Transparent Conducting Oxides for Photovoltaics: A fundamental investigation of their properties

Mutlucan BAYAT
*Faculty of Engineering, Department of Mechanical Engineering, Karabuk University, Karabuk, Turkey

Abstract

The utilization of photovoltaic has been an increasing interest in which many countries are attempting to supply their energy demands from the sun to reduce the cost of energy production and environmental concerns and also have secure, sustainable and affordable energy balance. Transparent conducting oxides (TCO_S) are one of the most powerful materials that simultaneously present optical transmission and electrical conductivity in photovoltaic (PV) devices. Thanks to these properties, TCOs are employed in wide range of applications as an important component such as electrode elements, structural templates, and diffusion barriers. The remarkable application, including multi-functional windows, solar cells and thin-film technologies have required the need of TCO materials for possessing new performance and increasing efficiency, depending on technological conditions and oxide films' resistivity. This paper reviews the fundamentals of TCOs and comparison of their properties.

Key words: TCOs, PV, solar cell, thin-film technologies.

1. Introduction

There is a unique class of materials that potentially houses the solutions to many problems formerly causes impairing film performance and cell efficiency. This family of materials known as the transparent conductive film oxides (TCOs) which are characteristically described as thin films that are highly conductive and transparent is generally based on tin oxide (SnO_2), indium oxide (In_2O_3), zinc oxide (ZnO), and cadmium oxide (CdO). As combinations of these materials (eg. InO_3:Sn: ITO) is possible and one property, particularly, conductivity, is strongly linked to a second, TCOs is recently undergoing renewed and reinforced analysis in many countries. Considering that, over the last 20 years, much of the these materials work on TCOs has been empirical with a focus on minor variants of ZnO, InO_2, and SnO_2, it is quite remarkable how dramatically this field has grown recently in both basic and applied science [8]. This is also how significant caution was given to technology and investigation of TCOs by very large application perspectives, such as photodiodes, electrochromic windows, flat-panel displays and solar cells [2,5,6,11,17].

*Corresponding author: Address: Faculty of Engineering, Department of Mechanical Engineering Karabuk University, 78050, Karabuk, TURKEY. E-mail address: mutlucanbayat@karabuk.edu.tr, Phone: +903704332021 Fax: +90 370 4333290

2. Transparent Conducting Oxides (TCOs)

2.1. TCOs in General

TCOs have historically been dominated by a small set of oxide materials including predominately SnO_2, In_2O_3 , InSnO and ZnO [8] and consist of two components. Firstly, B, the nonmetal part that is oxygen, and A which is a key requirement to opto-electrical characteristics and consist of metal-combinations, controlling semiconductors by forms of A_yB_z. With intensifying this structure, doping with metalloids or nonmetals (for instance: A_yB_z:D form, and D is dopant), new results can be obtained in opto-electrical properties. Therefore, metals can be either a part of A or a dopant [15].

Doping of metal oxides with TCOs enables their use in optoelectronic devices. Proper characterization of optoelectronic and structural features are essential for materials processing. Band gap and low resistivity are critical for the transparency of materials. A band gap of higher than 3.1ev and resistivity lower than 10^{-3} ohm provides with almost %80 transparency to the visible light (400-700 nm) [8]. Transparency and conductivity are tricky features to combine. Metals and glasses are typical examples for high conductivity versus poor transparency and vice versa, respectively. TCOs provide materials with conductivity owing to defection of the crystal structures. Furthermore doping TCOs with aliovalent elements can improve the conductivity even further [1]. Table 1 shows TCOs and their dopants elements according to proper cell type.

Table 1: TCOs employed in photovoltaic cells (from Klein A. [11]).

Cell Type	TCO	Dopants
a-Si:H§	SnO_2	F, Sb
μc-Si:H§	In_2O_3	Sn
HIT-Si:H§	ZnO	Al, In, Ga
$Cu(In,Ga)Se_2$	In_2O_3	Sn
	ZnO	Al, In, Ga
CdTe	SnO_2	F, Sb
	Cd_2SnO_4	-
Dye-sensitized Graetzel	TiO_2*	-
	SnO_2	F, Sb
	In_2O_3	Sn
OPV	high work-function‡	-

§a-Si: amorphous silicon, μc: microcrystalline, HIT: heterojunction with intrinsic layer
* anatase TiO 2
‡ higher work function required than currently available

2.2. The Current Use of TCOs

TCO materials mostly demonstrate n-type conductivity whose free carriers are electrons (e.g. In_2O_3, SnO_2 and ZnO)[5], however p-types do also exist (e.g. $CuAlO_2$, $SrCu_2O_2$ and NiO). In both types, defecting the crystal structure leads to formation of donor states; near the conduction band for the n-type and the valence for the p-type. These states are needed to be shallow for maintaining the transparency. These materials are of use in a wide range of applications in the PV industry, including but not restricted to: Dye sensitized solar cells (DSSC), thin film a-Si solar cell transparent electrodes, flat panel displays [1]. In Table II, individual TCO materials that need to meet exact properties, depending on ultimate application purposes and cell type have been respectively presented.

