

Diamond Phase III Beamline Proposal 059- S

Versatile Soft X-ray Beamline at the Diamond Light Source

(VERSOX)

A proposal prepared for the SAC March 2011

Acknowledgements

This document was compiled by the members of the working group: Andrew Evans (chair), Georg Held, Sven Schroeder, Bruce Hamilton, Nigel Mason, Karen Wilson, Andreas Lang, Richard Smith, James O'Shea, Sarnjeet Dhesi, Hongchang Wang, Tien-Lin Lee and Federica Venturini with contributions from the VERSOX community, listed below with affiliation and principal science themes. The letters of support are listed in alphabetical order in the Appendix.

Name	Affiliation	Department	Science 1	Science 2
Attard, Gary	Cardiff University	Chemistry	CATAL	
Baddley, Christopher	St Andrews	Chemistry	CATAL	
Bennet, Roger	Reading University	Chemistry	CATAL	PHOTO
Bowker, Mike	Cardiff University	Chemistry	CATAL	
Cafolla, Tony	Dublin City University	Physics	PHOTO	ENVIR
Chao, Yimin	University of East Anglia	Chemistry	PHOTO	
Chass, Greg	Bangor University	Chemistry	CATAL	
Clifford, Charles	N.P.L.	Engineering	PHOTO	
Cookson, James	Johnson Matthey	Industry	CATAL	
Crossley, Alison	University of Oxford	Materials	CATAL	
Davies, Philip	Cardiff University	Chemistry	HERIT	CATAL
Dhanak, Vin	University of Liverpool	Physics	PHOTO	ENVIR
Downes, Sandra	University of Manchester	Materials	PHARM	
Dryfe, Robert	University of Manchester	Chemistry	PHARM	
Egdell, Russell	University of Oxford	Chemistry	PHOTO	
Ellis, Peter	Johnson Matthey	Industry	CATAL	
Evans, Andrew	Aberystwyth University	Mathematics & Physics	PHOTO	ENVIR
Fraser, Helen	University of Strathclyde	Physics	SPAC	
Freestone,	Cardiff University	Archaeology	HERIT	
Greaves, Neville	Aberystwyth University	Mathematics & Physics	CATAL	HERIT
Halsall, M	University of Manchester	PSI	PHOTO	
Hamilton, Bruce	University of Manchester	Electronic Engineering	PHOTO	
Held, Georg	Reading University	Chemistry	CATAL	
Hofmann, Stefan	University of Cambridge	Engineering	PHOTO	CATAL
Hughes, David	Qioptic Ltd	Industry	PHOTO	
Irvine, Stuart	Glyndwr University	Solar Energy	PHOTO	ENVIR
Jones, Robert	Nottingham University	Chemistry	PHOTO	CATAL
Kavanagh, Anne	AstraZeneca	Industry	PHARM	
Kirkby, Karen	University of Surrey	Engineering	PHOTO	
Lang, Andreas	University of Liverpool	Earth Sciences	ENVIR	
Langstaff, David	Aberystwyth University	Mathematics & Physics	PHOTO	
Lee, Adam	Cardiff University	Chemistry	CATAL	
Lindsay, Robert	University of Manchester	Materials	CATAL	
Maffeis, Thierry	Swansea University	Engineering	PHOTO	
Martineau, Philip	DTC Ltd	Industry	PHOTO	ENVIR
Mason, Nigel	Open University	Chemistry	SPAC	ENVIR
McConville, Chris	Warwick University	Physics	PHOTO	
McCoustra, Martin	Heriott Watt University	Chemistry	SPAC	
McGovern, Iggy	Trinity College Dublin	Physics	PHOTO	
McGrath, Ronan	University of Liverpool	Physics	PHOTO	
McGuinness, Cormac	Trinity College Dublin	Physics	PHOTO	
Moggridge, Geoff	University of Cambridge	Chemical Engineering	PHARM	
Moloney, Mark	University of Oxford	Chemistry	PHOTO	CATAL
Moriarty, Philip	Nottingham University	Physics	PHOTO	ENVIR
Murrer, Barry	Johnson Matthey	Industry	CATAL	
O'Donnell, Kevin	University of Strathclyde	Physics	PHOTO	
O'Shea, James	Nottingham University	Physics	PHOTO	ENVIR

Ormsby, Bronwyn	Tate Britain		HERIT	
Pantos, Emmanuel	STFC	Heritage	HERIT	
Papakonstantinou, Pagona	University of Ulster	Engineering	PHOTO	
Pfrang, Christian	Reading University	Chemistry	CATAL	
Poolton, Nigel	Aberystwyth University	Mathematics & Physics	ENVIR	PHOTO
Roberts, Kevin	University of Leeds	Chemical Engineering	PHARM	
Schofield, Paul	Natural History Museum	Mineralogy	HERIT	ENVIR
Schroeder, Sven	University of Manchester	Chemical Engineering	CATAL	
Shard, Alex	N.P.L.	Engineering	PHOTO	
Siller, Lidija	University of Newcastle	Chemical Engineering	PHARM	CATAL
Smith, Richard	Johnson Matthey	Industry	CATAL	
Strilc, Matjia	University College London	Heritage	HERIT	
Teng, Vincent	Swansea University	Engineering	PHOTO	
Thomas, Andrew	University of Manchester	Physics	PHOTO	
Thornton, Geoff	University College London	Chemistry	CATAL	
Tildesley, Dominic	Unilever	Industry	PHARM	
Twitchen, Daniel	E6 Ltd	Industry	PHOTO	
Watson, David	Reading University	Chemistry	CATAL	
Wess, Tim	Cardiff University	Optometry	HERIT	
Wilson, Karen	Cardiff University	Chemistry	HERIT	CATAL
Withers, Philip	University of Manchester	Materials	CATAL	
Woodruff, Phil	Warwick University	Physics	PHOTO	
Yacoot, Andrew	N.P.L.	Engineering	PHOTO	

VERSATILE SOFT X-RAY BEAMLINE

1 Summary

The driving force behind the VERSOX beamline proposal is the new and diverse range of science that would flow from the combination of beamline and end-stations. The beamline design will make a cost effective use of a bending magnet, and the high brilliance and focussing properties of the Diamond light source will provide a beam quality that will easily serve a whole range of fundamental and applied science.

The VERSOX configuration will provide a unique combination of synchrotron radiation probes; it will be a distinctive facility both for the UK community and on the world stage. Our aspiration is that VERSOX will not only provide a platform for excellent research, but that the concentration of complementary spectroscopic and imaging modes in a single facility will help to connect synchrotron radiation science more closely to the great body of materials research taking place in academic and industrial labs. The soft x-ray photon energy range proposed is ideally tuned to the study of elements in the first-row of the Periodic Table, including carbon, nitrogen and oxygen – the building blocks of not only bio-pharmaceutical molecules but also of many semiconductors, polymers, ceramics, pigments, oxides, minerals and planetary atmospheres. Soft x-rays also have great sensitivity to surface (or equally importantly, near-surface) chemistry and electronic structure and are ideal probes for molecules or solids which are organised on the nano and meso scales; it is the synthesis and organisation of such systems which will drive new technologies to meet the pressing challenges posed by energy supply, information technology, healthcare and climate change.

The letters of support which have informed the detail of this case reflect these wide range of research interests that would populate the beamline initially; we are confident though that the versatile capability of VERSOX will rapidly generate important new collaborations.

The VERSOX beamline will have the capacity to switch X-ray photons between two end-stations; the combination of measurement probes across the two end-stations does not exist on any other single beamline worldwide. One end-station is designed for atmospheric or solution based (i.e. true environmental) measurement using photoelectron spectroscopy. This will allow the study of catalytic processes under realistic conditions. Equally environmental conditions are vital for the study of pharmaceutical molecular systems which need to be understood and characterised under the normal atmospheric pressure and temperature conditions for which they are designed to operate. These areas of work underpin two sectors of huge economic importance to the UK. This kind of end-station exists in Berlin and at Berkley; similar atmospheric pressure XPS facility is also planned at other synchrotrons. The other end-chamber is designed for vacuum experiments that make maximum use of photon and electron flux; it will have facilities for electron spectroscopy of surface chemical and electronic structure; optical detection of x-ray matter interactions at low temperature for chemical imaging of surface and sub-surface structure; scattered x-ray detection for more bulk sensitivity; scanned probe imaging and spectroscopy during x-ray excitation (normal mode and tip detection of x-ray interactions), time resolved spectroscopy for in-situ thin film growth and surface processing. UHV end-stations, equipped for optical detection, exist at the Canadian Light Source and Tskuba, and one is planned for Lund. End stations with scanning probe microscopy are becoming more common, but incorporation of scanning probe measurements directly into the x-ray beam exist only at the ERSRF and SPRing8.

2 Science Case

2.1 Introduction

The research enabled by the VERSOX beamline will be multidisciplinary bringing together a community that will engage with research focused on the developing energy sector, climate change, the environment, medicine and heritage. The science case is organised in six research themes.

