Chapter 1

Transparent Conducting Oxide

1.1 Introduction

Transparent conducting oxides (TCOs) are a special class of materials that can simultaneously be both optically transparent and electrically conducting and, as such, are a critical component in almost all thin-film photovoltaic devices. TCOs are generally based on a limited class of metal oxide semiconductors such In$_2$O$_3$, ZnO and SnO$_2$, which are transparent due to their large band gap and can also tolerate very high electronic doping concentrations to yield conductivities of 1000 S/cm or higher.

TCO’s consists of a group of materials that can be thought of as ‘conjugate property materials’ in which one property, [in this case conductivity], is strongly coupled to a second property, namely, the extinction coefficient. In this regard, it can be stated that materials like metals, that are highly conductive, will not normally transmit visible light, while highly transparent media like oxide glasses behave as insulators. The challenge for achieving materials that are both electrically conducting and optically transparent is to understand the fundamental material structure/property relationships that control these properties so that they may be decoupled such that the material retains transparency while becoming electrically conductive. To an extent, many phenomenological approaches based upon well-understood physical principles have been reported to achieve materials having these properties. More recent studies push the envelope of the earlier work through understanding, at a fundamental level, the microscopic nature of the conductivity process in order to discover the role of chemical structure, bonding, and film morphology on charge transport.

The first realization of a TCO material occurred a century ago when a sputtered film of cadmium metal experienced incomplete thermal oxidation upon post-deposition heating in air [1]. Certain metal oxide systems can show n-type electrical conductivity provided the charge-compensating electrons can be promoted to the conduction band of the material from defect levels lying close to the conduction band minimum. Since this early discovery, appreciable values of electrical conductivity had been achieved in many single, binary,
ternary and quaternary metal oxide systems [2–7]. Even though optical transmission through these materials in the visible region of the spectrum was quite good, electrical conductivities still remain considerably lower than that of metals.

For most optoelectronic devices especially the ones with flat panel displays, it is essential to have a transparent electrode with TCO. Although tin-doped indium oxide (commonly called indium-tin oxide, or ITO) thin films deposited using magnetron sputtering have been in practical use for most of the transparent electrode applications, there are many reports on other TCO’s as well as deposition methods [8–13]. A stable supply of ITO for the fast expanding market for optoelectronic devices may be difficult because of the cost and scarcity of indium, the principal material of ITO. In addition, recent developments in optoelectronic devices require thin-film transparent electrodes with specialized properties. Recent research on materials and techniques for making TCO’s is mainly focused on resolving these problems. For example, there are several research groups working all over the world aiming at the modification of zinc oxide (ZnO) as an alternative to costly ITO[10, 14, 15]. Recent developments in optoelectronic device applications make it necessary to have improvements in the physical and chemical properties of TCO films used as thin-film transparent electrodes. In order to develop TCO films suitable for specialized applications. Minami et al. reported new TCO semiconductors in 1994, ZnO–SnO\(_2\) multi-component oxides, that not only had the advantages of ZnO but also those of SnO\(_2\) [16]. In addition, TCO films using multi-component oxides composed of combinations of binary compound TCO materials and/or ternary compound TCO materials were developed. Several examples of multi-component oxides composed of combinations of binary compound TCO materials, such as ZnO–In\(_2\)O\(_3\), In\(_2\)O\(_3\)–SnO\(_2\) and SnO\(_2\)–ZnO systems are at present developed and studies elaborately.

1.2 Reviews of TCO

The research progress for TCO materials have been repeatedly reviewed from time to time. Holland [17] reviewed the early work of TCO film in 1958. Vosser [18] and Hacke [19] reported comprehensive reviews to the mid 1970s. Manfacier [20], Jarzebski[21] and Chopra et al. [22] published reviews covering all the important works in this area up to the
early 1980s. Hartnagal et al. [9] reviewed the growth technique, properties and application of TCOs. Some critical issues related to new TCO material, such as criteria for application and theoretical model were addressed in the MRS Bulletin [24]. Exarhos et al. [25] summarised up-to-date TCO research with an emphasis on the microscopic description of electronic conduction properties and guidelines for designing new TCO materials. S.Calnan et al. [26] reviewed importance of carrier mobility in doped TCOs. In this article strategies used to improve the carrier mobility in degenerately doped TCO thin film were reviewed. T.Minami et al. [5] reported the present status and prospects for further development of polycrystalline or amorphous TCO semiconductor used for practical thin film transparent electrode application.

1.3 General properties of TCO

TCOs are unique materials that combine optical transparency (band gaps > 3.1 eV) and electrical conductivity (carrier concentration of at least $10^{19}$ cm$^{-3}$). Band gap > 3.1 eV ensures that visible light photons cannot excite electrons from the valence band (VB) to the conduction band (CB).
These transparent materials are thus made electrically conducting by the introduction of defects, [intrinsic or extrinsic] into the system. TCOs can be classified as n-type or p-type, according to the defects and type of conduction of the material. These defects form split off acceptor (unoccupied) levels above the valence band maximum (VBM) in the case of p-type conduction, and donor (occupied) levels below the conduction band minimum (CBM) in the case of n-type conduction.

