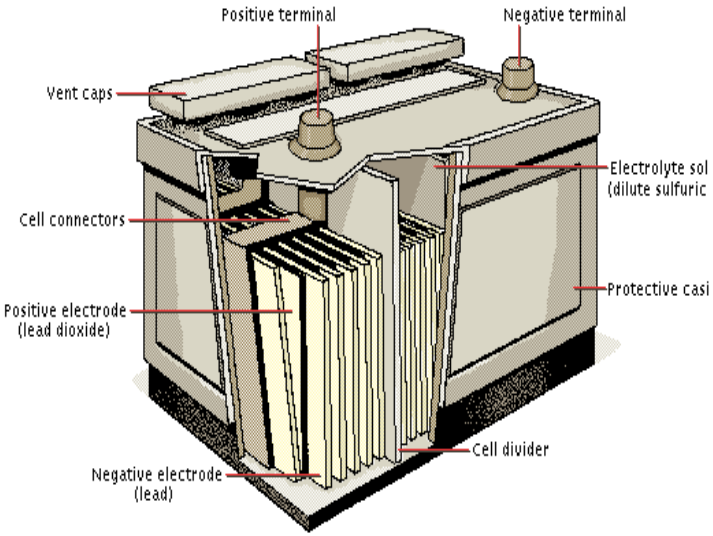
PROBING S ELECTRON STATES IN METAL OXIDES WITH HARD X-RAY PHOTOEMISSION

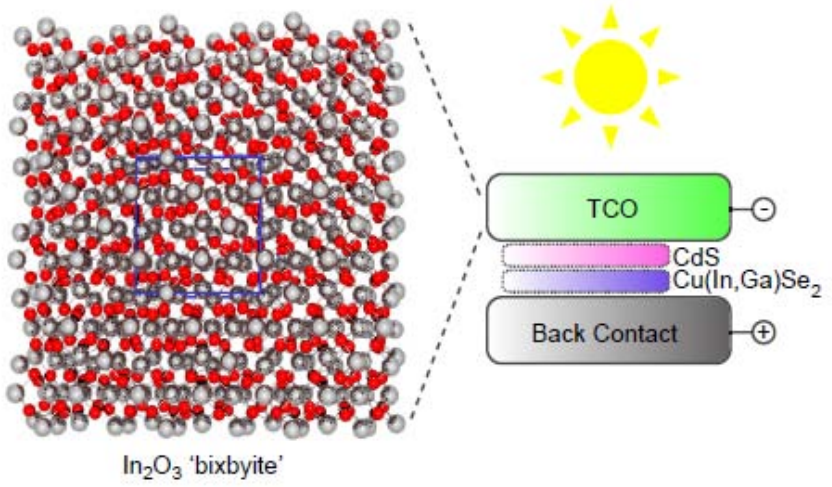
D. J. Payne[1] , K.H.L Zhang[1], G. Panaccione[2] and **R.G. Egdell[1]**

(1) University of Oxford, Inorganic Chemistry Laboratory, S. Parks Road, Oxford OX1 3QR, UK

(2) IOM-CNR , Lab. TASC, S.S. 14, Km 163.5, 34149 Trieste, Italy



PbO_2

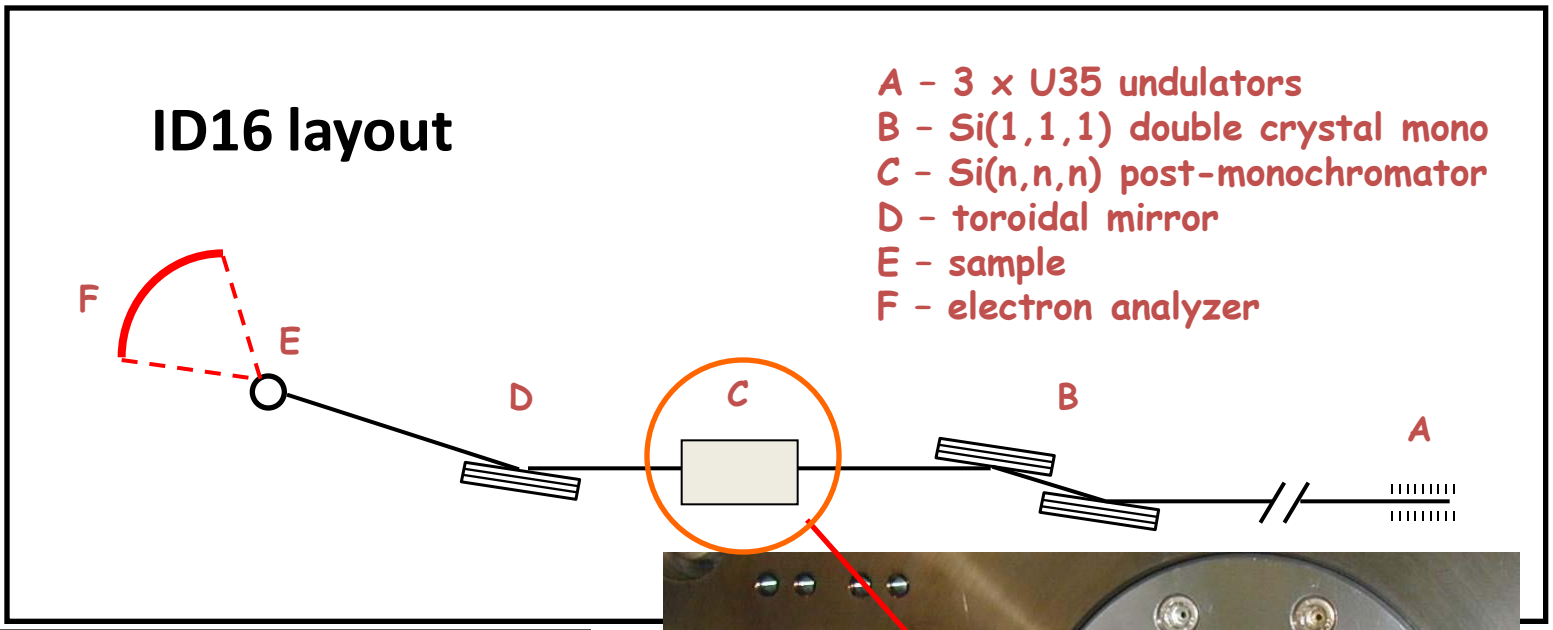


In_2O_3

UNIVERSITY OF OXFORD

The VOLPE experiment on ID16 of ESRF (Grenoble, France)
Beamline designed for inelastic X-ray scattering

p polarised
θ = 45°
45° incidence



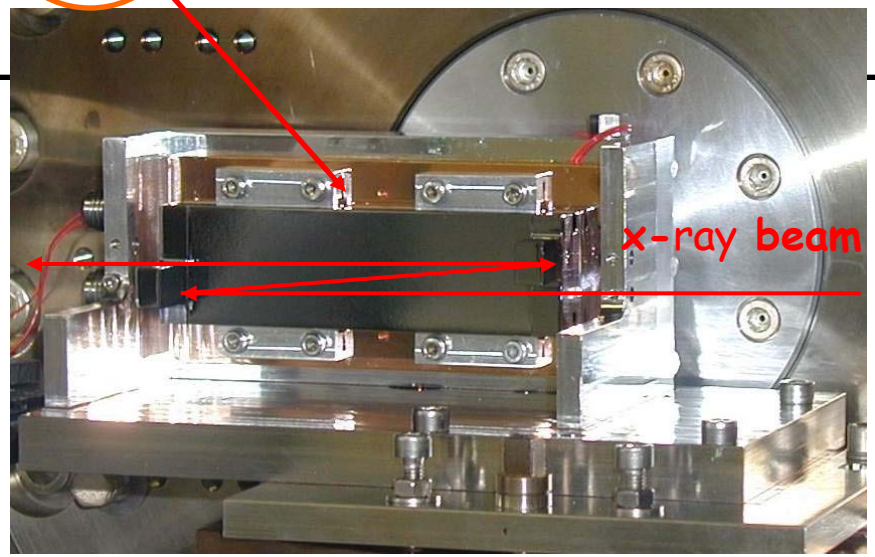
Channel-cut in backscattering (87°)

(4,4,4) @ 8 keV:

ΔE=40 meV & $6 \cdot 10^{11}$ ph/sec/100 mA

(5,5,5) @ 10 keV:

ΔE=15 meV & $2 \cdot 10^{11}$ ph/sec/100 mA



VOLPE spectrometer

MB SCIENTIFIC AB

Dispersive element

(Univ. Rome III and INFM)

Input lens

High retarding factor

Constant linear mag.

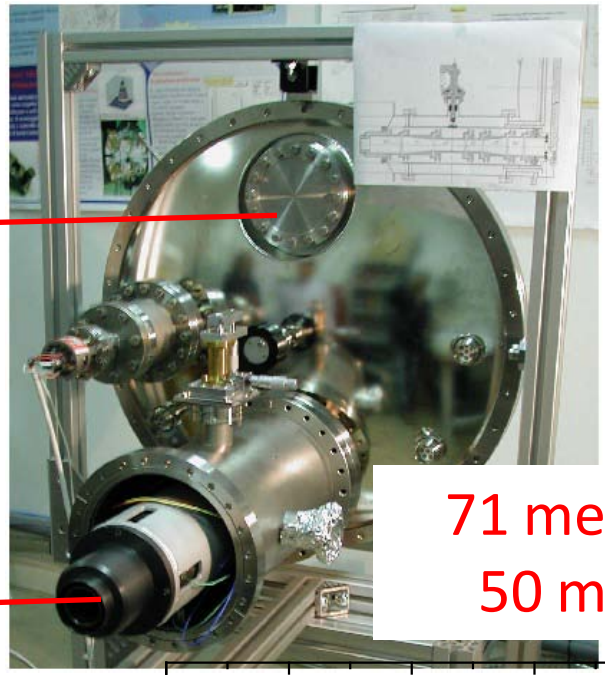
Small field of view

(ELETTRA)

