

Optimization of the Characteristics of Tin Oxide (AlSnO₂) Thin Film Doped with Aluminum

Emmanuel Ifeanyi Ugwu^{1,2*}; Usman Rilwan¹; Idu Hyacinth Kevin²; and
Huhammad Ja'afar¹

¹Department of Physics Nigerian Army University, Biu, Nigeria.

²Department of Physics, Taraba State University, Jalingo, Nigeria.

E-mail: ugwuei2@gmail.com*
ugwuei@yahoo.com

ABSTRACT

The study of the optimization of aluminum doped Tin Oxide thin film deposited using chemical bath deposition technique, was embarked on this work where the influence of the aluminum dopant on as-deposited SnO₂ thin film was analyzed in order to ascertain its effect on the characteristic properties especially as regards the optical and solid state properties of the material because of the peculiar nature of Tin Oxide thin film as a well-known perovskite oxide based thin film whose properties are of great interest due to its applications in various areas of optoelectronics and also its amenability for optimization in order to achieve the effective utilization in the areas of solar energy harnessin and other electronic device applications.

The properties of interest were analyzed using scanning electron microscope (SEM), X-ray diffraction machine, Shidmazu UV-VIS 1800 and four-point probe. While the other aspect such as solid-state properties, optical conductivities were computed using well known formulas using data from the optical properties. The electrical properties were determined using four-point probe and then the effect of aluminum dopant in each of these properties were analyzed.

(Keywords: *optimization, tin oxide, doping, semiconductors, characteristics, influence, aluminum, chemical bath deposition, analysis*)

INTRODUCTION

SnO₂ thin film is a material that is well known semiconductor based material that has a lot of applications as it belongs to the family of Perovskite oxide based thin film [1-5] and

because of its unique characteristics when it comes to its application especially in terms of next generation of optoelectronic devices that operate in the short (ultra-violet) wavelength region This is due to its wide energy band gap in the near UV spectral region [6-10] coupled with a large free -exciton binding energy such that the excitonic emission processes persist even at above room temperature [11,12].

It has a unique characteristic as it crystallizes in the Wurtzites structure which is similar manner to GaN material though in contrast to GaN it is more common and cheaply available as large bulk single crystal [11], but unlike GaN which is usually not easily grown because it is normally grown on sapphire, with a large lattice mismatch of ~16%. This factor creates room for an exceedingly high concentration of extended defects that ranges within (106–109 cm⁻²).

Just like ZnO counterpart that is grown with epitaxial technique, SnO₂ films grown on substrate results in pure thin film layers of the material with reduced concentration but with an extended defects and as such it consequently performs better in electronic and photonic devices when compared to GaN and some other oxide based thin films. Another added advantage which it has over GaN is that it is amenable to wet chemical etching like ZnO counterpart. Therefore because of its unique properties there has been interest in the study and characterization of the SnO₂ right from early days of semiconductor electronic [13-15].

It has similar characteristics to some of the group II-VII semiconductors, though its use in semiconductor electronic devices is being restricted due to lack of control with regards its conductivities poses a problem that is yet to be

resolved by researchers. Therefore, it has been the interest of material scientists to devise a means of reducing the defects to the barest minimum within the range that may have less significant effect on the electrical and optical properties of the material [17].

Since SnO₂ has a wide application as it exhibits a Perovskite oxide based thin film characteristics as well as transparent conducting oxide thin film (TCO) there has been a veracious quest for research to develop the thin film that would yield appreciable results for the past decade. Also in this recent time, there has been in continuation of the same quest with a worldwide desire due to the discovery of its good amenability in solar energy as well [18-20].

Therefore, different deposition techniques are being utilized for the fabrication of the thin film [21] such as RF sputtering, photochemical deposition, dip coating, sol-gel processes, chemical vapor deposition, spray pyrolysis, and spin-coating [22-25]. Research is also progressing in processes that involve use of various precursors in order to realize the achievement of an optimal SnO₂ thin film that can be capable of realizing the application associated to the thin film.

