NEAR-SURFACE X-RAY DIFFRACTION UNDER CONTROLLED SAMPLE ENVIROMENT.

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1. INTRODUCTION

The goal of this beamline is to provide to the scientific community a beamline with surface diffraction set-up for surface or near surface studies with controlled sample environment.

The interest of this project is to combine two different scientific aspects. On the one hand to be able to explore a novel scientific field of increasing interest as it is the study of the growth of organic layers in surface with special attention to the quiral behaviour. On the other hand, to combine these studies with other scientific studies of diffraction at surfaces or near the surface which are largely present within the Spanish scientific community.

Thin films is a technologically effervescent area of physics that represents a branch of material science that marks the convergence of physics, electronic engineering, material science and metallurgy. Measuring less than one micron thick, thin films play an important role in the development of next generation semiconductor devices. Key application areas of thin films include communication, coating, microelectronics, optical electronics, and renewable energy generation systems, among others. The market is expected to benefit from the ever growing demand for smaller, miniaturized electronic devices with energy efficient high-speed computing performance.

Research is currently underway to explore methods to grow thin films of germanium crystals, the fruition of which can result in thin films replacing silicon in semiconductors. In the medium term however, growth in the market will largely benefit from advancements in deposition processes, improvements in surface characterization, and developments in nanomaterials, optical materials, organic thin films, magnetic thin films, and nano-metal oxide thin films, among others.

In this regard the study of thin organic films growth is of great interest due to their great possibilities in biocompatibility applications as well as in electronic nanotechnology with the development of organic logic gates.

Moreover, the possibility to apply external fields, such as defined synchrotron light polarization, external magnetic or electrical fields, will permit to study their influence, i.e., on chiral systems as well as on the growth of magnetic thin films among others.

2. SCIENTIFIC CASES

The proposed beamline project is basically consisting on a substation hosting a multipurpose open configuration diffractometer with a surface adapted configuration, able to host different user-specific apparatuses with the objective to offer several sample environments to the users. Real-time experiments would give the possibility of studying growth processes or reaction at surfaces (as heterogeneous catalysis or electrochemistry). The equipment would be able to offer the possibility to follow the evolution of morphological changes in surfaces as well as to monitor their structural changes in a vast range of pressures (from ambient pressure to UHV) and temperatures (30K to 1500 K). With this proposed beamline configuration and all the different sample environment available at the beamline under user demand, a large number of scientific fields of newest or high interest science could profit of such beamline, not only within the Spanish scientific community but also international which have largely demonstrate the power of the surface diffraction as tool in the structure determination in different scientific fields

The sections that follow do not provide an exhaustive list of the measurements that will be carried out but are intended to identify the areas of high quality research that will be possible to reach with such a flexible and powerful beamline.

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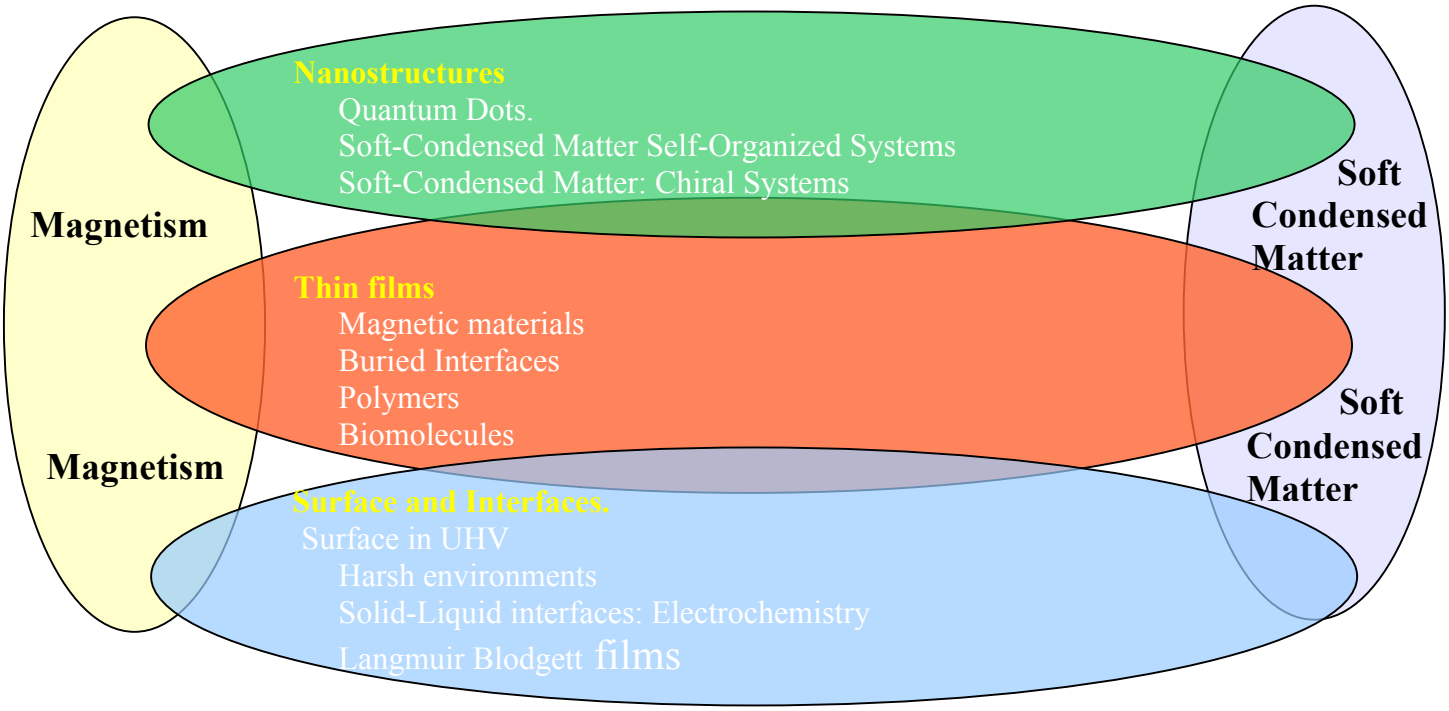
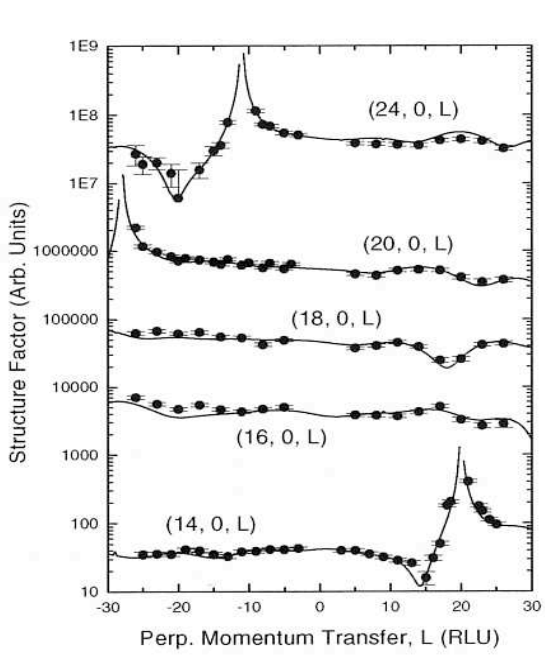
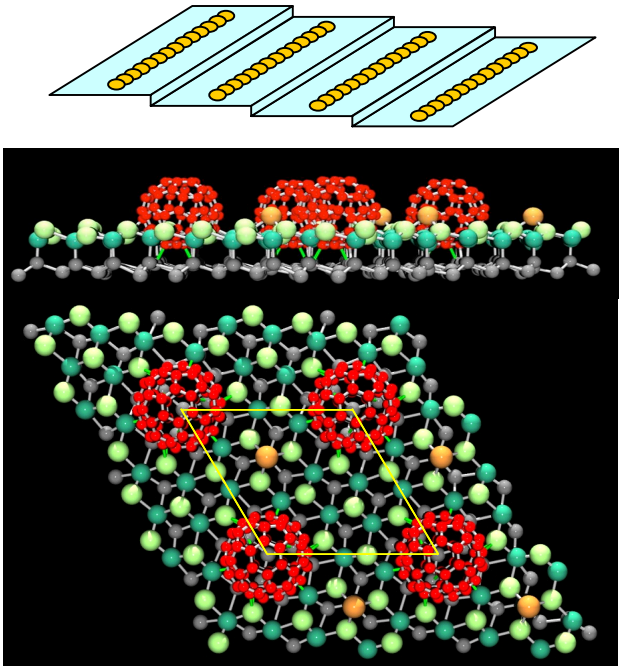


2.1 TARGET SCIENTIFIC CASE: ORGANIC THIN FILM AND CHIRALITY

The more ambitious scientific goal for this project is the study of the growth of organic layers in surface with special attention to the chiral behaviour of this system.

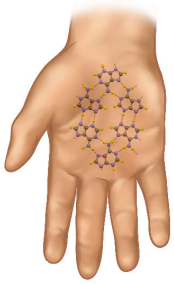
A large number of studies has demonstrated that the surface diffraction is a valuable tool for the characterization of the organic molecules order grown over a substrate. The interaction between substrates and organic or carbon based molecules induces large lateral arrangements on the substrate surface generating surface reconstructions with large unit cells. Usually, the intensities coming from these types of atomic periodicities are small, so intense X-ray beams impinging onto the sample are desirable. The $(13^{1/2}x13^{1/2})R14^{o}$ surface structure induced by fullerene molecules onto the Ge(111) surface is an example of intermediate superstructure. Its structure determination involved the measurement of more than 2000 non-equivalent superstructure reflections with intensities sensitively lower than those containing bulk contributions. One picture showing its crystallographic structure is represented below. The surface unit cell contains one Ge-adatom and the C60 molecule is sinking into the surface, because six Ge surface atoms are missing forming nano-pits [Torrelles 2003 and related].