- Heterogeneous Catalysis (CATAL)
- Pharmaceuticals and Biomaterials (PHARM)
- Photonic and Electronic Materials (PHOTO)
- Environment and Atmospheric Sciences (ENVIR)
- Space Science (SPACE)
- Heritage Science (HERIT)

2.2 Heterogeneous Catalysis

Surface science experiments in general and soft X-ray techniques in particular have been extremely successful in elucidating reaction mechanisms in heterogeneous gas-phase catalysis (see e.g. [1] and references therein). However, the behaviour of catalysts at high pressures, under which they are operated in industrial processes (typically 1-50 bar), may be different from that under the ultrahigh vacuum (UHV) conditions in which they are traditionally studied. Even seemingly well-understood reaction mechanisms such as that of CO oxidation on transition metal surfaces have been scrutinised recently after highly active surface oxide phases have been discovered which only exist at higher pressures [2,3]. Slow processes, such as oxidation or carbidisation, can dramatically affect the nature and, hence, the catalytic activity of the surface involved in the steady-state reaction [4,5,6]. Although the pressure range covered by the VERSOX Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) endstation (section 4) is still lower than that of industrial processes, this is only by 1-2 orders of magnitude, whereas UHV experiments differ from realistic pressure conditions by at least a factor 10^{10} . Importantly, the 10-100 mbar pressure regime, which will be accessible with the proposed instrument, ensures laminar gas-flow conditions – as opposed to molecular flow at lower pressure – and allows reaction temperatures similar to those in industrial processes. This will enable a major step up towards bridging the “pressure gap” between fundamental catalysis research and industrial processes within the catalysis and energy sector and is critical for the design and development of next-generation clean and sustainable catalytic technologies.

Notably in heterogeneous catalysis soft X-ray techniques can elucidate surface chemical processes in-situ, via time-resolved (on the sub-second timescale) X-ray photoelectron spectroscopy (XPS). Many groups world-wide have exploited time-resolved synchrotron XPS to gain valuable insight into the operation of commercial catalysts for pollution abatement and selective hydrocarbon oxidation/hydrogenation [1]. However, the constraint of ultra-high vacuum operation has greatly restricted the phenomena amenable to study. Hydrogenation reactions, in particular, usually require pressures at least in the mbar range. Currently there are only two synchrotron facilities with soft X-ray beamlines (BESSY and the ALS) capable of performing ambient/high-pressure measurements in the range offered by VERSOX. Both are heavily over-subscribed by the international community with a large contingent of UK researchers. The ability to determine molecular orientation of adsorbed reactants, intermediates and products via high-resolution X-ray Absorption Spectroscopy in particular focusing on Near-Edge Fine Structure (NEXAFS) under reaction conditions will provide additional invaluable insight into the structural constraints and steric effects of catalytic reactions.

The other VERSOX end-station, offering laterally-resolved XPS/XAS, will also accelerate the ability to screen combinatorial arrays of multi-metallic and mixed metal oxide libraries. While such libraries can enable rapid optimisation of complex catalyst formulations, there are few methods to efficiently screen the surface chemistry of individual library members necessary to evaluate e.g. resistance to carbon deposition. Spatially-resolved spectroscopy at VERSOX would thus provide a

unique opportunity to quickly identify and quantify the nature of such deposits, and thus develop core science discoveries into patented technologies for commercialisation.

2.2.1 Surface alloying and segregation

Within bimetallic single crystal and nanoparticulate catalysts the surface composition can change when they are exposed to reactive environments (temperature, ambient gas pressure). This phenomenon is driven by the change in the gas phase chemical potential and can, therefore only be studied under ambient conditions.

2.2.2 Catalytic poisoning/promotion

Phenomena such as sulfiding/sulfation and oxidation/reduction can be studied under conditions of steady-state turnover. Processes affected are e.g. selective alcohol oxidation, trans-esterification of algal/plant oils to biodiesel, and automotive pollution abatement over metal and metal oxide single crystals and nanoparticles. For example, it is thought that, during selective oxidation, the surface (and bulk) of Pd nanoparticles is carbided and therefore shows relatively low reactivity. A major effect of alloying with Au may be to stop this process occurring [7], leaving the metal available for reaction. Recently, Schlögl et al. could show, using the high-pressure XPS instrument at BESSY, that dissolved carbon leads to dramatic changes in the selectivity of a Pd model catalyst in ethane synthesis [4].

2.2.3 Direct CO₂ photoreduction

The direct reduction of CO₂ to fuel over semiconductor nanoparticles is at the very heart of green technologies. The sticking probability of CO₂ at higher temperatures is too low to get sufficient signal under UHV conditions. Therefore the relevant catalyst systems can only be studied using ambient-pressure X-ray photoelectron spectroscopy.

2.2.4 Oxide catalysis

In many cases oxide surfaces are superior to metal catalysts in terms of selective oxidation. The adsorption rates on oxide surfaces are, however, often relatively low compared with metals, due to their low surface energy and lack of electron density at the Fermi level. Thus elevated pressures are necessary for studying adsorption and surface reactivity. The use of high-pressure XPS it will enable the simultaneous identification of adsorbate chemical states, the active oxygen species and metal oxidation states, and surface segregation (in the case of mixed oxides). Amongst many others, one particularly interesting example is the behaviour of ferric molybdate, which is the industrial catalyst of choice for the selective oxidation of methanol to formaldehyde [8]. It is a mixed oxide with the cations normally in the highest oxidation state. The reactivity of this system is only partly understood, in particular the nature of the active site during the reaction eludes us. Another, famous, example is TiO₂, with its excellent photocatalytic properties [9]. Despite a massive body of work under UHV conditions, the behaviour and electronics of this material under reaction conditions is barely studied at a fundamental level.

2.2.5 Liquid phase heterogeneous catalysis, electrochemical and biochemical interfaces

Water is the “matrix of life”. Therefore practically all reactions involving bio-molecules or their building blocks take place in aqueous solution or involve other solvents. Solution-catalyst interfaces are far less well understood than the catalyst interfaces for gas-phase reactions because both solvent and reactants interact at the solid surface and make the adsorption complex more complicated in many ways. For example, the interaction of reactants with each other and/or the catalyst surface will depend on whether they are embedded in a hydrogen-bonded solvation shell or clathrate of solvent molecules. The application of conventional surface science techniques is very limited in this context as the coadsorption of the relevant surface species cannot be modelled under reaction conditions in UHV, where water only forms stable condensed layers below 150K. At these temperatures the kinetic barriers are too high for the key reaction steps, the exchange of molecules between surface layer and solution and chemical reactions between the surface species. Reactions in aqueous solution require temperatures near 300K where the vapour pressure is in the mbar range. First

experiments using the ambient-pressure beamline at ALS showed that even the adsorption behaviour of pure water changes dramatically under ambient conditions compared to UHV [10]. Even more dramatic effects are found for organic adsorbates in the presence of water [11]. Clearly, the presence of solvents has a profound influence on any surface reaction, therefore relevant reaction mechanisms can only be found if bio-related reactants are studied under appropriate ambient pressure conditions.

By balancing the vapour pressure and temperature it is possible to keep thin films (sub-monolayer to several layers) of water or other solvents on a catalyst surface. This approach, in combination with ambient-pressure photoemission provides a new way to study the chemical composition and electronic structures of solid-liquid interfaces and, thus, opens access to a number of technologically important material systems which could not be studied by soft X-ray spectroscopies at all so far. These include electrochemical and biological interfaces and liquid-phase heterogeneous catalysts. Using VERSOX, adsorption, exchange, corrosion and diffusion processes near such solid surfaces can be studied at realistic reaction temperatures. Fundamental studies of new technologies, such as biodiesel production and the synthesis and/or enantioselection of fine chemical and pharmaceuticals, will benefit immensely from permitting the investigation of key chemical processes such as competitive solvent adsorption, gas-liquid phase reactions and catalytic deactivation. Many of the most important commercial chemical syntheses (e.g. cross-couplings to produce liquid-crystals and medicinal drugs) involve volatile organics with vapour pressures between 10-100 mbar; VERSOX offers an unprecedented opportunity to understand the solid catalyst-liquid interface, and thereby increase reaction efficiency.

In addition to chemical research, medical research and new energy technologies will also benefit from knowledge created by the proposed beamline. For example, VERSOX will enable studies of

- adsorption and surface-reactions of bio-molecules in their native aqueous environment, relating to bio-mineralisation, bio-compatibility of implants, and drug discovery;
- key processes at solid-solution interfaces such as the charge-transfer interaction between the adsorbed dye and the electrolyte in a dye-sensitised solar cell;
- photocatalytic splitting of water using organometallic dye complexes on oxide surfaces;
- adsorption, dissociation and recombination processes on fuel cell electrodes.

