

# TRANSPARENT CONDUCTING OXIDE FILMS FOR VARIOUS APPLICATIONS: A REVIEW

**Rakesh A. Afre, Nallin Sharma, Maheshwar Sharon and Madhuri Sharon**

Walchand Center for Research in Nanotechnology and Bionanotechnology, W-H Marg, Ashok Chowk, Solapur, Maharashtra, 413006, India

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**Abstract.** This review encompasses properties and applications of polycrystalline or amorphous, Transparent Conducting Oxides (TCO) semiconductors. Coexistence of electrical conductivity and optical transparency in TCO depends on the nature, number and atomic arrangements of metal cations in oxides, on the resident morphology and presence of intrinsic or introduced defects. Therefore, TCO semiconductors that are impurity-doped as well as the ternary compounds and multi-component oxides consisting of combinations are discussed. Expanding use of TCO is endangered by scarcity, cost of In, fragility of glass, limited transparency to visible light, instability above  $>200$  °C, non-flexible for application of flexible solar cell; thus driving search for alternatives such as graphene or CNT, that are more stable under acidic, alkaline, oxidizing, reducing and elevated temperature. There are reasons to conclude that there is need to develop large area deposition techniques to produce TCO films with high deposition rate. TCOs are mostly n-type semiconductors, but p-type are also being researched.

## 1. INTRODUCTION

All the optically transparent and electrically conducting oxides (TCO) are binary or ternary compounds, containing one or two metallic elements. Their resistivity could be as low as  $10^{-4}$  Ω cm, and their extinction coefficient  $k$  in the optical visible range (VIS) could be lower than 0.0001, owing to their wide optical band gap ( $E_g$ ) that could be greater than 3 eV. This remarkable combination of conductivity and transparency is usually impossible in intrinsic stoichiometric oxides; however, it is achieved by producing them with a non-stoichiometric composition or by introducing appropriate dopants. Badeker [1] discovered that thin CdO films possess such characteristics. Later, it was recognized by Haacke [2] that thin films of ZnO, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub> and their alloys were also TCOs. Doping these oxides resulted in improved electrical conductivity without degrading their optical transmission. Al doped ZnO

(AZO), tin doped In<sub>2</sub>O<sub>3</sub>, (ITO) and antimony or fluorine doped SnO<sub>2</sub> (ATO and FTO), are among the most utilized TCO thin films in modern technology. In particular, ITO is used extensively.

The actual and potential applications of TCO thin films include: (i) transparent electrodes for flat panel displays; (ii) transparent electrodes for photovoltaic cells; (iii) low emissivity windows; (iv) window defrosters; (v) transparent thin films transistors; (vi) light emitting diodes; and (vii) semiconductor lasers. As the usefulness of TCO thin films depends on both their optical and electrical properties, both parameters should be considered together with environmental stability, abrasion resistance, electron work function, and compatibility with substrate and other components of a given device, as appropriate for the application. The availability of the raw materials and the economics of the deposition method are also significant factors in choosing the most appropriate TCO material. The selection decision is

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Corresponding author: M. Sharon, e-mail: sharonmadhuri@gmail.com

generally made by maximizing the functioning of the TCO thin film by considering all relevant parameters, and minimizing the expenses. TCO material selection only based on maximizing the conductivity and the transparency can be misleading.

Recently, the scarcity and high price of Indium needed for ITO, the most popular TCO, as spurred R&D aimed at finding a substitute. Its electrical resistivity ( $\rho$ ) should be  $\sim 10^4 \Omega \text{ cm}$  or less, with an absorption coefficient ( $\alpha$ ) smaller than  $10^4 \text{ cm}^{-1}$  in the near-UV and VIS range, and with an optical band gap  $> 3 \text{ eV}$ . A 100 nm thick TCO film with these values for  $\alpha$  and  $n$  will have optical transmission ( $T$ ) 90% and a sheet resistance ( $R_s$ )  $10^4 \Omega \text{ cm}^2$ . At present, Aluminium doped zinc oxide (AZO) and Gallium doped zinc oxide (GZO) semiconductors are promising alternatives to ITO for thin-film transparent electrode applications. The best candidates is AZO, which can have a low resistivity, e.g. of the order of  $10^4 \Omega \text{ cm}$ ,<sup>1</sup> and its source materials are inexpensive and non-toxic. However, the development of large area, high rate deposition techniques is needed.

Another objective of the recent effort to develop novel TCO materials is to deposit p-type TCO films. Most of the TCO materials are n-type semiconductors, but p-type TCO materials are required for the development of solid lasers. Such p-type TCOs include: ZnO:Mg, ZnO:N, ZnO:In, NiO, NiO:Li, CuAlO<sub>2</sub>, Cu<sub>2</sub>SrO<sub>2</sub>, and CuGaO<sub>2</sub> thin films. These materials have not yet found a place in actual applications.