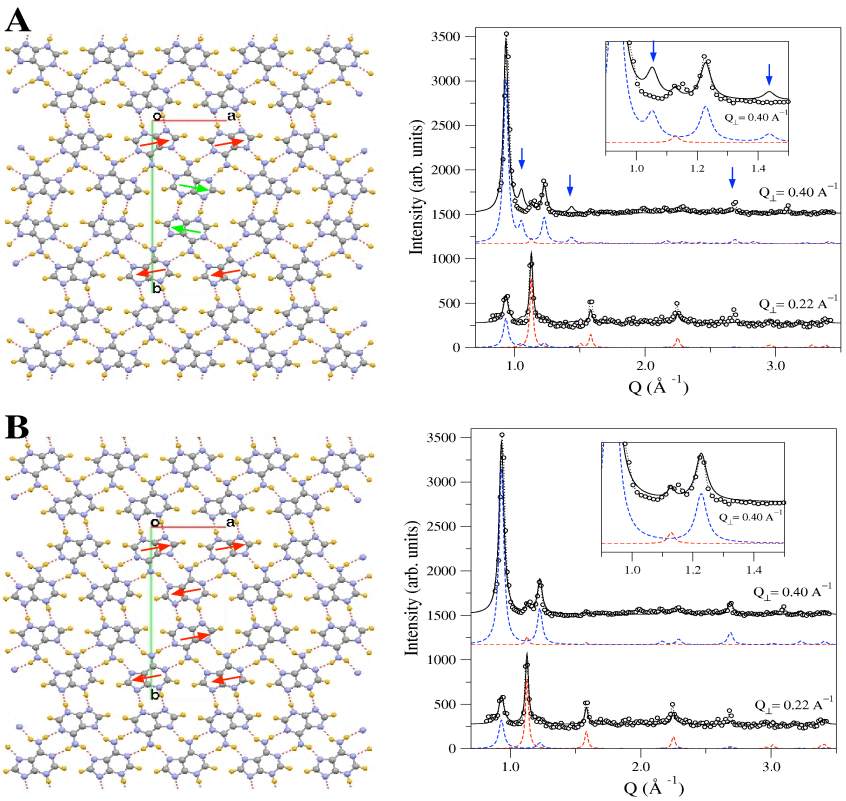
The creation of ordered arrangements of molecules is important in several areas of research. The substrate induced organization of the molecules to produce long-range order is an extension of the concepts of atoms forming reconstructions.

A field that is acquiring a great importance in the last years is related to the organic film and their chirality capabilities. It has potential benefits in the ability of the surface to selectively adsorb one enantiomer in preference to the other [Weckesser 2001 and related]. In many molecular systems it is very important in many molecular systems to ensure the purity of the molecules and can be very difficult to separate molecules that have the same chemical composition but differ only in the handedness of their structure. Such studies are invaluable as the effectiveness of many drugs depends on this distinction, as demonstrated by thalidomide. The ability of specific surfaces to adsorb certain molecules has therefore tremendous potential in the role of molecular purification. Recently, asymmetries in the scattering probability of polarized electrons from chiral molecules have been demonstrated [Mayer 1995 and related]. Even for unpolarized electrons, enantio-selective scattering has been predicted.



Prochiral molecules can produce chiral structures upon adsorption on surfaces or interfaces in which the interface plane breaks the mirror symmetry of the molecule. An example of this is the adenine [Capitán 2011 and related]. The deposition of DNA basis on surfaces is receiving significant attention opening the way for new bio-medical and farmacological applications.

X-ray diffraction is a valuable tool that can be used to study these systems. The chiral arrangement of prochiral molecules can be easily distinguished from the racemic mixture of molecules due to the differences in symmetry of the unit cell that results in the appearance or the disappearance of diffracted features.



In the case of the growth of adenine on Au(111) it has been found that two crystalline phases (alpha-beta structure) exist. Both phases are energetically quasi-degenerated and exhibit a very similar structure consisting in the "pile-up" of adenine planes. In the case of the alpha-adenine the stacked planes are enantiopure planes while in the beta structure the stacked planes are a racemic mixture of both chiralities. It has been found that under certain conditions the growth of the alpha phase is favored resulting in surfaces covered with adenine islands which are chiral from the first stages of the growth. Another example of the viability of these types of chiral studies by means of surface diffraction can be found in [Kuzmenko 1998] who study the growth of PVBA over a substrate.

In the quest of the genesis of chiral structures there is a inspiring question: "Can the asymmetry of a chiral field – such as a specifically oriented magnetic field, radiation field, or the combination of both – be transferred to racemic or prochiral organic molecules in a manner that an enantiomeric enhancement is induced, that is to say, transferred from the mass-less chiral field into the organic molecule?" And indeed, the answer to this question is "yes".

The combination of chirality and magnetism stems from Pasteur's work is particularly appealing. In the 80's, Barron reformulated and generalized the definition of chirality given by Lord Kelvin to include motion; a chiral system is thus defined as one in which space parity is broken, while time parity is conserved [Mayer 1995 and related]. This point of view has recently been confirmed by experiments: it has been demonstrated how chirality can be introduced in a system by the so-called "magnetochiral anisotropy" effect, combining a magnetic field parallel to the direction of propagation of an unpolarized light beam [Mayer 1995 and related]. In this way enantiomeric excess is generated in a chemical reaction. The setup envisaged for this beamline would also allow to explore this highly suggestive subject.

In that way it has been proposed four pathways to induce an enantiomeric enhancement via absolute asymmetric photochemistry. We distinguish between magnetic and magneto-optical effects and pure photochirogenesis. Circularly polarized light is a true chiral field and offers possibilities to induce the enantiomer excess via well-defined processes called photolysis, isomerization, and synthesis.

Conversely it has been found that planar chiral structures are an intriguing new type of optical meta-material which offer the possibility of effective manipulation of the polarization state of light in the far and near fields, as well as manifesting a range of new phenomena such as 2D optical activity.

2.2. NANOSTRUCTURES

The final goal is to develop procedures to fabricate well-ordered nanostructured materials with tailored properties for specific applications. Thus, the study of nano-objects becomes very important, not only from a fundamental point of view in order to understand how the structural confinement influences the physical properties of the material but also for its broad technological impact. Nanostructured systems concern physics, chemistry and biology communities, interested in their optical, magnetic, electrical and catalytic properties.

The self-organization processes have been observed at the surface of systems of very different character. Often the assembled systems present well-defined order with periodicities at the nanometer scale. These self-assembled nanostructures potentially represent a new patterning technology, able to surpass in speed and quality the present standard methods, such as lithography, in fields as diverse as magnetic recording media or light generation in semiconductor lasers. Two methods can be employed for this aim: first, by depositing soft condensed matter layers with self-organized nanostructures on flat substrates, and, second, by using nanostructured substrates.

The self-organized nanostructured substrates are created employing a wide range of self-assembly mechanisms to provide well ordered arrays of surface objects such as pits, dislocations, step bunches or pyramidal mounds. One family of techniques involves the ion bombardment of either metal or semiconductor single-crystal substrates, giving an ordered pit morphology. Whereas another uses strain driven self-organization in very thin-films or alloys. The strain-driven relaxation can take different pathways depending on the experimental system and different nanostructures as dots, wires or rings can be self-assembled. Misfit dislocations can be generated, and often in metal systems, they develop into very well ordered surface patterns. On semiconductor systems a competition of relaxation mechanisms occurs, such as ripple formation, coherent 3D island growth

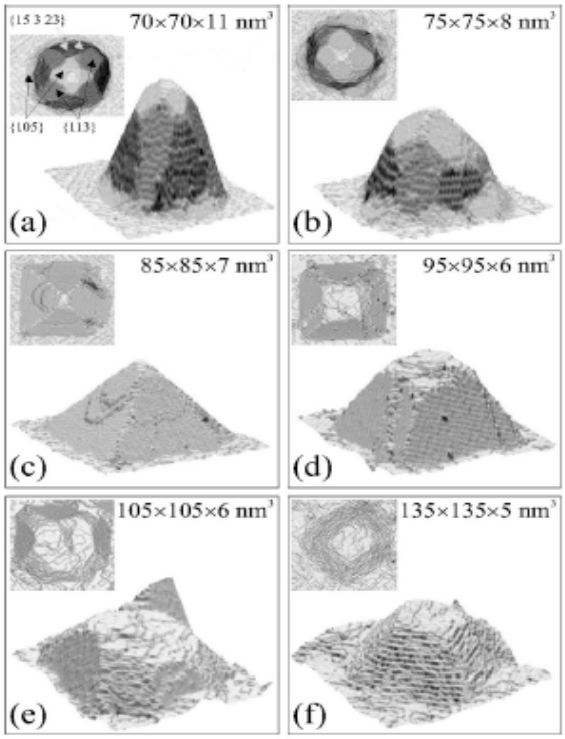


FIG. 11. Typical Ge island shapes obtained by STM during Si capping of Ge domes grown on Si(001): (a),(b), domes; (c) pyramids; (d)–(f) prepyramids. The Si coverages are 0, 1, 2, 4, 8, and 16 ML's for panels (a)–(f). From Rastelli *et al.*, 2001.

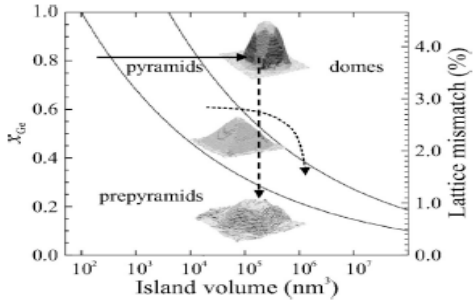


FIG. 14. Shape transition of Ge or SiGe islands grown on Si(001) during growth (solid arrow), postgrowth annealing (dotted arrow), and Si capping (dashed arrow). The solid curves represent the critical volumes for pyramids and domes. From Rastelli, Kummer, and von Kaenel, 2002, reprinted with permission from Elsevier. Copyright 2002.

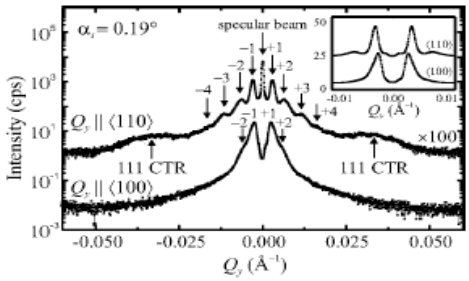
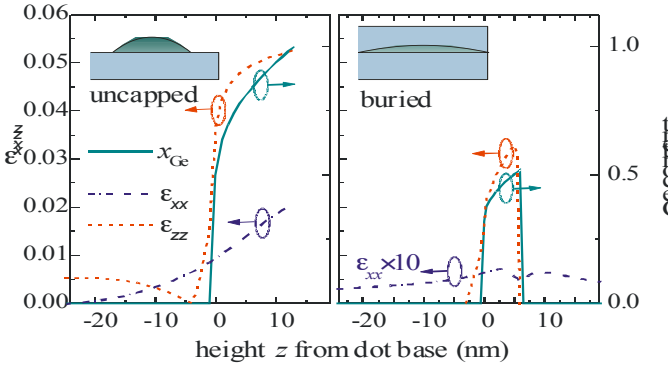