- [1] A. F. Lee, V. Prabhakaran and K. Wilson, *Chem. Commun.*, 2010, 46, 3827–3842.
[2] H. Over et al, *Science*, 2000, 287, 1474 – 1476.
[3] B. L. M. Hendriksen and J. W. M. Frenken, *Phys. Rev. Lett.*, 2002, 89, 046101.
[4] D. Teschner et al, *Science*, 2008, 320, 86 – 89.
[6] G. A. Somorjai and C. Aliaga, *Langmuir*, 2010, 26, 16190 – 16203.
[5] M. Salmeron and R. Schlögl, *Surface Science Reports*, 2008, 63, 169–199.
[7] M. Bowker and C. Morgan, *Catalysis Letts.*, 98, (2004) 67.
[8] M. Bowker et al., *Top Catal* 48 (2008) 158.
[9] U. Diebold, *Surface Science Reports*, 48 (2003) 53-229.
[10] K. Andersson, et al., *J. Phys. Chem C*. 111, 14493 (2007).
[11] A. Shavorskiy, F. Aksoy, M. E. Grass, Z. Liu, H. Bluhm, and G. Held, *J. Am. Chem. Soc.* accepted.

2.3 Pharmaceuticals and Biomaterials

In-situ characterisation of soft matter systems in environmental cells by synchrotron X-ray scattering in the hard and medium X-ray ranges are already well-established techniques. In contrast, X-ray spectroscopy in the soft X-ray region (i.e., at photon energies below 2 keV) has been confined to studies under high vacuum conditions, despite the fact that XPS and XAS have for some time been considered to be part of the core instrumentarium for studies of biomaterials and interfaces in medical research [1]. In-situ studies under practical conditions in the soft X-ray region have been scarce, even though the important K-edges of the ‘soft matter elements’ of the second period (especially C, N, O, F) but also third period elements such as Na, Mg, Al, Si, S, P lie in this energy range. The pioneering NEXAFS and XPS work on liquids at BESSY in the last few years [2-8] has shown how structural studies of solution species by soft XAS can be performed with windowed flow cell systems, while laminar-flow liquid jet systems permit XPS, XAS and XES studies. The ability to probe phases containing these elements *in situ* and/or *operando* as liquids or

in environmental cells under control of environmental conditions is extremely beneficial in the context of applications of contemporary interest, including biomolecular and pharmaceutical systems, organic and organometallic solution state chemistry and multicomponent products and formulations. The high pressure branch of VERSOX seeks to establish such a facility, world-wide for the first time for routine XAS measurements (ultimately permitting service measurements) while the main scanned microfocus XPS/XAS facility will provide more incisive insight into the physical properties of those systems for which a deep understanding is desired.

2.3.1 H-Bonding and Proton Transfer in the Organic Solid State

Recent work with XPS has indicated that core level spectroscopy of organic materials provides remarkably detailed and clear-cut insight into the composition and local interactions in the organic solid state, complementing and enhancing structural information that is traditionally provided through X-ray crystallography and solid-state NMR measurements [9-11]. These studies have opened up an avenue towards reliably detecting and assessing the influence of H-bonding and proton transfer on structure formation in the organic solid state in considerably more detail than is hitherto possible in the absence of neutron scattering analysis and solid state NMR measurements.

2.3.2 Crystal Growth and Nucleation

The process of phase transformation and the resulting creation of crystalline materials from liquid phase precursors are central to the *science* and *process engineering* of materials in their broadest sense. The classic kinetic models of a first order phase transition involving crystal nucleation assume spontaneous formation of molecular clusters (embryos) having a range of sizes between 1 and 10 nm whose viability is size-dependent. The concept of a critical size at which the gain in bulk free energy is balanced by the penalty of the surface free energy is well known as a model that describes the major macroscopic kinetic features of the nucleation process. In the context of current concepts of crystallisation as a supra-molecular assembly process this visualisation of the nucleation event is limited and void of structural considerations. Thus, the nature and importance of intermolecular interactions within supersaturated solutions as well as the existence and structural nature of pre-crystalline transition states do not form part of conventional considerations of nucleation theory. In the broad context of materials chemistry and especially in the field of crystal engineering, the ability to control the molecular assembly process from solution will be crucial in developing the molecular-scale process design capabilities needed for the future. Exemplars of this, as highlighted by the setting up of a new ‘Directed Assembly of Extended Structures with Targeted Properties’ (DAESTP) network as part of the Chemical Sciences and Engineering Grand Challenges, include design and control of the physico-chemical properties of condensed materials such as oily dispersions, liquid crystals, amorphous, nano-crystalline or micro-crystalline states. Elucidating the fundamental physics and chemistry that govern the structure of the nucleation transition state remains one of the truly unresolved ‘grand challenges’ of the physical sciences. The spectroscopies provided by VERSOX, would provide, for the first time in the UK, an incisive XAS/XPS measurement capability for following the chemical and physical state of molecules across short-range molecular interaction scales. Combined with complementary longer-range X-ray scattering measurements it will facilitate following the structural evolution from individual molecules in solution through molecular clusters to embryonic crystals *in situ*. This approach to studying nucleation phenomena is the subject of a new Manchester/Leeds EPSRC critical mass grant involving BESSY and the NSLS. The arrival of VERSOX as a UK facility for continuing such work in the future would therefore be extremely timely.

2.3.3 Multicomponent Systems / Complex Soft Matter

The ambient pressure environment and liquid handling capability of VERSOX provides a route to studying soft matter and multicomponent systems of technological relevance. The element specificity of soft X-ray techniques will permit structural characterisation in complex multicomponent systems when one element is associated with only a single component. An example would be studying the salvation structure around surfactant head groups and the organophosphorus

species used as capping agents and phase transfer ligands in liquid-liquid extractions and reactions. Dryfe and Schroeder are currently pioneering this approach in an NSF/EPSCRC-sponsored programme of liquid-liquid interface investigations using hard X-ray absorption spectroscopy [12]. Liquid-liquid and liquid-polymer interfaces are also the basis for biointerfaces and many consumer products in which the microstructure determines, usually in a complex fashion, the macroscopic properties. The local structure provided by core level spectroscopies complements the long-range information accessible through established X-ray scattering techniques.

- [1] D.G. Castner and B.D. Ratner, *Surf. Sci.* 2002, 500, 28-60
- [2] B. Winter and M. Faubel, *Chem. Rev.* 2006, 106, 1176-1211
- [3] E.F. Aziz et al, *Nature* 2008, 455, 89-91
- [4] E.F. Aziz, et al, *J. Phys. Chem. B* 2008, 112, 12567-12570
- [5] D. Nolting et al, *J. Am. Chem. Soc.* 2007, 129, 14068-14073
- [6] J. Grasjo et al, *J. Phys. Chem. B* 2009, 113, 8201-8205
- [7] E.F. Aziz et al, *Nature Chemistry* 2010, 2, 853-857
- [8] Ph. Wernet et al, *Science* 2004, 304, 995-999
- [9] J.S. Stevens et al, *Cryst. Growth Des.* 2010, 10, 1435-1442
- [10] J.S. Stevens et al, *J. Pharm. Sci.* 2010, 11, 4453-4457
- [11] J.S. Stevens et al, *J. Phys. Chem. B* 2010, 114, 13961-13969
- [12] K. Luo et al, *Chem. Mater.* 2009, 21, 4172-4183

2.4 Photonic and Electronic Materials

The development of new photonic and electronic technologies depends on understanding and controlling the electronic structure of materials. Electronics technology currently accounts for over 70% world GDP and is fuelled by a wide ranging fundamental science base. Continued growth of this sector is vital for the future in energy, health and security. As the technology becomes more sophisticated, the underpinning materials become more complex: quantum confinement of electrons and chemical inhomogeneity are used to gain new functionality. Discovering and understanding new materials requires the ability to probe and to correlate electronic and chemical properties on very local scales. The next two decades will see great changes in these technologies as new solutions will be needed to maintain data processing, transfer and storage and to operate at lower power consumption. In photonics, solid-state lighting will transform the urban environment and greatly reduce carbon emission and new materials for photovoltaic devices giving significantly higher efficiency will be a major world focus.

Synchrotron radiation, and in particular soft x-rays directly probe electronic states and chemical bonding enabling local structure to be directly correlated with electronic and photonic performance. The VERSOX facility will directly permit such measurements; moreover it will enable nanoscale size and shape to be factored into the understanding of electronic properties, it will represent a unique advanced tool for future materials development. High detection efficiency and precise lateral resolution will enable the study of structure-function relationships in new materials with demanding nanostructured geometries and will enable real-time monitoring of processing steps such as functionalisation and fabrication.

2.4.1 Organic Electronics and Sensors

Organic semiconductors are replacing their inorganic counterparts in an increasing number of applications (e.g. displays, photovoltaics (PV), sensors) but there remain challenges in optimising fundamental parameters such as current transport and light absorption/emission and in improving the lifetime and reliability. This is being realised using new molecules and new architectures, in particular using composites and blends [1]. There is also a growing activity in the fabrication of new structures using nanostructured organic and inorganic templates [2]. VERSOX will be able to apply parallel spectroscopies optimised for determining the chemical state of elements such as C, N and O and which directly reveals the nature and density of both occupied and unoccupied states that are responsible for light absorption/emission and charge transport.