One of the major drawbacks with TCO glasses are that they are fragile, cannot stand high temperature and not suitable for all pH. Graphene is being considered as TCO materials, because they can be deposited on any material after they have been formed, hence there is no temperature problem, and they are highly inert and can be used in any pH range, optical and electrical properties of graphene is much superior to any other TCO materials. In this review special section is allotted to discuss graphene and compare it with other TCO glasses.

Published reviews on TCOs have exhaustively reported on the deposition and diagnostic techniques, on film characteristics, and expected applications [3,4,5]. The present paper has three objectives: (i) to review the theoretical and experimental efforts to explore novel TCO materials intended to improve the TCO performance, (ii) to explain the intrinsic physical limitations that affect the development of an alternative TCO with properties equivalent to those of ITO, and (iii) to review the practical and industrial applications of existing TCO thin films.

## 2. ELECTRICAL CONDUCTIVITY

### 2.1. Effect of band gap of semiconductors

TCOs are wide band gap ( $E_g$ ) semiconducting oxides, with conductivity in the range  $10^2 - 1.2 \times 10^6 \text{ S}$ . The conductivity is due to doping either by oxygen vacancies or by extrinsic dopants. In the absence of doping, these oxides become very good insulators, with  $\rho > 10^{10} \Omega \cdot \text{cm}$ . Most of the TCOs are n-type semiconductors. The 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,  $\sigma$  is conductivity and  $e$  is the electron charge. The mobility is given by:

$$\mu = \frac{e\tau}{m^*},$$

where  $\tau$  is the mean time between collisions, and  $m^*$  is the effective electron mass. However, as  $m^*$  and  $\tau$  are negatively correlated, the magnitude of  $\mu$  is limited. Due to the large energy gap ( $E_g > 3 \text{ eV}$ ) separating the valence band from the conducting band, the conduction band can not be thermally populated at room temperature ( $kT \sim 0.03 \text{ eV}$ , where  $k$  is Boltzmann's constant), hence, stoichiometric crystalline TCOs are good insulators [6]. 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 done by Mizoguchi and Woodward [7].

In the case of intrinsic materials, the density of conducting electrons has often been attributed to the presence of unintentionally introduced donor centers, usually identified as metallic interstitials or oxygen vacancies that produced shallow donor or impurity states located close to the conduction band. The excess or donor electrons are thermally ionized at room temperature, and move into the host conduction band. However, experiments have been inconclusive as to which of the possible dopants was the predominant donor [8]. 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<sup>+</sup> donor state, could be responsible for the presence of carrier electrons [9]. In the case of SnO<sub>2</sub>, 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 [10]. They showed that Sn interstitials and O vacancies, which dominated the defect structure of  $\text{SnO}_2$  due to the multivalence of Sn, explained the natural nonstoichiometry of this material and produced shallow donor levels, turning the material into an intrinsic n-type semiconductor [11]. 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,  $\text{SnO}_2$  could have a carrier density with minor effects on its transparency [11].

## 2.2. Effect of electrical conductivity:

The electrical conductivity is intrinsically limited for two reasons. First,  $n$  and  $\sigma$  cannot be independently increased for practical TCOs with relatively high carrier concentrations. At high conducting 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 that the conductivity is not increased, and it decreases the optical transmission at the near-infrared edge. With increasing dopant concentration, the resistivity reaches a lower limit, and does not decrease beyond it, whereas the optical window becomes narrower. Bellingham *et al.* [12] were the first to report that the mobility and hence the resistivity of transparent conductive oxides (ITO,  $\text{SnO}_2$ , ZnO) are limited by ionized impurity scattering for carrier concentrations above  $10^{20} \text{ cm}^{-3}$ . Ellmer [11] and Bellingher [12] also showed that in ZnO films deposited by various methods, the resistivity and mobility were nearly independent of the deposition method and limited to about  $2 \cdot 10^{-4} \Omega \text{ cm}$  and  $50 \text{ cm}^2/\text{Vs}$ , respectively. In ITO films, the maximum carrier concentration was about  $1.5 \cdot 10^{21} \text{ cm}^{-3}$ , and the same limits were of conductivity and mobility limits [13]. This phenomenon is a universal property of other semiconductors [14,15]. Scattering by the ionized dopant atoms that are homogeneously distributed in the semiconductor is only one of the possible effects that reduce the mobility. The all recently developed TCO materials, including doped and undoped binary, ternary, and quaternary compounds, also suffer from the same limitations. Only some exceptional samples had a resistivity of  $\leq 1 \times 10^{-4} \Omega \text{ cm}^2$ .

