Chapter 4

Transparent Conducting Electrodes for Optoelectronic Devices: State-of-the-art and Perspectives

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Abstract

This chapter brings a concise review of the transparent conducting materials, films and electrodes (TCM, TCF and TCE, respectively), its state-of-the-art and outlooks ahead. Initial part of the chapter gives a general introduction of the topic, followed by a feasible road map as proposed and collated by the authors based on several other reviews. Fundamental physics behind the transparent conductors is discussed in the latter part. Established and potential oxide based TCMs, namely the transparent conducting oxides (TCOs) are reviewed which are being used commercially and will see application in the near future. Non-conventional TCMs, which are mostly non-TCOs, such as graphene, carbon nanotubes (CNT), metallic nanowires (MNWs) and their hybrids are described in brief. Scalability and large area fabrication which are most important concerns for commercialization of TCMs are discussed. The general prospects are given at the end.

Keywords

Transparent Conductors, Thin Films, Metallic Nanowires, Graphene

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1. Introduction

One of the important components of the optoelectronic devices like touch screens [1,2], flat-panel displays [3,4], light-emitting diode (LED) [5], solar cells [6], photosensors [7] and e-papers [8] are transparent conducting electrode (TCE). TCEs are transmitting the light and conducting the electrical current, simultaneously, mostly in the visible region. Flexible, bendable, stretchable transparent electronic devices have gained a huge interest in the academic as well as industrial research in the recent years.

The first example of TCE materials was thin metal films prepared by evaporating and sputtering reported in the end of the nineteenth century [9]. Baedeker [10] reported the development of CdO, Cu₂O and PbO in 1907 which are the early examples of the transparent conducting oxides (TCOs) [11]. The resistivity of CdO was $1.2 \times 10^{-3} \Omega$ with a yellowish appearance. This resistivity is around one order less than the ITO films. Currently, indium tin oxide (ITO), a transparent conducting oxide (TCO), is dominating the TCEs for almost four decades due to its excellent conductivity ($10 \Omega \text{ sq}^{-1}$ on glass) and high optical transmittance (>90%) [11]. Growing technologies and demand in the display industries for the flexible displays demands transparent conducting electrodes with excellent flexibility which is retaining its transmittance and electrical conductivity [12]. However, ITO has few serious drawbacks *viz*, poor flexibility and brittleness because ITO is a ceramic material [13]. Also, the cost of indium is increasing rapidly due to its low-availability in the earth's crust; however, synthetic procedure of the ITO is more expensive. Other oxide-based transparent electrodes such as SnO₂:F (FTO) [14] and ZnO:Al (AZO) [15] are also studied due to low-cost when compared to the ITO. However, they are also having the same limitation as of ITOs; like vapour phase synthesis and poor flexibility. This demands the suitable replacement for the conventional ITO with new materials with good transmittance and electrical conductivity along with excellent flexibility for the future devices [16].

Poly (3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) is a conducting polymer which has been widely studied for the TCEs. PEDOT:PSS is also used in organic photovoltaic and organic light emitting diode as the hole conducting layer [17]. It has huge advantage such as low-cost, transparent, flexible and solution-processable for the large scale fabrication of conducting polymer based-TCEs. However, the conducting

polymers have the disadvantage of low specific conductivities when compared to ITO. Nanocarbons such as graphene [18-20] and carbon nanotubes (CNTs) [21-23] are extensively studied for the TCE applications due to excellent electrical conductivity and optical transparency. Especially, single-walled carbon nanotube (SWCNT) films and single-layer graphene (SLG) have attracted significant research interest due to such properties [24,25].

One-dimensional metal nanostructures gained significant importance because of its high aspect ratio, ability to form conducting network and good crystallinity [26-28]. When compared to the CNT network films, 1D metal nanostructures show good contact between the nanowires whereas CNT shows high contact resistance in tube-tube junction [29,30]. Silver (Ag) [31-35] and copper (Cu) nanowires (NWs) [1, 36-39] networks are widely studied for the TCEs. The advantages of the metal nanowires are solution-processable, high optical transparency, low sheet resistance and more importantly, compatible with the flexible substrates.

The materials studied for the TCEs are diverse and exhibit spectrum of properties that find different applications in displays, heaters and sensors. In this chapter, critical description of the recent research progress in the field of TCEs with emerging new materials, which have the potential replacement for the conventional ITO, the technological roadmap for the TCEs in the commercial markets, the physical aspects of the materials used in the TCEs, overview of oxide-based TCEs, focuses on the hybrids of materials used for the TCEs and the applications of these materials in various optoelectronic devices with a comparison with ITO is given.

2. Roadmap to the transparent electrode technologies

The market for transparent conductive films and materials (TCF and TCM) has been changing at a rapid pace. Such a transformation is taking place at all levels of the value chain, including the technologies, applications and supplies [40]. New materials and technologies beyond expensive (indium doped Tin Oxide) ITO are imperative, for example, metallic nanowire (MNW), such as, Ag-nanowires and nanoparticles, nano-carbon (graphene and carbon nanotubes) and conductive polymer (PEDOT etc based transparent conductors. These new materials should be compatible with applications such as, add-on and embedded touch technologies in mobiles, smart watches, tablets, notebooks, all-in-one display-based gadgets (AiOs), automotive displays, smart windows, organic LEDs (OLEDs), organic photovoltaics (OPVs) and other thin film photovoltaics, in-mold electronics (IME), OLED lighting, transparent heating, and so on. Among these fixed as well as flexible OLED display markets are in immediate forefront in the recent decade. A major technology shift has been observed since 2008 when touchscreen-based

devices and gadgets started invading the commercial sectors and consumer durables. In more recent years, projected capacitive touch screen (PCAP) technologies demand TCMs with higher mechanical flexibilities without compromising the electrical conductivity and optical transparency. Not just the PCAP, but the rise of embedded touch screens in various microelectronic products and systems, which needs TCF to be stable and more durable under operations in stringent environmental conditions, like high ($>40^{\circ}\text{C}$) or low ($<0^{\circ}\text{C}$) ambient temperature, shear and vibrations etc.

In view of the above considerations, the roadmap of the TCF and TCM technologies should be set based on the fundamental materials properties, their realization and the market trends as illustrated in Figure 1. In following subsections, each one has been elaborated.

Figure 1 Representation of competing electrical mobility vs. free carrier concentration in TCO materials. The red marked region is where most of the TCOs as on date falls. The blue marked zones are where R&Ds are ongoing as transmittance (T) of visible photons is good for the materials falling in them. Some challenges exist as well in terms of materials design and process feasibility. The green marked region is where more R&D is required as obtaining a large mobility at lower carrier concentration will satisfy both high T and electrical conductivity.