2D delay line detector

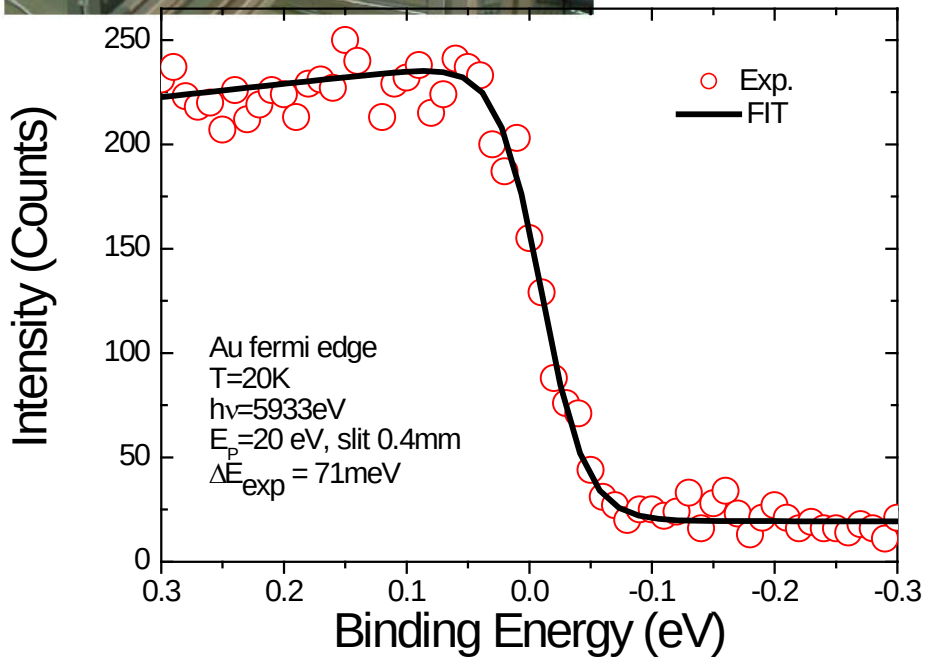
High stability power supplies

Working resolution in our experiments was 200 meV – 300 meV



71 meV @ 5933 eV

50 meV analyser



P. Torelli *et al*. Rev. Sci. Instr. 76, 023909 (2005)

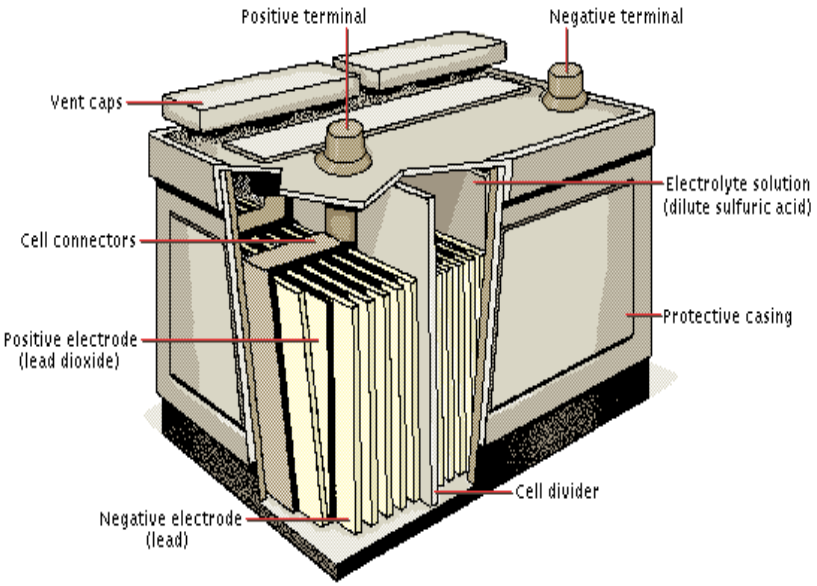
F. Offi *et a*l. NIM A, 550, 454 (2005)

G. Panaccione *et al*. NIM A 547, 56 (2005)

Metallic lead dioxide and the operation of lead-acid batteries

* PbO_2 is the medium for storage of chemical energy in lead-acid batteries.

* These batteries are still used in cars despite environmental problems.



** Discharge Process*

$$Pb + PbO_2 + 2HSO_4^- + 2H^+ \longrightarrow 2PbSO_4 + 2H_2O$$

$E° = 2.04$ V

* PbO_2 is a metallic conductor.
This is crucial to the ability of lead-acid batteries to deliver very large currents needed to turn over a starter motor.

Why is lead dioxide metallic with a carrier density of about 1-2 x 10^{21} cm^{-3} ?

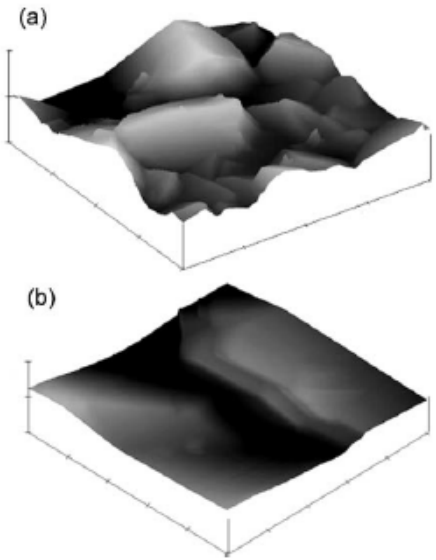
HAXPES of β-PbO_2

β-PbO_2 films prepared by electrochemical deposition on Pt discs.

Deposited from solution of 0.4M $Pb(NO_3)_2$ in 0.1M HNO_3. A current density of around 10mA cm^{-2} at 60°C gives β-PbO_2 with good phase purity.

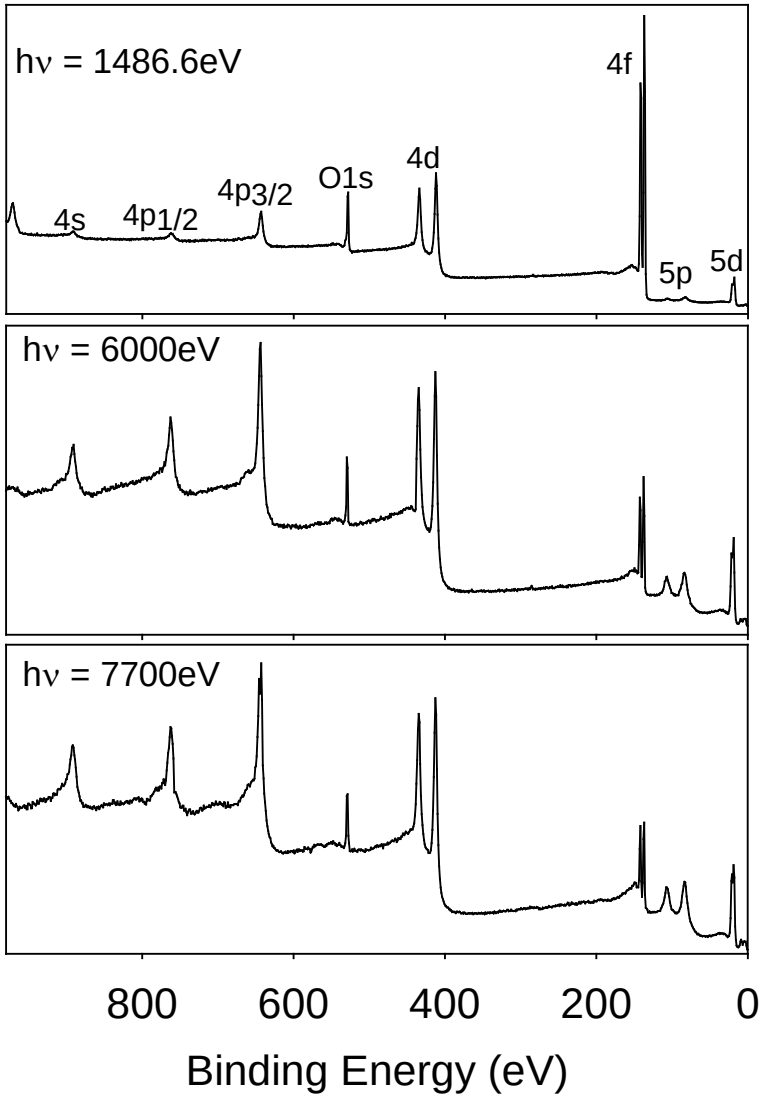
Rutile structure with predominant (110) texture.

Decomposes in air above 293°C to give the defect fluorite $Pb_{12}O_{19}$

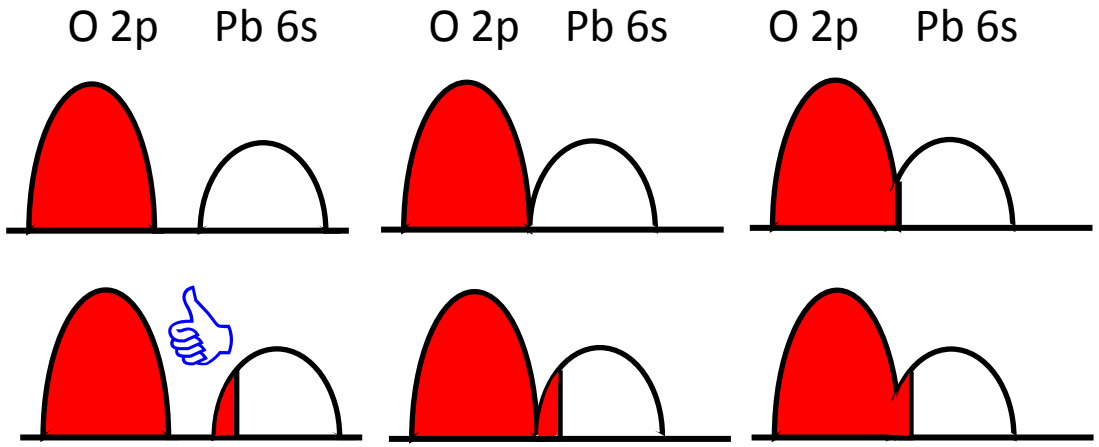


(a) AFM image of β-PbO_2 (20x20 μm).

(b) Image of same sample (5x5 μm).



Why is PbO_2 metallic?

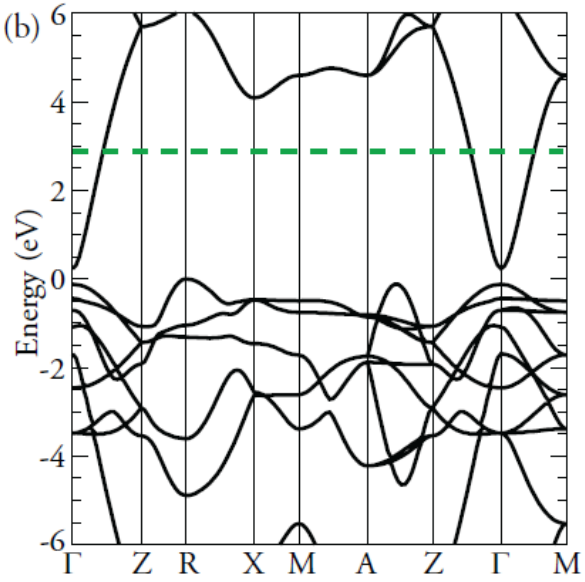


Stoichiometric PbO_2
($SnO_{2.0}$ is a 3. 6eV gap insulator)

With electrons in CB
introduced by donor defects
e.g. O vacancies

- O vacancies have low formation energy.
- O vacancies act as 2e donors resonant with conduction band.
- Oxygen site occupancy measured to be 0.984 by time of flight neutron diffraction.
- 1.6% O site vacancies gives carrier concentration of *1.5 x 10^{21} cm^{-3} .*