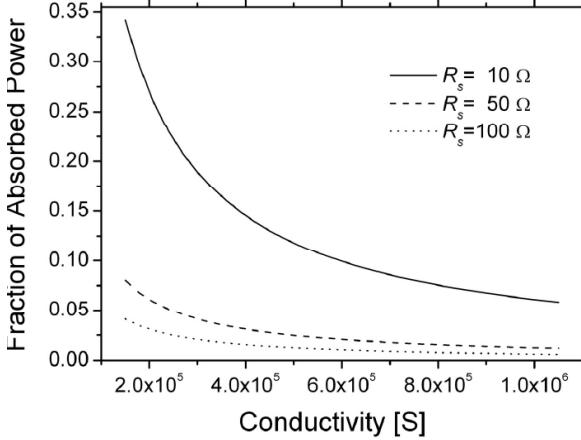
In addition to the above mentioned effects that limit the conductivity, high dopants concentration could lead to clustering of the dopants ions [16], which increases significantly the scattering rate, and it could also produce nonparabolicity of the conduction band, which has to be taken into account for degenerately doped semiconductors with filled conduction bands.

## 3. OPTICAL PROPERTIES

As mentioned, earlier, besides high conductivity ( $\sim 10^6 \text{ S}$ ), effective TCO thin films should have a very low absorption coefficient in the near UV-VIS-NIR region. The transmission in the near UV 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.

The 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 the position of the IR absorption edge, but 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.

The width of the VIS transmission window of a TCO film with thickness 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. The refractive index  $n_{\text{sub}}$  of the most common substrates are  $\sim 1.45$  for fused silica and  $\sim 1.6$  for various glasses. The extinction coefficient of the substrate ( $k_{\text{sub}}$ ) is generally  $< 10^{-7}$ , hence any light absorption would take place in the film, because generally  $k_{\text{film}} > k_{\text{sub}}$ . For films thicker than 100 nm, several interference bands could be formed due to scattering of light, producing maximal and minimal values of transmittance  $T$  when either the wavelength or thickness is varied, if  $k_{\text{film}} \approx 0$ , the peak transmission ( $T_{\text{max}}$ ) is equal to the transmis-



**Fig. 1.** Fraction of absorbed power as function of TCO conductivity.

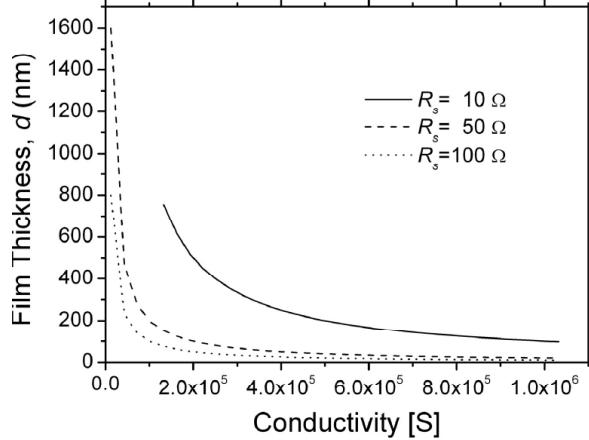
sion of the substrate [16]. Hence, assuming that the sample is in air,  $T_{\max} = 90\%$  and 93% for films deposited on glass and fused silica, respectively. The minimum sample transmission ( $T_{\min}$ ) in air is expressed by:

$$T_{\min} = \frac{An^2 n_{\text{sub}}}{(1+n^2)(n^2 + n_{\text{sub}}^2)}.$$

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.  $T_{\min}$  is closely approximated by the relation:  $T_{\min} = 0.051n^2 - 0.545n + 1.654$ . As  $n$  in the VIS decreases with wavelength,  $T_{\min}$  increases with wavelength, but will not exceed ~0.8. When the film extinction coefficient is not negligible and affects the transmission,  $T_{\max} < T_{\text{sub}}$ , and  $T_{\min}$  also decreases. By decreasing the TCO film thickness,  $T$  is increased but the sheet resistance decreases. Combining the optical and electrical properties of the film, the fraction of the flux absorbed in a film ( $A$ ) is given by the expression:

$$A \approx 1 - \exp^{-\frac{\alpha}{\sigma R}},$$

where  $A$  is flux absorbed in a film,  $\alpha$  absorption coefficient,  $\sigma$  electrical conductivity, and  $R$  is reflectance. Fig. 1 presents plots of the fraction of the absorbed power at wavelength of 400 nm and  $k \sim 0.02$  as a function of the conductivity for three representative values of  $R_s$ . For a given  $\sigma$  low values of  $R_s$  necessitate using thick films and lower conductivity requires the use of even thicker films, resulting in an increase in the loss of radiative power. The dependence of film thickness on the conductivity for three values of  $R_s$  is presented in Fig. 2.



