1.1 Past contributions of the Tonner research group to BL-7 development

The Tonner research group has been involved with the SpectroMicroscopy Facility since its inception as a workshop concept in 1985. Tonner and Tobin were the authors of the original field-task proposal that created the SpectroMicroscopy Facility, and Tonner served as the first PRT spokesperson. Certain basic underlying concepts of the design, such as the "mirror switchyard" concept which allowed the expansion of the project from a simple, one-technique at a time beamline to its current sophisticated around-the-clock operation, were initiated by Tonner and his collaborators during his service as project leader. The decision to expand the scope of the microscopy program, by building both a UHV and an air microscope, was made during this time. Tonner and his research group were primarily responsible for design of the "ultraESCA" XPD apparatus, and for certain basic elements of the STXM and SPEM zone-plate microscopy designs, such as the specification of high-resolution scan stages for both instruments, and the decision to break with tradition and build a SPEM with a scanning x-ray beam rather than a scanned sample stage.

1.1.1 Research using ultraESCA

We have constructed a photoemission system using a multi-channel detector photoemission

spectrometer and automated 5-axis sample manipulator, to get the best performance from the combination of small-area, high intensity, and high energy resolution that the undulator beamline can provide. This project is called "ultraESCA", which stands for UnduLaToR Assisted Electron Spectroscopy for Chemical Analysis. The group nickname for this system is the "XPD chamber."

The idea is to try to simultaneously make major improvements in X-ray photoelectron spectroscopy (XPS or ESCA) in terms of small analysis area, overall spectral resolution, and counting rate. This results in a figure of merit, $G=I/(dA^*dE)$, which characterizes the sensitivity of the tool. Compared to most laboratory ESCA instruments (G=1). ultraESCA has an enhancement in merit of G=10,000. Even compared to the highest performance, million-



Fig. 1: Scanning photoelectron spectroscopy image of a small particle of Cm compound, where the image intensity is proportional to the Cm 4f core-level count rate. The bright spot in lower right is the Cm oxide particle.

dollar-plus class Scienta 300 ESCA system, ultraESCA has a performance gain of two orders of magnitude[1], when we use the fact that we can vary the photon energy to optimize surface sensitivity and cross-section). Some examples of surface-sensitive, high energy resolution, high statistical quality core-level spectra from reconstructed silicon surfaces have been taken with total spectrum acquisition times of 15 seconds or less. Surface sensitive core-level spectra from Si(100) and Si(111) give count rates in excess of 1 Mhz from areas of less than 100 micron diameter, with total system energy resolution of 0.08 eV[2]. This type of performance is having a tremendous impact on the field of XPD (see below).

The ultraESCA instrumentation allows us to create maps, or images, of photoelectron spectra as a function of position on the sample, with a spatial resolution set by the monochromator spot size. Using the adaptive refocussing optics of BL7, this spot size can be adjusted to about 30 microns, with no penalty in count rate, at high energy resolution ($R \sim 8000$). There are numerous applications of this technique of scanning ESCA, but one in particular has had interesting initial results

We have used ultraESCA to study small particles of actinide compounds, primarily Cm and Pu compounds to date. Ordinarily, the problems



Fig. 2: Photoelectron spectrum of a small Cm containing particle, located by scanning photoemission microscopy using ultraESCA.

associated with radioactivity and toxicity of actinides makes it extremely difficult to perform spectroscopic measurements at facilities, without extraordinary sample handling precautions. By reducing the sample dimensions and volume, and immobilizing the samples on substrates, these problems can be greatly simplified. We have shown that photoemission cross-sections, as a function of incident photon energy, can be readily measured from samples of less than 3 nanograms mass and 3 picoCuries of activity. Some of the first soft X-ray absorption spectroscopy on actinides has been done this way, as well.

In an ultraESCA experiment on a small particle, the mapping capability is first used to locate the particles on the substrate. An example image is shown in Fig. 1, where the intensity of emission from Cm 4f core-level is plotted as a function of position on the substrate. The substrate appears dark, with a high-contrast bright white dot showing the location of the actinide particle. This specific particle is large, about 250 micron by 500 micron, so individual points on the particle surface can be chemically analyzed. A typical photoemission binding energy spectrum from a spot on the particle is shown in Fig. 2. The core-level spectrum shows features in addition to the 4f-7/2 and 4f-5/2 main lines, which may be due to additional chemical states. The area of analysis is about 75 microns.

1.1.2 X-ray Photoelectron Diffraction (XPD)

Photoelectron diffraction is a method for getting precise structural information about atoms at surfaces from the energy and angle dependent variations in emission intensity of photoelectron peaks. Since photoelectron binding energies are sensitive to the local chemical environment, photoelectron diffraction techniques are one of the few structural probes available that can map out bond lengths and angles for individual chemical species in a material.