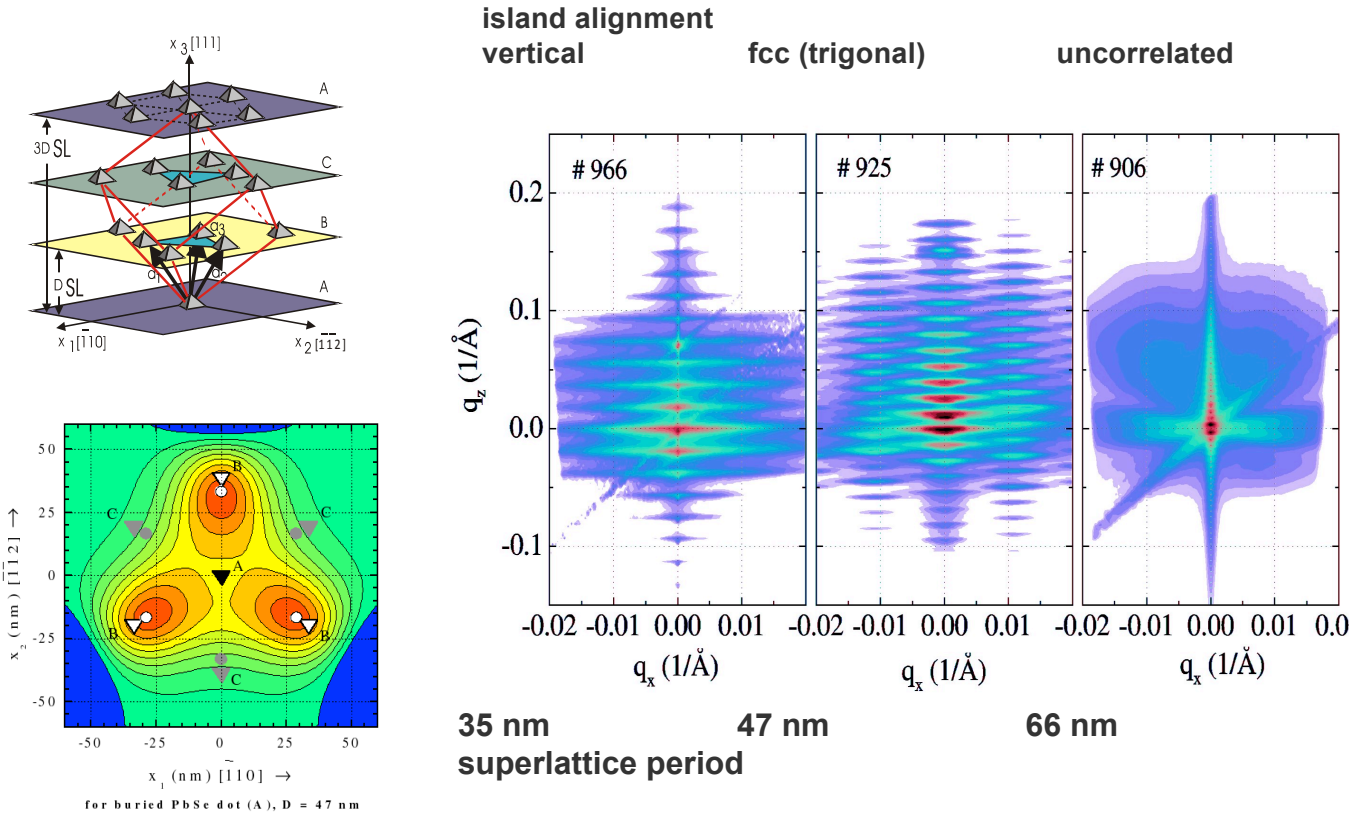
FIG. 33. GISAXS intensity distribution for two different sample orientations. Satellite peaks due to the positional correlation are visible as well as facet streaks due to island shape. From Schmidbauer *et al.*, 1998.

and misfit nucleation [Stangel 2004 and related]. A final technique will use crystal-lattice-mediated self-assembly to generate ordered arrays of nanoparticles over the surface of microcrystals. This variety of mechanisms will produce patterns of different length scales.

One very important power of this technique it is the fact that it is possible to study the shape and the self organization of quantum dots embedded in a matrix or covered by a capping layer. This allows determining the sort range correlation between these entities, as well as the shape modification induced by the capping layer [Roch 2002].



A main advantage of the buried intefaces studies by means of x-ray diffraction is the possibility to study the correlation between nanostructures buried at different layers. Here we show that the correlation between nanostructures depends on the interlayer thickness. At low interlayer thicknesses, i.e. 35 nm, only vertical correlation between nanostructures exist. At high interlayer thicknesses no correlation is observed. At intermediate thicknesses, i.e. 47 nm, both vertical and horizontal correlations are present.



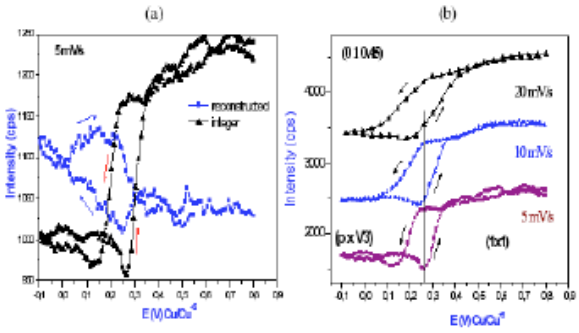
2.3. MAGNETIC SYSTEMS

The temporal evolution in semiconductors and magnetic recording devices has followed both an exponential law (Moore's law). Nonetheless, the continued growth in both fields is technologically limited. Improvements in both, recording and reading medias are necessary. Since the beginning of the manufacturing of magnetic hard drives in the 60s, the physical processes of recording remained the same. The increase of the areal storage density by six orders of magnitude took place by simple scaling. In spite of this continuity, researchers expect fundamental limits of this evolutionary process in the next five to ten years. The superparamagnetic effect limits the miniaturisation of the bit cell size because the stability of the magnetisation towards thermal fluctuations scales with the volume of the bit cell.

Spin Valves are the key element in giant magnetoresistive (GMR) read heads for magnetic recording disk drives. The technological trend has been associated to a decreasing in the film thickness. In the order side Magnetic Tunnel Junctions (MTJ) are attracting renewed interest due to their possible use as non-volatile Magnetic Random Access Memories (MRAMs) that could replace the semiconductor RAMs. MTJs are formed by two magnetic metals separated by a nanometer-thin

insulator layer. Today's MTJs are made of polycrystalline materials, which originate a large number of problems, of both basic and technological nature. There is much interest in growing epitaxial, single-crystal MTJs. This requires crystallographic and processing compatibilities for the materials involved. The decreasing in the film thickness has been so important that the interface nature from the chemical, physical and electronics point of view starts to play a fundamental role [Weichel 2000 and related]. X-ray diffraction is a powerful tool for non-destructive analysis of the layer structure and moreover of the physical and chemical state of their interfaces. From this point of view the evolution in the next future of both scientific fields go by the hand of the development of the structural studies by means of x-ray diffraction.

Determining the properties and morphology of buried layers and interfaces remains an important experimental problem in solid-state science. Many of the technological end products of this science are based on thin-film devices, which consist of a series of such layers. Characterization of the physical microstructure and degree of disorder of these films is commonly carried out by reflectivity, diffraction and diffuse scattering studies. The past few years have seen an enormous amount of activity in the development of magnetic devices for data storage, ultra-low field sensing and quantum computing applications. In such systems, a thorough knowledge of the magnetic microstructure is also required. Magnetic x-ray scattering is presently a burgeoning area able to study the magnetic structure in thin magnetic layers and more recently the induced polarization in magnetic/non-magnetic systems. Importantly the "photon-in, photon-out" nature of the experiment means that the applied magnetic field does not affect the measurements [Muzenberg 2000 and related]. So far the studies have concentrated on transition metal and rare-earth multilayers but one expects that this will extend to actinide systems in the near future.



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 differnt scan rates.

A detailed knowledge of the magnetic structure of such systems, combined with the possibility of controlling the physical structure on the length scale of magnetic domain sizes and smaller (patterned magnetic nanostructures), is thus of capital importance for the development of the field. Such structures may be artificially created through patterning or by deposition on miscut surfaces. As device sizes are continually being shrunk the interplay between magnetic structure and physical microstructure is of ever increasing importance.

In recent years, there has been significant interest in accessing the magnetic order at surfaces. Given the break in crystal symmetry at the surface one might expect to observe magnetic structures and critical behaviour different to those found in the bulk [Scholl 2001 and related]. The experimental difficulty is that the surface charge scattering is typically 5 orders of magnitude weaker than the bulk scattering. For this reason, high brightness synchrotron grazing incidence X-ray scattering techniques are required to characterise the chemical structure of the surface [Robinson 2004 and related]. The magnetic intensity is then further reduced by another 5-6 orders of magnitude, and so the XRMS enhancement is required to observe any magnetic contribution from the surface. Such difficult measurements will provide a significant and unique insight into surface magnetic ordering: an area of solid state magnetism that has not been exploited.

In the article [Sarthour 1999], authors have shown the utility of surface resonant magnetic

diffraction in multilayer. In this article they have shown that there is magnetic order induced in the

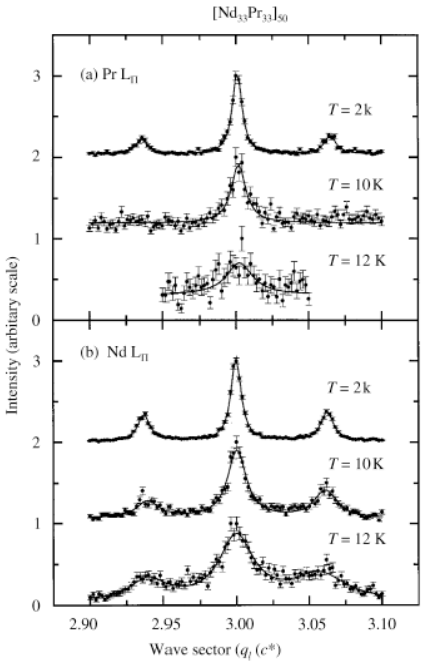


Fig. 2. Scans in the c^* direction through the magnetic Bragg reflection, at (q_h 0 3), for (a) Pr L_{II} and (b) Nd L_{II} edges.