2.1 Roadmap towards improvement of material properties

In general, the transmission cut-off in a TCF/TCM is determined in short-wavelength (UV) and long wavelength (IR) regions, by intrinsic band gap absorption and the

absorption onset by concentration dependent conduction band electron plasma oscillation, respectively. The figure of merit of the TCM may be determined by high electrical conductivity (σ) and optical transmittance (T) in visible region of spectrum. A higher T is warranted in different TCMs through different mechanisms. For example, in oxide based TCMs, such as SnO_2 , ZnO , CdO , In_2O_3 etc, high T is obtained through wide band gap (>3 eV) without the presence of colour centres (defect states within gap). In MNW based TCMs, the spatial density of nanowires is to be critically optimized. The high visible photon transmission also requires that the plasma resonance frequency should be large to shift absorption peak towards IR photon energies. The wavelength corresponding to the plasma resonance frequency (λ_p) is a function of the free carrier concentration (n) as,

$$\lambda_p \sim \frac{1}{\sqrt{n}} \quad (2.1)$$

As the lower magnitude of absorption is desirable in the visible photon energy, the shift of λ_p at longer wavelength demands the TCMs are provided low doping concentration. This however will compromise the electrical conductivity (σ) of the semiconductor through the standard expression:

$$\sigma = q(n\mu_n + p\mu_p) \quad (2.2)$$

where, q is the electron charge, n/p is free electron/ hole concentration, and μ_n/μ_p is the electron/hole mobility. Therefore, in order to enhance σ , the carrier mobility should be enhanced which can be done by modifying the band structure of host crystal near the band edges.

2.2 Roadmap towards new technology realization

2.2.1 p-type TCOs

At present, a great majority of TCMs available in market are n-type semiconductor based transparent conducting oxides (TCOs) because of their easy dupability to achieve a long range of doping (e.g. from 10^{14} - 10^{19} cm^{-3}). This doping is usually done through substitution at host compound through aliovalent species or hetero-atoms both via solid state or solution processes. Another reason behind the popularity of n-type TCOs is that conduction band of most TCO crystals are populated by delocalized s-orbitals, which ensures a very high electron mobility. On the other hand, p-type TCOs are suffering from low conductivity originating from large effective mass of holes leading to low hole

mobility in most oxide materials [41]. This is one of the great hindrances in the commercialization of p-type TCO materials. The valence band maximum in the wide band gap oxides are predominantly occupied by localized oxygen *p* orbitals, which causes deep acceptor levels and hence a poor hole mobility. Therefore, in order to promote p-type TCM technologies, a number of fundamental aspects need to be thoroughly addressed in further research [42]:

1. Create shallower acceptor levels by reducing defect ionization energy through transition or rare earth metal doping, co-doping, multivalent impurity doping etc.
2. Increase defect solubility through non-equilibrium synthesis method, such as hydrothermal, solvothermal, non-stoichiometric routes, or through increasing host energy by surfactants.
3. Engineer the band structure to achieve higher hole mobility by reducing the hole-effective masses. Increasing the doping concentration at degeneracy level needs to be controlled to reduce visible photon absorption as well as its reflections.

2.2.2 Metallic nanowire based TCMs

Metals with low bulk resistivity, such as Al, Ag and Cu in their nano-mesh forms are promising TCMs. A great number of developments have been seen in past decade over Ag- and Cu- based nanowires and patterns [28]. However, due to their high free carrier concentration $\sim 10^{22}$ - 10^{23} cm⁻³, the corresponding plasma wavelengths lie in visible to deep ultraviolet regime and it is therefore, challenging to make them highly transparent in the visible photon energies. Owing to this, the metallic films would be highly reflective in the visible region and have a large absorbance in the UV region. However, many such metal films and their nano-mesh are highly transparent in the IR region by virtue of the above consideration of blue shifted plasma wavelength. Therefore, the nano-metallic films would be an interesting option in IR applications, such as IR-sensors, IR-photo detectors and IR-solar cells (or thermophotovoltaic devices).

Optoelectronic applications of metallic TCMs are promising as transparency of the TCFs can be made as high as 85% or above by optimizing the size (length, diameter etc) and shape of the metallic nanostructure. However, their sheet resistance (*R_s*) has been found to increase in reduced dimension due to intrinsic grain boundary scattering of free carriers. Beside their physical aspect, chemical stability is another important factor for the development of metallic TCMs. For example, oxidation resistance of Ag is good and therefore Ag-nanowires need not have much protection from ambient. However, oxidation probability increases from Ag to Cu to Al (by virtue of their position in the electrochemical series). In nano-metallic TCFs therefore, few important aspects should be

well addressed before they can be integrated into commercial optoelectronics: 1. Cost effectiveness at large scale, 2. Transparency in visible region, 3. Sheet resistance and 4. Oxidation resistance. In table 1 [27,39,43,44] a scope is defined for their future development based on above four aspects and the untapped applications as on date.

Table 1 *A roadmap towards metal nanowire based TCE*

Metal option	Timeline	Transparency in visible region (Transmittance)	Sheet resistance R_s ($\Omega/\square$)	Cost effectiveness at large scale	Oxidation probability	Application target
Silver (Ag)	To date	~ 80% [43]	~ 38 $\Omega/\square$	Not feasible	Low	Thin-film, Organic PV and LEDs
	Future target	<ul style="list-style-type: none"> Low cost processing Immediate deployment in touch screen technologies 				
Copper (Cu)	To date	~ 85% [27,39]	~ 60 $\Omega/\square$	Highly cost effective	Moderate	Organic PV and OLED
	Future target	<ul style="list-style-type: none"> Reduction in R_s through nano engineering. Improve oxidation resistance Application over thin film PV modules (replacing ITO) 				
Aluminium (Al)	To date	~ 80% [44]	~ 45 $\Omega/\square$	Highly cost effective	Very high at nanoscale	
	Future target	No much promise due to low mobility and chemical stability.				

2.2.3 Carbon based TCMs

There are two major carbon based TCMs studied and developed so far: carbon nanotubes (CNTs) and graphene. The conducting polymers, such as PEDOT:PSS may be included in this category, however, such polymeric TCFs suffer from poor sheet resistance-transmittance trade-off, as well as chemical and thermal instability of their electrical conductivity limiting these types of TCMs in sustainable applications [45]. Amid high interflake resistances in graphene, the graphene as TCM holds some remarkable advantages over the ITOs in especially organic photovoltaic (OPV) and organic LED (OLED) devices. Novoselov et al. [46] has provided an excellent roadmap for the use of graphene in next 15 years in his review. The review anticipates a transition from medium quality graphene in touch screens, e-papers and foldable OLEDs as of now to high quality large area graphene in future developments. The graphene is expected to finally see a market in composited forms, such as that with CNTs, polymer matrices etc.

