

The Effect of Aluminum dopant on the Optical and solid State Properties Nickel Sulphide Thin Film

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ABSTRACT

Nickel sulphide thin film was doped with different concentration of aluminum using chemical bath deposition technique for which the effect of the concentration of aluminum as a dopant is the key focus to see how it will affect the optical and solid state properties of the deposited thin film. From the results, the spectral absorbance, transmittance from a UV-VIS double beam Spectrophotometer, XRD machine and also from the computed results of the absorption co-efficient, energy band gap, and the depicted preferred plane of orientation peak, it was seen that the dopant concentration did actually affect those aforementioned properties of NiS thin film which invariably may influence its application to solar energy harnessing and optoelectronics device application.

ARTICLE'S INFO

Article No.: 011526008

Type: Research

Full Text: [PDE](#), [PHP](#), [HTML](#), [EPUB](#), [MP3](#)

DOI: [10.15580/gjps.2026.1.011526008](https://doi.org/10.15580/gjps.2026.1.011526008)

Accepted: 18/01/2026

Published: 20/02/2026

Keywords: Nickel Sulphide, Aluminum, Doping, Effect, Solid State and optical properties

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Article's QR code



1.0 INTRODUCTION

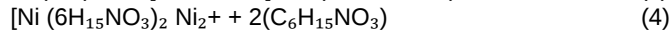
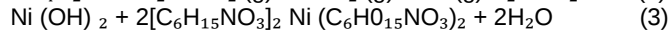
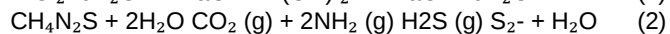
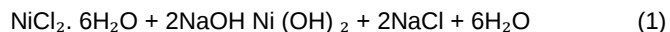
NiS is one of the sulphide based chalcogenide thin films that have received a great deal of attention because of their potential application in the area of electronic, optoelectronic devices and solar cell devices. This why in recent time more effort has been focused on the synthesis of such metal chalcogenide thin films which include tin sulphide, manganese sulphide, copper sulphide, cadmium sulphide, zinc sulphide, lead sulphide [1-8] etc in addition to Telluride, Selenide that are also of the same family with sulphide. These materials are of practical interest because of their optical, mechanical and electrical properties [9] which are unique coupled with the fact that they can be deposited in a large surface area using a simple and less costly deposition mechanism such as chemical bath method unlike some other categories of thin film whose deposition process are cumbersome and very costly to come by such as CVD, sputtering, spray-pyrolysis and sol-gel pulse laser techniques [10-15]. In case of the aforementioned sulphide based thin films, they can be deposited on metals, glass and polymer substrates that are immersed in solutions containing metal complex ions and a source of sulphide which normally Thiourea, [16]. The material have been increasingly studied in the search for new semiconductor materials for efficient solar energy conversion, sensor, photoconductors, optical mass memories coupled with the fact that these materials have been known to be potential candidates for photoelectrochemical characteristics and based on the anticipation to see if their properties can be further enhanced by any parameter [17-18] we decided by to dope our research material on focus, NiS with aluminum element which on its own has unique property in order to assess its effect on the as-deposited NiS thin film.

2. MATERIALS AND METHODS.

Where the substrates were first scrubbed thoroughly with clean cotton wool and soap solution which and then rinsed with water. They were then placed inside a bath containing a solution of HCl acid (30%) for some time in order to ensure that any dirt was remnant was completely removed after they were rinsed with deionized water and then dried in an open furnace at a moderate temperature. To facilitate smooth adherence of the films to the surface of the substrate during the growth process. The chemical bath on its own was prepared by sequential addition of 0.5M of Nickel Chloride Hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), 0.5M of Thiourea, 0.5M of Sodium Hydroxide (NaOH) to neutralize the acidity of the solution, 0.5M of Tri-ethanol-amine (TEA) as the ligand ($\text{C}_6\text{H}_{15}\text{NO}_3$) into three different baths (N, AN_1 and AN_2). Aluminum Chloride (AlCl_3) which is the source of Aluminum (Al) which will serve as the doping agent was also added into the second and third bath (AN_1 and AN_2) with varying concentration of aluminum dopant from

0.2M to 0.4M. After distilled water was further added until the volume of the solution reached 70ml and the PH of the solution measured using digital PH meter and kept constant for few hours at a specific temperature and further heated and then thoroughly stirred on a magnetic stirrer for a specific time in order to aid homogeneity. The cleaned and dried substrates were then clamped vertically using retort stand, clipped and then lowered into the three beakers (100ml) containing the CBD solution. Then, 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; N, AN_1 and AN_2 . After that, the three samples will be 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.

