



HAL
open science

Transparent Conductive Oxides. Part II. Specific Focus on ITO, ZnO-AZO, SnO₂-FTO Families for Photovoltaics Applications

Christelle Habis, Jean Zaraket, Michel Aillerie

► **To cite this version:**

Christelle Habis, Jean Zaraket, Michel Aillerie. Transparent Conductive Oxides. Part II. Specific Focus on ITO, ZnO-AZO, SnO₂-FTO Families for Photovoltaics Applications. Defect and Diffusion Forum (Online), 2022, 417, pp.257-272. 10.4028/p-6fqmfi . hal-03759771

HAL Id: hal-03759771

<https://hal.science/hal-03759771>

Submitted on 24 Aug 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

Transparent Conductive Oxides. Part II. Specific Focus on ITO, ZnO-AZO, SnO₂-FTO Families for Photovoltaics Applications

Christelle Habis^{1,a*}, Jean Zaraket^{2,b} and Michel Aillerie^{1,c}

¹Université de Lorraine, CentraleSupélec, Laboratoire Matériaux Optiques, Photonique et Systèmes, LMOPS, F-57070 Metz, France

²Université de Lorraine, Institut Jean Lamour, IJL, ENSTIB, F-88051 Epinal, France

^{a*}christelle.habis@univ-lorraine.fr, ^bjean.zaraket@univ-lorraine.fr, ^cmichel.aillerie@univ-lorraine.fr

Keywords: Transparent Conductive Oxides; Indium Tin Oxide, Zinc Oxide; Aluminum Zinc Oxide; Fluorine Tin Oxide.

Abstract. This contribution is the second part of a presentation of transparent conductive oxides, TCO. After a general overview in the first publication of properties and applications of TCO related to the type of oxide and dopant, the growth techniques and the temperature, we focus in the current one on three families of TCO used as transparent electrodes in photovoltaic, PV, cells and modules. Indeed, new generations of solar cells need optimizing TCO with improved conductivity and transparency depending on substrate, type of PV cells, and conditions of used. Thus, ITO, ZnO-AZO, and SnO₂-FTO TCO families are considered. ITO presents the best combination of electrical and optical properties but TCO based on the two other families are challenging in many photovoltaic applications for obtaining low cost and environmental friendly electrodes with comparable performances. Due to the high number of publications on TCO for PV applications, this contribution does not claim to be exhaustive but makes it possible to summarize the main information concerning these materials by approaching them in a common methodology.

Introduction

Transparent conducting oxides (TCOs) are becoming a more common component of photovoltaic (PV) devices, where they serve as electrodes, structural templates, and diffusion barriers, and their work function regulates the open-circuit device voltage. They're used in everything from organic PV polymer solar cells to crystalline-Si heterojunction with intrinsic thin layer (HIT) cells. The requirements of TCOs for PV technologies are similar to those for TCOs for flat-panel display applications, and include excellent optical transmissivity throughout a wide spectrum and low resistivity. TCOs for PV applications must also use low-cost materials, with some requiring device-technology specific features.

This work is a second part of a general presentation of TCO based on a literature review. The first contribution of this review on TCO is presented in a previous publication title: "*Transparent Conductive Oxides. Part I. General review of structural, electrical and optical properties of TCOs related to the growth techniques, materials and dopants.*" It introduces a general review of structural, electrical and optical properties of TCOs related to the growth techniques, materials and dopants. Based on this first one, the current one is more specifically focus on applications of TCOs as electrodes for photovoltaic applications. As specified above, and as for the first part, with the large number of works and publications present in the literature on TCOs, half of which relate to their use as electrodes in PV applications, with in addition publications presenting some given contradictory results, this contribution does not claim to be exhaustive but makes it possible for PV applications to summarize the main information, concerning these materials by approaching them in a common methodology. Considering the two parts of this contribution on TCO as a whole, mainly oriented to photovoltaic applications, it can be considered as a useful summary tool for researchers working in this domain of electrical engineering topics.

It is to be of note that, the last few years, a new generation of nanostructured TCO is currently being the subject of many researches. These aspects of materials are not considered here, and will be the subject of a future publication work.

Thus, currently, three families of TCO are considered: ITO, ZnO-AZO, and SnO₂-FTO used as electrodes in PV cells and modules. Based on the presentation done in Part. I, we will consider in this contribution the possible growth methods, the specific dopants and the main electrical and optical properties of this TCO for PV applications. The properties of these TCO films and families are finally compared in the final discussion.

Indium oxide (In₂O₃) and Indium Tin Oxide (ITO)

Indium Tin Oxide, ITO is a mixture of indium oxide (In₂O₃) and tin oxide (SnO₂) typically in a ratio of 90/10 wt%. [1] It is widely used in transparent heating elements of aircraft and car windows, antistatic coatings over electronic instrument display panels, heat reflecting mirrors and antireflection coatings, high temperature gas sensors. ITO is also widely integrated in other electro-optic devices as transparent electrodes for solar cells, light emitting diodes, phototransistors and lasers. In addition, ITO offers the best available FoM, i.e. best performance in terms of conductivity and transparency along with excellent environmental stability, reproducibility and good surface morphology.

General properties of Indium Tin Oxide

Indium oxide mostly has a cubic structure of bixbyite type as reported in Fig. 1. Substitutional doping with Sn replaces the In³⁺ ion to get indium tin oxide and Sn atoms form an interstitial bond with oxygen atoms. Tin is present with a dual valence and exists as either SnO or SnO₂ which gives a direct impact on the conductivity of ITO. For lower valence state, a drop in carrier concentration occurs caused by the creation of holes acting as traps and thus reducing conductivity.

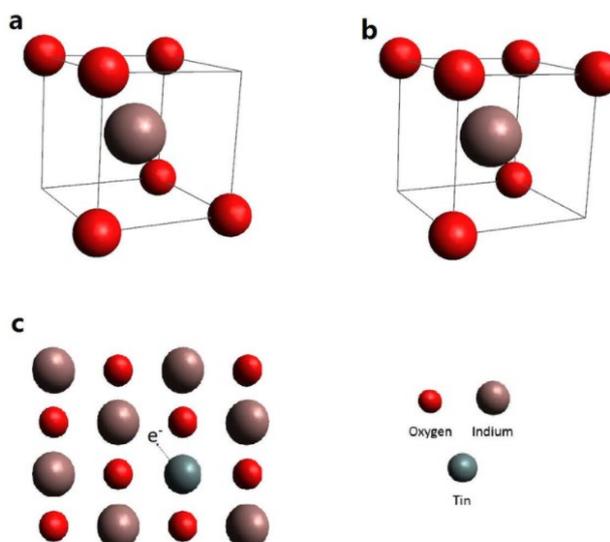


Figure 1. Indium oxide bixbyite structure. (a) Eight oxygen atoms are situated within a compressed octahedron and have six equidistant oxygen atom neighbors. (b), Eight indium atoms are situated at the corners of a highly distorted octahedron. (c), Sn doping sites in In₂O₃ lattice. [2]

However, for the case of SnO₂ state, Sn⁴⁺ releases electrons to the conduction band, thus acting as n-type donor. Moreover, ITO films have lattice parameters close to that of In₂O₃ and are in the range 10.12 Å to 10.31 Å. [3]

Tuna *et al.* [4] reported the effect of substrate temperature and film thickness on the electrical, optical and structural properties of ITO thin films deposited by RF and DC magnetron sputtering on glass substrates. In their study they found out that the substrate temperature mostly affects the crystallization and resistivity of the samples. The characteristic peak (222) indicating the crystallization of ITO was observed starting from the annealing temperature of 150 °C up to 300 °C.