Presently, graphene has already been attempted as TCMs in optoelectronic technologies, such as flexible-OLEDs, touch screens and e-papers. However, it is only partial due to the high cost involvement in the chemical vapor deposition (CVD) process involved in the graphene fabrications. Therefore, dependency on ITO has not been fully eliminated. In the next 10 years (by 2030), touch screens will be required to be interactive, such as car windscreens, industrial process and control view interfaces etc. Besides, read-write on e-paper will be done on foldable interface with radius as small as 5mm. The high contact resistance during folding has been a challenge which is required to be resolved. Graphene based TCFs will also be required on flexible solar panels by that time. In the next 20 years (by 2040) above technologies in wearable forms will be significant. They are also expected to be interactive and internet of things (IoT) based. As these wearables will be used in various weather conditions, such as high/low temperature/ humidity, their structural and thermal stability are required to be investigated in detail. In the next 30 years, the graphene based TCMs are expected to invade biotechnology where embedded soft electrodes can handle various functionalities of vision such as photochromic, electrochromic etc. implants in human eyes (Figure 2).

Figure 2 A 30-years roadmap for graphene and reduced graphene oxide based TCMs in optoelectronic applications.

2.3 Market trends of transparent conductors

The market of transparent conductive films is expected to reap \$5.86 billion by 2020 according to a private market survey [47], with a cumulative annual growth rate (CAGR) of 17.2% during the last forecast period of 2014 - 2020. The largest use of TCF as

discussed above in display technologies is either on glass or on films. The market is now growing primarily due to an escalating demand for touch enabled devices. Declining cost of new smartphones, continuous adoption of touch-based user interfaces (self-service kiosks *etc*), energy efficiency, light weight, low-cost materials, flexibility and robustness are the key drivers of this market. Apart from this, OLED lighting, OPV and DSSSC are also potential markets. However, these are expected to register a slower growth initially, but shall escalate in coming decade.

The TCF market is also segmented on the basis of technology, application and demographic acceptability. Key technologies which are implemented in manufacturing include ITO on PET, ITO on glass, non-ITO oxides, silver nanowires, graphene, carbon nanotubes, metal mesh, micro fine wire, and PEDOT [47]. The application industries include smartphones, tablets, notebooks, all-in-one PCs, monitors, TV displays, and OLED lighting. The geographical demand goes to North America, Europe, Asia Pacific (AP) and Latin America, Middle East and Africa (LAMEA). Among these, AP has been the leading region in the TCF market followed by North America. As per the above, the key companies in this market include (not limited to) 3M, Nitto Denko Corp, Toyobo Corp, Dupont Teijin Films, Eastman Kodak, Fujifilm Holdings Corp, Canatu Oy, DONTECH Inc, Cambrios Technologies Corporation, and Rolith. Various other companies are also growing in China, South Korea and Taiwan.

3. Physical aspects and materials for TCEs

The most common and vital requirements for a TCE are high conductivity and transparency. Typically, semiconductor oxide films with wide band gaps are best suited for its transparent nature (transparent conducting oxide, TCO). Besides, there can also be metallic mesh or nano-carbon networks which may be considered as TCEs. Transparency in the later class materials depends on their spatial density in most cases. As their material properties are totally different from TCO to metallic or nano-carbon TCEs, their electrical conductivity needs to be reviewed in different manner. These three classes of TCEs with respect to their physical properties are discussed below.

3.1 Physical requirement and materials for TCOs

In semiconducting oxide (TCO) materials a high conductivity σ can be warranted through a high carrier concentration n (electrons) of p (holes) and/or a sufficiently high carrier mobility $\mu_{n,p}$ according to following equation:

$$\sigma = q(n\mu_n + p\mu_p) \quad (3.1)$$

where, q is the electron charge.

By virtue of small effective mass, electrons have larger mobility than that of holes, and therefore, n-type TCOs are usually preferred over the p-type. However, the carrier concentration cannot be taken as a design parameter to improve the electrical conductivity because it is limited by the absorption of light by free electron gas, which compromises the visible light transmittance. According to classical Drude theory electrical field of a light wave causes the collective plasma excitation in electrons and defines a plasma frequency given by [48]:

$$\omega_p = \sqrt{\frac{ne^2}{m^* \epsilon_r \epsilon_0}} \quad (3.2)$$

where m^* is the effective mass of the electron carriers and $\epsilon_r \epsilon_0$ is the permittivity of the material. In most of the TCOs (Table 2) therefore, it is essential to keep the free carrier concentration below few 10^{21} cm^{-3} to keep the plasma wavelength in the infra-red region. Therefore, the higher electrical conductivity must be assured through the carrier mobility in these materials. Therefore, the electronic band structure plays vital role to control the effective mass of their free carriers. Table 2 below summarizes some common TCO materials with their reported physical properties [29].

3.2 Physical requirement and materials for metallic TCEs

In metallic TCEs nanostructures such as metallic nanowires or nanomesh are adopted to ensure large transmittance values, electrical conductivity needs to be critically evaluated due to two reasons: (1) metals have already very large free carrier concentration ($n \sim 10^{23} \text{ cm}^{-3}$), which makes them to absorb visible light due to their low values of plasma wavelength cut-off, and (2) poor interconnects at their nano-domain.

3.3 Physical requirement and materials for nano-carbon TCEs

Among various nano-carbon variants, graphene has attracted highest attraction in the field of TCE due to its outstanding two-dimensional electron gas at room temperature. Graphene shows exclusive electronic band structure where the valence band is formed by bonding π -orbitals, whereas the conduction band is formed by the anti-bonding π^* -orbitals. The conduction band eventually meets the valence band at a single point crystal momentum, $k = 0$, commonly known as a Dirac point [49]. At this point, the electron energy (E) is linearly dependent on k . This linear dispersion relation results in massless excitons, and thus electrons in graphene behave like massless Dirac fermions which can

travel large distances (in μm to tens of μm) as compared to their domain size (typically 10-100s nm) without scattering (ballistic transport). This leads to very high electron mobility at low carrier concentrations (table 2- indicative values). This intriguing property of graphene shifts the plasma wavelength to the far-infrared and it becomes highly transparent to visible light. Although single layer graphene is characterized with high intrinsic mobility $\sim 5000 \text{ cm}^2/\text{V.s}$, large area TCFs using graphene face real challenge of the presence of wrinkles, cracks, few-to-multi layers and other mobility-reducing defects and therefore, are yet to be addressed.

Table 2 Parameters (reported so far) of various possible TCMs which determine its application merit.

