

Assessing the Influence of Aluminum Dopant on the Morphological and Structural Characteristics of NiS Thin Film Material Deposited by Chemical Bath Deposition Technique

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ABSTRACT

Based on the influence of dopant like aluminum on some sulphide based thin film materials it has become paramount to carry out an assessment of chemical bath deposited Nickel sulphide doped with aluminum has been carried with the intension to ascertain the impact of the dopant concentration on the morphological and structural properties of the as-deposited NiS thin film sample and the aluminum doped, AlNiS thin film with different concentration of aluminum. It was revealed from the result as obtained from the work that both the morphological and structural properties that there were tremendous effect on the crystallinity, grain-size as depicted in figures and computed values in which the values of the lattice constant, dislocation density, micro-strain and grain-size as computed at the same preferred plane within the same diffraction angles are found to vary thereby indicating that there is clear evidence of the effect of aluminum doping concentration on the Nickel sulphide thin film developed with aluminum.

Keywords:

Assessment,
Aluminum,
Structural and Morphological
properties,
Chemical Bath Deposition,
Dopant,
Nickel sulphide.

INTRODUCTION

In the recent years, nanocomposites have been occupying a major focus of research. These nanocomposites are multiphase materials formed by mixing two or more materials. For instance, so many metals especially transition metals (Ti, Sn, Ca, V, Cr, Mn groups) can easily form binary chalcogenide with S, Se, Te etc), and can be synthesized by different methods as such they also exhibit different nanostructures and properties suitable for applications in various fields. Some of them are sulphide, selenide based chalcogenide while some are oxide based. Among the various nanocrystalline materials that are chalcogenide based nanocomposites that are often binary in composition are CdS, CdSe, Bi₂S₃, PbSe, PbS, As₂S₃, Ag₂S, Cu₂S, Sb₂Se₃, ZnS, CaS, PbTe, and NiS while some are ternary CdZnS, CdSSe, CuInSe₂, PbHgS, CdPbSe, AlNiS etc. (Gupta and Compaan, 2004; Adeyeba *et al.*, 2022; Nefzi *et al.*, 202). Their properties make them beneficial in various applications such as solar energy absorbers, electroconductive coatings, tabular solar collectors, microelectronic devices and gas sensing applications, ion batteries, in superconductors, and heterojunction photodetectors such as Cu₂S/CdS,

ZnO/Cu₂S, Cu₂S/ZnS, and Cu₂S/n-Si, and sensors (Adelifard *et al.*, 2012; Kassim^a *et al.*, 2011; Guo *et al.*, 2014; Ismail *et al.*, 2020; Zhan *et al.*, 2019; Khan *et al.*, 2018; Soonmin *et al.*, 2022).

However for whichever form appear to be, they can be grown using various deposition techniques the synthetization of sulphide and other chalcogenide based thin films especially NiS and AlNiS thin films viz; vacuum evaporation, photochemical deposition, chemical bath deposition, sputtering, continuous flow microreactor, spray pyrolysis, and successive ionic layer adsorption and reaction technique, (SILAR) (Busar *et al.*, 2020; Kadhim *et al.*, 2017; Leskelä and Ritala, 2003; Kumar and Sankaranarayanan, 2009; Aydin *et al.*, 2014; Owoh and Ugwu, 2009). However, chemical bath deposition technique which is the method we used is one of the most popular techniques for the deposition of thin films due to its advantage over other deposition techniques, such as cost, low pressure, ability to deposit large areas, and low-temperature requirement. It should also be bore in mind that the properties of chemically deposited thin films strongly depend on some deposition parameters, such as deposition time, pH value, bath

temperature, and substrate nature, complexing agent or ligand, doping and annealing (Gashaw and Abza, 2019; Khalil *et al.*, 2019; Ouchtari *et al.*, 2011; Ahmed *et al.*, 2021; Okoli *et al.*, 2016; Anuar *et al.*, 2011; Benhaoua *et al.*, 2014; Nefzi *et al.*, 2020; Abdallah *et al.*, 2018; Patel *et al.*, 2016; Obasi *et al.*, 2016).

In general, in whichever form chalcogenide thin films appear to be whether binary or ternary etc they have interesting characteristic associated with many of them. This is a general trend, they are always dark and diamagnetic in nature, insoluble in all solvents, and exhibit semiconducting properties especially n-type semiconductor coupled with the fact that most of them especially NiS have crucial properties, such as non-toxicity, low cost with an ideal energy band gap for so many application (Hedlund *et al.*, 2020; Adeyeba *et al.*, 2022; Kadhim *et al.*, 2017).

