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Transparent Conductive Oxides. Part I. General Review of Structural, Electrical and Optical Properties of TCOs Related to the Growth Techniques, Materials and Dopants

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Abstract. This contribution, based on literature review, presents a general overview of properties and applications of transparent conductive oxides, TCO. The requested properties of TCO are a high conductivity associated to high transparency in a wide wavelength range. The relation between the techniques used for deposition or growing TCO and the possibility of their doping with appropriate dopant and concentration were discussed relatively to their applications and properties. Thus, we present in this part, the various possible techniques for growing TCO and discuss the effect of the temperature on the functional properties. This self-consistent presentation is also considered to introduce a better understanding of the expected requirements for TCO integrated as transparent electrodes in photovoltaic cells and modules. These developments of TCO for photovoltaic applications will be presented in a second publication.

Introduction

The original known discovery of Transparent Conductive Oxide, TCO was in 1904 when Badeker[1] observed an oxidation of Cadmium (Cd) metal thin films deposited in a glow discharge chamber. He observed that after oxidation, the Cd films became transparent while conserving their electrical conductivity. Ever since, the value of these films grew commercially and the list of TCO expanded to other oxide materials as ZnO, TiO₂, GdInO_x, SnO₂, In₂O₃, pure or doped with elements as Fluorine (F) or Aluminum (Al), and many more.[2] Currently, at the date of this contribution, the properties of TCO layers and their optimization remain a subject of intense research all around the world and the number of publications concerning TCO continues to grow to reach 250,000 (Google Scholar, 2021) publications in rank A journals.

This enthusiasm is justified by the unique properties of these TCO layers which are directly linked to their transparency and conductivity. TCO thin films have a wide range of applications including transparent heaters, heat mirrors, smart windows, and optoelectronic devices in particular the market for transparent electrodes used in touch panels, flat panel display or lamps, and thin film solar cells which is still expanding linked to the increase of new emerging solar cells technologies and devices as organic and perovskite ones. [3] Based on the precursor tin oxide, SnO₂, applications can be classified into two dominant markets: architectural applications such as energy efficient windows which currently, employ fluorine doped tin oxide, FTO, deposited by pyrolytic process, thanks to its efficiency in preventing radiative heat loss due to tin oxide low emissivity. Such coated windows are ideal for low temperature applications as, for example, glass freezer doors or for airplane cockpit windows. The second current application domain of TCO is flat panel applications such in the case of PV modules, touch screens and plasma displays which mainly employ indium doped tin oxide, ITO as external surface transparent electrodes. [4] Beside ITO, zinc oxide (ZnO) is also a major material used for such applications.

These last decades, an emergent third market is linked to the development of renewable energies and more specifically to the production of electricity from photovoltaic, PV solar cells, modules or panels. The resulting increase in the need for PV panels, flat or not, rigid or more recently flexible, leads to technological new developments with the development of thin-film PV panels requiring the replacement of the surface electrodes made up of metal ribbons with transparent electrodes and therefore based on TCO layers.

Among all studied materials, ITO was the most employed for TCO applications, mainly for large screens due its advantageous and unique set of electrical and optical properties. Moreover, as ITO is a non-friendly material, over the years and with the increasing demand, the conception of employed TCO started to change. The change in the basic material opens the way to overcome limitations and improve the devices performance. Indeed, the urgent need of new materials for TCOs allowing the development of large area and/or flexible photovoltaic cells and display devices is accompanied by the need to increase their conductivity and transparency, which is made possible by a better understanding of the relationship between their structure and their electrical and optical properties.

It is in this context that we are carrying out this review, more specifically focus on applications of TCOs as electrodes for photovoltaic applications. Of course, as we have specified above, with the huge number of publications and work 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, it is not possible to make an exhaustive review of the properties of TCO materials and layers. It is for this reason that this contribution based on results validated in several publications, has a first main objectives to introduce a general review of structural, electrical and optical properties of TCOs related to the growth techniques, materials and dopants. This contribution as done in the current publication is the first part of a complete presentation done in two relative publications considered as a whole.

Thus, the second contribution of this review on TCO is presented in a second publication title: "*Transparent Conductive Oxides. Part II. Specific focus on ITO, ZnO-AZO, SnO₂-FTO for photovoltaic applications*". It corresponds to the second main objective dedicated to the presentation of the three main families of transparent conductive materials, ITO, ZnO-AZO, SnO₂-FTO, used as electrodes in PV cells and modules. Based on the presentation done below in the current Part. I, we will consider in the second contribution the possible growth methods, the specific dopants and the main electrical and optical properties of these TCO for PV applications. The properties of these materials are finally compared in the final discussion.

General Properties of TCO and their Relevance to some Applications

The requirements for TCO are good electrical conductivity and high transparency in the visible spectrum of light. These properties are achieved in wide band gap oxides made degenerate by the introduction of dopants. [5] However, a lot of parameters influence the choice of a TCO depending on the application to which it is intended to be used for. These parameters include stability (physical, chemical, thermal), etchability, conductivity, plasma wavelength, thickness, deposition temperature, uniformity, toxicity and cost. Table 1 shows the most important property of each transparent conductive material studied in various works around the world. Hence, for a given application, performance is defined by a number of electrical and optical but also by physical and chemical properties.