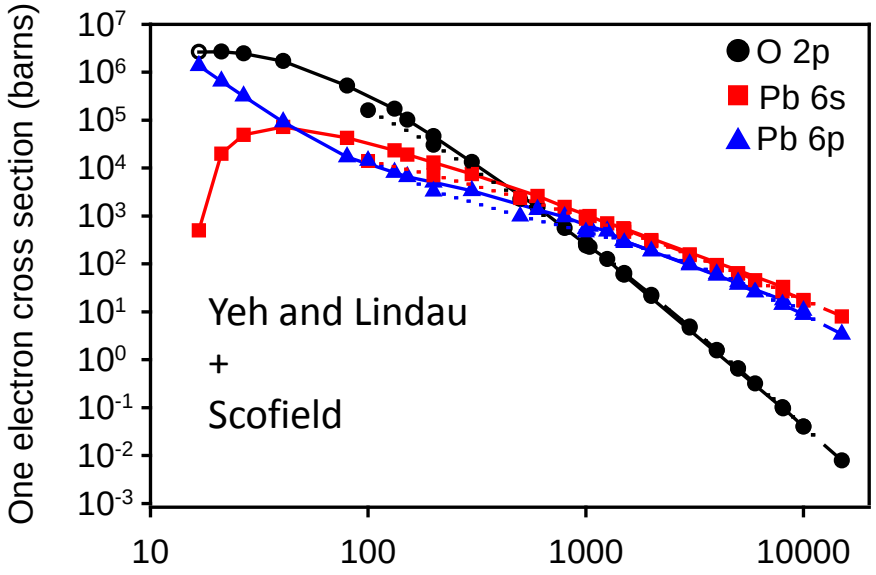
- *(Walsh et al., unpublished)*

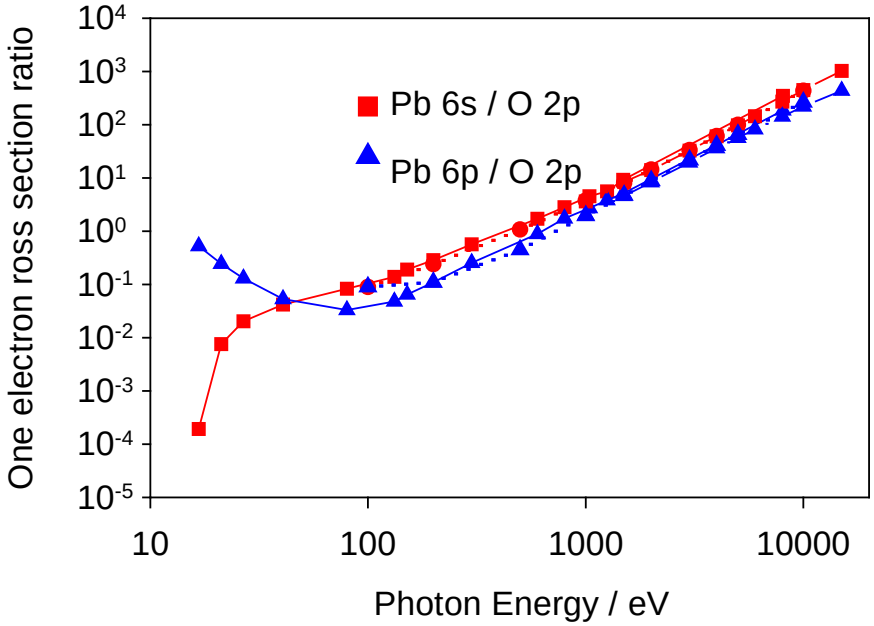


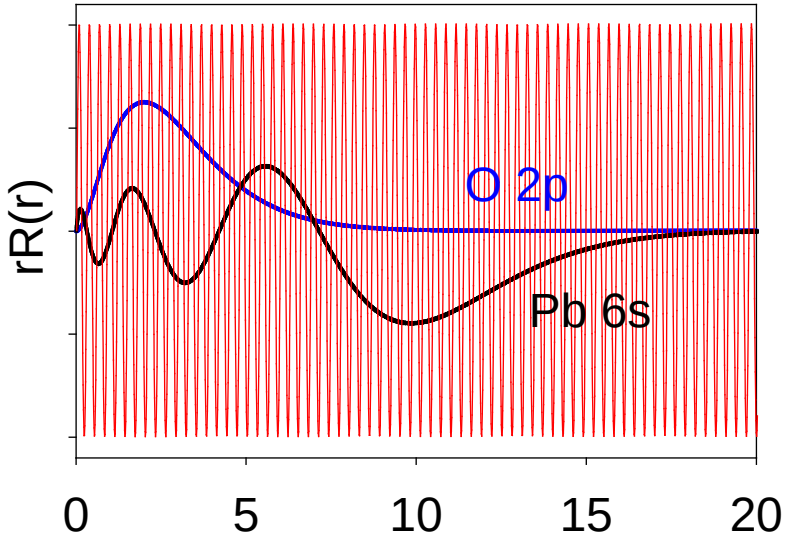
charge neutrality level

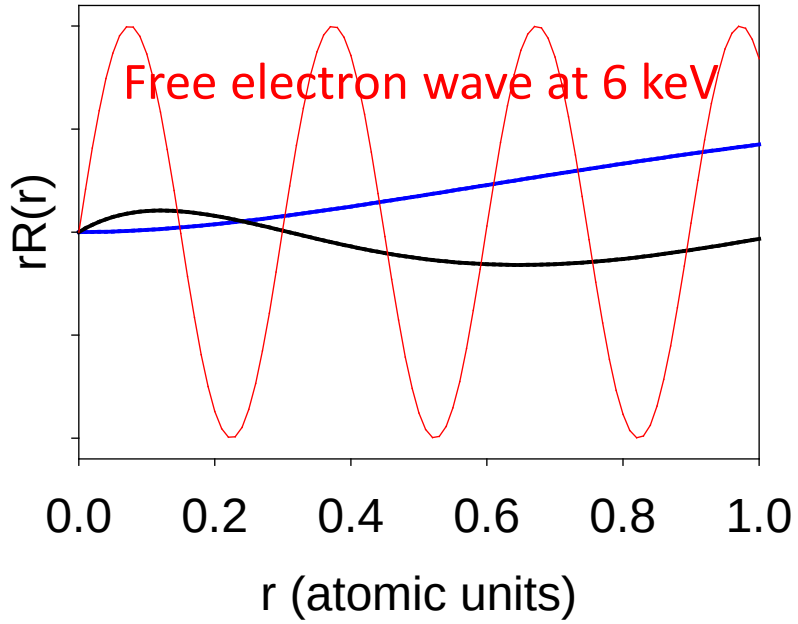
HSE06 Hybrid functional

Ionisation cross sections at high photon energies

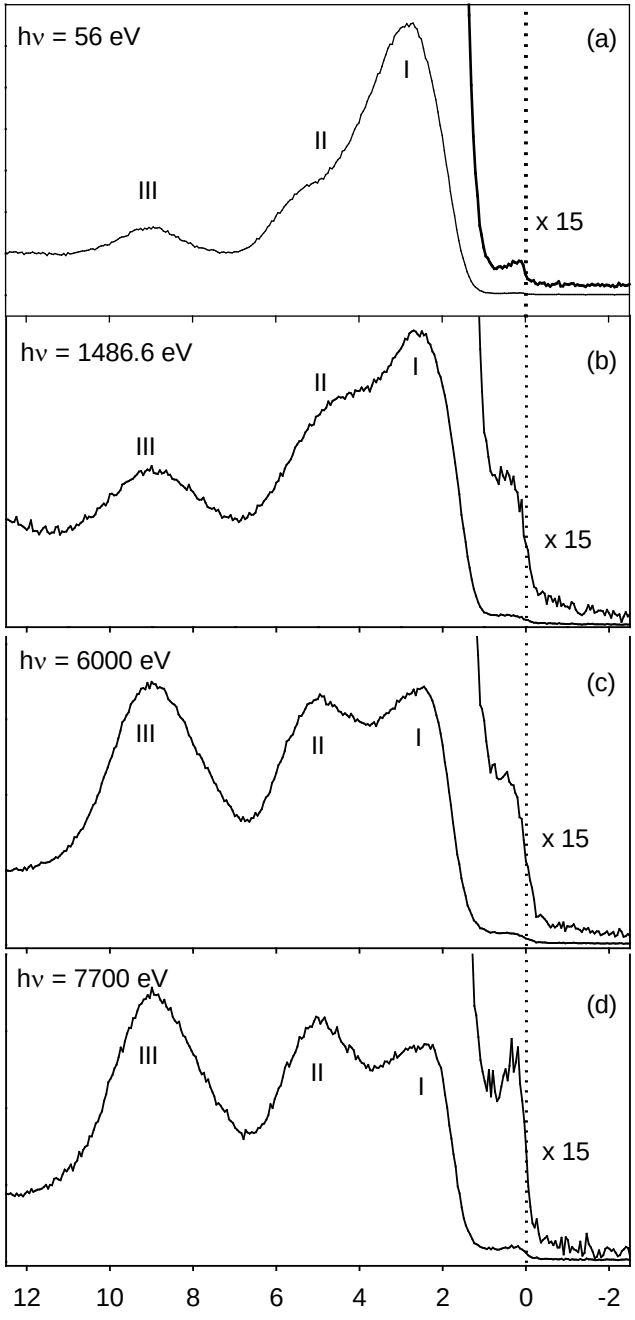




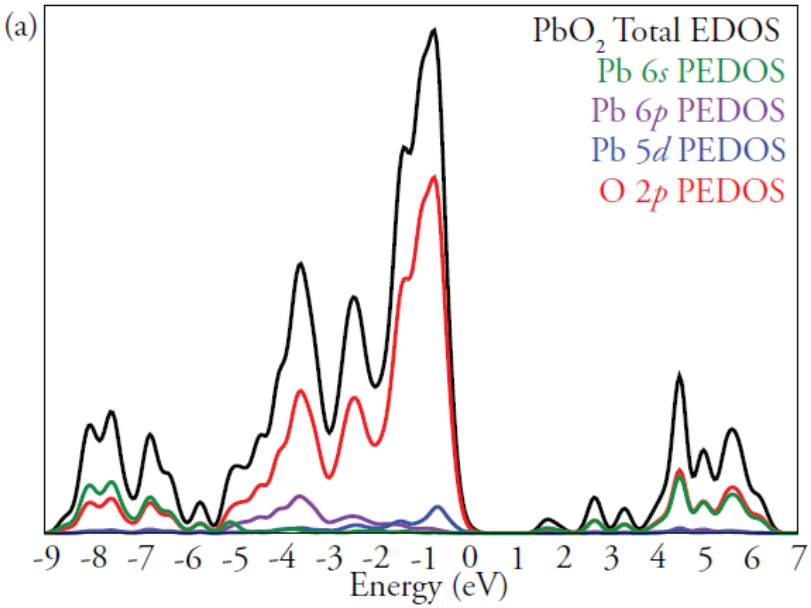


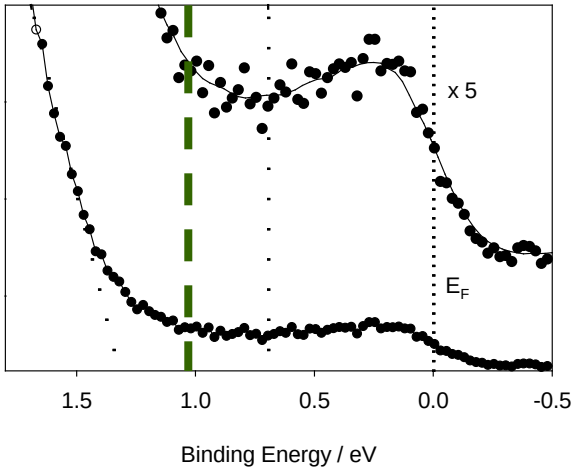


Valence and conduction band HAXPES of β-PbO_2



HAXPES
p polarised
θ = 45°
45° incidence

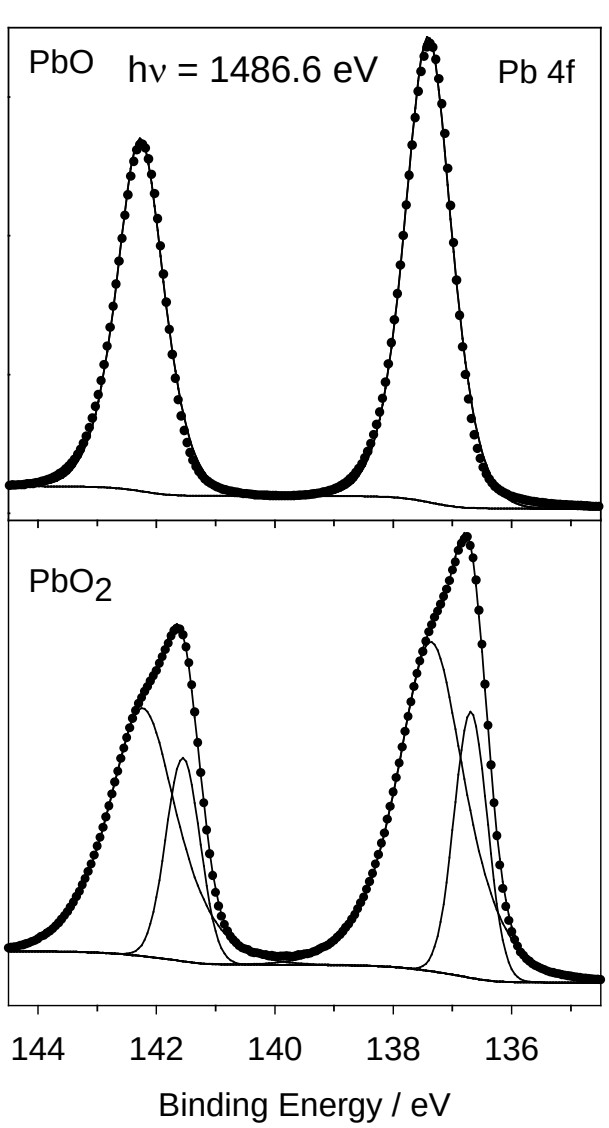


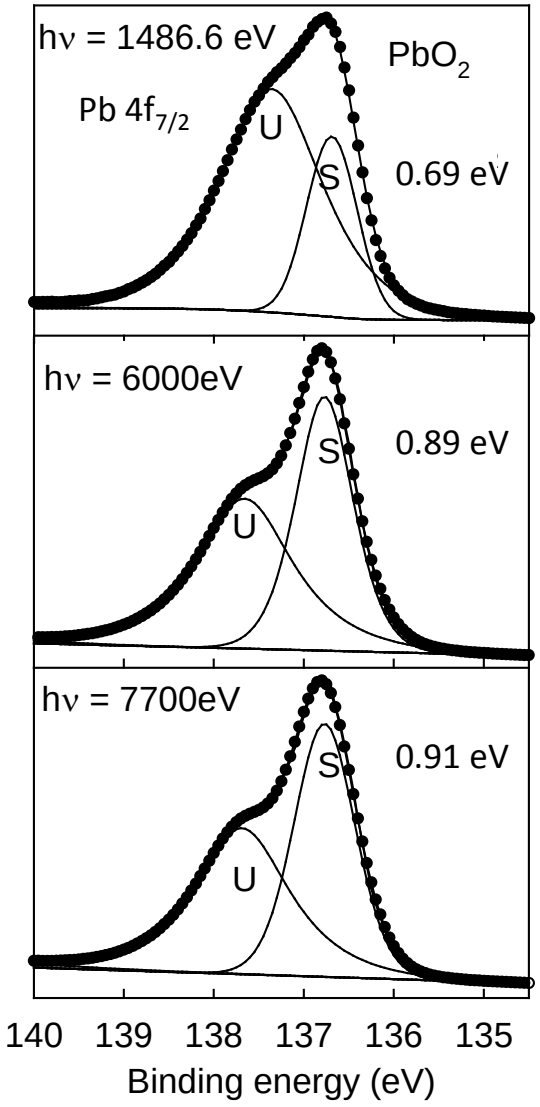


PRB 2007 **75** 153102

And to be published