However, in our own case, we intend to dope SnO₂ with varied concentration of aluminum as a dopant coupled the use of chemical bath deposition technique which is more simple and reproducible than other methods for growing the thin film in order to assess the dopant role in optimization of those properties such as optical and solid state property characteristics of the SnO₂ thin film which are the determinant of its amenability to the enumerated applications of the thin film.

MATERIAL AND METHOD

The thin films of Tin Oxide (AlSnO₂) were deposited onto the chemically cleaned glass substrates using pure chemicals by Chemical Bath Deposition (CBD) process. The chemical bath was prepared by sequential addition of 0.5M of Tin Chloride Di-hydrate (SnCl₂.2H₂O), 0.5M of Sodium Hydroxide (NaOH) to neutralize the acidity of the solution, 0.5M of Triethanolamine (TEA) (C₆H₁₅NO₃) into three different baths (T, AT₁ and AT₂).

Aluminum Chloride (AlCl₃) which is the source of Aluminum (Al) serving as the doping agent was added into the second and third bath (AT₁ and AT₂) varying from 0.2M to 0.4M. Distilled water was added until the volume of the solution reached 70ml and the pH of the solution was measured using digital pH meter and was kept constant at 9.

At a specific temperature, the bath solution was heated and then thoroughly stirred on a magnetic stirrer for a specific amount of time to aid homogeneity. The cleaned and dried substrates were clamped vertically using retort stand, clipped, and then lowered into the three beakers (100ml) containing the CBD solution where the Aluminum foil was used as a cover at the top of each beaker in order to prevent dust or unwanted particles from entering the solution.

The deposition time was kept constant throughout for each of the samples labelled; T, AT₁ and AT₂. After that the three samples were taken out of the bath solution, rinsed in distilled water, and dried in an open furnace at moderate temperature at a specific time to remove residual water content and other possible adsorbed surface impurities.

A Shimadzu UV-VIS 1800 double beam spectrophotometer was used to determine the optical characterization while a four-point probe was used for the electrical properties and a SEM for the morphological properties. The solid state and optical conductivity were computed from the data obtained from the optical properties using the appropriate equations, respectively.

RESULTS AND DISCUSSION

The morphological features of both as-deposited and annealed AlSnO₂ Tin Oxide thin film were presented in Figures 1 to 3 as obtained from SEM indicates that the morphological features of the material the influence of the of the aluminum dopant on SnO₂ coarseness as observed in the morphological features is clear. This is also seen in Table 1 showing the grain size and other lattice parameters such as microstructure, dislocation density for both as-deposited and aluminum doped SnO₂ thin film.

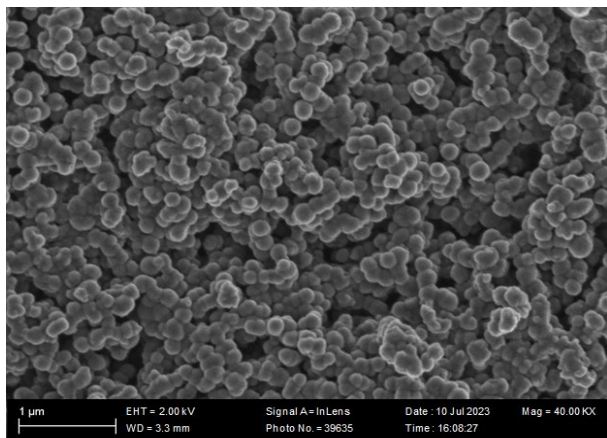


Figure 1: SEM Image of the Sample of Pure SnO₂ Thin Film (T).