2.4.1.1 Organic monolayers

The ability to fabricate and probe single molecular layers is important for understanding the fundamental interactions that underpin applications such as precursor decomposition at the earliest stages of thin film growth [3] and charge transfer in PV cells [4]. The structure of the substrate surface can also be used as a template to form new organic structures that do not form naturally [2]. Soft x-ray spectroscopies at VERSOX will be applied to model systems that isolate key molecule-substrate interactions, as demonstrated for example in the adsorption of thiol molecules to metal surfaces [5] and fullerene adsorption on semiconductor surfaces [6]. VERSOX has the sensitivity to monitor more complex systems involving new substrate and molecular design in particular using nanostructured and functionalised templates such as self-organised nano-particles, graphene and quasicrystals for the adsorption of a wide range of molecules that are not limited to simple vacuum-depositable films. A further advance is the ability to monitor changes in adsorption, self-organisation and templating as a function of coverage, dosing and temperature.

2.4.1.2 Organic films and blends

Soft X-ray methods will also be applied to the formation of organic thin films and blends to directly measure chemical bonding and energy band alignment at key interfaces. VERSOX will remove experimental constraints such as long data collection time and ex-situ fabrication to enable entire device structures to be measured, vastly improving throughput and exploration of parameter space. It will also enable organic blends (e.g. small molecule/fullerene, polymer/fullerene and polymer/nanoparticle) to be measured as a function of growth conditions and temperature.

2.4.1.3 Transparent conductors

In many photonic devices, the performance of the transparent electrode is a limiting parameter and there is a drive to find alternatives to indium tin oxide (ITO) as the world supply of indium becomes an increasing concern. Transparent semiconductors are also being developed for UV photonics using materials such as oxides, nitrides and diamond. Parallel probes of light emission/absorption and local chemical structure provide essential tools in this quest, especially in relation to impurity or defect states in the bulk of new wide-gap materials.

2.4.1.4 Oxides

Oxides are used as transparent conducting electrodes (TCO) in most PV and display technologies and also as active charge/light generation materials in applications such as dye-sensitised solar cells (DSSC). Such devices are often limited by interface issues such as the nucleation of thin PV materials on TCOs during growth and charge transfer across these boundaries. The exploitation of semiconducting oxides and in developing new TCOs require improved understanding of growth and on the interplay between light absorption and conductivity. Soft x-ray methods can for example determine the initial surface reactions during growth [3], the interface energetics at oxide-thin film interfaces [7] and have led to a new appreciation of the optical and transport gap of ITO [8]. They have also elucidated the timescale for charge transfer in TiO₂/dye interfaces crucial to the operation of DSSCs [4]. The combined VERSOX techniques measuring local bonding, electronic structure, charge transfer and luminescence will be applied to oxide fabrication, surface processing and thin film growth.

2.4.1.5 Diamond

Synthetic diamond, as a high quality electronic material and as crystalline nanoparticles, is opening up new applications in electronics and the bio-sciences that can operate in environments where Si devices cannot (e.g high temperature, in-vivo). The diamond surface strongly influences such applications; for example surface conductivity in undoped diamond can be controlled by transfer doping, elucidated using photoemission experiments [9]. Photoemission has also been applied in real-time to demonstrate correlations between conductivity and bonding at diamond interfaces at high temperature [10]. C 1s core level spectra were measured in 1s by parallel and direct electron counting using a laboratory x-ray source; using soft x-rays, this is reduced to 25 ms. VERSOX

researchers will apply parallel and in-situ soft x-ray methods to probe interfaces between diamond, nanodiamond and organic molecules for applications in electronics and the bio-sciences.

2.4.1.6 Graphene

Graphene is increasingly becoming available in larger areas by methods such as the exfoliation technique developed in the UK, growth from the gas phase using and growth on solid surfaces. Each of these methods are used by VERSOX researchers to understand its growth and modification during for example oxidation and heating for fuel cell application [11]. Graphene also has considerable potential as a transparent conducting substrate for PV applications. Graphene's optical transparency derives from its reduced dimension in the absorption direction but retains high conductivity in the growth plane. The VERSOX combination of optical and electron detection will probe both light absorption/emission and electronic structure during processing of graphene films and adsorbate interactions on these surfaces [12].

2.4.2 Low-dimensional materials

Inorganic nanoparticles (clusters quantum dots etc.) offer new opportunities for engineering electronic and photonic materials. The impact of spatial confinement on the quantum scale can hugely modify behaviour, switching on light emission, modifying density of states functions, producing Coulomb blockade. The fact that such functional properties are size dependent and, in principle, controllable makes them central to the quest for new materials systems. There are many application for these quasi zero dimensional solids: medical sensors, quantum computing elements, photovoltaic devices, displays, and catalysts. Many nanostructures are also light emitters through band-gap or defect processes. Materials systems of interest include metals, silicon, silicon dioxide, diamond, compound semiconductors, oxides and nitrides. The surfaces of nanoparticles can be as influential as the bulk in determining their properties; in fact the majority of atoms in a given nanoparticle may reside on the surface or at the interface with a matrix material For example, surface states can either quench or produce luminescence in excited nanoparticles and the surface functionalisation is a crucial design parameter to ensure correct bonding and charge exchange with the surrounding matrix. Soft x-ray methods are particularly well-suited due to their intrinsic depth sensitivity and selectivity especially where complementary spectroscopic probes are collocated [13,14], SPM is of course a key tool for the characterisation of individual nanostructures and combined with X-ray excitation nanoscale imaging can be extended to the nanoscale [15].

- [1] Y. Kim et al, Nat Mater, 2006, 5, 197
- [2] M. C. O'Sullivan et al Nature, 2011, 469, 72–75
- [3] R.A. Bennett et al, Phys Rev Lett, 2007, 98 056102
- [4] L. C. Mayor et al, J Chem Phys, 2008, 129, 114701
- [5] A Chaudhuri et al, Phys Rev Lett, 2009, 102 126101
- [6] P. J. Moriarty, Surf. Sci. Rep, 2010, 65, 175
- [7] T.D. Veal et al Appl. Phys. Lett, 2008, 93 202108
- [8] A Walsh et al, Phys Rev Lett, 2009, 100 167402
- [9] L. Ristein Science, 2006, 313 1057-8
- [10] D.A. Evans et al, Appl Phys Lett , 2007, 91 132114
- [11] N. Shang et al, J Phys Chem C, 2010, 114 (35)
- [12] M Halsall et al, Science, 2009, 323 ,613,
- [13] B.Hamilton et al, Nature, 1998, 343, 443
- [14] K.P. O'Donnel et al, Phys.Rev B, 2010, 81, 08529
- [15] S. Dhesi et al, Appl Phys Lett, 2009, 96, 093101

2.5 Energy and Environment

Combining materials chemistry, physics, and biology in multidisciplinary combinations offers the most effective way of meeting the challenges presented by climate change, environmental protection and the emergent demands of the low carbon economy. The agenda for Energy and the Environment is demanding new and improved catalysts (section 2.2), more efficient harvesting of light energy (section 2.4), efficient energy storage in batteries and fuel cells, and a better

understanding of the fundamental processes that take place in the Earth, in the atmosphere and in space (section 2.5).

2.5.1 Environment and Atmospheric science

Environmental samples typically have a high degree of elemental and chemical heterogeneity in their composition that is closely related to environmental chemical speciation and mobility as well as the potential for incorporating pollutants and contaminants from their physical environment. Characterization of these heterogeneities is of primary importance in the area of environmental science, particularly in the new interdisciplinary area of environmental science christened molecular environmental science (MES) which studies chemical, biological, and geological processes occurring at environmentally relevant interfaces. Thus, from the early stage of MES, synchrotron-based spectroscopy has been recognized as an important analytical tool with several beamlines being available in major synchrotron facilities in the United States (e.g., SSRL, ALS, APS, NSLS). The VERSOX beamline will provide an equivalent soft x-ray facility for environmental scientists in the UK requiring access to x-ray photoelectron spectroscopy (XPS), X-ray electron, fluorescent and luminescence absorption spectroscopy (NEXAFS, FY-XAS and LY-XAS).

2.5.1.1 Particulate Matter

Identification of source specific signatures is of utmost importance for subsequent source attribution and apportionment. Signatures are not easy to obtain for PM. Classification typically exists in terms of elemental and organic carbon only: EC and OC. This distinction is too primitive for source apportionment. Soft X-ray techniques such as C(1s) NEXAFS spectroscopy may be developed for the characterization and molecular speciation of carbonaceous PM, For example distinction between diesel exhaust and wood smoke is possible since there is an absence of graphitic structures in woodsmoke while graphitization of diesel soot can strongly depend on engine operation conditions and fuel doping [1]

Another important environmental issue related to carbonaceous materials is their ability to absorb (often toxic) hydrophobic organic compounds (HOCs), such as PCBs (polychlorinated biphenyls) and PAHs (polycyclic aromatic hydrocarbons) in soils and sediments and its relationship with its chemical characteristics [2]. XPS, NEXAFS, FY-XAS and LY-XAS may all be used to explore the uptake of such compounds which is an essential pre-requisite for study of toxicology of such PM for example Cl L3-edge NEXAFS spectra have shown that there is a positive correlation between local chemical properties of carbonaceous PMs and their PCB sorption properties [3].

