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Electrical and Solid State Properties of Aluminum Doped Nickel Sulphide Thin Film by Chemical Bath Method

***[1]Emmanuel Ifeanyi Ugwu, [2]Barnaba Abel Adeiza, [3]Hilary Uche Igwe and [1]Ikpughul Sunday Iyua**

[1]Department of Physics, Nigerian Army University Biu, Borno State, Nigeria.
[2]Department of Mechanical Engineering Nigerian Army University, Biu, Borno State, Nigeria.
[3]Department of Industrial Physics, Ebonyi State University Abakaliki, Ebonyi State, Nigeria.

*Corresponding Author's Email: ugwuei2@gmail.com
ORCID ID: https://orcid.org/0000-0001-7045-0814

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ABSTRACT

The rule of the electrical and solid state properties of sulphide based thin film has made it interesting for us to carry out a study on the electrical and solid-state properties of aluminum doped NiS deposited by chemical bath deposition method has been carried out in this work in order to ascertain the influence of the concentration of aluminum as a dopant on the electrical and solid state properties of NiS thin film material as pointed out. And from the results, it was obviously seen as showcased from the results such as the index of refraction, extinction coefficient, dielectric constants, optical conductance that there were significant influence of Al on the trends of these properties, in particular the electrical properties as obtained using four point probe that they were variations in trend of the graphs as the concentration of dopant, aluminum were varied indicating its effect on the behavior of the aforementioned properties of the thin film in question thereby clarifying the belief that generally doping is one of the parameters that can be used to modify the sulphide based chalcogenide.

INTRODUCTION

Sulphide based chalcogenide is like other chalcogenide thin film materials that can be deposited by using various methods of deposition techniques such as chemical bath, successive ionic layer adsorption reaction, atomic layer deposition technique etc (Sankapal *et al.,* 2000; Kadhim *et al.,* 2017; Nwali *et al.,* 2009; Guzeldir *et al.,*2012; Panda *et al.,*2014; Sartale *et al.,* 2001; Wang and Yushin, 2015; Cheon *et al.,* 1997). A great deal of research efforts has been geared towards the synthesis of NiS nanoparticle in particular and other nanoparticles of that family. Apart from the above-mentioned methods which may involve both "wet" and "dry" methods of deposition such as Vacuum evaporation, hot-wall epitaxy, molecular-beam epitaxy (Inumaru *et al.,*2007) were amongst the most successful techniques that have been successful deposition methods used in synthesis of these types of thin films. Other "dry" and "wet" methods that have been successfully used includes spray pyrolysis and electrochemical deposition. These categories of thin films can be influenced by some deposition parameters such deposition time, annealing temperature and doping etc. (Anuar *et al.,* 2010; Preetha *et al.,* 2015; Anuar *et al.,* 2011; Igwe and Ugwu, 2012; Benhaoua *et al.,* 2014; Adeyeba *et al.,* 2022; Nefzi *et al.,* 2020). Sequel to the ability of their properties to be modified based on these conditions, it become imperative that they can be adoptable to so many applications and these are more reasons why they being extensively investigated (Owoh and Ugwu, 2009; Rajini *et al.,* 2019; Sadovnikov *et al.,* 2010; Ugwu and Onah, 2007; Franzen *et al.,* 1968) because it now become obvious that their potential applications in electronic and optoelectronic and a wide direct band gap semiconductor is very high (Khan *et al.,* 2018). Some of them have unique properties that make them applicable to photovoltaic cell, (Penda *et al.,* 2014; Soonmin *et al.,* 2022) while several other such as $CuInSe_2$, CdTe and Cu_2S including PbS have also various applications in different fields such as IR detectors, display devices, solar control coatings (Tejuca *et al.,* 1989; Gupta and Compaan, 2004; Romayuk and Tiwari, 2011) LEDs, humidity and temperature sensors and in optical switching due to their third-order nonlinear optical properties.. However, attention has been focused more chemical bath deposition because of it's a simple nature, though with highly efficient effectiveness. It provides a powerful and versatile control of the size and surface density of nanoparticles and therefore can be used in preparation of high quality nanocrystalline NiS and some other form of thin films requiring large area .The characteristics of the deposited layers depend strongly on growth conditions (i.e. composition, temperature of solution duration of deposition process) as well as on the chemical and topographical nature of the substrate coupled with other parameters such as dip time, ligand or complexing agent and doping element (Abbas *et al.,* 2011; Peter *et al.,* 2010; Patel *et al.,* 2016). Chemical bath deposition of thin NiS and others such as PbS, C_2 S, ZnSe nano crystalline films has been investigated thoroughly (Brown *et al.,* 2019) for different of substrates viz. glasses, polymers and other materials for which semiconducting, optical, structural morphological properties have been investigated, but, however, there has been no vivid investigation on the effect of using aluminum as dopant on the solid state and solid state and electrical properties of NiS thin film. Therefore, we intend to dope NiS with aluminum and analyze its effect on aforementioned properties

MATERIALS AND METHODS

The Chemical Bath Deposition (CBD) technique was used to deposit NiS thin films at different concentrations of aluminum. CBD involves controlled precipitation and deposition of the desired compound in a simple constituent, which is low-temperature and less expensive (Sankapal *et al.,* 2000; Kadhim *et al.,* 2017).