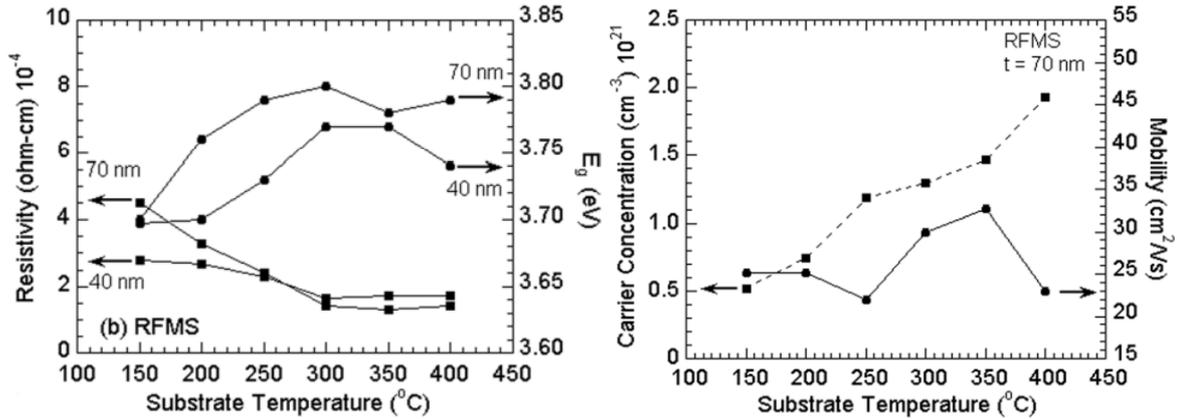


Figure 2. (a) Variation of resistivity and band gap as function of substrate temperature for ITO films. (b) Substrate temperature dependence of carrier concentration and Hall mobility of ITO 70 nm thickness. [5]

Generally, the resistivity of the ITO layer was noted to decrease as the substrate temperature increases due to the increment in carrier concentration, crystallization and grain size. Nevertheless, the resistivity of the films at 400°C is found to be slightly higher than the obtained resistivity at 350°C (Fig 2.a). This small variation might be the result of the growing number of oxygen vacancies under increased substrate temperatures. In addition, Nisha *et al.* [5] previously reported that the diffusion of alkali ions from the substrate into the film structure at higher temperature might have a negative effect on the mobility. The increase in mobility (Fig. 2.b) for temperatures above 250 °C is attributed to the higher degree of crystallinity resulting in less grain boundary scattering. However, the increase of carrier concentration for temperature above 350 °C limits the mobility which by consequence suddenly decreases. Therefore, to get the optimum electric properties, the preferable growth temperature for ITO films is around 350 °C.

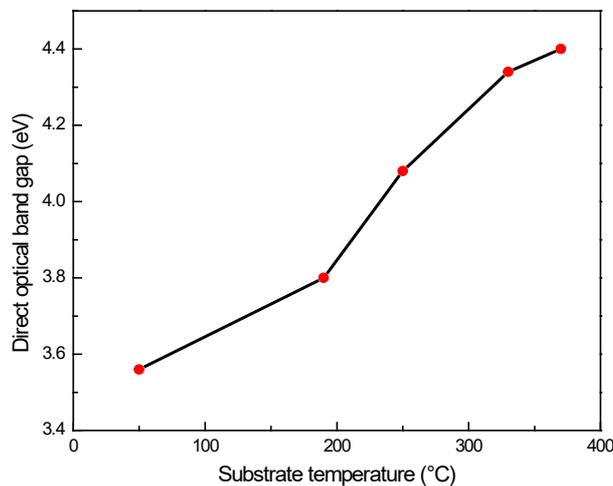


Figure 3. Variation of optical band gap with different substrate temperature for ITO thin films deposited by magnetron sputtering. [6]

High conductivity of ITO films is assumed to be owed to high carrier concentration rather than high mobility of hole. Compared to In_2O_3 , the low mobility of hole in ITO and its dependence on substrate temperature is attributed to scattering mechanisms by ionized impurities or grain boundaries. At higher substrate temperature, an enhance of the crystallinity contributes to the increase of mobility.

The band gap of ITO has generally a value greater than 3.7eV. It ranges from 3.5 to 4.40 eV depending on the growth method and conditions as illustrated in Fig. 3 with the dependence of the band gap with the temperature of the substrat for ITO thin films [6].

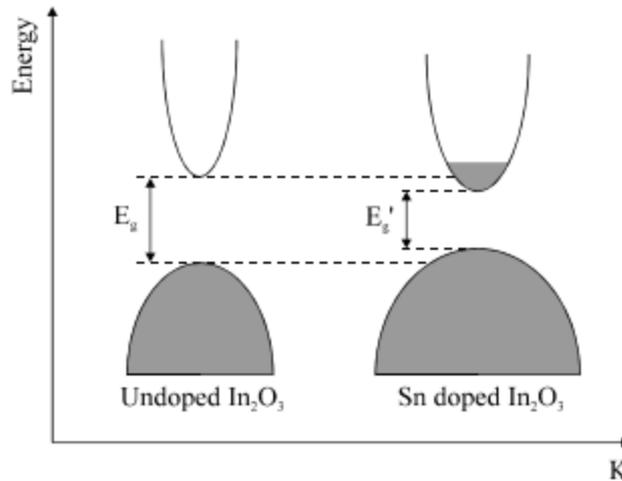


Figure 4. Assumed parabolic band structure of pure In_2O_3 and mixed $\text{In}_2\text{O}_3\text{-SnO}_2$ (ITO) compound. [7]

The doping with elements as tin in indium oxide, contribute in the formation of donor states at a level below the conduction band. With increasing the doping density up to a critical density, these states merge with the conduction band as illustrated in Fig. 4. The ITO film becomes degenerate when the density of free electrons from the donor atom exceeds this critical value. By consequence, the coulombic interactions shift up the valence band and down the conduction band which narrows the bandgap (Fig. 4). This shift partially compensates the Burstein Moss effect.