Table II: Transparent Conducting Oxides (TCOs) Employed in Photovoltaic Devices (from Fortunato E. [7]).

Cell Type	TCO in Current Use	TCO Needs	Materials Goals
Heterojunction with intrinsic thin layer (HIT) cell	Indium tin oxide (ITO)	Smooth, good interfacial properties, very good conductivity, low-temperature deposition, light trapping	Indium zinc oxide (IZO), indium-free materials, ZnO
Copper indium gallium selenide (CIGS)	Intrinsic-ZnO/Al:ZnO	Interfacial stability to CdS, low-temperature deposition, resistance to diffusion and shorting, need to make/improve the junction	Single-layer TCO to replace two layers and CdS layer
CdTe	(SnO_2) Zn_2SnO_4/Cd_2SnO_4	Stable interface to CdS/CdTe at temperature, diffusion barrier	Doping of ZnSnOx materials, single-layer TCO
Nano-hybrid polymer cell	ZnO, SnO_2, TiO_2	Nanostructure with right length scale, work-function matching, interface with organic, correct doping level for carrier transport	Self-organized structures core–shell structures, new nonconventional TCOs
Grätzel cell	TiO_2	Nanostructure with high electron mobility	Improved TiO_2 morphology and possible use of doped materials, new non-TiO_2 materials
Amorphous Si	SnO_2, ITO, and ZnO; many cells employ two TCOs	Temperature stability, chemical stability, and appropriate texture for both TCO layers	Higher conductivity, texture, and ohmic contact for both TCO layers

2.3. Properties of TCOs Used in PV Applications

The widespread architectural use of TCO used in a-Si and cadmium telluride (CdTe) thin films, is fluorine-doped tin oxide (SnO2:F) and it is used for energy efficient windows. Tin-doped indium oxide (ITO) is also extensively used in PV modules, including flat-panel displays (FPD), high-definition TVs and certain types of solar cells based on a-Si, or (CIGS). Currently, crystalline and polycrystalline silicon solar cells which dominated TCO market for PV cells, are representing over 93% of the market at present [8]. For instance, in Figure 1, the two-sided Sanyo HIT cell which actually uses TCO layers on both the front and back is shown. Moreover, thin film photovoltaics based a-Si, CdTe and Cu(In,Ga)Se 2 (CIGS) absorber layers all depend on one or more layers of a high performance TCO as shown in Figs. 1 and 2 [5,8].

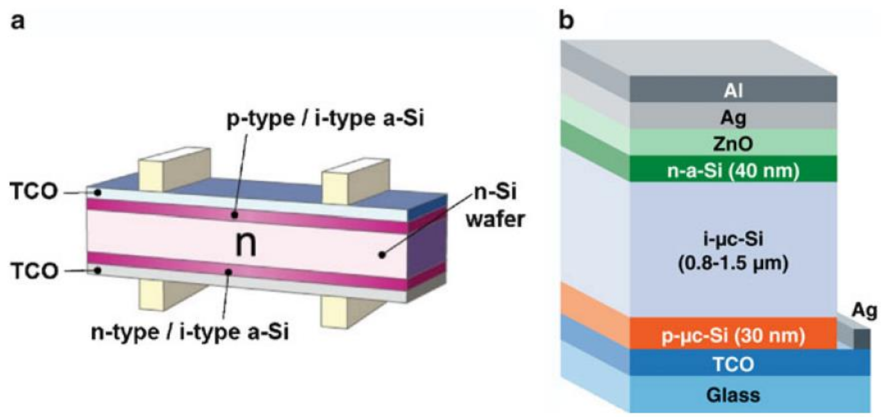

Figure 1: Typical configuration for (a) the Sanyo HIT cell and (b) for an amorphous-Si cell (from Ginley D. S. [8])