Prior to the deposition, the glass slide substrates were cleaned by scrubbing them thoroughly with cleaned cotton wool and soap solution, rinse with running tap water, then ultrasonicate using ultrasonic bath of acetone, Methanol and distilled water at room temperature for few hours. Then they were rinsed with deionized water. The substrates were dried in an open moderate temperature. All these cleaning processes were taken to remove possible impurity (organic or Inorganic) substances from the surface of the substrate which is very important for adherence of the films to the surface of the glass substrate. The thin films of nickel Sulphide (NiS) were deposited onto the chemically cleaned glass substrates using highly pure chemicals by Chemical Bath Deposition (CBD) process. The chemical bath was prepared by sequential addition of 0.5M of Nickel Chloride Hexa-hydrate ($NiCl_2.6H_2O$), 0.5M of Thiourea, 0.5M of Sodium Hydroxide (NaHO) to neutralize the acidity of the solution, 0.5M of Tri-ethanol-amine (TEA) (C_6H15NO_3) into three different baths (N, AN_1 and AN_2). Aluminum Chloride (AlCl) which is the source of Aluminum (Al) served as the doping agent was added into the second and third bath (AN1 and AN2) 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 8. At a specific temperature, the bath solution was heated and then thoroughly stirred on a magnetic stirrer for a specific amount of time (30min) 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 labeled; N, AN_1 and AN_2. 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.

Reaction Equations

$NiCl_2.\ 6H_2O + 2NaOH\ Ni\ (OH)_2 + 2NaCl + 6H_2O$ (1)

$CH_4N_2S + 2H_2O\ CO_2\ (g) + 2NH_2\ (g)\ H_2S\ (g)\ S_2- + H_2O$ (2)

$Ni\ (OH)_2 + 2[C_6H_{15}NO_3]_2\ Ni\ (C_6H0_{15}NO_3)_2 + 2H_2O$ (3)

$[Ni\ (6H_{15}NO_3)_2\ Ni_2+ + 2(C_6H_{15}NO_3)$ (4)

$Ni^{2+} + S^{2+} = NiS$ (5)

After this preliminary reaction, then two different concentration of aluminum were prepared and made to be deposited on as-deposited NiS in order to completely form AlNiS thin film as in AN_1 and AN_2 respectively.

Mathematical Relations used for Calculating the Solid-State Properties

The solid-state properties such as absorption coefficient, extinction coefficient index of refraction, optical conductivity was deduced from the quantities obtained directly from spectral photometer as the instrument that was used for the optical characterization using some well-known mathematical relations

Absorption Coefficient (α),

$In(\frac{I}{I_0}) = 2.303A = \alpha d$ (Inumaru *et al.,*2007) (6)

Whereby A is the absorbance as obtained from optical characterization. Therefor in general, the absorption coefficient could be deduced within a given region using Lambert law as given in equation (6)

I, I_o are the intensity of incident and transmitted radiation respectively, A is the optical absorbance and d is the film thickness. That of the extinction coefficient (k) is given by

$$\kappa = \frac{\alpha\lambda}{4\pi} \quad (7)$$

λ, is the wavelength of the photon energy. While the index of refraction, n is deduced from the relation $n = \frac{1}{T} + \left(\frac{1}{T-1}\right)^{1/2}$ (8)

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \quad (9)$$

Where T and R stand for spectral transmittance and reflectance respectively. The optical conductivity is on the other hand deduced from

$\sigma = \alpha n c \varepsilon$ (Ugwu and Onah, 2007) (10)

RESULTS AND DISCUSSION

The solid state and electrical properties of the deposited films would be characterized using various characterization techniques. UV-VIS spectrophotometer were used for determining the solid state characterization while four point probes (FPP) technique was used to investigate the electrical property of the deposited thin films while the solid state characterization involves studying the properties of materials in a solid state such as the Extinction coefficient, refraction index, optical conductivity, and dielectric constant which are the key parameters in this context:

Extinction Coefficient (k)

Extinction coefficient is a measure of light loss due to scattering and absorption per unit volume of a material, K is generated from equation 7. Figure 1 shows the plot of K as a function of photon energy of NiS thin films deposited at different concentration of dopant (Al) at constant time frame (30 min of stirring with magnetic stirrer). It has been noticed from the graph that the extinction coefficient increases in the UV region with increase in photon energy, as observable, the increase in K at photon energy below 4.125 eV for AN_1 and AN_2 respectively and N shows no change on the extinction coefficient up to 4.10 eV before showing a rough behavior from 4.125 eV to 4.20 eV. And this is due to the high absorption within those regions which is ascribed to smoothness of the surface of the films. It can be thus be deduced that increase in dopant concentrations increase the extinction coefficient from the absorption edge of the visible range in the NiS thin films.