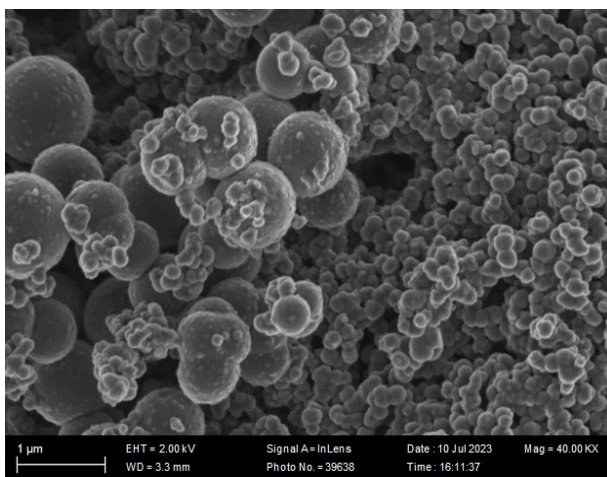


Figure 2: SEM Image of the Sample of Al-Doped SnO₂ Thin Film (AT₁) at 0.2M.

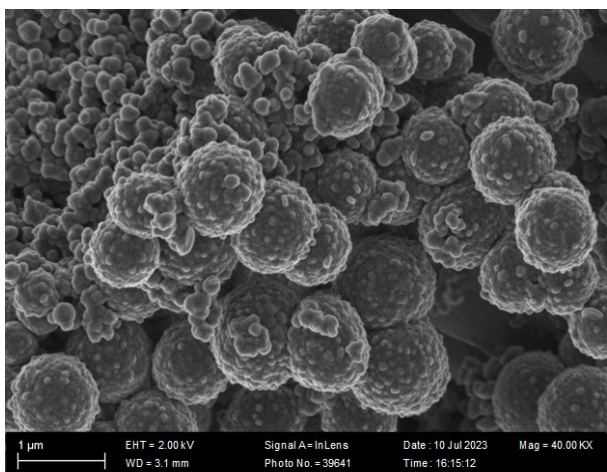


Figure 3: SEM image of the sample of Al-doped SnO₂ Thin Film (AT₂) at 0.4M.

Table 1: Energy Band Gap for the three Samples of SnO₂ Thin Films.

Samples	Energy Band gap (eV)
T	2.70
T ₁	1.87
T ₂	1.40

The absorbance spectra of AlSnO₂ thin film for the three samples are shown in the plot of absorbance against wavelength in Figure 4 where it is seen that the absorption strength is generally dependent on the dopant concentration.

It is noticed that sample T₂ has the highest absorption power across the wavelength region and as observed, SnO₂ thin film as deposited showed a sharp absorption power at wavelength below 380nm but after the addition of Al, the absorption profile changed with shifted in the absorption spectra of the film while the transmittance spectra the for three samples are shown in the plot of transmittance against wavelength (Figure 5) which exhibited high transmittance values greater than 60% in the visible region.

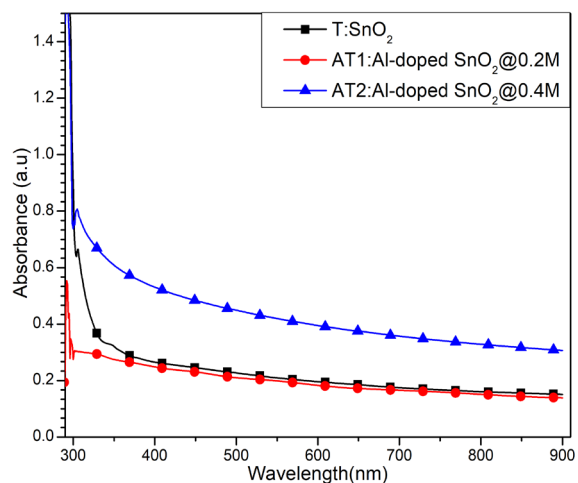


Figure 4: Absorbance as a Function of Wavelength for the three Samples.