In an attempt to identify the effect of grain size on the optical and electrical properties of ITO thin films under different annealing temperatures, Ahmed et al, deposited ITO thin films by high frequency magnetron sputtering. After deposition, the films were annealed at 250, 350, 450 and 550°C for 1 hour.[8]

Table 1. Table showing the increase in grain size as the annealing temperature increases. [18]

Temperature (°C)	Average crystallite size D (nm)
As grown	35.05
250	40.98
350	41.17
450	41.54
550	51.62

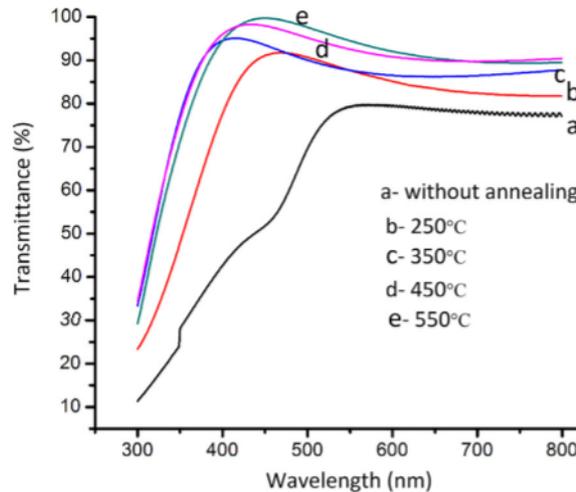


Figure 5. Optical transmittance spectra of ITO thin films deposited by high frequency magnetron sputtering. [8]

The study showed that as the annealing temperature increased, the microstructure of the ITO films improved and caused a decrease in the band gap of the film. This change is attributed to the possibilities of oxidation, more realignment and strong interaction between film and substrate. It results, as shown in Fig. 5 an increase of the transmission response with the increase of the annealing temperature. In addition, as showed in Table 1, authors in reference [8] observed an increase in grain size (calculated from XRD spectra using Scherrer's formula) with the increase of the annealing temperature. Finally, the main output of this study displayed that at an annealing temperature of 450°C the optimum characteristics of the film were obtained.

Finally, it should be noted that indium tin oxide (ITO) thin films are mainly used as transparent electrodes for most different types of liquid crystal displays (LCDs). ITO is not widely considered as transparent electrodes for traditional silicon photovoltaic sources or panels, but only for certain thin-film solar cells. For the latter, substitutes for ITO have already been developed, such as Al-doped ZnO (AZO) or Fluorine-doped SnO₂ (FTO). However, the properties of TCOs used for flat screens require improved optical and electronic qualities. It is for these reasons that, in applications such as flat screens, the ITO has not yet been replaced. Nonetheless, the total consumption of indium used for flat screens and alkaline batteries has increased dramatically in recent years and it is widely believed that a shortage of indium may arise in the near future. Currently, researches in various teams are intensively focused on possible alternatives to the transparent ITO electrodes used in displays, focusing on the development or optimization of materials that can be produced at low cost. Among them, we note the transparent conductive oxides (TCO) and particularly the importance of zinc oxide, mainly when it is doped with metal ions as Al or Ga (AZO or GZO) and tin dioxide mainly doped with fluorine (FTO).

Thus, for photovoltaic applications as concerned in the current contribution, it is therefore these two oxide-based materials, ZnO and SnO₂, which will attract our attention in the following paragraphs.

Zinc oxide (ZnO) and Aluminum doped Zinc oxide (AZO)

ZnO doped with metal ions is often chosen as an alternative to ITO in optoelectronic devices properties as its functional properties achieved currently a good level of performance and as, in addition to being a very abundant element which makes it relatively cheap. By else, it possesses an interesting set of properties that can be individually used (or manipulated) in various kinds of applications. [9] For example, the large excitonic binding energy of ZnO about 60meV at room temperature makes this material an efficient light emitter in the UV spectral region interesting for optoelectronic applications. Its high conductivity and transparency, i.e. yielding to an interesting FoM makes it important for applications, not only as transparent conducting oxides (TCO) but also as thin-film transistors (TFT). Furthermore, crystalline transparent and highly conductive ZnO thin film

production can be deposited by various techniques on large scale and at room temperature making it compatible with a lot of substrate types; rigid or flexible, plastic, glass, organic and inorganic ones. Moreover, optical, electrical, magnetic, piezoelectric, catalytic and gas sensing properties make ZnO specifically attractive for nanoelectronic, optoelectronic and piezoelectric devices.

General properties of Zinc Oxide

In zinc oxide crystal lattice, the atoms are arranged in tetrahedral geometry where each Zn atom is surrounded by four O atoms and vice versa. ZnO generally crystallizes in wurtzite form (Fig.6), but depending on the growth conditions, other crystal forms like zinc blende and rock salt exist for ZnO.

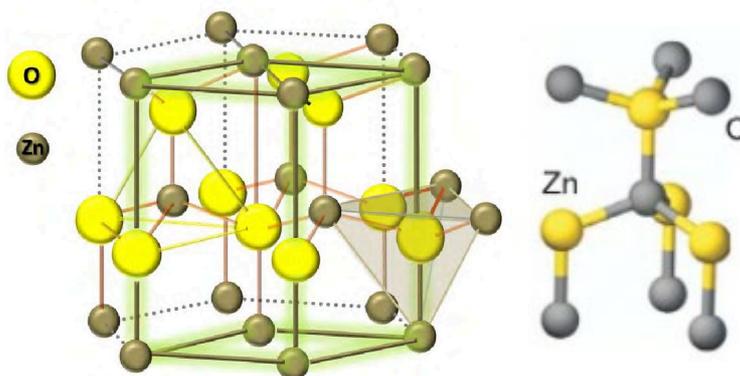


Figure 6. Zinc oxide structure: crystallizes in wurtzite form. [10]

Table 2. Basic properties of zinc oxide. [11]

Parameters	Value
Bandgap	3.4eV
Density	5.606g.cm ⁻³
Crystal structure	Wurtzite, rock salt, zinc blend
Stable phase at 300K	Wurtzite
Melting point	1975°C
Nature of oxide	Amphoteric oxide
Lattice constants at 300K	a ₀ = 0.32495nm c ₀ = 0.52069nm
Relative dielectric constant	8.66
Refractive index	2.0041
Solubility in water	0.16mg 100mL ⁻¹
Intrinsic carrier concentration	10 ²⁰ cm ⁻³

Zinc oxide is a direct band gap semiconductor with a high refractive index (~2) having $E_g = 3.4\text{eV}$ at room temperature. The concentration and mobility of electrons in ZnO were found to be in the range $10^{16}\sim 10^{17}\text{ cm}^{-3}$ and $20\sim 400\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. The resistivity of ZnO extends over several orders of magnitude, with values ranging from $10^{-4}\ \Omega\cdot\text{cm}$ to $10^{12}\ \Omega\cdot\text{cm}$. [12] According to the procedures used for the deposition of ZnO, a low resistive ($\rho = 10^{-4}\ \Omega\cdot\text{cm}$) i.e. high conductive or high resistive ($\rho = 10^3\ \Omega\cdot\text{cm}$) i.e. low conductive films can be developed.