Table 1. Summarizing table of the most important property for different Transparent Conductive Materials (TCM).[6]

Property	Material
Highest transparency	ZnO:F, Cd ₂ SnO ₄
Highest conductivity	In ₂ O ₃ :Sn
Lowest plasma frequency	SnO ₂ :F, ZnO:F
Highest plasma frequency	Ag, TiN, In ₂ O ₃ :Sn
Highest work function, best contact to p-Si	SnO ₂ :F, ZnSnO ₃
Lowest work function, best contact to n-Si	ZnO:F
Best thermal stability	SnO ₂ :F, TiN, Cd ₂ SnO ₄
Best mechanical durability	TiN, SnO ₂ :F
Best chemical durability	SnO ₂ :F
Easiest to etch	ZnO:F, TiN
Best resistance to H plasmas	ZnO:F
Lowest deposition temperature	In ₂ O ₃ :Sn, ZnO:B, Ag
Least toxic	ZnO:F, SnO ₂ :F
Lowest cost	SnO ₂ :F

Generally, a compromise must be found by the manufacturers and designers of systems between all these properties in order to find the best material allowing to obtain the electrode adapted to the intended application. As an example, low emissivity windows reflect infrared radiation for wavelength longer than the plasma wavelength by free electrons. For cold weather, the plasma wavelength should be fairly long in order to transmit most of the solar spectrum into heat inside the substrate or the background volume. For this application FTO is the best material because it has the convenient wavelength along with excellent durability and low cost. On contrary, for hot weather, a short plasma wavelength is better so that the near IR is reflected out of the substrate. For this application silver and titanium nitrides are suitable, since silver has poor durability, it is sealed inside double-glazed panes for protection against moisture and air.

Electrical and Optical Properties of TCO

For the transparent conductor to be effective, it should have a high electrical conductivity along with low absorption of visible light. [6]

The first interest to control the charge carriers concentration and mobility in the TCO film is to offer the possibility of an optimization of its electrical properties. This possibility is closely related to the intrinsic material of the TCO and the type and concentration of dopant. Indeed, the conductivity of thin film is highly dependent on the carrier concentration and mobility which are related by the following relation:

$$\sigma_{n,p} = nq\mu \quad (1)$$

Where n is the density of electron (hole) in the conduction band (valence band), q is the charge of the electron (1.6×10^{-19}) and μ is the mobility of charge carriers. It can therefore be seen that to become conductive, the films must either deviate from stoichiometry or by intrinsic doping such as oxygen

vacancies, or more generally, be doped with appropriate external impurities to form an extrinsic doping.

According to eq. 1, the possibility of increasing the conductivity of the films consists either in improving the concentration of carriers by doping, or in improving the electronic mobility μ .

Depending on material or on type of dopant, the doping can be realized by substitution, vacancies or interstitial implantations. Considering the valence of the dopants or of the type of implantation on acceptor or donor sites, the doping will induce n or p type conductivity. Thus, with the TCO presented in this contribution, the doping can be done by substitution of cation (metal ion) or anion (oxygen).

However, the increase in the dopant concentration is limited by the fact that at high concentration, the ionized dopant atoms can play the role of diffusion centers reducing the mobility of electrons but also can deteriorate the optical properties by an increase of the absorption of the film at long wavelengths (near infra-red). Thus, as far as possible, it is preferred to improve the conductivity by increasing the electronic mobility μ . Grain boundary scattering and ionized impurity scattering are generally considered to be the two main interacting mechanisms in conductivity. These two phenomena will then depend directly on the quality of the layers, on their thickness and therefore also on the growth or deposition methods. In particular, Minami *et al.* [7] for ZnO films obtained by different methods, and Rey *et al.* for FTO films have shown that the conductivity is primarily affected by grain boundaries scattering in thin films while for thicker films the ionized impurities scattering dominates. [8]

Direct bandgap and high exciton energy are basic requirements for materials to be used in optical emitting devices. Whereas for TCO to be used as electrodes in solar cells, they have to exhibit a minimum carrier concentration of the order of 10^{20} cm^{-3} and a band gap greater than 3.2eV to avoid absorption of light over most of the solar spectra. [9] The Hall Effect measurements are used to determine the electrical properties of TCO thin films. This characterization method permits to find the resistivity, charge carrier density and mobility. In the optoelectronic field especially for photovoltaic devices, it is preferable to have low resistivity to facilitate current transport.

The second interest to the doping of TCO concerns its optical properties. The first concerned optical effect is related to the Burstein Moss effect which shifts the transparency limit of a semiconductor towards short wavelengths with the increase in energy required to produce an interband electronic transition. [10] However, the increase in the density of carriers has the effect of increasing the Fermi energy and therefore of decreasing the transparency limit when the doping level increases. Nevertheless, corresponding to the second optical effect, the doping of TCO will strongly influence the interaction of photons and excitons. Below the higher wavelength limit of the transparency band (called plasma wavelength), but above the lower transparency limit, TCO is transparent and has a dielectric type behavior. Beyond the plasma wavelength, it behaves like a metal and absorbs or reflects light. The effect of the doping is then a shift in the plasma wavelength and therefore a reduction in the transparency of the TCO in the infrared. A compromise must then be found for the TCOs used in photovoltaic applications as a function of the spectral response of the absorber. Thus, in general, with TCOs whose plasma wavelength is typically between 1 and 2 μm , the type of oxide and its doping are optimized to have a transparency range ranging from near UV to near infrared depending on the material used and its doping.