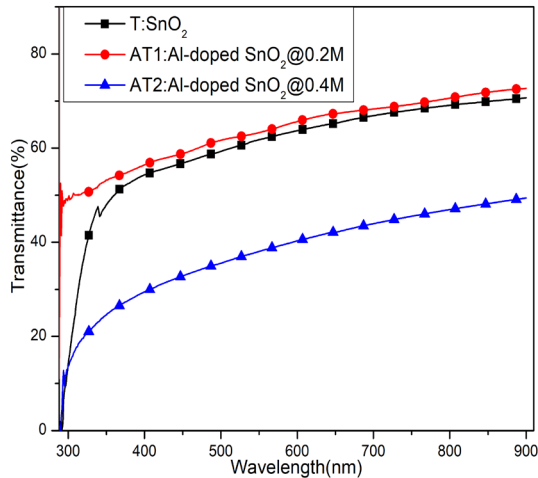


Figure 5: The Transmission Spectra as a Function of Wavelength for the three Samples.

Absorption coefficient or edge of the films (α) as displayed in Figure 6 as indicated in the value shows that α is considerably high for all the samples up to 340nm. The energy band gap for the three samples T, T₁ and T₂ of the AlSnO₂ thin films was calculated and estimated using the Tauc plot as displayed in Figure 7 and based on the estimation, the band gaps of the samples were obtained by extrapolating the linear portion of the plot $(\alpha h\nu)^2$ against the photon energy, $h\nu$ considered when $(\alpha h\nu)^2 = 0$.

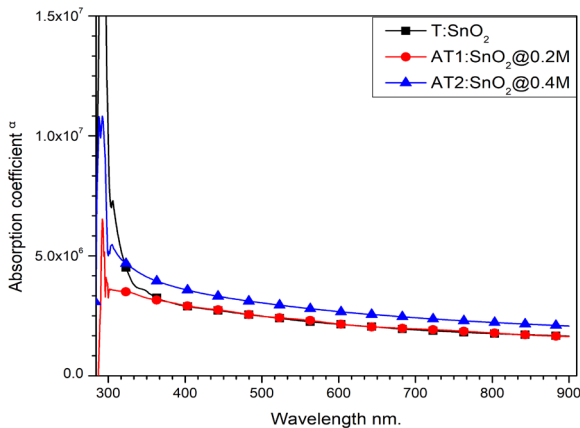


Figure 6: The Plot of Absorption Coefficient of the three Samples against Wavelength.

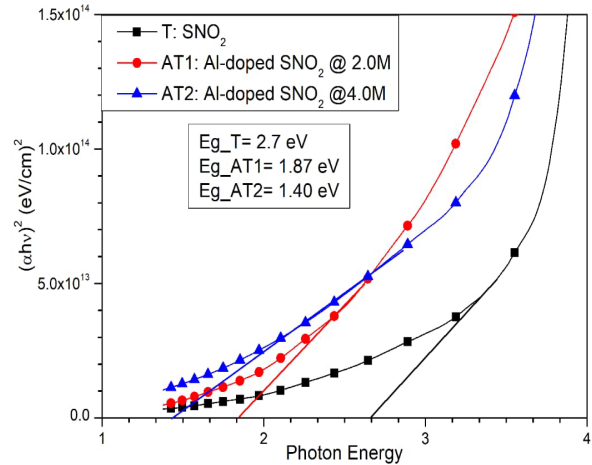


Figure 7: The plot of $(\alpha h\nu)^2$ as a Function of Photon Energy for the three Samples,

The values of energy band gaps were shown in Figure 7 to be 2.7eV, 1.87eV and 1.40eV respectively for the samples T, T₁ and T₂. It is observed that the thin films with lower concentration of dopant as in T and T₁ has a wider band gap as compared to T₂ which has a higher concentration of the dopant thereby agreeing the literature that there are some factor that may affect the band gap of SnO₂ doping or annealing the material at a given temperature [21].

The value of the absorption coefficient α however seems to agree with the trend of the absorbance of the thin film which decreases with increase in the wavelength as shown in Figures 4 and 6. Coming on side of the solid state properties, it appears as seen on the graph of the index of refraction that the refractive index for the three samples lies close within 0.20 and 0.22 as in figure 8, while the real and complex dielectric constant as in Figures 9 and 10 indicates that real dielectric has higher value within the UV and visible region and slightly decreases within the near infrared region of the electromagnetic wave spectrum, but the graphs of the extinction coefficient and optical conductivity followed the same trend as in Figures 11 and 12.