Therefore, in this work we intend to assess the effect of variation of aluminium doping on the morphological and structural properties of NiS as a sulphide based chalcogenide thin film using chemical bath growth technique. That is to ascertain how the variation of concentration of aluminum dopant affects the morphological and structural properties of the thin film.

MATERIALS AND METHODS

Prior to the deposition, the glass slide substrates were first of all cleaned by scrubbing thoroughly with cleaned cotton wool and soap solution, rinse with running tap water in order to ensure that all contamination on their surface is removed then further they were ultrasonicate using ultrasonic bath of acetone, methanol and distilled water at room temperature for some hours. After that, they were rinsed with deionized water and dried in an open moderate temperature. These cleaning processes were taken in order to ensure complete removal of all the 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 ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), 0.5M of Thiourea, 0.5M of Sodium Hydroxide (NaOH) to neutralize the acidity of the solution, 0.5M of Tri-ethanol-amine (TEA) ($\text{C}_6\text{H}_{15}\text{NO}_3$) into three different baths (N, AN₁ and AN₂). Aluminum Chloride (AlCl₃) 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 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; N, AN₁ and AN₂. 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.

Deduction

The structural grain size were deduced from the well-known mathematical as outlined below

The grain-size, of crystallites was calculated using a well known Scherrer's formula

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Where D is the grain-size, λ is the wavelength of X-ray used, where ($\lambda = 1.54184\text{\AA}$) gotten from the XRD data, β is the diffraction peak's FWHM and θ is the Bragg's diffraction angle. The estimated grain-size and some other structural data are presented in Table 4.03. This was confirmed that the D values of the films were dependent on the dopant molar concentration

The micro-strain of the films can be calculated using the equation (Busari *et al.*, 2020)

$$\gamma = \frac{\beta}{4 \tan \theta} \quad (2)$$

Where ϵ is the micro-strain, β is the diffraction peak, θ is the Bragg's angle.

The dislocation density of the films was calculated using the equation below (Adewinbi *et al.*, 2021)

$$\delta = \frac{1}{D^2} \quad (3)$$

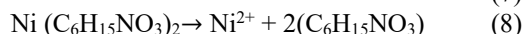
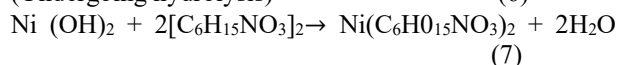
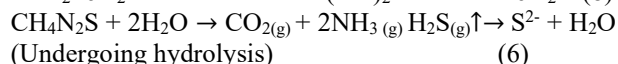
Where δ is the dislocation density and D is the grain-size as obtained from equation 1, the constants was also determined using the equation below

$$\frac{1}{d^2} = \frac{4}{3} \left[\frac{h^2 + k^2}{a^2} \right] + \frac{1}{c^2} \quad (4)$$

Where (d) is the interplanar distance or lattice spacing, (h, k, l) are the miller indices, (a) and (c) are the lattice constants for the film structure. Inter planar spacing can be calculated from Bragg's law as:

$$d = \frac{\lambda}{2 \sin \theta} \quad (5)$$

Reaction Equations



The samples were analyzed using the following techniques such as; X- Ray Diffraction (XRD) and Scanning Electronic Microscopy (SEM) EDX

RESULTS AND DISCUSSION

Energy Dispersive X-ray (EDX) Analysis

The Energy Dispersive X-ray (EDX) analysis (Energy Electron Diffraction Spectrometer) is a technique used for investigating the chemical composition of particles/elements and also the energy decomposition (Kassim *et al.*, 2021). In figure 1a shown below is the

EDX analysis for pure and Aluminum-doped nickel sulphide samples, which shows the sample composed of the nickel with significant amount of Sulphur elements.

The EDX result in figure 1a shows the presence of nickel and Sulphur in the pure sample. Also, in figure 1b, the presence of nickel and Sulphur elements are observed together with the presence of Aluminum in the Aluminum-doped samples.

It is observed that both pure and Aluminum-doped samples show the dominance of nickel element which is shown in the figure 2.