To compare the performance of transparent conductive materials, TCM quantitatively, a pertinent figure of merit, FoM is defined as the ratio of the electrical conductivity (σ) on the visible absorption (α) and is given by Eq.2

$$\frac{\sigma}{\alpha} = -[R_s \ln(T + R)]^{-1} \quad (2)$$

where R_s is the sheet resistance in ohms per square, T the total visible transmission, and R is the total visible reflectance. A larger value of FoM indicates better performance and quality of the TCM.[11] Another expression of FoM was proposed by Jain *et al.* [12] but without taking into account the reflection. It will not be considered here. Table 2 lists the FoM for different TCO materials.

Table 2. Figure of Merit for some transparent conductors. [6]

Material	Deposition method	FoM ($\times 10^{-2} \Omega^{-1}$)	Ref
ITO	Commercial	5.9	[13]
ITO	Atomic Layer Deposition	1.3	[14]
AZO	Pulsed DC magnetron sputtering	1.99	[15]
FTO	Ultrasonic Spray Pyrolysis	0.9	[16]

Table 2 indicates that for the case of zinc oxide and tin oxide, doping with fluorine gives better material performance compared to when doped with metallic elements. This difference could be explained by the conduction band in oxide semiconductors being derived from metal orbitals. A metal dopant is electrically active when it substitutes for the primary metal (zinc or tin). In this way, the conduction band receives a strong perturbation from each metal dopant, the scattering of conduction electrons is enhanced and thus the mobility and conductivity are decreased. In contrast, fluorine substitutes for oxygen, which confining the electronic perturbation to the filled valence band and minimizing the scattering of conduction electrons. The bulk properties of TCMs such as conductivity and absorption depend on the crystallite grain size which increases with increasing film thickness. Hence, one should note that as the electrical and optical properties depend on the film thickness, FoM also dependent on it and will increase with increasing thickness.

It is to be noted that the FoM is not the only qualification criteria occurring in the development of TCO on an industrial scale. All the production processes need to be considered from the origin, the chemical and toxicity of the constituting elements and the environmental aspects for the production and treatment at the end of life. From the industrial point of view, currently the most used material is indium tin oxide (ITO). Despite its flaws imperfections and instability of purchasing price, ITO is still dominating the transparent and conductive oxide industry. As a result, effort is made in order to find a competitive transparent material having similar or overpassing performance. Indeed, Indium is a rare element on earth, which is found in small quantities in the zinc, and lead mines. Indium is then produced in much smaller amount compared to zinc and tin.

Table 3. Abundance of Indium, Tin and Zinc in ppm. [17]

Element	Abundance (ppm)
Indium (In)	0.049
Tin (Sn)	2.2
Zinc (Zn)	75

Due to its rarity and the world increasing demand from the photovoltaic panel industry, its price has incredibly risen. For this reason, a renewed interest has grown in finding replacements for ITO. With today's environmental challenges, using natural and renewable resources or abundant elements became prior for sustainable development of efficient TCO and systems. [18]

Doping of Transparent Conductors

In this part, we focus on the influence of the type of extrinsic dopants on the properties of TCO and discuss the two types of doping, i.e. n and p doping. As previously shown a double interest exists in the doping of a TCO allowing respectively improving optical and electrical properties. Electronic, chemical and physical parameters of the components such as the size of the dopant ion and growing

process and technique parameters such as the solid solubility of the dopant in the host material network will also influence the possibility of doping and the final quality of the film. We report in Table 4 the ionic radius of the main elements considered in TCOs either as constituent elements of pure TCMs or as dopants, it is obvious that the substitution will be facilitated by ions having similar diameters.

Table 4. Table representing the ionic radii of the elements used as TCO. [19]

Element	Ionic radius (Å)
Oxygen (O)	1.40
Zinc (Zn)	0.74
Tin (Sn)	0.69
Fluorine (F)	1.33
Aluminum (Al)	0.53
Chlorine (Cl)	1.81
Gallium (Ga)	0.62
Antimony (Sb)	0.76
Indium (In)	0.80

Thus, we will see below that the size of the different ions involved in the doping process will be taken into consideration in the choice of the dopant in addition to the consideration of the electronegativity, the crystal structure and other optical and electronic parameters of host and dopants.

N-type doping

Many doping are based on cation substitutions for example, indium oxide can be doped with transition metal ions as molybdenum, titanium or tin ions giving the well-known indium tin oxide, ITO intensively used as TCO for photovoltaic cells of new generation. Zinc oxide ZnO is currently doped with metallic elements such as Al, Ga, In [20]–[22] and tin oxide SnO₂ with elements such as Sb, Nb, or metal ions such as Cu, Fe and Co.[23]–[26] The list of dopant candidates presented above, as example is not exhaustive and there is a great deal of works on many kinds of doping. Moreover, co-doping of TCO was already studied to enhance some specific properties and results can be found in literature, such as for the Al-Ti co-doping of ZnO.

Doping TCM by substitution of the oxygen anion is rare. However, this substitution process is still applied for SnO₂ with fluorine dopant substituting oxygen.

All dopants mentioned above are associated with the creation of an intermediary energy level under the conduction band of the host. The increase in dopant concentration develops an energy band overlapping the conduction band which reinforce the n type nature of the host semiconductor TCOs. Thus, compared to a pure undoped TCO, a larger number of electrons will participate to the circulation of the charges yielding to an increase in conduction by doping.

