High-pressure XPS of transparent conducting oxides:
Fermi level position and composition at ITO surfaces

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Tin-doped indium oxide (In_2O_3:Sn or ITO) is a degenerately doped semiconductor with a high transparency in the visible optical regime. Its high electron concentration of up to ~ $10^{21}cm^{-3}$ is obtained by substitutional doping with tin. ITO is largely used as a transparent electrode in optoelectronic thin film devices and also as sensor material. For these applications the electric surface potentials (Fermi level and vacuum level) are important. The use of ITO in organic light emitting diodes (OLEDs) combines two apparently excluding properties: The bulk of ITO needs to be as conducting as possible requiring a Fermi level as high as possible with respect to the band edges or the vacuum level. In contrast, the low injection barrier is reached by a Fermi level at the interface to the organic conductor as low as possible. Obviously both features can be combined using ITO. In order to assess the influence of ITO on the stability of OLEDs, the influences which change the ITO surface potentials must be understood. ITO thin films deposited by radio frequency magnetron sputtering exhibit changes of up to ~ 1 eV in XPS binding energies depending on deposition conditions when measured in-situ directly after deposition [1]. The Fermi level in these measurements is found as low as ~ 2.2 eV above the valence band maximum for the most strongly oxidized samples. These large shifts are interpreted in terms of a surface depletion layer and a change of the Fermi level position with respect to the band edges.

At BESSY we have investigated the changes of the ITO surface potentials using high-pressure XPS. The experiments were performed at the U49/2-PGM 2 undulator beamline. The photoelectron spectrometer system uses a differentially pumped lens system. ITO films prepared at 400 °C substrate temperature with pure Ar as sputter gas have been used for the experiments. Samples were heated using light from a laser diode array fed into the vacuum system with a glass fiber and placed ~ 2 mm before the entrance slit of the electron lens system. All spectra were recorded in normal emission. Hydrogen and oxygen gas was dosed via leak valves. For measurements at pressures above 0.1 Pa, the pumping speed was reduced by closing the valve between the measurement chamber and the turbomolecular pump. Residual pumping was thereby maintained through the small entrance slit of lens system. Pressures were measured using a Pfeiffer PKR full range gauge at lower pressures and a Baratron at higher pressures. All spectra were recorded using a photon energy of hv = 600 eV to avoid changing of the excitation energy because of the importance of energy calibration.

An overview of ITO surface potentials where the ITO was exposed to different gases with changing pressure and substrate temperature is shown in Figure 1. Here the core level and valence band maximum binding energies were determined after a saturation of the shifts was almost reached. Three important features are noticed: i) As expected oxygen leads to a lowering of the Fermi energy in the band gap whereas hydrogen raises the Fermi level and thus reduces the surface. ii) The variation in binding energy for the In 3d core line is significantly lower than variation of the valence band maximum. This phenomenon is explained by a screening of the core holes caused by metallic surface states [2]. iii) At higher temperature the surface seems to be stronger oxidized. This unexpected behavior has been reproducibly observed in different gas environments and for different samples. However, at present we can not give an explanation.

The change of the $In3d_{5/2}$ kinetic energy with time as a response to a sudden raise of the oxygen pressure at a substrate temperature of 400 °C is shown in Figure 2. The changes of kinetic energy correspond to changes of the surface Fermi level position, which is the expected mechanism leading to the sensor response of such materials. A high temporal resolution (~5 seconds / spectra) was possible due to the high intensity of the In 3d core-level. The changes occur much slower than expected for adsorption/desorption equilibria. This suggests that the changes are not caused by changes of surface coverage but rather by changes in the substrate oxygen stoichiometry, leading to changes in doping. As this was not expected, the stoichiometry was not recorded systematically during the beamtime. However,

High-pressure XPS of transparent conducting oxides: Fermi level position and composition at ITO surfaces, Y. Gassenbauer et al., BESSY Annual Report 2005 (2006) 286-288

