ESRF

ESRF	Experiment title: Normal Incidence X-ray Standing Wavefield Surface Structure Determination with Chemical-state Specificity and High Sensitivity	Experiment number: SI407
Beamline:	Dates of experiments: September1998, June 1999 and December 1999	Date of report: 20/2/2000
Shifts: 3x21	Local contact(s): Vincenzo Formoso initially Bruce Cowie latterly	*Received at ESRF:* 28 FEV. 2000

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Report:

This interim report relates to a Long Term Proposal awarded in the Spring of 1998 for which the final 6-month scheduling period is still underway (and indeed the final experimental run is being conducted at the time of writing. This project is concerned with the development and application of the normal-incidence X-ray standing wave (NIXSW) method which we originally developed using the SRS at Daresbury. ID32 at the ESRF offers a combined gain in both flux and resolution which opens up entirely new applications of this general method, notably in the exploitation of 'chemical shifts' in core level photoelectron binding energies to allow chemical-state selectively in NIXSW studies, but also offering the possibility to study low coverage adsorbates systems or other adsorption structures involving weak absorbers.

Our efforts have so far focussed on testing and exploiting the chemical-shift NIXSW (CS-NIXSW) method. The experiments involve *in situ* preparation of the sample surface (low index transition and noble metals surfaces - so far Ni(111) and Cu(111) plus appropriate adsorbates) in UHV in the special end-station for this purpose which is equipped with an electron spectrometer to measure the emitted Auger and photoelectrons following X-ray absorption, and which also requires resources for *in situ* surface characterisation. Until early

1999 this work was performed in the orginal UHV system for this purpose, but its very small size was a major limitation and the low energy electron diffraction (LEED) optics never worked satisfactorily. Despite these problems, the early experiments did make great progress in developing the ESRF-specific aspects of the methodology and the software needed to analyse the chemical-state specific raw data. The scientific outcome so far is on four/five adsorption systems:

1. Ni(111)/PF_x: a prior chemical-shift photoelectron diffraction study of this system meant that this was intended to be a 'simple' model system for our first tests. Adsorbed PF_3 fragments in the SR beam, and this previous work indicated PF_3, PF_2 and PF coadsorption in atop, bridge and hollow sites respectively. Our ESRF study has shown that while this may be true at the lowest temperatures, the system in general is much more complex due to a strong temperature dependence in the surface photochemistry. A full report of the reults appeared in *Surface Science* in 1999 (**441** (1999) 515-528)
2. Cu(111)/CH_3SH; methanethiol interacts with Cu(111) through initial deprotonation to form methyl thiolate, CH_3S- in two different forms, one mainly at low temperature, one mainly at high (room) temperature. At higher temperatures further fragmentation to atomic S occurs. The CS-NIXSW results have allowed major advances in understanding this system and a manuscript describing the main findings has very recently appeared in *Physical Review Letters* (**84** (2000) 119-122)
3. Ni(111)/CH_3SH; data for this closely related system (which has also been the subject of controversy in the literature) are currently being analysed
4. (& 5.) Ni(111) and Cu(111) + SO_x; SO_2 is known to interact with these surfaces to form at least one SO_x species in addition to atomic S. Our data suggest that probably x=3 in both cases (although this is rather controversial) and provide extensive local structural information on coadsorbed SO_x/SO_2/S species. The work on Cu(111) is about to be submitted for publication and the Ni(111) paper is in preparation.

Related work measuring non-dipole photoemission asymmetry factors, needed to interpret some of the data, has been performed mainly at the SRS but also with some work at ID32. A paper describing some of this work has recently been accepted for publication in *Physical Review Letters.*

An entirely new UHV end-station for this type of experiment at ID32 was commissioned in the early summer of 1999. This chamber incoporates proper *in situ* characterisation facilities (including LEED) and should permit investigations in which knowledge of the long-range ordered surface phase is known. Our first scheduled use of the chamber was for June 1999; unfortunately, having spent 2 weeks at the beamline helping to commission the new chamber and perform pre-preparation of our samples, the main manipulator bellows sprung a large leak one day before our first day of beamtime. The manufacturers were unable to complete the repair until after the end of our beamtime, so no experiments were performed in this run. Our first actual use of this chamber was therefore in December 1999. This run was significantly hindered by beamline problems (including difficulties with two separate beams of slightly different photon energies), but did permit a far more realisric evaluation of the capabilities and limitations of the new chamber and its associated sample handling facilities. These should be invaluable in making further scientific progress in the final run of this LT award in February 2000.