TCM example	Bulk resistivity ($\Omega\text{-cm}$)	Free electron concentration (cm^{-3})	Plasma wavelength (nm)	Electron mobility ($\text{cm}^2/\text{V.s}$)	Merit (M)/ Demerit (D)
Semiconducting oxides					
ITO (In:SnO_2)	$\geq 10^{-4}$	$< 3 \times 10^{21}$	770	$\sim 20\text{-}100$	M: High visible transmittance, very large electrical conductivity, low roughness. D: Highly brittle (low mechanical strength)
FTO (F: SnO_2)	$\geq 5 \times 10^{-4}$	$< 10^{21}$	1100	$\sim 15\text{-}50$	M: (Close to ITO) D: High roughness, higher processing temperature than ITO – application limitations.
AZO ($\text{Al 2\%:ZnO}$)	$\geq 3 \times 10^{-3}$	$< 3 \times 10^{20}$	1100	~ 20	M: Cheaper than ITO & FTO due to ZnO D: RF-sputtering only best reported technique for TCF (process limitation)
BZO (B_2O_3 2%: ZnO)	$\geq 2 \times 10^{-2}$	$< 10^{20}$	1100	$\sim 2\text{-}5$	M: Visible transmittance better than AZO D: Low electrical conductivity due to low mobility as well as carrier concentration.
Metals based					
Cu	$\sim 2 \times 10^{-6}$	$\sim 8.5 \times 10^{22}$	110	~ 50	M: Highly conductive, cheap D: Prone to oxidation, visible light absorption (high haze)
Ag	$\sim 1.5 \times 10^{-6}$	$\sim 6 \times 10^{22}$	140	~ 72	M: Very large conductivity, oxidation resistant. D: Cost, high haze.
Al	$\sim 2.5 \times 10^{-6}$	$\sim 1.8 \times 10^{23}$	80	~ 14	M: Cheap D: Very high visible absorption and haze factor.
Carbon based					
Graphene	$> 5 \times 10^{-6}$	$< 3 \times 10^{20}$	1900	< 5000	M: Extremely large electrical conductivity in single layer 2D form, highly transparent. D: Scaling up not easy.
SW-CNT	$> 1.5 \times 10^{-4}$	$\sim 3 \times 10^{17}$	250	< 10	M: Cheap and ductile. D: High haze above certain concentration / surface coverage.
Conductive polymer	$> 7 \times 10^{-4}$	$\sim 10^{20}$	800	< 1	M: Highly ductile (best suited as flexible TCM) D: Sheet resistance-transmittance trade-off

4. Oxide based TCMs: The TCOs

This section provides a brief account of TCOs from fundamental material in relation to the viewpoint of physics and industrial applications. A brief review of two well-known TCOs, namely the ZnO and In₂O₃, and their doped forms are given. Their crystal and electronic structures are also discussed. The research challenges in the field of transparent electronics and solar energy are discussed in specific. In later part, the developing field of hole transporting TCOs (or p-type TCOs) are also accounted.

4.1 Physical and chemical basis of TCO materials

The TCOs are class of heavy metal oxides, which are wide band gap semiconductor by virtue of low-lying O-2p orbitals which mostly constitute the top of valence bands (VB). Their electrical conductivity (σ) is determined by the product of carrier mobility ($\mu_{n/p}$) and their concentration (n/p) along with the fundamental charge (1.6×10^{-19} C). Fundamentally, large σ may be warranted by either large n/p (degenerate semiconductor) or a large $\mu_{n/p}$. However, as will be discussed later degeneracy in TCEs are not advisable to prevent visible light absorption by plasmon resonance phenomenon. A best strategy is therefore, selecting oxides that will provide large $\mu_{n/p}$. The electron mobility (n-type semiconductor) is proportional to the width of conduction band (CB) and therefore, a large overlap between electron sharing orbital is required. A number of metal oxides, containing of a heavy metal cation with an outermost shell electronic configuration of $(n-1)d^{10}ns^0$ ($n \geq 4$) and oxygen anions satisfy this condition (Figure 3) [50].

As mentioned above, the top of the VB is constituted by the O-2p orbitals and the bottom of the CB is mostly populated by the metal-ns (M-ns) orbitals (preferably to remain unoccupied) as illustrated in Figure4 for ITO (Sn doped In₂O₃). The spatial spreading of these M-ns is large and the overlap between them with spherical symmetry is also large. Metals with larger overlap integral between their n-s orbital offer higher mobility. Table 3 [51] below summarizes some common TCO metal candidates with their s-orbital overlap integrals. As is clear from table 3, s-orbital overlap is large in case of Zn and In, in ZnO and In₂O₃, respectively. Therefore, these two oxides are offering very high carrier mobility. SnO₂ also offers reasonably good electrical properties. Remaining candidates are either containing scare (Ga/Ge) or toxic (Cd) elements.

Representative elements		Representative elements										Noble gases	
GROUP NUMBER		GROUP NUMBER										18	
1 2												0	
IA IIA												He	
3	4											2	He
Li	Be											1s ²	
11	12											10	Ne
Na	Mg											2s ² 2p ⁶	
19	20											18	Ar
K	Ca											3s ² 3p ⁶	
37	38											54	Xe
Rb	Sr											5s ² 5p ⁶	
55	56											86	Rn
Cs	Ba											6s ² 6p ⁶	
87	88											118	Og
Fr	Ra											7s ²	

Figure 3 Heavy metal cations as suitable candidates for TCOs. Periodic table ref [47].

Figure 4 Typical band structure and projected density of states (PDOS) of an ideal TCO material (ITO here).

Table 3 Metal conduction band orbital overlap integral values in some representative metal candidate for TCOs according to ref [51].

TCO example	Orbital overlap	Overlap integral value	References
ZnO	Zn-4s/Zn-4s	0.604	[51]
In ₂ O ₃	In-5s/In-5s	0.561	[51]
β-Ga ₂ O ₃	Ga-4s/Ga-4s	0.463	[51]
GeO ₂	Ge-4s/Ge-4s	0.284	[51]
CdO	Cd-5s/Cd-5s	0.69	[51]
SnO ₂	Sn-5s/Sn-5s	0.452	[51]

4.2 Overview of common TCOs

As discussed above, both In₂O₃ and ZnO are non-toxic and have relatively large overlap integrals, which lead to a high electron mobility ensuring high electrical conductivity. In₂O₃ has a bixbyite cubic crystal structure which is a vacancy-defect oxide. The bixbyite structure is similar to that of fluorite and has a face-centred cubic array of indium atoms with all the tetrahedral interstitial positions filled with oxygen atoms. The MO₈ (metal centred- cornered oxygen) coordination units are replaced by missing oxygen from either the body or the face diagonal as depicted in Figure 5. The removal of two oxygen atoms from the MO₈ to form the MO₆ coordination units forces indium from the centre.

Figure 5 Crystal structure of In₂O₃ and ZnO which are basis of common TCOs.