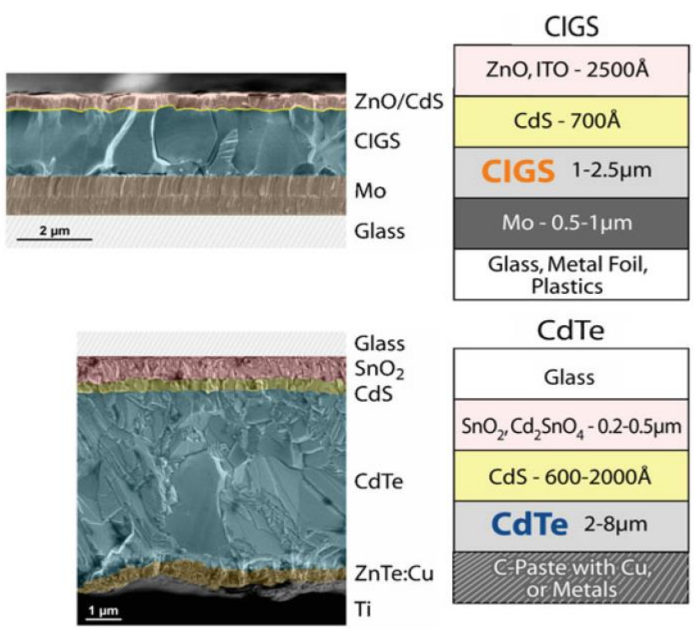

Figure 2: CIGS (top) and CdTe (bottom) PV structures seen in cross-section using SEM (left side of panel) and viewed schematically right side of panel (from Ginley D. S. [8]).

In general, TCO is needed in most types of thin solar cells to be used as the current-collecting electrode on the sun-facing side of the cell because of too high lateral conductivity. The principal types of solar cells that use TCOs are shown schematically in Figure 3 [5].

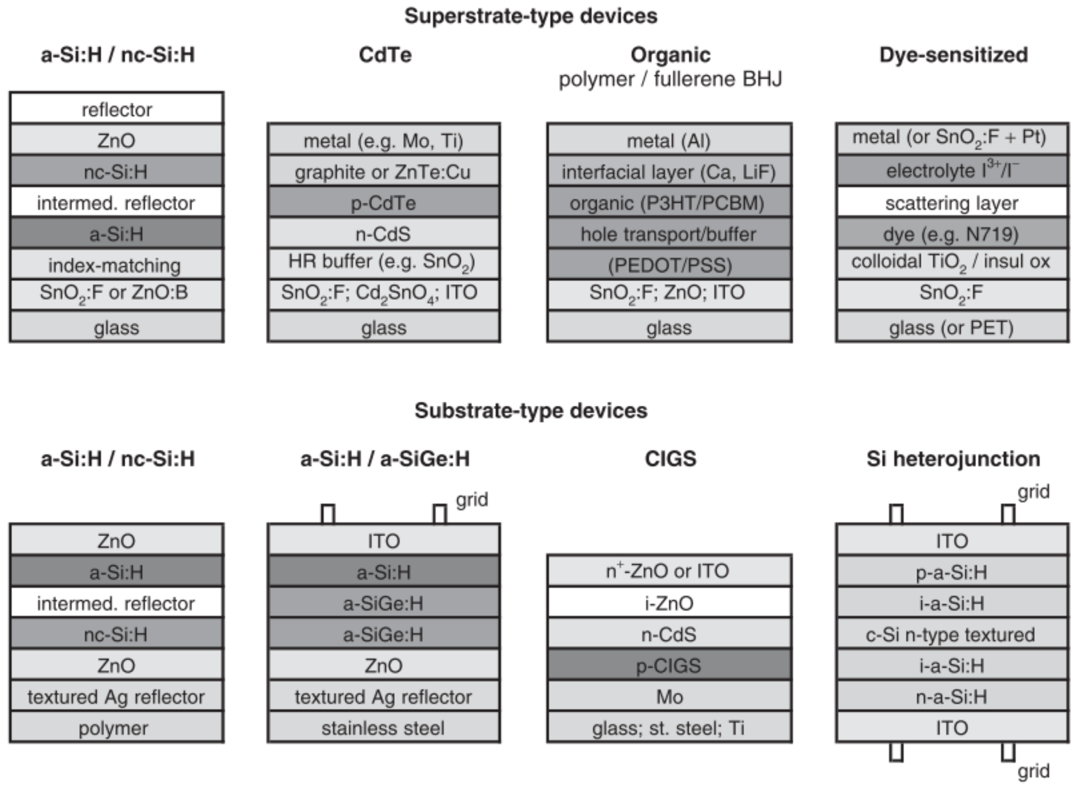

Figure 3: The principal types of solar cells that utilize one or more TCO layers in their construction. Top row: superstrate type devices; bottom row: substrate-type devices (from Delahoy A. E. [5])