The results of the electrical behavior of the material as obtained from four point probe shows that current voltage relationship appears linear manifesting a slight change as the dopant varies as shown in Figures 13, 14 and 15.

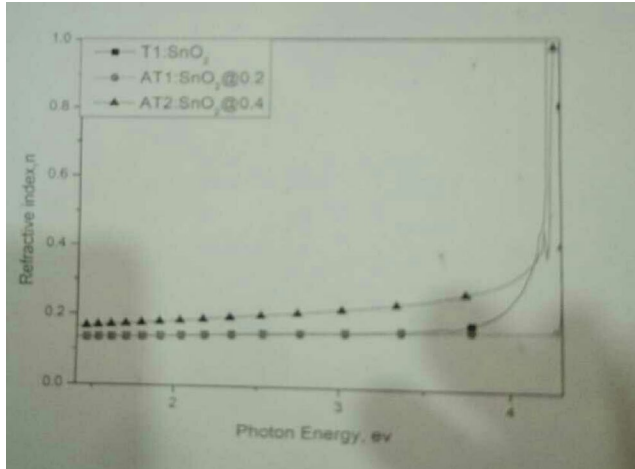


Figure.8: Index of Refraction as a Function of Wavelength.

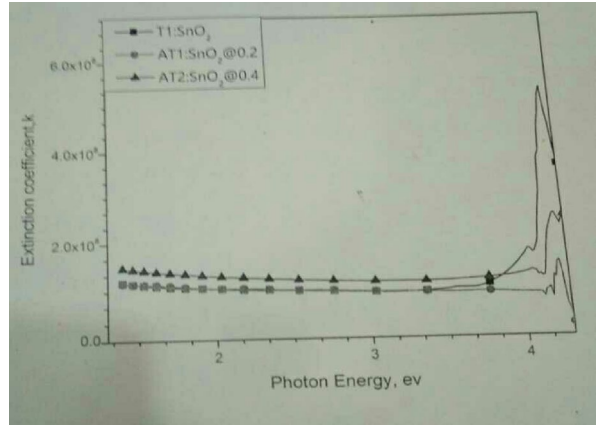


Figure 11: Extinction Coefficient, k , as a Function of Photon Energy.

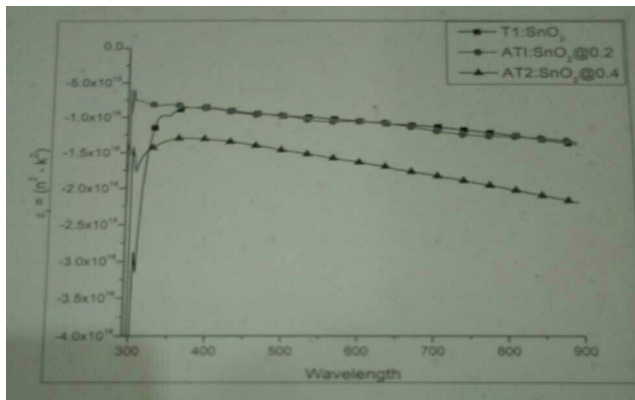


Figure 9: Real Dielectric Constant against Wavelength.

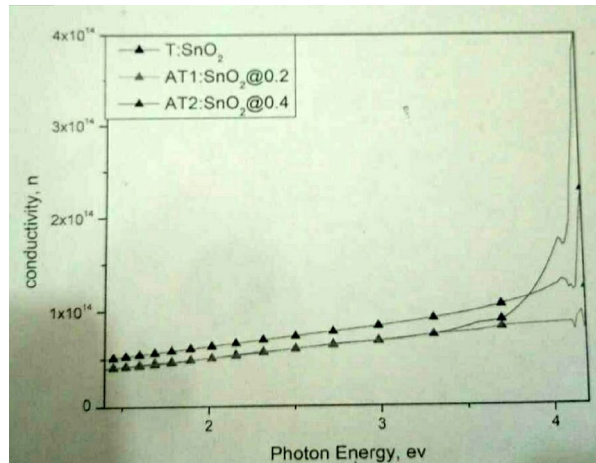


Figure12: Optical Conductivity against Photon Energy.

