Review on Transparent Conductive Oxides Thin Films deposited by Sol-gel spin coating technique

Olayinka Ezekiel Oladigbo*, Oluwaseun Adedokun**‡, Yekinni Kolawole Sanusi**

*Bola Ige Mechatronics Institute, Osun State College of Technology, P.M.B. 1011, Esa-Oke, Nigeria

**Department of Pure and Applied Physics, Ladoke Akintola University of Technology, P.M.B. 4000, Ogbomoso, Nigeria

(yinka.oladigbo@bimi.com.ng, oadedokun@lautech.edu.ng, yksanusi@lautech.edu.ng)

‡ Corresponding Author: Oluwaseun Adedokun, P.M.B. 4000, Ogbomoso, Nigeria, Tel: +2347031195750, oadedokun@lautech.edu.ng; adedokunoluwaseun2@gmail.com

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Abstract- The discovery of transparent conducting oxides, TCO's, has been a major breakthrough across electro-optical industries as significant durability, portability and flexibility of products have been achieved without compromising the efficiency and cost effectiveness of such product. Indium tin oxide, ITO, being the most widely used has shown appreciable performance with its high transmittance range of values coupled with high conductivity. Its toxic nature and continuous scarcity in the earth crust has however raised a concern, thereby necessitating an urgent need for adequate and effectual alternatives. With some of these alternatives already in use, the method applied in the preparation of TCO thin film is another factor that affects its performance. Sol-gel spin-coating method being one of the many deposition methods available is of great importance due to its simplicity and relatively low cost. This study therefore, seek to appraise the performance of aluminium-doped tin oxide (ATO), fluorine-doped tin oxide (FTO) and aluminium-doped zinc oxide (AZO) as sustainable alternatives to ITO with focus on spin-coated thin film.

Keywords - Sol-gel; spin coating; transparent conducting oxide; transmittance; electrical conductivity, thin films.

1. Introduction

Transparent conducting films as the name implies are essentially fabricated from optically transparent and electrically conductive materials called Transparent Conductive Oxide (TCO). TCO films are class of materials of importance because of their applications in optoelectronics and solar cells [1]. The film is a layered material deposit whose thickness is of order of a given wavelength of electromagnetic radiation.

TCO film when used as a window for light to pass through to the active material beneath, serves as an ohmic contact for carrier transport out of the photovoltaic. It also acts as a transparent carrier for surface mount devices used between laminated glass and light transmissive composites. Transparent materials possess bandgaps with energies corresponding to wavelengths which are shorter than the visible range of 380 nm to 750 nm. As such, photons with energies below the bandgap are not collected by these materials and thus visible light passes through. However, applications such as photovoltaic may require an even broader band gap to avoid unwanted absorption of the solar spectra.

TCOs have been on the bane of research in recent years just as many advances in technology are based on the application of TCO materials. The extensive studies being witnessed are due to their distinct characteristics which include: high optical transparency in the visible range, appreciable level of electrical conductivity, and high infra-red reflectivity. These properties are what made TCO an important component of modern opto-electronics. TCOs have high transmission in visible wavelength range which characterizes them as materials with a comparably low absorption of light [2]. They also have high electrical conductivity close to that of metals [2,3] and are highly flexible intermediate states with both of these characteristics.

Underlying the performance and economics of thin film components are the manufacturing techniques [4]. In an attempt to understand the efficacy of each deposition technique so as to maintain good performance of TCO thin films, some of the deposition processes that have been researched upon include: chemical vapour deposition [5], spray pyrolysis [6], pulse laser deposition [7,8], Sputtering techniques [9,10], evaporation techniques [11], sol-gel dip-coating [12] and sol-gel spin coating method [13].

Among these varieties of deposition process exists sol-gel spin coating, a technique suitable for large applications because of the easy control of the coating process from a drop of solution, followed by heat treatment in air [14]. The application of this process in commercial applications such as coating on window glass necessitate the focus of this study on thin film synthesized by this distinctive process.