**Fig. 2.** TCO film thickness as function of film conductivity.

TCO films are normally used as substrate for solar energy application, where one requires high transmission and highest conductivity. But characteristic of TCO film as shown in Fig. 1 suggests that fraction of absorption is highest for lowest conductivity, which is contrary to the requirement of TCO films for solar energy application. Dependence of thickness of TCO film with conductivity also suggest that higher thickness will show lower transmission which also contrary to the requirement of TCO film for solar energy application. Both these properties suggest that some other types of substrate is needed which has higher transmission for highest conductivity.

Using the same film conductivity, applications requiring the lowest  $R_s$  will be thicker and, the absorbed fraction will be higher. At present, only high quality ITO is compatible at present with the condition that the absorbed power fraction be lower than 10% and  $R_s = 10 \Omega$ . At lower extinction coefficient ( $k$ ) films with lower conductivities can be used, e.g., when  $k = 0.002$  instead of 0.02, the absorbed power  $A$  is lower by a factor of ~8, and allows the use of thicker films. The combination of film thickness, conductivity, and extinction coefficient determine the absorption of the radiation flux. However, when the total transmission  $T$  is considered, reflection and interference must be considered, which depend on the refractive indices of the substrate and the film, and the film thickness. A general formula for  $T$  and  $R$  was given by Cisneros [17].

#### 4. TRENDS IN THE DEVELOPMENT OF TCO MATERIALS

While the development of new TCO materials is mostly dictated by the requirements of specific ap-

**Table 1.** TCO Compounds and dopants.

TCO	Dopant
$\text{SnO}_2$	Sb, F, As, Nb, Ta
$\text{ZnO}$	Al, Ga, B, In, Y, Sc, F, V, Si, Ge, Ti, Zr, Hf, Mg, As, H
$\text{In}_2\text{O}_3$	Sn, Mo, Ta, W, Zr, F, Ge, Nb, Hf, Mg
$\text{CdO}$	In, Sn
$\text{GaInO}_3$	Sn, Ge
$\text{CdSb}_2\text{O}_3$	Y

plications, low resistivity and low optical absorption are always significant pre-requisites. There are basically two strategies in managing the task of developing advanced TCOs that could satisfy the requirements. The main strategy dopes known binary TCOs with other elements, which can increase the density of conducting electrons.

As shown in Table 1, more than 20 different doped binary TCOs were produced and characterized by Minami [18] of which ITO was preferred, while AZO and GZO come close to it in their electrical and optical performance. Doping  $\text{In}_2\text{O}_3$  with Sn to form ITO substantially increased conductivity. It is believed that substituting  $\text{Sn}^{4+}$  for  $\text{In}^{3+}$  provides carrier electrons, as  $\text{Sn}^{4+}$  is supposed to act as a one-electron donor [19]. Similarly, aluminum is often used for intentional n-type doping of  $\text{ZnO}$ , but other group III impurities, such as Ga and In, and group IV, such as Sn and Ge, also work. Doping by Al produced the relatively high conductivity AZO [3]. Doping with non-metallic elements is also common, e.g.,  $\text{ZnO:Ge}$  (GZO),  $\text{SnO}_2:\text{F}$  (FTO) and  $\text{SnO}_2:\text{Sb}$  (ATO) [20,21]. Recently, AZO films with  $\Omega \sim 8.5 \cdot 10^{-5} \Omega \text{ cm}$  was reported by Agura *et al.* (2003) [21]. An even lower resistivity of  $\sim 8.1 \cdot 10^{-5} \Omega \text{ cm}$  was reported for GZO [22]. This resistivity is very close to the lowest resistivity of ITO [23] of  $7.7 \cdot 10^{-5} \Omega \text{ cm}$ , with a free carrier density of  $2.5 \cdot 10^{21} \text{ cm}^{-3}$ .

The above described metallic dopant ions should have appropriate valency to be an effective donor when replacing the native metallic ion. However, when an  $\text{O}^{2-}$  ion is replaced with a  $\text{F}^-$  ion, a donor level is again produced. Thus, doping  $\text{SnO}_2$  by F increased the carrier electron mobility by a factor of ~2 and their concentration also by a factor of 2, reducing the resistivity by a factor of 4 [23]. The concentration of  $\text{F}^-$  dopant ions should not exceed an upper limit, as an increase in carrier scattering by F ions led to a decrease in the conductivity [24]. Doping  $\text{SnO}_2$  with Sb initially introduces  $\text{Sb}^{5+}$  ions that act as donors. When the doping concentration was in-

creased beyond a certain level, however,  $\text{Sb}^{3+}$  ions began to replace the  $\text{Sn}^{4+}$  ions. The introduction of  $\text{Sb}^{3+}$  ions generates an acceptor level that compensates the donors and increases the resistivity [25].