The low electrical conductivity of pure ZnO, when compared to ITO, is noted as a drawback. But doping by foreign elements showed to remarkably improve the conductivity and lower the sheet resistance to values of $4.3 \times 10^3\ \Omega/\text{cm}$ and $3.3 \times 10^3\ \Omega/\text{cm}$ for Al and Ga doping, respectively. [13] Thus, semi-conductive oxides being also often used as gas sensor and ZnO having good physical and chemical stability, it is perfectly suited for applications such as air pollution control, fire detection, leaks of harmful gases or tests for alcohol and other substances. ZnO having a high grain density and porosity, thus makes it possible to easily manufacture very sensitive gas sensors.

Various techniques can be used for the deposition of ZnO. The choice of a given technique will be driven by some practical criteria and of course, function of the targeted applications. Thus, TCO thin films must be prepared using appropriate deposition techniques that can produce low resistivity films at high deposition rates on large surface area substrates. Table 3 summarizes some deposition techniques along with the resulting associated ZnO properties. In addition, for specialized ZnO thin film materials, it is necessary to use deposition techniques that can achieve the lowest resistivity. Table 4 shows a number of deposition techniques that are usable for ZnO based thin film growth and their features.

Table 3. Electric properties of ZnO for different deposition methods.

Deposition method	Temperature (°C)	ρ ($\Omega\cdot\text{cm}$)	$n\nu$ (cm^{-3})	μ ($\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$)	Ref
Spray	350	2.70×10^3	2.4×10^{15}	0.34	[14]
	450	2.40×10^{-2}	-	-	[15]
Sputtering	150	1.00×10^3	-	3	[15]
PLD*	400	3	1.6×10^{17}	12.3	[16]
ALD**	250	5×10^{-2}	3×10^{19}	5.5	[17]

*Pulsed Laser Deposition **Atomic Layer Deposition

Table 4. Zinc oxide thin film growth methods and features.

Deposition method	Large area deposition	Applications
Magnetron sputtering deposition	Yes	LCDs, solar cells, touch panels
PLD	no	LEDs
Molecular beam deposition	No	LEDs
Spray pyrolysis	Yes	Solar cells
Chemical vapor deposition	Yes	Solar cells

Doping of Zinc Oxide

As mentioned above, for applications in optoelectronic devices, especially photovoltaic cells, doping ZnO is mandatory. This is how the conductivity of zinc oxide can be increased, or even optimized for the intended application thanks to the existence of intrinsic defects (vacancies and presence of interstitial atoms) allowing the introduction of doping ions, not only on these defect sites but also possible by substitution of zinc or oxygen. The presence of such intrinsic defects leads to n-type conduction. To improve its properties as transparent conductive oxide, ZnO must be doped by group III elements (B, Al, Ga, In...) or group IV element (Pb, Sn). Aluminum, indium and fluorine are the most common doping elements for ZnO. [18] The use of different dopants leads to remarkable changes in the film properties.

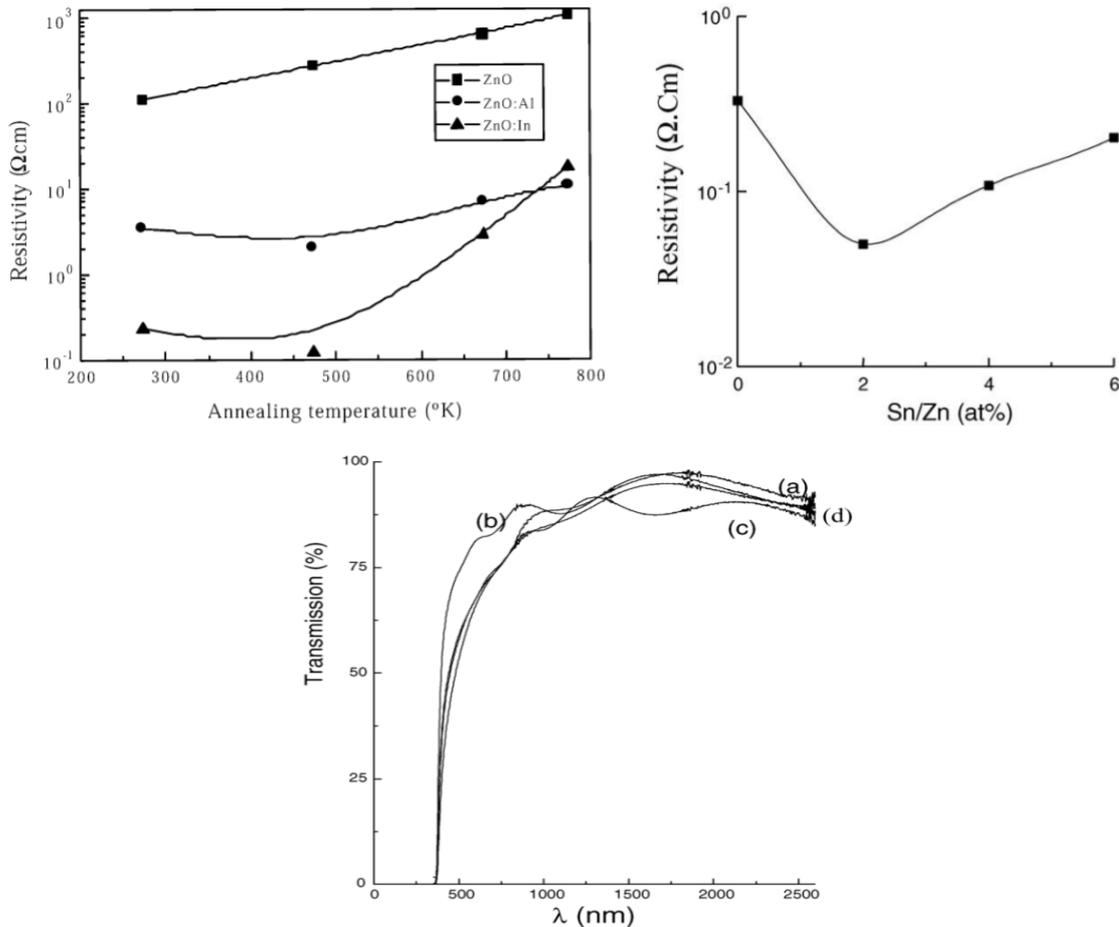


Figure 7. (a) Resistivity variation of doped and pure ZnO at different annealing temperatures. [19] (b) resistivity variation of tin doped ZnO at different concentrations.[20] (c) Optical transmission of the ZnO:Sn as function Sn/Zn ratio: (a) 0 at.%, (b) 2 at.%, (c) 4 at.% and (d) 6 at.% [20]

