Uniport Journal of Engineering and Scientific Research (UJESR)

Vol. 6, Issue 2, 2022, Page 204-212
ISSN: 2616-1192

(www.ujesr.org)



# Optical and Electrical Characterization of Synthesized Lead Zinc Sulphide Nanostructured Thin Films

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**Abstract**
*The effects of zinc concentrations on the optical and electrical properties of lead zinc sulphide (PZS) thin films have been described. Chemical bath deposition (CBD) method was used to deposit the ternary material on glass substrates. In the present work, the PZS films were grown using lead nitrate, Zinc (ll) Chloride and Thiourea as sources of Pb, Zn and S respectively. The transmittance was found to be high in the near infrared regions of the electromagnetic radiation and, also increase with zinc concentrations. The band gap energy was found to increase from 1.34 to 2.11 eV with zinc concentrations. The study indicates that CBD is an excellent method in depositing good quality films for various device applications.*
***Keywords:*** *Thin films, Substrates, Lead zinc sulphide, Deposition, Optical properties*
*Received: 20th July, 2022* *Accepted: 30th August, 2022*

## 1. Introduction

The search for clean and renewable forms of energy is a function of the ever-growing world population. To achieve this search for eco-friendly energy, the usual forms of energy (petroleum, natural gas, fossil fuel, coal etc.) are used (Emegha *et al*., 2022a). Naturally, the issue associated with these conventional sources of energy, (polluting and finite nature) have demanded a critical need of a recyclable sources of energy that is renewable (Jagadale *et al*., 2016). Solar energy as a more efficient and renewable alternate source of energy has been fully evolved and developed by researchers to convert photons (sunlight) into functional or useful electrical energy which are relevant in numerous optoelectronic applications such as digitalized watches and advanced calculators. Currently, thin films application in solar cells fabrications have been of immense interest to researchers as well as industrialist owing to their excellent properties like; tunable band-gap, low cost of production, ease of forming charge pairs which enables the conversion of photons to electricity (Choge, 2016; Jagadale *et al*., 2016)

Lead zinc sulphide (PZS) has attracted interest from scientists and industrialists globally for the development of window materials for the production of solar cells and optoelectronic semiconductor devices due to the fulfillment of certain requirements that are essential for device fabrications (Adeoye et al., 2015). Most importantly, PZS thin films have flexible properties that are beneficial for solar cell fabrication. Additionally, the energy band structure varies continuously with the elemental compositions within the ternary matrix; hence, influencing the p-n junction (Adeoye et al., 2015). This is due to the fact that the optoelectronic properties of PZS thin films as well as the dielectric constants are greatly dependent on the changing elemental constituents; and thus, offers great flexibility in optimizing higher efficiency in solar cells production (Ngahu, 2016).

Various chemical and physical deposition techniques have been employed or utilized for the synthesis of material thin films, viz.; chemical spray pyrolysis (Ahmed *et al*., 2019), spin and dip coating (Samarasekaran*et al.*, 2017; Ghediya *et al*., 2020), pulse laser deposition (Mahdavi*et al*., 2008), electro-deposition method (Fulari *et al*., 2014), Successive ionic layer absorption and reaction (SILAR) (Pradhabhan and Sakthivelu, 2019), metal organic chemical vapour deposition (MOCVD) (Efe *et al.*, 2019) and chemical bath deposition (CBD) (Ganesh *et al.*, 2014; Sharma *et al*., 2016). However, these methods come with their various merits and demerits.

In the present study, CBD technique was used to prepare the crystalline PZS thin films. This technique (CBD) was chosen because of its

simplicity, low cost, low temperature of operation and suitability for large scale deposition (Anuar *et al.*, 2010). Additionally, the CBD procedure and its related parameters such as the concentration and the pH of bath, the deposition time as well as the temperature influences the nucleation and the growth of the films. Up-to-date, the CBD technique has not been effectively utilized for the deposition of PZS thin films for different applications and characterizations. Hence, the intention of this research study is to investigate some optoelectronic properties of semiconducting PZS thin films that are necessary for device applications like solar cells.

