Chapter 20
Transparent Conductive Oxide Semiconductors

Many of the most important semi-conductors are oxides.
A.H Wilson, 1939 [65]

Abstract Typical materials in the class of transparent conductive oxides are mentioned. Their physical properties and the limits of conductivity versus transparency are discussed.

20.1 Introduction

Transparent conductive oxides (TCO) are semiconductors that are simultaneous transparent and highly conductive. Therefore they can serve as transparent contacts, e.g. as a solar cell front contact or in display applications. The materials are typically fabricated in the form of thin films on glass, polymers or similar substrates and devices. The crystallographic structure is polycrystalline or amorphous. The first TCO investigated was CdO in pressed powder [1387] and thin film form [31]. The recent historic development of the resistivity of the most important TCO materials in the last 30 years is shown in Fig. 20.1. Further information on TCO films can be found in [1388–1390].

20.2 Materials

Any wide-gap ($E_{\mathrm{g}} > 3\,\mathrm{eV}$) semiconductor that is conductive, e.g. due to intrinsic defects or by chemical impurities (doping), can be considered to be a TCO. Practically only a few, non-toxic materials that can be easily deposited are of importance. The first TCO application was heating of air plane windows. As always in semiconductor technology, price drives the suitability for applications. This in particular true for TCO applications since they include large area devices such as solar

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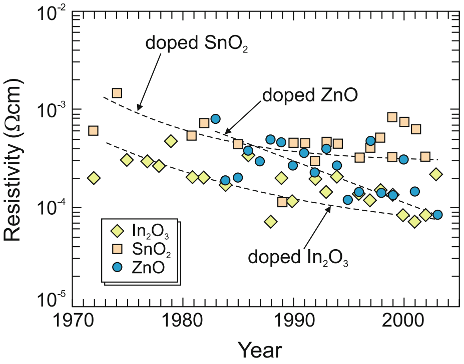


Fig. 20.1 Historical development of the resistivity of doped ZnO (*circles*), In_2O_3 (*squares*) and SnO_2 (*diamonds*) TCO films. Adapted from [1390]

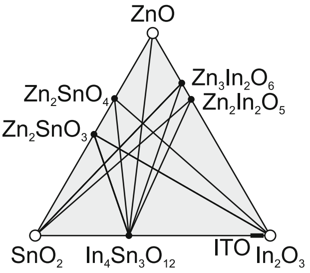


Fig. 20.2 Practical TCO materials

cells, displays and also large glass panes for electromagnetic shielding and architectural heat and IR transparency management. Therefore large quantities of TCO are needed. The popular ITO (indium-tin-oxide) suffers from large indium price and potential indium scarcity, opening the field for aluminum-doped ZnO (ZAO) which is abundant. Possible other compounds including Cd are of no practical interest due to toxicity. Conductive GaN has not been considered due to its large processing temperatures. All practical TCO materials contain either Zn, Sn or In (Fig. 20.2). A number of TCO materials is reviewed in [1391]. TCO are mostly n-conducting. Also p-conducting TCOs have been reported, e.g. $CuAlO_2$ delafossite [1392] with room temperature conductivity of $\sigma = 1\,\mathrm{S/cm}$, $ZnIr_2O_4$ [1393] with $\sigma = 2\,\mathrm{S/cm}$ and $ZnCo_2O_4$ spinel [1394] with $\sigma = 20\,\mathrm{S/cm}$. However, there has been so far no report on a practical transparent highly conductive p-type electrode.

The term ITO stands for a variety of Sn-doped indium oxide (In_2O_3) materials, the Sn content being typically in the 5–10 % range but not strictly defined. The crystal structure of In_2O_3 [1395] is shown in Fig. 20.3. The effect of the replacement of indium by tin atoms in In_2O_3 on mechanical, electrical and optical properties of ITO has been calculated in [1396] using DFT. In Fig. 20.4 the band structures of pure In_2O_3 and $(Sn_{0.065}In_{0.935})_2O_3$ (one out of 16 indium atoms was replaced in the calculation) are compared [1397]. The fundamental band gap is slightly lowered, the high doping introduces a gigantic Burstein-Moss shift. Additionally another band gap opens that splits the lowest conduction band. Also the conduction mechanism in amorphous oxides has been discussed [1398].