Satellite structure in core XPS of β-PbO_2





Two-peaked core level structure due to final state screening effects in metallic β-PbO_2.

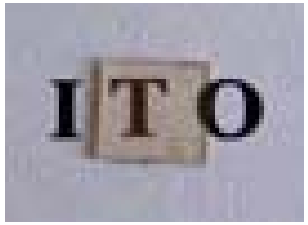
Screened final state structure enhanced in HXPS and moves to higher energy

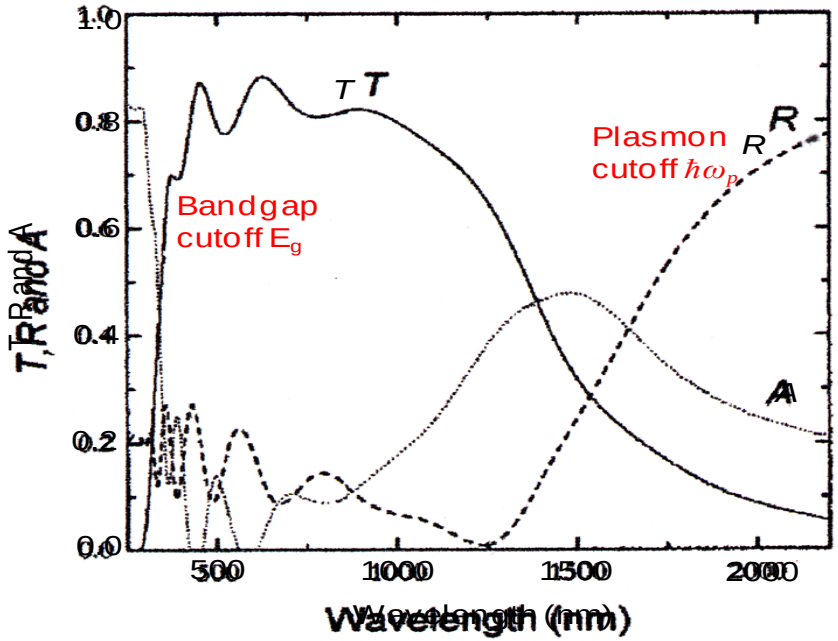
Transparent conducting oxides (TCOs)

* TCOs combine properties of high conductivity with optical transparency in the visible region.

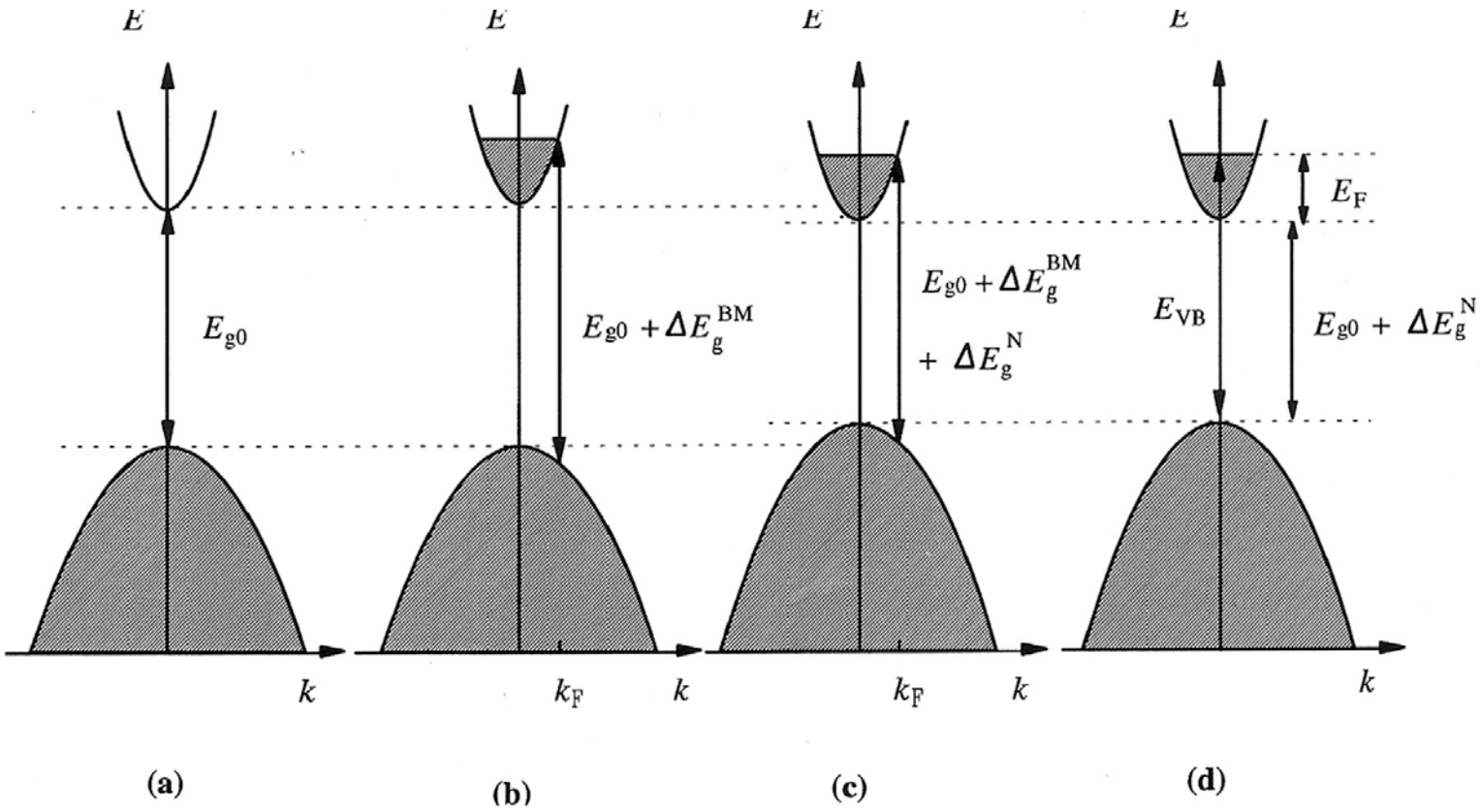
* Sn-doped In_2O_3 aka ITO is one of the most important TCOs with applications in liquid crystal displays, solar cells, electroluminescent display devices etc.