P-type doping

All the TCOs mentioned above are n-type semiconductors and the interest of p-type doping for TCO applications currently remains discussed and controversial. In fact, in the literature, the difficulty of creating transparent conductive oxides of p-type has been attributed to the significant localization of the holes in the oxygen levels and to the ionicity of the metal atoms. As a result, these holes are confined and require a considerable amount of energy to overcome a large barrier height to migrate inside the crystal lattice, causing poor hole mobility and conductivity. [27], [28] Despite that, the first attempt to make a p-type TCO was by Sato et al [27] in 1993. They reported a p-type semi-transparent TCO (40% visible transmission) and the possibility to form acceptor levels through doping in ZnO. It was then until 1997 when Kawazoe et al [29] reported the properties of an oxide material (CuAlO₂) that combines p-type conductivity up to 1 S.cm⁻¹ with good optical transparency. According to the authors, this value is not comparable to the best n-type conducting oxides, but is sufficient for some applications. In recent years, more and more experimental works have focused on

thin films of p-type TCO more specifically on ZnO doping with Ga, N, F, P, Sb and As. Even though some research teams obtained ZnO:Sb having a conductivity of 0.5 S/cm, mobility of 9-20 cm²/Vs and a hole density of 4.10 16 cm⁻³, with transmission of 85%,[30] the challenge to grow p-type TCO having a resistivity in the order of 10⁻³ Ω.cm or better still exists.

Development and Growth of TCOs

In this section, we highlight a variety of used methods for the deposition of oxide thin films. These different deposition conditions and methods affect significantly the optical and electrical properties of ITO thin films. We finally discuss the link between the process temperature and the stability and properties of the TCO.

Generalities of growth techniques

The first developments of TCO layers on a substrate such as glass, silicon or photovoltaic cells were low-cost techniques of liquid chemistry, such as electrochemical deposits [31] hydrothermal growth [32] or even deposition by the Sol-gel process. [33] In order to improve the control of the growth process and therefore the quality of the layers, the first methods of producing TCO layers on a substrate by sputtering [34], [35] and spray pyrolysis were introduced in the 1970s. The spray pyrolysis is also called atmospheric pressure deposition or aerosol-assisted chemical vapor deposition technique. More sophisticated techniques have emerged in recent decades, such as pulsed laser assisted deposition [36] or molecular beam epitaxy. [37] The development of these latter methods were motivated by the large-scale development of commercial TCOs requiring better control of reproducibility while improving the crystallinity of the layers, or even obtaining monocrystalline films and allowing the integration of dopants.

Furthermore, it should be noted that the development of nanostructured layers based on nanoparticles, nanowires or nanofibers have been recently developed to respond either to an improvement in the electrical and optical performance of TCO layers and / or to new applications such as for example photovoltaics on a flexible substrate. Some of the techniques mentioned above can also be used for the growth of nanostructured layers such as the deposition technique in a chemical bath, or in the vapor phase, others are then more specific such as for example the electro-spinning technique (not discussed in this article) used, for example for the development of ZnO nanofibers.

In the following part, we describe the main deposition and growth techniques of TCO films, illustrated by various examples relating to particular TCO films, in order to highlight the experimental and growth considerations to be taken into account specifically.

Sputtering

Sputtering is a widely used technique for the deposition of TCO thin films. Sputtering includes a variety of techniques that can be used in a wide range of temperature such as radio frequency (RF) or direct current (DC) sputtering, or at only high temperature as magnetron reactive and ion beam sputtering. Out of the mentioned techniques, RF and DC were found to be interesting for the industrial field since they offer high deposition rates, reproducibility and large area sputtering systems. But, the major drawback of RF deposition at room temperature is the poor electrical and structural properties since the temperature is not enough for the crystallization of ITO. Additionally, ITO films deposited by DC magnetron sputtering at room temperature, are most of the time amorphous with high electrical resistivity as reported by Quaas et. al. [38] and Teixeira et. al. [39] The deposition temperature of ITO films by magnetron sputtering ranges from room temperature to 500°C [40], [41]. Nevertheless, solar cells or electronic systems on plastics are types of substrates or applications requiring a low deposition temperature because higher temperatures could directly damage them or even damage the structure of the electronic device. [42]

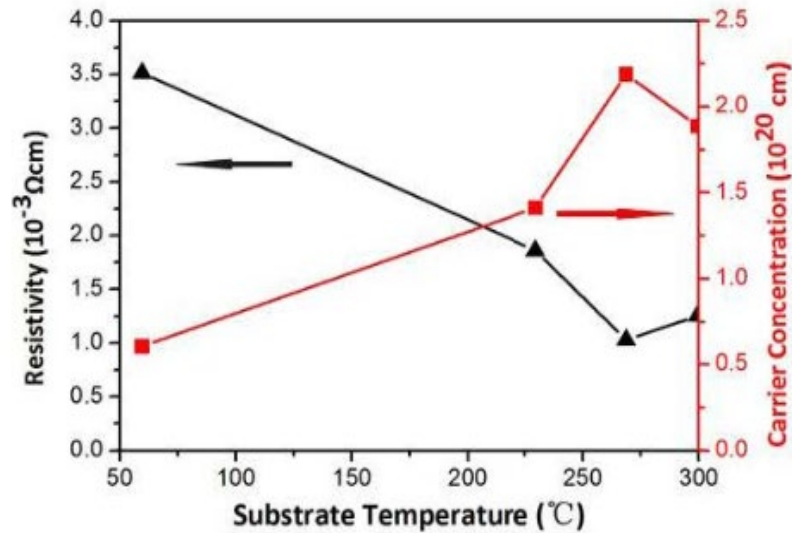


Figure 1. Variation of resistivity and carrier concentration in ITO layers with temperature grown by RF magnetron sputtering .[43]

As an example, we report in Fig. 1 the evolution of the resistivity and of the carrier concentration with the substrate temperature during the RF magnetron sputtering process made in discharge plasma modes. We can see at first, that resistivity and carrier concentration are inversely correlated.