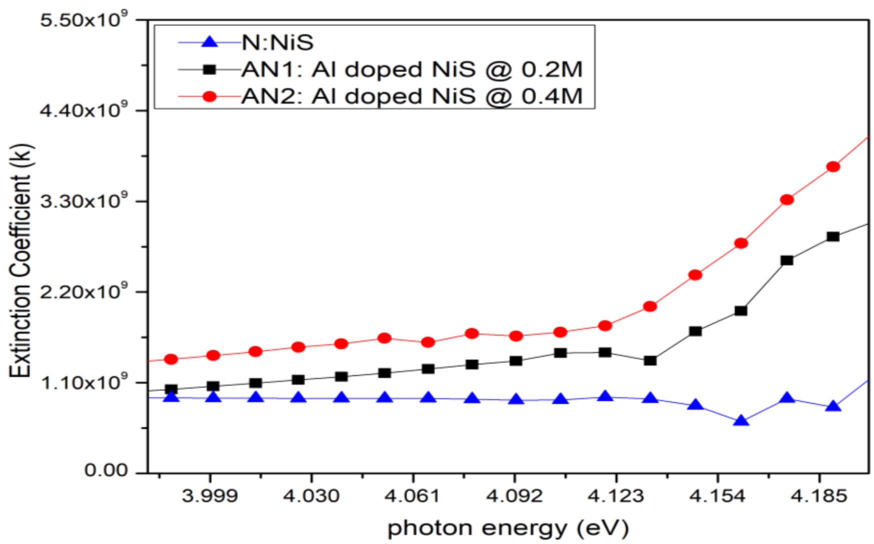

Figure 1: the variation of K as a function of photon energy for the three samples N, AN_1 & AN_2

Refractive Index (n)

The refractive index is the rate at which light is slowed down in a material. It is one of the significant properties of an optical material in optoelectronics. The plot of refractive index as generated using equation 8 as a function of photon energy for the three deposited samples of AlNiS thin films is shown in figure 2. It is observed from the graph that n for sample AN_1 is slightly high and for AN_2 is high (about 4.20 and 4.15 respectively) within the visible region of the films, which is attributed to the increase in the thickness of the films as a result of the smaller concentration of the dopant used in the preparation. In comparison with N which exhibit the lowest value of refractive index in the UV region. Therefore, it can be deduced from this observation that, increasing the concentration of the Al as the dopant in the chemical deposition of AlNiS thin films consequently increases the refractive index of the films within the UV region.

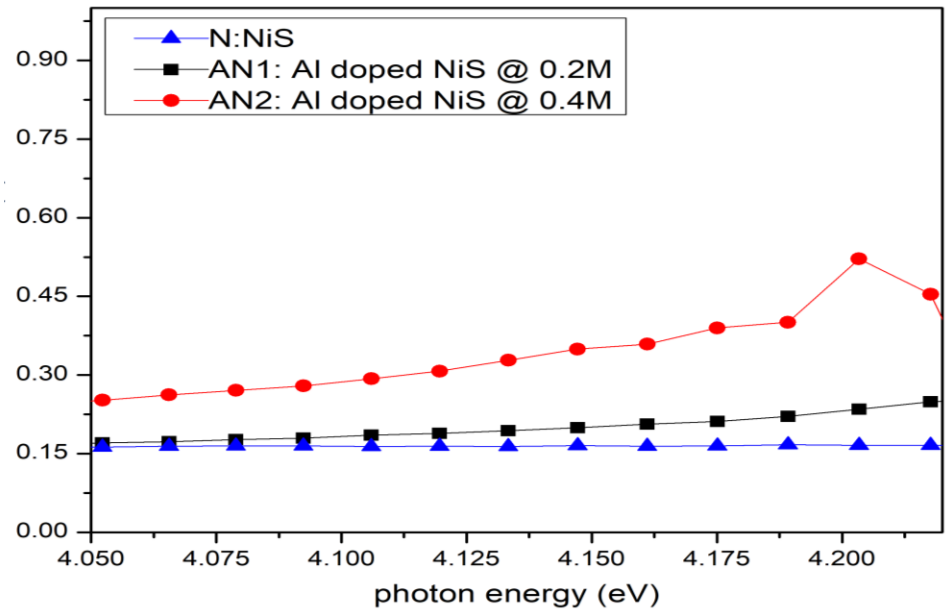

Figure 2: the plot of the refractive index (n) against the photon energy for sample N, AN_1 & AN_2