* Ongoing controversy about the bandgap of In_2O_3 until 2008





The influence of doping on electronic structure and optical absorption in In_2O_3 and related TCOs

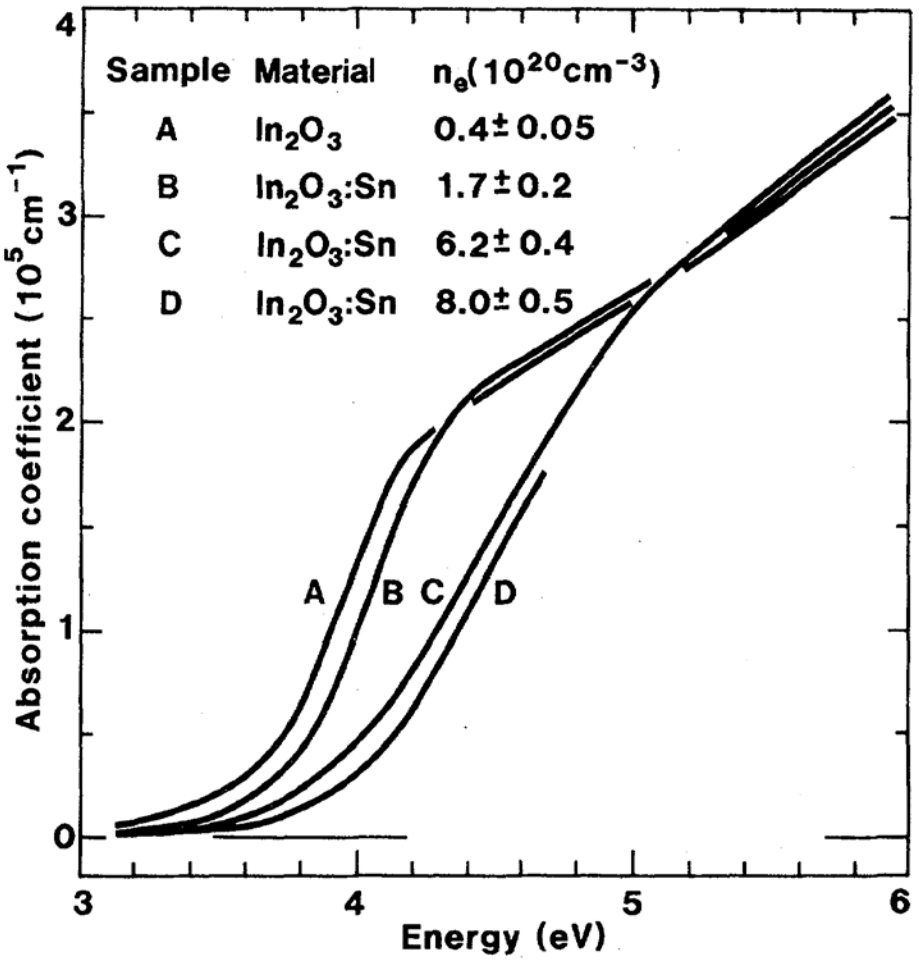


In 5s conduction band

O 2p valence band

(a) Undoped oxide.
(b) Degenerately doped oxide with rigid bands.
(c) After bandgap renormalisation. Information from optical absorption.
(d) After bandgap renormalisation. Information from photoemission.

Effect of doping on band gap in ITO



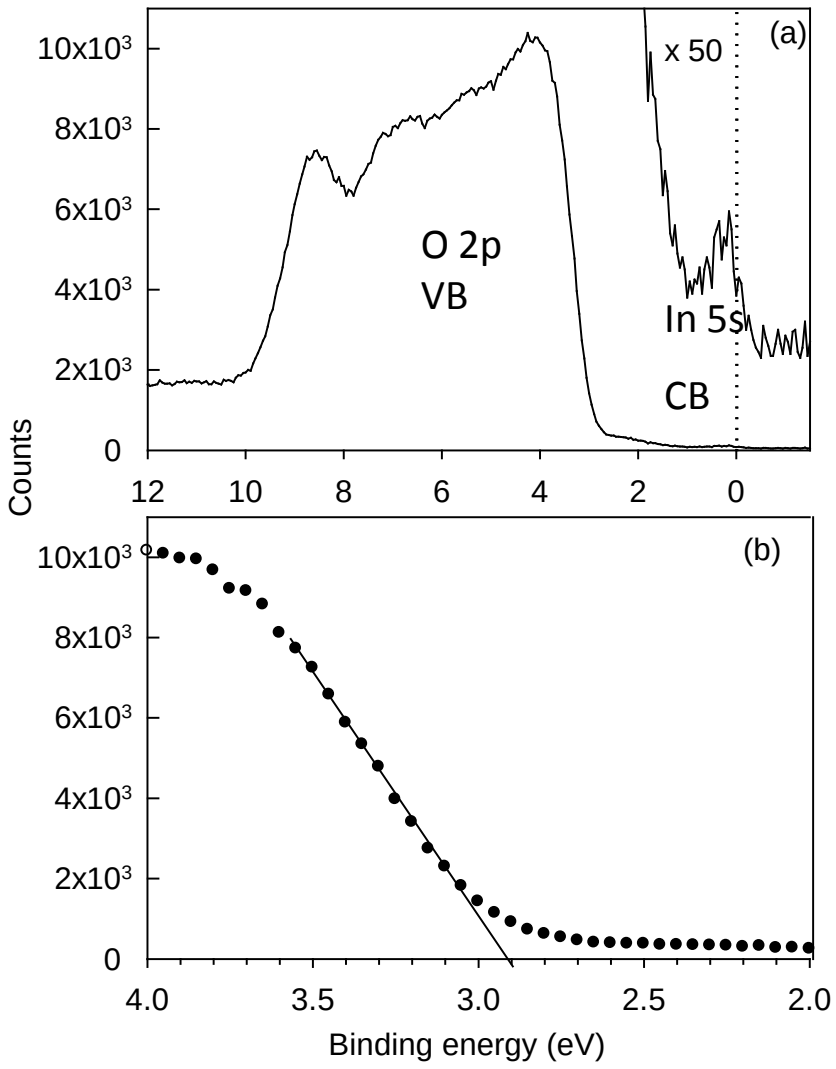
Hamberg *et al.*,
Phys. Rev. B 1984 **30** 3420.

Bandgap widens with increasing doping.

The "bandgap" of undoped In_2O_3 was inferred to be 3.75 eV and this value has been widely quoted ever since.

>12,500 papers on ITO and indium oxide films since 1985 – where bandgap is quoted, values usually between 3.5 eV and 3.8 eV.

Al Kα Photoemission of Nominally Undoped In_2O_3(001) MBE Film



Valence band edge is found at 2.9 eV below Fermi level.

This is almost 1 eV less than the widely quoted bandgap of 3.75 eV even though the conduction band appears to be partially occupied with an effective carrier concentration in the near surface region of around 2×10^{20} cm^{-3}. This would place the Fermi energy about 0.33 eV above the bottom of the conduction band and widen the optical gap.

Note that bulk doping level is only 7×10^{18} cm^{-3}

Similar results from polycrystalline thin films and (111) oriented thin films.

J. Appl. Phys. 2000 **88** 5180
Appl. Phys. Lett. 2008 **92** 092117

Does In_2O_3 have an indirect gap below 3.75 eV?

JOURNAL OF APPLIED PHYSICS VOLUME 37, NUMBER 1 JANUARY 1966

Optical Properties of Indium Oxide

R. L. Weiher and R. P. Ley
Central Research Laboratories, Minnesota Mining and Manufacturing Company, St. Paul, Minnesota

(Received 12 August 1965)

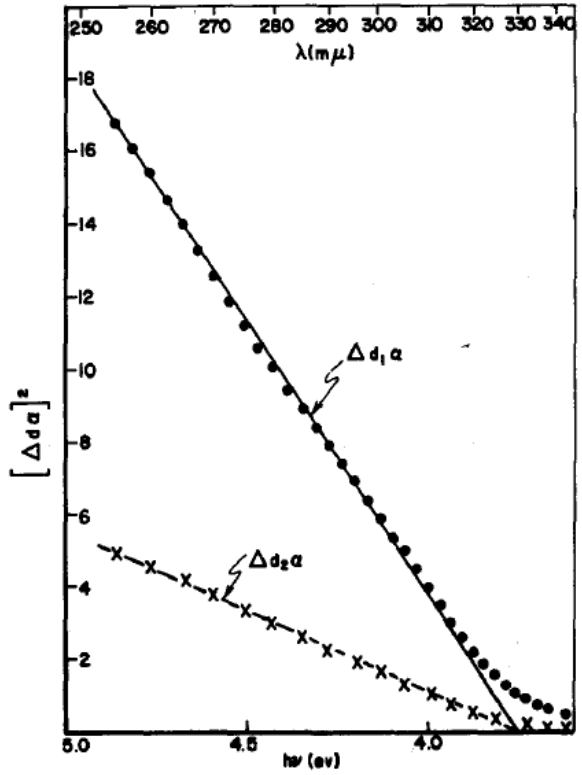


FIG. 1. Square of the absorption coefficient of indium oxide thin films as a function of photon energy.