Numerous studies have been carried out on the properties of layers doped with different elements depending on the nature of dopant, its concentration and the deposition techniques. For several decades, these studies have made it possible to improve the structural, electrical and optical behavior of thin films. The works have been carried out mainly for ZnO dopants such as Al, Ga, In and Sn. As example of the change in the ZnO properties, we report in Fig. 7.a the dependence of the resistivity with the annealing temperature of pure, Al and In doped ZnO films grown by the spray pyrolysis technique.[19] We also report in Fig 7.b the huge influence of the resistivity with the concentration of dopant (here with Sn ions) in the film allowing large possibilities of optimizations.[20] These studies have shown that the conductivity could reach a maximum value between 10^2 and $10 \Omega^{-1}\cdot\text{cm}^{-1}$ (Fig. 7.a and 7.b). Obviously, the optical properties are also modified by doping and growth techniques. It was reported that the transmission can varies between 70% and 95% observed for different concentrations (Fig. 7.c) thicknesses and deposition or annealing temperatures. [21]

Originally, for ZnO applications as gas sensors, aluminum and gallium were the most studied dopants and remain the most used today even for other applications because of its availability and its great electrical conductivity. [22], [23] Moreover, the deposition method also influences the choice of dopant specifically at high doping concentration. For example, in films developed by the metallic ions used as dopants are preferably locate at Zn sites in the lattice but the result of growing doped ZnO based TCO by spray pyrolysis technique, give films having more efficient optical and electrical properties with indium and gallium than with aluminum. This can be explained by looking at the ionic radius of each element; the ionic radii of Ga and In are 0.62 \AA and 0.80 \AA respectively which is close to that of Zn (0.74 \AA). Since the doping element replaces a Zn ion, the similarity in these values cause less lattice distortion at high concentration, when compared to the Al doping having 0.53 \AA as ionic

radius. Within this technique, the lowest resistivity of the doped ZnO film was obtained with In dopant at a concentration of 1 at %, but for a doping concentration above 2 wt%, a weakening of the film properties occurs. [24]

Focus on Aluminum doped ZnO (AZO)

Despite the better performance of TCOs based on indium and gallium doped ZnO compared to aluminum doping, it is the latter which is the most studied and developed, thanks in particular to its abundance and its comparatively attractive cost. Aluminum doped ZnO (AZO), with its unique electrical and optical characteristics, is the potential candidate to replace the expending ITO and FTO in TCO applications.

Table 5. Comparative table of ITO and AZO properties required to be used as TCO.

Property	ITO	AZO
High conductivity	✓	-
High carrier mobility	✓	-
High transparency	✓	✓
Suitable refractive index	✓	✓
Ease of processing	✓	✓
High stability	-	✓
Low toxicity	-	✓
Low cost	-	✓

In the attempt to find a material having comparable properties to that of ITO, AZO appears to be a good candidate since it has a good balance regarding the last six properties listed in Table 5. Whereas, AZO is not poor in completing the first two criteria, ITO has a good balance in fulfilling the first five but it fails with stability, toxicity and cost. [25] In this scope, many research work is carried on to sort out limitations of AZO considering different approaches to treat this material. Different approaches are adopted to overcome the limitations in AZO, some researchers changed the doping concentration of Al in ZnO, [26] others used different annealing temperatures, [27] or annealing duration, [28] and atmospheres, [29] while others focused on changing the substrate temperature and precursor concentration. [30] As already mentioned in the first part of this presentation, each of these parameters has a specific influence on the electrical and optical properties of the material.

It was reported that the incorporation of Al dopant enhances the transparency of the deposited film compared to the undoped ZnO (Fig. 8). The transmittance observed to increase up to a certain concentration limit where the transmittance is slightly reduced due to the increase in scattering and absorption photons by the crystal defects and free charge carriers. [31] Therefore, the upgrade in transmittance is attributed to the Al- induced crystal defects rather than the reduction of surface roughness. [32]

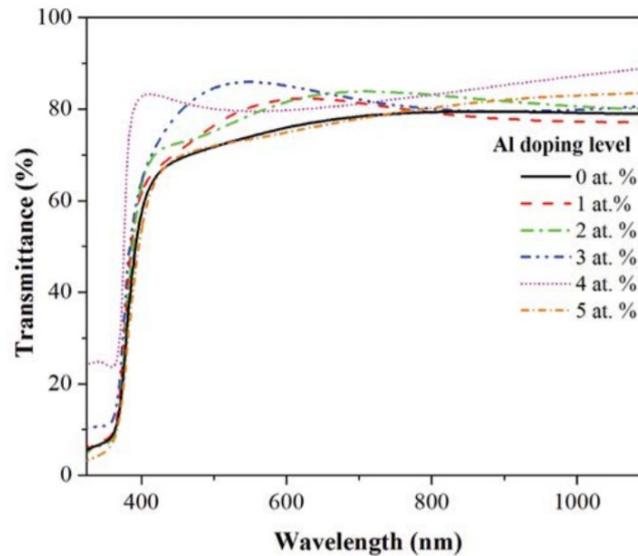


Figure 8. Transmittance of as deposited AZO thin films. [33]

Moreover, the choice of substrate also showed to have an influence on the optical properties of AZO films where glass and quartz substrates showed better optical transparency in the visible range when compared to FTO substrates. [34], [35]

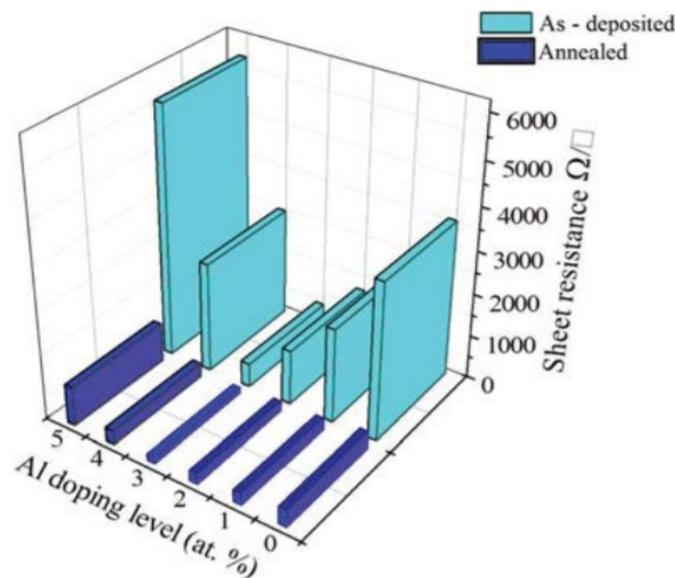


Figure 9. The variation of the sheet resistance of ZnO thin films as a function of Al doping level for as-deposited and annealed films.[33]

Besides the good transparency that is a requirement for a material to be used as TCO, conductivity is also considered a crucial property to be considered. This leads the researchers to have to study the impact of different process parameters on the electrical properties of AZO films. Concerning the annealing process of AZO films, a decrease in the resistivity value to half of that of the as deposited films was observed (Fig. 9). An explanation to this phenomenon is given by some studies where they suggest that annealing causes Al atoms to migrate from the grain boundaries to electrically active sites and this leads to an increase in the concentration of free carriers. Nonetheless a certain annealing temperature limit should be respected above which a reevaporation of the film takes place and an increase in resistivity takes place caused by the creation of zinc vacancies or antisite defects. [36]