N-type TCOs (SnO$_2$, ZnO, In$_2$O$_3$ etc) are already utilized in a range of technological applications. However p-type TCOs have proved to be harder to manufacture. Most of the wide band gap binary oxides have valence bands dominated by O 2p states. Hence on acceptor formation, the acceptor states (holes) are localized on oxygen ions, leading to low conductivity. Designing p-type TCOs with good conductivity has therefore still remains as a major challenge for materials scientists. Cu$_2$O is a known p-type TCO, in which good p-type conductivity is caused by favourable mixing between Cu (I) 3$d^{10}$ and the O 2p states, causing a more delocalized VB. However Cu$_2$O is not transparent as it has a band gap of 2.17 eV. In 1997, Kawazoe et al. [4] first reported p-type conductivity in CuAlO$_2$, which crystallizes in the “delafossite” structure. CuAlO$_2$ combines the p-type conduction properties of Cu$_2$O, with the wide band gap of Al$_2$O$_3$, producing for the first time, a native p-type TCO. They had realised that a suitable cation is needed to mix with the O 2p states, like in the case of Cu$_2$O, and identified Cu(I) and Ag(I) as the best candidates.

![Diagram of N-type and P-type TCOs](image-url)
It has been shown that Cu based TCOs are superior to Ag based TCOs, and many other Cu based TCOs have been synthesized, including delafossites CuInO$_2$ [27], CuGaO$_2$ [28], CuScO$_2$ [29], CuCrO$_2$ [30], CuYO$_2$ [31] and the SrCu$_2$O$_2$ [32]. To date, the p-type material with the highest conductivity is Mg doped CuCrO$_2$ [33].

1.3.1. Electrical conductivity

TCOs are wide band gap ($E_g$) semiconducting oxides, with conductivity [$\sigma$] in the range $10^2 – 1.2 \times 10^6$ (S), which is due to doping either by oxygen vacancies or by extrinsic dopants. In the absence of doping, these oxides become very good insulators, with $\rho > 10^{10}$ Ω cm. Most of the TCOs are n-type semiconductors. Electrical conductivity of n-type TCO thin films depends on the electron density in the conduction band and on their mobility: $\sigma=\mu n e$, where $\mu$ is the electron mobility, $n$ is its density, and $e$ is the electron charge. The mobility is given by:

$$\mu = e\tau / m^*$$ .......................................................   (1.1)

Where $\tau$ is the mean time between collisions, and $m^*$ is the effective electron mass. However, as $n$ and $\tau$ are negatively correlated, the magnitude of $\mu$ is limited. Due to the large energy gap ($E_g > 3$ eV) separating the valence band from the conducting band, the conduction band cannot be thermally populated at room temperature (kT~0.03 eV, where k is Boltzmann’s constant). Hence, stoichiometric crystalline TCOs are good insulators [34].
To explain the TCO characteristics, various population mechanisms and several models describing the electron mobility were proposed. Some characteristics of the mobility and the processes by which the conduction band is populated with electrons were shown to be interconnected by electronic structure studies [35]. For example, the mobility is proportional to the magnitude of the band gap.

In the case of intrinsic materials, the density of conducting electrons has often been attributed to the presence of unintentionally introduced ‘donors’ usually identified as metallic interstitials or oxygen vacancies that produced shallow donor or impurity states located close to the conduction band. The donors are thermally ionized at room temperature, and move into the host’s conduction band. However, experiments have been inconclusive as to which of the possible dopants was the predominant donor [36]. Extrinsic dopants have an important role in populating the conduction band and some of them have been unintentionally introduced. Thus, it has been conjectured in the case of ZnO that interstitial hydrogen, in the H⁺ donor state, could be responsible for the presence of carrier electrons [37]. In the case of SnO₂, the important role of interstitial Sn in populating the conducting band, in addition to that of oxygen vacancies, was conclusively supported by first-principle calculations of Kiliç and Zunger [38]. They showed that Sn-interstitials and O-vacancies, which dominated the defect structure of SnO₂ due to the multi-valence of Sn, produced shallow donor levels, turning the material into an intrinsic n-type semiconductor [39]. The electrons released by these defects were not compensated because acceptor-like intrinsic defects consisting of Sn voids and O interstitials did not form spontaneously. Furthermore, the released electrons did not make direct optical transitions in the visible range due to the large gap between the Fermi level and the energy level of the first unoccupied states. Thus, SnO₂ could have a carrier density with minor effects on its transparency.

