



**Experiment title: A study of band bending at SnO<sub>2</sub> and In<sub>4</sub>Sn<sub>3</sub>O<sub>12</sub> surfaces**

**Experiment number:**  
HE3306

<b>Beamline:</b> ID16	<b>Date of experiment:</b> from: 27/02/ 2010 to: 04/03/ 2010	<b>Date of report:</b> 28/09/2010
<b>Shifts: 12</b>	<b>Local contact(s):</b> Dr. Roberto Verbeni, Dr. Giulio Monaco	<i>Received at ESRF:</i>

**Names and affiliations of applicants (\* indicates experimentalists):**

R.G. Egdell<sup>a</sup>, Dr. D.J. Payne<sup>a\*</sup>, Dr. G. Panaccione<sup>b</sup>, P. Torelli<sup>\*c</sup>, F.Offi<sup>\*d</sup>, F. Borgatti<sup>\*e</sup>

<sup>a</sup>Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK

<sup>b</sup>Laboratorio TASC, INFN-CNR, Area Science Park, S.S. 14, Km 163.5, 34012 Trieste, Italy

<sup>c</sup>CNR-INFN-S3, Via Campi 213/A, I-41100 Modena, Italy

<sup>d</sup>CNISM and Dip. di Fisica, Universita Roma Tre, Via della Vasca Navale 84, I-00146 Roma, Italy

<sup>e</sup>TASC-INFN National Laboratory, S.S. 14, Km 163.5 in Area Science Park, 34012 Basovizza, Trieste, Italy

## Report:

### Aims of the experiment and scientific background.

Transparent conducting electrodes are an important component of liquid crystal and electroluminescent display devices, but there is also a rapidly growing demand for transparent electrodes in solar cells. Tin doped indium oxide (also known as indium tin oxide or ITO) is the material of choice in many of these areas of application, but the world supply of indium is limited and the metal has become a precious commodity with prices at one stage almost reaching levels of \$1000/kg. There is therefore a growing interest in development of transparent conducting oxides with a lower or zero indium content. Amongst these SnO<sub>2</sub> and In<sub>4</sub>Sn<sub>3</sub>O<sub>12</sub> are of particular interest because the cost of tin is only around \$15/kg: even though In<sub>4</sub>Sn<sub>3</sub>O<sub>12</sub> is not indium-free the metal cost is reduced by 42% as compared to In<sub>2</sub>O<sub>3</sub>. Based in part on experiments conducted on the ESRF we have recently shown that the transparency of In<sub>2</sub>O<sub>3</sub> arises from the fact that although the bandgap lies within the visible region (2.7 eV), optical transitions from states within 1eV of the top of the valence band are either dipole forbidden or have very weak dipole intensity, so that the onset of strong optical absorption is shifted to 3.7 eV [1,2]. At the same time the very strong dispersion of the conduction band gives rise to a charge neutrality level that lies well above the conduction band minimum. This ensures a high intrinsic dopability. A further consequence of the position of the charge neutrality level is that the Fermi level at In<sub>2</sub>O<sub>3</sub> surfaces is pinned above the conduction band minimum by surface states and gives rise to spontaneous carrier accumulation at surfaces of In<sub>2</sub>O<sub>3</sub> with low bulk doping levels: the space charge region is typically around 5 nm thick [3]. Band bending of this sort is important in determining the performance of transparent conducting oxides in devices involving junctions between the oxide and other active layers of the device. The aim of the current experiments was to extend the work on In<sub>2</sub>O<sub>3</sub> to SnO<sub>2</sub> and In<sub>4</sub>Sn<sub>3</sub>O<sub>12</sub>, combining the synchrotron results with conventional Al K $\alpha$  photoemission. Both of these materials are

potential lower cost alternatives to  $\text{In}_2\text{O}_3$ .  $\text{SnO}_2$  has a bandgap of 3.6 eV and  $\text{In}_4\text{Sn}_3\text{O}_{12}$  a lower gap of 2.71 eV, very close to that of  $\text{In}_2\text{O}_3$  itself [4].