Indium-doped tin oxide otherwise called Indium Tin Oxide (ITO) is the most widely used TCO [6]. This is as a result of its outstanding characteristics including strong physical and chemical interaction with absorbed species, low operating temperature and strong thermal stability in air (up to 500 ˚C) [15]. These properties make ITO good candidates for many applications in optoelectronic devices [16], infrared reflectors, antireflection coatings, thin film resistors [17], flat panel display [18], solar cells and organic light emitting diode [19].

The scarcity and high cost of indium in the earth crust has however necessitated the need and discovery of several alternatives which include: aluminium-doped zinc oxide (AZO), flourine-doped tin oxide (FTO), un-doped zinc oxide, barium stannate, etc. Many of these alternatives are being employed in several applications. Hence this review will focus on how well the so called alternatives have successfully replaced indium tin oxide (ITO) with emphasis on film synthesized through sol-gel spin coating process.

2. Applications of TCO Thin Film

Thin film technology has a wide range of applications as their structures range from simple single coating to intricate arrangement of 100 or more layers (multiple dielectric coating). Such applications include: fabrication of optical elements, such as interference splitters and polarizers; and antireflection coatings which greatly reduces the surface reflectiveness of an optical element.

From the study of indium-doped tin oxide films, it has been concluded that uniform, homogenous and highly transparent films with small grain size can be prepared by indium doping on tin oxide. The films are however highly resistive; implying that SnO_2:In coatings can be used in areas where only a moderate electronic conductivity is required [16]. Flourine-doped tin oxide, SnO_2:F, deposited by chemical vapour deposition has also found application in the making of energy efficient windows [5] while Cheng *et al*., has also reported that doping SnO_2 nanoparticles with Al, enhances the property that makes it considerable as potential materials for device fabrication. [20].

The application of thin films has furthermore extended to the following fields: optical coatings, photovoltaic, semiconductor, flat panel displays, data storage, photo-electrochemical cell (PEC), optical device, optoelectronic, ultra-capacitor, gas sensor, and warfare and space exploration.

3. Properties of TCO Thin Film

3.1. Optical Properties

The optical property of a material is defined as its interaction with electro-magnetic radiation in the visible region. The visible region spans electro-magnetic radiation with wavelengths ranging from 0.39 to 0.77 μm. As tin oxide thin film is a solar application semiconductor material, it is important to explain the behaviour of thin film to solar electromagnetic radiation. Understanding optical properties requires the study of some parameters. These parameters are: refractive index ‘n’ and extinction coefficient ‘k’ also called attenuation coefficient. The refractive index ‘n’ refers to the relative velocity of light passing through a medium: thin film in this case, while extinction coefficient ‘k’ is the measurement of how strongly a medium absorbs light at a given wavelength.

A beam of light incident on a surface is absorbed, reflected or transmitted or partially undergoes two or all of the three processes. No material is fully transparent in all optical frequencies and hence there will always be some absorption in some region of the spectra [16].

These processes also form some other parameters employed in studying optical properties. They are termed absorbance, reflectance and transmittance respectively. The reflectance ‘ρ’ of a medium is the amount of flux reflected by that medium, normalized by the amount of flux incident on it. Transmittance ‘τ’ defines the amount of flux transmitted by the medium, normalized by the amount of flux incident on the same medium; while absorbance ‘*A*’ refers to any flux not reflected or transmitted. The law of conservation of energy implies that the sum of these three parameters equals a unit.

$$\rho + \tau + \alpha = 1 \qquad (1)$$

Optical properties of thin films are not constants because they are influenced by various factors such as the substrate temperature, film thickness, crystallinity, nature and amount of dopants. These factors also affect the electrical properties of thin films [16].

Reflectance, absorbance and transmittance, among various optical properties, are of interest when attention is being focused on a thin film because they actually determine how the film behaves to incident beam of light (e.g. X-rays). These quantities are defined by ratios of radiant power values and as such they are dimensionless.