A photoelectron diffraction pattern is a map of the emission intensity, from a particular binding energy peak, into the hemispherical space above the sample substrate, $\chi(\theta, \phi)$. An energy dependent photoelectron diffraction curve is the intensity oscillation for a specific emission direction, but with the kinetic energy varying, $\chi(\mathbf{E})$. Both of these types of diffraction experiment, angle and energy dependent, contain structural information which results from the complicated scattering of the outgoing photoelectron wave from the neighboring atoms in the solid. With modern multiple scattering calculations, it is possible to model experimental data and achieve excellent agreement with theoretical models[3]. This can result in bond-length measurements with an accuracy of 0.05 Angstroms or better[4].

The XPD experiments are done using the ultraESCA chamber. This has been designed explicitly with high accuracy photoelectron diffraction experiments in mind. The manipulator, incident x-ray beam, and electron detector axis are aligned to exploit certain symmetry properties of XPD that lead to improved surface sensitivity and smoother 'instrument functions'[5].

of One the main project goals for the Facility SpectroMicroscopy was to optimize the experimental acquisition of complete photoelectron diffraction data sets, covering both the angle- and energydependence. Since the angular dependence can be expressed in terms of electron momentum parallel to the surface, and the energy dependence is in terms of perpendicular momentum, a data set comprehensively showing the diffraction pattern in K_x , K_y , and K_z space can be thought of as a photoelectron diffraction "volume". In order to see the value of such a large data set, we have constructed a diffraction volume for a Cu(100) surface. In Fig. 3 we show the full angle-dependent patterns for a set



Fig. 3: Set of complete photoelectron diffraction patterns from Cu(100) crystal at several kinetic energies.

due

to

of discrete photon energies. The patterns show the high sensitivity to the electron kinetic energy, since each has its own unique signature. Common features include bright spots at directions corresponding to atomic rows, which arise from forward scattering along the atom chain.



Photoelectron diffraction is a powerful structural tool, but its full potential places high demands on the sensitivity of a photoemission experiment. In order to fully exploit the technique, high energy resolution is needed to extract small chemical shifts, and high intensity is needed to accumulate the large required data sets in a reasonable time. An

example of a challenging problem is to use photoelectron diffraction with very high energy resolution to study the diffraction effects of surface atoms in the Si(111)-7x7 reconstruction.



Fig. 4: Photoelectron diffraction "volume" in momentum space constructed from a set of individual patterns. The energy dependent XPD appears as vertical columns, the horizontal planes are patterns for a specific energy.

The high resolution spectrum of the Si 2p atoms from Si(111)-[7x7] is shown in Fig. 5. The overall envelope of the 2p corelevel surrounds emission from as many as five different atomic species, "bulk" atoms plus four types of surface atoms in the [7x7] reconstruction. Very clean, well ordered surfaces, and high energy resolution, are needed to see the small distortions (shoulders) in the 2p envelope that uniquely pin down the parameters of the multi-peak curve-required for this complex surface.

There remains a considerable debate over the origin of the various spectral components in core-level spectroscopy from this surface. We have used the high intensity and energy resolution of the SpectroMicroscopy Facility, along with a photoemission "robot" to scan the angles and energies, to collect a photoelectron diffraction "volume" for the [7x7] surface reconstruction. The



Fig. 5: High resolution spectrum of Si 2p core-levels from a Si(111)-[7x7] surface, showing four surface atom peaks in addition to the bulk peak.

results have superb statistics, and reveal the diffraction patterns of each of the components in the 2p line. Since each atom which has a distinct local structure will produce a unique diffraction pattern, we can identify the origin of the spectral features with certainty. The data analysis employs both the conventional approach of model calculations, and direct inversion using photoelectron holography techniques.

Related experiments which have been completed are a surface core-level shift photoelectron holography study of Si(100)-[2x1], and a surface-shift diffraction study of W(110).

1.1.3 "Complete experiment" photoelectron holography

Given the extraordinary capability of the BL-7 ultraESCA station, we have been able to push the limits and quality of photoelectron holography as a tool for surface structure to new levels. The best recent example of our results is from a study of a magnetic surface alloy, Mn on Ni(100).

For modern high-tech materials, the atomic geometries of surfaces and interfaces are frequently a key factor in performance, but measuring these geometries directly is not a simple matter. Most current methods rely on comparing experimental data with calculations from various models, to determine which model



Fig. 6: Ball-and-stick model (left) of Mn (green) on Ni (blue), compared with the experimentally derived, direct-inversion holographic image (right).

matches the observations most closely in general configuration and then to refine details of the model such as bond lengths. Quantitative X-ray photoelectron diffraction (XPD, in which experiments are compared to full multiple-scattering simulations, is one means of gathering experimental data for such comparisons.