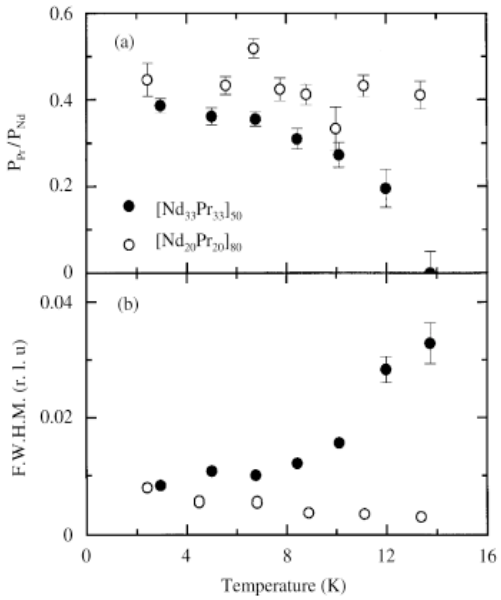
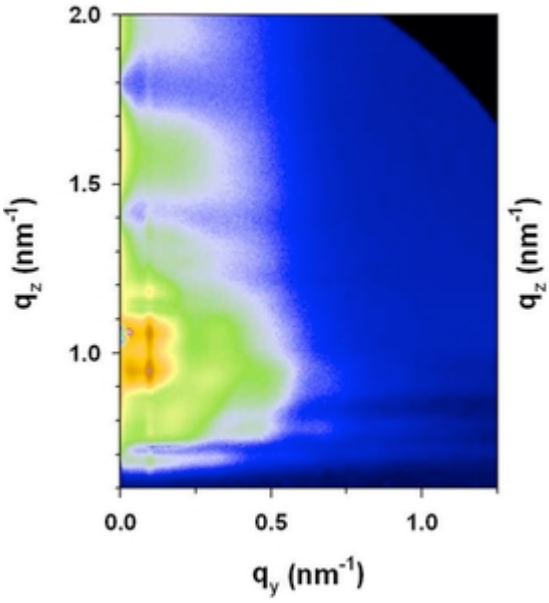
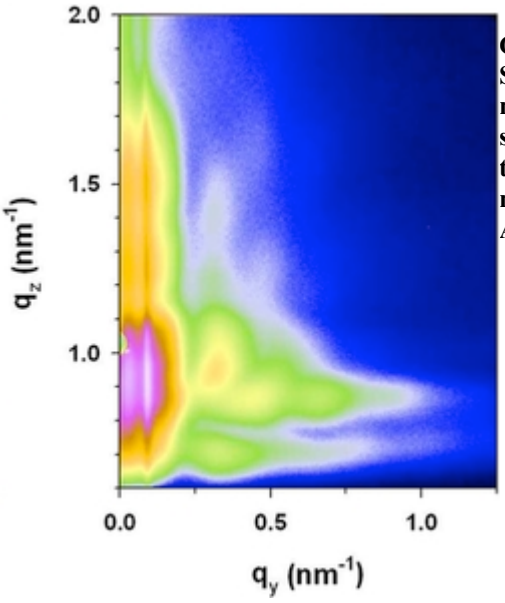


Fig. 3. (a) The polarisation of Pr 5d band relative to Nd versus temperature. (b) The width of the main magnetic Bragg peak in the c^* direction versus temperature, at the Nd L_{II} edge.

Pr in the case of Nd/Pr multilayer.

Another example of near-surface diffraction on magnetic system can be found on [Franz 2008]. Magnetic nanostructure arrays are created using di-block copolymer micelles with silica-loaded cores. The generated dots were made of (Co/Pt)2-multilayers. They show different magnetic behavior, depending on their size, inter-particle distance and milling time. In this case they have found that the GISAXS patterns change drastically after ion milling. The strong oscillations along qz disappeared, indicating that the complete Co/Pt multilayer was eroded between the metal oxide particles while along qy the interference increased due to the formation of the Co/Pt dot array.



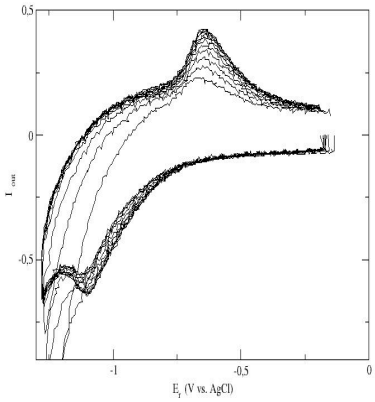


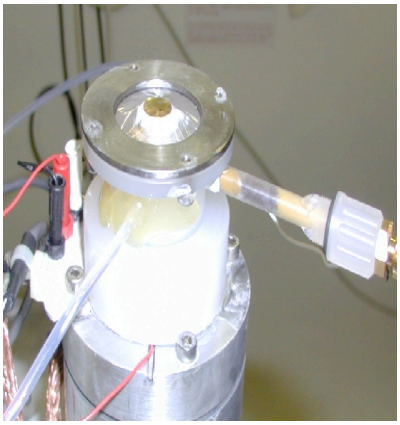
GISAXS pattern of SiO2 particles on Co/Pt multilayer before sputtering (left) and of the fabricated magnetic dot array by Ar+-ion milling (right).

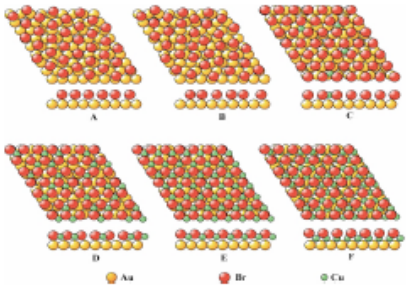
2.4. SOLID-LIQUID INTERFACE.

X-rays are able to penetrate through matter and probe the interface of interest, even in buried environments such as at the liquid-solid interface.

An important scientific area that relies on studies of the interface between a solid and a liquid is electrochemistry [Herrero 2000 and related]. In this case, the changes in the solid-liquid interface are controlled by the applied potential. One of the most important cases is the deposit of layers or multilayers of metals or other compounds, in a process that can be considered analogous to the ordered reconstructions that occur in samples grown by molecular beam epitaxy (MBE). The high flux and careful cell design would allow the real-time study of deposition process. These studies are



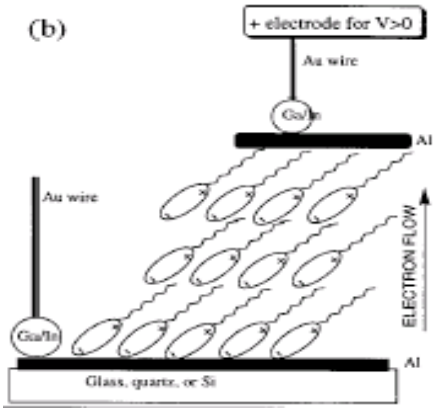


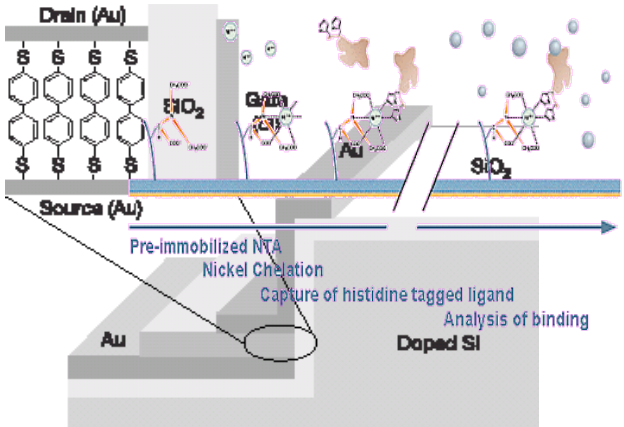


Changes in the structure of a single Copper monolayer onto Au (111) in presence of Br- as dopant induced by the electrochemical potential

very useful in order to obtain tailored surfaces with very specific properties. Another important advantage of the X-rays is that they can monitor the interface during an electro-catalytic reaction, such as hydrogen oxidation, oxygen reduction, carbon monoxide adsorption and oxidation, oxide formation…, reactions that are very important in fuel cell technology and corrosion.

Some researchers have extensively used X-ray scattering techniques to determine the structures that can be formed by self-organization of molecules, such as long chain thiols on gold surfaces [Torrelles 2004 and related]. Such measurements are beneficial not only for the role they have in understanding the structure of the interface, but also because it aids the understanding of the self-assembly process. This is a key area for the development of devices built using a `bottom-up' approach, which are predicted to supersede the current generation of silicon `top-down' structures. There are already electronic devices based in the use of the thiols or dithiols layers. For instance, a molecular rectifier and a molecular transistor devices have been presented.

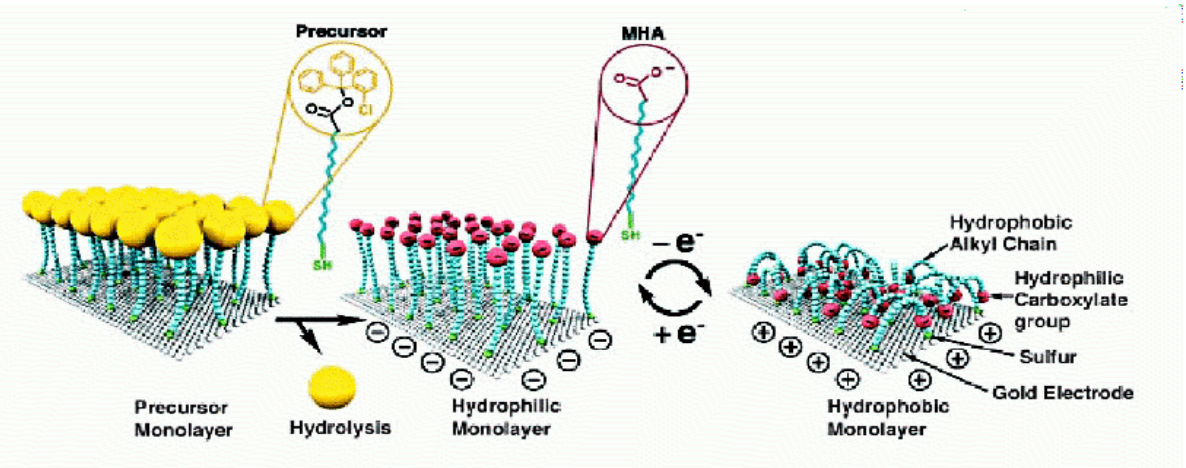




These thiols can be functionalized in order to a have the possibility of connect selectively other

molecules. One very interesting example is the formation of organic logic gates over the self-assembled monolayer. These devices are able to modify their conductivity (logic state) as a function of the environment conditions [Clemente-León 2003 and related].

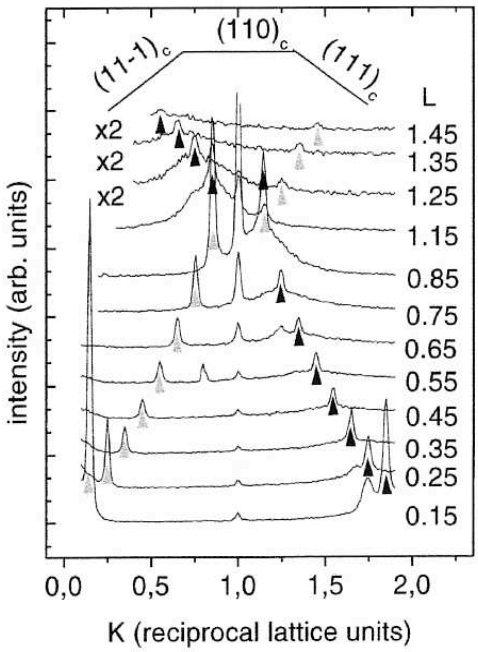
The study of the formed thiol layer under controlled humidity has open new aspect of the thiols system. In this case the thiols order has been shown that depends on the water content of the system. It has been shown that they act as switchable surfaces based on organic layer.