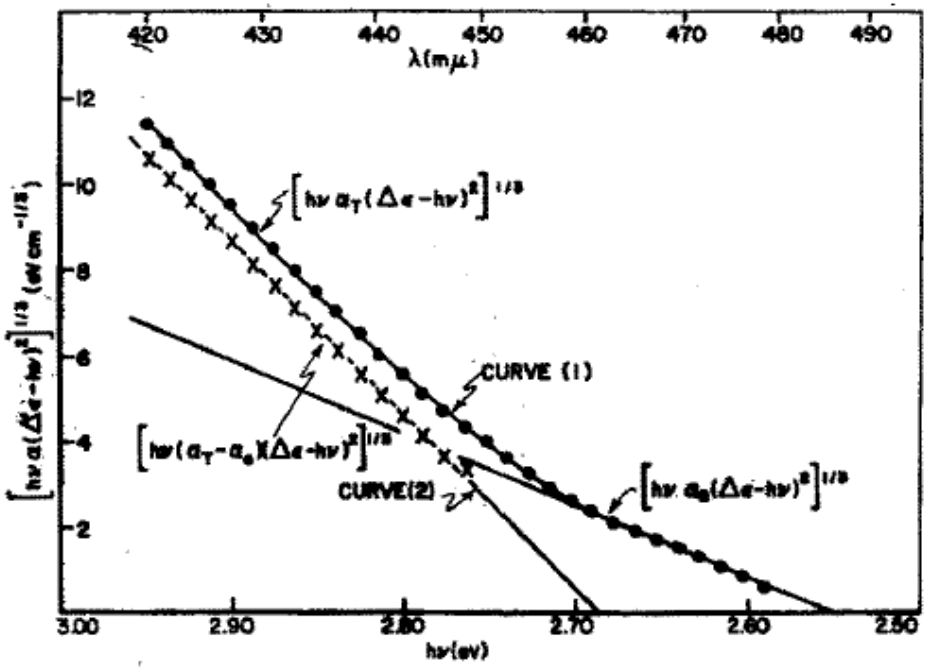
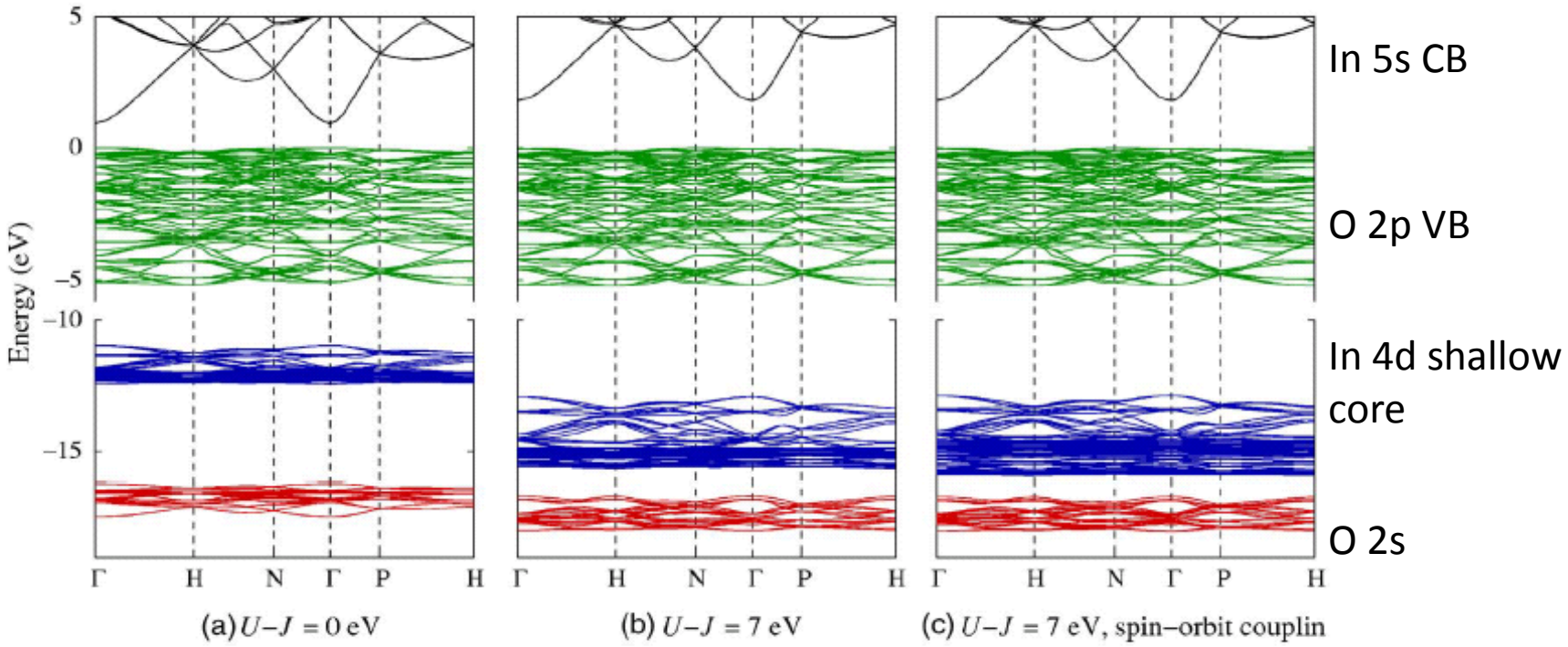


FIG. 5. Graphical analysis of absorption data (shown in Fig. 4) denoting forbidden-indirect transitions.

Does shallow core hybridisation give an indirect gap in In_2O_3?



The answer is no!

P Erhart, A Klein, R G Egdell and K Albe, Physical Review B 2007 **75** 153205

The Klein Model for the Band Edge Position in In_2O_3 and ITO

PHYSICAL REVIEW B 73, 245312 (2006)

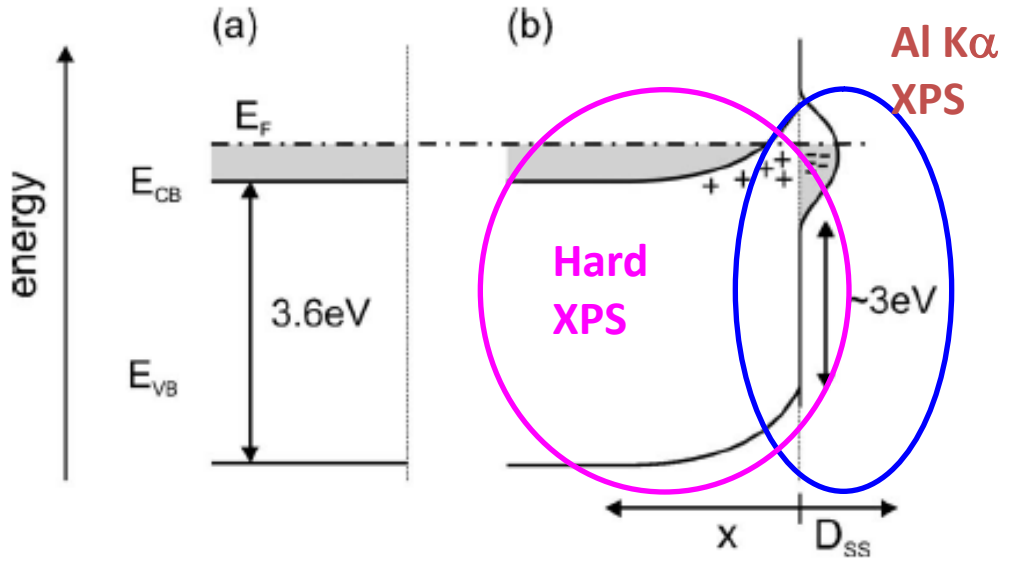
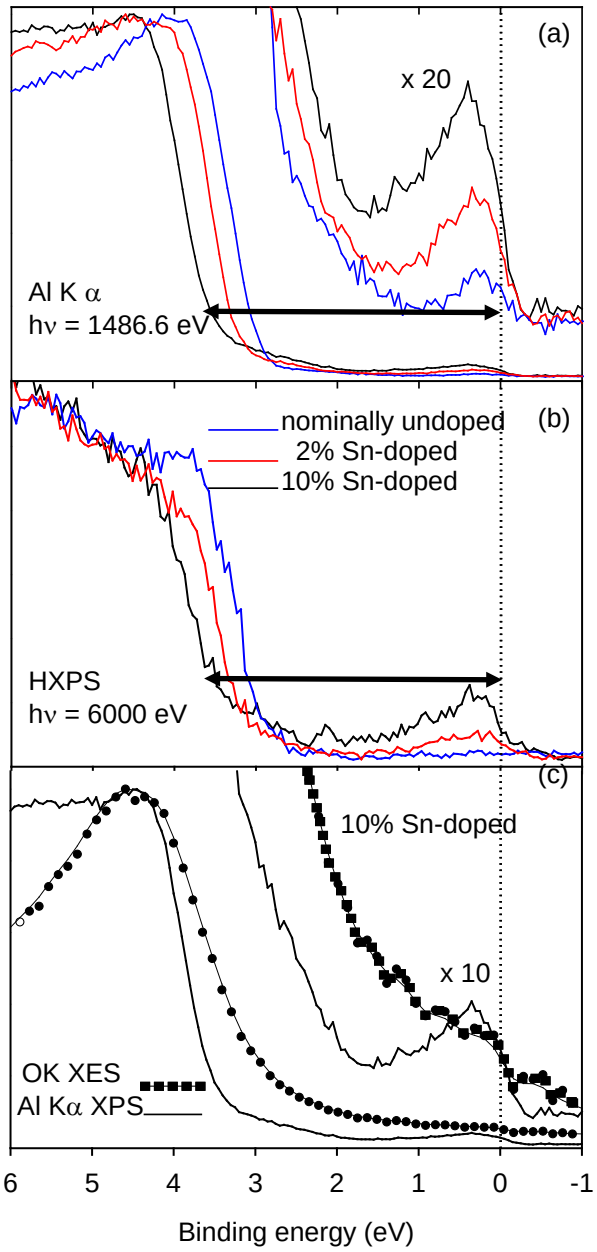


FIG. 8. Possible surface potential distributions leading to the observation of photoelectron emission at the Fermi level from a degenerately *n*-doped semiconductor. (a) Flat band situation: the Fermi level at the surface is inside the conduction band as in the bulk of the material; (b) Surface potential drop: the emission can only occur if a high density of surface states is present at the Fermi energy compensating for the space charge.

If this model is correct we might expect to observe a shift in the position of the valence band edge on changing the excitation energy in photoemission from the Al Kα value of 1486.6 eV to "hard" X-ray energies above 6000 eV – hard XPS is much less surface sensitive.



Photoemission and XES of In_2O_3

*The valence band onset in XPS of nominally undoped In_2O_3 is less than 3eV below the Fermi energy, suggesting a bandgap of about 2.9 eV after allowance for surface doping and experimental broadening of VB onset.

* Doped ITO shows Moss-Burstein type shifts.

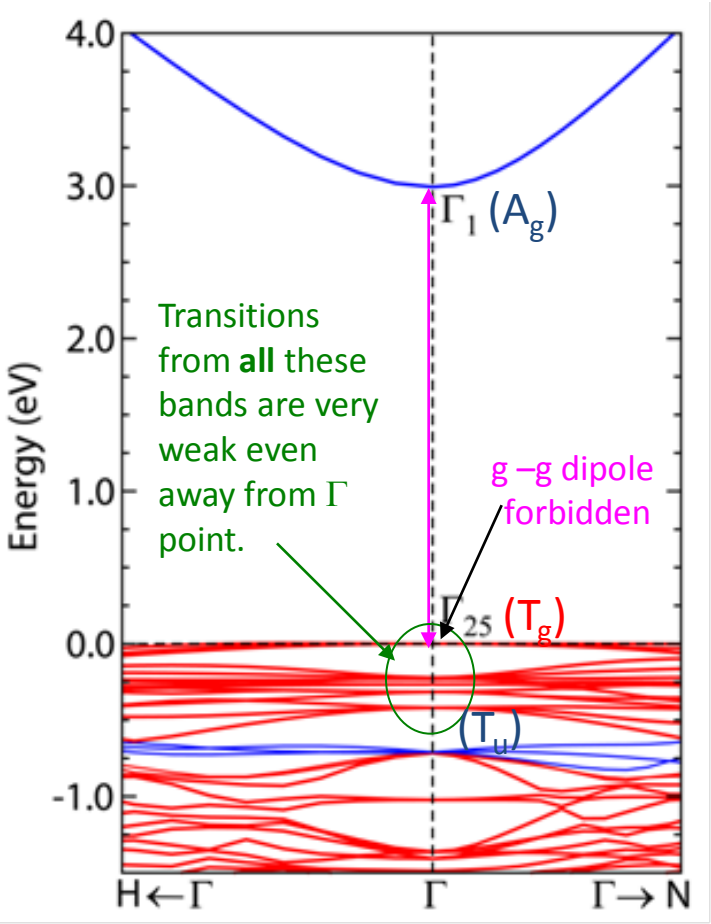
*The same onset energies are observed in hard XPS of doped ITO samples excited at 6000 eV photon energy even though this technique is much less surface sensitive.