An alternative approach is to attempt direct inversions of the experimental data to form atomic "images" of the surface structure. Our group recently used XPD with both these approaches to study a surface alloy of manganese and nickel on a nickel substrate. Our results not only extend

the general characteristics of an unusual earlier model for the alloy structure based on low-energy electron diffraction (LEED) measurements, but also lend hope for x-ray photoelectron holography as a method of direct, quantitative determination of surface structures. The experiments, performed using the ultraESCA endstation, use complete photoelectron diffraction sets to create images of atomic positions using a simple Fourier transform, with no need for prior knowledge of the structure.

We measured x-ray photoelectron diffraction patterns for a large number of x-ray photon energies and then used both comparative techniques and holography to examine the surface buckling in more detail. Given the complexity of full multiple-scattering simulations, the direct imaging approach of holography is potentially a way to begin a structural refinement close to the final answer, greatly improving the accuracy and confidence in the final result.

In Fig. 6 we show the holographic reconstruction from our experimental data. No a-priori information about the structure was needed as input to this inversion algorithm. The image shows virtually no artifacts, no twin image, and gives a direct indication both of the local symmetry and the "buckling" of the Mn atom. The main reason for the



Fig. 7: Photoemission microscopy image of a Au grid, using the Au 4f core levels, acquired in 34 seconds with the PRISM instrument. The grid spacing is $25 \mu m$.

improved quality of the reconstruction, and the reason we do not need to use complex inversion algorithms, is that the data set is "complete". That is, it contains full hemispherical XPD patterns over a wide range of kinetic energy, thereby spanning the three-dimensional momentum space of diffraction.

1.1.4 PRISM

A series of important benchmarks were reached in the PRISM photoemission microscopy project. PRISM, which stands for Paraxial Ray Imaging SpectroMicroscope, is the result of a collaboration between UW-Milwaukee and IBM-Almaden. It is a new design of a direct-view imaging photoelectron microscope, which uses electron optics to make a magnified image of a sample surface using the photoelectrons that are emitted[6]. The electron optics consist of a high-voltage electrostatic magnification stage, bridged to a low-energy hemispherical electron spectrometer for selection of the electron kinetic energy. By tuning the instrument to pass low energy secondary electrons, which are copious, high spatial resolution images of the surface can be viewed at standard video rates. To map the surface chemical composition, the analyzer is set to pass electrons from a specific core-level or valence band feature, and the image is integrated to build up statistics.

An example of the first photoelectron core-level test pattern images taken with this instrument is shown in Fig. 7. The sample was a mesh of Au (a standard electron microscopy mesh), which was sputtered to remove the contamination layer. After sputtering, the



Fig. 8: PRISM photoemission binding energy spectrum of Au 4f core-levels from a small section of one of the grid bars (about 2 microns in diameter). This high quality spectrum was acquired with 3.3 seconds of time per point.

strong Au 4f core-levels are nicely resolved, as shown in Fig. 8. The photoelectron microscope image was acquired by setting the analyzer to pass the Au 4f core-level. The image displayed took 34 seconds to build up the statistics shown, which are sufficient to see the main structures of the grid.

Earlier tests of the spatial resolution of PRISM were made using lithographically printed photoresists, and video-rate microscopy with secondary electrons. Line widths as small as 0.2 micron were easy to see at these speeds, and 0.1 micron is discernible in frame-grabbed pictures. The secondary-electron mode of PRISM also is used for chemical analysis, by sweeping the incident photon energy to generate an X-ray absorption near-edge spectrum (XANES). Micro-XANES mapping is being applied to a variety of problems, from magnetic domain imaging to the identification of the chemistry of contamination particles.

1.1.5 Scanning Zone-plate microscopy

Research using the scanning zone-plate microscopes, both UHV (SPEM) and atmospheric pressure based (STXM), has spanned the range from microelectronics to environmental studies.

Using the STXM, we have made the first measurements of transition metal L-edge spectra in liquids. While more common at high photon energies, where the penetration of the x-rays is very high, until our work there were no core-level spectra ever taken below 1000 eV from ions in liquids. Using these spectra, we are able to measure the changes in ligand-field strength that occur in the transition from solid to liquid. We also see changes, for certain ions, in the shape of the spectra which indicates a change in local bonding.

We are now applying this new experimental technique to the study of chemical reactions in liquids. This is the first example of a high-resolution core-level spectroscopy, in this energy range, to be applied to a reaction in solution. As we improve the spectral resolution and signal-to-noise, we expect to be able to directly map out speciation diagrams in liquids. Although we began our work with transition metals, the technique is obviously also well suited to studies at the carbon and nitrogen edges.

We have used the STXM, and 'wet cells', to study the local chemistry of the mineral-microbe interface. Micro-organisms attach to and chemically modify a variety of minerals. The mechanism of the attachment process, such as whether or not a polysaccharide film is produced, depends on the mineral substrate. We are using a combination of transmission and surface x-ray microscopy experiments to learn about the chemical changes that take place during the interaction between the micro-organisms (primarily S. Putrefaciens) and mineral surfaces.