2.1; Reaction equations



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.

3. RESULTS AND DISCUSSION

After these processes, the three samples were taken to the laboratory for analysis using spectrophotometry, Ellipsometry, and Photoluminescence Spectroscopy and XRD from where the spectral absorbance, reflectance, transmittance, energy band gap and structural characteristics of the thin film were determined.

3.1; Optical Properties of NiS Thin Film

The influence of aluminum (Al) doping on the optical properties of nickel sulphide (NiS) thin films using a cost-effective chemical bath deposition (CBD) technique at room temperature would be examined and discussed in this section. The aluminum (Al) influence doping on spectral absorbance, transmittance, absorption coefficient and Energy band gap at photon wavelength region of 200 to 900 nm are sequentially studied using a UV-VIS double beam Spectrophotometer.

3.2; Thin Film Absorbance.

The absorption behavior of the grown thin films in the wavelength range of 300 to 900 nm is shown in the

Figure 4.1 below. The figure shows the absorbance spectra of the NiS and AlNiS thin film samples of different concentrations of aluminum (Al); N is the standard sample of the NiS thin film, AN₁ is the Aluminum (Al) - doped NiS thin film at 20 ml concentration and AN₂ being the Al- doped NiS at 25 ml concentration. It is easily observed from the graph plot in the Figure 4.1 that the standard sample N shows the least absorption property in the absorption spectra which is in line with the result obtained by (T. H. Johnson, 1984). While samples AN₁ and AN₂ increases in absorbance behavior at a longer wavelength as the concentration of aluminum (Al) doping increases in the region of the absorption spectra respectively. As a result of these observations, it can be easily concluded that the increase in the concentration of Al- doping of NiS thin film increases and enhances the absorbance property of the film material as seen in figure

3.3; Thin Film Transmittance.

The transmittance spectra in percentage (%) of NiS thin films for the standard and control samples N, AN₁ and AN₂ are respectively shown in the plot of transmittance against wavelength in figure 4.2 below. It can be deduced from the plot that there was no transmittance between the wavelength ranges of 200 nm to 300 nm for the three (3) samples. The transmittance increases exponentially as the wavelength increases from 300 nm upward and this reason may be attributed to the thickness of the films.

However, it is obviously observed from the graph plot in figure 4.2 that the standard sample N has the highest value of transmittance in the transmission spectral region. The control samples AN₁ and AN₂ decreases exponentially as the concentration of the Al-doping increases and AN₂ with the highest concentration of Al has the least value of transmittance. With the aforementioned reasons and observations as seen from the graph plot, it can be concluded that the increase in the concentration of Al- dope in NiS thin Film decreases the transmittance of the material in the transmission spectral region. Therefore, aluminum doping lowers the transmittance of NiS and AlNiS thin film.

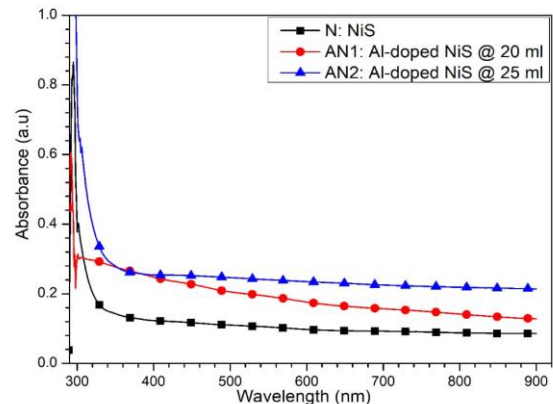


Figure 1; The Absorption spectra of the standard and controlled samples of Pure NiS and AlNiS Thin Film

