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Overview on Transparent Conducting Oxides and State of the Art of Low-cost Doped ZnO Systems

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Abstract

Transparent conducting oxides (TCOs) have become an integral part of modern life through their essential role in touch screen technology. The growing demand for cheap and superior transparent conducting layers, primarily driven by the smart phone market, has led to renewed efforts to develop novel TCOs. Currently, the most widely used material for transparent conducting applications is Sn-doped indium oxide (ITO), which has outstanding optical and electrical properties. This material is expensive due to the extensive use of In, and efforts to develop new low-cost transparent conducting oxides (TCO) have become increasingly important. Similarly attempts to reduce the cost of the fabrication and post-sintering steps used in making doped ZnO systems through innovative technologies have gained a lot of attention as discussed in this review.

Keywords: Transparent; Conducting oxides; Low-cost; ZnO; Microwave

Overview

In the fast growing electronics market, transparent conducting oxides (TCOs) have become essential components in a large number of modern devices including touch screens, portable electronics, flexible electronics, optics, biochemical/environmental sensors, transparent heaters, multifunctional windows and solar cells [1]. The demand for all of these technologies is continuously increasing in the developed world [2]. The heavy use of TCOs in modern applications, the high cost associated with the current TCO materials and the potential opportunities for future applications has stimulated intense research interest over the diverse transparent conductor field.

Generally, TCOs are metal oxides with high optical transmittance and high electrical conductivity [3]. They are also referred to as wide-bandgap oxide semiconductors (band gap > 3.2eV). These materials have high optical transmission at visible wavelengths (400 - 700 nm) and electrical conductivity close to that of metals, which is often induced by doping with other elements. They also reflect the near infrared and infrared wavelengths [4]. Since the bandgaps of these materials lie in the ultraviolet wavelength region they hardly absorb visible light, so they appear to be transparent to the human eye. These unique properties make TCOs widely applicable in current electronics which requires optical access behind electrical circuitry. In order to be considered as a TCO substrate, the film needs to possess a low electrical resistivity ($\sim 10^{-3}$ - 10^{-4} Ω.cm) as well as a high optical transparency towards visible light (>80% transmittance), due to their wide band gap (>3.0eV).

The first TCO material was found by Bädeker in 1907, when he realised the electrical conducting properties of transparent CdO thin films prepared by a thermal oxidation of sputtered cadmium [5]. Later, it was discovered that many binary oxides systems, primarily formed from p-block heavy metals, show good transparent conducting properties. Examples of these include SnO_2, In_2O_3, ZnO, CdO, Ga_2O_3, Tl_2O_3, PbO_2, and Sb_2O_5 [6,7]. Recently it has been found that ternary and quaternary transition metal oxides such as Cd_2SnO_4, $CdSnO_3$, $CdIn_2O_4$, Zn_2SnO_4, $MgIn_2O_4$, Y-doped $CdSb_2O_6$, $ZnSnO_3$, $GaInO_3$, $Zn_2In_2O_5$, and $In_4Sn_3O_{12}$ are also good candidates for TCOs [7]. Out of this wide array, Sn-doped In_2O_3 (ITO) and F-doped SnO_2 (FTO) have become the most widely used TCOs in current industries, as they have superior electrical and optical properties. The relative scarcity and high cost associated with indium are significant drawbacks for ITO; whilst FTO is far more cost effective, it requires higher deposition temperatures, which limit its applicability in flexible devices [6].

Over low cost, high durability and being non-toxic makes ZnO an attractive alternative to the commonly used ITO [8]. ZnO has a direct and wide band gap in the near-UV spectral region and a large free-exciton binding energy so that excitonic emission processes can persist at or even

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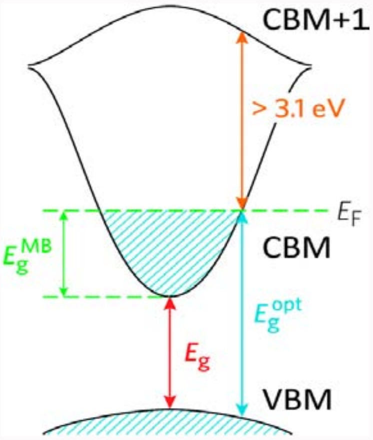