## 2. Materials and methods

### 2.1 Materials

To produce the nano-structured PZS thin films, chemicals of analytical grade (AR) were used without further purification; The chemicals used for the films preparation are listed as follows; Lead Nitrate, [Pb $(NO_3)_2$], Zinc (ll) Chloride [$ZnCl_2$], Thiourea [$NH_2.CS.NH_2$], EDTA Disodium salt, Ammonia solution [$NH_4OH$] and distilled water.

### 2.2 Deposition of lead zinc sulphide ($Pb_{1-x}Zn_xS$) thin films

Solutions of 1.0M of zinc, lead and thiourea were prepared from accurately weighed analytical solids. 25 ml of each solution was taken into a separate beaker to form 75 ml of the solution. Then 25 ml of distilled water was added to top the solution to 100 ml at room temperature. It was then stirred for about 30 minutes for proper harmonization of the ions. During the deposition, EDTA Disodium salt was used as a complexing agent. 25% of Ammonia solution was added drop-wise using a burette to maintain the pH of the solution at 9.0. For all the films deposited constant volumes of lead nitrate, thiourea, ammonia solution and the EDTA Disodium was maintained. When doping with zinc, varying volumes of uniform concentration of zinc (II) chloride [$ZnCl_2$] solutions was used by varying the value of x in terms of volume using Equation (1).

$$X = \frac{[Zn^{2+}]}{[Pb^{2+}+Zn^{2+}]} \quad (1)$$

where $Zn^{2+}$ is the number of moles of zinc (II) chloride, $Pb^{2+}$ is the number of moles of lead nitrate and the value of x varied from 0.0 to 0.6 according to the equation $Pb_{1-x}Zn_xS$. Table 1 indicates how the deposition conditions were varied.

Equations (2) and (3) were used to calculate the various concentrations of the solutions used.

$$Molarity = \frac{No.\ of moles\ x\ volume\ used}{1000} \quad (2)$$

and,

$$Concentration = \frac{massed\ used}{RMM\ \text{X}\ 1000}\ in\ moles\ per\ litre \quad (3)$$

The films were characterized as-deposited. The chemical bath deposition set-up illustrated in Fig. 1 was used.

**Table 1:** Parameters of depositing $Pb_{1-x}Zn_xS$ thin films

| Samples | Values of x | Formula. $Pb_xZn_{1-x}S$ | Vol. $Pb^{2+}$ (mL) | Vol. $Zn^{2+}$ (mL) |
|---|---|---|---|---|
| AX1 | 0.2 | $Pb_{9.8}Zn_{0.2}S$ | 9.80 | 0.20 |
| BX1 | 0.4 | $Pb_{9.6}Zn_{0.4}S$ | 9.60 | 0.40 |
| CX1 | 0.6 | $Pb_{9.4}Zn_{0.6}S$ | 9.40 | 0.60 |