2

we found evidence for changes in the surface tin concentration with gas atmosphere and temperature. The intensity ratio [Sn]/([Sn]+[In]) is plotted in Fig. 3 in dependence on the surface Fermi level position. The changes in E_F are induced by changes in substrate temperature, gas environment (H_2, O_2) and pressure. For substrate temperatures >300°C there is a clear correlation of the surface tin concentration with the position of the Fermi level. Only for a sample temperature of 250°C the tin concentration deviates from the observed general dependence, which is indicated by the dashed line. This can be explained by a too slow diffusion of Sn. The segregation of tin is most likely driven by changes in the surface potential gradient [2].

High pressure XPS allows a detailed insight into the changes of electronic and chemical surface properties of conducting oxides, which can not be directly assessed otherwise. The results from only 1 week of beamtime already revealed several unexpected dependencies, which have and will significantly improve the understanding of these materials and their applications.
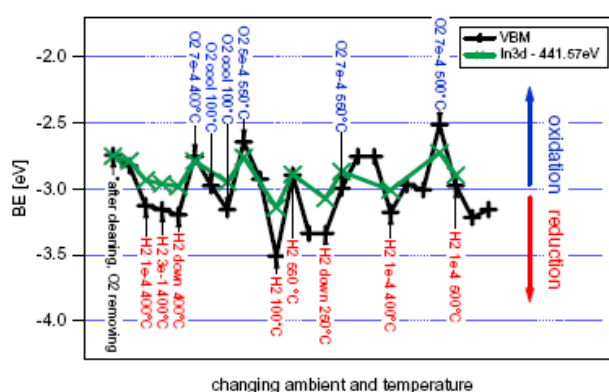

Figure 1: Variation of core level and valence band maximum binding energy with changing temperature and gas exposure.
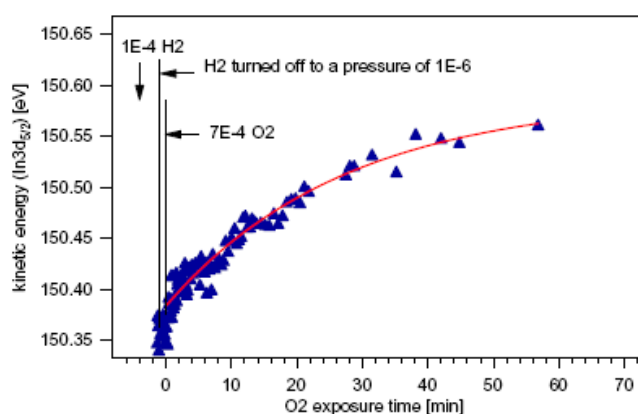

Figure 2: Variation of In3d5/2 kinetik energy with exposure time to pure oxygen ($p(O_2) = 7*10^{-4}$ mbar) at a substrate temperaure of 400 °C. Excitation energy $h\nu = 600$ eV. The stepwise change of kinetic energy gives a hint on several overlapping processes with different time constants.
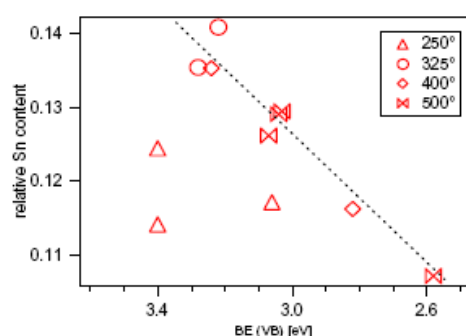

Figure 3: Dependence of relative tin content for different temperatures of Fermi level position. The straight line represents the tin-concentration expected for an equilibrium situation.

[1] Y. Gassenbauer, A. Klein; Solid State Ionics Vol. 173 (2004) pp 141-145
[2] Y. Gassenbauer, R. Schafranek, A. Klein, S. Zafeiratos, M. Hãvecker, A. Knop-Gericke, R. Schlõgl; Physical Review B, submitted