Electron beam and direct thermal evaporation

Electron beam and direct thermal evaporation methods use powders of metallic Sn and In for the growing of ITO films. Indium will be favorably vaporized altering the composition of alloys caused by the higher vapor pressure of In relative to Sn. Diniz *et al.* [44] investigated the effect of various post deposition heat treatments on the microstructure, electrical and optical properties of $\text{In}_2\text{O}_3:\text{Sn}$ (ITO) thin films deposited by electron beam evaporation. The thin films were deposited on microscope glass substrates and silicon single crystal wafer. After deposition, the samples were annealed in air for 30 minutes at temperatures of 200, 250, 300, 350, 400, 450, 550°C. They observed that at low temperature, the film was amorphous while the crystallite size remarkably increases with the temperature. It was noted that for a temperature of 300°C the average grain size was about 10 to 25 nm, whereas it increases to reach 15 to 50 nm for higher temperatures. This link between temperature and structure was also reported in literature and is attributed to the fact that for a given driving force, the migration rate increases as the temperature increases. [45], [46], [47]

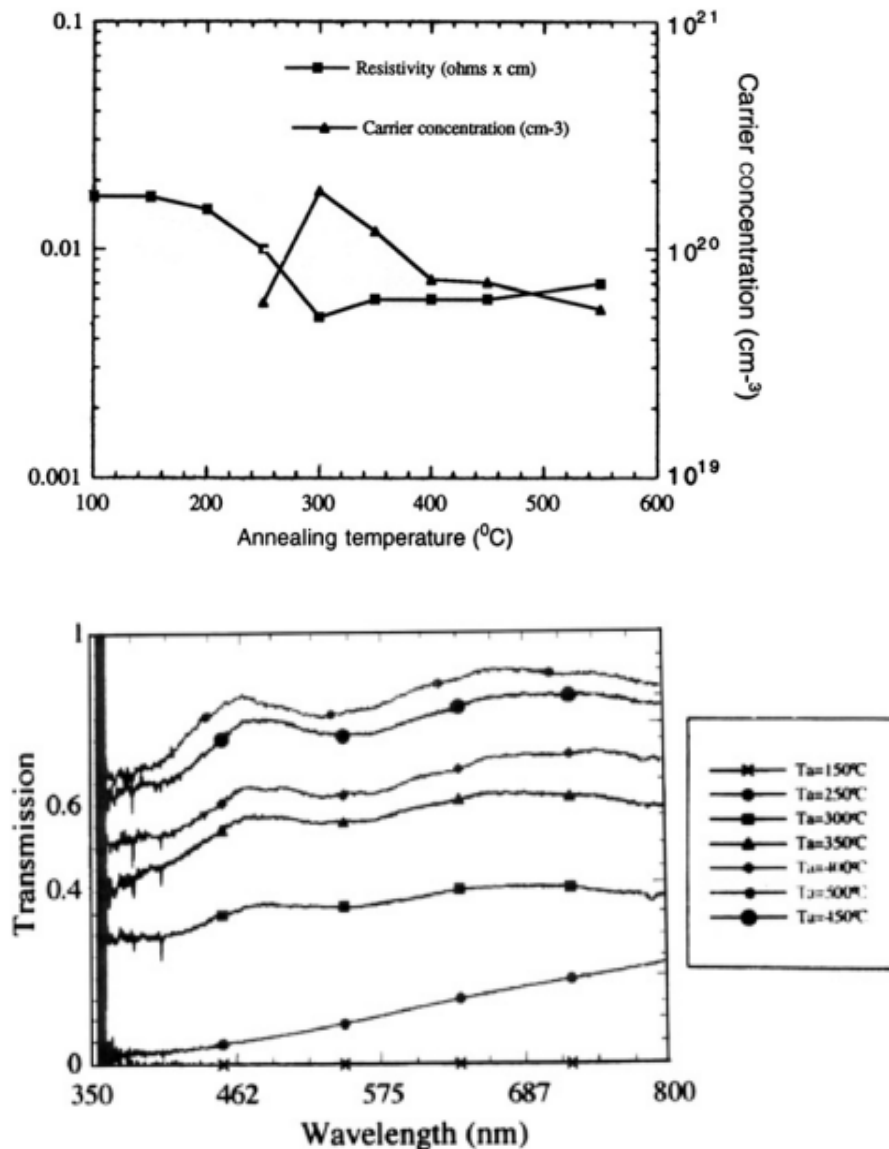


Figure 2. a) variation of electrical resistivity and carrier concentration as function of annealing temperature for ITO films. b) optical transmission curves for a series of ITO/glass films annealed at different temperatures.

Fig. 2.a summarizes the electrical properties (resistivity and carrier concentration) of the ITO films at various temperatures. At the annealing temperature of 300°C a sharp decrease in film resistivity as well as an increase in carrier concentration are observed. The increase in film resistivity as we go further in annealing temperature is explained by the diffusion of more oxygen into the film that contribute to the decrease in the concentration of oxygen vacancies. This reduces the carrier concentration and hence the film resistivity. It is noted that optical transmission increases with increasing annealing temperatures since one of its effect is film crystallization (Fig 2.b). Many earlier works explained the decrease of transmission for $\lambda < 400$ nm by the absorption of ITO band gap which may vary in the range of $3.5 \text{ eV} < E_g < 3.8 \text{ eV}$. [48], [49] Higher annealing temperatures resulted in improvement in optical transmission is a result of the transition from amorphous to microcrystalline then polycrystalline. This transition reduces the disorder level and assists the incorporation of tin atoms into the indium oxide lattice so that E_g becomes more defined.

