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Electronic properties of In_2O_3 surfaces

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Surfaces of reactively evaporated In_2O_3 films were investigated *in situ* by synchrotron-excited photoemission. Work function, valence band maximum, and electronic states in the band gap were determined as a function of oxygen pressure. Surface and bulk electronic properties can only be explained consistently with the assumption of a surface depletion layer. © *2000 American Institute of Physics.* [S0003-6951(00)01339-5]

The material properties of In_2O_3 are generally described by a high optical transparency for visible light and a high electrical conductivity.[1,2] To increase the conductivity it is generally doped with Sn and then known as indium–tin–oxide (ITO). ITO is used as a transparent electrode in a large number of optoelectronic devices such as flat panel displays or solar cells and is therefore of particular technological importance.[1] The surface properties of ITO are poorly known. Only recently a number of photoemission studies were stimulated because of the relevance of ITO surfaces in organic light emitting devices.[3–5] In these devices ITO acts as hole injection electrode which requires a large work function. However, in solar cells ITO is used as electron collector[6–8] being more efficient for low work function material. These different material requests are inherent in sensor applications of ITO which are based on a varying surface conductivity by adsorbate induced work function changes (see Ref. 1 and references therein).

Values for the work function of ITO are given in the literature between 4.1 eV and more than 5 eV (see Refs. 5, 9, 10, and references therein). These large differences are difficult to combine with the standard picture of ITO being a degenerate semiconductor with the Fermi level fixed some 100 meV above the conduction band minimum.[1,2] Unfortunately, many photoemission studies of ITO gave only values for the work function and not for the Fermi level position within the band gap which is also easily accessible with this technique. Cox *et al.*[11] determined the distance between the Fermi level (E_F) and the valence band maximum (E_{VBM}) to be $E_F - E_{VBM} \approx 3$ eV, a value which is considerably less than the optical band gap of $E_g = 3.6$ eV.[2] No value for the work function is reported. A peak at the Fermi energy is attributed to filled conduction band states. The energy difference between the conduction band and the valence band maximum is determined to be ≈ 2.6 eV which was explained by the presence of an indirect gap at this energy.[11] An indirect band gap of ITO with $E_{g,i} \approx 2.6$ eV is reported in the literature.[2,12,13] However, the assumption of an indirect band gap with this energy is in contradiction with the observed Burstein–Moss shift of the optical gap which requires a Fermi level position $E_F - E_{VBM} \geqslant 3.6$ eV[2] (see also discussion in Ref. 9).

In this work the surface electronic properties of polycrystalline In_2O_3 have been investigated by photoelectron spectroscopy using synchrotron radiation. It is found that the Fermi level generally lies well below the conduction band minimum at the surface. A consistent explanation of both volume and surface properties of In_2O_3 hence requires the assumption of a surface depletion layer. It is supposed that this result is not restricted to In_2O_3 but also valid for ITO.

In_2O_3 films were deposited on different substrates using reactive evaporation of In at a substrate temperature $T_S = 220\,^\circ$C. Material properties of films prepared by this technique are described in the literature.[9,14,15] In particular are the crystallographic, optical, and electrical properties of the films representative for high quality films when prepared at an oxygen pressure of $p_{ox} \approx 5 \times 10^{-4}$ mbar.[9] The deposition chamber was directly connected to a VG ADES 500 photoelectron spectrometer which was attached to the TGM 7 beamline of the BESSY storage ring in Berlin. Sample transfer from the deposition chamber (base pressure 10^{-9} mbar) to the analysis chamber is possible in ultrahigh vacuum.

Photoemission spectra excited with $h\nu = 21$ and 35 eV synchrotron radiation are shown in Fig. 1. A sample bias of -6 V has been applied during measurement of the 21 eV spectra. An oxygen pressure of $p_{ox} = 5 \times 10^{-4}$ mbar and a substrate temperature of $T_S = 220\,^\circ$C have been used. Identi-

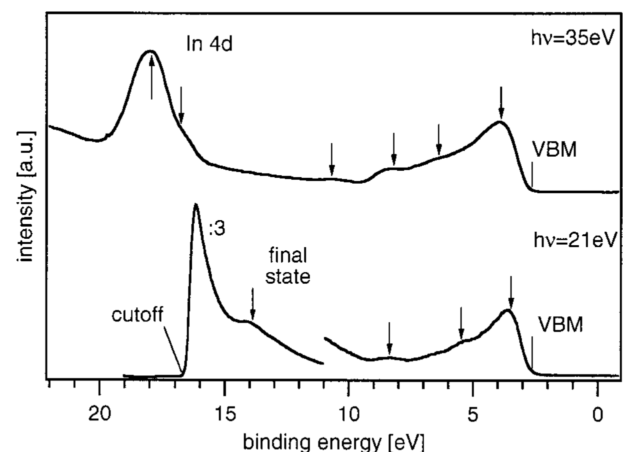

FIG. 1. Synchrotron excited photoelectron spectra of reactively evaparated In_2O_3. During deposition the substrate temperature was kept at $T_S = 220\,^\circ$C the oxygen pressure was $p_{ox} = 5 \times 10^{-4}$ mbar. Characteristic emission features are indicated by arrows.