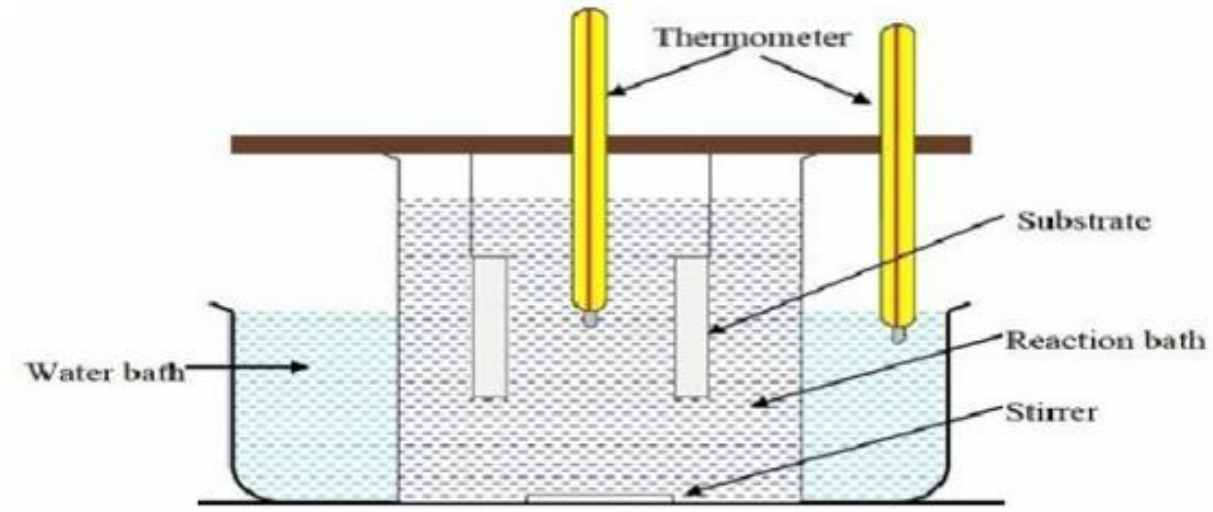


**Fig. 1:** Experimental set-up of Pb-Zn-S deposition (Zein and Alghoraibi, 2014)

### 2.3 Reaction mechanism

The deposition process of $Pb_{1-x}Zn_xS$ via CBD is based on the slow release of $Pb^{2+}$, $Zn^{2+}$ and $S^{2-}$ ions by the corresponding complexing agents (EDTA Disodium salt), and subsequently the nucleation of films on the substrates. The chemical mechanism of the films formation and deposition is as follows: The decomposition of thiourea in alkaline solution (Fekadu, 2015):

$$SC(NH_2) + (3OH^-) \leftrightarrow (CN_2)^{2-} + HS^- + 3H_2O \quad (4)$$

$$HS^- + OH^- \leftrightarrow S^{2-} + H_2O \quad (5)$$

When ammonia is added to the various salts' solutions ($Zn^{2+}$ and $Pb^{2+}$) tetra-amine complexes are produced; thus:

$$[Zn^{2+}(NH_3)_4]^{2+} \leftrightarrow Zn^{2+} + 4NH_3 \quad (6)$$

Similarly,

$$[Pb^{2+}(NH_3)_4]^{2+} \leftrightarrow Pb^{2+} + 4NH_3 \quad (7)$$

Finally,

$$Pb^{2+} + Zn^{2+} + S^{2-} = (PbZnS)\ PZS \quad (8)$$

When reaction (5), (6), and (7) are adequately slow, a heterogeneous nucleation of the material would occur on the inner walls of the beakers as well as on the immersed substrates (Emegha et al., 2021a), and the deposition of the material can be expected in each reaction.

### 2.4 Characterization techniques

The optical measurements were done through a (UV-1800S) Spectrophotometer in a wavelength range of 350 to 800 nm at normal room temperature, while four-point probes (FPP) measurement was employed to determine the electrical properties.

## 3. Results and discussion

### 3.1 Optical characterization of PZS thin films

A plot of the optical transmittance spectra against wavelength is shown in Fig. 2. It was found that the films had a very high transmittance of above 75% in the visible and near infrared regions. Sample BX1 had the least transmittance in the infrared region while Sample CX1 had the highest in same region. Also, zinc concentrations were found to increase with transmittance within the regions. This increase in transmittance with zinc concentrations may be attributed to the formation of zinc-lead-sulphide nano-crystals. As the nano-crystals are increasing, the transparency also is increasing. Therefore, rise in zinc concentrations makes the films more transparent. The high transmittance observed in this study was as a result of the enhanced crystallinity of the films, which in turn, reduces the defects in the grain boundaries. Films of such high transmittance indicated that the films could be used for several applications, including solar cells, transparent conducting materials in LEDs and photonic devices and it can also be a good material for thermal control window coatings for cold climates and anti-reflection coatings (Emegha et al., 2021b).