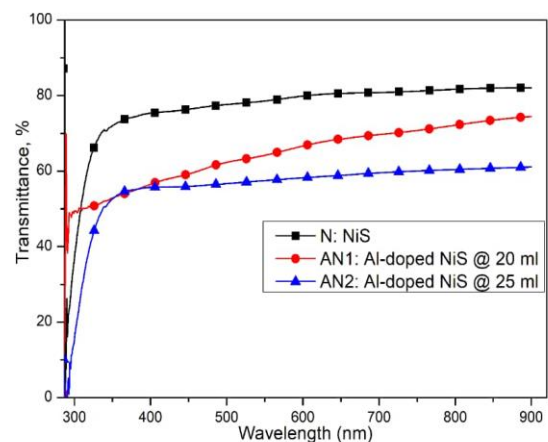


Figure 2; The transmission spectra of the standard and controlled samples of Pure NiS and Al-doped NiS Thin Films.

3.4; Absorption Coefficient)

Absorption coefficient of a thin films is usually utilized in determining the nature of the optical band gap of the films. Equation (7) was used in generating the absorption coefficient of the film, the optical absorption coefficient of NiS thin films with different concentrations of Al- doping at room temperature; AN₁ and AN₂ respectively is plotted as a function of wavelength in figure 4.3. The figure shows a similar behavior to that of the absorption spectra discussed earlier in figure 4.1. The results obtained from the standard sample AN₁ corresponds to the result obtained by [19] . It can be deduced from the graph plot in the figure 1 and figure 3 that the increase in the concentration of Al- doping in NiS thin film increases the absorbance and absorption coefficient of the films material respectively .Therefore, aluminum doping enhances the absorption coefficient of NiS thin film.

3.5; Energy band gap, E_g

The energy band gap of the three samples N, AN₁ and AN₂ of the deposited and Al- doped NiS thin films was estimated using Tauc plot as shown in figure 4 below. In the figure, the value of $(\alpha h\nu)^2$ was plotted against the photon energy in accordance with the expression for direct band gap estimation. The respective band gap for each samples was obtained by extrapolating the linear region or portion of the curve of different concentrations of aluminum was determined as plotted in figure 4. The photon energy axis at a point where the term $(\alpha h\nu)^2$ is zero. Indicate the band gap for each graph. The obtained results for the three samples are tabulated in table 1.

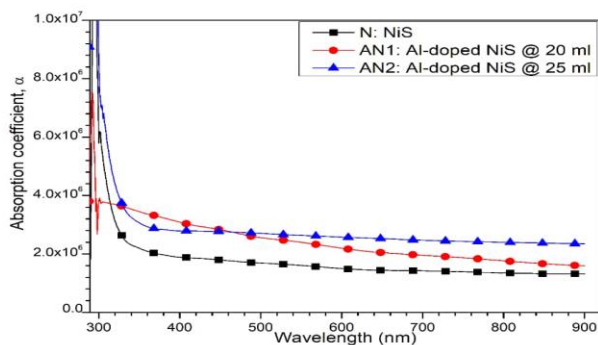


Figure 3: The absorption coefficient of the standard and controlled samples of Pure NiS and Al-doped NiS Thin Films.

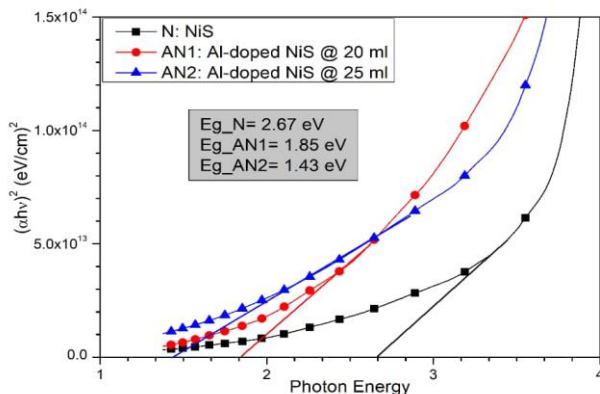


Figure 4: The Tauc plot of the energy band gap of the three samples of NiS thin films as a function of photon energy.

Table 4.1; Energy band gap for the three different samples of NiS thin films.