Figure 1: Diagram of the optical widening by the effect of the Moss–Burstein shift [11].

above room temperature [9]. One of the key challenges in developing ZnO based TCOs is investigating the best metal dopants and the optimal dopant contents, in order to achieve the highest electrical conductivity. Unlike in SnO_2 and In_2O_3 based TCOs, efficient doping of group III elements into the ZnO structure could decrease the resistivity significantly, potentially realising a future low cost TCO for electronic and optoelectronic applications [10].

Opto-electrical Properties of TCOs

The induction of electrical properties of TCOs can be understood by the semiconductor band theory. For electrical conduction to occur within the semiconductor material, ground state electrons must be excited from the valence band to the conduction band minimum (CBM), across the band gap by absorbing photon energy. A wider band gap requires a higher-energy photon in order for an electron to become excited into conduction. Therefore, widening the band gap (i.e. Eg > 3.0eV) in a material permits transparency to the visible portion of the spectrum by placing a greater separation between the valance band maximum (VBM) and CBM of the material, thus decreasing the probability of exciting an electron into conduction [11].

TCOs have been developed by doping materials in order to facilitate the charge carrier generation within the structure. In the description of the band model, there is an important difference between the fundamental band gap (i.e. the energy separation of the E_{vb} and E_{cb}; an intrinsic property of the material) and the optical band gap (an extrinsic property), which corresponds to the lowest-energy allowed for an optical transition. The optical band gap determines the transparency of a material which is important in TCO applications. In order to achieve n-type conducting properties, electrons are injected from a nearby defect donor level directly into the conduction band. The point defects in a metal oxide crystal, such as oxygen vacancies, proton or metal interstitials and certain substitutional defects, effectively create an excess of electrons close to the defect site in n-type TCOs. If there is sufficient orbital overlap, it permits delocalisation of electrons from the defect sites such that electronic states at the CBM become filled or in other words Fermi level shifts above the CBM. This leads to an effect known as the Moss–Burstein shift, which effectively widens the optical band gap.

$$E_g = E_{CBM} - E_{VBM} \tag{1}$$

$$E^{opt}_g = E^{MB}_g + E_g = E_F - E_{VBM} \tag{2}$$

Since the Moss–Burstein shift is:

$$E^{MB}_g = E_F - E_{CBM} \tag{3}$$

where E_g is the fundamental energy gap separating the VBM and CBM, E^{opt}_g is the optical band gap corresponding to the smallest allowed optical transition from the VB to the CB, E^{MB}_g is the Moss–Burstein shift and E_F is the Fermi level (Figure 1). Thus, lattice defects in TCOs can simultaneously promote both electrical conductivity and optical transparency.

Apart from the Moss–Burstein shift the fundamental band gap is tapered due to the band gap narrowing effect which led by exchange interactions in the free-electron gas and electrostatic interactions between free electrons and ionized impurities [10].

The optical band gap is a key aspect in designing a TCO. However, the CBM depth or electron affinity (EA) in other words, the difference between vacuum energy and CBM which affects the 'dopability' of the TCO is also equally important in determining the conducting properties. A higher value of EA indicates greater ease of introducing charge carriers, i.e. a greater dopability [12,13]. A large separation ($Eg > 3.0$eV) between the Fermi level in the conduction band and the next electronic energy level (CBM+1) helps to prevent excitation of electrons to higher states within the conduction band, which prevents undesirable optical absorption [14].