This effort to increase the conductivity without degrading the transparency was paralleled by a more elaborate strategy in which phase-segregated two-binary and ternary TCOs were synthesized and characterized. The phase-segregated two-binary systems include  $\text{ZnO-SnO}_2$ ,  $\text{CdO-SnO}_2$ , and  $\text{ZnO-In}_2\text{O}_3$ . In spite of the expectations, the electrical and optical properties of the two-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 [21,26] based on known binary TCO compounds. Accordingly, the ternary TCO compounds could be formed by combining  $\text{ZnO}$ ,  $\text{CdO}$ ,  $\text{SnO}_2$ ,  $\text{InO}_{1.5}$ , and  $\text{GaO}_{1.5}$  to obtain  $\text{Zn}_2\text{SnO}_4$ ,  $\text{ZnSnO}_3$ ,  $\text{CdSnO}_4$ ,  $\text{ZnGa}_2\text{O}_4$ ,  $\text{GalnO}_3$ ,  $\text{Zn}_2\text{In}_2\text{O}_5$ ,  $\text{Zn}_3\text{In}_2\text{O}_6$ , and  $\text{Zn}_4\text{In}_2\text{O}_7$ . 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  $\text{In}_6\text{WO}_{12}$  and the p-type  $\text{CuAlO}_2$ .

The first-principle model of Kiliç and Zunger [10] showed the importance of the composition in turning an insulating oxide into a TCO. However, structural considerations should also be included. Hosono *et al.* [26] investigated the conditions for depositing wide-gap *amorphous* oxides with high electron mobility. They indicated that since the mobility is proportional to the width of the conduction bands, a large overlap between relevant orbitals is required. In addition, the magnitude of the overlap needs to be insensitive to the structural randomness that is intrinsic to the amorphous state. They assumed that since the spatial spreading of the ns orbital is large and the overlap between these ns orbitals with spherical symmetry is large and insensitive to any angular variations in the M-O-M bonds (where M is a metal cation) compared with p-p or d-p orbitals having high anisotropy in geometry. Oxides composed of metal cations with an electronic configuration  $(n-1)d^{10}ns^0$  would satisfy these requirements, as the lowest part of the conduction band in these oxides is primarily composed of ns orbitals [27]. Hosono *et al.* [26] also conjectured that because of this, ternary oxides are preferred to binary oxides for the formation of amorphous TCO thin films. Scanning the periodic table, they identi-

fied 105 combinations of elements as promising ternary oxide candidates.

As indicated by Mizoguchi and Woodward [7] not only do binary n-type TCO materials contain a metal with  $(n - 1)d^{10}ns^0$  electronic configuration, but also the ternary and quaternary complex TCOs. In a study of  $CdSnO_3$ ,  $Cd_2SnO_4$ , and  $CdIn_2O_4$ , Shannon et al. [28] conjectured that the formation of a transparent conductor could result from edge sharing of  $Cd^{2+}$ ,  $In^{3+}$ , and  $Sn^{4+}$  octahedra.<sup>2</sup> Nearly all of the complex TCOs found to date possess cations in octahedral coordination, as do most binary TCOs, with the exception of  $ZnO$  (wurtzite structure) and  $\beta\text{-Ga}_2O_3$ . These and other studies show that similar complex oxides may be a rich source of new TCO materials [28-31]. Mizoguchi and Woodward [7] based on their research concluded that the only necessary condition for an oxide, binary or complex, to be a transparent conductor was to have a structure causing the lowest energy band to be dispersed and split off from the rest of the conduction band, whereas continuous edge sharing of the structural octahedra is only accidental.

The lowest energy band in the conduction band of an effective transparent conductor should be wide so that carriers introduced upon doping will be highly mobile. This condition is met when the anion coordination environment is fairly symmetric, as is the case in binary TCOs. This is a necessary but not sufficient condition for transparent conductivity. The second condition for a good TCO material is that it must be possible to effectively populate the conduction (or valence) band by doping, and that the doping should not seriously degrade the carrier mobility or the optical transmission [8,31].

Considering the ternary TCO compound  $(A_xM_yO_z)$ , where A is a lower valency cation and M is a main group ion with higher valency, if the valence of the A-O and M-O interactions were not too different, as they would be when the A-cation has an  $(n - 1)d^{10}ns^0$  electron configuration, the oxygen bonding was likely to remain reasonably symmetric and a disperse conduction band would result, in agreement with the necessary condition specified above. The dispersion of the conduction band energy in such compounds may not be as large as in a binary oxide, yet, there could be extra freedom to manipulate the composition and structure of such oxides, facilitating the adaptation of the electronic energy levels for applications with specific needs [7].

