Journal of Advances in Applied Sciences and Technology

ISSN : 2393-8188 (print)
2393-8196 (online)
www.milliyasrcollege.org.journal.php

TRANSPARENT CONDUCTING OXIDES—AN OVERVIEW

Shaikh Asif Karim*[*1], Shaikh Mujeeb[2]

[1] Sir Sayyed College, Physics Dept. , Aurangabad

[2]EngineerignCollege, Rotegaon, Aurangabad.

* asifkarim93@rediffmail.com

ABSTRACT:

Transparent conducting oxides (TCOs) are electrical conductive materials withcomparably low absorption of electromagnetic waves within the visible region of thespectrum. They are usually prepared with thin film technologies and used in opto-electricalapparatus such as solar cells, displays, opto-electrical interfaces and circuitries. Here, basedon a modern database-system, aspects of up-to-date material selections and applications fortransparent conducting oxides are sketched, and references for detailed information aregiven. As n-type TCOs are of special importance for thin film solar cell production,indium-tin oxide (ITO) and the reasonably priced aluminum-doped zinc oxide (ZnO:Al),are discussed with view on preparation, characterization and special occurrences.

***KEYWORDS*:** transparent conducting oxide; oxide; TCO; ITO; ZnO:Al.

1. INTRODUCTION

Transparent conducting oxides (TCOs) are electrical conductive materials with a comparably lowabsorption of light. They are usually prepared with thin film technologies and used in opto-electricaldevices such as solar cells, displays, opto-electrical interfaces and circuitries. Glass fibers are nearlylossless conductors of light, but electrical insulators; silicon and compound semiconductors arewavelength dependent optical resistors (generating mobile electrons), but dopant dependent electricalconductors. Transparent conducting oxides are highly flexible intermediate states with both thesecharacteristics. Their conductivity can be tuned from insulating via semiconducting to conducting as well as their transparency adjusted. As they can be produced as n-type and p-type conductives, theyopen a wide range of power saving opto-electrical circuitries and technological applications.

A still valuable overview of transparent conductive oxides is given in [1], basics to material physicsof TCOs are discussed in [2], some structural investigation of TCOs was made e.g., in [3], preparationof TCOs was discussed in [4] and substitutes for the most popular transparent conducting oxide,namely ITO (indium-tin oxide), are listed in [5]. Here, based on a modern database-system, aspects ofup-to-date material selections and applications for transparent conducting oxides are sketched, andreferences for detailed information are given. As n-type TCOs are of special importance for thin filmsolar cell production, ITO and the reasonably priced aluminum-doped zinc oxide (ZnO:Al) arediscussed with view on preparation, characterization and special occurrences. For completion, therecently frequently mentioned typical p-type delafossite TCOs are described as well, providing avariety of references, as a detailed discussion is not reasonable within an overview publication.

As transparent conducting oxides are usually compound semiconductors—where the nonmetal partis oxygen—they are discussed along their metal elements. Metals were used as compound materials ordopants (with just a few percent content).

2. TRANSPARENT CONDUCTING OXIDES (TCOS)

2.1. TCOs in General

In transparent conducting oxides (TCOs), the nonmetal part, B, consists of oxygen. In combination withdifferent metals or metal-combinations, A, they lead to compound semiconductors, AyBz, with differentopto-electrical characteristics. These opto-electrical characteristics can be changed by doping, AyBz:D(D = dopant), with metals, metalloids or nonmetals. Hence, metals can be part of the compoundsemiconductor itself, A, or can be a dopant, D. Scanning the periodic table of elements, with a view onthe utilization of metals for

TCOs, results in Table 1 (regarding the 2nd and 3rd period,exclusively aluminum).