3.1.1. Reflectance

Reflectance 'ρ' is defined by the ratio of reflected radiant power to incident radiant power. For a given area 'dA' of the reflecting surface, the (differential) incident radiant power is given by the surface's irradiance 'E_e', multiplied with the size of the surface element, thus

$$dF_{e,\ incident} = E_e\ dA \qquad (2)$$

and the (differential) reflected radiant power is given by the exitance M_e, multiplied with the size of the surface element:

$$dF_{e,\ reflected} = M_e\ dA \qquad (3)$$

Thus,

$$\rho = \frac{d\Phi_{e,reflected}}{d\Phi_{e,incident}} = \frac{M_e\ \mathrm{dA}}{E_e\ \mathrm{dA}} = \frac{M_e}{E_e}$$

or

$$M_e = \rho\ E_e \qquad (4)$$

3.1.2. Absorbance

Absorbance '*A*' of a medium is defined by the ratio of absorbed radiant power to incident radiant power. As radiation passes through a medium, it is absorbed to an extent depending on the nature of the substance and its thickness. Each layer of a thin film will absorb the same fraction of the energy that reaches it thus reducing the energy of the wave by a fractional amount that is proportional to the thickness of the film. The measure of the change in energy as the wave passes through the film is called Absorption coefficient 'α'. The relationship between absorption coefficient and absorbance is given as:

$$\alpha = \frac{Absorbance}{t} \qquad (5)$$

where 'α' represents Absorption coefficient and 't' is the Film thickness. Absorption coefficient is also related to band gap energy by:

$$\alpha h\nu = A\left(h\nu - E_g\right)^{n/2} \qquad (6)$$

Where 'α' is the absorption coefficient, '$h\nu$' is the photon energy, 'E_g' is the band gap, 'A' is a constant and 'n' is equal to one for a direct-gap material and to four for an indirect-gap material.

3.1.3. Transmittance

Transmittance 'τ' of a medium is defined by the ratio of transmitted radiant power '*I*' to incident radiant power 'I_o'.

$$\tau = \frac{\mathrm{I}}{\mathrm{I}_o} \qquad (7)$$

Because the intensity of the transmitted light '*I*' is never greater than the intensity of incident light 'I_o', transmittance 'τ' is always less than 1. τ is usually multiply by 100 to obtain the percentage transmittance '%τ' which ranges from 0 to 100%.

$$\%\tau = \tau \times 100$$

Transmittance and absorbance are inversely related as

$$A = -\log_{10}\tau$$

$$A = 2 - \log_{10}\%\tau$$

and related with absorption coefficient and film thickness as

$$\alpha = \frac{\ln(1/\tau)}{t} \qquad (8)$$

where α = Absorption coefficient, τ = Transmittance and t = Film thickness

3.2. Electrical Properties

The electrical performance of TCO is another factor that characterizes this range of materials as very important. The high conductivity of TCO films results mainly from non-stoichiometry. The conduction electron in these films is supplied from donor sites associated with oxygen vacancies or excess metal ions. These donor sites can easily be created by chemical reduction. One of the major factors governing the conductivity of TCO films is the carrier mobility. The mobility of the carriers in the polycrystalline film is dependent on the mechanism by which carriers are scattered by lattice imperfection. The electrical conductivity of TCOs are somewhat inversely related to its optical transmittance.

4. Factors that affects the Properties of Thin Film

The process of making TCOs into usable products involves deposition processes and these processes involve variables such as deposition time, temperature involved in the process of heat treatment, atmospheric conditions, deposition apparatus and the source of materials being used. All these variables have their respective influence on the result of the deposition thereby necessitating countless number of researches on deposition techniques.

The pros and cons of deposited TCOs are examined through a process known as characterization. Some of the characterization methods being utilized are optical characterization using UV-Vis-IR spectroscopy; morphological characterization using atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM); electrical characterization using four point probe method; and structural characterization through X-Ray Diffraction (XRD) [13].

4.1. Nature of Substrate

TCO thin film fabrication involves the layers of materials to be coated on substrate which can be plastic, glass (quartz), metal or sapphire to achieve desirable effect. Different substrates however appeared to influence the sheet resistance of the films and as such the interaction between the substrate and the solution are important [21]. Factors such as the type, thickness, side and temperature of the substrate has a deal of effect on the performance of TCO.

An example is a TCO deposited on a glass substrate to form a thin film. This glass substrate, apart from providing a support that the oxide can grow on, has the additional benefit of blocking most infrared wavelengths greater than 2μm for most silicates, and converting it to heat in the glass layer. The thickness of the substrate also varies the distance travelled by the incident light thereby affecting the optical properties of the film.