Electrical conductivity [σ] is intrinsically limited due to two reasons. First, n and µ cannot be independently increased for practical TCOs with relatively high carrier concentrations. At high electron density, carrier transport is limited primarily by ionized impurity scattering i.e., the Coulomb interactions between electrons and the dopants. Higher doping concentration reduces carrier mobility to a degree so that the conductivity cannot be increased. More over it decreases the optical transmission at the near-infrared edge. With
the increase in dopant concentration, the resistivity reaches a lower limit, beyond which it cannot decrease. But the optical window becomes narrower. Ellmer also showed that in ZnO films, deposited using various methods, resistivity and mobility were nearly independent of the deposition method and limited to about $2 \times 10^{-4}$ $\Omega$ cm and 50 cm$^2$/Vs, respectively [40,41]. In ITO films, the maximum carrier concentration was about $1.5 \times 10^{21}$ cm$^{-3}$[42]. This is a universal property of other semiconductors too [43,44]. Scattering by the ionized dopant atoms that are homogeneously distributed in the semiconductor is only one of the possible effects that reduce the mobility. Recently developed TCO materials, including doped and undoped binary, ternary, and quaternary compounds, also suffer from the same limitations. Only some exceptional samples had resistivity of $\leq 1 \times 10^{-4}$ $\Omega$ cm.

In addition to the above mentioned effects that limit the conductivity, high dopant concentration could lead to clustering of the dopant ions [45] which increases significantly the scattering rate. It could also produce ‘nonparabolicity’ of the conduction band, which has to be taken into account for degenerately doped semiconductors with filled conduction bands [46].

### 1.3.2 Optical properties

As mentioned above, besides high conductivity ($\sim 10^6$ S/m), good TCO thin films should have very low absorption coefficient in the near UV-VIS-NIR region. Transmission in the near-UV region is limited by $E_g$, as photons with energy larger than $E_g$ are absorbed. A second transmission edge exists at the NIR region, mainly due to reflection at the plasma frequency. Ideally, a wide band gap TCO should not absorb photons in the transmission “window” in the UV-VIS-NIR region. However, there are no “ideal” TCOs thin films, and even if such films could be deposited, reflection and interference would also affect the transmission. Hence, 100% transparency over a wide region cannot be obtained.

Optical properties of TCOs transmission [$T$], reflection [$R$], and absorption [$A$], are determined by its refraction index $n$, extinction coefficient $k$, band gap $E_g$, and geometry. Geometry includes film thickness, thickness uniformity, and film surface roughness. $T$, $R$ and, $A$ are intrinsic, depending on the chemical composition and solid structure of the material, whereas the geometry is extrinsic. There is a negative correlation between the carrier density and position of the IR absorption edge; but there is positive correlation.
between the carrier density and the UV absorption edge, as $E_g$ increases at larger carrier density (Moss-Burstein effect). As a result, the TCO transmission boundaries and conductivity are interconnected.

Width of visible transmission window of a TCO film deposited on a transparent substrate is affected not only by the optical parameters of the TCO film but also by the optical properties of the substrate. Refractive index $n_{sub}$ of the most common substrates are ~1.45 for fused silica and ~1.6 for various glasses. Extinction coefficient of the substrate ($k_{sub}$) is generally $< 10^{-7}$. Hence light absorption would take place only in the film, where generally $k_{film} > k_{sub}$. For films thicker than 100 nm, several interference bands could be formed, producing maximal and minimal values of $T$ when either the wavelength or thickness is varied. When $k_{film} = 0$, the peak transmission ($T_{max}$) is equal to the transmission of the substrate. Hence, assuming that the sample is in air, $T_{max} = 90\%$ and 93\% for films deposited on glass and fused silica, respectively. The minimum sample transmission ($T_{min}$) in air is expressed by:

$$T_{min} = \frac{4n_{film}^2n_{sub}}{(1+n_{film}^2)(n_{film}^2+n_{sub}^2)^{1.5}}$$

(1.2)

As most TCO films have values of $n$ in the VIS in the range 1.8 – 2.8, $T_{min}$ will be in the range 0.8 – 0.52. $T_{min}$ and is closely approximated by the relation,

$$T_{min} = 0.051n^2 - 0.545n + 1.654.$$  

As $n$ in the visible region decreases with wavelength, $T_{min}$ increases with wavelength. But it will not exceed ~0.8. When the film extinction coefficient is not negligible and affects the transmission, $T_{max} < T_{sub}$, and $T_{min}$ also decreases. By decreasing the TCO film thickness, $T$ is increased. But the sheet resistance increases.
1.3.3 Work function

Energy difference between Fermi energy level and vacuum level corresponds to the work function ($\Phi$) which is the minimum amount of energy needed to remove an electron from the metal. In metals, work function and ionization energy are the same. Condition of the surface can strongly affect the work function. Presence of minute quantity of contamination (less than a monolayer of atoms or molecules), or the occurrence of surface reactions (oxidation or similar) can change the work function substantially. Changes of the order of 1 eV are common for metals and semiconductors, depending on the surface condition. These changes are due to the formation of electric dipoles at the surface, which change the energy an electron needs to leave the sample. Due to the sensitivity of the work function to chemical changes on surfaces, its measurement can give valuable insight into the condition of a given surface. In a nondegenerate semiconductor (having a moderate doping level), the Fermi level is located within the band gap. This means that work function is now different from the ionization energy (energy difference between valence bands maximum (VBM) and vacuum level). In a semiconductor, the Fermi level becomes a somewhat theoretical parameter since there are no allowed electronic states within the band gap. This means that Fermi distribution needs to be considered, which is a statistical function that gives the probability to find an electron in a given electronic state. Fermi level refers to the point on the energy scale where the probability is just 50%. Work function of untreated ITO is generally equated at ~4.7eV [47], where the plasma cleaning of the TCO in O$_2$ generally increased the work function by about 0.1-0.3 eV.

