2. TRANSPARENT CONDUCTING OXIDES

In this Chapter we provide some information on transparent conducting oxides.

A metal oxide in the thin film form transparent to visible light and conducting to electricity is called a transparent conducting oxide. The dual property is called as the transparent conducting. The material exhibits both transparent and conducting property is known as the transparent conductor. The basic electromagnetic theory does not permit a material to be transparent and conducting simultaneously. Maxwell’s electromagnetic theory demands that no material can be both transparent and conducting simultaneously. For example copper or silver cannot be transparent. NaCl, CaF$_2$, TiO$_2$ etc cannot conduct. So, in order to get a material which is to be a transparent conductor mix a metal oxide with a metal. Because, in general, all metals are conductive to electricity and all metal oxides are transparent & insulators (because of wide band gap). Generally all insulators are transparent and all metals are conducting. So mixing a metal oxide with a metal under suitable preparation conditions would definitely yield a transparent conductor.

Transparent conductive oxides (TCO) are materials that exhibit a low resistivity of the order of $1 \times 10^{-4} \Omega \text{cm}[1]$ and high carrier concentration in the range $0.1-1.0 \times 10^{21} \text{cm}^{-3}[1]$ while being transparent in the visible part of the electromagnetic spectrum, typically having an average visible transmittance of $80\%[1]$. For some applications such as flat panel display (FPD) it is necessary to have conductive electrodes to switch pixels in a display. Metal electrodes could be used to achieve this,
but such electrodes may be completely opaque, therefore light may not be transmitted through the electrodes. Although a very thin layer of metal could be used as an electrode, there would still be some optical absorption that would decrease the overall brightness of the display. For this reason TCO’s are used in applications (FPD) where a conductor is required that is also transparent. Other products in which TCO’s are used, are, electrochromic windows (and mirrors)[2], heating [3], gas sensors [4], biosensors [5], organic light emitting devices (OLED) [6], polymer light emitting devices (PLED) [6] and architectural glazing (cold heat mirrors) [7], antistatic coatings [8], write once read many times memory chips (WORM) [9] and electronic ink [10].

For the majority of the aforementioned applications, indium sesquioxide (In$_2$O$_3$ - a wide band gap semiconductor material) heavily doped with tin (Sn) is used. Typically the dopant concentration for commercially available material is 5% Sn. This material is n-type due to the excess of electrons conferred by the Sn dopant.

Most of the TCOs are binary or ternary compounds, containing one or two metallic elements. The resistivity of the TCOs may be as low as $1.0 \times 10^{-4}$ Ωcm, and their extinction coefficient k in the optical visible (Vis) spectral range could be as low as $1.0 \times 10^{-4}$, owing to their wide optical band gap ($E_g > 3.0$eV). This remarkable combination of conductivity and transparency is usually impossible to obtain in intrinsic or undoped stoichiometric oxides. For obtaining high conductivity in these materials, either they have to be non-stoichiometric in composition or should be doped with appropriate element.
The first TCO discovered by Badeker (1907) was the CdO in thin film form [11]. Later, it was observed that thin solid films of ZnO, SnO₂, In₂O₃ and their alloys are also good TCOs [12]. Controlled doping of these oxides could improve their electrical conductivity without degrading their optical transmission. For example Al doped ZnO, tin doped In₂O₃ and antimony or fluorine doped SnO₂ are among the most utilized TCO thin solid films in modern technology. In particular, tin doped In₂O₃ is the most extensively used.

Recently, the scarcity and high price of indium, the principal component of indium tin oxide (ITO) led to the search for alternative TCOs for industrial applications. For technological applications, the TCO should have electrical resistivity (ρ) ~ 1.0 x 10⁻⁴ Ω cm or less, with an absorption coefficient (α) smaller than 1.0 x 10⁴ cm⁻¹ in the near UV and Visible range, and with an optical band gap >3.0eV. Films of TCO with 100 nm thick, with these values for α and ρ will have optical transmission (T) in the order of 90% and a sheet resistance (Rₛ) 10Ω. At present, ZnO: Al and ZnO:Ga semiconductors are promising alternatives to ITO for thin film transparent electrode applications. The best candidates is ZnO: Al which can have a low resistivity, e.g. of the order of 1.0 x10⁻⁴ Ω cm [13], with source materials being inexpensive and non-toxic. However, the development of large area needs high rate deposition techniques.