4.2. Doping Concentration

Apart from the substrate applied during deposition process and the nature of the TCO itself, the performance of TCO can also be altered by the addition of dopant(s). Elements such as Al, In, Zn, F, Ga and Sb have been employed as dopants in the preparation of SnO_2 films [22]. Dawood et al., found that optical transmittance is closely related to doping concentration, which is associated with free electrons in indium-doped tin oxide (ITO) thin films. It was discovered that as conductivity increases, the optical transmittance of ITO thin films also increase with doping concentration. [6]. Transmittance decreases for heavily doped sample of indium doped tin oxide while light doping of about 2 at. %

In can make the transmittance to improve significantly from the un-doped one. The decrease of transmittance at higher doping concentrations may be due to the increased scattering of photons by crystal defects created by doping. [16].

As doping concentration and the deposition method applied affects transmittance, it also affects other TCO performance properties. For instance, ITO films that have different preparations that alter sheet resistance also affect the optical properties in a systematic fashion [23]. The introduction of fluorine atoms into the SnO_2 lattice could also improve the stability of SnO_2 sol as well as promotes a change in the sheet resistance. [24].

Apart from tin dioxide, the general effect of doping on other transparent conductive oxide has been of immense contribution to the success recorded in the wide application of TCO. Salam et al., for example, used doping to improve the electrical and optical properties of ZnO films prepared by sol-gel deposition techniques. It was discovered that the addition of Al^{3+} ions to Zn^{2+} sol solution increases the number of nucleation sites, resulting in higher grain boundary density. [25].

With the various effects noticed on TCO thin film due to the nature and concentration of dopants, adequate attention has to be paid to the choice of dopant and the corresponding concentration during deposition processes.

4.3. Deposition Techniques

The vast varieties of thin film materials have their deposition processes and fabrication techniques depending on the purpose for which the thin film is being prepared. For instance, energy efficient windows for architectural purpose can be made from FTO deposited by chemical vapour deposition [5] while the same FTO was deposited using sol-gel techniques in an attempt to study its electrical properties [26]. Mohagheghi et al., also reported the synthesis of Al doped SnO_2 thin films via spray pyrolysis process [27]. With the varieties of deposition techniques available, it is possible to classify them in two ways viz.: physical process and chemical process [28].

Physical method covers the deposition techniques which depend on the evaporation or ejection of the material from a source, i.e. evaporation or sputtering, whereas chemical methods depend on physical properties. Chemical methods offer many advantages compared to the physical deposition techniques, such as cost, simplicity and readily control of homogeneity and composition, combined with no need for vacuum in the deposition chamber [21]. With many of these deposition techniques showing good performance, the onus is therefore on the researcher to make a decision based on factors such as: cost; compatibility with the materials to be deposited; controllable deposition rate; moderate temperature compatibility; and the volume of materials to be deposited. This particular study, however emphasize sol-gel spin coating method.

4.3.1. Sol-Gel Spin Coating Process

The "sol-gel" process may be described as formation of an oxide network through poly-condensation reactions of a molecular precursor in a liquid. The idea behind the synthesis is to dissolve the compound in a liquid so as to bring it back as a solid in a controlled manner. The process which usually results in sinterable small particles also prevents the problems with co-precipitation.

Sol-gel synthesis may be used to prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and thin films. The technique is suitable for large applications because of the easy control of the coating process from a drop of solution, followed by heat treatment in air [14].

When compared with other techniques, the sol-gel route presents some advantages such as possibility of depositing on complex-shaped substrates, easier control of the doping level, rather inexpensive starting materials and simple equipment [12]. This fabrication method in general is cost-efficient and also provides a possibility to deposit thin films even on a large area. [29]. Wet chemical method (sol-gel technique) is a promising technique that provides a control over variety of properties, including stoichiometry, porosity, crystallinity, and morphology. [25].

Deposition by sol-gel method involves steps namely; mixing, gelation, aging, drying, and sintering. The solution is then coated on a substrate through either of dip-coating or spin-coating to obtain a thin film. While dip coating offer the advantage of having the same coat on both side of the substrate, spin coating process appears simpler and less costly.