1.3.4 Thermal and Chemical stability

Thermal stability temperature is a threshold temperature, above which TCO films show appreciable change or degradation in its properties. The reported thermal stability temperatures for ZnO, SnO$_2$ and Cd$_2$SnO$_4$ are 250, 500 and 700°C, respectively [12]. Above these temperatures, chemical decompositions of the films occur, which degrade the quality of the films. Many commercial substrates are temperature sensitive (glass < 500°C, polymer <200 °C) and hence, restrict the processing temperature. Moreover, observations of chemical reaction of the TCO films with the substrate and the subsequent layers have been reported in the literature [48]. Thermal stability is essential for the developed TCOs from
the application point of view as these TCOs may be exposed to various extreme environments. Chemical stability of a TCO is determined by its ability to resist corrosive environment and treatment. For applications such as amorphous Si solar cells, sensitivity of TCO to reducing atmospheres is an important concern. ITO undergoes heavy reduction when exposed to hydrogen environments. Comparatively, doped ZnO films are much more stable in reducing atmospheres and plasmas containing hydrogen species [12, 5]. Therefore, ZnO based TCOs may be preferred for the applications involving hydrogen plasma processing. In contrast, for oxidizing atmospheres, especially at high temperatures, ITO shows better stability compared to other TCOs.

1.3.5 Surface morphology

Surface texture should be such that it nicely scatters the sunlight so as to increase the path length of light inside the cell. The texture, however, does not mean the steep and rugged surface because it makes the smooth and junction formation difficult. One of the smooth, coherent texture was reported on CVD deposited SnO$_2$: F film in 1990 [49]. Also the chemical stability of ZnO on top of the textured SnO$_2$: F has been clarified to be better than SnO$_2$:F bare surface [50]. It consists of regular, smooth surface microcrystals with good coherence and is recognised as standard texture for a-Si solar cells.

TCO coated substrates for use in solar cell comprises of three main features
1) Resistivity as low as possible to minimise the loss due to Joule heat
2) Absorption of sunlight (Covering from near UV to near infrared) as low as possible to better conversion efficiency
3) A proper texture to confine as much sunlight as possible in the junction region of the cell.

The second requirement is now recognised as more important because the light utilization ratio of near infrared/ visible in increasing in a-Si:H/mc-Si:H tandem structures recently available on the market. This means that the TCO having higher mobility is better because of lower absorption in the infrared.
1.3.5.1 Function of TCO texture

Effect of texture can be explained in more detail as shown in Fig1.1. **The first** is reduction of reflection (or suppression of reflection) provided by the rugged structure with characteristic length equal to somewhat smaller than the quarter wavelength of the average sunlight. This give rise to graded refractive index layer which serves as anti reflection (AR) layer at the interface (TCO/a-Si). Taking into account the refractive index 2.0 of tin oxide and that of a-Si c.a 4.0, this material combination well satisfy the amplitude condition of the AR coating. **Second** is strong scattering power to extend the travelling length of light in i-layer where photoelectron and holes are generated. Multiple passage of light increases the electron–hole pair generation. The generated electron- hole pair must be separated as soon as possible and this is caused by the electric field between p- and n-layers. Accordingly the separation efficiency goes up as the i-layer thickness decreases. This trade-off relation suggests that there is an optimum thickness of i-layer. Multiple scattering of the light helps semiconductor to generate more electron–hole pairs so that its thickness can be reduced and the separation field is strengthened. Thickness reduction may also serve as saving the Si raw materials.

**Third** is light confinement. The sunlight yet not absorbed in the photoactive i-layer suffers from diffuse scattering and sent back again into the active i-layer where it takes part in the electric power generation. The higher the diffuse back scattering broader the wavelength region covered by the texture, its contribution to the power generation is enhanced.
1.4 TCO Materials

Three oxides have emerged as commercially important transparent conductors: indium oxide, tin oxide, and zinc oxide. Properties and crystal chemistry of the transparent conducting indium oxide family of materials is discussed in some detail in the following sections because it is probably having the highest performance and hence the best-understood/studied material in the TCO class. By volume, however, the most deposited TCO today is SnO$_2$, which is used in IR-efficient architectural window applications. ZnO is also primarily used in window coatings (multilayer stacks with Ag), but recent processing-related improvements and low cost make it an attractive replacement for high-cost In-based TCOs.