The conductivity of a TCO is determined by the number of charge carriers and their mobility within the crystal lattice, which is inversely proportional to their effective mass. The effective mass is a quantity used to express the mass that the electrons appear to have when moving within a crystalline solid, in which their mobility is affected by their response to local forces within the crystal, expressed relative to their true mass (m_e). The local forces in TCO crystal lattice is controlled by the orbital overlap between the metal cation in a host lattice and the oxygen. The electron mobility, electron density and conductivity of inorganic materials are linearly related as described in the Boltzmann equation:

$$\sigma = ne\mu \tag{4}$$

where σ is the electrical conductivity defined in S cm^{-1}, n is the density of free charge carriers (*i.e.* electrons in an n-type TCO), e is the electronic charge and μ is the electron mobility. The electrical resistivity (ρ), expressed in Ω.cm, as below:

$$\rho = \frac{1}{\sigma} \tag{5}$$

There are three distinct domains amongst inorganic materials regarding electrical properties: namely the semimetals (high carrier density, low electron mobility), highly conductive metals (both high carrier density and mobility) and semiconductors (low carrier density, high mobility). While the introduction of a donor level close to the conduction band permits a wide optical band gap from the VBM to the CBM, the optical absorption associated with the promotion of electrons from the CBM to higher states places an upper limit on the carrier concentration in the CBM, such that the absorption coefficient α of the TCO is proportional to the density of free electrons n as found in equation 6:

$$\alpha = \sigma n \tag{6}$$

where σ is the absorption cross-section and n is the carrier density.

Therefore, a compromise must be made when designing doped

Table 1: An overview of different doped ZnO based TCOs and different deposition techniques reported in the literature.

Semiconductor	Dopant	Synthesis/ deposition method	Reported Resistivity/ Conductivity/ Sheet resistance	Reference
ZnO	Al, Na and Al Na co-doped	Sol-gel	-	[39]
ZnO and $Zn_{1-x}Mg_xO$	Al	magnetron sputtering	Resistivity ~ 0.001 Ω.cm	[40]
ZnO	Al	Solvothermal Method	-	[41]
ZnO	Al	aqueous solution deposition (Al is immersed in the alkaline aqueous precursor solution)	Resistivity of 5 x 10^{-3} Ω.cm	[42]
ZnO	Al and Ga	sol–gel and spin-coating	Sheet resistance of Ga:ZnO is 3.3 × 10^3Ω/□ and for Al:ZnO is 4 × 10^3Ω/□	[43]
ZnO	Al	Pulsed laser deposition	Resistivity of 8.54 x 10^{-5} Ω.cm	[44]
ZnO	As	magnetron sputtering and *in situ* rapid annealing	Sheet resistance ~3 × 10^5 Ω/□	[45]
ZnO	In	Sputtering	Conductivity of 3 x 10^3 $Ω^{-1}.cm^{-1}$	[46]
ZnO	Al	Sol-gel	Resistivity of 1.94x10^{-2} Ω.cm	[47]
ZnO	Al	Chemical spray	Resistivity of 1.8×10^{-2} Ω.cm	[48]
ZnO	Al	Magnetic sputtering and post annealing	Resistivity of 8.76 ×10^{-4} Ω.cm	[49]
ZnO	Al	Magnetron co-sputtering and post annealing	Resistivity of 8.30 ×10^{-4} Ω.cm	[50]
ZnO	Al	Microwave assisted nonaqueous sol-gel synthesis	Resistivity of 2.35 x 10^{-2} Ω.cm	[51]
ZnO	Si	Aerosol Assisted Chemical Vapor Deposition	Resistivity of 2.0 x 10^{-2} Ω.cm	[52]
ZnO	Al and Ga co-doped	High-throughput continuous hydrothermal flow synthesis	Resistivity of pellets 9 x 10^{-3} Ω.cm	[53]
ZnO	Al and Ga co-doped	Aerosol Assisted Chemical Transport	Resistivity of pellets 5.6 x 10^{-4} Ω.cm	[54]

TCOs because of this relationship between the free electron density and the optical absorption.[19] With this limitation, ideal TCO materials need to have a high charge carrier mobility (typically μ = 50–70 $cm^2\ V^{-1}\ s^{-1}$) and a low electrical resistivity (ideally $\rho = 10^{-3}$ - 10^{-4} Ω.cm) whilst keeping the carrier concentration below $2 \times 10^{21}\ cm^{-3}$, to prevent undesired optical absorption [11].