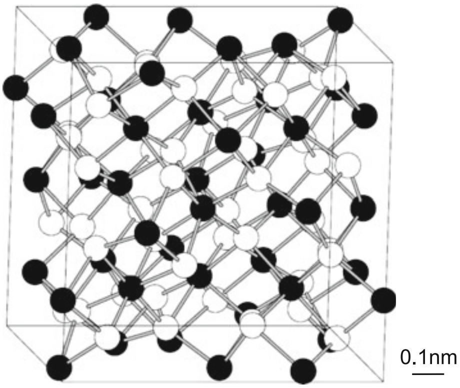


Fig. 20.3 The bixbyite crystal structure of indium oxide ($In_{32}O_{48}$) showing one unit cell where the indium and oxygen atoms are represented by the *full* and *empty circles*, respectively. Adapted from [1396]

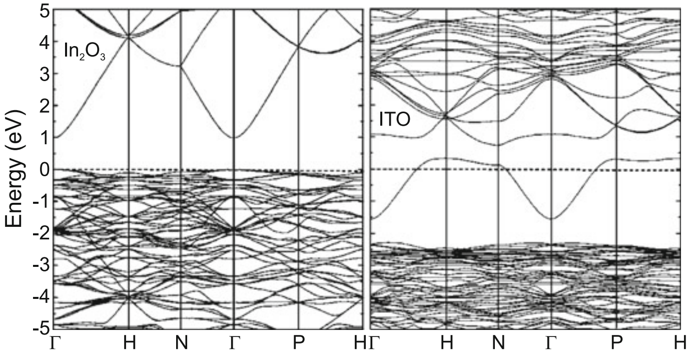


Fig. 20.4 Comparison of the band structure of In_2O_3 (*left*) and $(Sn_{0.065}In_{0.935})_2O_3$ (*right*). The position of the Fermi level is for both cases at $E = 0$. Adapted from [1397]

20.3 Properties

The best conductivity of TCOs is in the range of $10^{-4}\,\Omega$cm for the specific resistivity. Such value is about three orders of magnitude smaller than that of metals. However, the TCO meanwhile is highly transparent in the visible region, while metals become transparent only in the UV region because of their high plasma frequency (cf. Sect. 9.8.1).

The conduction mechanism in ZnO:Al is band transport in a highly doped semiconductor. The carrier concentration is typically around $10^{21}\,\text{cm}^{-3}$. One of the best results is a (Hall) mobility of $47.6\,\text{cm}^2$/Vs, leading to a specific resistivity of $8.5 \times 10^{-5}\,\Omega$cm [1399]. The mobility is limited by (doping level dependent) ionized impurity scattering (Sect. 8.3.3) as shown in Fig. 20.5 for various films. A detailed discussion of ionized impurity scattering in doped ZnO films can be found in [1400].

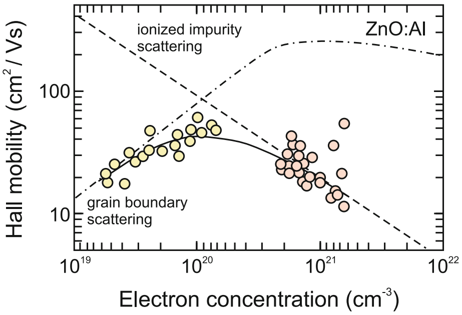
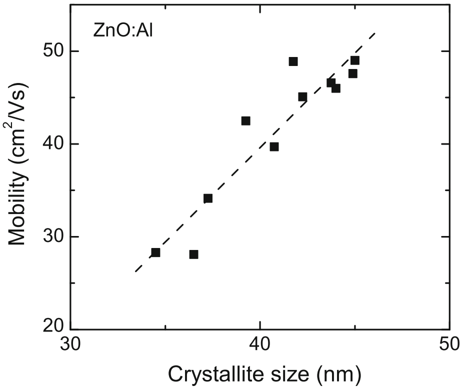