In many cases environmental samples are extracted under hydrous or wet conditions and typically need in situ characterization methods. VERSOX's ambient pressure end station will make it possible to conduct such studies in situ upon directly collected field samples. For example the interactions of soils and natural colloids under wet and hydrous conditions may be explored using VERSOX, knowledge that is essential for understanding how pollutants are transported through ground water.

2.5.1.2 Aerosols

The role of atmospheric aerosols is one of the largest uncertainties in assessing the anthropogenic contributions to radiative forcing and climate change. Studies of chemical properties of the atmospheric aerosol is therefore central to ongoing climate research. Much of the aerosol is of a biogenic and other natural origin (e.g. seaspray) and is hygroscopic such that chemical and physical properties are rapidly changed upon uptake of water. Such phase changes in atmospheric aerosols have recently been recognized to be of key importance [4] but they are still very poorly understood. The atmospheric pressure end station of VERSOX will provide a unique facility for study of aerosol systems of atmospheric importance, in particular since it will allow investigations at pressures one order of magnitude above those accessible elsewhere. Specifically oxidation-induced changes in the viscosity and phase of a range of liquid and solid aerosols may be explored to improve the understanding of chemical and physical ageing processes of atmospheric aerosols. VERSOX may

also be used in investigations of the behaviour of monomolecular organic layers covering such aerosols. XPS, NEXAFS, FY-XAS and LY-XAS may all be used to explore such phenomena.

Furthermore the construction of a controlled humidity chamber to allow for experiments on solid-liquid/humid interfaces over the terrestrial atmosphere temperature range between -50° C and 50°C and the development of liquid and droplet jets will provide an ideal set up for experiments related to atmospheric chemistry.

- [1] A Braun (2005) *J. Env. Monitoring* **7**, 1059-1065; A Braun et al, (2007) *Environ. Sci. Technol* **41**, 173-178.
- [2] R.G. Luthy et al (1997) *Environ. Sci. Technol.*, **31**, 3341–3347
- [3] T.H. Yoon, et al (2006) *Environ. Sci. Technol.*, **40**, 5923–5929.
- [4] Virtanen et al., (2010) *Nature*

2.5.2 Space Science

Astronomy is the oldest of the sciences, and it has received a spectacular boost in the last sixty years from observations outside the original optical waveband. The Universe which has been revealed continues to inspire deep questions regarding our origins, to which we have only partial answers. Current questions include: Where do planets come from? How did life originate? These are not purely philosophical questions, but issues that can be addressed by modern science.

2.5.2.1 Earth and Planets

Planetary exploration missions are driving a need to better understand the local geology and atmospheres in comparison to terrestrial counterparts. The associated materials challenges are working with rare, small volume and spatially heterogeneous systems that require non-invasive and efficient probes. The new facility will, for example, help identify electron-hole recombination at defects in minerals and artificial materials using micro-imaging luminescence and XAS. Such experiments will provide the correlation between local chemistry and electronic structure of defects, revealing their origin and fluorescence mechanisms. This information is essential for improved environmental and personal dosimetry; it will also aid the analysis of the elemental abundances of planetary surfaces using X-ray techniques. Similar techniques will also be used to better understand charge recombination pathways in minerals from the Earth's surface to improve Geological dating techniques – essential for better understanding past climate change, as well as human evolution and dispersal.

2.5.2.2 Interstellar space

Galactic gas exists in several phases, from hot collisionally ionised plasma to the dense, cold molecular clouds from which stars form. Numerous physical and chemical processes control the matter cycle of the Galaxy from interstellar gas to stars and back again to gas. Spectroscopy is a key tool in modern astronomy, revealing the Universe at a multitude of wavelengths. To understand what we see, we must complement our observations with laboratory studies. The capabilities of the VERSOX beamline will permit us unrivalled access across the soft X-ray spectrum for such laboratory studies providing a focus for laboratory studies that will help to unravel the details of astrochemistry and astrobiology, including the origins of life.

Chemistry plays a key role in the cycle of matter through the Universe [1]. Understanding the formation of molecules in the interstellar medium is a key question facing the astronomy and astrophysics communities. In the gas phase, the pathways from atoms and atomic ions to molecules and molecular ions are reasonably well mapped out [2,3]. However, simulations highlight a limitation of gas phase only models in that they fail to accurately predict the observed concentrations of many simple gaseous chemical species, including molecular hydrogen (H₂). Astronomers are now convinced therefore that the contribution from gas phase chemistry must be complemented by chemistry occurring on the surfaces of the dust grains that make up around 1% of the mass of a typical dense cloud [4,5]. Surface science has the potential to contribute significantly to our understanding of the gas-grain interaction [6] with experiments aimed at probing the

formation of molecules such as H₂, the desorption of icy grain mantles by heating and other energy sources, and the processing of icy mantles into pre-biotic materials. Although there is already much activity in astronomical gas-grain interaction, with UK-based groups often leading the way, key areas remain to be visited. The capabilities of the VERSOX beamline will allow us to address one of those areas and to open potential international dimensions associated with 4th generation light sources elsewhere in world to address others in this field.

Soft X-rays represent a minor but very important part of the interstellar radiation field. X-rays are much more penetrating into cold dense environments than radiation with ultraviolet and optical wavelengths. Hot, young stars are intense sources of such X-rays and are embedded in the remains of the protostellar disk from which the newly born star emerged. These disks are the building blocks of planetary systems retaining the icy grain population of the pre-stellar core and retain significant potential for chemical processing driven by the penetrating soft X-ray emission from the nascent star.

To understand what happens to an icy grain surface as it is irradiated with soft X-rays the combination of reflection-absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) used by McCoustra and others [7] will be deployed to probe both physical and chemical changes in the surface. Such measurements complement and extend the work already being undertaken to investigate photon-driven chemistry on icy grains at longer wavelengths [8]. They will allow us to identify potential mechanisms driven by core excitations with the goal of ultimately developing pump-probe experiments utilizing fourth generation light sources such as FLASH and XFEL to investigate the energy flow subsequent to soft X-ray absorption. In particular this may allow us to investigate excitation transport in icy solids that is often cited as responsible for desorption in such systems [9].

The second issue that might ultimately be addressed by VERSOX is the origin of the primary asymmetry in biological molecules. All biological relevant amino acids are left handed while the sugars that form the energy source and constructional material in many biological systems are right handed. Already numerous experiments are showing us the photon- and low energy electron-induced processes in simple ice mixtures can result in the formation of pre-biotic molecules. But this chemistry is achiral – it does not introduce a handedness into the reaction products. Such experiments require coupling the output of VERSOX with additional external light sources including lasers. Additional enantiospecificity brought to enantiospecific desorption by enantiospecific gas phase photolysis could enhance the effectiveness of this mechanism for producing the primary asymmetry. But careful quantification of each of these mechanisms is urgently needed.

2.6 Heritage Science

The UK and mainland Europe are home to some of the world's most diverse cultural heritage sites and historical artefacts. However threats from the combined impact of atmospheric pollution, negligence and inappropriate restoration measures, which often results in irreversible damage, pose a major challenge for heritage scientists. In a proactive response, the ARHC/EPSRC Science and Heritage Program was launched to ensure that knowledge and innovation in UK cultural heritage research is strengthened by developing new capacity within the research community to support interdisciplinary scientific research to tackle complex archaeological challenges that face the 21st century [1].

The application of non-destructive synchrotron techniques to probe changes in the surface and structural properties of materials under reactive environments will prove pivotal to improving our ability to conserve historical artefacts [2]. Such capabilities are central to aiding our understanding of the interactions between the surfaces of historical artefacts and their surrounding atmosphere, and in turn identifying processes which lead to weathering or decay phenomena observed in many conservation projects. The brightness of modern synchrotron facilities allow improved analytical

sensitivity for time-resolved measurements during exposure of historical artefacts to reactive environments, while also permitting simultaneous multi-technique characterisations (e.g. Raman, XRF and XAS). Since the closure of the SRS, only the LUCIA beamline at Soleil is capable of measuring XAS on light elements (e.g. Na, Mg Al K-edges) [3]. However, LUCIA is a dedicated μ -focus beamline and cannot analyse first row elements or permit time resolved environmental studies, thus VERSOX will fill an important gap in the armoury of spectroscopic techniques for heritage science.