ZnO Based TCOs; Structural and Electrical Properties

ZnO has been shown to be an extremely promising material for transparent conducting applications [10]. It has a wide and direct band gap in the near-UV spectral region, with a larger free-exciton binding energy and a higher electron effective mass which could give rise to high optical transparency. Also ZnO can persist excitonic emission processes at or even above room temperature, hence it is possible to prevent thermal excitation of electrons and avoid the unwanted optical absorption [11]. ZnO crystallizes in the wurtzite structure [15]. The properties of ZnO for semiconductor electronics have been widely studied, but the use of ZnO as a semiconductor in electronic devices has been hindered by the lack of control over its electrical conductivity. The n-type conductivity in ZnO thin films is mainly controlled by electrons generated by oxygen vacancies and charge donation [10]. However, theoretical studies, specifically first-principles calculations based on density functional theory (DFT), have also given a deeper understanding to the role of native point defects and impurities on the ZnO n-type conductivity [9].

The native defects in the ZnO crystal lattice can influence the structure, which in turn affects the optical and electrical properties producing a naturally n-type material [9]. The structural defects of ZnO can be dependent on the atmosphere in which the material is grown as well as post synthesis annealing conditions. Therefore, characterising the nature of defects in ZnO helps to tune the materials properties, including their conductivity. Oxygen vacancies are the most discussed defect in ZnO, as it was once believed to be one of the main sources for the natural n-type behaviour. However, density-functional theory calculations disclosed that oxygen vacancies are very deep donors rather than shallow donors ("deep and shallow" in terms of the energy needed to remove an electron/hole from the trap to the valance or conduction band compared to the characteristic thermal energy kT, where k is the Boltzmann constant and T is absolute temperature) and consequently, cannot contribute to n-type conductivity [9]. Though, these deep donors can be manipulated under different annealing atmospheres (e.g. hydrogen) in order to change the electrical and optical properties [16].

In n-type ZnO, zinc vacancies can easily form as a deep acceptor. Higher concentration of zinc vacancies are formed in oxygen rich atmospheres. Hydrogen rich atmospheres also have an effect on these zinc vacancies as the hydrogen is incorporated into the structure and passivates the charge state of the zinc vacancies. This in turn increases the n-type conductivity [17].

Zinc interstitials carry two electrons above the conduction band minimum in order to stabilize its +2 charge state. Zinc interstitials are believed to be a shallow donor because they always donate electrons to the conduction band as they have low ionization energy, but it is still unclear if it is related to sublattice defects or a zinc-interstitial complex. Zinc interstitials have shown mobility at room temperature, creating a complex with ambient nitrogen which also acts as a shallow donor and can increase the conductivity of ZnO [9]. The native defects such as zinc antisites, oxygen interstitials and oxygen antisites with higher formation energies are not expected to deliver n-type conductivity in ZnO under equilibrium conditions [9].

The electrical and optical properties of ZnO, can be significantly affected by relatively low concentrations of native point defects and impurities [18-21]. Hence, understanding the role of native point defects (i.e. vacancies, interstitials, and antisites) and the incorporation of impurity dopants is key toward tuning the conductivity in ZnO. For a long period, it has been hypothesised that the unintended n-type conductivity in ZnO is caused by the presence of oxygen vacancies or zinc interstitials. Though, recent state-of-the-art density functional calculations and optically detected electron paramagnetic resonance measurements of high quality ZnO crystals have exhibited that this provenance to native defects cannot be correct. It has been shown that oxygen vacancies are deep donors and cannot contribute to n-type conductivity. Moreover, it was found that the other point defects (e.g. Zn interstitials and Zn antisites) are also unlikely to cause the n-type conductivity in ZnO [9].