For instance, FTO thin films were prepared by sol-gel, followed by spin coating technique. [30]. The starting materials used were tin chloride ($SnCl_4.5H_2O$), ethyl alcohol and ammonium fluoride ($NH_4.F$). Various solutions of different concentration of fluorine compound were made to obtain F:Sn ratios of 1.0, 2.5, 5.0, 7.5, 10.0 and 12.5 at %. 5 ml of 0.1N concentrated hydrochloric acid was then added into the solution as a catalyst to increase the solubility of the solute and to induce simultaneous condensation and gelation. The solutions were stirred and refluxed for one hour at 60°C, cooled in the ambient and then aged in open beakers at room temperature. The required FTO thin film was obtained by dispensing 3 ml of the resulting gel on the glass substrate mounted over the turn table, which was thereafter spanned for 3000 rpm for 10 seconds. The coating was repeated 9 times and heat treated at varying furnace temperature, ranging from 325ºC to 450ºC for about 30minutes to get different sample.

In another study of sol-gel spin-coating method, Kim *et al.*, deposited Al-coated zinc oxide thin films on quartz substrates using sol-gel spin-coating method. [31]. Zinc acetate dehydrate [$Zn(CH_3COO)_2\cdot 2H_2O$] was used as a starting material; monoethanolamine [C_2H_7NO] and 2-methoxyethanol [$CH_3OCH_2CH_2OH$] were used as the stabilizer and solvent, respectively. The dopant source was aluminium nitrate [$Al(NO_3)_2\cdot 9H_2O$]. The molar ratio of dopant in the starting solution was varied to give a [Al:Zn] ratio of 1-3 at.%. The resultant solution was stirred at 60ºC for 2 hours to yield a clear and homogeneous solution followed by aging at room temperature for a period of 24hours. For deposition, the solution was dropped on the quartz substrates, which were rotated at 3000 rpm for 20 seconds and pre-heated at 300ºC for 10 minutes to evaporated the solvent and remove the organic residuals. The AZO films were cooled at a rate of 5ºC/min to avoid cracks before repeating the spin coating and pre-heating procedure for five times. The obtained layers of AZO thin film were then heated in a furnace in air atmosphere at 550ºC for 60 minutes.

Just like the discussed sol-gel preparation methods for FTO and AZO, Jafan et al., also prepared ITO thin films via sol-gel spin coating technique, using indium nitrate hydrate ($In(NO_3)_3.H_2O$, 99.99 %) and tin chloride anhydrate ($SnCl_4$ 98 %) as inorganic reactants, polyvinyl alcohol as polymerizing agent and binding material, double-distilled water, absolute ethanol and acetyl acetone (98%) as solvents and hydrochloric acid (37 %) as dispersing solvent. [32].

For the purpose of the sol, 1.1 g polyvinyl alcohol (PVA) was dissolved in 30 ml double-distilled water and the resultant solution was refluxed at 80ºC for 3hours. $In(NO_3)_3.H_2O$ was dissolved in double-distilled water, and the resultant solution was refluxed at 60ºC for 30 minutes. The required amount of $SnCl_4$ (0.025 mol (0.29 mL) was then dissolved in 5 mL absolute ethanol and 5 mL acetyl acetone and stirred for 30 minutes to obtained an initial molar ratio of 9:1 for In:Sn. The two obtained solutions A and B were separately added to solution 1 and refluxed at 60ºC for another 2hours (pH 2.3) under stirring. Several drops of hydrochloric acid were added to the solution to prevent hydrolyzation of $SnCl_4$ during a refluxing until a transparent ITO sol was achieved (pH 1.6). The obtained sol was finally aged for 2 days at room temperature, spins coated at 2,500 rpm for 20seconds and heated at 150ºC for 20minutes between each deposition until the desired thickness of film was achieved.

One of the most important factors in sol-gel spin coating is repeatability. Subtle variations in the parameters that define the spin process can result in drastic variations in the coated film. A typical spin process, following the preparation of the coating solution, consists of a *dispense step* in which the resin fluid is deposited onto the substrate surface, a *high speed spin step* to thin the fluid, and a *drying step* to eliminate excess solvents from the resulting film.