A related issue is the study of a widely important but poorly understood phase of iron oxide. This phase, commonly called 'green rust', has important catalytic properties. It is a mixed-valence compound, but the precise structure and certainly the electronic structure are not known. We have obtained very high resolution spectra of various natural and synthetic green-rust oxides, and have concluded that the electronic structure is unique: that is, it is not the spectral sum of Fe(II) and Fe(III), as for the simpler case of various minerals such as magnetite.

This project is now a large interdisciplinary program, focussed on issues in biologically mediated remediation of contaminants in soils. The project involves microbiologists (JPL), physical chemists (NASA), and physicists (UWM). The unique capability of the BL7 instrumentation to tackle complex materials from the environment is essential to this program.

2. Near-term plans

2.1 New X-PEEM microscope

The X-PEEM that we have designed has shown a spatial resolution of better than 50 nm, with monochromatic x-rays, in micro-XAFS imaging experiments. This is a world's record for the technique, and actually surpasses the spatial resolution of the STXM and SPEM. We are nearly finished with the construction of XPEEM-II, which has an improved optical system and will reach even better spatial resolution limits. We plan to move the XPEEM to the ALS for experiments on BL-7 in a "roll up" mode. This will add an important new capability to the types of imaging experiments that can be done at ALS. The construction of the new XPEEM is supported by an instrumentation proposal from the NSF. The same grant is supporting our development of an aberration-corrected X-ray PEEM. This instrument will drive down the spatial resolution to 100 angstroms or smaller.

2.2 On-going projects

The following projects are funded, and are nearly entirely dependent on the ALS and BL-7.

2.2.1 Bio-remediation

This is a project from the DoE "Natural and Accelerated Bio-Remediation Innovative Research" (NABIR) program. Our study uses surface science techniques, such as photoemission, XPD, and XAFS, as well as in-situ x-ray spectromicroscopy. We are studying the formation of micro-mineral deposits by microbial respiration, which then serve as the substrates for adsorption of contaminants in soil or liquids.

2.2.2 Spectro-microscopy of mineral interfaces

This project is supported by DoE BES and OBER. It is a support project for the NABIR program, but a basic science project in its own right. We are studying the surface chemistry and structure of mineral surfaces, both as single crystal "model" surfaces and as natural minerals as inclusions in rocks. These studies of complex materials, which are exposed to the environment, require high spatial resolution and novel sample handling to get reliable information.

For example, much of the work is done on anaerobic specimens. The samples must be studied by our techniques, with complete control over exposure to the atmosphere. At no time can the samples be exposed to oxygen. We have developed an experimental protocol in which samples (which include microbial cultures) can be grown or processed in an anerobic chamber, and transferred to the BL-7 equipment with no uncontrolled exposure to air. Without this capability, the study of such important compounds as the mixed-valence 'green rust' would be impossible.

2.2.3 Photoelectron diffraction of complex surfaces

We are attempting to determine the adsorption sites of uranium and chromium contamination species on single-crystal mineral substrates. The adsorption step is a critical one in the bioremediation scheme. Photoelectron diffraction is a powerful structural probe, but it has almost never been applied to such complicated materials as a mineral sample with multiple adsorption sites, different metal cations, and mixed adsorbed species. The problems of getting this experiment to work in 'environmental' applications are daunting, but we are putting a large amount of effort into solving them.

The first experiments involve relatively simple mineral substrates, such as galena and pyrite. The next substrates we will investigate are Mn, Fe, and mixed Fe-Mn oxides, including bixbyite, magnetite, and various forms of manganese dioxide.

- 1 The comparison is made using data from the Scienta 300 in Prof. G. Margaritondo's laboratory at the EPFL in Lausanne, Switzerland.
- 2 Recent advertisements of electron spectrometers from the Physical Electronics company feature data taken on the ultraESCA station.
- 3 "Effect of the Reference Wave in Auger Electron Holography," D. K. Saldin, G. R. Harp, and B. P. Tonner, Phys. Rev. B **45**, 9629 (1992).
- 4 "The Structure of Cu on Ir(111): a case study in photoelectron holography and quantitative photoelectron diffraction," B. P. Tonner, J. Zhang and Z.-L. Han., Applied Surface Science **70/71**, 378-385 (1993).
- 5 "Angular instrument response for photoelectron diffraction using focused, plane-polarized synchrotron beams," J. D. Denlinger, J. Zhang and B. P. Tonner, Nucl. Inst. and Methods in Phys. Res. A **347**, 475-479 (1994).
- 6 "Energy-filtered Imaging with Electrostatic Optics for Photoelectron Microscopy," B. P. Tonner, Nucl. Inst. and Methods **A291**, 60-66 (1990).