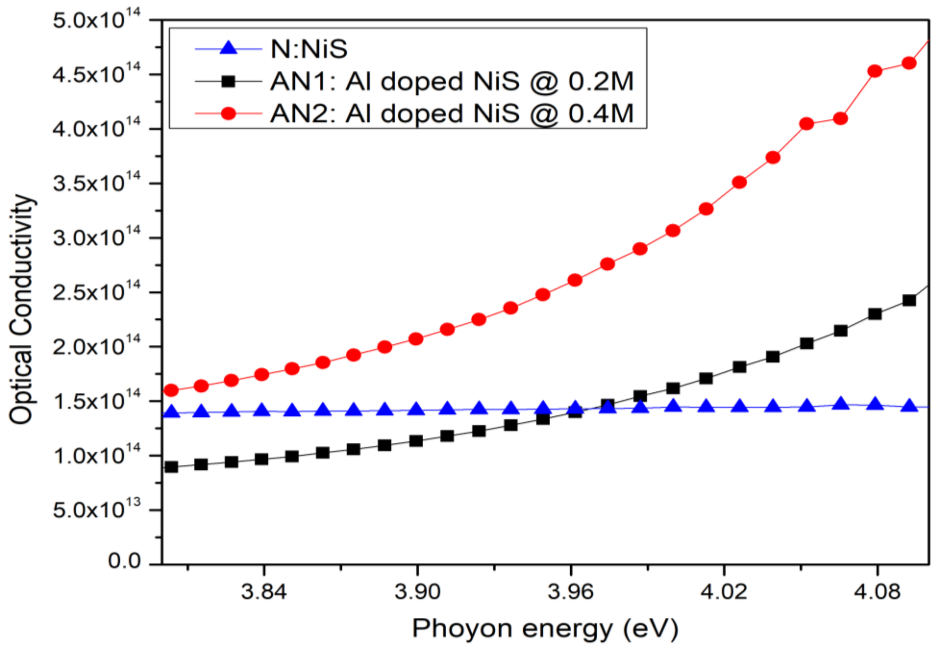

Figure 3: The variation of δ_{opt} with the photon energy for the three samples N, AN_1 & AN_2 of NiS thin film

Optical Conductivity, σ

Optical conductivity is a measure of the frequency response of a material when irradiated with light. The optical conductivity of the three samples of the deposited NiS thin films is calculated using the relation in equation 19, which is strictly dependent on α and n only. The plot of δ_{opt} against the photon energy is presented in figure 3 below, it is observed from the plot that, δ_{opt} displays the trend as that of n discussed above. AN_2 is said to have the highest optical conductivity (nearly $5.0x10^{14}$), followed by AN_1 (nearly $1.5x10^{14}$) and N which shows poor optical change (nearly $1.5x10^{14}$). This indicates that the optical conductivity of AlNiS thin film materials increases as we increase the concentration of aluminum. It is also interesting to know that the sample N shows a no change in the optical conductivity but as the dopant is added, sample AN_1 shows the lowest optical change while as the concentration of the dopant increase in sample AN_2, it indicates the highest optical conductivity.

Thus, it can be concluded from the sight of this as a result of increase in concentration of the dopant, there is increase in the optical conductivity of the AlNiS thin film.

Dielectric Constant (ε_r)

Real and imaginary part of the dielectric constant parameters were obtained from equation 14 and 15, which are purely n and k dependent. Figure 4(a) shows the graph of real dielectric constant against the wavelength range from 299 nm to 315 nm of AlNiS thin film at different concentration of dopants. As observable from the graph, all the three samples exhibit similar behavior as that of refractive index because, the respective values of K^2 is greater than n^2 as shown in the equation 14 of chapter two. This implies that ε_r mainly depend on n. in comparison to ε_i in equation 15, which is mainly dependent on K. the obtained value of the real dielectric constant ($\leq 10^{18}$) is considerably smaller than that of the imaginary part as observed in figure 4(b), Furthermore, it is observed that ε_r increases as the concentration of dopant increases but for ε_i decrease, also the dielectric constants increase as the wavelength of the incident radiation increases. Therefore, the dopant influences the behavior of the real and imaginary part dielectric constants of chemically deposited AlNiS thin film.