4.4. Heat Treatment

The process of deposition of thin film often results in some defects in the crystal of the film which consequently alter some of the properties of the film. This defects in the crystals can be corrected by heat treatment – the process of changing the structures of a specimen by heating it to a predetermined temperature for a prescribed period of time and cooling it at a prescribed rate. This improves its physical morphology and widens its applications thereby improving the structure, because the atoms must have rearranged themselves in a regular manner giving rise to better specified properties.

The majority of the preparation methods currently involved a relatively high substrate temperature (≥300˚C) in order to obtain thin films with a reasonably good conductivity. This requirement may be restrictive for some applications, for example, for flexible electro-optical devices, hetero-junction solar cells, and photovoltaic devices based on amorphous silicon which may seriously deteriorate at elevated temperature [17].

Yildirim *et al.*, investigated annealing effects on structural, electrical and optical properties of CuS, CuZnS and ZnS thin films. It was observed that the increasing annealing temperature decreases the optical band gap and the annealed films have more resistance than the grown films. [33].

Heat treatment processes are of various kinds viz.: annealing; normalization, hardening, and tempering. The most suitable heat treatment method for TCO thin film is *annealing*. Hardening and tempering will further disorganize the crystal rather than improve it.

Annealing involves heating a material to above its recrystallization temperature, maintaining a suitable temperature long enough for the transformation to take place, and then cooling slowly. In annealing, atoms migrate in the crystal lattice and the number of dislocations decreases, leading to change in ductility and hardness. The crystallinity or grain size of a film is not altered due to thermal annealing [21].

Increasing the heat treatment temperature and annealing in reducing atmospheres significantly improves the conductivity of the films. The increase in conductivity is achieved by removing oxygen interstitials. Annealing at higher temperatures could, thereby, increase the conductivity by strengthening the physical contact between the layers [21].

4.5. Coating Layers

The number of coating layers directly affects the thickness of the film. Thicker layer of coated film contains a relative higher carrier concentration but the consequently accumulated higher internal stress might crack the film and retard the carrier mobility. For many TCO, electrical resistivity usually decreases with increase in thickness until a certain critical thickness is reached. Other properties such as structural and optical properties also follow this trend – changing the course of response to change in film thickness at a critical thickness.

5. Performance Evaluation of TCO Thin Films

After the deposition of TCO, it is important we evaluate its performance. This evaluation is carried out through a process called characterization which can be optical, morphological, structural or electrical depending on the property under study. Below is the summary of optical and electrical performance of various TCO understudy in this review.

5.1. Optical Characteristics

The optical characteristics of TCO are one of the major properties that brought about the importance attached to this category of material both in the research and application world. For any thin film to be qualified for a practical application, it must demonstrate a good optical attributes such as Reflectance, Absorbance and Transmittance. Flourine-doped tin oxide (FTO) obtained by sol-gel spin coating method appears to show good reproducibility and excellent opto-electronic properties at a heat treatment temperature of 375ºC.

For instance, Subramanian *et al.* reported a FTO thin film deposited at varying temperature between 350ºC and 400ºC to show an increase in average transmittance value up to 94.4% at 375ºC and decreases to low value of 67.77% at 400ºC [30]. The increase in transmittance value was attributed to the decrease in absorption, diffuse and multiple reflection caused by fall in grain size, increase in surface smoothness, and uniformity in film thickness whereas the decrease observed as temperature increases further from 375ºC to 400ºC was attributed to the increase in scattering and perturbation effect due to large grain size and crystal aggregate. The refractive index observed at wavelength range of 325 to 700nm was found to vary between 1.422 and 2.011 with the lowest value observed for the film treated at temperature 375ºC at wavelength 550nm. The low refractive index correlates with the high optical transmittance due to low crystallite size and low absorption coefficient of the film. These observation undoubtedly portray FTO as a potential n-type material for solar cell applications.