In the In₂O₃, O²⁻ ions occupy 3/4th of the tetrahedral interstices of an fcc In³⁺ array. Consequently, valence band of In₂O₃ consists of filled oxygen-2p states. The indium-3d core lies below the valence band edge. On the other hand, the conduction band is

characterized by indium-5s band maintaining a gap of 3.75 eV with valence band. At high concentration of oxygen, an oxygen vacancy band forms and overlaps at the bottom of the conduction band. It makes In_2O_3 a degenerated semiconductor. In this case, the oxygen vacancies act as doubly ionized donors and contribute a maximum of two electrons to the conduction band. Additional improvement of conductivity can be done via doping Sn into In sites. Since indium exists as In^{3+} , the Sn^{4+} substitution results in an n-type doping by providing an extra electron to the conduction band in order to preserve the overall charge neutrality.

The second TCM of interest is ZnO, which crystallizes in a highly stable wurtzite structure as shown in Figure 5. The electronic structure of ZnO has been widely studied by many researchers [52]. In ZnO, the lowest two valence bands correspond to the $\text{O}^{2-} : 2s$ core-like states and the next six valence bands are populated by $\text{O}^{2-} : 2p$ bonding states. On the other hand, first two conduction bands (lowest of which is 3.4 eV apart from the valence band) are strongly localized by unoccupied $\text{Zn}^{2+} : 4s$ levels to support electronic conduction. The undoped ZnO is slightly conducting, whereas higher conductivity occurs from the self-doping from the oxygen vacancies and/or Zn-interstitials. The donor levels can also be produced by the incorporation of foreign atoms such as H, In, Ga, B etc.

4.3 Emerging TCO substitutes of ITO

In the past few decades there have been only incremental developments with respect to basic n-type crystalline TCO properties and such a class of materials has almost reached a maturity. Hosono and co-workers [53] first pointed out that, amorphous oxides can be promising TCOs. Later, Narushima and co-workers [54], Nomura et al. [55], Hosono [56] and Taylor et al. [57] independently established the potential of amorphous oxides as TCOs [54-57]. In these reports, the ionic amorphous mixed oxides $(\text{In}_2\text{O}_3)_x(\text{ZnO})_{1-x}$ and $(\text{Ga}_2\text{O}_3)_x(\text{In}_2\text{O}_3)_{1-x}$ constituted a new class of TCO materials that could be used both as TCEs and for transparent field-effect transistors. These amorphous semiconductors have unique electrical conductivity that stems from very high electron mobility ($\sim 10 \text{ cm}^2/\text{V.s}$) despite large structural disorders. Such extraordinary electrical property exists because their conduction band is composed of spherical, isotropic 5s orbitals of the metal cation, the overlap of which does not change greatly in their amorphous state. Another promising new TCO material is doped TiO_2 , which was first invented as TCE by Hasegawa and co-workers [58] in 2005. The resistivity reported in this system was remarkably low $\sim 5 \times 10^{-4} \Omega \text{ cm}$. Although, this could be reached only at relatively high substrate temperatures of more than 300 °C, which is a drawback in many practical devices. A big advantage,

however, with doped TiO_2 is its excellent chemical stability and further research is necessary to make it colourless as well.

4.4 Hole transporting or p-type TCOs – Challenges and perspectives

The transparent conducting oxides are crucial to many technologies from transparent electronics to thin film solar cells. While majority of the transparent conducting oxides in commercial sectors as mentioned above are n-type, their p-type counterparts are not well commercialized, as they exhibit much lower carrier mobilities that originates from large effective masses of hole in most oxides. Therefore, a primary objective to develop p-type TCO is to identify crystal structures which will offer low hole effective masses without compromising their wide band gap and low free carrier concentration. A fundamental difficulty in developing high-mobility p-type TCOs lies in the valence band in most oxides which is mostly populated by localized oxygen $2p$ -orbitals. This makes the valence band quite flat across the Brillouin zones and it leads to a large hole effective masses (m_h^*) [59]. Kawazoe et al. [60] in 1997 first demonstrated that, delafossite compound and a p-type semiconductor, CuAlO_2 could show encouraging electrical conductivity and high optical transparency in visible light. In the crystal a large hole mobility was explained by a large hybridization of the oxygen orbitals with $3d^{10}$ electrons of Cu^{+1} p-closed shell, which lowers the oxygen's localized character and ultimately leads to dispersive valence band. Since then, the presence of Cu in p-type oxide semiconductor compounds has been believed to be a determining factor towards TCO development. In 2012, Hautier et al. [41] presented a design principle to identify the best suited candidates for p-type TCOs based on first-principles calculations. According to this design, several oxides can show p-type conductivity with wide band gap ($> 3\text{eV}$) but with effective masses ($0 < m_h^* < 1.5$) as compared to existing p-type TCOs, including CuAlO_2 (where $m_h^* \sim 2.5$ or above). This provides an opportunity to make them competitive with their n-type counter parts where the electron effective mass ranges between 0 and 0.5 (Figure 6- the target region of development). Apart from the copper d -orbital, hybridization in existing Cu-based p-type TCOs, there are also a number of cations, such as Sn^{2+} , Pb^{2+} , Tl^{1+} etc. where hybridization of s -states from $(n-1) d^{10}ns^2$ ($n \geq 5$) is possible with the oxygen- $2p$ states, making its effect benign. As the s -orbitals are more delocalized than d -orbitals, a higher dispersion of the valence band is possible to ensure lower effective masses of hole. Therefore, wide band gap compounds, such as $\text{K}_2\text{Sn}_2\text{O}_3$, $\text{Rb}_2\text{Sn}_2\text{O}_3$, PbTiO_3 , PbZrO_3 , PbHfO_3 , $\text{K}_2\text{Pb}_2\text{O}_3$, Tl_4O_3 and $\text{Tl}_4\text{V}_2\text{O}_7$ are quire promising candidate as p-type TCOs provided feasible synthetic routes and their environmental stabilities (especially for Pb and Hg-based candidates) are ensured.

Figure 6 Existing state of the art of p-type TCOs and their opportunity region of development in comparison to the existing ideal n-type TCOs.

5. Nano-carbon based TCMs: Graphene and CNTs

5.1 Graphene based TCEs

Graphene is a two-dimensional nanomaterial where carbon atoms are arranged hexagonally planar one-atom thick layer. Graphene has been studied theoretically in the second half of the 20th century. In 2004, graphene was successfully synthesized by mechanical cleavage method from graphite. After that, graphene has been successfully prepared by various techniques and studied for different applications. Even though various preparation techniques are available, for graphene based TCEs are generally prepared from CVD grown graphene or from the graphene oxide (GO) [61]. GO can be directly coated over the substrate and can be reduced. In case of CVD grown graphene, the graphene has to be transferred into the device substrate which involves etching and stamping, thermal release method, photoresist method, roll-to-roll method and general method.

$$T = \left(1 + \frac{Z_0}{2R_S} \frac{G_0}{\sigma_{2D}}\right)^{-2}$$

where $Z_0 = 1/\epsilon_0 c$ is the free-space impedance, ϵ_0 is the free-space dielectric constant, and c is the speed of light. For graphene sheet, $\sigma_{2D} = n\mu e$, where n is the number of charge carriers per unit volume, e is the electronic charge and μ is the mobility.

