a very high angular accuracy ($1/10000^\circ$) and an excellent stability. In addition, the arms supporting the detectors will be robust and correctly dimensioned, in both cases, to receive various systems of detection (CCD camera, analysers with additional circles for polarization analysis ...etc.)

UHV Diffractometer.

The “ Z-axis ” geometry well adapted for the study of surfaces in ultra-high vacuum seems mandatory for this device. The UHV chamber of this diffractometer will be equipped with a large semi-cylindrical beryllium window that allows an extended reciprocal space access. A double differential pumping rotating axis will ensure the rotation of the sample around its normal, with the base pressure below 10^{-10} mbar (see 10^{-11} mbar). This chamber should be equipped with various evaporators, gas lines, ion gun and an AUGER spectrometer in order to prepare and control the samples. It is also important to provide a view-port suitably located to allow evaporation by laser ablation, with the targets facing the sample. The sample should be heated or cooled in a convenient range of temperature (from 10K to 1500K).

Another important point is the surface magnetic experiments. The chamber must be equipped with an adjustable intense magnetic field (5000 Gauss). In order to exploit GISAXS technique, it is also necessary to consider a set of slits inside the UHV-chamber, like the one developed on SUV (BM32 ESRF), to eliminate the diffusion from the impact of the incident beam on the Be window.

« multi-purpose » diffractometer

If the decision concerning the geometry for the UHV diffractometer appears clear, the one for the multi-technique diffractometer is still open. To work with the sample surface horizontal has many advantages from a mechanical point of view to its capability to accommodate heavy and cumbersome chambers. In addition, the possibility of working with a vertical polarization and the tilted mirror at 45° makes this geometry perfectly equivalent to

the vertical one. The definition of the specific chambers adapted to this diffractometer will be carried out by the laboratories interested by the different experiments, in collaboration with the SOLEIL staff.

D - Additional Chambers

In addition, it is fundamental to develop “mobile additional preparation chambers” easily connectable with the beamline permanent set-up. These chambers will allow to optimise the operation of the line (preparations of specific samples prior to the allocated beam time for the experiment) and to be free from contaminations of the various evaporated elements (specific chambers: III-V; II-VI, metals...etc.). These chambers will be equipped with the tools for sample cleaning and characterisation (quartz monitors, RHEED, LEED, ion gun ...). It will be equally necessary to develop small UHV portable chambers enabling the sample transfer among the various SOLEIL beamlines. Moreover, it will be also necessary to envisage a clean room close to the beamline to accommodate these additional chambers, and also a room equipped with the proper chemistry tool, which is mandatory to prepare the substrates prior to the growth. A detailed survey of the high performance surface equipment available at LURE should be made in view of constituting an efficient surface support laboratory for all the concerned beamlines.

E - Data acquisition

Various systems of detection are to be envisaged:

- Solid State Detector with a good resolution in energy (optimal use for the low counting rates)
- Scintillation Detector, NaI type, with analyser (for the reduction of the background level or for polarization analysis).
- CCD Camera 16bit (see 32bit) for GISAXS and diffuse scattering measurements.

F - Beamline Software

A comprehensive software, controlling the undulator and beamline optics adjustment, the sample orientation and the data collection, at the level of the SPEC- software performances should be available.

G - Provisional diagram of establishment of the line

The location of all components of the beam-line is given in table II

Component	Distance from the source (m)
Slit	12
Mirror 1	18
Monochromator (horizontal focusing)	22.5
Polariser (¼ wave plates)	24
Tilted mirror at 45°	28
“multi-purpose” diffractometer	32 (13 mm)
UHV-Diffractometer	42 (45 mm)

Table II : Preliminary lay-out of the beam line components

H - Financial estimation

Infrastructure	2,5 MF	375 k€	
Undulator U20	2,5 MF	375 k€	
First Mirror	1 MF	150 k€	Cooled
Monochromator	1,5 MF	225 k€	
¼ wave plates	1 MF	150 k€	
Tilted mirror at 45°	0,5 MF	75 k€	
UHV-Diffractometer	4 MF	600 k€	
YAG laser quadrupled in frequency*	1.2 MF	180 k€	
“multi-technique” diffractometer	3,5 MF	525 k€	
One preparation chamber	1 MF	150 k€	per chambers
detection	1 MF	150 k€	
TOTAL	19,7 MF	2955 k€	

(*) This laser although slightly more expensive to purchase, appears indeed less expensive to operate than an excimer laser. An additional advantage comes from the fact that it does not require any safety installation for dangerous gases (F₂) contrary to the case of the excimer laser.

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