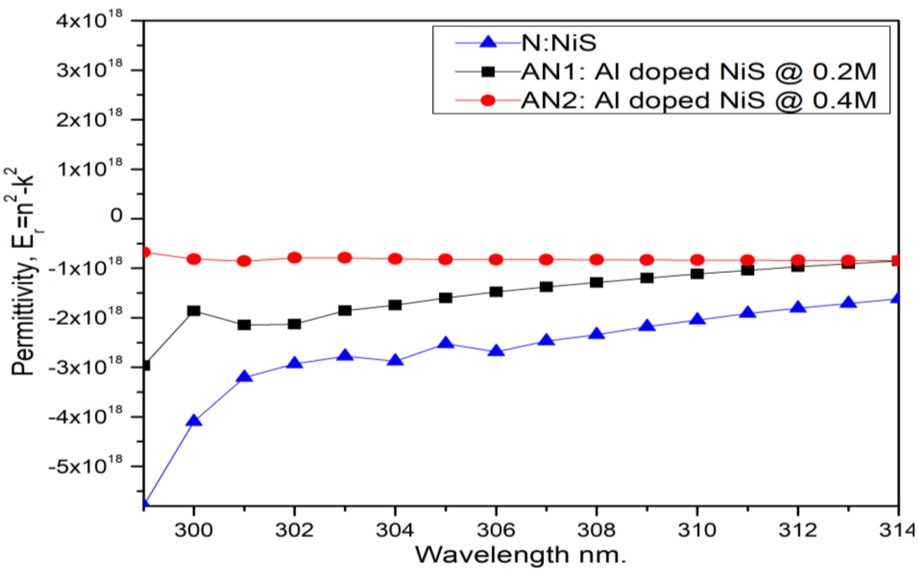

Figure 4(a): Real dielectric constant, ε_r against the wavelength of sample N, AN_1 & AN_2 of AlNiS thin films

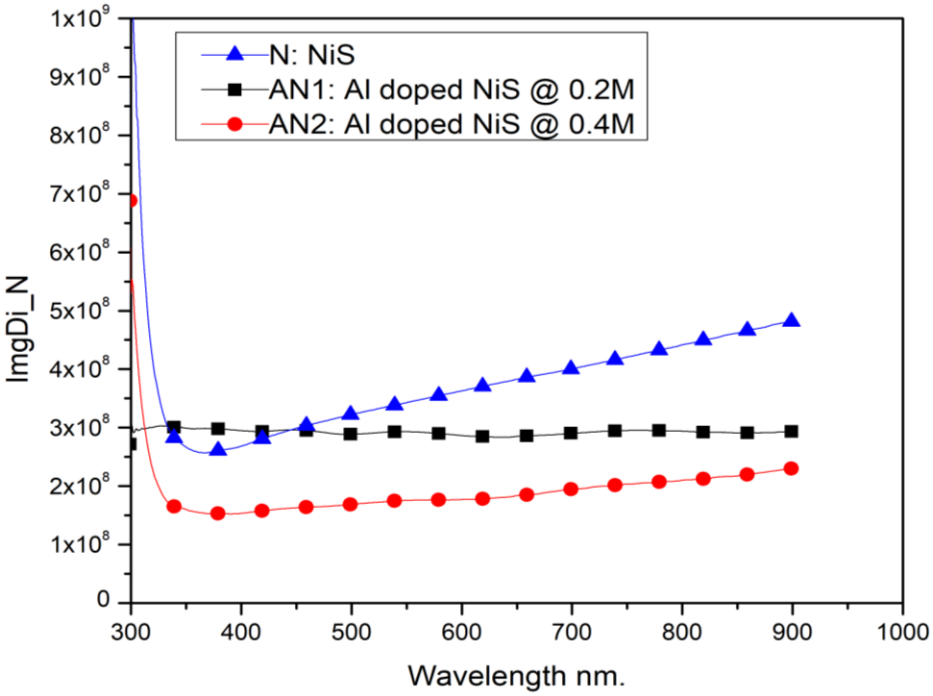

Figure 4(b): Complex dielectric constant, ε_i against the wavelength of sample N, AN_1 & AN_2 of AlNiS thin films

Electrical Characterization

The electrical analysis of the chemically prepared AlNiS thin film was obtained using four-point probe (FPP) technique. Figure 5(a), 5(b) and 5(c) illustrate the plot of I-V characteristics of sample N, AN_1 and AN_2 respectively. As observed from the plot, currents flow through the films linearly with the applied outer voltage. This is an indication that AlNiS for both as-deposited and the ones aluminum doped with exhibit Ohmic characteristics, i.e. it obeys Ohm's law since the plot of the graph of current as a function of voltage shows linear relationship manifesting smooth linear relation as the concentration of the dopant increase because it can also be observed from the graph in figure 5(a) that N shows the poorest linear behavior of I-V characteristics compared to AN_1 and AN_2 in figure 5(b) and 5(c). The obtained results of the average electrical conductivity, resistivity and sheet resistance of the three samples of NiS thin film are presented in the table 1 below where could be easily deduced from the table that the average conductivity of the thin films increases as the concentration of dopant increases which is in agreement with the graphs as elucidated. Thus, a clear indication that there is a decrease in the average resistivity and the average sheet resistance of the films with increase in the concentration of the dopant. Therefore this evidencing observed consistency in the increase in electrical conductivity and decrease in the sheet resistance as the concentration of the dopant increases shows the suitability of the AlNiS thin film in so many applications especially in photoconductor and detectors and also in solar control system which is invariably in agreement with the observation as indicated in the literature.