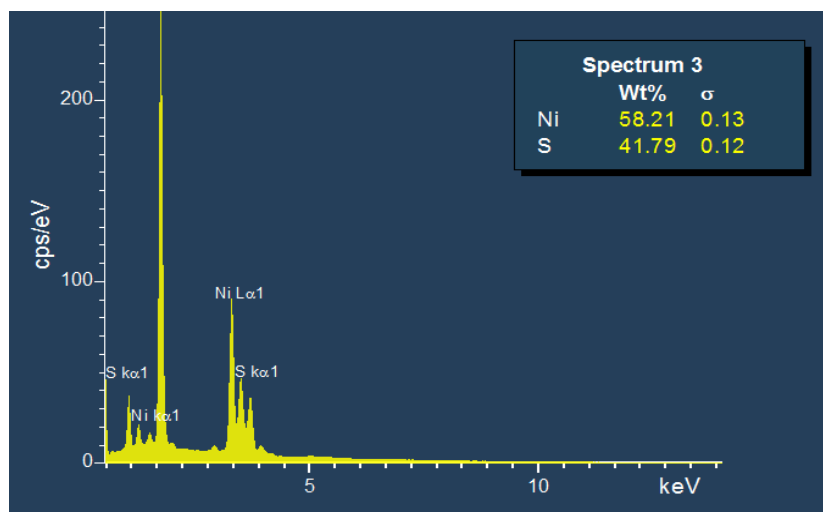


Figure 1(a): EDX image for Pure Sample of Nickel Sulphide

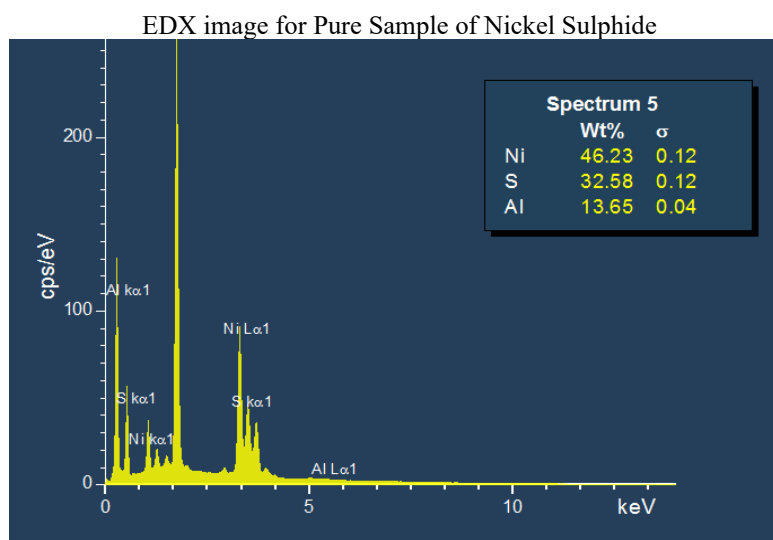


Figure 1(b): EDX image for Aluminum-Doped Sample

Surface Morphology

The scanning electron microscopy (SEM) analysis revealed significant differences in surface morphology between pure nickel sulphide (NiS) films, as shown in the figure 2(a), and those doped with aluminum (Al). The microstructure of undoped NiS film (N) consisted of

unevenly distributed flaky layers with irregular shapes and jagged edges, indicating disrupted growth. Presence of noticeable gaps and porosity between the haphazard clusters evidenced lack of uniformity and discontinuity in the film (Ugwu, 2013; Zhang *et al.*, 2021). Low level Al-doping (AN₁) led to increased uniformity in layered

structure distribution as flakes appeared smoother with tighter packing, as shown in the figure 2(b), (Chen *et al.*, 2014). Distinct spherical nanocluster formations were observed on the surfaces along with unique cauliflower multivariate shapes implying doping introduced favorable alterations in growth mechanisms as in literature (Patel *et al.*, 2016).

Higher Al-doping AN_2 further enhanced inter-linking between layers, with densely packed smooth textures and negligible porosity between them, as shown in figure 2(c). The surfaces were homogeneously coated with uniformly spread nanoclusters having larger size variants

compared to the low doped films, AN_1 affirming profound impacts of Al-incorporation. The pure NiS, N morphology indicated poor crystalline quality with high structural defects. In contrast, Al doping facilitated reorientation of layered structures leading to significant improvements in density, continuity and nano-structuring. Increased doping concentrations resulted in progressive grain structure modifications, consistent with literature as it affects the doped metal sulphide thin film systems as in (Tejuca *et al.*, 1989) and (Rajathi *et al.*, 2014; Patel *et al.*, 2016).