Table 1. *Published results regarding transparent conducting oxide (TCO)-layers,containing metallic elements e.g., from the 2nd and 3rd period of the periodic table of the elements (PE, excluding aluminum), including examples for the later discussed ZnO's.*

Compound semiconductor	Dopant	Preparation	Reference
NiO	Li	Pulsed Laser Deposition (Different Li-concentr.)	[6]
ZnO	Na, Al	Sol-gel,	[7–9]
Cr2O3	Mg, N	Spray Pyrolysis	[10]
CuCrO2	Mg	Sol-gel Technique	[11]
Mg1−xZnxO	In	Pulsed Laser Deposition	[12]
Mg1−xZnxO	Al	Radio Frequency Magnetron Sputtering (different substrates)	[13]

Outstanding good optical characteristics have been provided by tin-, indium- and zinc oxides (A = tin,indium, zinc). Well known is, for example, indium tin oxide (ITO), and the doping of zinc oxide withless than 5% aluminum (ZnO:Al). Moreover, doped delafossite and mayenite compounds are ofupcoming interest (see Table 1). A variety of preparation and characterization methods was applied toinvestigate their different chemical structures and physical characteristics. These shall be briefly discussed.

2.3. Aluminum Doped Zinc Oxide (ZnO:Al)

Transparent conducting, aluminum doped zinc oxide thin films (AlxZnyOz, ZnO:Al) [14,15] contain about 2%wt aluminum and can be produced with spray pyrolysis [16–21], sol gel technology [22–28],electro deposition [29,30], vapor phase deposition [31,32], magnetron DC sputtering [33–37],magnetron RF sputtering [38–41] or a combination of both the sputter deposition methods [42–58].

Moreover, high quality deposition methods using thermal plasmas [59, 60], (low pressure (LP), metal organic (MO), plasma enhanced (PE)) chemical vapor deposition (CVD) [61, 62], electron beam evaporation [63], pulsed laser deposition [64–69] and atomic layer deposition [70] can be applied.

The underlying substrate—crystalline, amorphous or organic—may have an influence on the grown structure and the opto-electronic properties of the thin film [71–75], independent of the used deposition method. For example, in the case of solar cell production, an ultra-thin CdS buffer layer is usually the basis for ZnO:Al deposition [76,77]. Even if the substrate is identical, the layer thickness (deposition time, position upon the substrate) itself influences the physical values of the deposited thin film [78].

A variation of the physical values from the grown thin films can also be reached by changing process parameters, as temperature [79] or pressure [80,81], or by additions to the process gas, as oxygen [82] or hydrogen [83].

Commonly, pure zinc oxides [84,85] are n-doped with aluminum [86,87]. Alternatively, n-doping can be done with metals such as copper, Cu, silver, Ag, gallium, Ga, magnesium, Mg, cadmium, Cd, indium, In, tin, Sn, scandium, Sc, yttrium, Y, cobalt, Co, manganese, Mn, chrome, Cr, and boron, B [88,92]. P-Doping of ZnO is technologically difficult, but apart from nitrogen, N, phosphorus, P, seems to be an adequate dopant [93–101].

Theopto-electronic properties [102] of these TCO thin films can be changed by post process thermal annealing in an inert gas or reactive gas atmosphere [38,102-103]. Especially surface and interface states can be influenced [104,105]. The deterioration of ZnO:Al thin films is discussed in [106].

3. Further Aspects to Technological Advances of Transparent Conducting Oxides

Reasons for technical advances in transparent conducting oxides are manifold—influencing aspectsare: The investigation of adequate novel materials and material-combinations, as for example the firstdelafossites by Charles Friedel in 1873 an increasing financial support for research according to political decisions, as forexample the increased financial support of solar cell investigations and therefore of TCOs by thepresent nuclear power phase-out in Germany; the publication of new results, as research groups inindustrial companies often reserve important information; and the efficiency of modern literaturedata-bases, as only included literature can be found and selected.

4. CONCLUSION:

Based on a modern database-system, aspects of up-to-date material selections and applications for transparent conducting oxides have been sketched; references for detailed information have been given for the interested reader. As n-type TCOs are of special importance for thin film solar cell production, indium-tin oxide (ITO) and the reasonably priced aluminum-doped zinc oxide (ZnO:Al) have been discussed with view on preparation, characterization and special occurrences. As transparent conducting oxides are usually compound semiconductors—where the nonmetal part is oxygen—they have been discussed along their metal elements. Metals were used as compound materials or dopants.

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