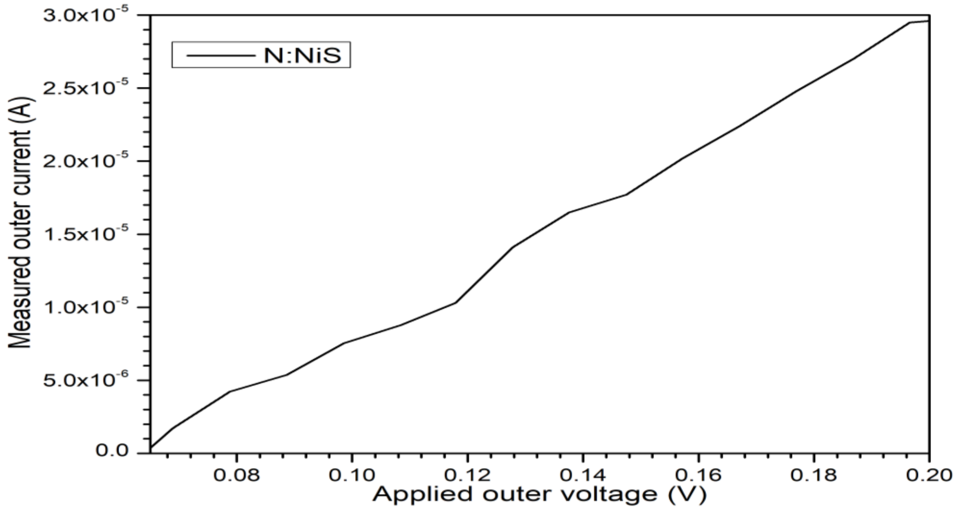

Figure 5(a): I-V characteristics for N

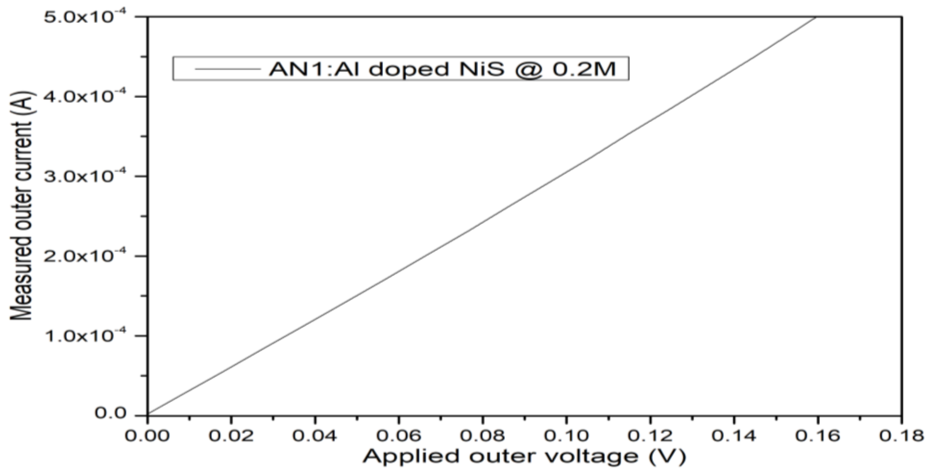

Figure 5(b): I-V characteristic for AN_1

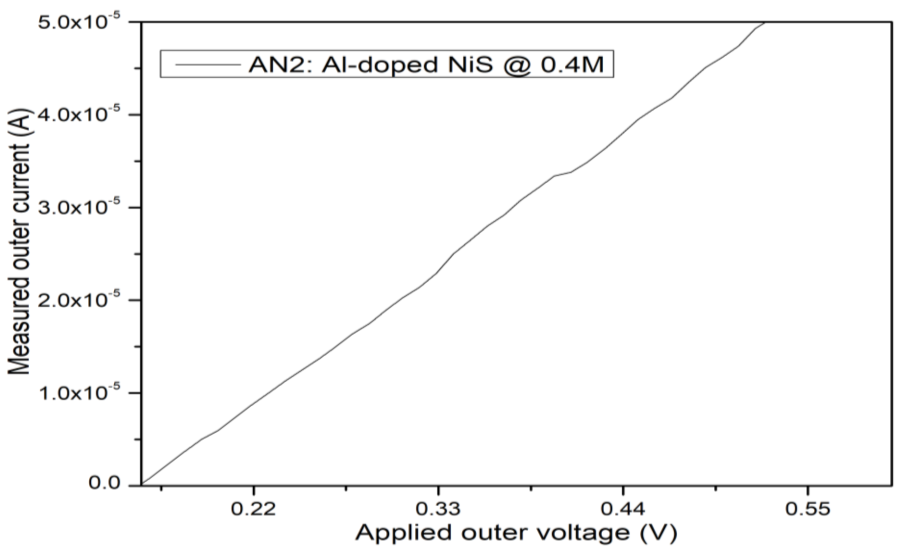

Figure 5(c): I-V characteristics for AN_2

Table 1: I-V Characteristics of Chemical Bath Deposited NiS Thin Film

SAMPLES	$R_{sheet}(\Omega)$	Resistivity (Ωm)	Conductivity $(\Omega\text{m})^{-1}$
N	6673.676	0.000667	4179.438
AN_1	2540.062	0.000254	6094.218
AN_2	550.9423	$5.51\text{x}10^{-5}$	54134.14

CONCLUSION

In this work, NiS thin film has been successfully grown at different concentration of dopant (Al) using chemical bath deposition technique. The influence of Al on solid state and electrical properties of the deposited films has been characterized and investigated. The solid-state parameters such as absorption coefficient, optical conductivity, refractive index and dielectric constant were obtained using various existing equations. The graphs that were plotted as a function of wavelength in some cases and also as a function of photon energy in other cases have been presented revealed some major interesting characteristics while the electrical properties of the films that were analyzed using four-point probe (FPP) technique. Showcased the electrical behaviour. However, the results obtained show that Al doping has a considerable influence on the various properties of NiS thin films. For instance, there was variation in refractive index, real and complex dielectric constant with the photon energy with the concentration of the aluminum as a dopant as indicated in the figures as presented here in the results, it was observed that there were slight variation in some of these properties as analyzed here occasioned by different concentration of the aluminum. The effect also manifested on the electrical propertied as obtained from the four point probe which is indicated on table 1.0.Thus from the observation as shown in the result, the sulphide based and other type of chalcogenide thin films can be tailored into so many applications since the properties of the thin film are amenable to modification by some parameters such as this. There from this, it could be inferred that the film has a trend of the properties with such features that make it suitable for so s many applications such as sensors, photo-detectors and energy devices and also in photovoltaic applications.