If an oxide is completely stoichiometric, it can only be an ionic conductor. Such a material is obviously of no interest as transparent conductors because of high activation energy required for ionic conductivity. However, real oxides are hardly, if ever, completely stoichiometric. The oxides used for transparent conductors are invariably with anion vacancy. Consider the formation of an oxygen vacancy in perfect crystal. In the process of removing an oxygen atom, two electrons of oxygen ions are left in the crystal. If both these electrons are localized at the oxygen vacancy, the charge is same as in the perfect crystal and the vacancy has zero effective charge. Such a vacancy is neutral. If one or both of the localized electrons are excited and transferred away from the vacancy, the vacancy is left with an effective positive charge with respect to the perfect crystal. The charged vacancy becomes ‘electron trapping site’. But in the process one or more electrons are made available for conduction. If the cation is multivalent (e.g. Sn), the creation of too many oxygen vacancies results in the structure change from SnO$_2$ to SnO. Somewhere in such a transition, there occurs a compositional change where excess of oxygen in the SnO structure will exist. Cation vacancies resulting from excess oxygen have the opposite effect. They produce holes rather than electron. Creation of an anion vacancy results in a cationic valence charge. Clearly, for conduction to be efficient, volume fraction of trap must be small. Binary oxides used for transparent conductors are relatively unstable and are relatively easy to oxidise or reduce.
If, instead of creating oxygen vacancies by chemical reduction, one incorporates into the host lattice substitutional cations with a valency higher than that of the host, it has electrically the same effect of creating anion vacancies. Since overall charge neutrality must be preserved, substitution of higher valency cation requires the addition of an electron. Conversely, incorporation of lower valency cation produces a hole. [If one incorporates Sb\textsuperscript{5+} substitutionally in SnO\textsubscript{2}, an additional electron is added to the lattice. If instead, In\textsuperscript{3+} is substitutionally added, a hole is produced which, in an n-type semiconductor, becomes a trap.] As with the oxygen vacancies, not all higher valency dopants incorporated into the lattice produce charge carriers. Some simply remain as neutral point defects. Electrically equivalent effects can occur if anion sites are doped with atoms whose valency is lower than that of oxygen. Among the anion dopants employed, F\textsuperscript{−} and Cl\textsuperscript{−} are the most popular.

Ionic radius of the dopant must be the same or smaller than that of the ion it replaces, and no compounds or solid solutions of dopant oxide with host oxides are formed. Even in the absence of solid solution or compound formation, a dopant may not be usable based on its ionic radius. If the dopant ions are too large, an interstitial, rather than a substitutional site is favoured, and the dopant will act as a scattering site rather than a source of charge carriers.

1.4.1 ITO or Tin–Doped Indium Oxide

ITO is a solid solution of indium oxide and tin oxide, typically 90% In\textsubscript{2}O\textsubscript{3}, 10% SnO\textsubscript{2} by weight. It is transparent and colourless in thin layer while in bulk form it is yellowish to grey. In the infrared region it is a ‘metal like’ mirror. ITO is one of the most widely used transparent conducting oxide having electrical conductivity and optical transparency. Thin films of ITO are mostly deposited using electron beam evaporation, physical vapour deposition and sputter deposition techniques.

Tin–doped indium oxide films prepared with the help of various techniques are always polycrystalline and retain a crystal structure of bulk – undoped In\textsubscript{2}O\textsubscript{3}. However lattice constant values are usually larger than those of bulk-undoped In\textsubscript{2}O\textsubscript{3}. Increase in lattice constant depends on the deposition parameters like the partial oxygen pressure p(O\textsubscript{2}) in the sputtering process [58]. For the lowest value of p(O\textsubscript{2}), a\textsubscript{0}=10.15 Å while for p ( O\textsubscript{2} ) >5×10\textsuperscript{−5} Torr, a\textsubscript{0}≈10.23 Å. Increase in the value of lattice constant up to 10.23 Å has been
observed by many workers [52-54]. ITO film, in general, exhibits a strong (111) or (100) preferred orientation depending on the deposition condition.

**1.4.2 Tin oxide (SnO$_2$)**

SnO$_2$ has tetragonal rutile structure with space group D$^{14}$ (P4$_2$/mmm) [55]. The unit cell contains six atoms –two tin and four oxygen. Each tin atom (cation) is at the centre of six oxygen atoms (anions) placed approximately at the corners of regular octahedron, and every oxygen atom is surrounded by three tin atoms approximately at the corners of an equilateral triangle. The lattice parameters are [56] are a=b=4.737 and c=3.185, while c/a ratio is 0.673. Ionic radii of O$^{2-}$ and Sn$^{4+}$ are 1.40 and 0.71 Å respectively [57]. The lattice has 15 optical normal modes of vibration, five of which are Raman active (Frequencies 100-800 cm$^{-1}$). Seven modes are IR active (frequencies 250-600 cm$^{-1}$) and two are inactive [58].