Spray pyrolysis

In the spray pyrolysis (already mentioned above and also called atmospheric pressure deposition or aerosol-assisted chemical vapor deposition technique), a chemical reaction of gaseous species takes

place with a heated substrate surface. The advantages of this technique, which has become quite common for the development of electrodes, is the relatively low cost of the deposit frame, the low temperature used for the deposit allowing the deposit to be deposited on various substrates, and the possibility of depositing over large surfaces. For the experimental point of view, an additional advantage is that it enables the production of coatings having good properties on different substrate shapes with no need of vacuum use. Moreover, it is considered to be relatively cheap with respect to the apparatus. But for ITO films the main drawback is the lack of volatile and thermally stable material source.

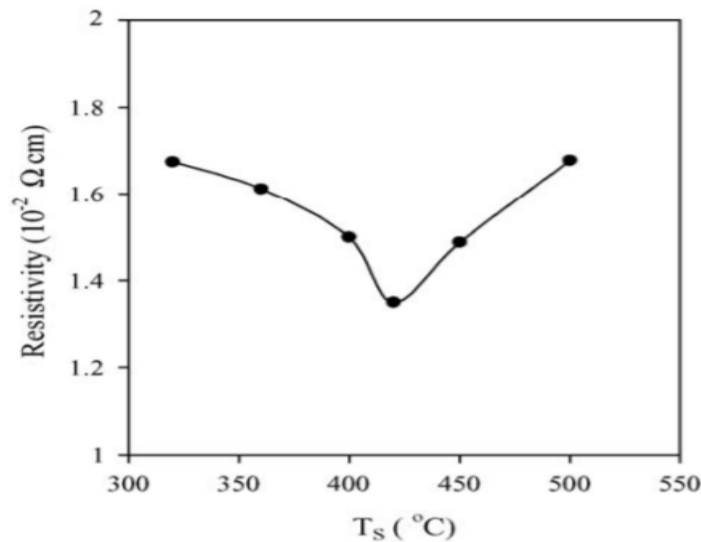


Figure 3. Dependence of the resistivity of ZnO films on the substrate temperature. [50]

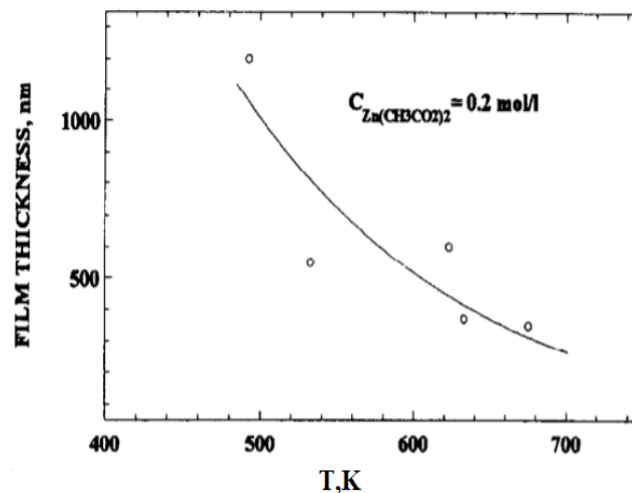


Figure 4. Dependence of film thickness on the growth temperature. [51]

Numerous research for ZnO thin films deposition on glass substrates by the spray pyrolysis technique was made in the purpose to investigate the change in properties of the films with varying deposition parameter. ZnO thin films deposited on glass substrates with different thickness and different deposition temperature revealed the dependence of the resistivity on the substrate temperature and spraying rate (Fig. 3). In addition, the substrate temperature during the deposition process showed an effect on the film thickness; [51] it was found to decrease with increasing temperature (Fig. 4). This decrease is explained by the decrease in mass transport to the substrate at higher temperature and by the increase of reevaporation rate.

Thermal Stability of Transparent Conductors

The deposition temperature is decisive during a deposit because it defines the kinetics of the various reactions between the chemical species present and the deposition regime. It follows a link between this temperature and the thermal stability of the so-grown layer.

Generally, thermal stability of TCM is tested by heating the material to temperature greater than the deposition temperature. Generally, it leads to an increase in the resistance of the TCM if heated for a long period of time. Tests were made and reported in the literature to check the thermal stability of several TCMs and the results are shown in Table 5. The tested materials remained stable with no increase in sheet resistance for temperatures slightly above the deposition temperature.

Table 5. Thermal stability of some transparent conductors. (LPCVD and APCVD are Low and Atmospheric pressure CVD, respectively). [6]

Deposition method and material	Deposition temperature (°C)	Stability temperature (°C)
LPCVD ZnO:B	200	<250
APCVD ZnO:F	450	<500
APCVD SnO ₂ :F	650	<700

As mentioned in the Introduction paragraph, following this general review of structural, electrical and optical properties of TCOs related to the growth techniques, the materials and their dopants, the three main families of transparent conductive materials, ITO, ZnO-AZO, and SnO₂-FTO, used as electrodes in PV cells and modules will be presented in a second contribution.