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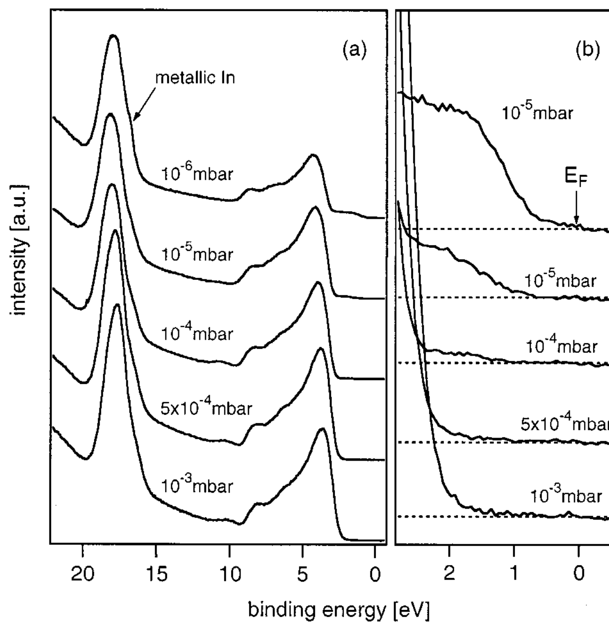

FIG. 2. Valence band spectra of reactively evaporated In_2O_3 films (a) deposited at a substrate temperature of $T_S = 220\,°C$ in dependence of oxygen pressure p_{ox}. Spectra were excited with $h\nu = 35\,eV$ synchrotron radiation. The valence band maximum is shown on an expanded scale in (b). Only for $p_{ox} = 10^{-6}$ mbar a metallic Fermi edge and a metallic In 4d species can be identified.

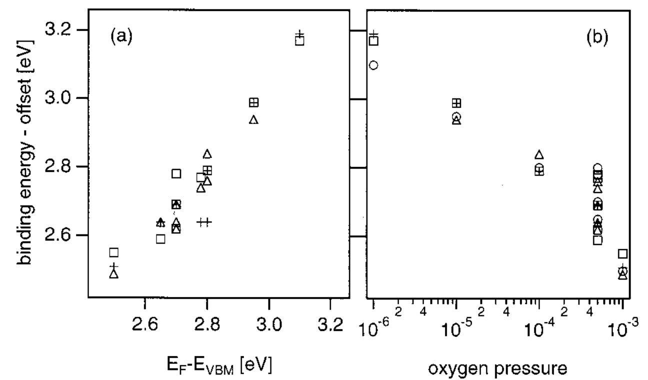

FIG. 3. Binding energies—offset of the valence band maximum (○), O 2p (+), secondary electron cutoff (□), and In 4d (△) of reactively evaporated In_2O_3 films. Offset values are 1.11 eV (O 2p), 13.93 eV (cutoff) and 16.16 eV (In 4d), respectively. The abszissa correspond to the binding energy of the valence band maximum of each film in (a) and to the oxygen pressure during deposition in (b). The parallel binding energy shifts of all levels is characteristic for a movement of the Fermi level and a constant ionization energy.

cal spectra were observed for a large number of samples. Characteristic emission features are indicated by arrows. The valence band maximum is determined by linear extrapolation of the leading edge of high energy electrons and lies at binding energy $E_{VBM} = 2.7 \pm 0.05\,eV$ in both spectra. The secondary electron cutoff is determined by linear extrapolation of the leading edge of low energy photons. Its binding energy is given by $16.6 \pm 0.05\,eV$ giving a work function of 4.4 ± 0.1 eV.

A characteristic shoulder is present close to the In 4d level at lower binding energies. At present its origin is not clear. However, it is definitely not due to metallic indium which should occur at similar binding energies [BE(In $4d_{met}$) = 16.7 eV].[16] This is evident from spectra which were recorded from films prepared with different oxygen pressures (Fig. 2). Metallic indium can be identified only for $p_{ox} = 10^{-6}$ mbar from the sharp features in the In 4d level and from the occurence of a metallic Fermi edge.