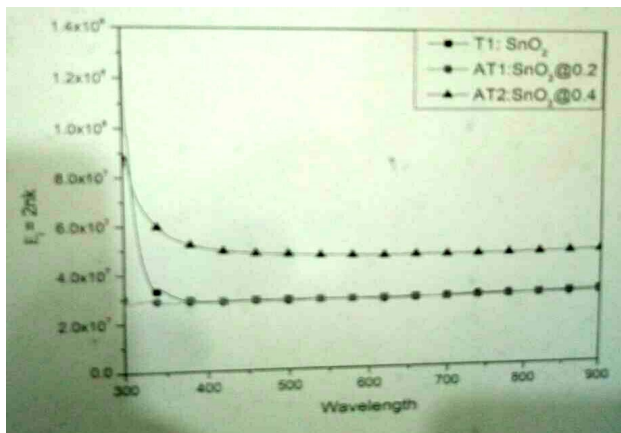


Figure 10: Complex Dielectric Constant as a Function of Wavelength.

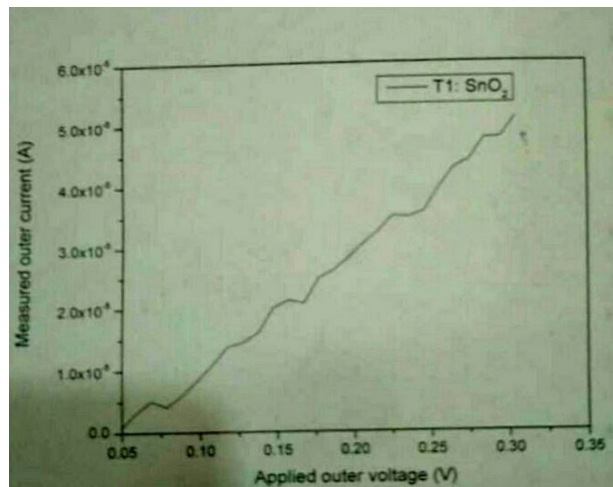


Figure 13: Current as a Function of Voltage for As-Deposited SnO₂.

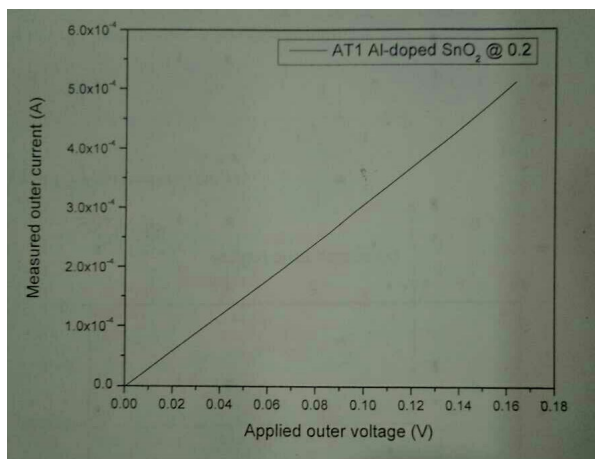


Figure 14: Current as a Function of Voltage for T₁.

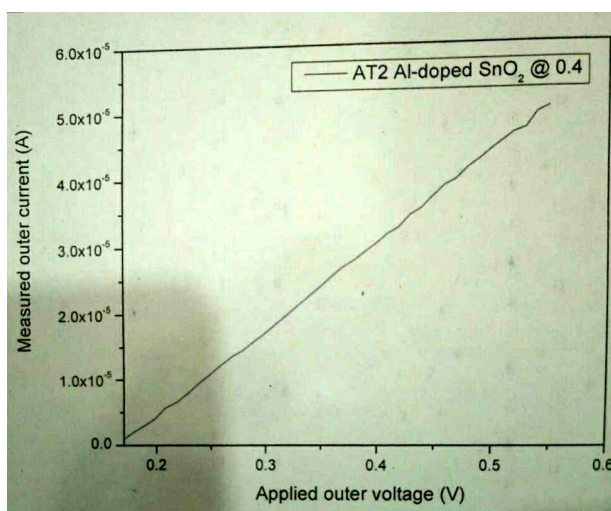


Figure 15: Current as a Function of Voltage for T₂.