If SnO$_2$ was completely stoichiometric, it would be an insulator or at the most an ionic conductor. However the practical material is never stoichiometric and is invariably anion deficient. This is due to the formation of oxygen vacancies in the otherwise perfect crystal. These vacancies are responsible for making electrons available for the conduction process. In the case of SnO$_2$, because the cation is multivalent, the creation of too many oxygen vacancies also results in structure change from SnO$_2$ to SnO.

**1.4.3 Indium Oxide(In$_2$O$_3$)**

In$_2$O$_3$ single crystal has the cubic bixbyte structure (also called c-type rare earth oxide structure) and belongs to the space group (T$_h^7$.Ia$_3$). The lattice parameter of In$_2$O$_3$ is 10.117 Å and co-ordination is six fold for the indium atoms and four fold for the O atoms. One can assume that there are two crystallographically non-equivalent In-sites. One of this is associated with an In-O separation of 2.18 Å, and oxygen atom lying nearly at the corners of the cube with two body diagonal opposite corners unoccupied. The other is associated with non-equal In-O separations of 2.13, 2.19 and 2.23 Å, and O atoms lying nearly at the corners of a cube with two face diagonal opposite corners unoccupied.

In$_2$O$_3$ is a non-stoichiometric compound under various conditions with In /O ratio larger than 2/3. This non-stoichiometry makes it an n-type semiconductor [or even a semimetal at high electron concentration]. During the crystal growth, large number of native
donors is produced because of the oxygen vacancies. These donors also create an intense ‘free carrier absorption’ in the infra red reflection spectrum.

1.4.4 Zinc Oxide (ZnO)

Most of the group II-VI binary compound semiconductors crystallize in either cubic zinc–blende or hexagonal wurtzite structure where each anion is surrounded by four cations at the corners of the tetrahedron, and vice versa. Zinc Oxide occurs in the nature as the mineral called ‘zincite’. Zinc Oxide crystallizes in the hexagonal wurtzite (B4 type) lattice. Zinc atoms are nearly in the position corresponding to ‘hexagonal close pack’ structure. Every oxygen atom lies within the tetrahedral group of four zinc atoms and all these tetrahedral points are in the same direction along the hexagonal axis giving the crystal its polar symmetry. The lattice constants are $a= 3.24 \text{ Å}$ and $c= 5.19 \text{ Å}$.

1.5 Important Electrical and Optical Properties of n-type TCO materials

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Cell Parameters ($\text{Å}$)</th>
<th>Electrical (Ω cm)</th>
<th>Band gap (eV)</th>
<th>Dielectric</th>
<th>Refractive Index</th>
</tr>
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<tr>
<td>SnO$_2$</td>
<td>B Schlöfl</td>
<td>$a_2$ $b_2$ $c_2$</td>
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<td>3.7 - 4.6</td>
<td>3-5</td>
<td>1.5 - 3.1</td>
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<tr>
<td>In$_2$O$_3$</td>
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<td>8.9</td>
<td>2.3 - 3.1</td>
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<tr>
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<td>$10^4$ $-10^5$</td>
<td>3.7 - 4.6</td>
<td>8.9</td>
<td>2.3 - 3.1</td>
</tr>
<tr>
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<td>B Schlöfl</td>
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</tr>
<tr>
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<td>Wurtzite</td>
<td>$a=3.24$ $b=3.19$</td>
<td>$10^4$ $-10^5$</td>
<td>3.7 - 4.6</td>
<td>8.9</td>
<td>1.83 - 1.99</td>
</tr>
</tbody>
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1.6 P-type TCO

The first report of a p-type TCO was NiO [59]. In 1997 there was a report of transparent p-type conducting films of CuAlO$_2$ showing considerable improvement over NiO [60]. Although the conductivity of 1 S cm$^{-1}$ was about three orders of magnitude smaller than that of n-type materials, the result was promising. Since then, a number of promising p-type materials have been prepared as a consequence of material exploration efforts following the design concept. Work by the groups of Kawazoe and Hosono over the
last few years has led to the discovery of a number of p-type TCOs [60–63] based on Cu⁺ bearing oxides.

1.6.1 Copper-based delafossite structure

Kawazoe and co-workers [60] proposed that one could modify the valence band edge by ‘mixing orbitals’ of appropriate counter cations that have filled energy levels comparable to O 2p. This would reduce the strong Coulomb force exerted by the oxygen atoms and thereby delocalize the positive holes. Copper was selected as one of the major constituents because of its ‘3d10 energy level’. Also, its closed d-shell makes it less prone to d–d transitions that could absorb light in the visible range. The chemical formula of delafossites is AMO₂ in which A is the monovalent cation and M is a trivalent cation. Delafossites have a hexagonal, layered crystal structure: the layers of A cations and MO₂ are stacked alternately, perpendicular to the c-axis [64]. As a class, p-type materials now include the copper-based delafossites CuMO₂.