Instead, the unintentional incorporation of impurities which act as shallow donors, is the most likely cause. An example of such unintentional incorporation could be hydrogen, which exists in almost all growth and processing environments [22,23]. Density functional theory has demonstrated that interstitial H forms a strong bond with O in ZnO and acts as a shallow donor, contrary to the amphoteric behaviour of interstitial H in conventional semiconductors [22]. Moreover, recent findings suggest that H can also substitute for O in the ZnO structure and act as a shallow donor [23]. Other shallow donors which give rise to the n-type conductivity in ZnO are impurity dopants such as Al, Ga, Cu, In or Se. However, these elements are not usually present in ZnO samples thus intentional doping will be required to alter the conductivity.

It has been shown that it is a very difficult to obtain p-type doping in ZnO, mainly due to its tendency towards n-type conductivity [24-28]. Additionally, the above-mentioned defects play a role as compensating centres in p-type doping, reducing its effect. Furthermore, there are very few candidate shallow acceptors for ZnO [9]. Group 1 metals (Li, Na, K) on the Zn site can be considered as either deep acceptors or stable like interstitial donors which compensate p-type conductivity [29-31]. Group 11 metals (Cu, Ag, Au) are deep acceptors hence do not contribute to p-type conductivity. As O is an electronegative element, only N is possible to result in a shallow acceptor level in ZnO. Group 15 elements (P, As, Sb) act as deep acceptors when substituted on to O sites in ZnO [31]. Even though, there are reports on obtaining p-type doping through incorporation of N, the reproducibility and the stability of this p-type doped ZnO is still under debate [9]. An overview of different doped ZnO materials and different deposition techniques reported in the literature is summarised in Table 1.

Deposition Methods

The electrical and optical properties of TCO thin films can be altered during the deposition and post-sintering steps, as they are frequently dependent on the film nanostructure, coverage and particle interconnectivity [32,33]. The cost of TCOs is not only dependent on the materials, but also on the film deposition process. TCO films have been fabricated through an extensive number of techniques, each of which has drawbacks [34,35]. TCO films have typically been deposited by magnetron sputtering or chemical vapour deposition methods. However these deposition techniques require a vacuum pressure (~ 10^{-6} Pa) or higher deposition temperatures (450 – 700 °C) both of which increase the energy demand and overall cost of the techniques [36]. In general, aerosol assisted deposition methods are considered to be one of the lower cost deposition techniques for TCO thin film fabrication as it does not require specially designed heated reactor lines or high vacuum systems [37]. However, the famous chemical vapour deposition technique, aerosol assisted chemical vapour deposition (AACVD) method require specially designed metal-organic precursors and high temperature heating zones [69,70]. Therefore, due to the disadvantages in the current deposition techniques a great amount of attention has been committed to developing low cost and energy efficient deposition and post-sintering methods. Aerosol assisted chemical transport (AACT) is one of the recently reported low cost deposition method which a physical vapour deposition method, was used to deposit TCO thin films using nanoparticle suspensions at relatively low temperatures [38]. In the AACT technique, aerosol droplets containing nanoparticles can be generated by nebulising a nanoparticle suspension using an ultrasonic generator, the droplets are then transported onto the substrate at a relatively low temperature using an inert carrier gas, thus depositing a thin film of nanoparticles on the substrate due to solvent evaporation.

Thermal Processing of TCOs

It is a well-known phenomenon that the electrical and optical properties of TCO thin films can be modified by carrying out post-deposition heat treatments [55-57]. The optical transmittance of a film is known to be strongly depend on its surface morphology. Yim et al. studied the effects of annealing on structure, resistivity and transmittance of Ga doped ZnO films [58]. Chang et al. reported the effects of post-annealing on the structure and properties of Al-doped zinc oxide films [49]. According to their findings, improvement in the film transparency can be observed after the post-heat treatment of doped ZnO thin films, which is a result of the enhanced crystallinity and reduced surface roughness. As the grain size increases with the post-heat treatment, the boundary scattering tends to decrease. This effects the transmittance of the films favourably. Furthermore, annealing doped ZnO under a reducing atmosphere widens the optical band gap, whereas annealing in an oxidising atmosphere makes the optical band gap narrower. The phenomenon that explains how the optical band gap increases with increasing carrier concentration in the conduction band is known as the Moss-Burstein effect as discussed. The Burstein relationship between the band gap shift ΔEg and the carrier concentration is linked in the following equation [58].

$$\Delta E_g = \frac{h^2 n^{2/3}}{8 m_e^* \pi^{2/3}} \qquad (9)$$

where m^*_e is the effective mass of the electron, n is the electron concentration, and h is Planck's constant.