CONCLUSION

AlSnO₂ thin films has been successfully developed using varied concentrations of aluminum dopant for chemical bath deposition technique was used. Here, consideration and attention was given to the influence of the aluminum dopant on optimization of the characteristics properties of the films as regards the optical and solid state characteristics for which the graphs of these characteristics were either plotted function of wavelength and in some cases as a function of photon energy.

The influence of the dopant on the optical and solid state properties of the dopant on SnO₂ thin film were critically analyzed and it was observed that there were clear indications of slight

variations in some of these properties as the concentration of the dopant is varied especially as showcased in the energy band gap where the value of band gap became narrower with increase in the concentration of the aluminum which suggest that the thin film characteristics were optimized by the dopant element.

REFERENCES

1. Ugwu, E.I. 2018. 'The Effect of Annealing, Doping on the Properties and Functionality of Zinc Oxide Thin Film; Review.' In: *Sol-Gel Method-Design and Synthesis of New Materials with Interesting Physical, Chemical and Biological Properties*. IntechOpen.Chapter2.
2. He, W.W. and C.H. Ye. 2015. "Flexible Transparent Conductive Films on the Basis of Ag Nanowires: Design and Applications: A Review". *J Mater Sci Technol*. 31: 581–588.
3. Samavat, F., P.T. Ahmad, F. Mahmoodi, M.F. Samavat, and M.H. Tavakoli. 2012. "The Effect of Annealing on the Size and Morphology of Palladium Nanoparticle". *Am J Cond Mat Phys*. 2(3): 73-6.
4. Lin, J.J. and Z.Q. Li. 2014. "Electronic Conduction Properties of Indium Tin Oxide: Single-Particle and Many-Body Transport". *J Phys: Condens Matter*. 26: 343201.
5. Shan, F.K. and Y.S. Yu. 2005. "Band Gap Energy of Pure and Al-doped ZnO Thin Films". *Journal of the European Ceramic Society*. 24: 1869-1872.
6. Kim, Y.S., W.P. Tai, and S.J. Shu. 2005. "Effect of Preheating Temperature on Structural and Optical Properties of ZnO Thin Films by Sol-Gel Process". *Thin Solid Films*. 491: 54-60.
7. Pogrebniak, A.D. N.Y. Jamil, and A.K.M. Muhammed. 2011. "Structural and Optical Properties of ZnO Prepared by CVD before and after Annealing". *Metallofiz. Noveishie Tekhnol*. 33: 235-241.
8. Alaeddin, A., I. Rachidi, F. Bahsoun, Y. Mohanna, O. Bazzi and F. El haji Hassan. 2009. "Influence of Al Dopant on the Optical and Electrical Properties of ZnO Thin Films Prepared by Spray Pyrolysis". *Journal of Applied Sciences*. 9(8): 1588-1592.
9. Leenheer, A., J. Perkins, M. van Hest J. Berry. R. O'Hayre, and D. Ginley. 2008. "General Mobility and Carrier Concentration Relationship in Transparent Amorphous Indium Zinc Oxide Films". *Phys Rev B*. 77: 115215.