All the TCOs discussed above are n-type semiconductors. In addition, p-type doped TCOs were also developed and could find interesting future ap-

plications, in particular in the new optoelectronic field of “transparent electronics” [32]. Fabricating undoped or doped p-type TCOs was found to be more difficult than the n-type. The first p-type TCO was made from  $CuAlO_2$  by Kawazoe in 1997 [33]. Prior to this, in 1993 Sato et al [34] had reported about a semi-transparent p-type TCO with ~40% visible transmission. 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 was hypothesized to result from the strong localization of holes at oxygen 2p levels or due to the ionicity of the metallic atoms. O 2p levels are far lower lying than the valence orbit of metallic atoms, leading to the formation of a deep acceptor level with the holes. 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 [34,35]. Following this 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 valence band. The recent detailed report of Banerjee and Chattopadhyay [36] 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 TCO have relatively lower conductivities, of the order of 1 S/cm, and lower 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 [37,38]. Based on first principle calculations, Yoshida et al. [39] 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. [40] 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 S/cm<sup>3</sup> p-type  $ZnO:\text{Sb}$  was deposited with a filtered vacuum arc equipped with a Zn cathode doped by Sb David et al. [41]. The conductivity was ~0.5 S/cm, the mobility 9–20 cm<sup>2</sup>/Vs and the hole density ~4·10<sup>16</sup> cm<sup>-3</sup>, with transmission of ~85%. It is evident that the challenge to grow p-type TCO with resistivity ~ 10<sup>3</sup> Ω cm, or better, still exists.

The need to produce n-type TCOs with higher conductivity and better transmission, without relying on In, inspired research and development effort to discover and study some unconventional TCOs. Novel transparent conductors were proposed using oxides with  $s^2$  electron configurations. Oxides of Mg, Ca, Sc, 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 could be achieved, the optical properties would not deteriorate at lower resistivity. Recently, mobility with more than twice that of commercial ITO was observed in Mo-doped  $\text{In}_2\text{O}_3$  (IMO) and it was shown that the conductivity can be significantly increased with no changes in the spectral transmittance upon doping with Mo [39,42]. Electronic band structure investigations of IMO by Medvedeva [43] 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.

Recently, new thin film geometries were also explored in search of TCO films with higher conductivity. Dingle et al. [44] showed that higher conductivity could 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 [45] used a zone confining process to deposit ITO with  $\rho = 4.4 \cdot 10^{-5} \Omega \text{ cm}$  and  $\mu = 103 \text{ cm}^2/\text{Vs}$ . The highly and lowly doped regions were laterally arranged in the films, rather than vertically as in superlattice structures. A theoretical outline of a method to engineer high mobility TCOs was presented by Robbins and Wolden [46], based on the high mobility transistor structure discovered accidentally by Tuttle et al. [47]. The film should consist of alternating thin layers of two semiconductors. One layer provides a high density of carriers, while the second is a high mobility material. Electrons are supplied by the former and transported in the latter, mitigating the limitations of ionized impurity scattering. The model of Robbins and Wolden [45] assumes that the electrons move into the high mobility material in response to differences in electron affinity. However, the success of the proposed TCO design depends upon controlling the layer thickness at nano dimensions, (e.g. ~5 nm). In addition, this approach depends on having mate-

rials of excellent quality and compatible crystal structure in order to avoid problems related to interface defects.

TCO materials with magnetic properties, which are ferromagnetic semiconductors with a Curie temperature well above room temperature, have also been explored recently, as they could be used for second generation spin electronics and as transparent ferromagnets. Ueda et al. [48] reported that Co doped ZnO thin film ( $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ) with  $x = 0.05 - 0.25$ , had a large magnetic moment of  $1.8 \mu\text{B}$  per Co ion for  $x = 0.05$ . High-temperature ferromagnetism was subsequently found by other groups, with varying magnetic moments [49].

## 5. COMPARING CARBON NANO TUBES (CNTS) WITH TCOs

Transparent conductors are fragile and tend to break down due to fatigue. The most commonly used TCO is Indium-Tin-Oxide (ITO) because of its good electrical properties and ease of fabrication. However, these thin films are usually fragile and such problems as lattice mismatch and stress-strain constraints lead to restrictions in possible uses for TCFs. ITO has been shown to degrade with time when subject to mechanical stresses. Recent increases in cost are also forcing many to look to CNT films as a potential alternative.

CNTs can also be used in addition to transparent conducting oxides (TCOs) in thin-film photovoltaic devices. Two TCOs which are often used are ZnO/Al and  $\text{In}_2\text{O}_3/\text{Sn}$  indium tin oxide (ITO). PV devices made with these TCOs attained energy-conversion efficiencies of 19.5% in  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ -based (CIGS) solar cells and 16.5% in CdTe-based solar cells. These photovoltaic devices had much higher efficiencies compared to the devices made with CNT thin films: Britz et al. [50] reported an efficiency of 8%, with an open circuit voltage ( $V_{oc}$ ) of 0.676 V, a short circuit flux ( $J_{sc}$ ) of  $23.9 \text{ mA/cm}^2$ , and a fill factor of 45.48%. However, CNT thin films show many advantages over other transparent electrodes in the IR range. CNT thin films were reported to have a transmittance of over 90% in this range (400 nm – 22  $\mu\text{m}$ ). This paves the way for new applications, indicating that CNT thin films can be used as heat dissipaters in solar cells because of this high transmittance.