REFERENCES

Sankapal B.R., Mane R.S. and Lokhande C.D. (2000). Successive ionic layer adsorption and reaction (SILAR) method for the deposition of large area (~10cm2) tin sulfide SnS_2 thin films. *Materials Research Bulletin*. 35:20.

Kadhim A., Al-Haddad A. and Abdullah H. (2017). Structural and Optical Properties of NiS Thin Films Grown on Glass Substrates by Pulsed Laser Deposition. *Journal of Materials Science and Engineering,* 19(3):789-802.

Nwali N.P. and Ugwu E.I. (2009). Optical properties of chemical bath deposited Cu_2S thin film within UV-VIS, and NIR radiation. *Metallurgy and material engineering,* 4(2):26-30.

Guzeldir B., Saglam M. and Ates A. (2012) Deposition and characterization of CdS, CuS and ZnS thin films deposited by SILAR method. *Acta Physica Polonica A*. 121:33-35.

Panda S.K., Rout C.S. and Fathima S.N. (2014). "Electronic and Spectral Properties of Hexagonal NiS: A First-Principles Study." Journal of Alloys and Compounds, 587:464-468.

Sartale S.D., Lokhande C.D. and Uplane M.D. (2001). Synthesis of NIS Thin Film Using Successive Ionic Layer Adsorption and Reaction (SILAR) Technique. Journal of Materials Research, 26(8):123-136.

Wang X. R. and Yushin G. (2015). Chemical Vapor Deposition and Atomic Layer Deposition for Advanced Lithium Ion Batteries and Supercapacitors. *Energy Environ. Sci. 8* :1889-1904.

Cheon J. W., Talaga. D. S. and Zink J. I. (1997). "Laser and thermal vapour deposition of metal sulfide (NiS, PbS) films and situ gas-phase luminescence of photofragments from $M(S_2COCHMe_2)_2$", *Chemistry of Materials*, 9:1208-1212.

Inumaru T., Kasahara A. and Yamoah N. (2007). Epitaxial Growth of Chromium Nitride (CrN) Thin Films on Special Substrates Using Pulsed Laser Deposition. Journal of Thin Film Deposition and Technology, 23(5):456-471.

Anuar K, Ho SM, Abdul HA, Noraini K, Saravanan N, (2010). Influence of the deposition time on the structure and morphology of the ZnS thin films electrodeposited on indium tin oxide substrates. *Digest Journal of Nanomaterials and Biostructures*.2010, 5:975-980.