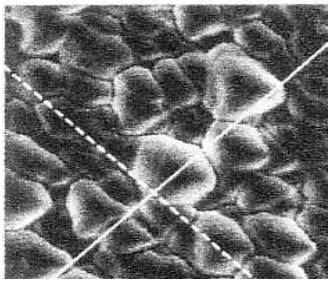


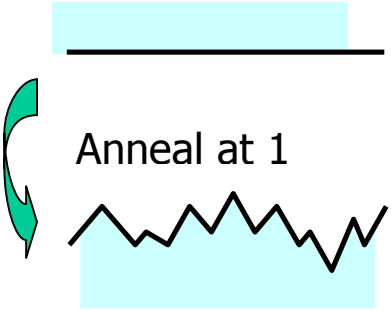
2.5 SOLID-GAS INTERFACE: CATALYSIS.

For harsh environments X-ray diffraction is unique in its ability to monitor (at the atomic scale) the surface structure of materials under real-world processing conditions [Quirós 2002 and related]. Such measurements will become increasingly important in future studies, where the opportunity to close the `pressure gap' will be taken and the true processes that occur in industry will be probed, in contrast to the artificial environments of many research studies. In addition to ultrahigh vacuum molecular beam epitaxy (MBE), processes that could be studied by this technique include metal-organic chemical vapour deposition (MOCVD) or laser ablation. These are much more prominent in technological applications because of the more rapid growth rates and more easily achieved sample environments.

Some investigations at the ESRF of samples held under high gas pressures have shown the creation of microfacets at elevated pressures and temperatures. Therefore, in addition to the growth opportunities in these environments, the study of important catalytic systems (e.g. ammonia synthesis over iron) under real operating conditions will be possible.

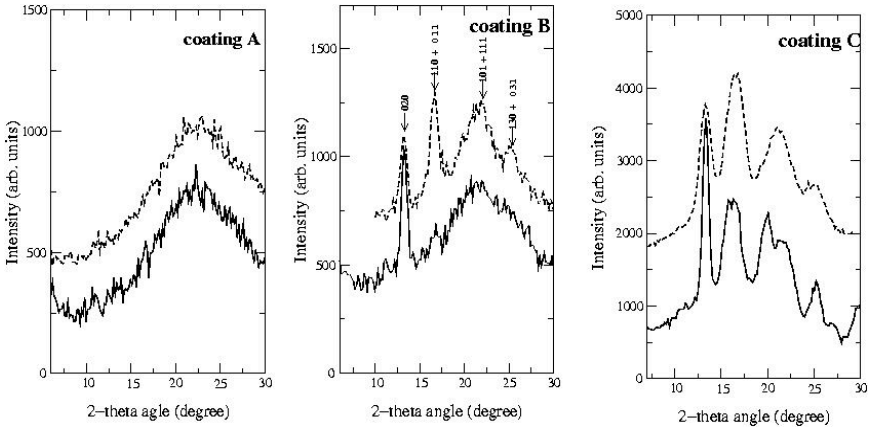


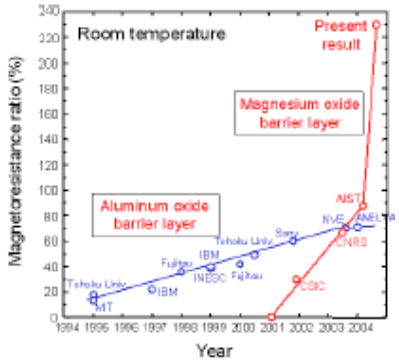




2.6 SOFT CONDENSED MATTER.

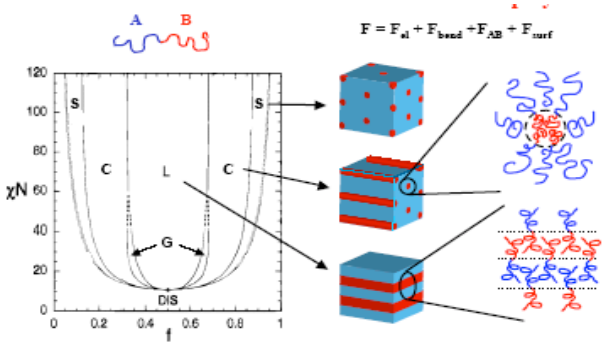
A fundamental understanding of the influence of free surfaces and buried interfaces on the properties of thin polymer films is important in many applications, including coatings, adhesion and the electronic behavior at interfaces in polymer-based optoelectronic devices. Both the free surface and the buried interface may differently affect properties such as the chain conformation, the composition of mixed systems and chain dynamics, while a combination of surface and finite size effects may also influence the character and temperature of the crystallization and glass transitions. In contrast to the extensive data available for semiconductors and other inorganic materials, indicating pronounced differences in the state of order between surfaces and bulk, very little information is available about the surface structure of polymers. Grazing incidence diffraction with synchrotron radiation is an ideal tool for such studies since the penetration depth is of the order of the molecular dimensions at the surface, and the surface and bulk structure can be compared by adjustment of the incident angle [Capitán 2004 and related]. Near-surface diffraction on PHB thin films have shown that the polymer crystallised under RT when the film thickness is small. In the same conditions the polymer is not able to crystallise in a thick layer. Furthermore these studies shown that the polymer has a preferential crystallization direction given by the substrate surface direction.



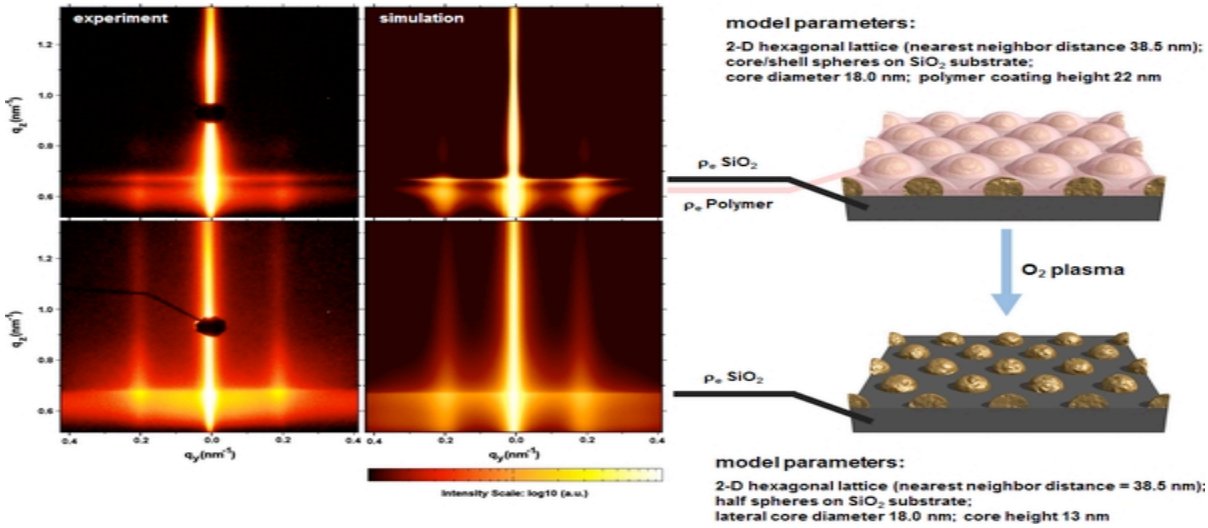


Semiconducting polymers for electronic devices are a big growth area both scientifically and commercially [Sirringhaus 1998]. Here polymers are used in thin films, often in multilayer structures. Since the device performance depends very largely on its interfacial properties, and as we know that electronic properties of polymers are strongly coupled to their chain conformations, we can anticipate that an understanding of the factors controlling chain ordering near surfaces and interfaces will be crucial to optimizing device performance. Structural studies of in-situ processing of semiconducting polymer films is likely to be an important growth area for the coming decade.

The block copolymer formed by asymmetric polymers is able to form phases in the equilibrium with a self-assembled morphology that can be changed as a function of the polymer blocks concentration ratio. The formation of these large size structures can be used as a chemical robust route to the fabrication of ultrahigh-density arrays of nanostructures [Thurn-Albrech 2000 and related]. One of the polymer blocks can be selectively eliminated by chemical methods. The resulting structure can be used as a mask for the formation of microelectronic nano-structures.

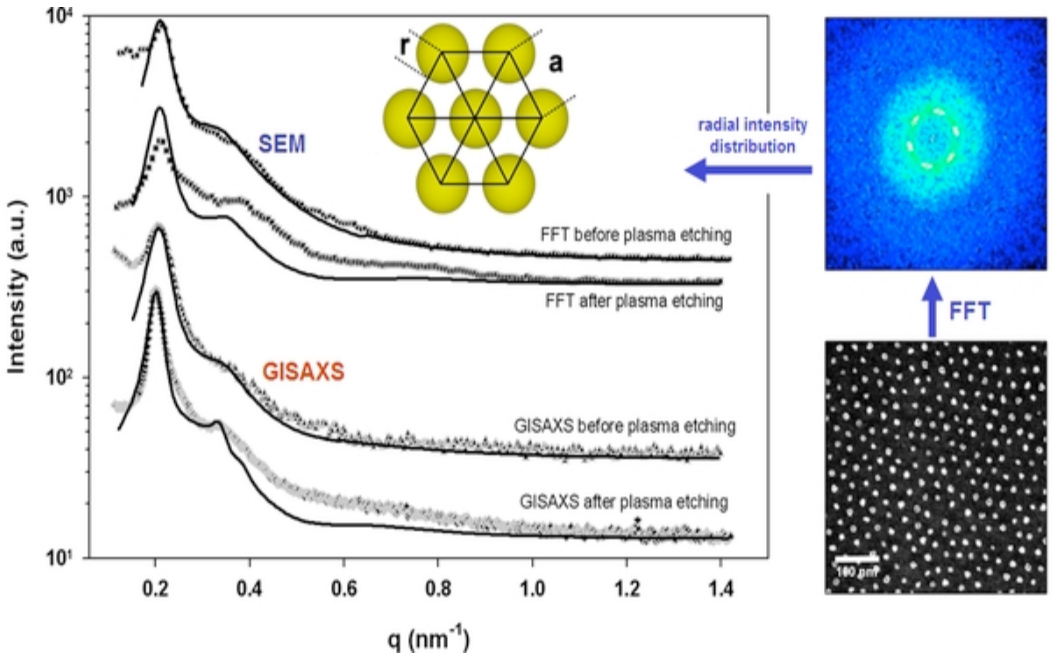


The next experiment [Frömsdorf 2007] show patterns and simulations for SiO2 loaded cores in a micellar monolayer before and after plasma treatment. Before O2 plasma treatment, the 2-dimensional hexagonal array has a period of 38.5 nm, the SiO2 particle radius is 9 nm and the height of the coating 22 nm. After removing the organic shell via oxygen plasma the height of the array decreases to 13 nm, while the lateral values are constant. This means that not only the organic shell on top of the SiO2 particles is completely removed but also the particles are etched from the top by 5 nm.