There are published reviews which have reported exhaustively on the deposition and diagnostic techniques, on film characteristics and expected applications [14 - 16 ].
2.1 Development of New TCO materials

The development of new TCO materials is mostly dictated by the requirements of specific applications, however, low resistivity and low optical absorption are always significant pre-requisites. There are basically two strategies in managing the task. The main strategy accounts for the doping known binary TCOs with other elements, which can increase the density of conducting electrons. More than twenty different doped binary TCOs were produced and characterized (See Table 2.1) [17], of which ITO was preferred, while ZnO: Al and ZnO : Ga having similar electrical and optical performance. Doping with low metallic ion concentration generates shallow donor levels, forming a carrier population at room temperature. Doping In$_2$O$_3$ with Sn to form ITO substantially increases the conductivity. It is believed that substituting Sn$^{4+}$ by In$^{3+}$ provides electrons, as Sn$^{4+}$ is supposed to act as a one-electron donor [18]. Similarly, aluminium is often used for intentional doping n-type ZnO, but other impurities, such as Ga and In of the group III, and Sn and Ge of the group IV may also be used. The doping by Al produced the relatively high conductivity ZnO:Al [13]. Doping with non-metallic elements is also common, e.g., ZnO:Ge, SnO$_2$: F and SnO$_2$:Sb [19,20]. Recently, ZnO:Al thin solid films with resistivity $\rho \sim 8.5 \times 10^{-5}$ $\Omega$ cm was reported by Agura et al [21]. An even lower resistivity was reported for ZnO: Ge, $\rho \sim 8.1 \times 10^{-5}$ $\Omega$ cm [22]. The resistivity is very close to the lowest resistivity of ITO [23] of $7.7 \times 10^{-5}$ cm, with a free carrier density of $2.5 \times 10^{21}$ cm$^{-3}$.

The effort to increase the conductivity without degrading the transparency was paralleled by a more elaborate strategy in which phase segregated binary and ternary TCOs were synthesized and characterized. The phase –segregated binary systems
include ZnO-SnO$_2$, CdO–SnO$_2$ and ZnO-In$_2$O$_3$. In spite of the expectations, the electrical and optical properties of these binary TCOs were much inferior to those of ITO. The phase diagram of the ternary TCOs could be schematically presented by a three –dimensional or four –dimensional phase combination of the most common ternary TCO materials [17,23] based on known binary TCO compounds. Accordingly, the ternary TCO compounds could be formed by combining ZnO, CdO, SnO$_2$, InO$_{1.5}$ and GaO$_{1.5}$ to obtain Zn$_2$SnO$_4$, ZnSnO$_3$, CdSnO$_4$, ZnGa$_2$O$_4$, GaInO$_3$, Zn$_2$In$_2$O$_5$, Zn$_3$In$_2$O$_6$ and Zn$_4$In$_2$O$_7$. However, as Cd and its compounds are highly toxic, the utilization of these TCOs is limited, though they have adequate electrical and optical properties. Other binary TCOs were synthesized from known binary TCOs and also from non-TCO compounds, such as In$_6$WO$_{12}$ and the p-type CuAlO$_2$.

All of the TCOs discussed above are n-type semiconductors. However, p-type doped TCOs have also been developed and may have interesting future applications, in particular in the new optoelectronic field of ‘transparent electronics’ [24]. Fabricating undoped or doped p –type TCOs was found to be more difficult than the n-type. In 1993 Sato et al [25] reported on a semi-transparent p- type TCO with ~ 40% visible transmission. Later p- type TCO was made from CuAlO$_2$ by Kawazoe in 1997 [26]. It has been reported that it is possible to form acceptor levels in ZnO, doping with N, P and As. The difficulty in producing p- type oxide is supposed to result from the strong localization of holes at oxygen 2p levels or due to the ionicity of the metallic atoms. Oxygen 2p levels are far lower lying than the valence orbit of metallic atoms, leading to the formation of a deep acceptor level. Hence, these holes are localized and require sufficiently high energy to overcome a large barrier height in
order to migrate within the crystal lattice, resulting in poor hole-mobility and conductivity [27,28].

Following the above hypothesis, an effort was made to grow p-type TCO based on 'chemical modulation of the valence band (CMVB)', where the oxide composition and structure were expected to delocalize the holes in the valance band. The recent detailed report of Banerjee and chattopadhyay [25] lists several groups of such synthesized p-type TCOs, e.g., CuM$_{iii}$O$_2$, AgM$_{iii}$O$_2$ where M$_{iii}$ is a trivalent ion. Compared with the n-type TCOs, these p-type TCOs have relatively lower conductivities, of the order of 1.0 mho/cm, and lower optical transmission, < 80%.