Graphene based TCEs were reported based on the solution processed GO for different photovoltaic devices. Wang et al. [62] showed that the GO prepared from the Hummer's method was deposited over the quartz substrate by dip coating and reduced by thermal treatment. The electrical conductivity of the graphene film was 550 S/cm and optical transmittance of 70%. The graphene based TCE was demonstrated for organic solar cells. Graphene-based TCE has also been used for the DSSCs [63]. The film thickness of <20 nm, the optical transmittance of >80% and the sheet resistance of the TCE was in the range of 5k to 1M ohm/sq. However, the GO-based method for the preparation of graphene and TCE was having disadvantage due to the high sheet resistance due to the introduction of the functional group on the GO.

CVD grown graphene is having high optical transmittance as well as good sheet resistance which makes the reliable method for the preparation of graphene-based TCEs. In this CVD technique, Cu foil is used as the substrate for the growth of graphene. The carbon solubility is low in Cu foil which limits the precipitation of carbon while cooling down the furnace. The growth of graphene on the Cu foil is mainly due to the catalytic decomposition of hydrocarbon on the surface and subsequent growth of graphene on the Cu substrate. Depending on the conditions, single-crystal or polycrystalline graphene can be grown on the Cu foil. Roll-to-roll production of graphene has been achieved by CVD technique on 30 inch Cu foil [64]. They have doped with p-type doping on graphene. The sheet resistance of $\sim 125 \text{ ohm sq}^{-1}$ with $T = 97.4\%$ and $\sim 30 \text{ ohm sq}^{-1}$ with $T = 90\%$.

5.2 Carbon nanotubes (CNTs) based TCEs

SWCNTs is a one-layer carbon atom thick seamless cylinder bounded together by sp^2 carbon bond [65,66]. Carbon nanotubes are one-dimensional carbon nanomaterials which can be prepared in single-walled (SWCNT) and multi-walled (MWCNT) forms [67]. It is having superior properties such as mobility as high as $100,000 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$, current carrying capacities of 109 A/cm^2 and ON/OFF current ratios as large as 10^5 [68,69]. SWCNTs also exhibit high surface area to volume ratio and excellent thermal stability. The CNTs can form a network structure as film due to its 1D structure and high aspect ratio [70]. The CNT network films are transparent below 100 nm and having high electrical conductivity. Thus, the CNT network films are widely studied for the possible candidate for the TCE. The CNT-based TCE mainly focused on the SWCNTs because MWCNTs usually accompanies with defect which reduces the conductivity and affects the TCE properties [21-23]. CNTs are produced in high quality using different techniques

such as chemical vapor deposition (CVD), arc-discharge technique and laser ablation technique [71-74]. The formation of SWCNTs and MWCNTs can be controlled by varying the synthesis conditions and parameters. SWCNTs can be formed into network with uniform, optically homogeneous film where thickness can be controlled [75]. The SWCNTs network can be formed by simple filtration technique, air brushing, drop-drying from solvent, Langmuir-Blodgett deposition and lithography techniques [75-80].

For using CNTs as the TCE materials, the impurities such as metal catalysts and carbon impurities need to be thoroughly removed. The purification process of the CNTs consists of removal of the other carbon impurities and defective CNTs by controlled oxidation followed by acid washing to remove the metal impurities which used as catalyst for CNT growth. The harsh purification induces the defects on the surface of the CNTs which leads to the increase in the sheet resistance. Thus, it is important to control the purification procedure for the CNTs to obtain high quality CNT-based TCEs. The purified CNTs need to be deposited on the substrate and mostly solution-based deposition technique is widely used. Due to strong Van der Waals interaction between CNTs, the dispersion of CNTs in solution is realized by surface functionalization on CNTs, by selective dispersion on organic solvents and using surfactants.

SWCNT film has been reported on plastic substrate using line patterned technique with high optical transparency of >80% and low-sheet resistance (<100 Ω/sq) [81]. Similarly, Lee et al. [82] reported the transparent SWCNTs (t-SWCNT) film for the optical transparent p-type ohmic contacts to GaN light-emitting diodes. The t-SWCNT was patterned using standard microlithography technique. A simple process for fabricating SWCNT film by filtration process which was transparent, electrically conductivities has been demonstrated with the transferring of the SWCNT film on various substrates [75]. The optical transparency and conductance of the SWCNTs film prepared by the vacuum filtration technique has been found to be dependent on nanotube length. It has been highlighted that the high intertube resistance limits the conductivity properties of the CNT films [83]. Geng and coworkers [84] studied the effect of acid treatment on CNTs on the electrical conductivity without affecting the transmittance. The acid treatment was observed to effectively remove the dispersing agent (sodium dodecyl sulphate) which subsequently found to improve the junction contact by reducing contact resistance.

The CNT-based TCEs are excellent replacement for the ITO due to its flexibility, scalability, solution processability and excellent optical and electrical properties which is very important for the TCEs. However, still, the CNT-based TCEs are limited by the high sheet resistance due to nanotube-nanotube junction contact resistance and roughness. Recently, Jiang et al reported network of isolated SWCNTs by modified CVD technique [85]. The pristine CNT film exhibited the optical transparency of 90% and sheet

resistance of $45\Omega.\text{sq}^{-1}$. The acid-treatment using HNO_3 further reduced the sheet resistance to $25\Omega.\text{sq}^{-1}$ without affecting optical transparency. The observed improvement is due to the welding of SWCNTs by graphitic carbon the intertube junction.

6. Metallic nanowire based TCEs

Metal nanowires have received considerable attention for the development of advanced TCEs because of the inherent electrical conductivity and optical transparency. The main advantages of metal nanowires are the solution-phase synthesis and solution-processable coating of TCE film, which drastically reduces the cost and increases the production capability.

Figure 7. Various processes of high throughput fabrication

6.1 Silver nanowires

Silver nanowires are studied for the TCE applications because of the very low resistivity of the silver in the bulk [86]. Silver nanowire-based TCE was first reported by Lee and co-workers [12]. They modelled the optical transmittance of the silver grating in the period of 400 nm, line-width of 40 nm and various heights. They showed that the metal grating is far superior to the ITO TCE with low sheet resistance. By this evidence, they deposited silver nanowire over the glass prepared by polyol synthesis using PVP as the capping agent. The silver nanowires were having the length of 103 ± 17 nm with diameter of 8.7 ± 3.7 nm. The nanowire suspension was drop-casted over the glass. The initial sheet resistance of the as-prepared silver nanowire mesh was $>1\Omega.\text{sq}^{-1}$ due to the thin-layer of PVP over the silver nanowire. The silver nanowire was heated at 200°C for 20 nm where the sheet resistance drastically decreased from >1 to $100\Omega.\text{sq}^{-1}$ due to the degradation of PVP and silver nanowire-to-silver nanowire contact and fuse together.