Tin oxide (SnO₂) and Fluorine doped Tin Oxide (FTO)

General properties of Tin Oxide

There are two main forms of tin oxide: the stannic oxide (SnO₂) commonly called tin oxide and the stannous oxide (SnO). The existence of these two oxides reflects the dual valence of tin, with oxidation states of 2+ and 4+. Stannous oxide is not as well characterized as the stannic form of tin oxide. For example, currently, its electronic band gap is not accurately known but lies somewhere in the range of 2.5–3 eV. Thus, SnO exhibits a smaller band gap than SnO₂, for which, the band gap is commonly quoted to be 3.6 eV. Also, there are no single crystals available that would facilitate more detailed studies of stannous oxide. Stannic oxide possesses the rutile structure and stannous oxide has the less common litharge structure (tetragonal crystal system). [37] Finally, stannic oxide is the more abundant form of tin oxide

Tin oxide is a material having a big technological importance. Thus, SnO₂ have been studied for a wide range of applications such as rechargeable lithium batteries, storage of solar energy, and it is the one of technological significance in gas sensing applications and oxidation catalysts. This variety of applications depends on the morphology, phase, crystallinity, and size of the nanocrystals of the material. But in fact, dedicated to various applications, many geometrical structures and forms of tin oxide were produced like spherical particles, thin films, networks of ribbons and sheets.

In ambient conditions and atmospheric pressure, SnO₂ crystallizes in tetragonal rutile structure with space group P4₂/mnm (Fig. 10) where the tin ions are at the center of the octahedral site formed by the oxygen ions. When doping with fluorine, the F ion replaces the oxygen.

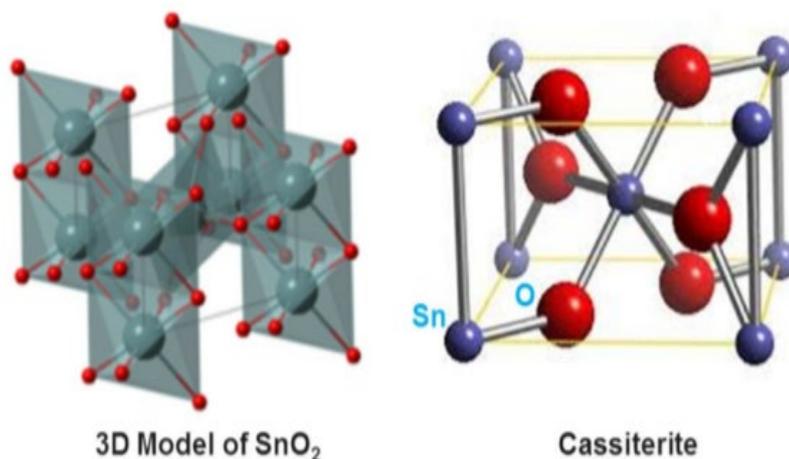


Figure 10. Crystal structure of SnO₂. [38]

Table 6. Tin Oxide properties.

Property	SnO ₂
Mineral name	Cassiterite
Crystal structure	Tetragonal, rutile
Space group	P4 ₂ mnm
Lattice constant	a=0.474 c=0.319
Band gap [eV]	3.6
Common n-type dopants	Sb, F, Cl

Nanostructured SnO_{2-x} thin films are usually prepared by chemical vapor deposition and by reactive DC-magnetron sputtering techniques. As for other materials deposited in film shapes, its crystallographic phase will be conditioned by the substrate temperature during the growth process. Thus, for SnO_2 films growth by DC magnetron sputtering technique, the pure tetragonal phase at low temperatures (below 90°C) and a mixture of tetragonal and orthorhombic phases at temperatures above was found. In this temperature range, the films present a wider band gap than that of a pure tetragonal phase. [39]

Doping of Tin Oxide

As for previous presented TCO, a great variety of dopants, mainly Al, In, Li was selected for tin oxide for the improvement or specialization of the SnO_2 layer properties optimized to specific applications. For TCO applications, the most commonly used dopants for tin oxide are Sb, Cl and F. In the case of Sb doping, antimony (+V) substitutes tin (+IV) ion. For high doping levels, the coexistence of Sb (+V) and Sb (+III) makes the later act as an acceptor by compensation of charge carriers liberated by Sb (+V). In addition, always for high doping levels, the ions mobility decreases attributed to formation of micelles, and, the thin film color changes to darker shades reducing the transparency and leading to a low Figure of Merit. [40]

Fluorine and chlorine doping share many similarities. Cl and F ions replace oxygen by releasing a charge carrier. The incorporation of these dopants also leads to the formation of uncharged micelles. Unlike Sb doping, the micelles do not carry an electrical charge, which does not cause disturbance of the tin network. In addition, films obtained by doping with chlorine or fluorine have better transparency compared to doping with antimony. Finally, fluorine doping offers an advantage over chlorine doping because of the close values of the ionic radii for fluorine (0.133 nm) and for oxygen (0.132 nm) while the ionic radius of chlorine is 0.181 nm. The consequence is that unlike the incorporation of Cl but also of Sb, the doping F can be incorporated into the tin oxide network without disturbance, thus making it possible to ensure better conductivity.

Focus on Fluorine doped SnO_2 (FTO)

Many deposition methods are adopted for the preparation of fluorine doped tin oxide such as chemical vapor deposition, [41] sputtering, [42] and most commonly spray pyrolysis [43] using tin chlorides as precursors. As expected, the fluorine doping concentration influences the properties of the film. Increasing the F-doping level leads to an increase in the Fermi energy until reaching the conduction band edge. Hence the optical band gap exceeds 4eV and the transparency of the film in the ultraviolet (UV) range is improved.

The effect of F/Sn atomic ratio on the structural, optical and nano-mechanical properties of FTO films grown by Ultrasonic Spray Pyrolysis on glass substrate was recently investigated by Tuyen L *et al.* [44] The films showed tetragonal rutile structure of SnO_2 with preferred orientation of (110) and an increased grain size with increasing F/Sn ratio. An important result of their study is the demonstration for the electrical and optical properties of FTO of a critical concentration of the fluorine dopant located approximately at a ratio $\text{F/Sn} = 0.5$ corresponding to a fluorine concentration of 5.1 at% in layer. We present in Fig. 11 the results of their studies of FTO as a function of fluoride concentration. Below the critical concentration, a sharp increase in the concentration of free charge carriers is clearly observed, leading to a decrease in resistivity. However, beyond this critical concentration, there is a decrease in the concentration of charge carriers attributed to the fact that the excess fluorine no longer being able to replace the oxygen ions, it is expelled to segregate at the grain boundaries. Moreover, FTO films are acceptable have interesting transmittance (around 90% in the visible range) below the concentration threshold, whereas it appears to be reduced above the threshold (down to 80% for $\text{F/Sn}=1$). Authors explained this decrease by the scattering effect due to the increase of the surface roughness.