As can be seen, SnO2:F is characterictically used for both a-Si and CdTe superstrate thin film PV technologies as TCO. However ZnO, doped with Al (ZnO:Al) or B (ZnO:B), is more often preferred in the next-generation a-Si/nc-Si cells. Another place of use for SnO2:F is dye-sensitized TiO2 type cells. When it comes to organic cells, most main types of TCOs have been employed. Substrate-based technologies may use either ZnO:Al or ITO as the sun-facing TCO. Another palce of use for ITO is the Sanyo HIT cells which also utilize a metal grid over the p-type a-Si/n-type c-Si base. On the other hand, crystalline Si wafer-based cells principally do not use a TCO but a metal grid and a heavily doped emitter for current collection[5].

2.4. Further Aspects and Selection Criteria

So far, the fundamentals of solar cells which consist of different TCO materials and exhibit various properties have been investigated in different aspects and our attenion was given to mostly transparancy, conductivity and resistivity. When considered with all aspects of materials, it can be seen that every material has indivudial advantages and drawbacks. For instance, ZnO is the preferred TCO to the front and back contacts of a-Si solar cells [18] due to supeorior properties, icluding a thin film resistivity as low as 2.4×10^{-4} Ω cm, but only in undoped status [7] and providing, high average optical transmittance rate is over than 85% [5]. Therefore, it seems to be appealing to be used PV window and display technology applications. However, SnO_2:F offers lowest cost among the other which makes it more commercially available. Tin oxide is also much more chemically and thermally stable than ZnO, possessing a high work function of 4.9 eV [5]. Further examples can be multiplied according to TiO_2 and In_2O_3. However, materials and their important fuctions are shown in Table III, resistivities of TCOs throught the years, comparing to each other are also given in Figure 4

Table III. TCO materials for various applications (from Ginley D. S. [8]).

Property application	Material		
	Simple	Binary	Ternary
Highest transparency	ZnO:F	Cd_2SnO_4	
Highest conductivity	In_2O_3:Sn		
Highest plasma frequency	In_2O_3:Sn		
Highest work function	SnO_2:F	$ZnSnO_3$	$Zn_{0.45}In_{0.88}Sn_{0.66}O_3$
Lowest work function	ZnO:F		
Best thermal stability	SnO_2:F	Cd_2SnO_4	
Best mechanical durability	SnO_2:F		
Best chemical durability	SnO_2:F		
Easiest to etch	ZnO:F		
Best resistance to H plasmas	ZnO:F		
Lowest deposition temperature	In_2O_3:Sn ZnO:B a-InZnO		
Least toxic	ZnO:F, SnO_2:F		
Lowest cost	SnO_2:F		
TFT channel layer	ZnO	a-InZnO, a-ZnSnO	$InGaO_3(ZnO)_5$, a-InGaZnO
Highest mobility	CdO, In_2O_3:Ti In_2O_3:Mo		
Resistance to water	SnO_2:F		

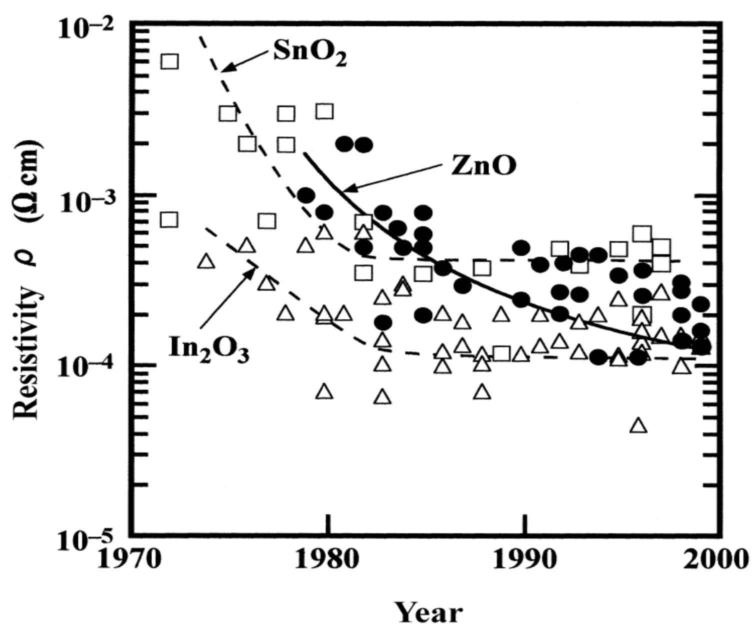

Figure 4. Reported (1970–2000) resistivities of binary transparent conducting oxide (TCO) materials: undoped and impurity-doped SnO 2 (□), In 2 O 3 (Δ), and ZnO (●) (from Minami T. [13])