Comparing the optical characteristics of FTO obtained by Subramanian *et al*., with the result obtained for ITO thin film deposited by sol-gel spin coating as reported by Jafan *et al.*, the latter thin film shows a maximum transmittance of more than 90%; a slight increase from the average transmittance value obtained for another ITO thin film deposited by jet nebulizer spray pyrolysis technique, which was found to be in the range of 82-87%. [32]. The increase in transmittance value as reported, can be linked with the introduction of dopant; if compared to pure indium oxide film with 77% transmittance. [34]. Jafan *et al* also reported a variation in transmittance value with change in the number of coating layers while the absorption spectra of the ITO films gave a broad band at around 310nm which is due to excitonic transition of the ITO nanostructures from the valence band to the conduction band. [32].

In another comparative study as shown in Fig.1, a plot of transmittance versus wavelength compares the transmittance value of undoped SnO_2 and various concentrations of aluminium doping on SnO_2. The plot shows an average of 80% transmittance in the visible region (wavelength range of 400nm to 2600nm) with the transparency decreasing with increase of Al doping in the films [35]. With the increase in the aluminum doping also comes an increase in the direct bandgap values of the films which is however related with the decrease of particle size.

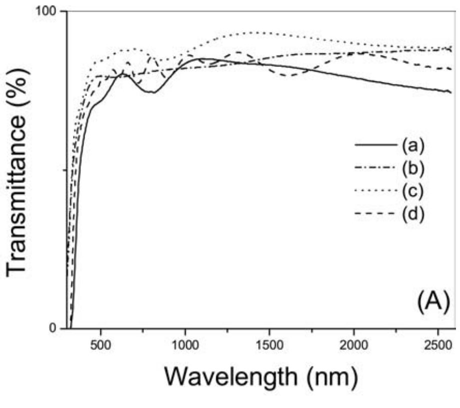

Figure 1. Transmittance (T) spectra of SnO_2 thin film for (a) 2.31%, (b) 8.16%, (c) 12.05% and (d) 18.56% of Al doped. [35].

The high transparency observed in the foregoing: FTO [30], ITO [32] and [34] and ATO [35], is also found in aluminium-doped zinc oxide (AZO) film as reported by Suganya *et al.*, The transmittance value of the film varies between 91 and 98% depending on the concentration of aluminium dopant as shown in Fig.2. In contrast, undoped ZnO film shows a high transmittance value of 98% while the value varies with increase in doping level to attain a lower value of 91% for a doping concentration of 2 at%. This decrease in the visible transmittance may be due to crystal defects generated by the incorporation of Al into the ZnO lattice. [36]. The transmittance in the near infrared region (NIR) is however better for the AZO films with Al doping level of 1.5 at.% when compared with other films. The effect of aluminium doping on zinc oxide was also observed by Kim *et al.* to be similar as shown in Fig.3. Kim *et al.*, found the optical transmittance of the film to clearly exhibit a shift in band edge with the variation in Al concentrations resulting in a value of 80% in the visible region. [31].

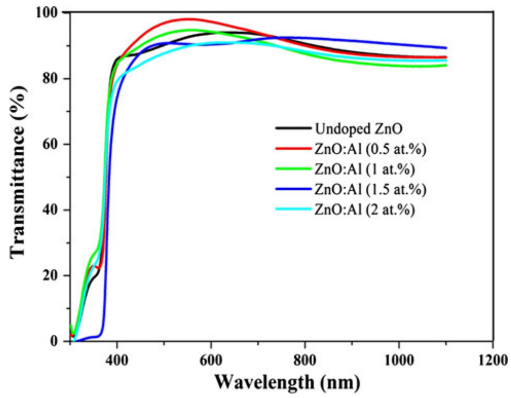

Figure 2. Transmission spectra of ZnO:Al thin films [36].

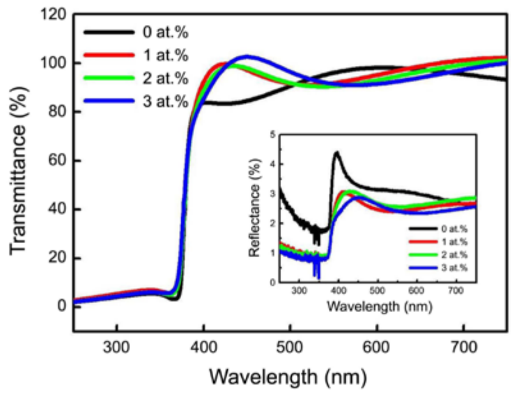

Figure 3: Optical transmittance of the AZO thin films with different Al concentrations and inset shows the reflectance of the AZO thin films. [31].