Heritage conservation requires an understanding of the kinetics of decay processes, and how to mitigate and manage deterioration of artefacts by adopting the most appropriate preservation policies. Materials conservation not only addresses our past, but also our future with aging behaviour of modern day materials (e.g. photographs, composites and polymers) selected for archiving also presenting a challenge. Climate change has a significant influence on both indoor and outdoor environmental conditions; understanding the interaction of variable microclimates with materials is thus key to deciding preservation policies and practices. Such climates can range from aggressive environments as in the case of atmospheric pollutants with surfaces of masonry, sculptures or ancient glass on buildings and monuments, to more subtle effects of humidity on artwork, textiles, parchment and photographs. There are only two soft x-ray beamlines in operation currently capable of performing the ambient/high-pressure measurements offered by VERSOX, both are heavily over-subscribed by the international community and lacking the proposed complementary high-throughput XAS facility on the second end-station. The capabilities of the VERSOX beamline will be invaluable for probing the transformations involved in all these projects, and it is anticipated that the range of applications will continue to expand as the new heritage community matures. Specific examples of project include:

2.6.1 Conservation of historical artefacts

2.6.1.1 Parchment

Hydration and relative humidity has a significant effect on the molecular and mesoscopic structure of parchment, with the surface-ink interface often undergoing degradation as a result of environmental damage [4,5]. Analysis of such ink-surface interactions on parchment using micro-focused X-ray spectroscopies to probe the upper few microns of the surface where writing is found will allow local changes at the surface of parchment to be probed shedding light on the mechanism of this important degradation process [6]. Given this information, new protocols for archive record maintenance, storage and novel cleaning techniques can be established.

2.6.1.2 Ivory

A pressing current challenge in conservation, archaeology, anthropology and art history is the fully-integrated study and management of artefacts made from animal tissues such as ivory. These materials are inherently complex and the authenticity and origin of the source of the material is often problematic and requires a non-destructive approach to more accurately catalogue the materials according to their elemental composition. It is essential that our ability to determine the origins, authenticity and date of ivory objects and working residues is substantially enhanced. μ -XRF and XAS analysis will a powerful method to map the elemental compositions and local structures of ivory-based materials.

2.6.1.3 Metallic and wooden artefacts

Many metallic artefacts are found to decay post-excavation, which is related to the presence of Chlorine. The processes by which corrosion phases form, and later evolve, strongly influence the conservation and restoration of these metal artefacts. The microscale variations of iron and chlorine speciation along the depth of the corrosion crust could be determined using μ -XAS. Furthermore environmental XPS would allow a greater understanding of the surface chemistry and dynamics of the initial stages of the decay process. Distribution of metals in composite materials can be probed

by μ -XRF, μ -XAS. e.g. swords comprised of Fe, As, Ni composites, or Fe and Cu in Egyptian bronzes where changes in oxidation state can be observed by deterioration.

Synchrotron studies also revealed the origins of decay in the timber frame of the salvaged Tudor warship *The Mary Rose*. Sulphuric acid formation, identified deep within the timbers, was observed to react with the timber surface leading to its decay. Unfortunately existing preservation methods are unable to prevent the acid formation, however, having identified the problem, new preservation methods can be sought to prevent the formation of sulphuric acid and retard the decay within the timbers and so save the historic remains of this ship.

2.6.2 Conservation of historical buildings

2.6.2.1 *Masonry and sculptures*

An understanding of how to combat pollution induced weathering of masonry from historic buildings and sculptures, such as York Minster [7] requires access to XAS facilities capable of measuring light elements (e.g. C, S, Mg, Al, Ca) and is ideally suited for the soft x-ray specification of the proposed VERSOX beamline. Imaging of light elements will prove valuable for mapping local regions of decay and elemental distribution within masonry samples and identifying the local structure of amorphous salts. XPS will permit the interaction of atmospheric gases with historic masonry to be examined to aid our understanding of the influence of hydration (relative humidity) upon salt formation. In addition the effect of organic acids with surfaces of building materials can also be investigated to assess the effect of modern day pollutants on historic buildings.

2.6.2.2 *Glass*

The effect of weathering on medieval stained glasses can result in changes in glass colour, as well as the formation of surface weathered phases. The combination of μ XRF and μ XAS information contributes to our understanding of the way chemical phases react as a function of the long-term weathering, but also to the conservation of these stained glasses [8,9].

2.6.3 Conservation of modern materials

2.6.3.1 *Photographs*

An improved understanding of the effects of micro- and macro-environmental conditions on the degradation of colour photographic media is essential for the preservation and management of colour photograph collections for future generations [10,11]. Artificial ageing methods are being employed to follow the aging of colour photographs under different environments. Analysis of the resulting changes requires by an array of spectroscopic techniques to map out the changes as the photographic dyes degrade. By constructing a model of the environmental effects on the stability of colour photographs using such non-invasive measurements will allow the life expectancy of colour photographs from The National Archives to be estimated.

2.6.3.2 *Polymers and Plastics*

Heat-set tissues were once applied to paper as a remedial conservation treatment. The nature of the substrate and adhesive, combined with the application of heat, can be detrimental to the long-term stability of laminated documents. The issues surrounding the identification and deterioration of synthetic polymers are of growing concern within the heritage sector. They pose significant stabilisation problems because of the processing methods, additives and treatments used. The routes of degradation are often complex, requiring an intimate knowledge of the interfacial chemistry between the paper and laminate in order to develop conservation and preservation protocols.

- [1] E. Pantos et al, *Physics Methods in Archaeometry*, 154, 2004, 299.
- [2] L. Bertrand et al *Applied Physics A*, 83 2006, 225
- [3] D. Fessas et al, *Thermochemica Acta*, 447 2006, 30.
- [4] I. Arcon et al, *X-ray Spectrometry*, 36, 2007, 199.
- [5] C.J. Kennedy et al, *Nanoletters*, 4, 2004, 1373
- [6] Science Heritage Research Cluster - <http://www.heritagescience.ac.uk/index.php?section=101>

- [7] Building a Future for our Past, Pioneer, 1, 2008, 28
- [8] D. Benedetti et al, Nuovo Cimento della Societa Italiana di Fisica C, 30, 2007, 27.
- [9] J.Roque et al, Physics Status Solidi B, 243, 2006, 1337.
- [10] <http://www.nationalarchives.gov.uk/information-management/projects-and-work/conservation-research-development.htm/egor.htm>
- [11] A. Fenech et al, Atmospheric Environment, 44, 2010, 2067.

2.7 Comparison with other facilities

The design parameters for the VERSOX beamline (section 3) are highly competitive in comparison with bending magnet beamlines elsewhere. The beamline will, for example provide a smaller spot size and higher brilliance than at most other facilities. However, the main advantage of the VERSOX beamline is the complementary range of techniques provided by the twin branch line design.

One will be dedicated to near-ambient XPS using commercial systems. Worldwide there are currently two synchrotron facilities, BESSY and ALS, with soft X-ray beamlines capable of performing ambient/high-pressure XPS with limited NEXAFS capabilities. BESSY operate a prototype instrument on an undulator beamline, which is owned by the Fritz-Haber Institute but also available to outside users; it is mainly devoted to gas-phase catalysis. ALS has two ambient/high-pressure XPS beamlines, one undulator and one dipole, which are used for a broad range of experiments from atmospheric studies to catalysis. All three beamlines are heavily over-subscribed (e.g. the two beamlines at ALS are 6-fold and 4-fold oversubscribed). Several European synchrotrons (e.g. MAXlab, ALBA, SOLEIL, SLS) are planning or in the progress of building high-pressure beamlines/endstations over the next years. The concepts published so far are less versatile and have an emphasis on gas-phase, rather than liquid interface studies, and on XPS, rather than XAS.

The other end-station will be a unique combination of detector technology that will provide parallel and efficient detection of electrons, light and x-rays and also to provide nanoprobe detection of local chemical bonding. Optical detection will be developed from mobile systems built in the UK that have been operated at many international centres that are based on optical microscopy coupled to sensitive CCD detection. UHV end-stations equipped for optical detection, exist at the Canadian Light Source and Tskuba, and one is planned for Lund. End-stations with scanning probe microscopy are becoming more common, but incorporation of scanning probe measurements directly into the x-ray beam exist only at the ERSRF and SPRing8. The VERSOX system will be unique in coupling such systems together with electron and x-ray detection.

The presence of both systems on the same beamline is unique and will particularly serve communities in areas such as Catalysis and Heritage science where both facilities are needed to provide a complete picture.

2.8 Industrial relevance

Research within many of the science areas are application driven. Research groups interact closely with industrial partners in collaborative programmes and there is an appreciation among these partners of the value of accessing advanced materials characterisation methods such as those offered by the VERSOX beamline and more broadly using synchrotron radiation. The design of the end-stations includes provision for the handling of complex, multi-phase materials and the measurement of their processing under realistic conditions such as during thin film growth and at near-ambient pressure. A further design parameter is rapid throughput realised by a modular architecture and small chamber volumes linked to fast loading from atmosphere. The relaxation of the UHV demands for the chambers that will enable operation without extensive baking in many cases will enable loading to measurement times of a few hours. The twin branch design will enable parallel scheduling for off-line preparation and shorter, rapid access for one-off samples. Potential industrial users recognise the need for such rapid access along with ease of use, strong local support and collaboration with experienced users.