In addition to improving the transparency, post-heat treatment under a reduced atmosphere is also found to improve the electrical properties of trials [57,58]. This is ascribed to the passivation of grain boundaries and zinc ions resulting in increases in the carrier concentration and mobility in ZnO based materials. Negatively charge oxygen species reside at grain boundaries and act as trap sites. These negatively charged species form depletion regions near the grain boundary surfaces, decreasing the free-carrier concentration and Hall mobility. If these depletion regions in the TCO films were removed by the passivation of the grain boundary surfaces during the post-deposition annealing in hydrogen atmosphere, the carrier concentration would increase, which in turn increases the conductivity.

In contrast, N_2 rich atmospheres are more advantageous for ITO thin film processing compared to the reducing atmospheres used for ZnO [59]. As the Sn dopant and oxygen vacancies play a major role in ITOs conductivity, controlling the oxygen content is an important factor. According to the literature, N_2 can induce oxygen vacancies or remove oxygen interstitials through the incorporation of a reducible defect, giving rise to the conductivity [60,61]. Whilst the hydrogen treatment can form hydrogen oxygen links and stabilize oxygen in the ITO lattice, reducing the number of oxygen vacancies and increasing the resistivity [62].

Microwaves for TCO Synthesis and Post Deposition Sintering

The use of microwave radiation for post-annealing of metal oxides, is a novel technological advancement and an alternative to conventional sintering [63]. This technique has recently gained particular momentum for the improvement of the chemical and physical properties of TCOs [64,65]. The improvement given by post-annealing with microwave irradiation is attributed to changes in the crystallinity and the particle necking properties and the densification of the TCO thin films. Recent examples demonstrate that microwave processing is a promising alternative to conventional sintering for thin film post treatments with better properties [66].

Heat generation in materials by microwave energy is fundamentally different from conventional radiant heating, conduction or convection heating. In the microwave process, the heat is generated within the material instead of originating from external heating elements. In other words, microwave heat generation is due to an energy conversion rather than a heat transfer process. As the material is being processed under microwaves, the absorbed radiation is converted to heat energy and the material becomes its own heating source.

For conventional thermal heating, the material always has a higher temperature at the surface compared to the core; this is due to heat being transferred from the heating element to the sample, then heat gradually transfers through the surface towards the core. The temperature profile for microwave heating is the reverse. As the heat is generated within the material, the temperature at the core of the sample is the greatest, but then decays towards the surface due to energy loss to the surroundings. Through use of hybrid heating, it is possible to create uniform heating throughout the sample by carefully tuning the microwave and thermal power. The use of hybrid heating offers significant advantages compared to using thermal or microwave heating alone [38,54,67,68]. By using hybrid heating, it is possible to create materials with more uniform properties. For example, if the phase of a material is dependent on the temperature, uneven heating could create a mixture of phases, which would lead to different properties, such as, differing levels of conductivity and catalytic activity, amongst others. As the dielectric constant of a material is temperature dependant, this offers significant opportunities for hybrid heating. For example, a material which does not absorb microwaves efficiently at room temperature, might, in fact, absorb much more efficiently at higher temperatures, opening up more possibilities to process low microwave absorbing materials.

Conclusions

The most widely used material for transparent conducting applications is Sn doped Indium oxide (ITO) due to its excellent optical and electrical properties. However, finding novel low cost transparent conducting oxide (TCO) materials and methods for fabricating and post-sintering doped metal oxide thin films has become an increasingly interesting area of research as current TCO market has a high production associated with the raw material (In) and high pressure/temperature thin film fabrication techniques. Recent findings demonstrate that ZnO doped systems attained by microwave assisted technology could be a potential way forward on achieving highly electrical conducting films as well as economic advantages through energy saving.

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