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. In the current contribution, we have focused on the general link between, the structural, electrical and optical properties from one side and the various possible growing processes, the operating temperature and the effect of the various dopants in term of electronegativity and concentration on the other side. Depending on the intended application and substrate, we point out the importance of choosing a suitable TCO within its specific dopant, and closely link, the choice of a appropriate growth technique at specific temperature. Thus, the presentation is based on general considerations illustrated by examples of various TCO.

This publication is the first part dedicated to general considerations of a review work on transparent conductive oxides. The second part will be more dedicated to specific families of TCO integrating photovoltaic cells and modules. It will be presented by the same authors in a second linked publication entitled "*Transparent Conductive Oxides. Part II. Specific focus on ITO, ZnO-AZO, SnO₂-FTO for photovoltaic applications*". It will covered the ITO, ZnO-AZO and SnO₂-FTO TCO families.

References

- [1] K. Badeker, Concerning the electricity conductivity and the thermoelectric energy of several heavy metal bonds, *Annalen der Physik*, 22 (1997) 749.
- [2] T. Minami, Transparent Conductive Oxides for Transparent Electrode Applications, *Semiconductors and Semimetals*, 88 (2013) 159–200.
- [3] B. G. Lewis and D. C. Paine, Applications and Processing of Transparent Conducting Oxides, *MRS Bulletin*, vol. 25 (2000)
- [4] D. S. Ginley and C. Bright, Transparent Conducting Oxides, *MRS Bulletin*, 25 (2000) 15–18
- [5] B. G. Lewis and D. C. Paine, Applications and Processing of Transparent Conducting Oxides, *MRS Bull.*, 25 (2000) 22–27
- [6] R. Gordon, Criteria for Choosing Transparent Conductors, (2000)
- [7] T. Minami, New n-Type Transparent Conducting Oxides, *MRS Bulletin*, 25 (2000)
- [8] G. Rey, C. Ternon, M. Modreanu, X. Mescot, V. Consonni, and D. Bellet, Electron scattering mechanisms in fluorine-doped SnO₂ thin films, *Journal of Applied Physics*, 114 (2013)
- [9] T. Minami, Transparent conducting oxide semiconductors for transparent electrodes, *Semicond. Sci. Technol.*, 20 (2000) 35–44
- [10] E. Burstein, Anomalous Optical Absorption Limit in InSb, *Phys. Rev.*, 93 (1954) 632–633
- [11] D. Ginley, A. Catalano, H. W. Schock, C. Eberspacher, T. M. Peterson, and T. Wada, Thin films for photovoltaic and related device applications
- [12] V. K. Jain and A. P. Kulshreshtha, Indium-Tin-Oxide transparent conducting coatings on silicon solar cells and their ‘figure of merit,’ *Solar Energy Materials*, 4 (1981) 151–158.
- [13] 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.
- [14] B. Dugrenil et al., AZO electrodes deposited by atomic layer deposition for OLED fabrication, in *Organic Photonics VI*, 9137 (2014) 127–132.
- [15] B. Sarma, D. Barman, and B. K. Sarma, AZO (Al:ZnO) thin films with high figure of merit as stable indium free transparent conducting oxide, *Applied Surface Science*, 479 (2019) 786–795.
- [16] B. Benhaoua, S. Abbas, A. Rahal, A. Benhaoua, and M. S. Aida, Effect of film thickness on the structural, optical and electrical properties of SnO₂: F thin films prepared by spray ultrasonic for solar cells applications, *Superlattices and Microstructures*, 83 (2015) 78–88.
- [17] Information on <https://courses.lumenlearning.com/geology/chapter/reading-abundance-of-elements-in-earths-crust>
- [18] D. R. Lide, G. Baysinger, S. Chemistry, L. I. Berger, R. N. Goldberg, and H. V. Kehiaian, *CRC Handbook of Chemistry and Physics*, 2661.
- [19] Information on <https://environmentalchemistry.com/yogi/periodic/ionicradius.html>
- [20] M. Asemi, M. Ahmadi, and M. Ghanaatshoar, Preparation of highly conducting Al-doped ZnO target by vacuum heat-treatment for thin film solar cell applications, *Ceramics International*, 44 (2018) 12862–12868.
- [21] E. Muchuweni, T. S. Sathiaraj, and H. Nyakoty, Effect of gallium doping on the structural, optical and electrical properties of zinc oxide thin films prepared by spray pyrolysis, *Ceramics International*, 42 (2016) 10066–10070.
- [22] R. K. Chava and M. Kang, Improving the photovoltaic conversion efficiency of ZnO based dye sensitized solar cells by indium doping, *Journal of Alloys and Compounds*, 692 (2017) 67–76