Experiment and simulation before and after O2-plasma treatment of SiO2 filled diblock copolymer micelles on a silicon wafer

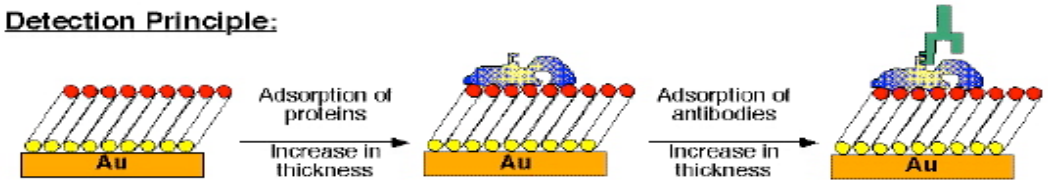
The microscopic methods SEM and AFM are not suitable to investigate the surface morphology on the scale of several mm. Micrographs show only a small part of the sample and for better statistics additional methods are needed. Here [Frömsdorf 2007] GISAXS is the first choice, as it reveals information from a large part (several mm2) of the surface. The scattering curves can be compared with the FFTs of the microscopic images, to demonstrate that the same nanostructure is uniformly spread over a large surface area.



SEM FFT spectra and GISAXS out of plane scattering curves (at Yoneda maximum) from silica filled micelles before and after O2-plasma etching

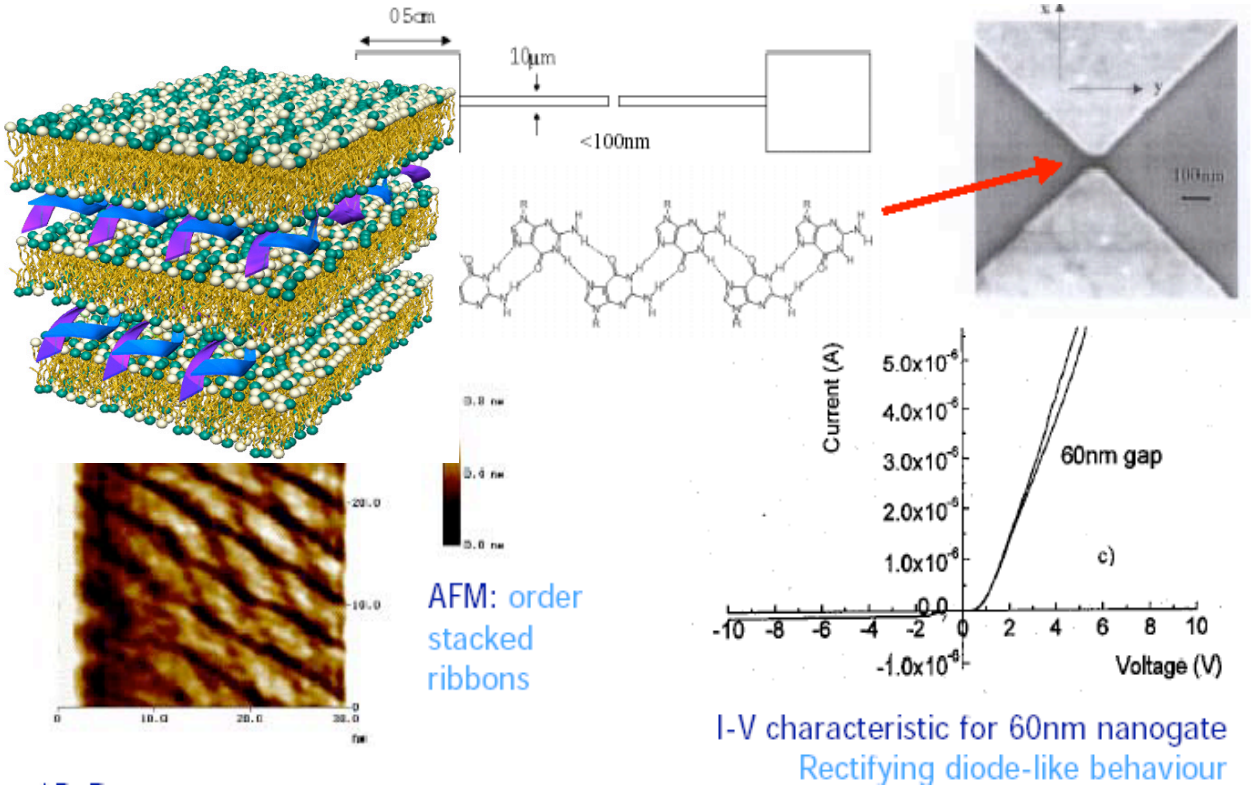
Within the soft-condensed matter the system containing biomolecules has a rising interest, specially when they used in a new development area as the technological production of biosensors and bio-devices.

The interface between biological molecules and a non-biological surface is a largely unexplored area of science, which is of relevance to important biological and medical technologies as well as future nanotechnology: medical implants, biosensors, bio-catalysis, biofouling-resistant surfaces, 'smart polymers' for controlled drug release, templates for tissue engineering and bio-electronic materials of the future i.e. bacteriorhopsodin, DNA networks [Prime 1991].



A central scientific issue is to understand and control the interactions at the interface between a solid material surface and its biological environment. In view of the hierarchy of structures occurring in proteins, these interactions need to be understood at the level of amino acids, peptide and polypeptide chains and protein molecules. Additionally, the effect of the aqueous solvent conditions and the chemical nature of the surface needs to be addressed. Vacuum-based surface techniques are therefore not applicable and a combination of synchrotron-based surface x-ray diffraction and photon-based spectroscopies is essential.

A longer-term benefit from understanding interactions of biological molecules with interfaces, and with the aqueous environment lies in nanotechnology [Rinaldi 2001]. In the search for new functional materials it is tempting to try to exploit the intriguing peptide and protein architectures that orchestrate the catalytic and other regulatory tasks in living systems. Detailed understanding of the supra-molecular interactions between biomolecules, interactions with interfaces and with the environment would thus be crucial to the design of such functional nanostructures.



Surface studies of membranes, and the molecules on their surfaces, are also hugely promising with applications for a large number of industrial processes [Koltover 2004 and related]. In the food and pharmaceutical sectors, surface science is vital to understanding activities such as protein denaturation, emulsification and phase separation, binding and unbinding, and the control of interfaces. Device development and biosensors also rely heavily on information derived from surface science studies at a solid-liquid interface. Increasing numbers of diseases are now being associated with the deposition of non-crystalline deposits in organs such as the brain, heart and pancreas.

2.7 LANGMUIR BLODGETT FILMS

Following the realization of Lord Rayleigh that a film of oil on water was just one molecule thick. Langmuir demonstrated that monolayers of fatty acids could be ordered on the water surface by application of lateral pressure, which triggers phase changes from a gaseous state of non interacting molecules to a "solid like" state, where the molecules interact in a rigid film. Langmuir and Blodgett demonstrated the transfer of such monolayers from the water surface to a solid substrate by slowly passing an appropriately treated substrate through the air/water interface. Films may be picked up on passing several times from air into water and vice versa, the so called Y type deposition, only on passing from water to air, Z type deposition, and on immersion from air into the water only, X type deposition. Therefore producing distinctive head to head, or head to tail,

orientations of the amhiphilic molecules in a well-ordered multilayer structure.
The Langmuir-Blodgett technique has demonstrated its ability to form quantum wells from organic molecules appropriately chemically engineered to provide both a conjugated region of high electron affinity and aliphatic side-groups. The tunneling barriers also act to provide the conjugated molecular constituent with its amphiphilic (hydrophobic and hydrophylic) components. Many of such molecules have been spread as Langmuir films on a sub-phase, and subsequently deposited on substrates as Langmuir Blodgett multilayers [Clemente 1998 and related].

Control of the transfer of charge through multilayer structures offers the possibility of achieving an increase in the density of information storage, in at least one dimension, down to molecular dimensions. The presence or absence of charge in a molecular layer, that forms part of a multilayer produced by the Langmuir Blodgett technique, represents a one or zero of binary logic [Matsui 2003 and related].

3. BEAMLINE REQUIREMENTS

The proposed project is basically consisting on a substation hosting a multipurpose open configuration diffractometer able to host different user-specific apparatuses with the objective to offer several sample environments to the users. Real-time experiments would give the possibility of studying growth processes or reaction at surfaces (as heterogeneous catalysis or electrochemistry). The equipment would be able to offer the possibility to follow the evolution of morphological changes in surfaces as well as to monitor their structural changes in a vast range of pressures (from ambient pressure to UHV) and temperatures (30K to 1500 K).

Surface X-ray diffraction is a well-established technique for studying surfaces and interfaces. Even if several other techniques allow a structural determination of surfaces, X-ray diffraction offers unique possibilities:

- Taken into account the low Z number of the organic system that has aimed of study of this project, it is necessary that the diffraction beamline has a **maximum photon flux with a great stability**.

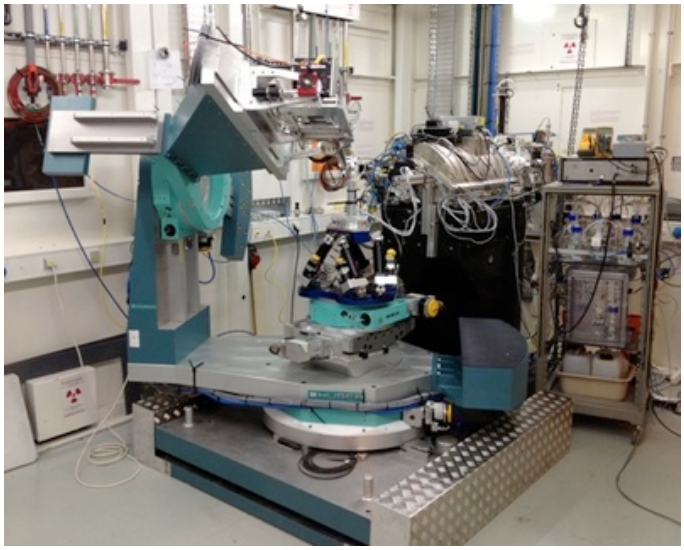
- The structural study to the chirality implies to determine the relative intensity of the Bragg peaks that are allowed/prohibited by the symmetry of the systems. That is to say, one of the fundamental characteristics that they are going to define if the growth of the organic layer is heterohiral or homochiral, is the fact that a growth or another one implies changes in the elements of symmetry characteristic of the cell unit of the growth. The direct consequence of this is that allowed tips of Bragg/prohibited by the symmetry of growth group will be present or absent. Due to this it is clear that it is necessary that **the system of detection of this line must be very clean of background noise for the relation signal as opposed to background noise is as high as possible**.