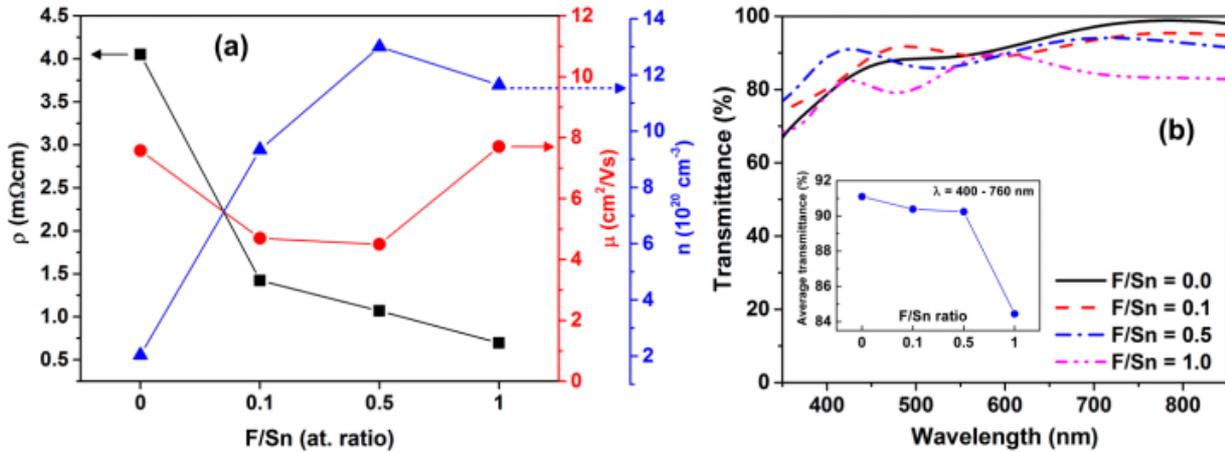


Figure 11. (a) F/Sn ratio-dependent resistivity (ρ , black squares), carrier concentration (n , blue triangular), and carrier mobility (μ , red spheres) of the FTO thin films. (b) Transmission spectra of FTO thin films as a function of F/Sn ratios. The inset in (b) presents the average optical transmittance (%) of the films in the visible range of 400–760 nm. [44]

In this review, different types of TCO materials such as ITO, ZnO, AZO and SnO₂, FTO were discussed and compared. Several works have been presented to show the influence of the nature of TCO materials and structures on PV performance. In addition, various research efforts on the development of TCO materials have been presented, which has many advantages in terms of PV. It was noted that no type of materials can be considered perfect. Finally, the development of TCO layers itself, and the development of PV system are by combining with different research areas such as chemistry, physics, and electronics.

Conclusion

Since their discovery, Transparent Conductive Oxides were the subject of intense studies and researches in view of the diversity of materials, their important features and the multitude of application fields mainly as detectors and as transparent electrodes in various optoelectronic devices and for photovoltaic cells and modules of new generation. After a general presentation of structural, electrical and optical properties of TCO in a first publication, by the same authors, entitled “*Transparent Conductive Oxides. Part I. General review of structural, electrical and optical properties of TCOs related to the growth techniques, materials and dopants.*”, the current one focus on TCO for photovoltaic cells and modules. Among these TCOs, Indium doped Tin Oxide (ITO), Zinc Oxide (ZnO) with its many dopants mainly aluminum (AZO) and tin oxide mainly fluorine doped (FTO), possess excellent transparency combined with high electrical conductivity. They are widely studied and were found to be the most suited for photovoltaic purposes. Due to its advantageous set of functional properties, ITO is still dominating the TCO industry. But a shortage in Indium supply started to emerge few years ago that makes it a rare and expensive material. By else, ITO thin films deposition requires vacuum based techniques and high temperatures, which is considered as a drawback since these conditions are hard to satisfy. In addition to certain risk of device damage, some substrate types are unable to handle such parameters. On the other hand, ZnO-AZO and SnO₂-FTO thin films could be deposited by simple techniques with no obligation of high temperature or vacuum chamber which is suitable for many substrates types as flexible substrates.

References

- [1] Information on <https://www.americanelements.com/indium-tin-oxide-ito-50926-11-9>
- [2] Z. Ma, Z. Li, K. Liu, C. Ye, and V. J. Sorger, Indium-Tin-Oxide for High-performance Electro-optic Modulation, *Nanophotonics*, 4 (2015) 198–213.
- [3] J. C. C. Fan and J. B. Goodenough, X-ray photoemission spectroscopy studies of Sn-doped indium-oxide films, *Journal of Applied Physics*, 48 (1977) 3524–3531.
- [4] O. Tuna, Y. Selamet, G. Aygun, and L. Ozyuzer, High quality ITO thin films grown by dc and RF sputtering without oxygen, *J. Phys. D: Appl. Phys.*, 43 (2010) 055402.
- [5] M. Nisha, S. Anusha, A. Antony, R. Manoj, and M. K. Jayaraj, Effect of substrate temperature on the growth of ITO thin films, *Applied Surface Science*, 252 (2005) 1430–1435.
- [6] S. Ray, R. Banerjee, N. Basu, A. K. Batabyal, and A. K. Barua, Properties of tin doped indium oxide thin films prepared by magnetron sputtering, *Journal of Applied Physics*, 54 (1983) 3497–3501.
- [7] L. Gupta, A. Mansingh, and P. K. Srivastava, Band gap narrowing and the band structure of tin-doped indium oxide films, *Thin Solid Films*, 176 (1989) 33–44.
- [8] N. M. Ahmed, F. A. Sabah, H. I. Abdulgafour, A. Alsadig, A. Sulieman, and M. Alkhoaryef, The effect of post annealing temperature on grain size of indium-tin-oxide for optical and electrical properties improvement, *Results in Physics*, 13 (2019) 102159.
- [9] Ü. Özgür *et al.*, A comprehensive review of ZnO materials and devices, *Journal of Applied Physics*, 98 (2005) 041301.
- [10] K. Ellmer, A. Klein, and B. Rech, *Transparent Conductive Zinc Oxide: Basics and Applications in Thin Film Solar Cells*. Springer Science & Business Media, (2007).
- [11] S. Johari, N. Y. Muhammad, and M. R. Zakaria, Study of zinc oxide thin film characteristics, *EPJ Web Conf.*, 162 (2017) 01057.
- [12] M. Bouderbala *et al.*, Thickness dependence of structural, electrical and optical behaviour of undoped ZnO thin films, *Physica B: Condensed Matter*, 403 (2008) 3326–3330.
- [13] M.-C. Jun, S.-U. Park, and J.-H. Koh, Comparative studies of Al-doped ZnO and Ga-doped ZnO transparent conducting oxide thin films, *Nanoscale Research Letters*, 7 (2012) 639.
- [14] T. Prasada Rao, M. C. Santhosh Kumar, A. Safarulla, V. Ganesan, S. R. Barman, and C. Sanjeeviraja, Physical properties of ZnO thin films deposited at various substrate temperatures using spray pyrolysis, *Physica B: Condensed Matter*, 405 (2010) 2226–2231.
- [15] T. V. Vimalkumar, N. Poornima, C. S. Kartha, and K. P. Vijayakumar, Effect of precursor medium on structural, electrical and optical properties of sprayed polycrystalline ZnO thin films, *Materials Science and Engineering: B*, 175 (2010) 29–35.
- [16] G. Epurescu *et al.*, p-type ZnO thin films grown by RF plasma beam assisted Pulsed Laser Deposition, *Superlattices and Microstructures*, 42 (2007) 79–84.
- [17] V. H. Nguyen *et al.*, Deposition of ZnO based thin films by atmospheric pressure spatial atomic layer deposition for application in solar cells, *Journal of Renewable and Sustainable Energy*, 9 (2017) 021203.
- [18] A. Douayar, R. Diaz, F. C. E. Moursli, G. Schmerber, A. Dinia, and M. Abd-Lefdil, Fluorine-doped ZnO thin films deposited by spray pyrolysis technique, *Eur. Phys. J. Appl. Phys.*, 53 (2011).
- [19] P. Nunes, E. Fortunato, and R. Martins, Influence of the post-treatment on the properties of ZnO thin films, (2001).