As stated previously, chirality of CNT is important in helping determine its potential aid to these devices. Before mass production can occur, more research is needed in exploring the significance of tube diameter and chirality for transparent conduct-

**Table 2.** General properties of graphene.

Density	0.77 mg/m <sup>2</sup>
Young modulus	0.05 TPa
Carrier density	10 <sup>12</sup> /cm <sup>2</sup>
Resistivity	10 <sup>-6</sup> Ωcm
Electron mobility at 300K	20,000 cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup>
Thermal conductivity (at 27 °C)	5000 W/m K

ing films in photovoltaic applications. It is expected that the conductivity of the SWCNT thin films will increase with an increase in CNT length and purity. As stated previously, the CNT films are made using randomly oriented bundles of CNTs. Ordering these tubes should also increase conductivity, as it will minimize scattering losses and improve contact between the CNTs.

Though CNT can show high conductivity, but it does not show transparency to visible light as much as ITO film. After the discovery of graphene for which a Nobel prize was given to Dr. A. Geim and K. Novoselov in 2010, it is observed that graphene can possess the following electrical properties which are unique for any material (Table 2):

Graphene also shows a well-defined ambipolar electric field-effect, which means it can conduct electron or hole with same mobility. In addition to these properties, transparency of graphene is 250 to 1750 nm in the range of 50 to 90% as compared to ITO film which shows transparency from 250 nm to 750 nm in the range of 50 to 90% (Fig. 3). Graphene is also stable at high temperature in absence of oxygen where as ITO cannot be used beyond about 200 °C. As a result various types of materials for

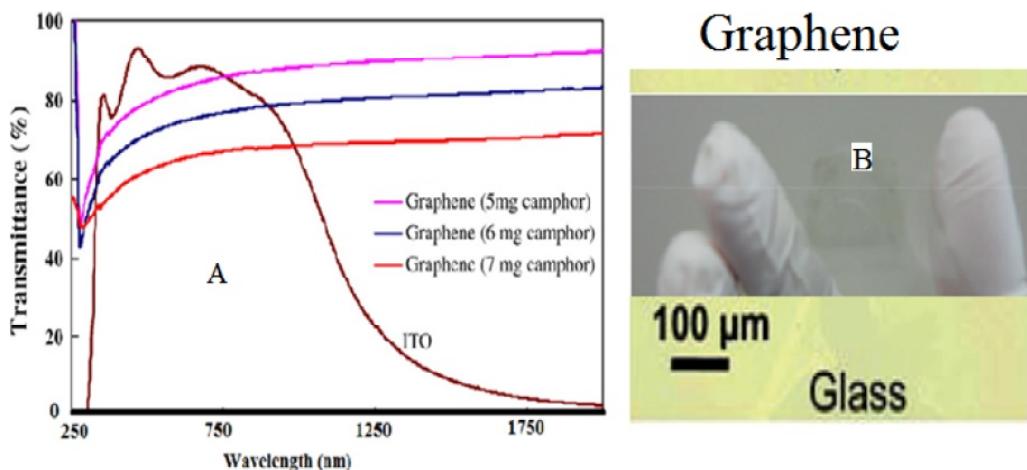
different applications can be deposited over graphene at higher temperature (in the range of 400 °C to 1000 °C or even higher). Since graphene is flexible, it is also possible to prepared flexible solar cell backed by graphene [51] which can act like a transparent conducting base material

## 6. INDUSTRIAL 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 buildup. In this application relatively high surface resistances (e.g. kΩ/cm<sup>2</sup>) can be tolerated.

### 6.1. Transparent heating elements

Transparent heating elements may be constructed from TCO coatings. These are applied 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 areas. This application requires either the use of very low surface resistance coatings (e.g. ~1 Ω/cm<sup>2</sup>), 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, as has been widely dis-



**Fig. 3. (a)** Transmittance by the large area Graphene sheets synthesized using different amounts of camphor and transferred on glass. (© 2010 Elsevier, Courtesy: Kalita et al., Materials Letters 64, 2010, 2180–2183, Ref. [53]); **(b)** A photograph of monolayer graphene film transferred to PET substrates. (© 2011 Elsevier; Courtesy: Kalita et al., Physica E 43, 2011, 1490–1493, Ref. [54]).

cussed, then this application may prove to be more commercially feasible in the future.

## 6.2. TCO coatings

TCO coatings may be used as shielding to decrease electromagnetic radiation interference (EMI) from providing visual access. This may be to either to keep radiation from escaping an enclosure, to avoid interfering with nearby devices, or 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, which 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.

