ESRF	**Experiment title: Distribution of Cu 4s states in transparent conducting p-type Cu(I) oxides probed by hard X-ray photoemission spectroscopy**	**Experiment number**: **HE- 2876**
Beamline: ID16	**Date of experiment**: from: 21st January 2009 to: 24th January 2009	**Date of report**: 28th August 2009
Shifts: 9	**Local contact(s)**: Dr. Laura Simonelli	*Received at ESRF:*

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Report:

Final state wave functions for the high energy photoelectrons produced in valence band hard X-ray photoemission have a short characteristic wavelength and oscillate rapidly over the length range which characterises the radial distribution of typical valence orbitals. However the wavefunctions of n*s* valence orbitals with $n \geq 4$ are highly penetrating, with rapidly oscillating inner radial maxima whose length scale may better match the final state wavefunctions. Thus the inner part of the n*s* wavefunction provides a contribution to the dipole matrix elements that determine ionisation cross sections that decays less rapidly with increasing photon energy than is typical for non penetrating orbitals such as O 2*p*. It follows that the n*s* contribution to the partial density of states is selectively enhanced at high photon energies. In previous work on beamline 16 of the ESRF we have established that that there is indeed a significant enhancement in the relative intensity of features associated with electronic states with significant metal *s* character in photoemission spectra of simple oxides measured at high photon energies [1-3]. This finding has aroused widespread interest and a publication from our group published in Physical Review Letters in April last year based on work on the ESRF has already received 23 citations [1].

The objective of the current experiment was to extend this work to study the distribution of metal 4*s* states in p-type transparent conducting oxides based on Cu(I) including Cu_2O itself and $CuCrO_2$. Prior to the experimental run we had completed high quality band structure calculations on Cu_2O and $CuCrO_2$ to provide a basis for interpretation of the hard XPS data [4-6].

Unfortunately during our experimental run electronic instabilities in one of the power supplies to the hard x-ray electron spectrometer endstation prevented us from obtaining definitive valence band photoemission spectra on the Cu oxides as intended. The nature of the electronic problems were however identified after our beamtime had finished. However during the course of our investigation of the origins of the instabilities we were able to obtain high quality hard X-ray photoemission data from a single crystal thin film of In_2O_3 with (111) orientation and a very low carrier density. Conventional X-ray photoemission spectra of this sample showed a well defined feature associated with occupied conduction band states in an electron accumulation layer about 5 nm thick. The conduction band states have substantial In 5*s* character and in a flat band situation would be selectively enhanced in HXPS. However the conduction band feature is actually weaker at $h\nu$ = 6000 eV than at $h\nu$ = 1486.6 eV. This is a consequence of the longer electron

pathlength at high photon energy and the consequent reduction in the contribution of the accumulation layer region to the overall spectrum. This experiment therefore provided definitive evidence of an accumulation layer, in agreement with our recent proposal published in Physical Review Letters last year [7]. This work is now in press in Chemistry of Materials [8].

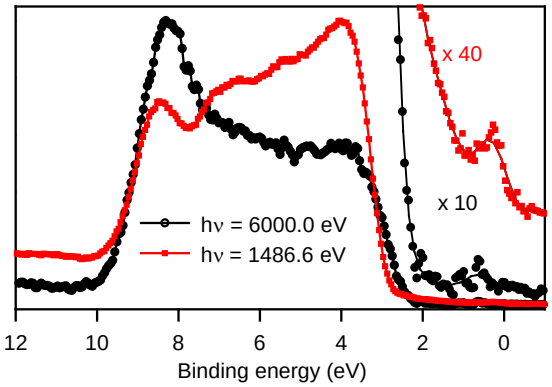

Figure 1. Valence band XPS of In_2O_3(111) on Y-ZrO_2(111) excited at 1486.6 eV and 6000.0 eV photon energies. The peak at 9 eV binding energy is associated with O 2p states strongly hybridised with In 5s states and undergoes pronounced enhancment in relative intensity at high photon energy. By contrast the peak close to the Fermi energy which is asscociated with conduction band states also with pronounced In 5*s* character (after allowance for cross section effects) is reduced in intensity at 6000 eV. This provided evidence for carrier accumulation close to the surface in this sample. The differing expansions of the conduction band structure at the two different photon energies corrects for cross section effects.

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