5.2. *Electrical Characteristics*

Photovoltaic, optoelectronic and other electrical applications of transparent conductive oxide (TCO) is based on its electrical properties and so electrical characterization of this material is also of high importance. The measure of electrical conductivity or resistivity of TCO varies to a large extent with the addition of impurities. Subramanian *et al* found the doping of tin-dioxide with fluorine to result in resistivity decrease with a rise in n-type conductivity which partially depends on the heat treatment temperature. At lower temperatures (325ºC to 375ºC), chemisorption mechanism predominates and the grain boundary scattering becomes low which reduces the film resistivity and increase carrier concentration whereas at higher temperatures (above 375ºC), oxygen desorption phenomena becomes predominant with higher grain boundary scattering, which increases the film resistivity while decreasing its carrier concentration. The sheet resistance and resistivity for the FTO thin film heat treated at 375ºC was found to be minimum with the value 40 Ω/cm^2 and 7.4 x 10^{-3} Ω.cm respectively. Similar observation of variation in resistivity and conductivity with changes in doping concentration was also made by [34]. Thirumoorthi *et al* observed that the resistivity of ITO thin film decreased to a minimum value of 3.9×10^{-4} Ω.cm; while the carrier concentration increased as well as mobility increasing with increase in Sn concentration. Apart from variation in doping concentration, TCOs electrical properties also depends on the heat treatment temperature. [37]. Chan *et al* reported that a higher annealing temperature leads to a decrease in the sheet resistance of ultrathin ITO films; which is due to the fact that the annealing treatment rearranges the structure of the ITO films, causing more Sn ions to become an effective dopant. The higher annealing temperature exceeding 20ºC caused a replacement of In^{3+} by Sn^{2+}. Similarly, the rise in conductivity with an increase in temperature was also observed in aluminium-doped tin oxide (ATO) thin film, just like other semiconductors. [35].

Ahmed *et al* also noted variation in electrical conductivity with increase in aluminum doping; with values lying in the range of 0.21 Scm^{-1} to 1.36 Scm^{-1} corresponding to a doping concentration of 2.31–18.56%. The decrease was found to be due to decrease in mobility resulting from the decrease of grain size with increase of Al doping. The conductivity however increased with increase in aluminium doping starting from a critical % of Al doping (12.05%); due to the generation of more free-carrier hole, which dominate the effect of mobility due to particle size decrement.

Similarly for aluminium-doped zinc oxide film, the grain boundary resistance and hence conductivity are also found to vary against the doping concentration of Al. [36]. It was observed that the grain boundary resistance values of all the Al doped ZnO films are lesser than that of bare undoped ZnO, though the doping content was very low as 0.5 at.%. Increase in the doping concentration of Al above 0.5 at.% has led to both increase and decrease of grain boundary resistance but the values are found to be lower than that of undoped ZnO. This was attributed to the changes in the number of substitutions of Al^{3+} ions in the Zn^{2+} sites and also the number of free electrons generated in ZnO.

Therefore, the overall change observed in the electrical properties of TCO films with changes in dopant concentration is a desirable phenomenon for transparent conducting oxide.

6. Conclusion

This study has reviewed the performance of various TCOs in order to establish the viability of the alternatives available to indium-doped tin oxide (ITO). Pure tin oxide (SnO_2), fluorine-doped tin oxide (FTO), aluminium-doped tin oxide (ATO) and aluminium-doped zinc oxide (AZO) were some of the TCO studied; in comparison to the commonly used ITO. The optical and electrical characteristics of these oxides were observed and compared against indium based thin film. All the alternatives shows good transmittance value, each showing an average value above 80% which can be taken to be comparatively good. They also demonstrate good electrical properties comparable to the ITO. The closeness of these physical properties to that of Indium doped oxides points to a conclusion that several alternatives can be explored, notwithstanding the non-availability of indium compound in the earth crust. Hence, having observed efficient performance for the various spin-coated TCO thin films studied other methods of deposition is recommended for further studies with additional aim of discovering more viable alternatives to ITO without having to depend on the few TCOs reviewed so far.

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