ESRF	**UPGRADE PROGRAMME – PHASE I** **CONCEPTUAL DESIGN REPORT**

X-ray standing waves, photoelectron spectroscopy, and diffraction beamline	
Current designated sector:	Facility goes to:
ID32	ID32

1.1 ID CARD

The ID32 beamline at the ESRF utilises surface X-ray diffraction and X-ray spectroscopic techniques such as hard X-ray photoelectron spectroscopy in combination with X-ray standing waves for investigating the structure, as well as the chemical and electronic properties of surfaces and interfacial regions, of crystalline materials. Samples are studied in ultra high vacuum and under “real” conditions e.g. immersed in a gas atmosphere or in a liquid.

1.2 SCIENTIFIC CASE

The scientific programme at ID32 will be centred on the combination of X-ray structural tools (X-ray standing waves and X-ray diffraction (XSW and XRD, respectively)), with high resolution spectroscopy (X-ray photoelectron-, fluorescence-, and absorption-spectroscopy (XPS, XFS, XAS, respectively)) for the investigation of surfaces and (buried) interfaces. XSW measurements in combination with XPS, XFS, and XAS allow *absolute* element and chemical species specific structural investigations on the atomic scale (Zegenhagen, 1993). XRD becomes element specific, though less sensitive, when combined with XAS (DAFS measurements).

A new UHV system for hard X-ray photoelectron spectroscopy (HAXPES) is presently in the commissioning phase. HAXPES (Zegenhagen & Kunz, 2005) permits a larger information depth (>10 nm) and higher energy resolution (<50 meV) for electron spectroscopy. A new area of application for HAXPES will be catalysis and sensor technology. Using hard X-rays, the chemical (and electronic) specification of gas/solid interface reactions during gas exposure can be obtained. The high electron kinetic energy of up to 15 keV and small sample size will permit, in conjunction with suitable differential pumping, to investigate catalytic processes at gas pressures up to (and even above) 10 mbar. Furthermore, with a micron sized beam with a moderate divergence of about 1 mrad, XSW/HAXPES measurements are possible on very small crystals. Such a HAXPES catalysis system is proposed to be installed in a third experimental hutch, constructed in the area of the new experimental hall. Due to the large source distance, a nanometre-sized beam can

be achieved at a sample distance necessary for the catalysis system. Thus, chemical information can be obtained on typical nano-sized catalysts.
The concept of the optical layout of the ID32 beamline with a two-stage post-monochromator and CRL and FZP focusing optics is unique in allowing the properties of the X-ray beam to be tailored to the specific needs in surface and interface science (SIS) research. Presently, two experimental hutches are available. A third hutch (EH3), constructed at a source distance of about 110 metres from the source, and proper optics will allow either a 50 nanometre focus size for microscopy or about a micron focus size to be obtained with moderate divergence for local XSW measurements. Furthermore, the third hutch will allow beamtime to be used at 100% efficiency: time demanding preparation in the catalysis UHV system in EH3 can be carried out whilst performing XSW/XPS experiments in EH2 and the UHV system in EH2 can be accessed when XRD or XSW experiments are being carried out in EH1, where all preparatory work can be carried out during machine dedicated time.

The ID32 beamline offers world-wide unique facilities for studies of surfaces and interfaces using XR, XSW, and spectroscopic techniques. XSWs are produced by single crystals, mirror surfaces, multilayer, or thin films. The present instrumentation permits the use of a multitude of diffraction planes for element specific and chemical sensitive high resolution imaging using XRF on the kappa diffractometer in EH1. Recent examples are the localisation of Al in zeolite crystals (Bokhoven et al, 2008) and the determination of the site distribution of 5% Mn in a thin film of GaMnAs (Lee et al, 2009). With the ongoing construction of a UHV compatible high precision three-circle goniometer, this potential is presently extended to allow XSW imaging in combination with XPS/HAXPES in UHV.

The surface characterisation laboratory (SCL) and electrochemistry laboratory (ECL) allow well prepared and characterised samples to be used for X-ray studies by employing various portable chambers. Samples are studied in UHV and various environments. Notably solid/liquid interfaces are studied in situ with externally applied electrical potential. In this way, for example, the corrosion of a Cu_3Au alloy was studied with X-ray diffraction (Renner et al, 2006). The optical concept of the beamline features a high degree of flexibility with the energy resolution $\Delta E/E$ ranging from about 10^{-3} down to better than 10^{-6} if necessary. At present the beam size on the sample ranges from about a few square millimetres down to a few square micrometres. Using XSW and XPS, the focus of the user programme is on studying the structure and chemical properties of large organic molecules on metal surfaces. With XSW and XFS, there is, at present, some emphasis on studying the site distribution of the magnetic impurities in dilute magnetic semiconductors for spintronic applications. Furthermore, the structure, chemistry and (electronic) structure of complex oxide interfaces is investigated with the unique combination of XSW and XPS.

The new UHV chamber with a new photoelectron spectrometer will allow hard X-ray photoelectron spectroscopy (HAXPES) investigation with electron kinetic energies up to 15 keV and, once fully commissioned, with energy resolutions better than 50 meV. The high kinetic energy of the electrons gives access to interfaces buried deeper than 10 nanometres. The new manipulator, which is presently under construction, will allow XSW measurements using single crystal Bragg reflections at any angle, while the old XSW/XPS setup with a 15 year old Perkin-Elmer (PHI) analyser is limited to backscattering geometry, kinetic energies of 4.8 keV, and energy resolution >200 meV. However, this rugged, simple XSW/XPS setup is appreciated by users and shall be refurbished with a new electron analyser within the next three years.