The optical absorbance of the films against wavelength is indicated in Fig. 3. In all the Samples, it was observed that the absorption was high in the ultraviolet region of the spectra. The high absorbency in this region may be attributed to the effects of light scattering from the nano-sized grains of the films as a result of variations in lead concentrations (Damisa *et al.,* 2017). Also from the spectra, the absorbance increases with increasing wavelengths. An indication of an improve transmission and crystallinity within the films (Moreh *et al.,* 2013).

Fig. 4 shows the plot of reflectance of the deposited PZS thin films as a function of the wavelength. It was noted that the reflectance decreases with the wavelength (>450 nm) for the material. Generally, all the film has low reflectance values that lie below 25%. However, at wavelength of 900 nm, the average value was about 11.0%, which may possibly be as a result of the decreasing tendencies of the thin films' density with rise in the wavelength. The high transmittance and low reflective properties of the film makes it a good material for several electronic applications such as solar cells, LEDs, thermal controlled window coatings for moderate climates as well as anti-reflective coatings.

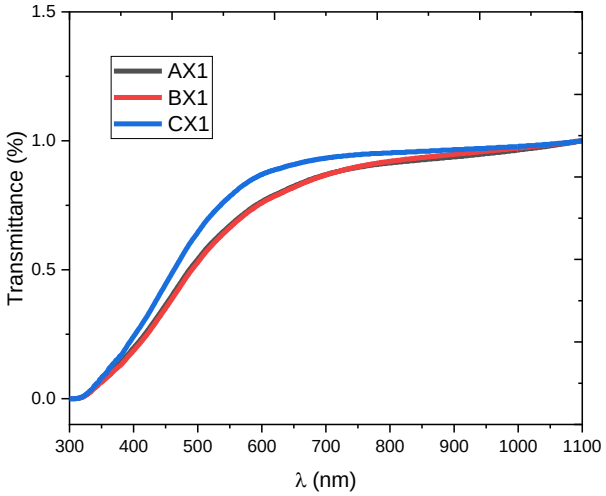


**Fig. 2:** Transmittance spectrum of PZS thin films

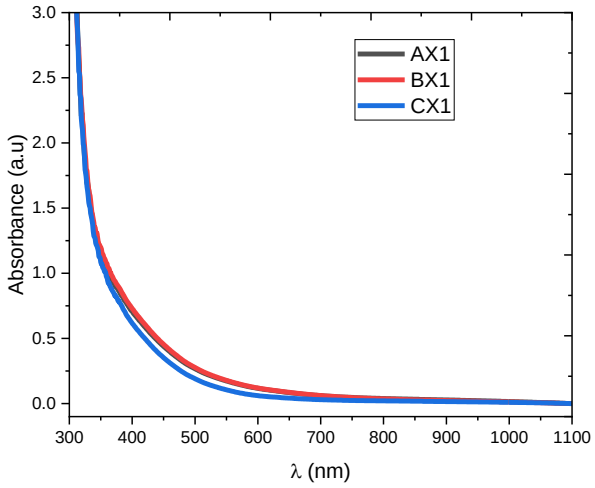


**Fig. 3:** Absorbance spectrum of PZS thin films

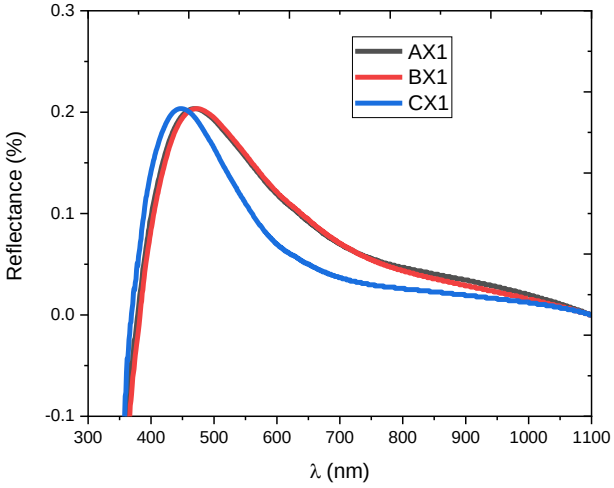