## 6.3. Flat panel displays

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. Thus 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, has reduced light transmission. Recently transparent field effect transistors (FETs) have been developed based on the zinc oxide, but using a Cr gate. These zinc oxide FETs have been incorporated into small 220 X 280 10  $\mu\text{m}$  pixel active matrix LCDs [52].

Small and medium LCDs are a 25 B\$/yr market which is growing by about 5%/yr, while large area

LCDs have a similar market size and a much higher growth. The explosive growth for demand of ITO coatings for this specific application has generated wide spread concern about Indium scarcity in the near future.

## 6.4. Solar cells

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, in as much as patterning is not required, but environmental stability is.

## 6.5. Coatings on architectural glass

TCO films are commonly applied to architectural glass, often as part of multi-layer stacks. In window glass applications, usually the conductivity *per se* is irrelevant, but rather the concurrent high infra-red reflectivity is exploited, in order to obtain good light transmission in the visible range, while minimizing heat transmission. This feature is used to minimize air conditioning costs in the summer, and heating costs in the winter, in buildings equipped with appropriately coated windows. Approximately 25% of flat glass is coated, and energy conserving coatings are now mandated in various regions. Most commonly the coatings are applied by two techniques. (1) Very enduring and inexpensive, but simple, coatings are produced with atmospheric pressure chemical vapor deposition (APCVD), in line with the float glass production process. This insures a fresh surface, and exploits the high temperature of the glass during its production. However, APCVD is not very flexible and there are only limited options available for the coating architecture. (2) A more flexible, but also more costly, process is magnetron sputtering. Commonly multiple (e.g. 20-60) rotary targets are mounted in long modular vacuum systems (e.g. 40-160 m length), and multilayer stacks are deposited as the glass panels pass beneath the various cathodes, traveling at velocities of ~1 m/s. Typically these systems operate continuously for 2 weeks, after which expended targets are replaced and other maintenance is performed.

## 7. COMMERCIAL AVAILABILITY OF TCO THIN FILMS

The coating industry is segmented into “captive shops” which provide coating service within a given

company for their products, and "job shops" which provide contract coating services for external companies. It is difficult to gather information about the former, since companies have no need to advertise their captive shops, and often prefer to guard their processes as trade secrets. More information is available concerning TCO availability from job shops, who often advertise their capabilities via the internet. A survey of these companies revealed that about 3/4 of them indicated that they provide ITO coatings; most of the remainder did not specify the coating composition, but most probably they also deposit ITO as their TCO of choice. Only one company advertised supplying FTO films, and another also advertised IZO and AZO. Surface resistances ranged from 5 to 500  $\Omega/\text{cm}^2$ . It should also be noted that float glass on-line coated by APCVD with FTO is readily available as an inexpensive commodity.

## 8. CONCLUSIONS

The expanding use of TCO materials, especially for the production of transparent electrodes for optoelectronic device applications, has developed into a world wide multi-billion \$US economy that in general depends on the availability of ITO. This economy is endangered by the scarcity and high price of In. The situation drives the search for alternative TCO materials to replace ITO, and motivates an intensive investigation of the physics and chemistry of TCO materials.

The main significant progress in the research and development of TCO thin films has been made in understanding the physics of TCO semiconductors. The physical processes that make possible the coexistence of electrical conductivity and optical transparency are well clarified and understood. In particular, the role of oxygen vacancies and various dopants in the formation of shallow donor levels is well established. In addition to binary TCOs, progress has also been made in developing new TCO compounds, consisting of combined segregated-binaries, ternary and quaternary oxides. However, the objective of developing new TCOs with conductivity similar or even higher than that of ITO has not been realized. The conductivity of the recently developed ternary, quaternary, and binary-combination TCOs is lower than that of ITO. It is now appreciated that the attainment of higher conductivity is limited by the negative correlation between carrier density and electron mobility. It is now realized that the development of TCOs with higher conductivity does not necessarily depend on higher dopant concentration that provides higher carrier density, but

could also be achieved by maintaining moderate carrier density with increased mobility. Spatial separation of the conduction electrons and their parent impurity atoms (ions) should significantly reduce carriers scattering and increase their mobility. Using this principle, the conductivity of ITO was successfully increased; however, it has not yet been applied to other TCOs. The effort to produce TCOs with higher mobility based on using the oxides with  $ns^2$  electron configuration, instead of the  $ns^0$  electron configurations found in typical TCOs, was only partially successful. These wide band gap oxides exhibited the desired optical and electronic features; however, their conduction was low due to too low p-type TCOs were obtained by doping ZnO with N, F, P, Sb, and As, however, it was also shown that such doping had some serious limitations, and the conductivity was lower than n-type ZnO.

In summary, AZO, GZO and FTO are at present the only TCOs with electrical conductivity close to that of ITO, and with appropriate high optical transmission in the near-UV, VIS and NIR. The objective of producing TCO materials with optical and electrical characteristics equivalent to those of ITO has not yet been achieved.

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