Light-induced heating on the junction of the silver nanowires for the plasmonic welding was introduced by Garnett et al. [87]. The small gap between the silver nanowires in the junctions can be used to localized heating by effective light concentration and welding the junction. This reduces the sheet resistance and improves the optical transmittance. The advantage of this technique is self-limited and heat sensitive materials because of the strong dependence of the plasmonic field due to the distance between the wires.

6.2 Copper nanowires

Copper is 1000 times more abundant than silver in the earth's crust and 100 times cheaper than silver and 6000 times cheaper than gold. The conductivity of the copper is slightly lower than the silver (6%). The main challenges in the synthesis of CuNWs are enhanced surface oxidation due to the large surface-to-volume ratio, stability and dispersity. There are various techniques available for the synthesis of copper nanowires. Synthesis of AgNWs is mainly based on the polyol route and it is well-established. However, the CuNWs can be synthesised by various techniques like solution-based technique, electrospinning, hydrothermal [88].

Solution-based synthesis can be broadly classified into aqueous and non-aqueous route for the synthesis of CuNWs. In aqueous route, one approach is the reduction of CuCl_2 under pressure at 175°C in water for 10-48 h in the presence of octadecylamine (or oleylamine or hexadecylamine). The low temperature modified method for the synthesis of the above mentioned approach is the reduction of glucose, temperature of 100°C and less than 6 h. This approach is known as alkylamine-mediated synthesis and the solvent used is water. The nanowires with the length >100 nm and diameter around 20 nm which yields high aspect ratio are prepared and is highly desirable for the TCE films. Another approach for the preparation of CuNWs is EDA-mediated synthesis [89]. Chang and coworkers [90] reported the synthesis of CuNWs using EDA with length of 40-50 nm and diameter of 90-120 nm and aspect ratio of >350 -450. High concentration of NaOH is necessary to avoid the precipitation of copper hydroxide. Wiley et al. [91] groups have developed EDA-mediated CuNWs are synthesized relatively mild reaction condition at 60°C in alkaline condition. Hydrazine is used as the reducing agent and EDA acts as the structural directing agent. The mechanism of formation of CuNWs is growing from the spherical seed.

Various other methods have been attempted to synthesize the CuNWs, such as non-aqueous route, disproportionation reaction, seeded, imine, amino acid, ascorbic acid, and hydrothermal route. Reduction of their junction resistance has been attempted by post-treatments like thermal annealing, wet chemical coating, nanoplasmonic welding and electric welding. Longer the NWs the junction resistance can be reduced. Cui et al. [92]

have been investigating the development of NWs through electrospinning in various architectures. In order to improve the junction resistance, photonic welding is widely used. CuNW-conducting polymer and transparent polymer composites are developed for the TCEs.

7. Hybrid nanostructured TCEs

The hybrid nanostructure based TCEs (HNS-TCEs) are featured TCEs that combines and inherit unique properties of their parental constituents at the nanoscale. Therefore, they possess a synergistic effect between individual components, provided they are designed carefully. In the HNS-TCEs the weakness of one component is compensated by the strength of the other component(s). In following sections, such HNS-TCEs are reviewed where physical or chemical limitation of the first component can be taken care by the other.

7.1 Metal nanowires-conductive metal oxide (MNW-MO) hybrids

Metal nanowires (MNWs) are promising for their excellent electrical properties. However, there are some issues which must be resolved before they can be successfully applied to optoelectronic devices. A few of them include i) surface roughness, ii) poor adhesion to substrates, iii) thermal instability, iv) high junction resistance, and v) limited contact area with the adjacent layer [93]. Hybrid structures composed of a metal nanowire mesh and conductive metal-oxide layer have been suggested as promising alternatives to resolve these issues [94]. It has been seen that incorporation of the conductive metal oxide into the host MNWs protects the nanowires from local melting-induced disconnection, which in turn enhances the thermal stability of the MNWs. In addition to this the metal-oxide overcoating layers improve the adhesion property of the MNWs to the substrate. Such composite electrode also facilitates effective charge transfer by filling the empty space unoccupied by the MNWs and by smoothing the electrode surfaces [95]. Table 4 [93, 96-98] lists some notable developments in literature as on date of MNW-MO based TCEs.

7.2 Metal nanowires-graphene (MNW-graphene) hybrids

As mentioned earlier, MNW networks have certain limitations towards commercialization. They exhibit high NW-NW contact resistance, high surface roughness, high oxidation probability (especially in CuNW) and poor adhesion to plastic substrates. The CVD graphene films are usually polycrystalline with grain boundaries that affect the charge mobility and hence the electrical conductivity. The transferred graphene electrodes also have intrinsic defects and dislocations leading to their

conductivity lower than that of exfoliated graphene. However, combining graphene and MNWs overcomes the weakness of individual component. In some cases, MNW-core/graphene or reduced graphene oxide (RGO)-shell structure has been shown to protect the MNW such as CuNW from oxidation [97]. Table 4 [99-101] lists some important developments in the literature as on date for MNW-graphene/GO based TCEs.

Table 4. TCE parameters reported in some hybrid nanostructured systems

HNS-TCE system	HNS-TCE example	Sheet resistance (Rs) $\Omega\cdot\text{sq}^{-1}$	Transmittance (%) at 550 nm	Research group/ year/ Reference
MNW/MO	ITO/AgNW	23.0	88.6	Yang/ 2012/ [96]
	AZO/AgNW/AZO-ZnO	11.3	93.4	Moon/ 2014/ [93]
	IZO/ AgNW	9.3	91.0	Subramanian/ 2016/ [97]
	SnO _x /AgNW	5.2	81.0	Riedel/ 2014/ [98]
MNW-Graphene	CVD graphene/AgNW	16	91.1	Zhang group/ 2014/ [99]
	spin coated AgNWs/CVD-graphene	33	94.0	Park group/ 2013/ [100]
	CuNW/RGO core-shell	28	90	Yang group/ 2016/ [101]
MNW-CNT	AgNW/SWNT (3:2)	120	90.8	Han group/ 2015/ [102]
Graphene-CNT	(CVD) Graphene/ (CVD) SWNT	420	~ 73	Tai group/ 2012/ [103]
	RGO/ SWNT	180	86	Kim group/ 2012/ [104]
Polymer composite based (CPC)	PEDOT:PSS/Graphene	0.2 S / cm (Conductivity)	~ 80	Chen group/ 2009/ [105] Yang group/ 2011/ [106]

Abbreviations: AZO – Al doped ZnO, ITO – In doped SnO₂, IZO – In doped ZnO, RGO – Reduced Graphene Oxide

7.3 Metal nanowires-carbon nanotube (MNW-CNT) hybrids

The main advantage of integrating MNW with SWCNTs has been the overcoming of the high haze factor in some MNWs, such as AgNW [102]. By the plasma resonance property of SWCNTs, they absorb light scattered from the AgNWs, which in turn reduces the haze of such MNWs. However, such composites have not gained much attention due to tricky optimization and trade-off between the sheet resistance and the haze values.