10. Bhosle V., A. Tiwari, and J. Narayan. 2006. "Metallic Conductivity and Metal Semiconductor Transition in Ga-Doped ZnO". *Appl Phys Lett*. 88: 032106.
11. Kim, D., I. Yun, and H. Kim. 2010. "Fabrication of Rough Al Doped ZnO Films Deposited by Low Pressure Chemical Vapor Deposition for High Efficiency Thin Film Solar Cells". *Cur. Appl. Phys.* 10: S459–62.
12. Steinhauser, J., S. Faÿ, N. Oliveira, E. Vallat-Sauvain, and C. Ballif. 2007. "Transition between Grain Boundary and Intragrain Scattering Transport Mechanisms in Boron-Doped Zinc Oxide Thin Films". *Appl Phys Lett*. 90:142107.
13. Jimenez-Gonzalez, A.E., J.A Soto-Ureta, and R. Suarez-Para. 1998. "Optical and Electrical Characteristics of Aluminum Doped ZnO Thin Films Prepared by Sol Gel Techniques". *Journal of Crystal Growth*. 192: 430-438.
14. Nworie, S.I. and E.I. Ugwu. 2020. "Study of the Optical Characteristics of Aluminum Doped ZnO Thin Film". *Pacific Journal of Science and Technology*. 21(1): 40-44.
15. Ugwu, E.I., S.I. Nworie. and N.E.J. Omaghali. 2021. "Influence of Variation of Aluminium Doping Concentration and Annealing Temperature on the Structural, Morphological and Dielectric Constant of ZnO Thin Film Grown Using Chemical Bath Deposition Process". *Applied Materials Science & Engineering Research*. 5(2): 15 –20. www.opastonline.com
16. Ugwu. E.I., U. Rilwan, I.A. Danasabe, and R.A. Busari. 2022. "Study of Transparent Conducting Oxide (TCO) Based Thin Films Grown by Different Growth Techniques". *Review. J. App Mat Sci & Eng Res*. 6(2):12 -22.
17. Ugwu, E.I. 2018. "The Effect of Annealing, Doping on the Properties and Functionality of Zinc Oxide Thin Film; Review". In: *Sol-Gel Method-Design and Synthesis of New Materials with Interesting Physical, Chemical and Biological Properties*. IntechOpen. Chapter 2.
18. Ugwu, E.I. and H.K. Idu. 2023. "A Brief Review on Prospect and Applicability of Perovskite Oxide based Nonmaterial". *Nanomed Nanotechnolj*. 8(4): 000279.
19. Igwe, H.U., O.E. Ekpe, and E.I. Ugwu. 2010. "Effects of Thermal Annealing on the Optical Properties of Titanium Oxide Thin Films Prepared by Chemical Bath Deposition Technique". *Research Journal of Applied Science, Engineering and Technology*. 2(5): 447-451.
20. Shan, F.K. and Y.S. Yu. 2005. "Band Gap Energy of Pure and Aldoped ZnO Thin Films". *Journal of the European Ceramic Society*. 24: 1869-1872.
21. Nwanna, E.C., P.E. Imoisili, and T.C. Jen. 2022. "Synthesis and Characterization of SnO₂ Thin Films using Metalorganic Precursors". *Journal of King Saud University – Science*. 34: 102123. <http://creativecommons.org/licenses/by-nc-nd/4.0/>
22. Nwanna, E.C., P.E. Imoisili, T.C. Jen. 2020. "Fabrication and Synthesis of SnO_x Thin Films: A Review". *Int. J. Adv. Manuf. Technol*. 111(9–10): 2809–2831. <https://doi.org/10.1007/s00170-020-06223-8>.
23. Kim, S.J., S. Yoon, and H.J. Kim. 2014. "Review of Solution-Processed Oxide Thin Film Transistors". *Jpn. J. Appl. Phys*. 53 (2S): 02BA02
24. Gu, F., S.F. Wang, M.K. Lü, X.F. Cheng, S.W. Liu, G.J. Zhou, X.U. Dong, and D.R. Yuan. 2004. "Luminescence of SnO₂ Thin Films Prepared by Spin-Coating Method". *J. Cryst. Growth*. 262(1–2): 182–185. <https://doi.org/10.1016/j.jcrysgro.2003.10.028>
25. Kolmakov, A., Y. Zhang, G. Cheng, and M. Moskovits. 2003. "Detection of CO and O₂ using Tin Oxide Nanowire Sensors". *Adv. Mater*. 15(12): 997–1000. <https://doi.org/10.1002/adma.200304889>

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