## Results and discussion.

Hard X-ray photoemission spectra (HAXPES) of  $\text{SnO}_2$  and  $\text{In}_4\text{Sn}_3\text{O}_{12}$  were measured using excitation at  $h\nu = 6989$  eV. The valence band spectra are shown in figure 1 along with earlier HAXPES data for  $\text{In}_2\text{O}_3$  [1,5] and conventional Al  $K\alpha$  data for all three compounds. As we have demonstrated in a recent publication [5] electronic states with substantial metal 5s character are selectively enhanced relative to states of pure O 2p character upon switching from  $h\nu = 1486.6$  eV to photon energies of 6 keV or higher. Thus for all three materials the structure at the bottom of the valence band associated with bonding states arising from in-phase mixing between O 2p and metal (In, Sn) 5s states is strongly enhanced in HAXPES relative to states at the top of the valence band. By contrast there is no enhancement in the relative intensity of states close to the Fermi energy arising from partial occupation of the conduction band, even though these states also have very significant metal 5s character.

These observations provide confirmation of the hypothesis that the conduction band photoemission intensity in conventional XPS for these nominally undoped materials arises from carrier accumulation at the surface due to downward band bending. Conventional XPS is dominated by the space charge region but the inelastic electron mean free path is much bigger in HAXPES so that the technique probes beyond the space charge region into the bulk of the material where the carrier concentration is lower.

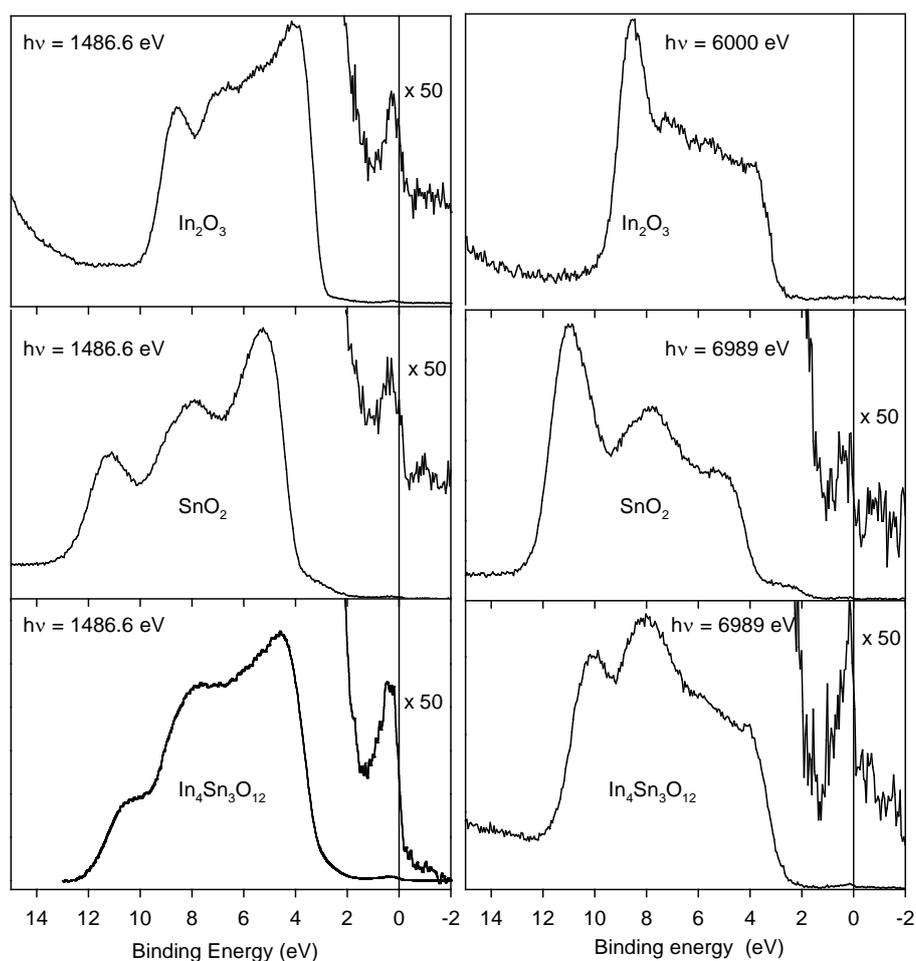


Figure 1. Conventional Al  $K\alpha$  XPS and HXPES of  $\text{In}_2\text{O}_3$ ,  $\text{SnO}_2$  and  $\text{In}_4\text{Sn}_3\text{O}_{12}$  measured in the valence band region. The  $\times 50$  expansions show structure associated with occupation of the conduction band.

This work is currently being written up for publication in Physical Review B and was presented at the EMRS Fall Meeting held in Poland in September 2010.

## References.

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