*The same energy referencing pertains in XES which is not at all surface sensitive.

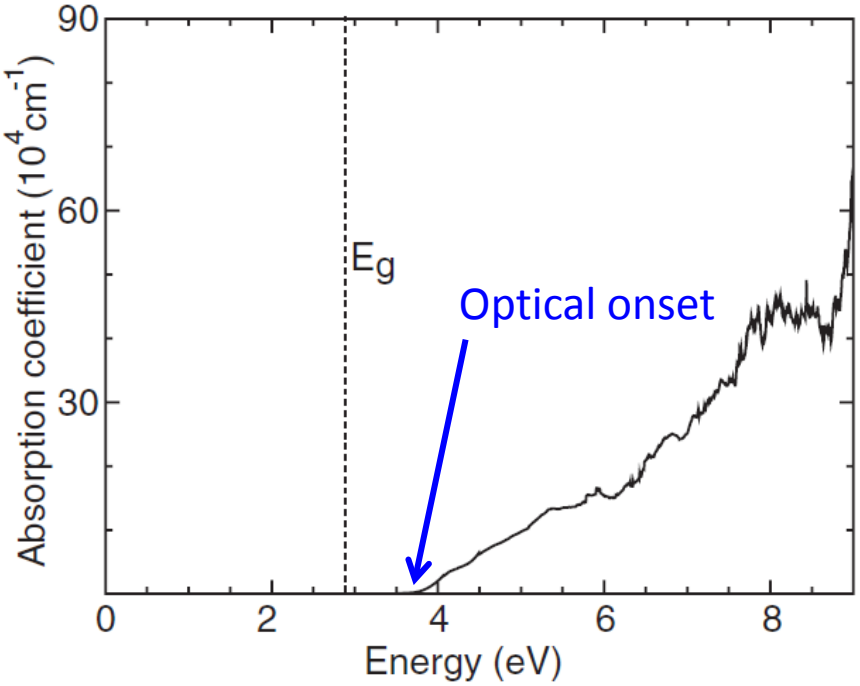
* Hybrid exchange DFT or screened exchange DFT give bandgaps of around 2. 6 eV – 3.0 eV, i.e. much lower than 3.75 eV and in agreement with X-ray spectroscopy but not optical data.

PRL 2008 **100** 167402

Resolution of the bandgap problem for In_2O_3



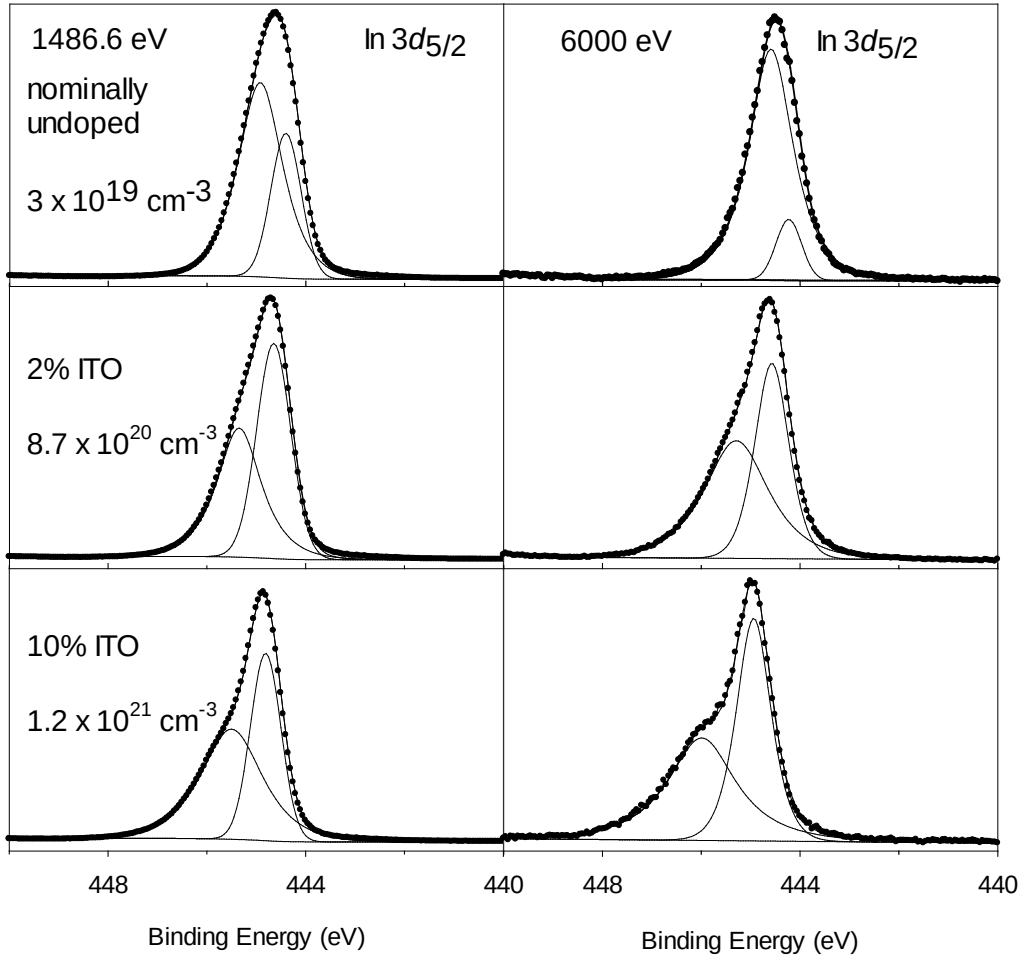
Band structure of In_2O_3 (along of the H-Γ-N lines). The highest energy valence band states promoting strong optical absorption into the conduction band are coloured blue.



Absorption spectrum of bulk In_2O_3, calculated with a fundamental band gap of 2.9 eV. Note that the onset of optical absorption is 0.8 eV higher in energy.
Optical transitions from the first 5 valence bands are all extremely weak across all k space.

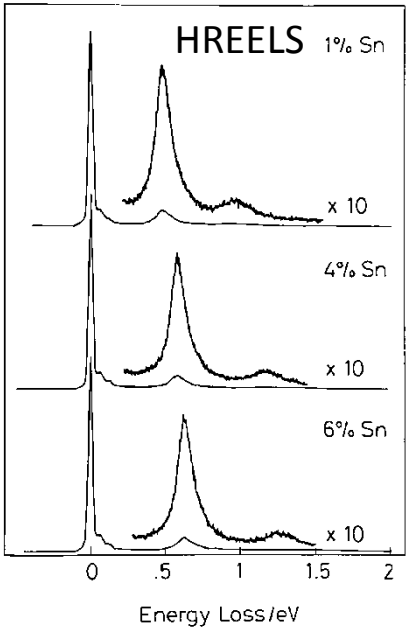
PRL 2008 **100** 167402

Satellites in core XPS of degenerately doped indium oxide



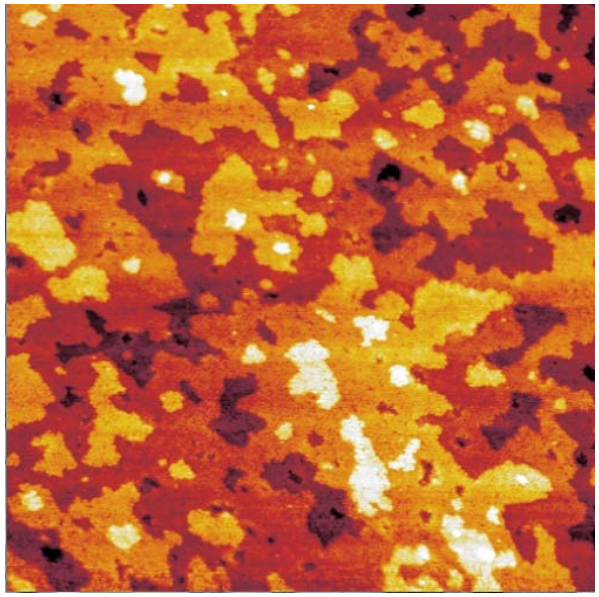
PRB 2010 **81** 165207

Final state screening or plasmon satellite in narrow band free electron metal?

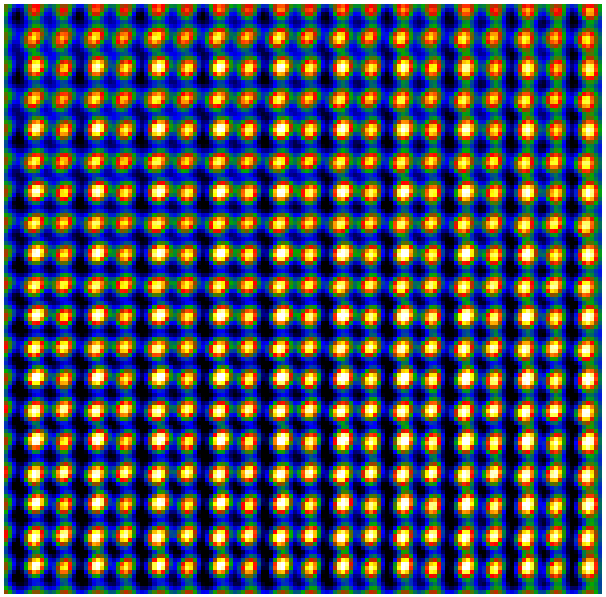


P A Cox, W R Flavell and R G Egdell
Journal of Solid State Chemistry 1987 **68** 340

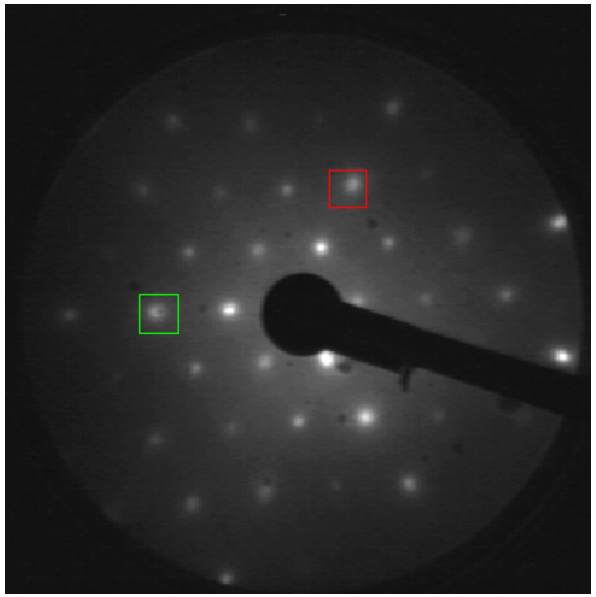
Epitaxial Growth of $In_2O_3(111)$ Thin Films on Y-$ZrO_2(111)$



200 nm x 200 nm STM of Sn-doped $In_2O_3(111)$ showing atomic scale steps of height $(a/2\sqrt{3}) = 0.29$ nm