- X-rays are weakly absorbed by matter. As consequence surface X-ray diffraction is not limited to free surfaces under UHV conditions but can be applied with success to buried solid interfaces, solid/liquid interfaces and high pressure gas/solid interfaces. This is of particular importance in the case of heterogeneous catalytic reaction where the role of the catalyst can be studied under real working conditions.

- In addition to crystallographic studies, surface diffraction is also suited for dynamical studies such as epitaxial growth, ion patterning, surface kinetics and phase transitions. In particular, ion erosion with ion beams in combination with grazing-incidence small-angle scattering has been employed to study the dynamical evolution of medium range correlations during nanopatterning.

- The possibility of tuning the photon wavelength allows carrying out experiments at resonance energies of particular elements. This is important to investigate surface magnetism in order to determine the depth distribution and magnetization of the resonant atoms. Resonance can also be used to determine the involvement and role of a particular atomic species in the surface/interface structure

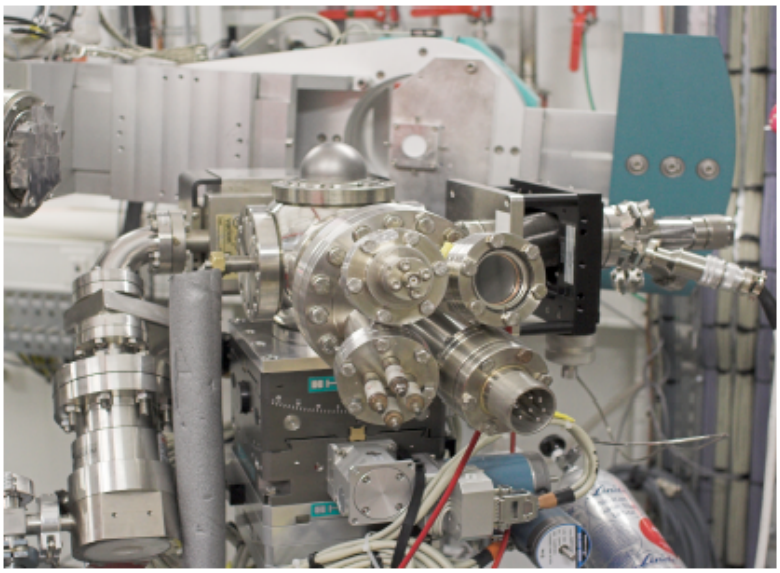
- Will be equipped with a z-axis vertical diffractometer specially suited for samples with a horizontal surface geometry where users' chamber could be mounted on the diffractometer. The maximum load supported by the mechanics would be in the range 150 to 200 kg. The possibility to tilt the incident beam downwards (~ 0.5°) by using vertical KB mirrors will make liquid surfaces accessible. For all the proposed scientific cases it is necessary to achieve the minimal confusion sphere that possible in the diffractometer. The main limitation can be given by the necessity of space in order to be able to install the sample environment proposed for such studies at the diffractometer. We consider that a minimum distance base to the centre of diffractometer of about 15 cm must be considered.



This station will be dedicated to the in-situ studies of the structure and morphology of surfaces, buried interfaces, thin films, liquid surfaces, magnetic experiments, nanotechnology (GISAX: in situ real time growth processes, evolution of catalyst nanoparticles morphology in reaction conditions,…) and to surface characterization during reactions (catalysis, electrochemistry, etc.).

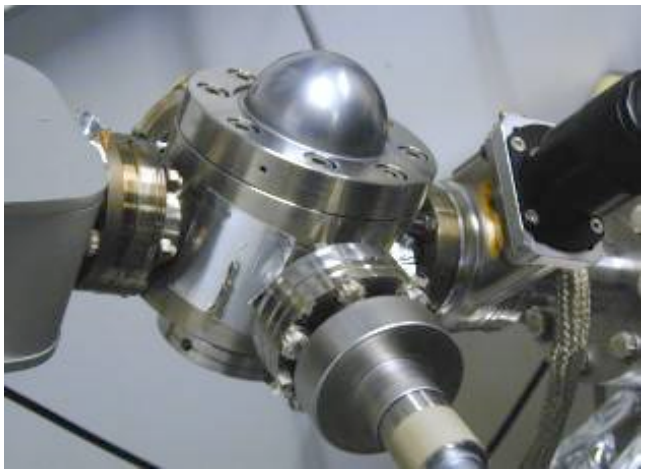
3.1. "In situ" PREPARATION MINICHAMBER

It is interesting to give the possibility of following "in situ" the process of growth of the organic layer. For that reason, it is needed that the beamline has the possibility of an **UHV chamber with surface cleaning system, organic evaporator and sample/substrate heating and cooling in liquid N2.** The figure shows a portable UHV diffraction chamber which allows "in situ" sample preparation. The chamber is equipped with a beryllium window. The cylindrical shape of the window imposes no limitations for the in-plane and out-of-plane diffraction directions. An ion gun and deposition cells are provided in the chamber. A gas inlet system is available for supplying different gasses to the sample under requirement. The sample holder can be cooling down to N2-liquid temperature, which is specially important for organic systems which can modify their structures at RT.



Ultra high vacuum in the 10^{-9} mbar regime can be achieved after baking the chamber at temperatures around 120◦ C. The vacuum is maintained by a turbo molecular pump (d) and an ion getter pump (e). On top of the chamber a gate valve (g) is mounted which allows the direct transfer of the sample from a UHV analysis chamber (described in the previous examples) into the portable chamber. This chamber would not be permanently fixed onto the diffractometer, but easily installed on it when required. So, an **open configuration diffractometer** is required to leave enough space available in the surroundings of the sample for mounting the instrumental equipment necessary for preparing and manipulating it.

3.2. BABY CHAMBER TRANSFER, FOR "ex situ" SAMPLE PREPARATION



For the structural studies of surfaces, thin layers, nanostrucutes,… prepared in outer UHV chamber and where that it would be transferred it is the already prepared sample. This chamber will be used to transfer the sample from an "external" surface preparation station to the diffractometer. The surface station would be equipped with a surface preparation laboratory for permitting the users to prepare the sample prior to its characterization using the X-rays techniques. Some experiments could require to clean the surface by applying several annealing/sputtering cycles and/or to deposit organic or inorganic compounds onto the surface before being transferred into a portable chamber (baby chamber) for its X-ray analysis.

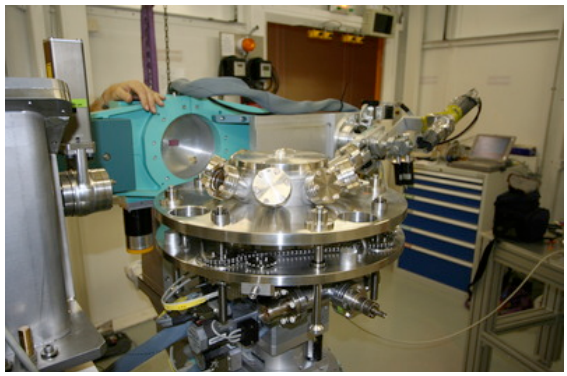
The UHV ALBA Surface Preparation Laboratory should be equipped with conventional surface science techniques as Low energy electron Diffraction (LEED), Auger Electron Spectroscpy (AES), Scanning Tunneling Microscopy (STM), polar and longitudinal Magneto Optic Kerr Effect (MOKE) setup, thickness monitor, Residual Gas Analyzer (RGA) and several evaporation sources. The preparation chamber should be able to transfer the sample holder to a small portable chamber for mounting it in the diffractometer.

However, users also could perform the experiments in this station by mounting their own baby chambers containing the already prepared samples in their host laboratories on the diffractometer.

3.3. A FLOW REACTOR CHAMBER WITH REMOTE CONTROLLED GAS SYSTEM FOR CATALYSIS

A Flow reactor equipped with in-situ UHV surface preparation tools would allow the study of reactions in real time and closer to real industrial conditions. The reactor is also equipped with a gas line having an automated system of gas flow controllers that improves the data acquisition procedure and gives the ability to follow the catalytic reaction from the beginning.
The flow reactor shown in the figure below has a lower and an upper part. The lower part is the UHV section whose upper big flange is holding the UHV tools and is equipped with Ion Sputter Gun for sample surface preparation, Residual Gas Analyser, RGA and Electron beam evaporator

The big flange can be moved up and down with respect to the sample position. When up, the sample is in UHV conditions and can be prepared with standard UHV tools. When the flange is down the region around the sample is sealed off having a small reactor volume (15 mL). Gases can flow through two capillaries. UHV conditions are preserved in the bottom section all the time.



The gas system has four mass flow controllers at the gas inlet. This allows mixing exact proportions of desired gases. It will be remote controlled via beamline control software.

3.4. ELECTROCHEMICAL CELL

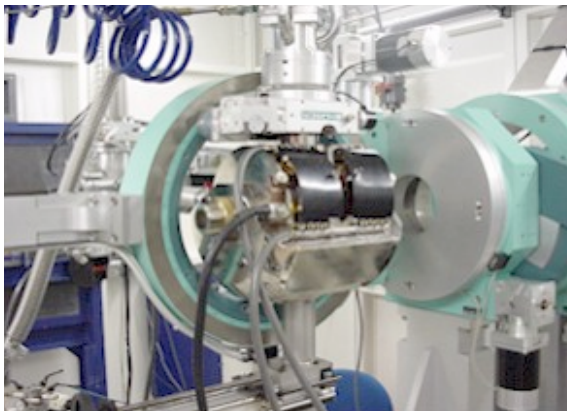
A Kel-f electrochemical cell will be available for electrochemical studies. The cell has a sealed Mylar window for the x-ray pass through.

The substrate is mounted at the end of a holed Kel-f road for electrical contact. The tube and substrate can be adjusted towards the Mylar window by means of a micrometer screw which is mounted on the male substrate joint.

Inlet and outlet lines to the cell can be opened/closed by valves to apply over and underpressure to the interior of the cell.