Fig. 20.5 Hall mobility for various ZnO:Al TCO thin films as a function of carrier (electron) concentration. The *dashed line* is the Brooks–Hering theory of ionized impurity scattering (taking into account non-parabolicity of the conduction band). The *dash-dotted line* is mobility in the presence of grain boundaries, the *solid line* is combined theory. *Symbols* are experimental data from two sets of samples. Adapted from [1390]

Also the mobility is correlated (Fig. 20.6) with scattering at structural defects such as grain boundaries [1401] (cf. Fig. 8.5). We note that the carrier mobility in a (polycrystalline) TCO is not very different from that in highly doped (crystalline) silicon (Fig. 8.7).

Conductivity and transparency are, however, linked. The high doping of the TCO leads to shifts in the band gap (renormalization and Burstein-Moss shift), band tails and the like that can introduce absorption in the visible spectral region. Also the infrared transparency is related to the conductivity by free carrier absorption and the plasma edge (Sect. 9.8.1). With increasing carrier density, the plasma edge shifts into the visible spectral range (Fig. 20.7a), limiting the possible maximum carrier density to several 10^{21} cm^{-3}, the exact value depending on the carrier mass. In Fig. 20.7b the transparency spectra of two SnO_2 films with different conductivity are compared. The higher conductivity due to larger carrier concentration leads to reduced IR

Fig. 20.6 Hall mobility of ZnO:Al films (of varying thickness) versus the crystallite size. Experimental data (from [1390]) are shown as *symbols*. The *dashed line* is a guide to the eyes



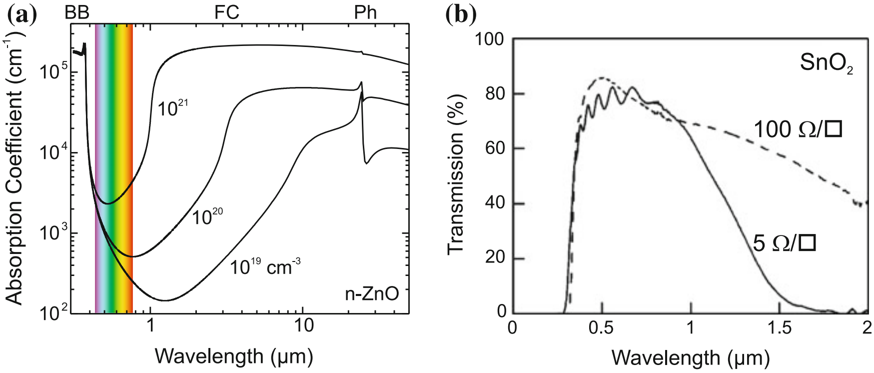


Fig. 20.7 (**a**) Absorption coefficient of n-type ZnO for various electron concentrations as labeled. Spectra synthesized from ellipsometric data of thin films. The visible spectral range is indicated. The contributing absorption processes are band-band transitions (BB), free carrier absorption (FC) and phonon-related absorption (Ph) as labeled. (**b**) Transparency versus wavelength spectra of two SnO_2 films with different conductivity as labeled. Adapted from [1402]

transparency. Generally, the transmission of a TCO is limited by the band edge on the high energy side of the spectrum and the plasma edge on the low energy side of the spectrum. The limited carrier concentration due to the onset of free carrier absorption in the visible spectral range ($\sim 3 \times 10^{21}\,\mathrm{cm}^{-3}$) and the limited mobility in the presence of such high impurity concentration (max. $50\,\mathrm{cm}^2/\mathrm{Vs}$) restrict the minimum resistivity of a TCO (or any transparent conductor) to about $4 \times 10^{-5}\,\Omega\,\mathrm{cm}$ [1403].