HRTEM viewed down <11-2>



LEED

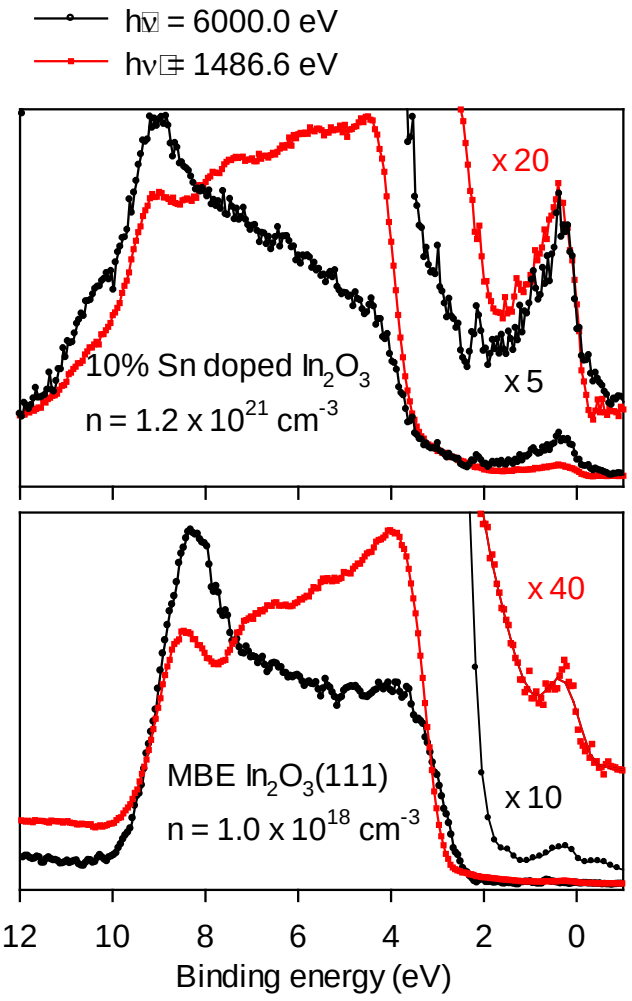
$In_2O_3(111)$ thin film grow epitaxially on YSZ(111) with atomically flat terrace areas separated by atomic scale steps - optimal temperature for flat films is 700 ºC.

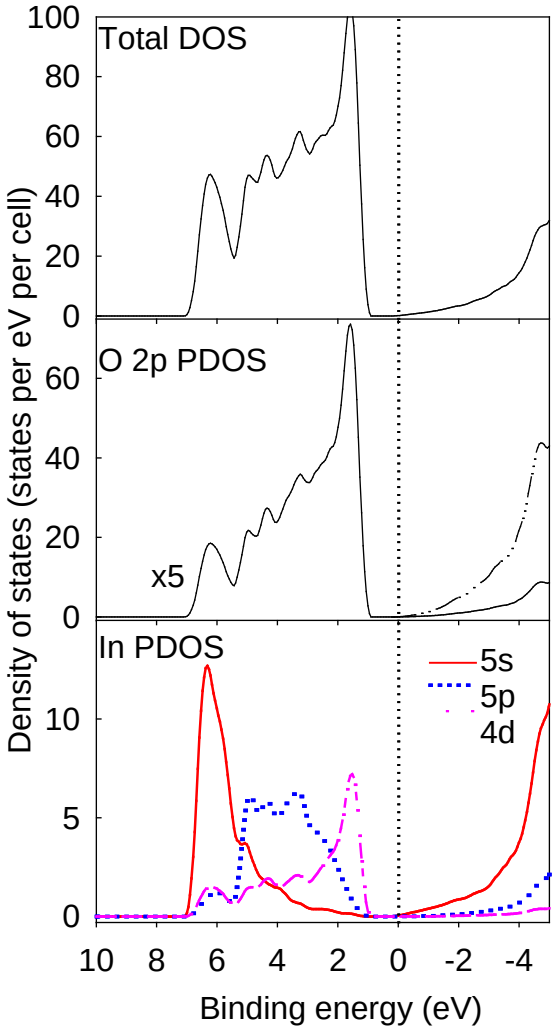
Film quality even better for Sn doped films as Sn doping reduces lattice mismatch.

(001) films may also be grown at 600 ºC.

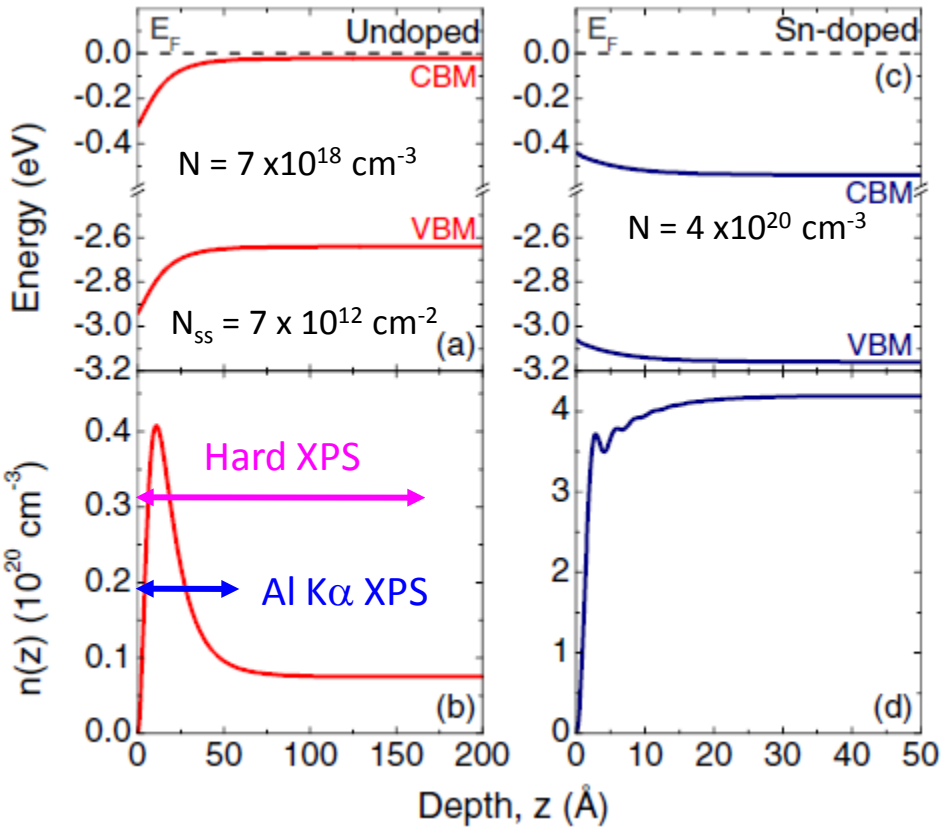
KHL.Zhang et al. Chem. Mater. ***21*** *4353 (2009)*

Hard X-ray and Al Kα X-ray photoemission of In_2O_3 and ITO





Carrier accumulation at nominally undoped In_2O_3 surfaces



Space charge calculations within modified Thomas–Fermi approximation

Conduction band feature in conventional XPS of nominally undoped In_2O_3 arises from pinning of the Fermi level about 0.4 eV above the conduction band minimum with consequent carrier accumulation at the surface.

Conventional XPS is dominated by the space charge region.

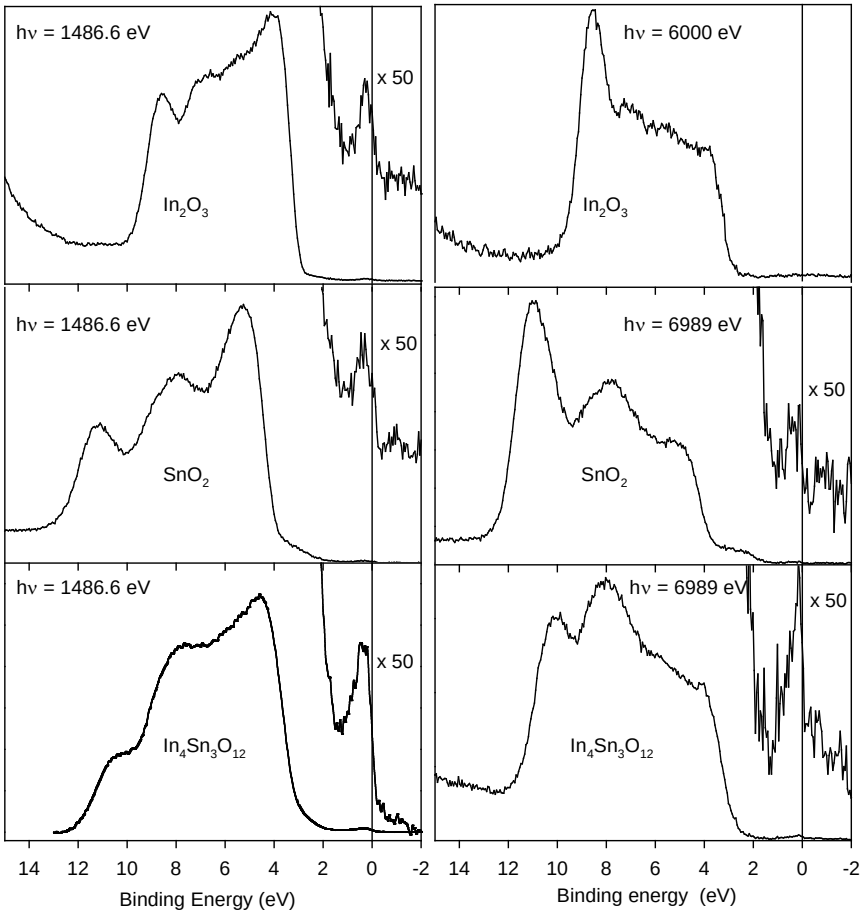
Longer path length in hard XPS means that the technique probes through the space charge region into the bulk where the carrier concentration is very low

Similar accumulation is observed on (100) and (111) single crystal surfaces, as well as poly crystalline surfaces.

Chemistry of Materials 2009 **21** 4353
Phys. Rev. Lett. 2008 **101** 116808

Conclusions and prospects

- HAXPES is an ideal technique for studying *s* electron states in oxides, especially *s*-derived conduction bands in post transition metal oxide semiconductors and TCOs.
- Combining HAXPES with soft XPS allows one to probe structure of space charge layers in oxide semiconductors.
- The TCO/oxide semiconductor community needs a beamline that will combine HAXPES with soft XPS – band bending at surfaces depends on sample preparation.



Acknowledgements

Waiting patiently for the signal to noise to improve.

David Payne

Hongliang Zhang

Guido Paolicelli
Giancarlo Panaccione

The rest of the VOLPE team:
Francesco Offi, Paulo Lacovig, Piero Torelli, Guido Paolicelli

ESRF support team:
G Vanko, G Monaco, A Fondacaro

Other collaborators:
Chris McConville, Philip King, Tim Veal (Warwick, UK)
Aron Walsh, JLF daSilva, S-H Wei (NREL, USA; Bath, UK: DFT)
Kevin Smith, Louis Piper (Boston USA: XES)
Andreas Klein, Christoph Korber (Darmstadt, Germany)

- Save the fox (VOLPE in Italian)
- Anyone with a few spare hard X-ray photons contact: giancarlo. panaccione@elettra.trieste.it