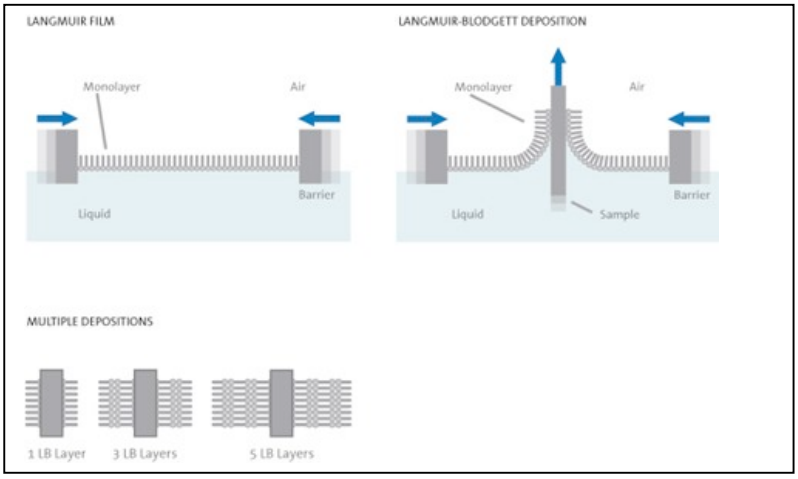
3.5. MAGNETIC FIELDS

Intense magnetic fields that could be set around the sample holder at the diffractometer in order to allow the study of the structural changes associate to the presence of an intense external magnetic field (i.e. 1T). Furthermore, it would be very interesting to allow that these magnetic fields were compatible with the UHV minichamber for studying the influence of the presence of a nonhomogenous field as is an external magnetic field in organic prochirals layer.



3.6. LANGMUIR & OTHER LIQUID TROUGHS

A large Nima langmuir trough (400 x 300mm) could be mounted on the diffractometer for experiments using the DCD (Double Crystal Deflector). This is combined with an active anti-vibration system to isolate the sample from any vibrations generated by the diffractometer. The trough can be placed inside a large controlled atmosphere enclosure as required. The films obtained can be highly organized ranging from ultrathin monolayer to multilayer structures built up of hundreds of monolayers. Irving Langmuir and Katherine Blodgett founded the science of LB films early in the 20th century.



Langmuir film, Langmuir-Blodgett depositions and Langmuir-Blodgett films of various thicknesses

Repeated deposition can be achieved to obtain well-organized multilayers on the solid substrate. There are several parameters that affect on what type of LB film is produced. These are the nature of the spread film, the subphase composition and temperature, the surface pressure during the deposition and the deposition speed, the type and nature of the solid substrate and the time the solid substrate is stored in air or in the subphase between the deposition cycles.

Density, thickness and homogeneity properties are preserved when transferring the Langmuir film

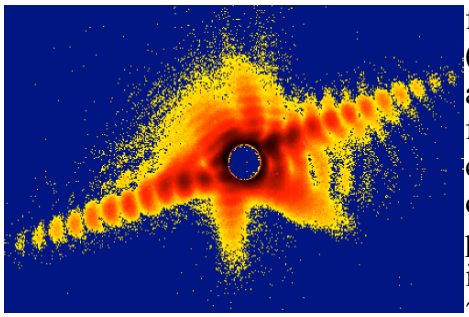
onto the substrate, giving the possibility to make organized multilayer structures with varying layer composition.

4. ANNEX: OPPORTUNITIES WITH MICROBEAM

The use of X-rays in diffraction has conventionally yielded the average structure of the ensemble, where the coherence length of the domains on the sample is inversely related to the width of the diffraction peaks. In such measurements, the coherence of the x-ray beam has not been a dominant factor. The advent of new-generation synchrotron sources with low source dimensions and the use of narrow band pass insertion devices, now ensures that x-ray diffraction with coherent beams will open up a whole new range of studies. The potential of using a coherent source of x-rays in diffraction experiments has only recently been realised with some preliminary experiments carried out at the European Synchrotron Radiation Facility (ESRF) and the Advanced Photon Source (APS). Several types of measurements and analysis have been identified including the reconstruction of the shape of nanocrystals due to oversampling [Robinson 2001] and the determination of dynamical processes by observation of x-ray speckle [Pitney 2000]. The first of these requires that the size of the coherent beam closely match that of the crystal, resulting in diffraction features with fringes arising from facets. The 'phase problem' usually associated with x-ray diffraction is overcome, as the pattern is oversampled by more than a factor of two relative to the Nyquist frequency. Inversion is therefore possible to produce a two-dimensional projection of the crystal shape.

4.1. COHERENCE

A striking manifestation of coherence is the appearance of a speckled intensity distribution whenever coherent radiation impinges on a statistical scatterer and is observed at some distance from it. The high contrast of the speckles and their fine, diffraction-limited, graininess are essential



for a wide range of applications at optical wavelengths (Goodman 2006) including the new laser optical mouse. As far as spatial coherence is concerned it can be improved by spatial filtering of the main beam with a pinhole, although at a considerable loss of power. This has enabled the development of a large number of X-ray speckle-based techniques like X-ray photon correlation spectroscopy (XPCS) or coherent diffraction imaging (Sutton 1991; Mochrie 1997; Miao 1999; Marchesini 2003).

XPCS is based on the generation of a speckle pattern by the scattered **coherent light** originating from a material where some spatial inhomogeneities are present. A speckle pattern is a diffraction limited structure factor, and is typically observed when laser light is reflected from a rough surface, or from dust particles performing Brownian motion in air. If the state of disorder of the system changes with time, the speckle pattern will change, thus by studying the time dependence of the scattered intensity at a fixed wavevector, one can probe the dynamics of materials in thermodynamic equilibrium or out of equilibrium. Consequently, this technique could provide detailed information on many processes including thermal roughening, evolution of growing surfaces, diffusion effects, grain boundary motion or nanocluster formation. X-ray speckle-based techniques studies have attracted significant interest at 3rd generation synchrotron sources, such as the Troika facility (ID10) at the ESRF.

The feasibility of using microbeam techniques at Alba to produce a well-defined beam will ensure

an extension to the range of samples that can be studied. This will include measurements of materials where the arrangement of atoms is more disordered, such as in 'real' environments like toxic atmosphere of a MOCVD reactor, in structures grown by laser ablation or in various adsorbates including biomolecules. The production of ordered nanocrystals (self assembly of nanoparticles into micron sized domains) would greatly benefit from the microbeta source option.

4.2. LAUE μ-DIFFRACTION

White beam microdiffraction is a very old technique, which has been commonly used to measure the orientation of crystals for almost a century now. The typical source for such experiment is the bremsstrahlung radiation from x-ray tubes. Bending magnet or wiggler sources from synchrotrons are also naturally well-suited sources for such experiments as they display a homogeneous spectrum of radiation centered at some critical energy depending on the magnetic field intensity and the energy of the stored electrons.

Together with the high brilliance of third generation synchrotron sources, this broad wavelength spectrum allows very demanding experiments to be performed like high spatial resolution scattering experiments with micrometer or even nanometer hard x-ray beams.
The interest for white X-ray microbeams has been demonstrated by the pioneering experiments of Ice (Chung 1999) at the Advanced Photon Source and MacDowell and co-workers at the Advanced Light Source (MacDowell 2001, Kunz 2009). In Europe, in addition to the present setup, white beam Laue experiments have been carried out at the Swiss (Maab 2009) and Diamond (Hofmann 2009) light sources.

Although white beams lack a scale reference (the wavelength) and cannot be used for absolute lattice parameter measurements, they can be used to measure angles of crystal planes accurately and hence obtain crystal orientations and deviatoric part (i.e., distortional part) of the crystal strains.
A major interest of white beam experiments is the possibility to obtain a scattering diagram whatever the orientation of the crystals in the beam, hence allowing fast collection of data in a well-defined geometry.

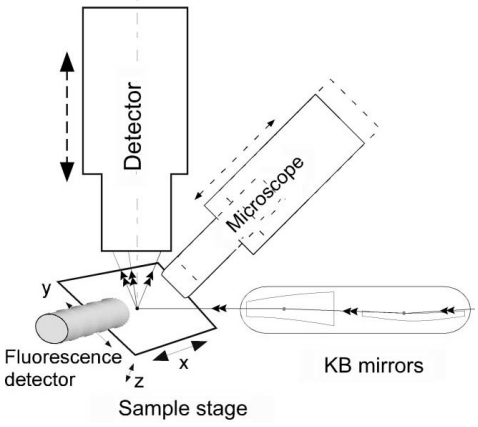
The interest of being able to obtain such data at the submicrometer scale is of special relevance to understand the microscopic origin of mechanical properties of polycrystalline samples, e.g., metals or oxide compounds. The understanding of the role of the microstructure on the mechanical and physical properties of a device is of special importance when the overall size of the system is comparable to that of the micrograins, which is the case for many systems in microtechnology and microelectronics (e.g., metal interconnect lines in integrated circuits). The large use of such materials in microtechnology is a motivation for proposing this setup.

Such information can hardly be obtained using other techniques as x-rays offer distinctive advantages over other orientation and strain probes (e.g., electron microscopy and Raman scattering). X-rays can be used on nonoptically transparent and insulating materials, and, due to their relatively high penetrating power, little or no sample preparation is requested before the measurements.

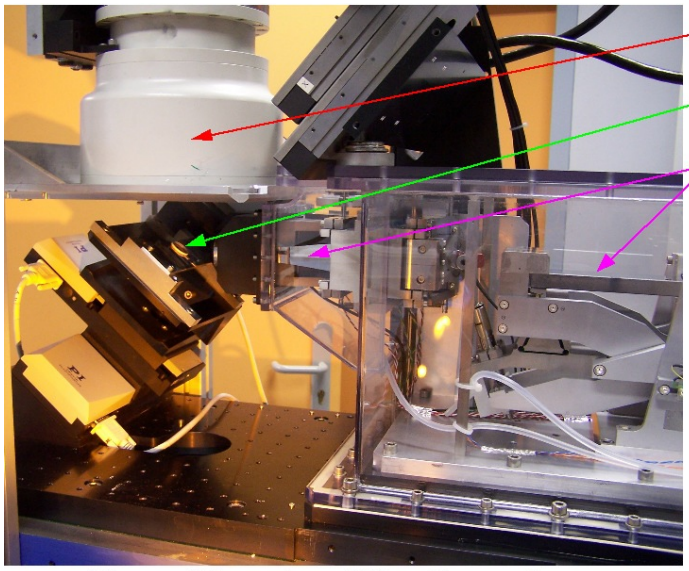
Keeping boundary conditions constant is especially important when the aim is to measure the strain state of a material. Also, (hard) x-rays are little absorbed and allow one to carry experiments in a nondestructive way with reduced amounts of energy deposited into the material.

Objectives:

- Fast mapping of crystal orientation and strain fields in polycrystals with a submicron spatial resolution in two dimensions. In the well crystallized parts of the grains, the analysis of Laue spot positions provides the local deviatoric strain tensor. The hydrostatic part of the strain tensor may also be obtained, at the cost of a longer measuring time, by measuring the energy profiles of the Laue spots using a variable-energy monochromatic beam.
- Possibility to position and raster scan the sample with submicron accuracy.
- Possibility to measure the energy profiles of Laue spots in X-ray Laue microdiffraction



Sample area sketch showing the focusing KB mirrors, the detectors, and the sample translations.



View of the microdiffraction setup

Photograph of a Laue µ-X-ray diffraction system showing the different elements

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