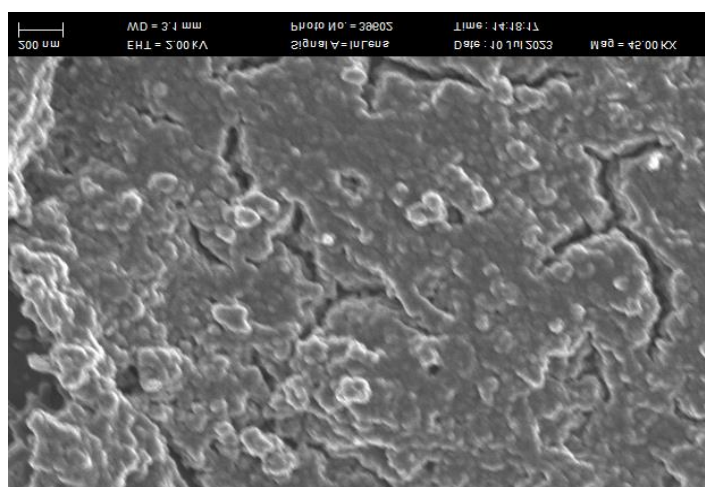


Figure 2(a): Pure Sample of NiS thin film

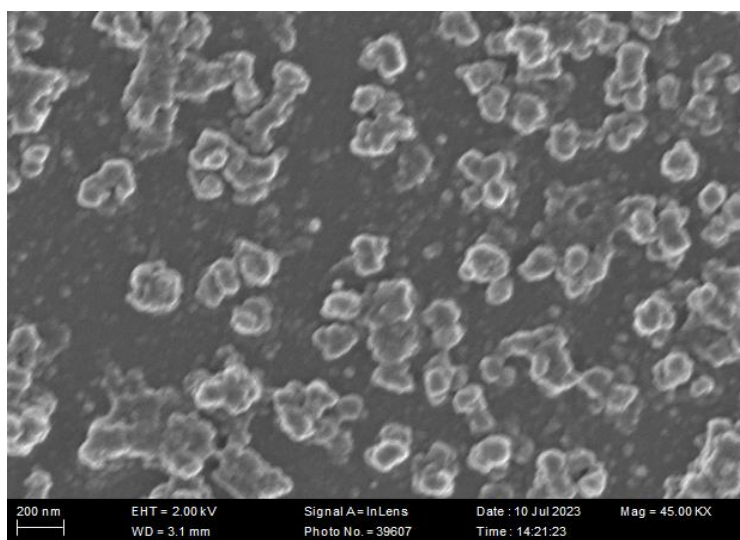
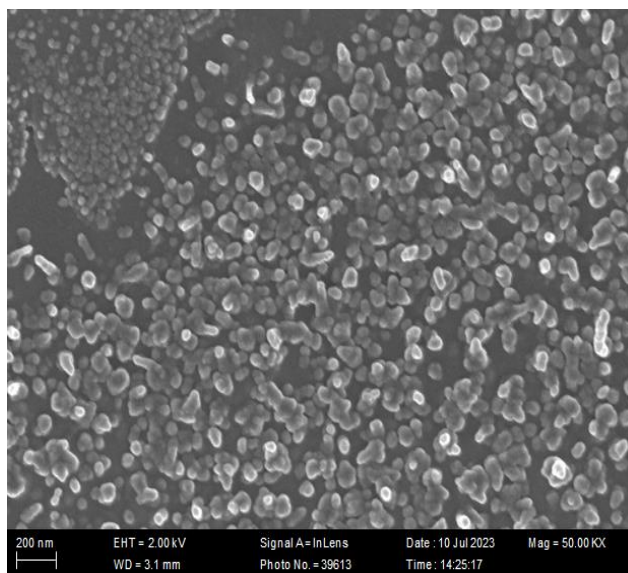


Figure 2(b): Al-doped NiS at 0.2M, N_1

Figure.2(c): Al-doped NiS at 0.4M, N₂

Structural X-Ray Diffraction (XRD) Analysis

The structural 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. The XRD patterns of the pure Nickel Sulphide thin film N and the Aluminum-doped Nickel sulphide thin films AN₁ and AN₂ at different

concentration of Aluminum doping is shown figure 3. The XRD pattern of Nickel sulphide thin film was taken within the range of Bragg's angle (2θ), from 10° to 65° . The peaks in the spectra are identified as originating from reflection of (111) and (311) planes indicating the structure of Nickel Sulphide film to be hexagonal in nature. Therefore, having strong orientation in (111) plane.