Samples	Energy band gap (eV)
N	2.67
AN ₁	1.85
AN ₂	1.43

It is easily observed from the graph plotted in figure 4 that this, the energy band gap become narrower as the Al concentration increased as shown on table 1.0 that the energy band gap of the standard sample N has the highest value of energy band gap 2.67 eV and it is in tally with the result obtained by [20] (K. Anuar, Z. Zulkanain *et al.*, 2004) for as-deposited NiS thin film while the other two samples AN₁ and AN₂ shows the a decrease in the value of the optical energy band gap as the concentration of aluminum increases respectively. Therefore, sample AN₂ with the highest concentration of aluminum having the lowest value of band gap. Thus, with this observation and it is obvious that Al- doping is found to affect the NiS thin films as it /narrows the optical energy band gap.

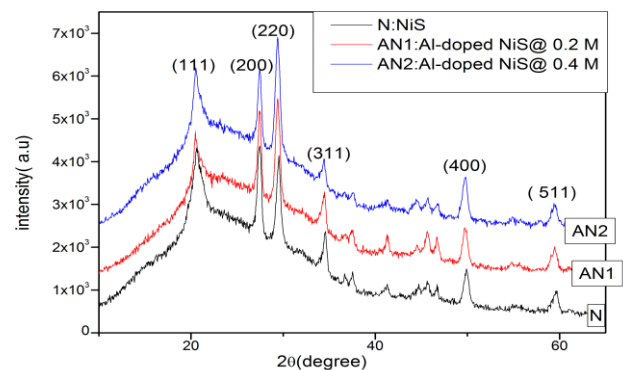


Figure 5; X-Ray Diffraction Pattern of Pure NiS and Al-doped NiS Thin Films

3.6; X-Ray Diffraction (XRD) Analysis

The solid state properties of Nickel sulphide thin film was analyzed using X-Ray Diffraction (XRD) analysis based on the following parameters: crystallinity, grain-size, micro-strain, and dislocation density and lattices parameters are the determinant of the solid state characteristics of materials. The XRD patterns of the pure Nickel Sulphide thin film (N) and the aluminum-doped Nickel sulphide thin films (i.e AN₁ and AN₂) at different concentration of aluminum doping is shown figure 3 depicting the orientation of each of the sample. The XRD pattern of as-deposited and aluminum doped Nickel sulphide thin film were taken within the range of Bragg's angle (2θ), from 10° to 65° from where the peaks in the spectra are identified within (111) (200) and (220), (311), (400) and (511) planes where the sample N₂ was identified to have the most intense peak indicating the effect of the dopant on the structure of the material, because it is obvious that the variation in the intensity of the peaks of N₂ and N₁ were enhanced due to the different concentration of the aluminum dopant on Nickel Sulphide thin film which is 0.2M and 0.4M

respectively which must have contributed in changing the orientation of the crystal structure.[21-22]

4. SUMMARY

In this research work, NiS thin films has been successfully grow and dope with different concentration of aluminum dopant using chemical Bath Deposition Technique for which the influence of aluminum doping on the optical properties of the deposited films has been characterized and investigated as it concerns the optical properties of the films such as the spectral absorbance, transmittance, absorption coefficient and energy band gap using UV-VIS spectrophotometer within the spectral range (300- 1000 nm) and from the results obtained there is an indication that aluminum doping has a considerable influence on the optical properties specifically absorbance, transmittance, absorption coefficient, energy band gap and the structural properties of NiS thin films. The absorbance and absorption coefficient has been observed to increase with the concentration of Al. In a similar manner, it was clearly revealed that the energy band gap of the thin film got narrowed as the concentration of Al dopant increases while the transmittance decreased with increase in the concentration of Al concentration. The structural properties as indicated in the XRD was also affected as the peak of the preferred plane of orientation increased with increase in the concentration of the aluminum [23]. Thus it is obvious that doping NiS with aluminum optimized its properties. In general as could be inferred from the literature, these categories of thin films could be influenced by some deposition parameters [23-24]. And this is more reason why chalcogenide categories of thin films can be tailored in to so many applications such as solar energy harnessing and optoelectronic.[26]

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Cite this Article: Ugwu, EI (2026). The Effect of Aluminum dopant on the Optical and solid State Properties Nickel Sulphide Thin Film. *Greener Journal of Physical Sciences*, 12(1): 1-6, <https://doi.org/10.15580/gjps.2026.1.011526008>.