7.4 Graphene-carbon nanotube (graphene-CNT) hybrids

Although graphene is a proven material with outstanding electrical mobility and very high transmittance to become the material of choice for TCEs, the practical issue associated with graphene deposition on the substrate is the domain size limitations and their interconnectivity. This leads to worsening its electrical merit. Carbon nanotubes can synergistically solve this problem to act as domain- to -domain interconnecting media. Typically, graphene sheet resistance has been shown to improve from 2.15 to 420 $\Omega\cdot\text{sq}^{-1}$ by CVD grown SWNTs. Although, the transmittance in such cases has been found to get affected from 85 to 73%. Therefore, density of spatial coverage of CNTs plays a crucial role on determining the transparency. Moreover, SWNTs have also been used with reduced graphene oxides (RGO), where introducing them between the RGO sheets is a sustainable approach for inhibiting the agglomeration of sheets after chemical reduction takes place. Table 4 [103,104] lists some of the best reported TCEs based on graphene-CNT composites.

7.5 Conductive polymer (CP) composite transparent electrodes

A conductive polymer matrix, such as PEDOT:PSS may be used as a bridging medium in the nanosheet-to-nanosheet electrical conduction in the graphene films such as by the CNTs as mentioned in the foregoing section. In addition to that, a CP can also act as flexible host and therefore, such CP-graphene composite can act as promising CP-composite TCE [105]. The CP has also been useful in MNW based TCEs. With organic polymers such as, PEDOT:PSS or amyl acetate (nail polish solvent) MNWs such as AgNWs have shown excellent adhesion property with the glass as well as flexible substrates [106]. Table 4 [105,106] enlists some reported TCE characteristics of such CP composites.

7.6 Graphene-metal oxide (graphene-MO) hybrids

As mentioned above, graphene needs a bridging matrix to reduce its sheet resistance originated from dispersed nanosheets over the substrate, amid exceptionally high

electronic mobility. Some metal oxide (MO), such as very thin layer of silica can serve as protective host as well [107].

8 Scalability and large area fabrication of advanced TCEs

Large-area fabrication of the advanced TCEs is important for the commercial applications. It is well-known that the solution-based deposition technique is considered promising for the large-area fabrication due to its low-cost, scalability and high-throughput. In solution-based deposition technique, the TCE materials are uniformly dispersed in the suitable solvents and the dispersed solution is subsequently coated onto the substrate. Some of the solution-based deposition techniques are vacuum filtration, spin-coating, dip-coating, spray coating, rod coating and ink-jet print coating.

The vacuum filtration method is a solution-based deposition technique for the thin film production. In this deposition technique, vacuum filtration is used for the deposition of thin film on the filtration membrane followed by transferring the deposited film on the targeted substrate from the filter membrane. The TCEs produced from this method exhibit highly homogenous and the process parameters can be used to control the properties of the TCEs by simply varying the concentration and volume of the solution. By using filtration techniques, CNTs, rGO, AgNWs and CuNWs and their hybrids are widely reported. The main limitation of the vacuum filtration technique is its scalability. This method is restricted to the development of small area TCE films. Similarly, another solution-based technique is the spin coating for fabricating uniform TCEs on the flat substrates. The properties of the TCEs are controlled by the rotation speed, duration, concentration of the solution, etc. However, this method is also limited for the scalability and large-area deposition.

Some of the scalable methods for the fabrication of large-area TCEs are spray coating, rod coating (Meyer rod) and ink-jet printing technique. These techniques can be adopted for the continuous production of TCEs by roll-by-roll coating. These are all solution-based deposition techniques which are simple, fast, low-cost, and scalable deposition method to obtain TCEs. The method can be adopted for the room temperature and different substrates can be used. In the spray coating method, the TC materials can be directly coated on the substrate by spraying the solution using air gun or ultrasonic spray gun. The advantage of this method is deposition of materials on the different types of substrate and in different geometries. The Meyer rod coating is a solution-based deposition method which is scalable and low-cost technique. This is a continuous roll-by-roll fabrication TCE fabrication technique in which high quality TCEs can be deposited on the substrate. The properties of the film can be controlled by the viscosity of the coating slurry, speed of coating and wetting property. Mainly, metal nanowire-based TCE

fabrication is widely reported by this technique. The ink-jet printing method is considered as the fast and low-cost printing technique because this method does not have any templates or mask for fabrication of thin TCE films. This method can be adopted for the large-area and roll-to-roll production of films.

9. Prospects

ITO is widely used TCEs in the commercial market for almost six decades and it is expected that the ITO will be continued to be used in the future. However, rapid growth in flexible, bendable, and stretchable devices in coming decades necessitates the development of the advanced TCEs. Also, availability of the indium and cost of manufacturing the oxide-based TCEs by vapor-based technique are driving to find suitable replacement of ITO.

CNT-based TCEs have made huge progress with the optical transparency and electrical conductivity comparable to the ITO. CNT film exhibits excellent conductivity, mechanical flexibility and required optical properties. However, the TCEs-based on CNT still need to reduce the sheet resistance which is high due to the contact resistance between the nanotubes and high roughness factor. Graphene is another promising candidate for the TCE. The SLG is having the optical transparency of ~97%. However, obtaining the continuous single-layer graphene without defects is limiting the large-scale fabrication and continuous roll-by-roll production. In this aspect, metal nanowires (NWs) such as AgNWs and CuNWs are most promising candidates which can be produced in large scale and processed at room temperature. The large-scale fabrication is possible by using Meyer rod coating, spray coating and ink-jet printing methods which enables to produce continuous roll-by-roll coating of metal nanowire-based TCEs. This also enables the fabrication of TCEs at lower-cost when compared to vapor-based fabrication of ITOs. AgNW-based TCEs are already available in the commercial market. However, the cost of Ag limits the future of the AgNW-based TCE. In this aspect, CuNW-based TCEs is having potential for the future TCEs because of the low-cost, scalable and good mechanical, electrical and optical properties. However, the CuNWs are prone to oxidation in the ambient condition. Recently, hybrid TCEs are widely studied for the TCEs and these hybrid TCEs need to be fabricated in the large-scale.

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