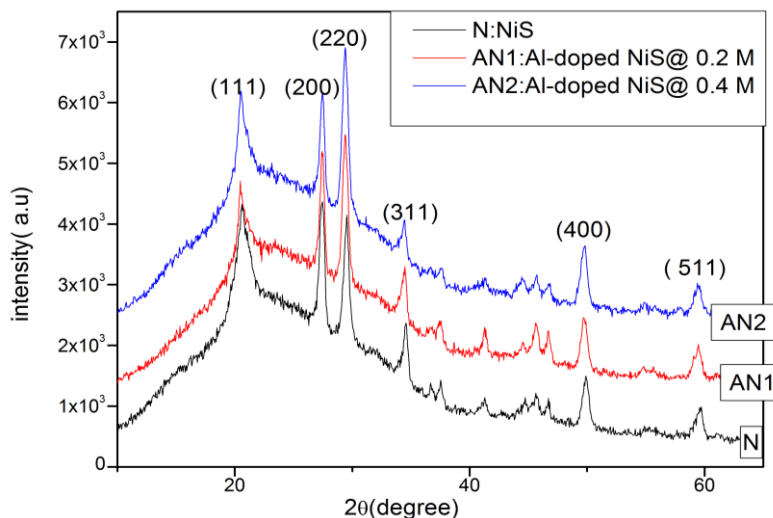


Figure 3: X-Ray Diffraction Pattern of Pure NiS and Al-doped NiS. Thin Films

In a polycrystalline material, the crystallites typically involve differential crystallographic orientation among their neighbors. In relation to some chosen frame of reference, this preference orientation may be dispersed randomly. Here, (311) diffraction plane is the preferred orientation exhibited by the films and similarly, this can be made reference to the XRD pattern of the work done on Cd-O thin film electrodeposited by two electrodes

(Busari *et al.*, 2020). The intensity of the peak is enhanced due to the different concentration in the aluminum-doped nickel sulphide films (i.e., 0.2M and 0.4M).

Where ($\lambda=1.54184$) is the wavelength used and θ is the incident angle at which maximum diffraction occurs (Patel *et al.*, 2016).

Table 1: Full Width at Half Maximum Angle, Crystallites Size, Micro Strain, Inter Planar Space

S/N	Thin Film/Sample	Bragg's Angle (2 θ) (°)	Preferred Plane (hkl)	d-space(Å)	Grain-size (D) (Å)	Dislocation Density (δ) (Å ⁻²)	Micro-strain (ϵ)	FWHM (β)	Lattice constant (a) (Å)	Lattice Constant (c) (Å)
1.	NiS (N)	27.4353	200	3.2666	3.8601	0.0671	0.3957	0.3864	1.7078	1.8229
2.	Al-doped NiS(AN ₁) @ 0.2M	29.4078	220	3.0375	3.3233	0.0905	0.4295	0.4508	1.6514	1.7716
3.	Al-doped NiS (AN ₂)@ 0.4M	29.4360	220	3.0351	2.4493	0.1667	0.5822	0.6118	1.5923	1.7694

Dislocation Density and Lattice Constant I at Preferred Plane (200), (220)

Contrary to expected outcomes, X-ray diffraction studies indicated reduced crystalline domain sizes in aluminum-doped nickel sulfide thin films, concurrently with heightened microstrain and dislocation densities (Shah *et al.*, 2021; Kim *et al.*, 2021). This unintuitive concurrence suggesting aggravated distortion incorporation was further validated through scanning electron microscopy, which evidenced proliferation of granular nanostructures with increasing inter-crystallite voids (Chen *et al.*, 2014). The collective microstructural analyses verify that excessive doping can breach lattice saturation thresholds in nickel sulfide matrices, thereby deteriorating structural arrangements despite additional dopant introduction (Kar *et al.*, 2021). The results emphasize the intricacies of judicious defect engineering by validating aberrant morphologies and porous discontinuities from surpassing optimum incorporation limits that generate accumulated strains without accruing anticipated benefits (Patel *et al.*, 2016). Careful calibrations of dopant quantities within permissible limits are therefore critical for enabling ideal microstructure and performance in synthesized chalcogenide thin films.

CONCLUSION

Using the chemical bath technique, nickel sulphide thin films were effectively produced in this work at concentrations of aluminum doping whereby it was seen from the EDX result that there was no contamination or impurities in deposited films samples for both as-deposited and aluminum doped NiS thin film. The evaluated and studied of the impact of aluminum doping on the structural and morphological properties of the deposited films obtained from X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) revealed the morphology and the structure characteristics of the deposited films analyzed whereby the outcomes demonstrate that the morphology and structural properties of nickel sulphide thin films are significantly influenced by aluminum dopant. It was observed that there were slight variations in the structural properties as analyzed here occasioned by different concentration of aluminum doping using XRD analysis. For instance, there is variation in grain-size, grain boundary, dislocation density, micro-grain, lattice parameters and

crystalline nature with the aluminum doping concentration as indicated in figures as presented. As from the aspect of the morphology, the SEM micrograph structure revealed that the grain-sizes of the films decrease as the concentration of the aluminum doping increase and this outstanding property of the thin films makes it suitable for various applications and as such can be concluded that the properties of NiS modified by Al dopant have an improved characteristics for optoelectronic, solar harnessing applications as outlined in the literature.

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