1.6.1.1 Copper Aluminum Oxide (CuAlO₂)

Structure of CuAlO₂ delafossite had been extensively studied by Ishiguro et al. [65] and they proposed an alternative stacking of CuI and layers of nominal AlO₂ composition consisting of Al–O₆ octahedral sharing edges. Each copper atom is linearly coordinated with two oxygen atoms to form an O–Cu–O ‘dumb-bell unit’ placed parallel to the c-axis. Oxygen atoms of the O–Cu–O dumb-bell link all Cu layers with the AlO₂ layers. After the report of p-type semiconducting transparent CuAlO₂ thin film, recently a research field in device technology has emerged known as “transparent electronics”. For the synthesis of CuAlO₂ thin films, the groups of Hosono [66], Gong [67,68], and Chattopadhyay [69-73] used pulsed laser deposition (PLD), “plasma-enhanced metalorganic chemical vapor deposition (PE-MOCVD)” and dc sputtering respectively. Band gap was observed between the valence band edge in the PES spectrum and the conduction band edge in the IPES spectrum, which was about 3.5 eV. The Fermi energy lies almost at the top of the valence band. This observation agrees with the fact that the sample is a p-type semiconductor.

1.6.1.2 Copper Indium Oxide (CuInO₂)

Of the copper-based delafossites, the CuInO₂ system is particularly interesting because it can be doped to form both p-type (with Ca) and n-type (with Sn), allowing p–n
homojunction to be produced [63, 75]. Thin films of CuInO\textsubscript{2} delafossite can also be made both p-type and n-type by doping appropriate impurity and tuning the deposition conditions. This is quite puzzling because CuInO\textsubscript{2} has the largest reported band gap of 3.9 eV. No similar trend has ever been observed in any other semiconductors. Using first-principles methods, Nie et al. [76] reported the unusual ‘bipolar dopability’ observed in this material by the exceptionally large disparity between its fundamental indirect band gap and apparent direct band gap. Unfortunately, the conductivity of CuInO\textsubscript{2} films (∼10\textsuperscript{−3} S cm\textsuperscript{−1}) has, thus far, been smaller than that of the other p-type TCOs. However, producing phase-pure targets is still challenging and has likely limited the subsequent research on CuInO\textsubscript{2}. However, the oxygen-rich Cu\textsubscript{2}In\textsubscript{2}O\textsubscript{5} phase of Cu–In–O is easily prepared by solid-state synthesis in air. Therefore, Teplin et al. used Cu\textsubscript{2}In\textsubscript{2}O\textsubscript{5} as a target to deposit single phase undoped and Ca-doped CuInO\textsubscript{2} thin films [77].

1.6.1.3 Copper Gallium Oxide (CuGaO\textsubscript{2})

CuGaO\textsubscript{2} is another p-type TCO with band gap energy of ∼3.6 eV [78]. This material has a larger lattice constant [a = 2.98 Å], than CuAlO\textsubscript{2} (a = 2.86 Å). The lattice constant of the a-axis in AgInO\textsubscript{2}, which is the only n-type conductive delafossite available at present, is 3.27 Å. Polycrystalline thin film of CuGaO\textsubscript{2} has been prepared by an rf sputtering method [79]. The deposited film was obtained in an amorphous state, and was subjected to post-deposition annealing for crystallization at 850 °C for 12 h under nitrogen atmosphere. For CuGaO\textsubscript{2} thin film, its activation energy was roughly estimated to be about 0.22 eV. The conductivity at room temperature was about 5.6 × 10\textsuperscript{−3} S cm\textsuperscript{−1}. Epitaxial CuGaO\textsubscript{2} films were prepared on α-Al\textsubscript{2}O\textsubscript{3} (001) single-crystal substrates by PLD without post-annealing treatment [78]. Electrical conductivity, carrier (positive hole) density, and Hall mobility at room temperature were found to be 6.3 × 10\textsuperscript{−2} S cm\textsuperscript{−1}, 1.7 × 10\textsuperscript{18} cm\textsuperscript{−3}, and 0.23 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1}, respectively.

1.7 Application of TCOs

TCO’s have diverse industrial applications; some of the more important ones will be described in this section. 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 build-up. In this application relatively high surface resistances (e.g. kΩ) can be tolerated.

The architectural use of TCOs is predominately for energy efficient windows. Fluorine doped tin Oxide (FTO) films deposited using chemical vapour deposition (CVD) process, are often used for this application [80,81]. Metal–oxide/Ag/Metal–oxide stacks such as ZnO/Ag/ZnO are common also [82,83]. Windows with tin oxide coating are efficient in preventing radiative heat loss due to their low thermal emittance ~0.15, compared to ~0.84 for uncoated glass [84]. Such “low-e” windows are ideal for use in cold or moderate climate. In addition, pyrolytic tin oxide is also used for heated glass freezer doors in commercial use. In this application, the doors can be defrosted by passing small current through the slightly resistive TCO coating. In 2007, the annual demand for low-e coated glass in Europe was 60×10^6 m^2 and this is projected to increase to about 100×10^6 m^2 in a few years [85]. Rapid growth in China is also increasing the demand of low-e glass [86].