**Fig. 4:** Reflectance spectrum of PZS thin films

The refractive index (n) is an important (optical) parameter in the fabrication of many optoelectronic devices such as switches, modulators, filters, waveguides, solar cells and detectors (Damise et al., 2021). Generally, the refractive index of a semiconductor is related to the optical band gaps. Moreover, the refractive index (n) against photon energy is indicated in Fig. 5. From the Figure, it was found that the refractive indexes were decreasing with photon energy above 2.5 eV. The highest refractive index was found to be approximately 1.02 in the high energy region. However, as the lead concentrations is increased, the average refractive indexes were found to fall and rise within the range of 0.7 and 1.02. This trend in the refractive index was possibly due to the trapped photon energy within the grain boundaries of the samples (Damisa *et al.*, 2017). The extinction coefficient (k) was estimated using Equation (9) (Emegha et al, 2022b).

$$k = \frac{\alpha\lambda}{4\pi} \quad (9)$$

where α is the absorption coefficient and $\lambda$ is the wavelength of the incident photon energy. Fig. 6 shows the variation of the extinction coefficient (k) as a function of photon energy for the deposited films. It is clear from the plot that the extinction coefficient increases with photon energy. It was also found that the average extinction coefficient falls and rises with lead/zinc concentrations. Thus, suggesting that the extinction coefficient depended on the high transparency of the films. The nature of extinction coefficient of this material as observed was due to the successive internal reflection within the film matrix (Damisa and Emegha 2021).

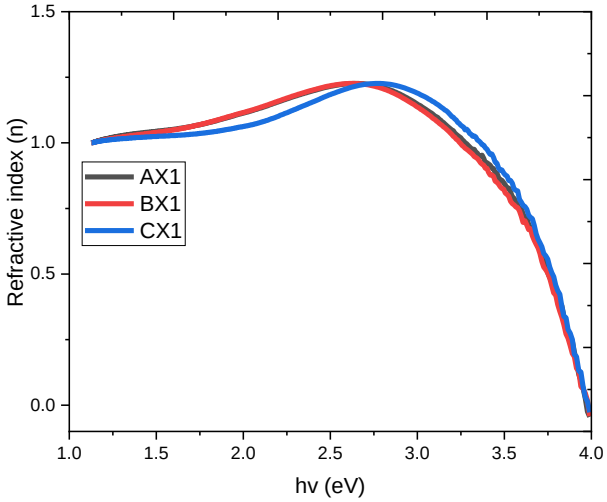


**Fig. 5:** Refractive index of PZS thin films

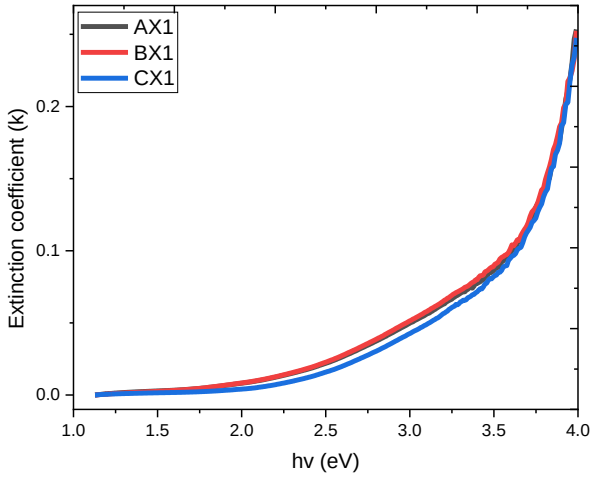


**Fig. 6:** Extinction coefficient of PZS thin films

The absorption coefficient (α) of PZS thin films was evaluated using the Equation (10) (Efe *et al.,* 2019).