4. Conclusions

There is an increasing understanding to conventional TCOs which have been described their work patterns as well as dopants materials. Although the component of materials and optoelectronic structures of films seems to be complicated, it is clear that TCOs are key compounds for PV applications to have better performance and efficiency. Doping materials into these film means new characterization and special occurrences. Considering all our data based on different extensive research, TCOs are not certain to meet all PV applications, accepting there are significant challengies in especially ZnO, promising to high transparancy and comparable resistivity for many applications, comparing with SnO2, and ITO. In this sense, exsisting materials, leading to discover a novel material, needs to have low resistance and better optical and higher mobility properties simultaneously to decide which one is the best. However, further research would be crucial to enlighten future novel materials fractions.

References

1. Bhachu D. S. The synthesis and characterisation of metal oxide thin films (Phd thesis). University of College London (UCL): 2013.
2. Calnan S, Tiwari A. N. High mobility transparent conducting oxides for thin film solar cells. *Thin Solid Films* 2010; 518: 1839-1849.
3. Coutts T. J, Young D. L, Li X, Mulligan W. P, Wu X. Search for improved transparent conducting oxides: A fundamental investigation of CdO, Cd_2 SnO_4, and Zn_2 SnO_4. *Journal of Vacuum Science & Technology A* 2000; 18: 2646-2660.
4. Coutts T. J, Young D. L, Li X. Characterization of transparent conducting oxides. *Mrs Bulletin* 2000; 58-65. Available from: Mrs Bulletin (August 2000).
5. Delahoy A. E., Guo S. Transparent conducting oxides for photovoltaics. In: Luque A, Hegedus S editors. *Handbook of Photovoltaic Science and Engineering*, 2nd ed, West Sussex: Wiley, 2011, p. 716-796.
6. Exarhos, G. J, Zhou, X. D. Discovery-based design of transparent conducting oxide films. *Thin Solid Films* 2007; 515: 7025-7052.
7. Fortunato E, Ginley D, Hosono H, Paine D. C. Transparent conducting oxides for photovoltaics. *Mrs Bulletin* 2007; 32: 242-247. Available from: Mrs Bulletin (March 2007).
8. Ginley D. S., Hosono H, Paine D. C. Handbook of transparent conductors. New York: Springer; 2010.
9. Hosono H. Recent progress in transparent oxide semiconductors: Materials and device application. *Thin Solid Films,* 2007; 515: 6000-6014.
10. Hough T. P. Trends in solar energy research, New York: Nova, 2006
11. Klein A, Körber C, Wachau A, S¨auberlich F, Gassenbauer Y, Harvey S. P. *et al.* Transparent conducting oxides for photovoltaics: Manipulation of fermi level, work function and energy band alignment. *Materials* 2010; 3: 4892-4914.

12. Liu Y, Li Y, Zeng H. ZnO-Based transparent conductive thin films: Doping, performance, and processing. *Journal of Nanomaterials* 2013; 2013: 1-9.
13. Minami T. New n-type transparent conducting oxides. *Mrs Bulletin* 2000; 38-44. Available from: Mrs Bulletin (August 2000).
14. Nakada T, Hirabayashi Y, Tokado T, Ohmori D, Mise T. Novel device structure for Cu(In,Ga)Se 2 thin film solar cells using transparent conducting oxide back and front contacts. *Solar Energy* 2004; 77: 739-747.
15. Stadler A. Transparent conducting oxides—An up-to-date overview. *Materials* 2012; 5: 661-683.
16. Wang D. Preparation and characterisation of transparent conducting oxides and thin films (Phd thesis). Department of materials Loughborough University: 2010.
17. Wu X, Coutts T. J, Mulligan W. P. Properties of transparent conducting oxides formed from CdO and ZnO alloyed with SnO_2 and In_2O_3. *Journal of Vacuum Science & Technology A* 1997; 15: 1057-1062.
18. Yamada A, Sang B, Konagai M. Atomic layer deposition of ZnO transparent conducting oxides. *Applied Surface Science* 1997; 112: 216–222.