Realization of p–n junction composed of TCOs is a requisite for the extension of application of TCOs to transparent semiconductors because a variety of active functions in semiconductors arise from p–n junction. Previous attempts to construct transparent electronic devices have been hampered by the lack of a p-type transparent semiconductor with good performance. To date, the group of copper based delafossites such as CuAlO_2 and CuGaO_2 and SrCu_2O_2, etc., seemed to be potential p-type materials for transparent p–n junctions and due to the development of these materials, it has become feasible to fabricate transparent p–n junctions. Several oxide transparent p–n junctions and LEDs have been successfully fabricated, such as n-ZnO/p-SCO [87–89], n-CuInO_2: Sn/p-CuInO_2: Ca and n-ZnO/p-CuAlO_2 [90]. For these oxide diodes, ZnO was selected as the n-type material due to its advantageous properties in carrier mobility, capability of film deposition at relatively low temperatures and controllability of electrical conductivity.

Amorphous oxide p–n junction diodes are also of interest. When the performance of crystalline devices often suffers from defects inherent to the rigid periodicity of the crystalline lattice, [e.g. grain boundaries and rough interfaces in polycrystalline materials and lattice mismatch at hetero interfaces], amorphous materials and devices are free of these
troublesome effects. Amorphous semiconductors are highly favourable for applications in large-area electronic devices such as solar cells and flat-panel displays because they have several advantages, i.e. homogeneous films can be deposited on a variety of large area substrates at low temperature. Research on p-type transparent amorphous oxide semiconductors and amorphous oxide p–n junction diodes has started to seek materials that meet these advantages. The first ‘all-amorphous’ oxide p–n junction diode was reported by Narushima et al. [91]. They fabricated a flexible p–n heterojunction diode on plastic substrate using an amorphous ZnORh$_2$O$_3$ film for the p-layer and a-InGaZnO$_4$ film for the n-layer at room temperature. The diode exhibited distinct rectifying electrical characteristics with threshold voltage (~2.1 V) consistent with the band gap of the a-ZnORh$_2$O$_3$ film and on–off current ratio of ~10$^3$.

Transparent heating elements may be constructed from TCO coatings. These are useful as defrosters in aircraft and vehicular windshields. Their advantage over traditional hot air blowers is that they can have a much shorter effective defrosting time and work uniformly over large area. This application requires either the use of very low surface resistance coatings (e.g. ~1 Ω/□), or a high voltage power source. Application of TCO coatings to passenger vehicles has proven to be technically successful. However there is a difficulty 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, as has been widely discussed, then this application may prove to be more commercially feasible in the future.

TCO coatings may be used as shielding to decrease electromagnetic radiation interference (EMI) while providing visual access. This may be either to keep radiation from escaping an enclosure to avoid interfering with nearby devices / detection, or from entering an enclosure [to prevent external radiation sources from interfering with electronic devices within]. One potential example is the window of domestic microwave ovens that today use a perforated metal screen, [which obscures clear visual observation], to 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 films were proposed 50 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 transparent conductive oxide thin 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 the 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, and hence patterning the films is required. ITO is the TCO of choice in this application, both because of its electro-optical properties, and the relative ease of acid etching.

The best LCDs utilize an active matrix comprising one amorphous silicon transistor which occupies a corner of each pixel and because the silicon is opaque, there is reduction of light transmission. Recently transparent field effect transistors (FETs) have been developed based on the zinc oxide, but using a Cr gate. Most solar cells use TCO films as a transparent electrode. Major considerations in the choice of the TCO for this application, besides the conductivity and transparency, are electronic compatibility with adjacent layers in the cell, processing requirements, and stability under environmental conditions. Often tin oxide based films are chosen for this application, where patterning is not required, but environmental stability is essential.

1.8 Importance of the present work

Current photovoltaic technologies as well as next-generation approaches to PVs, will place specific demands on the transparent contact layers beyond transparency and low resistivity. To date, the industry standard in TCO is ITO, or tin-doped indium-oxide. This material boasts a low resistivity of \( \sim 10^{-4} \ \Omega \cdot \text{cm} \) and a transmittance of greater than 80\%. However ITO has the drawback of being expensive. Indium, the film’s primary metal, is
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rare (6000 metric tons worldwide in 2006), and its price fluctuates due to market demand (over $800 US per ingot in 2006). For this reason, doped binary compounds such as aluminum-doped zinc-oxide (AZO) and indium-doped cadmium-oxide have been proposed as alternative materials. Among these, AZO is composed of aluminum and zinc, two common and inexpensive materials, while indium-doped cadmium oxide only uses indium in low concentrations. In many of the novel PV technologies currently under development, such as organic photovoltaics and Grätzel cells, control of the morphology and surface chemistry of the TCOs used is critical to device performance. Examination of current and future PV-TCO materials performance leads to the conclusion that new efforts to develop application specific TCO materials and processes are needed. As new device structures evolve, it will be necessary to expand the tool kit of TCO materials available to achieve very different film properties and surface chemistries.

References
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