For oxygen pressures $p_{ox} \leq 10^{-4}$ mbar there is emission intensity observed at binding energies between the valence band maximum and the Fermi edge which is evident from the expanded view shown in Fig. 2(b). These emissions must be attributed to electronic states within the In_2O_3 band gap. Their intensity obviously increases with decreasing oxygen pressure which is accompanied by an increase of optical absorption of the films as judged from thicker films deposited on quartz glass under the same conditions. It is assumed that these gap states have their origin in different substrate stoichiometries which, however, cannot be stated unambigously without a separate experimental determination, e.g., with x-ray photoelectron spectroscopy. The stoichiometric changes are most likely not restricted to the topmost atomic layer because this would be accompanied by changes in the work function due to different surface dipoles.

Changes of the surface dipole are present when the work function of a material changes without changing the Fermi level position relative to the energy bands (see e.g., Ref. 17). In semiconductors the Fermi level can be moved within the band gap which also gives rise to work function changes.[17] If the shift of Fermi level and work function are of the same magnitude there is no change of the surface dipole. To differentiate between band bending and surface dipole changes the binding energies of the valence band maximum, secondary electron cutoff, In 4d core level, and the most intense O 2p valence level in the 35 eV spectra (at BE≈4 eV) are plotted versus binding energy of the valence band maximum in Fig. 3(a) and as a function of oxygen pressure during film deposition in Fig. 3(b). A number of films have been deposited with $p_{ox} = 5 \times 10^{-4}$ mbar. The scatter of the data at this pressure is probably related to deviations in film composition due to imperfect reproducibility of deposition conditions.

It is evident from Fig. 3 that all levels show parallel binding energy shifts. The work function shift is therefore evidently explained by a shift of the Fermi level rather than by changes of the surface dipole. A higher oxygen pressure during deposition results in a lower Fermi level position in the band gap. For all oxygen pressures the Fermi level lies well below the conduction band edge which is assumed 3.6 eV above the valence band maximum.[2] The distance between the valence band maximum and the vacuum level, which is the ionization energy (I_P) or the electron affinity (χ) plus the band gap, is constant with a value of $I_P = 7.1 \pm 0.15\,eV$ ($\chi = 3.5 \pm 0.2\,eV$).

The range for the work function and $E_F - E_{VBM}$ given in Fig. 3 is in general agreement with recently published values on In_2O_3 and ITO[3–5,9,11] and therefore does not seem to be restricted to our deposition conditions. The tendency to higher work function with increasing oxygen content is also reported.[5] Unfortunately, Sugiyama *et al.*[5] do not give information about corresponding shifts of the valence band maximum. Therefore, it cannot be decided whether the work function changes observed as a result of the surface modifications are due to a change of the surface dipole or due to a movement of the Fermi level inside the band gap.

A movement of the Fermi level of In_2O_3 within the band gap and particularly a Fermi level position of up to 1 eV below the conduction band minimum seems to be in contradiction with the Burstein–Moss shift of the optical gap and the high electrical conductivity of the material. Both effects require a Fermi level position above the conduction band minimum. This discrepancy can be solved by considering the different information obtained from optical and electrical measurements on the one hand and from photoemission on the other. Electrical and optical properties are integral measurements of the whole material, while the information depth of photoemission is only about 1 nm (see e.g., Ref. 18). Hence, optical and electrical techniques mostly probe the Fermi level inside the bulk, while photoemission experiments give access to the Fermi level at the surface. The obviously different Fermi level positions deduced from the two kinds of measurement can therefore be explained by assuming a surface depletion layer with a band bending on the order of 1 eV.

Because of the high doping level of the In_2O_3 films[9] the depletion layer should be confined to a few angstroms from the surface being comparable to the escape depth for very low energy electrons. However, no shift of the valence band maximum could be observed for valence bands taken with photon energies down to 11 eV. The depletion layer should therefore reach deeper into the bulk than expected for homogeneous doping. Since doping in In_2O_3 is generally considered to be due to oxygen vacancies,[1,2] inhomogeneous doping should be related to changes in stoichiometry, or more precisely to changes in oxygen content. Pronounced changes in stoichiometry of ITO films were, e.g., observed by Mergel *et al.*[19] Vacancy concentrations and distributions in transparent conductive oxides depend on deposition temperature, oxygen pressure, and cooling rates (see Ref. 20 and references therein). A detailed description of the course of the electrostatic potential requires knowledge of the spatial dopant/defect distribution, which is presently not available.

It should be mentioned that depletion layers are also known for other transparent conductive oxides as SnO_2 and ZnO. They are the physical basis for applications like gas sensors[20] and varistors[21] and are known to depend on oxygen gradients.[21]

In light of the presented experiments and considering the comparable values for work function and Fermi level positions in the literature, the proposed surface depletion layer seems to be a general property of In_2O_3 and ITO. Such a depletion layer most likely also occurs at grain boundaries of polycrystalline films. The properties and the function of ITO should then strongly depend on the granular structure of the films. In this case tailoring of material properties of ITO films would require not only the optimization of doping concentration but also the selection of particular grain sizes.

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