$$\alpha = \frac{1}{t}\, ln\left(\frac{1}{T}\right) \quad (10)$$

where t is the thickness and T is the transmittance of the films. The observed variation of absorption coefficient for the material with respect to the doping concentration is shown in Fig. 7. The result showed that the absorption coefficient of the material increased with concentrations. Generally, the transitions (direct or indirect) in semiconductors depend on the band structure of the deposited materials. From the obtained absorption spectra, the value of optical band gap ($E_g$) can be determined from the Equation (11) (Tariq *et al.,* 2014):

$$\alpha hv = A(hv - Eg)^n \quad (11)$$

where, α is the absorption coefficient, A is a constant and n is an electronic transition index which can assumed the various values of $1/2$, $3/2$, 2 and 3. The index n = $1/2$ for allowed direct transition, n = $3/2$ for forbidden direct transition, n = 3 for forbidden indirect transition and n = 2 for allowed indirect transition. The electron transition can be determined from the absorption coefficient values. If the absorption coefficient is greater than $10^4$ $cm^{-1}$, the material is assumed to have a direct transition, and indirect transition when the absorption coefficient is less than $10^4$ $cm^{-1}$ (Alwan and Jabbar, 2010).

The value of the absorption coefficient shows that the deposited PZS thin films exhibit a direct allowed transition. The optical band gap was estimated from the straight lines of the plot of $(\alpha hv)^2$ against the photon energy (eV) as indicated in Fig. 8. However, the band gaps obtained for PZS were found to be 1.34 eV (sample AX1), 1.86 eV (sample BX1) and 2.11eV (sample CX1) respectively as shown in Fig. 8. This shows that the band gaps of the material increased with increase in doping concentrations of zinc. Different factors may be responsible for such rise in band gap as doping concentration increases. The band gap rise is possibly due to the increased grain sizes and crystalline nature of the films which thus influenced the band gaps (Emegha et al, 2022b). Additionally, it may also be the direct effect of elevation in transition tail width and shift effect, which can be describe in terms of increase in carrier concentration (Damisa *et al.,* 2017).

### 3.2 Electrical analysis of ZPS thin films

The electrical properties of the thin films were investigated using the four-point probe technique. The sheet resistivity and conductivity of PZS was measured and the results were indicated in Table 2. Fig. 9 shows the graph of resistivity and conductivity against zinc concentrations in the samples. The variation of direct-current electrical resistivity was studied for $Pb_{1-x}Zn_xS$ thin films for x= 0.2 to 0.6. From Fig. 9, the resistivity at very low concentration was found to be of the range of $10^6$ Ωcm and then decreases downwards in same order. It was observed that resistivity increases as the concentration of zinc in the films increases from BX1 to CX1, which shows that zinc doping influences the electrical conductivity of synthesized thin films. This might be owed to the quality of the films deteriorating which further increase in the dopant concentration. The observed increase in the conductivity (from AX1 to BX1) is attributed to the improved concentration of the charge carriers in the PZS system (Emegha et al., 2022c). This reflects the expansion and pairing of grains to form larger crystallites within the deposited films. Due to this modification, the charge carrier density is increased and, consequently increases the electrical conductivity. Similar observations have been reported in literature for ZnS and PbS thin films (Emegha et al., 2022c; Sebastian *et al.,* 2020; Ngahu, 2016)