3 Beamline Requirements

The Bending Magnet (BM) source will provide bright and continuously tuneable radiation (50 – 2000 eV) in two branched lines for fixed and scanned energy experiments. It will be optimum for handling radiation sensitive materials such as organic molecules where radiation damage from Insertion Device (ID) sources can be a concern. The 10x-100x reduction in flux compared to an ID beamline will be compensated by reduced beam damage and optimum detection efficiency. The efficient collection of light, x-rays and electrons optimised to the BM source intensities and sample environment will be realised by a fusion of the latest detection technologies in experimental environments that enable in-situ materials processing to be carried out whilst probing with soft x-rays. The following techniques will be provided:

- Photoelectron spectroscopy (PES) for real-time monitoring of surface processing and measurement at near-ambient pressures.
- Electron yield x-ray absorption spectroscopy (EY-XAS or NEXAFS) for surface-sensitive chemical state, unoccupied orbitals and molecular orientation.
- Scanned probe detection will uniquely enable local chemical mapping at the nanoscale
- Fluorescent yield x-ray absorption spectroscopy (FY-XAS or FY-NEXAFS) for bulk-sensitive chemical state, unoccupied orbitals and molecular orientation.
- Luminescence yield x-ray absorption spectroscopy and x-ray-excited optical luminescence (LY-XAS and XEOL) for probing light emission and bulk-sensitive local chemical state in non-metallic materials.
- Additional optical probes, such as lasers, can be coupled to the pulsed structure of the DLS x-ray beam in pump-probe experiments.

The experimental end-stations will be designed with performance, flexibility, high throughput and ease of use as primary design criteria. One line is designed around an ambient pressure photoelectron analyser. The other line is optimised for parallel detection and its efficiency will enable time and spatially resolved electron detection for real-time analysis.

4 Beamline Specifications

Diamond bending magnets (BM) emit synchrotron radiation with a critical energy of 8.39 keV, and power of 48 W/mrad(h) at 300 mA, with a peak power density of 184 W/mrad². The photon flux available from the bending magnets of Diamond is shown in Fig.1.

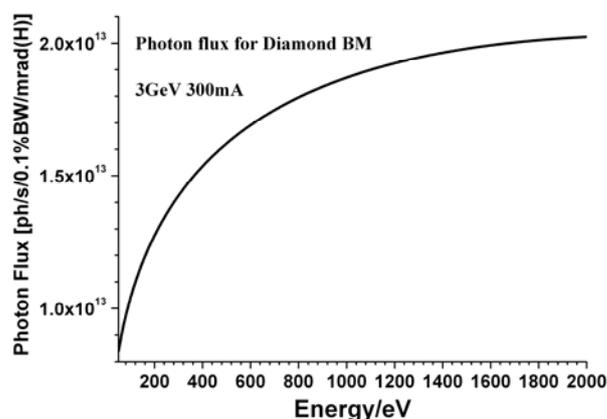


Fig.1: Photon flux from the bending magnet dipole as a function of energy

4.1 Beamline Optics

The beamline optics are designed to address a variety of competing requirements – the main ones being ability to provide a moderate energy resolution and high flux in a large energy range of 50-2000 eV. Two branches are required in this beamline. A beamline design based on collimated plane

grating monochromator (cPGM) is being proposed because of its many attractive features including the full flexibility of using it in many operational modes (high photon-energy mode, high spectral resolution mode or high harmonic suppression mode). Good experience in designing, building and operating of cPGM exists at Diamond. For example, the cPGM is already being used all of the three soft X-ray beamlines (I06 Nanoscience, I10 BLADE and I09 SISA), and it has also been designed for one Phase III beamline (I05 ARPES).

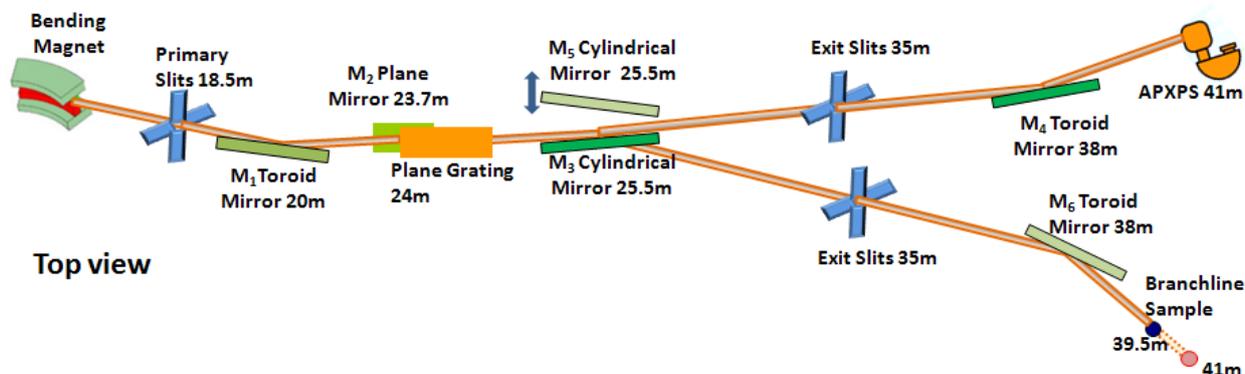


Fig.2: Schematic layout of VERSOX beamline

The beamline concept is shown in Fig. 2. The toroidal mirror will deflect the beam horizontally by 3° (*i.e.* 88.5° angle of incidence) by trading off the reflectivity and the beam footprint. The toroidal mirror will collimate the light in the vertical and perform 1:1 focusing of the light in the horizontal direction at the exit slit of the monochromator. The slope error on this mirror will be $1\mu\text{rad}$ rms along the tangential direction. The sagittal figure errors of this mirror reduced by the forgiveness factor, *i.e.*, the cosine of the angle of incidence on the mirror, will contribute to the monochromator resolution. The tangential figure errors will affect the horizontal size at the exit slit.

The mono vessel contains one plane mirror and several plane gratings. The plane mirror will deflect the beam upwards (along the dispersion direction) towards the grating. In the present design three gratings (300 lines/mm, 600 lines/mm and 1200 lines/mm) have been proposed. These gratings will cover the required energy range whereas the latter offers very high resolution.

After the grating, the beam intercepts by two retractable cylindrical mirrors 1.5 m downstream of the grating that focus the beam into an exit slit in the vertical direction. The beam will be deflected to either of the two branch lines by switching these two focusing mirrors. One can therefore get a much larger split between the two branches than in the case of the spherical grating monochromator design (where splitting needs to be done after the exit slits). The distance between the cylindrical mirror and the exit slit would be set to a large value, subject to space constraints, to achieve high spectral resolution. Since collimated light is incident on the grating the beam is always focused at the same position; the exit slits do not need to move along the beam when the energy is changed. Spectral resolution and spot size at sample depends on the exit slit size.

The intermediate focus at the exit slit is then refocused by a toroidal mirror to the sample position. In one of the branch lines, two refocusing mirrors with different focusing distance are suggested. This allows for potential location of other end-stations increasing the versatility of the beamline.

Radiation from a bending magnet is linearly polarized when observed in the bending plane. Out of this plane, the polarization is elliptical. The circularly polarized X-rays could be harnessed by moving the primary slit above or below the electron orbit plane of the storage ring.

Preliminary ray tracing has been done for performance prediction of the beamline. In the present study the bending magnet beam acceptance is set to $1\text{ mrad} \times 1\text{ mrad}$. The collimating mirror (M1), focusing mirror (M3) and refocusing mirror are assumed to be gold coated with grazing angles of

incidence of 1.5° . The terms contributing to the resolving power calculated for the 1200 lines/mm grating, $c = 2.0$, exit slit = $20\ \mu\text{m}$ and with the parameters chosen for the beamline as displayed in Fig. 2. Fig. 3 shows the ray traces at APXPS for 500 eV. From the energy distribution along the vertical direction one obtains a resolving power of 10000. The spot size along the vertical direction is very close to the width of the exit slit whereas in the horizontal direction the beam FWHM is around $120\ \mu\text{m}$, which will be matched to the requirements of the experiment.