Preetha K. C. Murali K. V., Dhanaya A. C. and Remadevi T.L. (2015). "Role of complexing agents on chemical bath deposited PbS thin film characterization". IOP *Conf. Ser. Mater. Sci. Eng*, 73:012086

Anuar K, Ho S.M., Lim K.S., Nagalingam S. (2011). SEM EDAX and UV-Visible studies on the properties of Cu2S thin films. *Chalcogenide Letters*. 8:405-410.

Igwe Hilary U, Ugwu Emmanuel. I., 2012. "Influence of the annealing temperature on the optical and solid-state properties of lead selenide (PbSe) thin films grown by chemical bath deposition (CBD) technique", *Adv. Appl. Sci. Res.,* 1(3):240-246

Benhaoua. A., Rahal. A. and Benhaoua. B. (2014). "Effect of Fluorine doping on the Structural, Optical and Electrical properties of SnO_2 thin films prepared spray ultrasonic". *Superlattices and Microstructures,* 70: 61-69.

Adeyeba O.A., Ugwu E.I. and Busari R. A. (2022). Influence of Ligand on the Morphological, Electrical, optical and Solid-State Properties of Chemical Bath Deposited Lead Sulphide Thin Film. *Journal of Materials Science Research and Reviews*. 10(4):16-31.

Nefzi. C., Souli, M., Y. Cuminal, N. Kamoun-Turki, 2020. "Effect of substrate temperature on physical properties of Cu_2Fe-SnS_4 thin films for photo-catalysis applications". *Mater Sci Eng B.* 114509

Owoh B., and Ugwu E.I. (2009). Growth and Optical characterization of Antimony selenide thin film using chemical bath deposition technique. *Metallurgy and material engineering, 4(1):38-41.*

Rajini M., Karunakaran M. and Kasirajan K. (2019). An investigation of SILAR grown CdO thin films. Chem. Chem. *Iran. J. Eng., Vol. 38, no. 4.*

Sadovnikov S. I., Kozhevnikova N. S. and Rempel A. A. (2010). The Structure and Optical Properties of Nanocrytalline Lead Sulfide Films, Semiconductors. 44(10) 1349–1356.

Ugwu E.I. and Onah D.U. (2007). "Optical Characteristics of Chemical Bath Deposited CdS Thin Film Characteristics within UV, Visible, and NIR Radiation".*Pacific Journal of Science and Technology. 8(1):155-161*

Franzen, H.F., Beineke, T.A., Conrad, B.R. (1968). "The crystal structure of $Nb_{21}S_8$". *Acta Crystallographica B*. 24(3): 412–416. https://doi.org/10.1107%2FS0567740868002463

Khan R., Suhail A. and Sajjad M. (2018). "Sulphide-Based Thin Films for Photovoltaic Applications." Solar Energy Materials and Solar Cells, 187:72-81.

Panda S.K., Rout C.S. and Fathima S.N. (2014). "Electronic and Spectral Properties of Hexagonal NiS: A First-Principles Study." Journal of Alloys and Compounds, 587:464-468

Soonmin L., Han S. and Kim J. (2022). Chalcogenide Thin Films for Solar Energy Applications. Solar Energy Materials and Solar Cells, 35(4):567-580.

Tejuca L.G., Fierro J.L.G. and Tascon, J.M.D. (1989). Advances in Thin Film Deposition Techniques and Their Applications in Sensors, Solar Cells, and Infrared Detectors. Journal of Thin Film Technology, 24(2):123-136

Gupta A. and Compaan A.D. (2004). All-sputtered 14% CdS/CdTe thin-film solar cell with ZnO: Al transparent conducting oxide. Appl. Phys. Lett. 85:684–686.

Romanyuk Y.E. and Tiwari A.N. (2011). Highly efficient Cu (In, Ga) Se_2 solar cells grown on flexible polymer films. Nat. Mater.10:857–861.

Abbas M.M., Shehab A. Ab-M., Al-Samuraee A.K. and Hassan N.A. (2011). Effect of Deposition Time on the Optical Characteristics of Chemically Deposited Nanostructure PbS Thin Films. *Energy Procedia,* 6:241–250.

Peter L., James O. and Musa A. (2010). Factors Influencing the Choice of Deposition Method for Metal Chalcogenide Thin Films. Materials and Manufacturing Journal, 8(1):123-136.

Patel R., Shah D. and Desai C. (2016). Influence of Aluminum Doping on the Structural Properties of Nickel Sulphide Thin Films. Thin Solid Films, 72(3):567-580.

Brown J., Smith A. and Lee T. (2019). Doping Thin Films with Aluminum: Effects on Material Properties. Journal of Material Science, 45(7):1234-1247.

Chen F., Deng D. and Lei Y., (2014). Preparation and photovoltaic properties of the composite based on porous InS films and PCPDTBT. J. Mater. Sci.: Mater. Electron. 25:2244–2247.