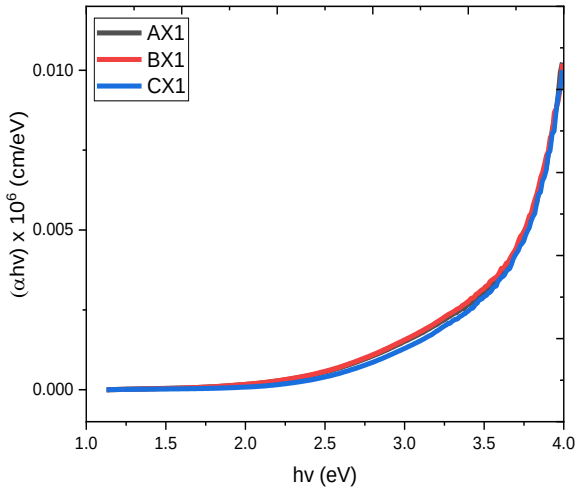


**Fig. 7:** Absorption coefficient of PZS thin films

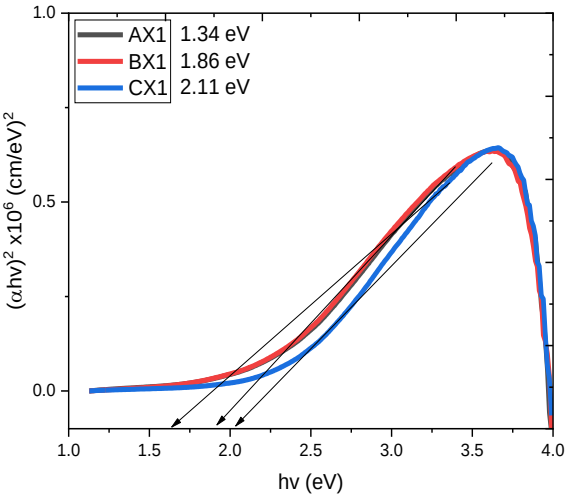


**Fig. 8:** Optical band-gaps of PZS thin films

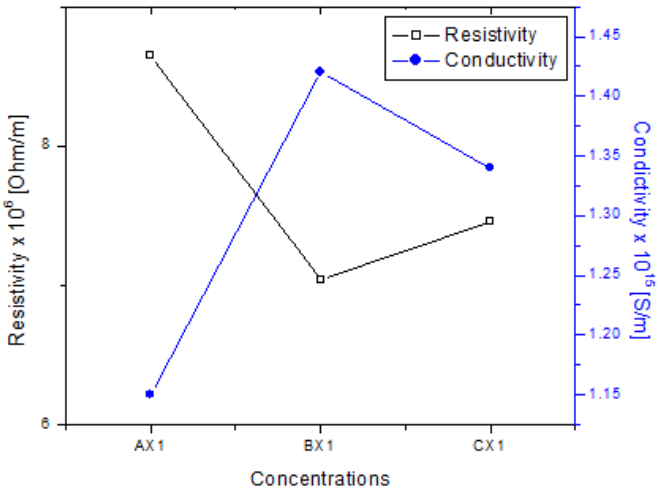


**Fig. 9:** Electrical properties of PZS thin films

**Table 2:** Electrical parameters of PZS thin films

| Samples Label | Thickness, t (nm) | Resistivity, **ρ**(Ω.cm) | Conductivity, **σ**(S/m) |
|---|---|---|---|
| AX1 | 111.64 | $8.65\times10^{6}$ | $1.15\times10^{15}$ |
| BX1 | 112.93 | $7.04\times10^{6}$ | $1.42\times10^{15}$ |
| CX1 | 113.69 | $7.46\times10^{6}$ | $1.34\times10^{15}$ |

## 4. Conclusion

Ternary ZPS thin films were obtained through the CBD techniques. The route offers a unique technique in preparing ZPS thin films utilizing chemical precursors. Optical and electrical properties were directly influenced by the deposition concentrations. The films exhibited high transmittance in the UV region with an energy gap that increased with increase in zinc concentrations. The refractive index and extinction coefficient showed that the optical constants of the deposited material were influenced by concentration variations. The electrical measurements indicate that the PZS thin films are naturally semiconducting. These properties exhibited by the deposited films confirm the films as good material for various optoelectronic device applications.

## Acknowledgements

The authors are grateful to the entire staff and students of the Department of Energy and Petroleum Studies, Novena University Ogume, Delta State, Nigeria for allowing the use of their facility for the production of this film.

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