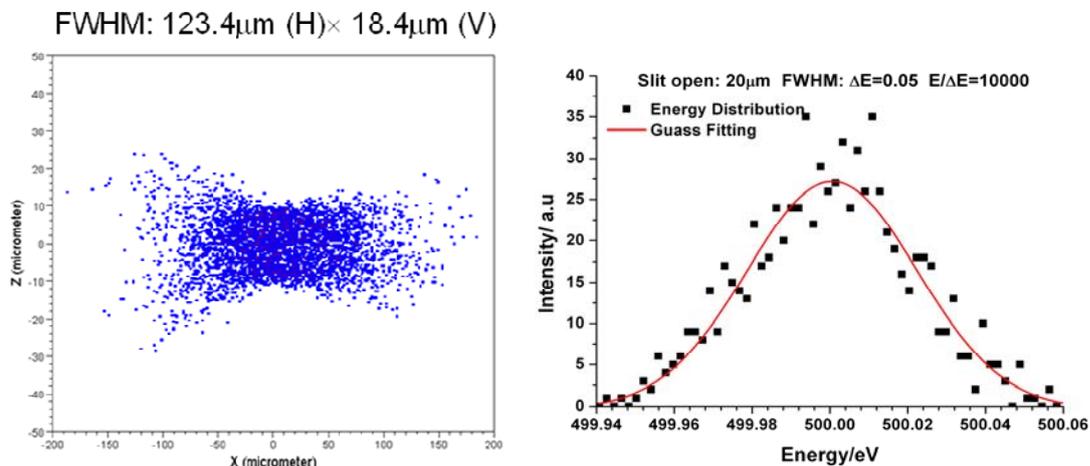


Fig.3: Beam profile and energy distribution at APXPS sample position for 500 eV

4.2 Experimental end-stations

There will be two end-stations, each located on one of the two branch lines. One end-station will provide parallel detection using maximum incident and emitted flux and the other will be devoted to ambient-pressure photoemission spectroscopy.

4.2.1 Parallel Spectroscopy

The technical objectives of this end-station will be to integrate spectroscopy and imaging with soft X-rays as real-time, in-situ probes of surface processing. The Bending Magnet source will be optimum for handling radiation sensitive materials such as organic and bio molecules where radiation damage from Insertion Device sources can be a concern. The vacuum environment will provide the maximum incident photon flux and electron emission for probing complex and nanostructured materials with high sensitivity. The technical solution will be to use efficient detectors of x-rays, light and photoelectrons. This will be realised by a fusion of optical, x-ray and photoelectron detection technologies in an experimental environment that enables in-situ materials processing to be carried out whilst probing with soft x-rays. The chamber will be modular to enable different experimental combinations of sample handling, treatment and characterisation to be rapidly interchanged without relocating the chamber infrastructure. Solid samples can be studied with all techniques; liquid samples can be studied using optical and x-ray detection. The simple, compact design will also facilitate rapid sample transfer and so the combination of throughput and fast measurement will make the facility attractive for new users and direct industrial access. Key design features are:

4.2.1.1 Photoelectron techniques

Photoelectrons will be detected by total and partial yield for XAS/NEXAFS and by a compact hemispherical analyser for XPS. The latter will be coupled to a direct electron counting array whose efficiency and pixel density will enable a compact, high performance analyser to be used. Technology developed in the UK provides such a high dynamic range detector with the current 38 mm chip offering 1500 channels with a pitch of 25 mm. This will enable spectral features to be collected with high speed ($\sim 10\text{ms}$) over many orders of magnitude of intensity; this is important when measuring weak band edges and strong core levels in parallel while completely attenuating

substrate emission during thin film growth. The compact size of the analyser will enable coupling to other detection systems, growth cells and gas/vapour/aerosol exposure.

4.2.1.2 *Soft x-ray techniques*

Soft x-ray emission detection, based on commercial designs, will be compact systems to enable parallel operation with the other techniques for example in probing unoccupied electronic states originating deeper in the bulk material than emitted photoelectrons.

4.2.1.3 *Optical luminescence techniques*

Luminescent photons emitted during x-ray exposure will be detected using sensitive photomultipliers for total yield XAS and using CCD detection coupled to a compact microscope for imaging studies. Imaging XAS and luminescence in parallel enables correlations between local structure and light emission to be determined for samples that are laterally inhomogeneous and that do not require complicated sample preparation. This is attractive in particular for rare and delicate materials such as historical artefacts and bio-structures. The UK has produced unique mobile spectrometers for optical detection that have been applied at many international centres and this leading position will be exploited within VERSOX by incorporating this technology for the first time with in-situ processing and other, electron and x-ray methods. Additional optical probes, such as lasers, can be coupled to the pulsed structure of the x-ray beam in pump-probe experiments where the laser populates or depopulates shallow electronic states while the x-rays probe the deeper core states.

4.2.1.4 *Scanning probe techniques*

In this VERSOX chamber, sample surfaces will be imaged in-situ using AFM topology or other mode to locate area of interest (e.g. single nanostructure). Excitation with fixed X-ray energy is used for chemically sensitive imaging; scanned X-ray energies, through appropriate atomic absorption edges is used for spectroscopy. For all electronic nanostructures (metallic or semiconducting) there is a tendency to acquire a net charge at a rate determined by the relative values local electron loss (ionisation) rate and the electron supply rate from the substrate. AFM configured in the electric field microscopy, Coulomb force mode, has great sensitivity for charge measurement, providing single electron sensitivity in UHV. The simultaneous imaging of charge and topology provides correlation between chemical variation and charge localisation and the physical localisation site may also be indicative of defects. For spectroscopy, the AFM tip is fixed at a site (guided by the topology image); as the photoemission rate varies due to scanning over an atomic edge, the electron supply rate is essentially constant. The net charge therefore rises and falls as the photon energy passes through the resonance and NEXAFS data localised to the single nanostructure can be measured.

4.2.2 *Ambient-pressure XPS*

Central to this end-station will be a differentially pumped electron energy analyser, which enables measuring photoelectron and NEXAFS spectra while the sample is exposed to an ambient pressure of up to > 10 mbar. This type of analyser became commercially available recently and is currently offered by two suppliers, Specs and VG Scienta, with similar specifications. The maximum sample pressure is determined by the aperture at the entrance to the lens system and the distance between this aperture and the sample, which cannot be shorter than twice the aperture diameter. The diameter, in turn should match the spot size. Currently available commercial systems have aperture diameters of 0.5 – 1.0 mm and can operate up to 10 mbar. Making use of the small spot size available at the VERSOX beamline, the aim will be to push the maximum pressure into the 100 mbar range, thus surpassing the capabilities of existing systems.

One of the key features of this endstation will be its versatile modular design, which will provide different sections of the user community with suitable sample environments (reaction chamber, sample holder) for:

- Gas-phase catalysis
- Solid-liquid/humid interfaces including biological interfaces
- Liquid surfaces / droplet jets / atmospheric

The modular concept will provide the optimum sample environment for every type of experiment without having to compromise. It will allow the use of additional detectors, if needed, and will minimise the danger of cross-contamination between different experiments. The design and commissioning of a suitable modular sample environment system meeting as many user requirements as possible, will be a major in-house development programme in parallel with the design and commissioning of the beamline. This will be done in collaboration with major vacuum-component manufacturers and some of the work can be out-sourced to key user groups.

Key components in addition to the electron analyser are experimental chambers and manipulators matching the specific requirements of each section of the user community, with versatile options for experimental chambers and a UHV preparation chamber. Sample load-locks and transfer will be designed to easy and rapid. Additional modular detector systems can be incorporated, e.g. partial yield electron detector, photodiode array, and x-ray spectrometer. In particular the X-ray detectors will extend the accessible pressure range beyond the limits imposed by absorption of electrons in the gas phase. These detector systems can be shared between the two endstations of the VERSOX beamline. Potential experimental environments include:

4.2.2.1 Reaction chamber for gas-phase heterogeneous catalysis

Gas phase catalysis experiments require a UHV compatible reaction cell with small volume and passivated surface to minimise reactions and adsorption on chamber-walls and to reduce bakeout/pump-down times. The system would cover a pressure range from 10^{-11} to 100 mbar and allow a controlled gas environment. The sample holder will allow variable temperatures between 300K and 1500K.

4.2.2.2 Controlled humidity chamber

Experiments on solid-liquid/humid interfaces require a similar small reaction cell and a temperature range between -50°C and 100°C . This requires a cooling system that ensures that the sample is the coldest spot in the chamber and avoids the build-up of ice at elevated pressures. Such a chamber would be equipped with mass flow controlled inlets for water vapour and other gases or solvents and suitable pressure and humidity gauges.

4.2.2.3 Liquid surfaces, Liquid or Droplet jet

A liquid jet or droplet train passing by the analyser aperture enables the study of a variety of liquids under well-defined conditions. The liquid surface is constantly replenished and can be exposed to gas environments without the risk of contamination over time. This is the ideal set up for experiments related to atmospheric chemistry. More viscous liquids may require different designs, which will be developed in collaboration with the respective user groups.

In addition to the elevated pressure experimental chambers the endstation could also be equipped with a separate conventional UHV preparation chamber providing standard surface science preparation and analysis techniques (LEED, ion-sputter gun, evaporator sources) and a load-lock and transfer system for sample transfer to the reaction and controlled humidity chambers. The sample holders will have integrated thermocouple contacts for accurate temperature measurements and control in both sample cells.