1.3 PROJECT HISTORY

ID32 came into operation in 1995. In order to provide state-of-the-art instrumentation and excellent beam conditions to the XSW/spectroscopic and diffraction community, the beamline has gone through a major refurbishment programme, taking in account all of the recommendations of the beamline review committee in 2002. The construction and commissioning of a second optics and a second experimental hutch required a shutdown of the user operation of the beamline for four months in winter 2002/2003. The most recent major piece of equipment installed is a UHV chamber with a 15 keV PHOIBOS 225 hemispherical electron analyser in EH2. Construction of a novel three-circle UHV manipulator and design of a preparation chamber for this unique instrument is ongoing. Together with the instrumentation, the beamline optics is developing and its operation is continuously improving. The mission and ongoing development of the ID32 beamline was strongly endorsed by the beamline review panel in autumn 2008.

The idea of constructing a third experimental hutch at about 110 m from the source relates to the HXPM (Hard X-ray Photoelectron Microscope) CDR which is contained in Volume 2 of the Purple Book. A sample distance of about 110 m from the source will allow a demagnification of the source of a factor of 1000 even with a reasonable focal length of 10 centimetres. The small beam allows the X-ray beam to be concentrated on small grains or particles, important for catalytic reactions. A HAXPES system with differentially pumping stages will allow the chemical and electronic characterisation of catalytic reactions by HAXPES at pressures up to 10 mbar. This will yield unique, new information in catalysis research. A slightly increased focal size of about 1 micrometre allows small sample crystals to be studied with HAXPES whereas the beam divergence is sufficiently small to allow XSW measurements.

1.4 BASIC TECHNICAL CONSIDERATIONS

ID32 will continue in the future to offer a range of techniques, aimed at linking structure and chemical/electronic properties of surfaces and interfaces. These techniques have largely similar requirements regarding the optical layout of the beamline. The concept of the beamline is also meant to assure 100% efficient use of beamtime allowing to service and prepare sophisticated UHV equipment while taking beam in (one of) the upstream hutch(es).

Within the next two years, the present (major) developments at the beamline will be finished and the configuration of ID32 will be consolidated in view of the optical capabilities of the beamline, i.e. energy range and energy resolution, and the XSW capabilities, such as XSW Fourier analysis in the HAXPES UHV chamber in EH2 with the help of the new UHV three-circle manipulator. During the same period and the following one to two years, the control and operation of the optics and instrumentation of the beamline will be further developed to become increasingly user friendly, dependable, and stable. This whole development programme for the next four years or so will follow closely the recommendations of the beamline review committee from November 2008, as given below:

1) Complete the beamline control and diagnostics systems for stable and flexible operation of the monochromator, CRLs, mirrors, and post-monochromator optical components. This combined hardware - software solution would allow the beamline to be easily and quickly tuned to the desired energy, energy band-pass, angular divergence and focal point. This will make a rather complicated optical system user friendly and relieve the beamline staff from routine adjustments.
2) Fabricate special sets of channel-cut crystals for the post-monochromator to allow for controlled angular and energy width necessary for the XSW in both EH1 and the XSW and HAXPES in EH2. The requirement is for several pairs of asymmetric- symmetric 2-bounce crystals with a piezo tweaked weak-link separating the 1^{st} and 2^{nd} bounce.
3) Complete the construction and commission the internal UHV goniometer to make it possible to perform XSW in combination with HAXPES. This is the primary world-wide unique capability of this station that will be used for site-specific spectroscopy and chemically-sensitive atomic imaging.
4) Work with SPECS engineers to achieve the stated specifications of the HAXPES system. The system is presently at 160 meV and should be improved to achieve the design specification of ~10 meV. Cryostat cooling will need to be added to reduce thermal broadening in order to exploit the ultimate resolving power and also to reduce radiation damage to organic films and possibly oxides.
5) A side preparation chamber for the HAXPES system that will allow *in situ* preparation of atomically clean surfaces, characterisation and deposition without contamination of the very delicate HAXPES unit.
6) A multi-element silicon drift-diode array XRF detector system to meet the high count rate demand for the XSW measurements in EH1. This can be supplied and supported by the ESRF detector pool, as it will be needed for less than 50% of the beamtime.
7) A 2D pixel array for the SXRD measurements in EH1 can also be made available and supported by the detector pool.
8) Upgrade CRL focusing system in OH2 by changing from 0.8 mm to 3.0 mm aperture lenses, including an auto-lens changer.
9) A modified mini-kappa goniometer to mount on the large EH1 diffractometer for XSW measurements of small single crystals down to 50 microns in dimension. The smaller goniometer will have a smaller sphere of confusion necessary for keeping the micro focussed beam on the small crystal while rotating between different hkl reflections.

Once this ongoing programme for ID32 is finished and the operation of the beamline is consolidated, a third hutch shall be constructed for the installation of a new HAXPES catalysis UHV system. There are no particular risks with the foreseen development. Challenges are the minimal focus size (50 nanometres) and the maximum tolerable pressure for HAXPES catalysis experiments (10 mbar). A schematic drawing of the beamline is given below. The third hutch will allow preparatory work at the catalysis system to be carried out, while XSW/XPS experiments are performed in EH2, which in turn can be accessed when XSW/XRF or XRD experiments are conducted in EH1.

1.5 References

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