-
- [20] A. Bougrine, M. Addou, A. Kachouane, J. C. Bérnède, and M. Morsli, Effect of tin incorporation on physicochemical properties of ZnO films prepared by spray pyrolysis, *Materials Chemistry and Physics*, 91 (2005) 247–252.
- [21] F. Hijazi, Etude des propriétés physiques et de transport dans des films d'ITO et de ZnO (dopé ou non) pour dispositifs optoélectroniques organiques, Limoges, (2010).
- [22] M. Hjiri, L. El Mir, S. G. Leonardi, A. Pistone, L. Mavilia, and G. Neri, Al-doped ZnO for highly sensitive CO gas sensors, *Sensors and Actuators B: Chemical*, 196 (2014) 413–420,
- [23] Y. Zhang *et al.*, ZnO-Decorated In/Ga Oxide Nanotubes Derived from Bimetallic In/Ga MOFs for Fast Acetone Detection with High Sensitivity and Selectivity, *ACS Appl. Mater. Interfaces*, 12 (2020) 26161–26169.
- [24] P. Nunes, E. Fortunato, P. Tonello, F. Braz Fernandes, P. Vilarinho, and R. Martins, Effect of different dopant elements on the properties of ZnO thin films, *Vacuum*, 64 (2002) 281–285.
- [25] J. Rombach *et al.*, The role of surface electron accumulation and bulk doping for gas-sensing explored with single-crystalline In₂O₃ thin films, *Sensors and Actuators B: Chemical*, 236 (2016) 909–916.
- [26] C. S. Prajapati, A. Kushwaha, and P. P. Sahay, Effect of Al dopants on the structural, optical and gas sensing properties of spray-deposited ZnO thin films, *Materials Chemistry and Physics*, (2013).
- [27] Z.-N. Ng, K.-Y. Chan, and T. Tohsophon, Effects of annealing temperature on ZnO and AZO films prepared by sol–gel technique, *Applied Surface Science*, 258(2012) 9604–9609.
- [28] X. Shu-Wen, A Study of Annealing Time Effects on the Properties of Al:ZnO, *Physics Procedia*, 25 (2012).
- [29] C. Lennon, R. Kodama, Y. Chang, S. Sivananthan, and M. Deshpande, Effects of annealing in N₂ on sputtered Al-doped ZnO thin films, *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena*, 27, (2009) 1641–1645.
- [30] D. S. Kim *et al.*, Effect of deposition temperature on the properties of Al-doped ZnO films prepared by pulsed DC magnetron sputtering for transparent electrodes in thin-film solar cells, *Applied Surface Science*, 259 (2012) 596–599.
- [31] B. J. Babu, A. Maldonado, S. Velumani, and R. Asomoza, Electrical and optical properties of ultrasonically sprayed Al-doped zinc oxide thin films, *Materials Science and Engineering: B*, 174 (2010) 31–37.
- [32] C. M. Muiva, T. S. Sathiaraj, and K. Maabong, Effect of doping concentration on the properties of aluminium doped zinc oxide thin films prepared by spray pyrolysis for transparent electrode applications, *Ceramics International*, 37 (2011) 555–560.
- [33] K. Ravichandran, N. J. Begum, S. Snega, and B. Sakthivel, Properties of Sprayed Aluminum-Doped Zinc Oxide Films—A Review, *Materials and Manufacturing Processes*, (2014).
- [34] M. Benhaliliba, C. E. Benouis, M. S. Aida, A. S. Juarez, F. Yakuphanoglu, and A. T. Silver, A comparative study on structural, optical, photoconductivity properties of In and Al doped ZnO thin films grown onto glass and FTO substrates grown by spray pyrolysis process, *Journal of Alloys and Compounds*, 2 (2010) 548–553.
- [35] A. E. Manouni *et al.*, Effect of aluminium doping on zinc oxide thin films grown by spray pyrolysis, *Superlattices and Microstructures*, 39 (2006) 185–192.
- [36] Y. Igasaki and H. Saito, Substrate temperature dependence of electrical properties of ZnO:Al epitaxial films on sapphire, *Journal of Applied Physics*, 69 (1991) 2190–2195.

-
- [37] M. Batzill and U. Diebold, The surface and materials science of tin oxide, *Progress in Surface Science*, 79 (2005) 47–154.
- [38] S. Das and V. Jayaraman, SnO₂: A comprehensive review on structures and gas sensors, *Progress in Materials Science*, 66 (2014) 112–255.
- [39] Information available on http://www.scielo.org.mx/scielo.php?script=sci_arttext&pid=S1665-35212013000300005
- [40] G. Rey, Etude d'oxydes métalliques nanostructurés (ZnO, SnO₂) pour applications photovoltaïques notamment oxydes transparents conducteurs et cellules solaires à colorant, Grenoble (2012)
- [41] M. M. Tavakoli *et al.*, Fabrication of efficient planar perovskite solar cells using a one-step chemical vapor deposition method, *Sci Rep*, 5 (2015) 14083.
- [42] Z. Banyamin, P. Kelly, G. West, and J. Boardman, Electrical and Optical Properties of Fluorine Doped Tin Oxide Thin Films Prepared by Magnetron Sputtering, *Coatings*, 4 (2014) 732–746.
- [43] M. A. Aouaj, R. Diaz, A. Belayachi, F. Rueda, and M. Abd-Lefdil, Comparative study of ITO and FTO thin films grown by spray pyrolysis, *Materials Research Bulletin*, 44 (2009) 1458–1461.
- [44] L. T. C. Tuyen, S.-R. Jian, N. T. Tien, and P. H. Le, Nanomechanical and Material Properties of Fluorine-Doped Tin Oxide Thin Films Prepared by Ultrasonic Spray Pyrolysis: Effects of F-Doping, *Materials*, 12 (2019).