-
- [23] N. Zhou, Q. Cheng, L. Li, and H. Zhou, Doping effects in SnO₂ transport material for high performance planar perovskite solar cells, *J. Phys. D: Appl. Phys.*, 51 (2018) 394001.
- [24] S. S. Roy and J. Podder, Synthesis and optical characterization of pure and Cu doped SnO₂ thin films deposited by spray pyrolysis, 7.
- [25] J. Kaur, J. Shah, R. K. Kotnala, and K. C. Verma, Raman spectra, photoluminescence and ferromagnetism of pure, Co and Fe doped SnO₂ nanoparticles, *Ceramics International*, 38 (2012) 5563–5570.
- [26] E. Halvani Anaraki et al., Low-Temperature Nb-Doped SnO₂ Electron-Selective Contact Yields over 20% Efficiency in Planar Perovskite Solar Cells, *ACS Energy Lett.*, 3 (2018) 773–778.
- [27] H. Sato, T. Minami, S. Takata, and T. Yamada, Transparent conducting p-type NiO thin films prepared by magnetron sputtering, *Thin Solid Films*, 236 (1993) 27–31.
- [28] H. Kawazoe, H. Yanagi, K. Ueda, and H. Hosono, Transparent p-Type Conducting Oxides: Design and Fabrication of p-n Heterojunctions, *MRS Bulletin*, 25 (2000) 28–36.
- [29] H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, and H. Hosono, P-type electrical conduction in transparent thin films of CuAlO₂, *Nature*, 389 (1997) 939–942.
- [30] T. David, S. Goldsmith, and R. L. Boxman, Electro-optical and structural properties of thin ZnO films, prepared by filtered vacuum arc deposition, *Thin Solid Films*, 447–448 (2004) 61–67.
- [31] J. S. Wellings, N. B. Chaure, S. N. Heavens, and I. M. Dharmadasa, Growth and characterisation of electrodeposited ZnO thin films, *Thin Solid Films*, 516 (2008) 3893–3898.
- [32] T. Sahoo et al., Hydrothermal growth and characterization of ZnO thin film on sapphire (0001) substrate with p-GaN buffer layer, *Thin Solid Films*, 516 (2008) 8244–8247.
- [33] L. Znaidi, Sol–gel-deposited ZnO thin films: A review, *Materials Science & Engineering B*, 1–3 (2010) 18–30.
- [34] S. Takayanagi, T. Yanagitani, and M. Matsukawa, Effect of metal mode and oxide mode on unusual c-axis parallel oriented ZnO film growth on Al/glass substrate in a reactive magnetron sputtering of Zn target, *Journal of Crystal Growth*, 363 (2013) 22–24.
- [35] W. Gao and Z. Li, ZnO thin films produced by magnetron sputtering, (2004)
- [36] S.-M. Park, T. Ikegami, K. Ebihara, and P.-K. Shin, Structure and properties of transparent conductive doped ZnO films by pulsed laser deposition, *Applied Surface Science*, 253 (2006) 1522–1527.
- [37] Information on [https://www.semanticscholar.org/paper/Basics-of-Molecular-Beam-Epitaxy-\(MBE\)-Rinaldi/c4b463caba1e85265210a62b5cb42b8dba4ce0fd](https://www.semanticscholar.org/paper/Basics-of-Molecular-Beam-Epitaxy-(MBE)-Rinaldi/c4b463caba1e85265210a62b5cb42b8dba4ce0fd)
- [38] M. Quaas, H. Steffen, R. Hippler, and H. Wulff, Investigation of diffusion and crystallization processes in thin ITO films by temperature and time resolved grazing incidence X-ray diffractometry, *Surface Science*, 540 (2003) 337–342.
- [39] V. Teixeira, H. N. Cui, L. J. Meng, E. Fortunato, and R. Martins, Amorphous ITO thin films prepared by DC sputtering for electrochromic applications, *Thin Solid Films*, 420–421 (2002) 70–75.
- [40] F. Kurdesau, G. Khripunov, A. F. da Cunha, M. Kaelin, and A. N. Tiwari, Comparative study of ITO layers deposited by DC and RF magnetron sputtering at room temperature, *Journal of Non-Crystalline Solids*, 352 (2006) 1466–1470.
- [41] Y. S. Jung and S. S. Lee, Development of indium tin oxide film texture during DC magnetron sputtering deposition, *Journal of Crystal Growth*, 259 (2003) 343–351.

-
- [42] W. Liu and S. Cheng, Photoelectric properties of ITO thin films deposited by DC magnetron sputtering, *J. Semicond.*, 32 (2011).
- [43] C. Chityuttakan, P. Chinvetkitvanich, S. Chatraphorn, and S. Chatraphorn, Influence of deposition parameters on the quality of ITO films for photovoltaic application, *AIP Conf. Proc.*, 2091 (2019) 3.
- [44] A. S. A. C. Diniz, The effects of various annealing regimes on the microstructure and physical properties of ITO (In₂O₃:Sn) thin films deposited by electron beam evaporation for solar energy applications, *Renewable Energy*, 36 (2011) 1153–1165.
- [45] I. A. Rauf and M. G. Walls, A comparative study of microstructure (in ITO films) and techniques (CTEM and STM), *Ultramicroscopy*, 35 (1991).
- [46] A. S. A. C. Diniz, C. J. Kiely, I. Elfalla, R. D. Pilkington, and A. E. Hill, The effects of post-deposition annealing on the microstructure of electron-beam evaporated indium tin oxide thin films, *Renewable Energy*, 5, (1994)
- [47] 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* 13 (2019)102159.
- [48] I. Hamberg and C. G. Granqvist, Evaporated Sn-doped In₂O₃ films: Basic optical properties and applications to energy-efficient windows, *Journal of Applied Physics*, 60, 123–R160.
- [49] L. Zhao, Z. Zhou, H. Peng, and R. Cui, Indium tin oxide thin films by bias magnetron rf sputtering for heterojunction solar cells application, *Applied Surface Science*, 252 (2005) 385–392.
- [50] A. Ashour, M. A. Kaid, N. Z. El-Sayed, and A. A. Ibrahim, Physical properties of ZnO thin films deposited by spray pyrolysis technique, *Applied Surface Science*, 252 (2006) 7844–7848.
- [51] T. Prasada Rao and M. C. Santhoshkumar, Effect of thickness on structural, optical and electrical properties of nanostructured ZnO thin films by spray pyrolysis, *Applied Surface Science*, 255 (2009) 4579–4584.