Growing p- ZnO was an important milestone in ‘Transparent Electronics’ allowing fabrication of wide band gap p-n homo junctions, which is a key structure in this field. It was anticipated that higher conductivity and optical transmission could be obtained by doping ZnO with N, F, P, Sb and As, however, it was also shown that such doping had some serious limitations[30,31]. Based on first principle calculations, Yamamoto and Yoshida [32] proposed that co –doping of donor –acceptor dopants (e.g. Ga and N, respectively) in ZnO might lead to p-type ZnO. Joseph et al [33] applied this principle to simultaneously dope ZnO with an acceptor (N) and a donor (Ga), where the acceptor concentration was twice that of the donor. The optical transmission was greater than 85%, but the conductivity was low, ~ 1 mho/cm. p-type ZnO: Sb was deposited with a filtered vacuum equipped with a Zn cathode doped by Sb [34]. The conductivity was ~ 0.5mho/cm, the mobility 9.20 cm$^2$/Vs and the hole density ~ 4.0 x 10$^{16}$ cm$^{-3}$, with transmission of ~ 85%. It is evident that the challenge to grow p-type TCO with ρ~ 1.0 x 10$^{-3}$ Ω cm, or better, still exists.
The need to produce n-type TCOs with higher conductivity and better transmission, without relayng on In, inspired research and development effort to discover and study some unconventional TCOs. Novel transparent conductors were proposed by using oxides with \( s^2 \) electron configurations. Oxides of Mg, Ca, Se and Al also exhibited the desired optical and electronic features; however, they have not been considered as candidates for achieving good electrical conductivity because of the challenge of efficiently generating carriers in these wide band gap materials. The approach suggested was to increase the mobility rather than the carrier density. If this goal is achieved, the optical properties will not deteriorate at lower resistivity. Recently, mobility with more than twice that of commercial ITO was observed in Mo-doped \( \text{In}_2\text{O}_3 \), and it was shown that the conductivity can be significantly increased with no changes in the spectral transmittance upon doping with Mo [35, 36]. Electronic band structure investigations of \( \text{In}_2\text{O}_3: \text{Mo} \) by Medvedeva [37] revealed that the magnetic interactions which had never been considered to play a role in combining optical transparency with electrical conductivity ensure both high carrier mobility and low optical absorption in the visible range.

Now thin solid films geometries were also explored recently in search of TCO films with higher conductivity. Dingle et al [38] showed that higher conductivity can be obtained by doping modulation, which spatially separates the conduction electrons and their parent impurity atoms (ions) and thereby reduced the effect of ionized and impurity scattering on the electron motion. Rauf [39] used a zone confining process to deposit ITO with \( \rho = 4.4 \times 10^{-5} \, \Omega \, \text{cm} \) and \( \mu = 1.0 \times 10^{3} \, \text{cm}^2/\text{Vs} \). The highly and
lowly doped regions were laterally arranged in the films, rather than vertically as in super lattice structures.

TCO materials with magnetic properties, which are ferromagnetic semiconductors with a Curie temperature well above room temperature, have also been explored recently as they can be used for second generation spin electronics and as transparent ferromagnets. Veda et al [40] reported that Co doped ZnO thin solid film (Zn$_{1-x}$Co$_x$O) with $x = 0.05 - 0.25$, had a large magnetic moment of 1.8 $\mu$B per Co ion for $x = 0.05$. High temperature ferromagnetism was subsequently found by other groups, with varying magnetic moments [12].

2.2 Applications of TCOs

TCO coatings are applied to transparent materials used for work surfaces and closet doors, particularly in clean rooms used for electronics assembly, in order to prevent harmful static charge buildup. In this application relatively high surface resistances can be tolerated.

Transparent heating elements may be constructed from TCO coatings. These are applied as defrosters in aircraft and vehicular windshields. The advantage over traditional hot air blowers is that they can have a much shorter effective defrosting time and uniformly large work areas. This application requires either the use of very low surface resistance coatings or a high voltage power source. The application of TCO coatings to passenger vehicles has proven to be technically successful but a commercial failure, due to the high cost of a supplemental alternator to deliver the requisite high voltage. If the automobile industry will adopt a higher bus voltage then this application may prove to be more commercial.
TCO coatings may be used as shielding to decrease electromagnetic radiation interference and to provide usual access. This may also be used to prevent the escaping of radiation from an enclosure and to interfere with nearby devices, or to detect, or to avoid the entering of radiation into an enclosure to interfere with electronic devices within. One potential example is the window of domestic microwave ovens, which today uses a perforated metal screen to obscure clear visual observation and reduce microwave leakage. Radiation leakage must be minimized to prevent harm to the users, as well as interference to proliferating wireless devices which use the unlicensed spectral band at 2.45 GHz. While transparent conducting thin solid films were proposed fifty years ago, an attempt to introduce microwave windows with TCO coatings into the market was not successful about a decade ago, due to the high cost. Low cost designs are currently being developed.

The three largest applications of TCO thin solid films, in terms of the surface area covered, and their total value, are flat panel displays, solar cells, and coatings on architectural glass. In general, transparent electrodes are needed for a large variety of electro-optical devices, of which flat panel displays and solar cells are the most important examples. In liquid crystal displays (LCDs), TCO films are needed for both electrodes, in order to allow backlighting to pass through the liquid crystal film while applying voltage to the various pixels. Generally these electrodes are in the form of a pattern of lines, with the alignment of the lines on the two electrodes perpendicular to each other. This allows addressing individual pixels by applying a voltage to the two lines which intersect at a given pixel.
References:


