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Comparative Assessment of the Effect of Dip Time, Dopants, and Ligand on the Structural and Solid-State Properties of Selected Sulphide-Based Chalcogenide Thin Films Grown by Chemical Bath Technique: PbS and NiS

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ABSTRACT

A comparative assessment of the effects of dip time, dopant, and ligand on the structural and solid-state properties of PbS and NiS thin films deposited by the chemical bath technique was conducted. The influence of these parameters, commonly employed during chemical bath deposition, was evaluated to ascertain their comparative impact on the morphological, solid-state, structural, and optical properties of the thin films. XRD patterns and selected solid-state properties were analyzed, revealing variations in peak intensities at different planes of orientation in the XRD patterns, depending on ligand/dopant concentration and dip time. Similarly, variations in the energy band gap, refractive index, dielectric constant, optical conductivity, and absorption coefficient were observed in accordance with changes in these parameters for the selected chalcogenide-based thin films.

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1.0 INTRODUCTION

In recent years, chalcogenide compounds and thin films have attracted significant research interest due to their anticipated applications and unique characteristics. Beyond their multipurpose applications, these materials exhibit fine crystallization, distinctive behavior at gas-solid interfaces, heterogeneous catalysis, and susceptibility to partial substitution at reactive positions [1]. Many naturally occurring minerals and ores are monosulfides [2]. Chalcogenide thin films can be readily synthesized, with their chemical and physical properties amenable to forming fine crystalline structures. They also readily form compounds with transition metals. Metal dichalcogenides have the general formula ME_2, where M is a transition metal and E is S, Se, or Te. Binary chalcogenides include CdS, CdSe, Bi_2S_3, PbSe, PbS, As_2S_3, Ag_2S, Cu_2S, Sb_2Se_3, ZnS, CaS, PbTe, and MnS, while ternary chalcogenides include CdZnS, CdSSe, $CuInSe_2$, PbHgS, and CdPbSe. Quaternary chalcogenides also exist. Many of these compounds can be grown using the chemical bath deposition (CBD) technique [3-4], while others may require alternative thin film growth methods [5-9]. For example, the growth and optical characterization of antimony selenide (Sb_2Se_3) thin films using the CBD technique have been performed in the UV, visible, and near-infrared (NIR) regions [10-11].

Generally, chalcogenide thin films—whether binary, ternary, or quaternary—are primarily composed of sulfides, tellurides, and selenides. A notable characteristic of these materials is their dark color, diamagnetic nature, insolubility in all solvents, and semiconducting properties. These novel chalcogenide films are of particular interest for the fabrication of large-area photodiode arrays, solar selective coatings, solar cells, photoconductors, sensors, and, notably, for their superconductive properties [12]. Many metals, especially those in the Ti, V, Cr, and Mn groups, can readily form binary or trichalcogenides, often described as $CM^{4+}(E_2^{2-})(E^{2-})$, where E = S, Se, or Te.

In this work, we assess the effects of dip time, ligand variation, and doping on sulphide-based chalcogenide thin films, specifically PbS and NiS, grown by the chemical bath technique, to determine how these parameters influence their structural and solid-state properties.

2. MATERIALS AND METHOD

Sulphide-based chalcogenide thin films were deposited exclusively by the chemical bath deposition technique, which generally involves three steps: preparation of substrates, preparation of anionic and cationic solutions, and film growth. Glass slide substrates (7.5 cm × 1 cm × 0.2 cm) were prepared by soaking in acid medium and subsequently cleaned chemically prior to deposition. For PbS films, the chemical bath was prepared using 5 ml of 0.5 M lead acetate ($Pb(CH_3COO)_2 \cdot 3H_2O$) and 6 ml of 1 M thiourea ($(NH_2)_2CS$). Sodium hydroxide (NaOH, 5 ml, 2 M) and triethanolamine ($N(CH_2CH_2OH)_3$, 2 ml, 1 M) were used to adjust the pH and as the ligand, respectively. The cleaned glass substrates were immersed vertically into the chemical solutions, positioned appropriately. Immersion was conducted for designated durations at bath/room temperature, depending on the specific experimental setup. For example, in the case of CdS growth, chemical baths were prepared with 5 ml of 0.03 M $3CdSO_4 \cdot 8H_2O$, 5 ml of 0.1 M thiourea, 1 ml ammonium hydroxide (NH_4OH), and 2 ml of 1 M triethanolamine as the ligand. CdS films were grown at 80°C for 1 hour [13–16].

For nickel sulphide (NiS) thin films, the same substrate preparation protocol was followed. The chemical bath was prepared by sequentially adding 0.5 M nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), 0.5 M thiourea, and 0.5 M sodium hydroxide (NaOH) to neutralize the solution's acidity, followed by 0.5 M triethanolamine (TEA, $C_6H_{15}NO_3$) into three separate baths. Aluminum chloride ($AlCl_3$), serving as the aluminum (Al) dopant source, was added to the second and third baths at concentrations of 0.2 M and 0.4 M, respectively. Distilled water was added to bring the total solution volume to 70 ml, and the pH was measured and maintained at 8 using a digital pH meter. The bath solution was heated to a specific temperature and stirred thoroughly on a magnetic stirrer for 30 minutes to ensure homogeneity.

Film deposition from solution involves a nucleation phase in which an initial layer of $Pb(OH)_2$ forms on the glass substrate and is chemically converted into PbS by reaction with S^{2-} ions generated from the hydrolysis of thiourea. The presence of $Pb(OH)_2$ in the as-prepared bath is essential for PbS thin film deposition. For NiS, a similar nucleation phase occurs, where an initial layer of $NiCl_2 \cdot 6H_2O$ forms on the substrate and is chemically converted to NiS by reaction with ions from thiourea hydrolysis. Doping of NiS is achieved by adding aluminum chloride to obtain AlNiS [17-18].

3. RESULTS AND DISCUSSION

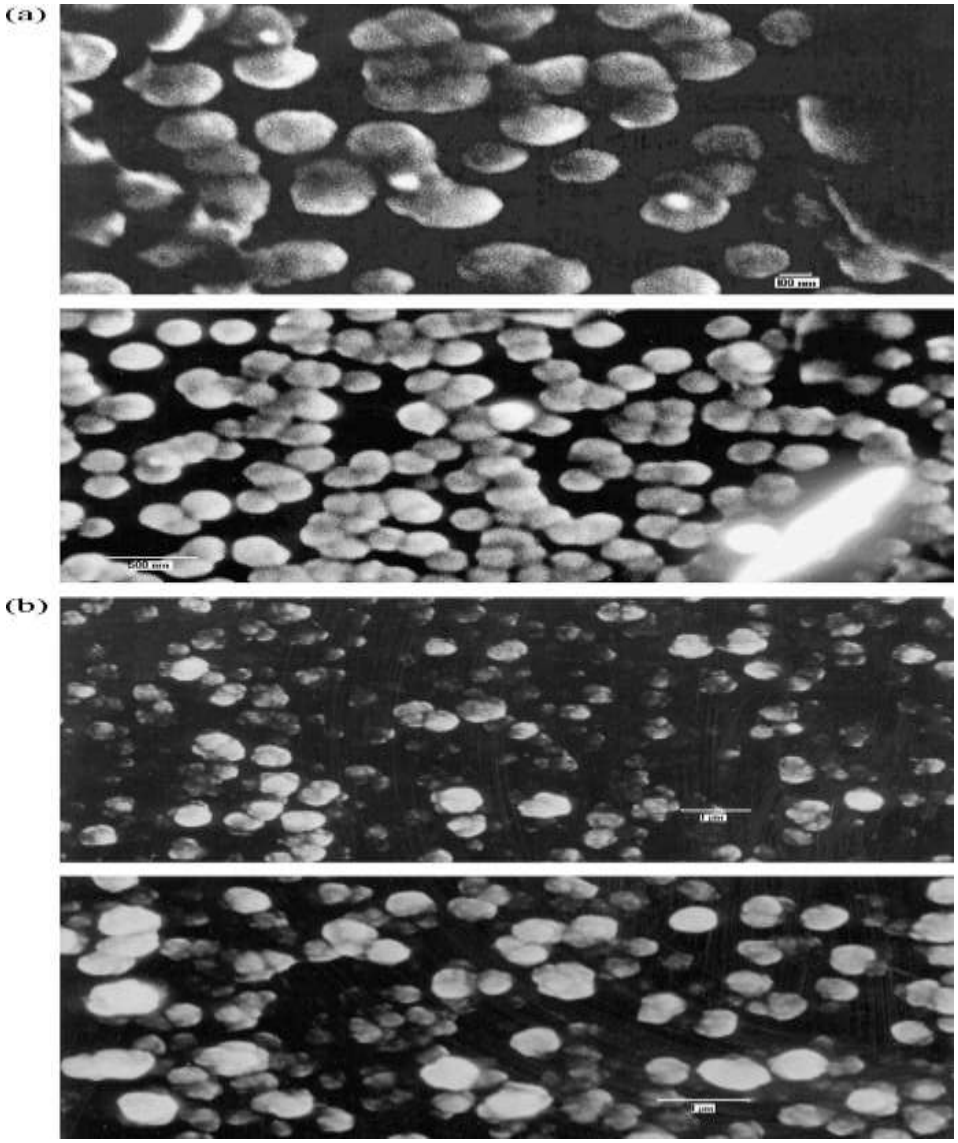

Figure 1: (a, b) PbS nanoparticles produced by chemical bath deposition at ~26°C for 1 hr (a) and 1.5 hr (b).

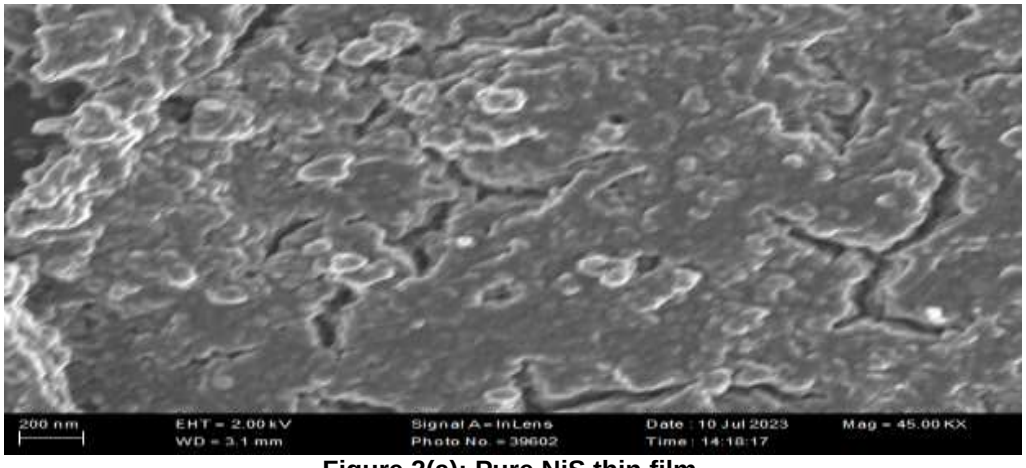

Figure 2(a): Pure NiS thin film.

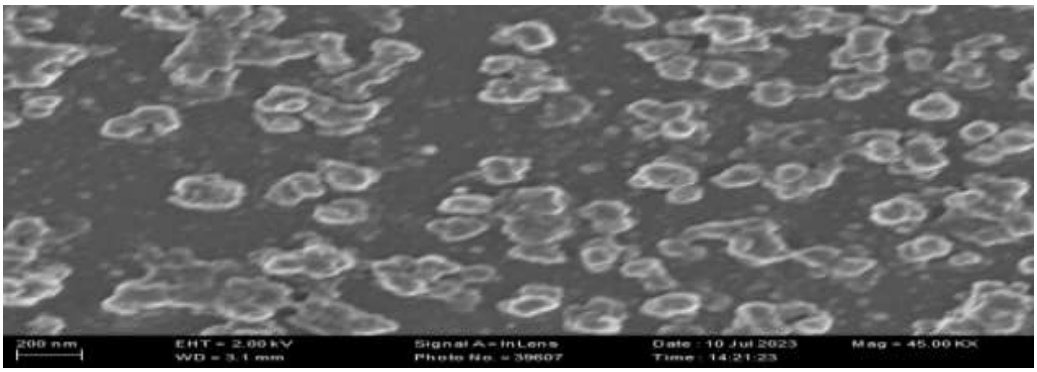

Figure 2(b): Al-doped NiS at 0.2 M aluminum.

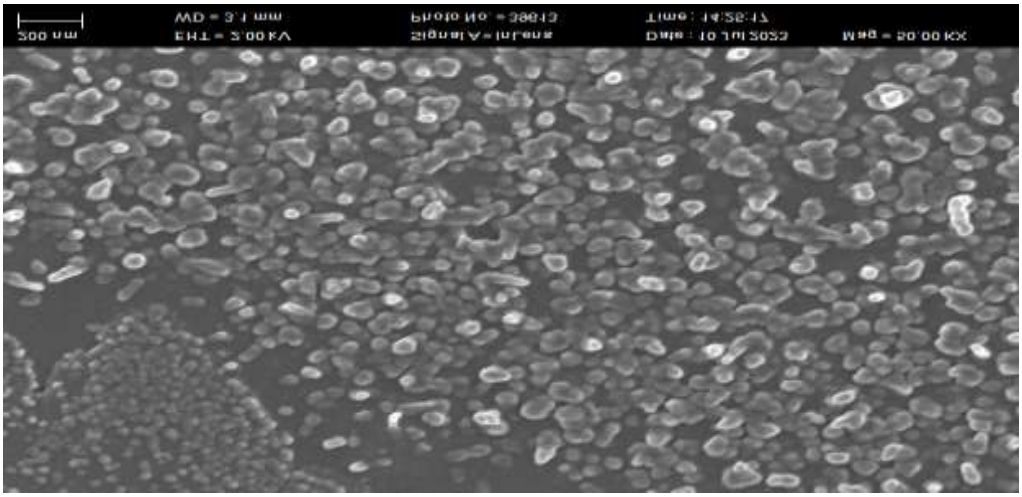

Figure 2(c): Al-doped NiS at 0.4 M aluminum.

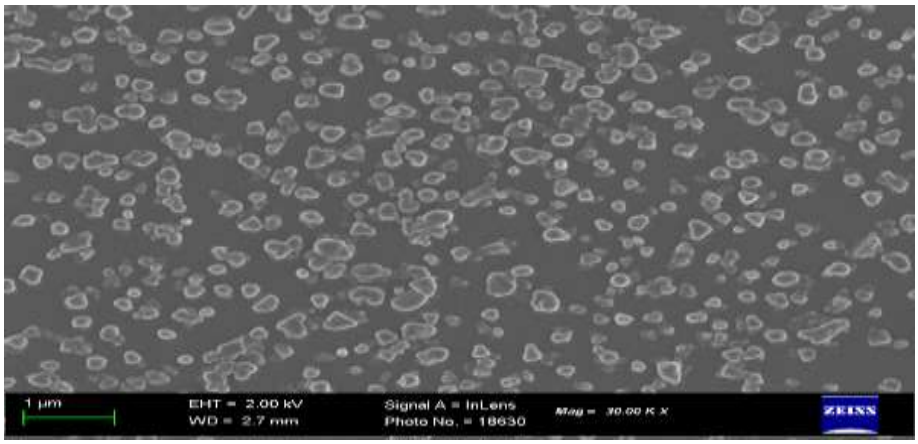

Figure 3(a): Morphology of PbS with 0.5 M ligand.

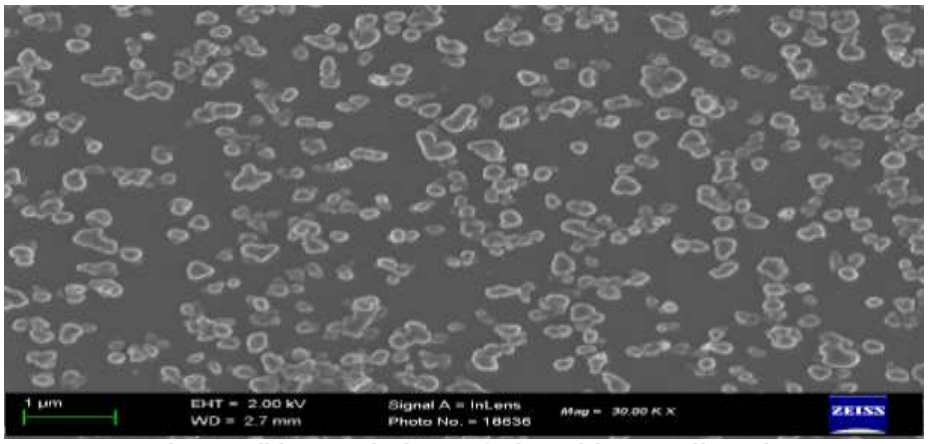

Figure 3(b): Morphology of PbS with 0.8 M ligand.

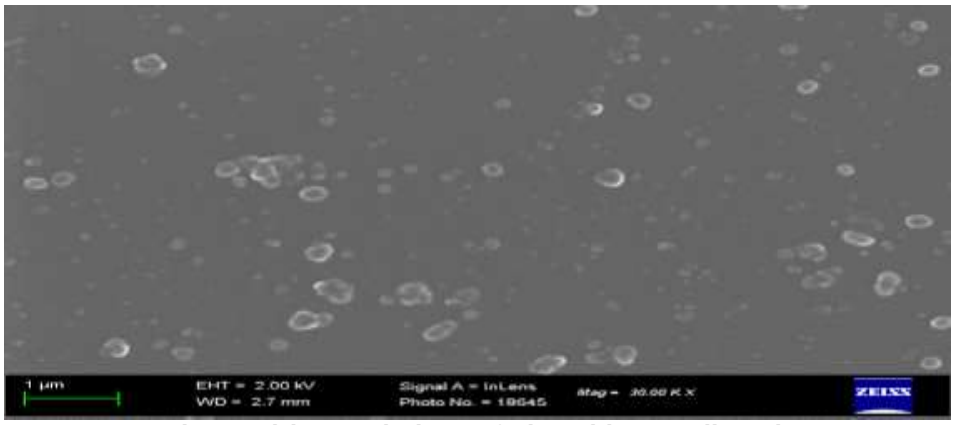

Figure 3(c): Morphology of PbS with 1.0 M ligand.

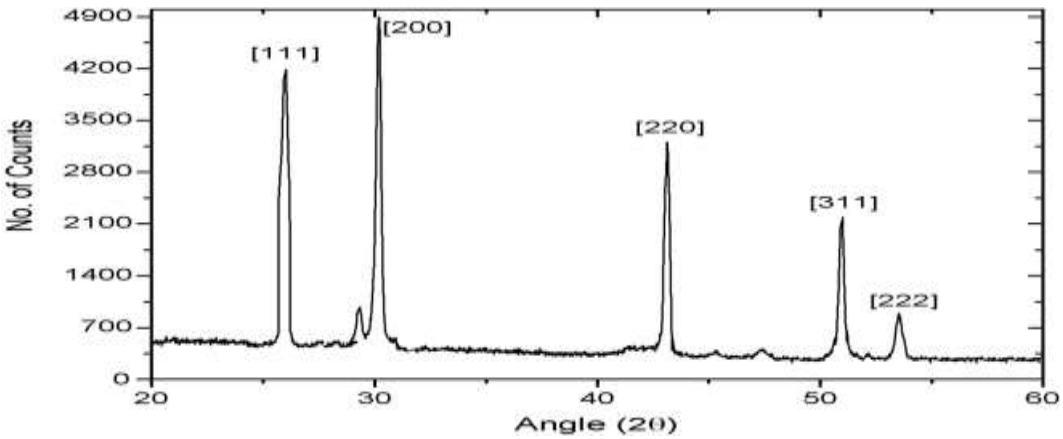

Figure 4: XRD pattern of PbS nanoparticles.

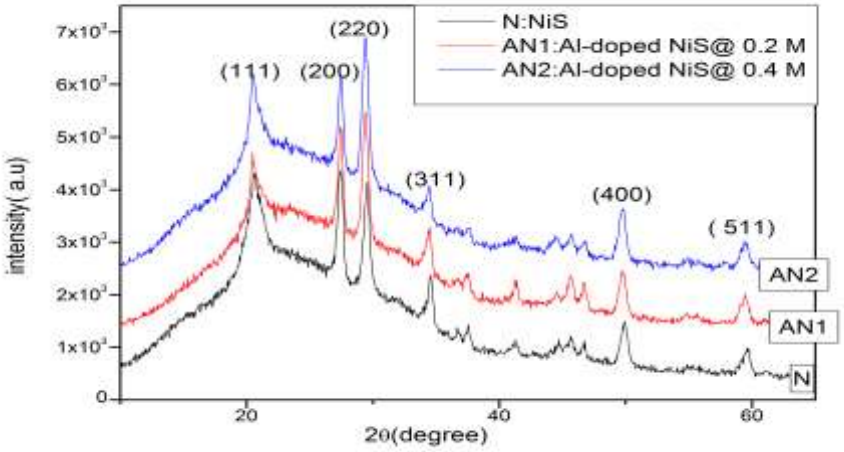

Figure 5: X-ray diffraction pattern of pure NiS and Al-doped NiS thin films.

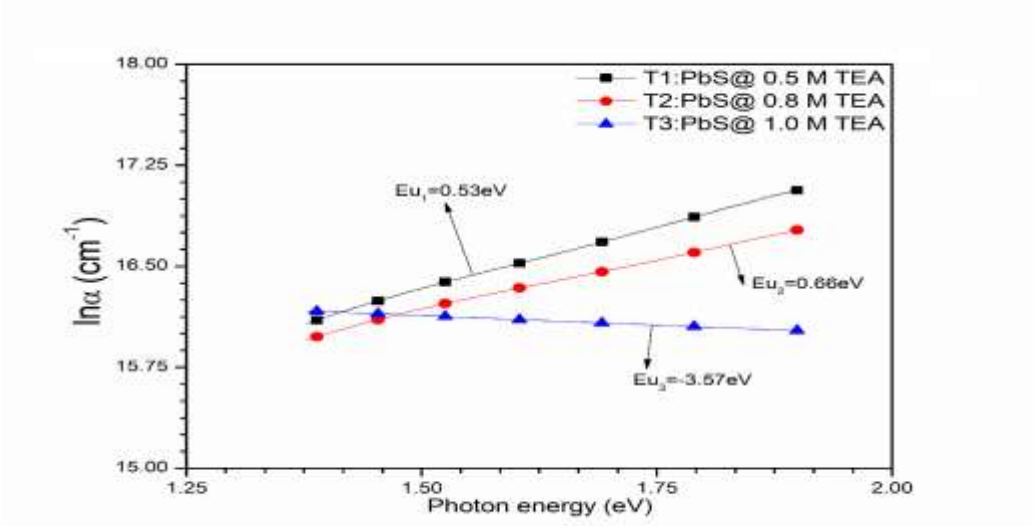

Figure 6: Variation of ln(α) as a function of photon energy for PbS thin film at various ligand concentrations.

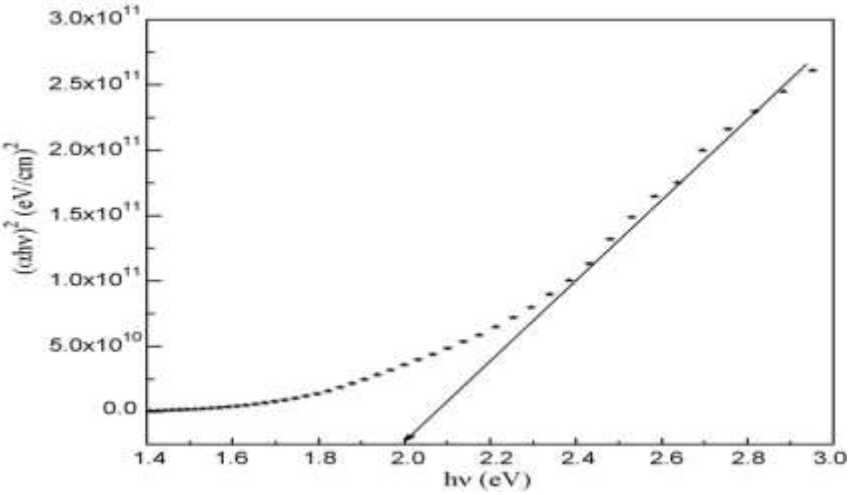

Figure 7(a): Variation of (αhv)² with energy for nanocrystalline PbS thin film grown with different dip times.

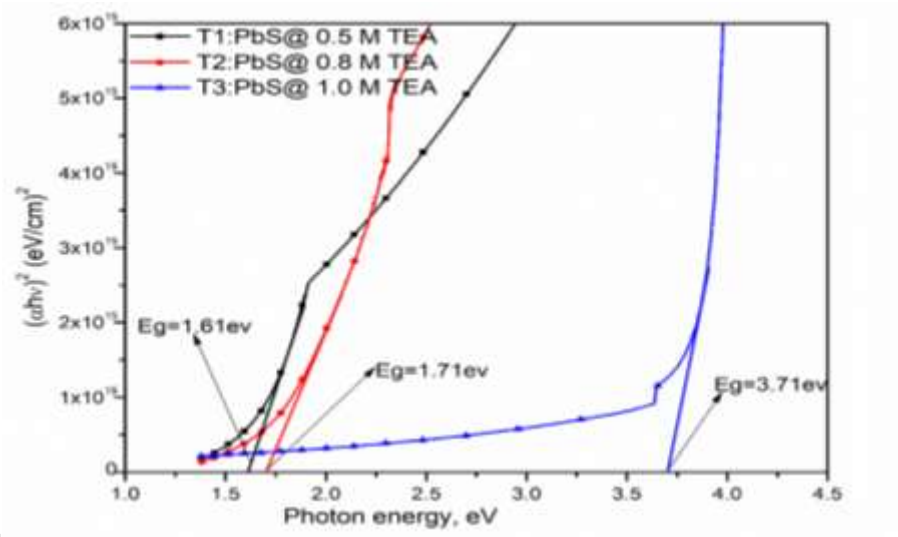

Figure 7(b): Variation of (αhv)² with energy for nanocrystalline PbS thin film at various ligand concentrations.

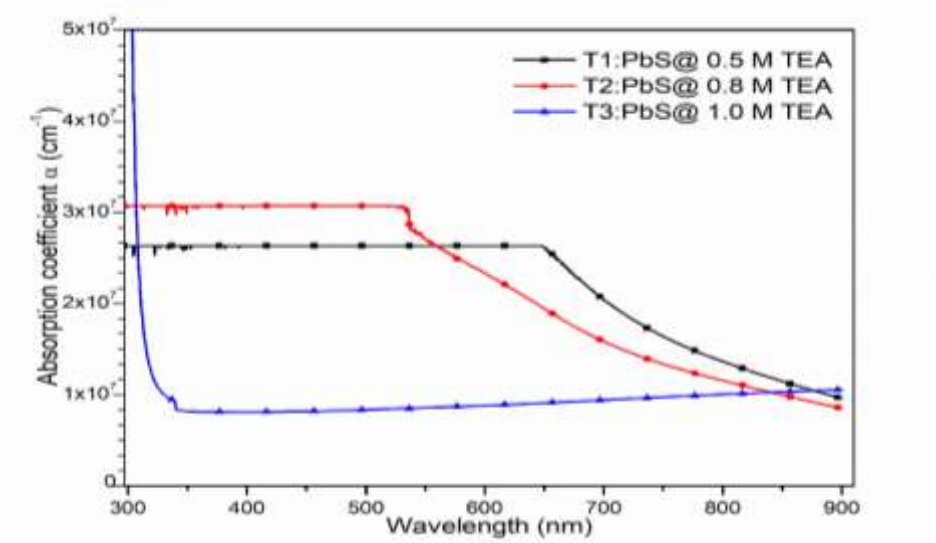

Figure 7(c): Absorption coefficient as a function of wavelength for PbS thin film at various ligand concentrations.

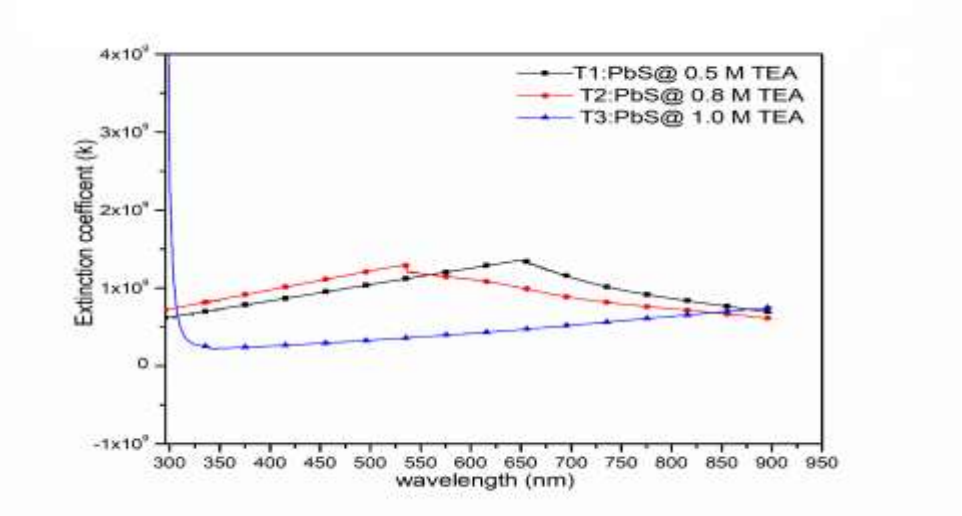

Figure 7(d): Extinction coefficient (k) of PbS thin film at various ligand concentrations.

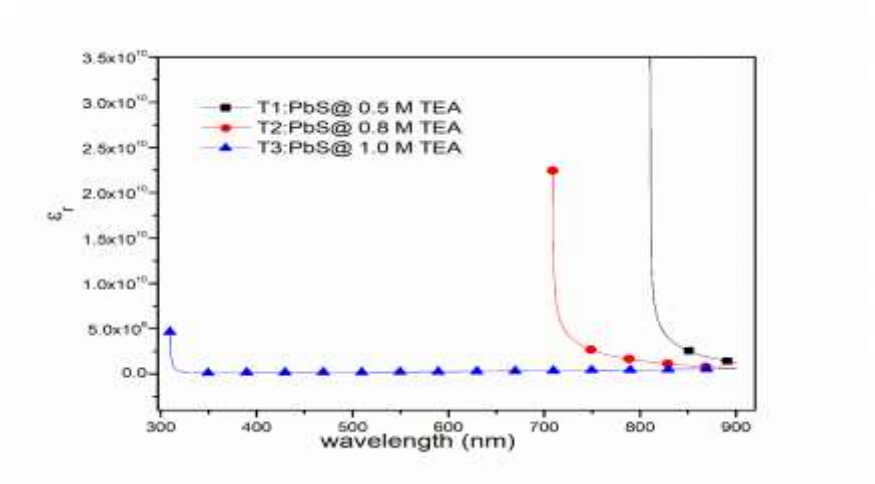

Figure 7(e): Real dielectric constant (εr) of PbS thin film at various ligand concentrations.

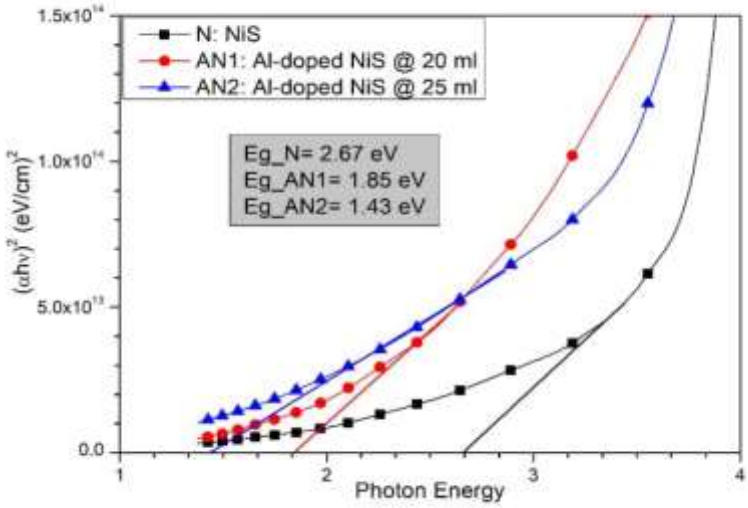

Figure 8(a): Variation of (αhv)² with energy for nanocrystalline NiS and AlNiS thin films.

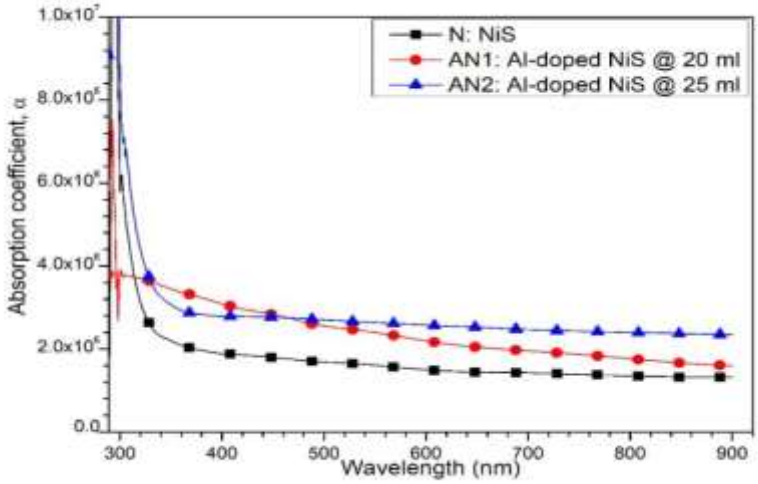

Figure 8(b): Absorption coefficient of AlNiS thin film.

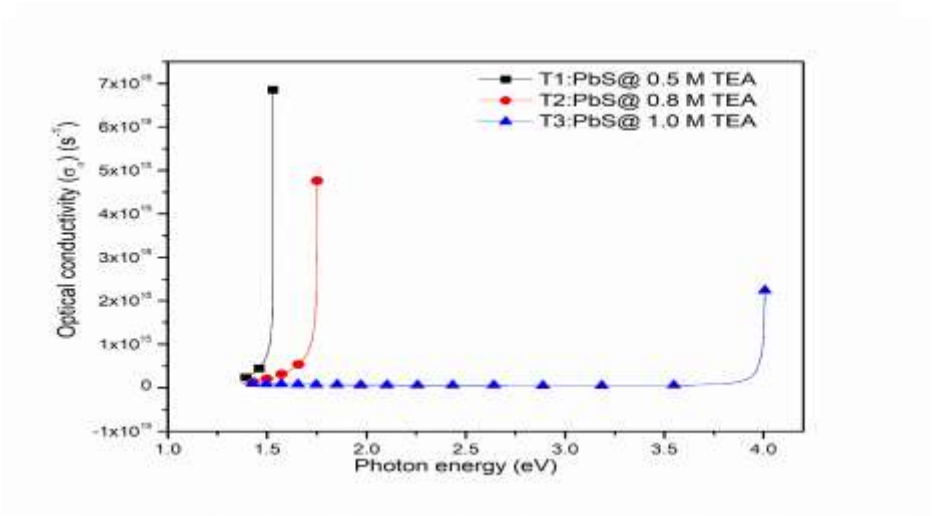

Figure 8(c): Optical conductance of PbS thin film.

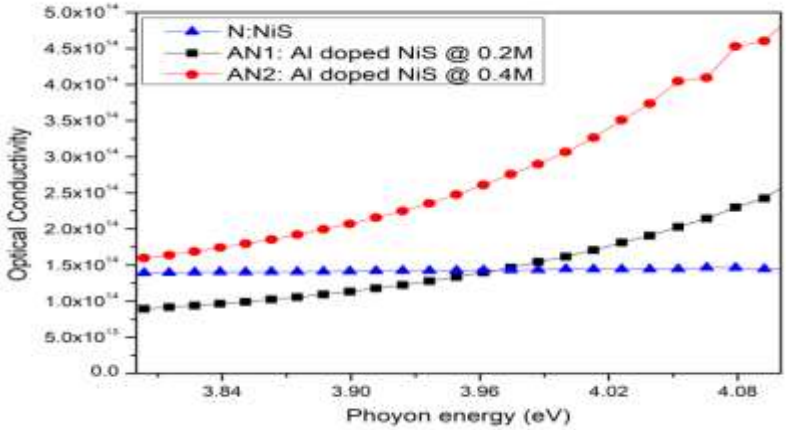

Figure 8(d): Optical conductance of AlNiS thin film doped with various aluminum concentrations.

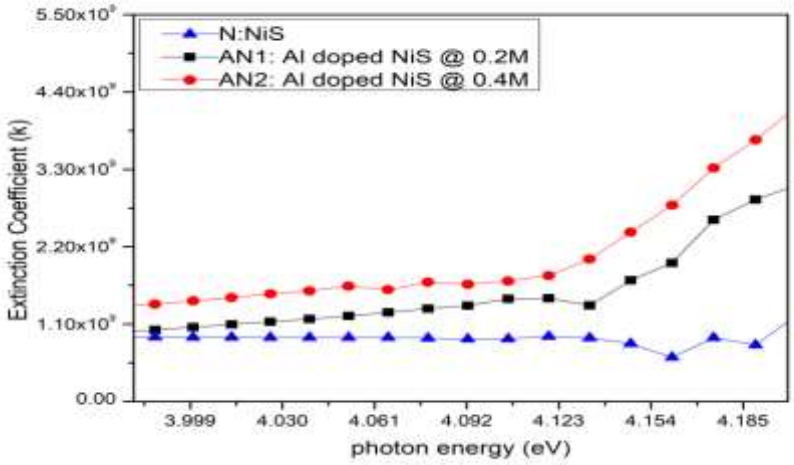

Figure 8(e): Extinction coefficient of AlNiS thin film.

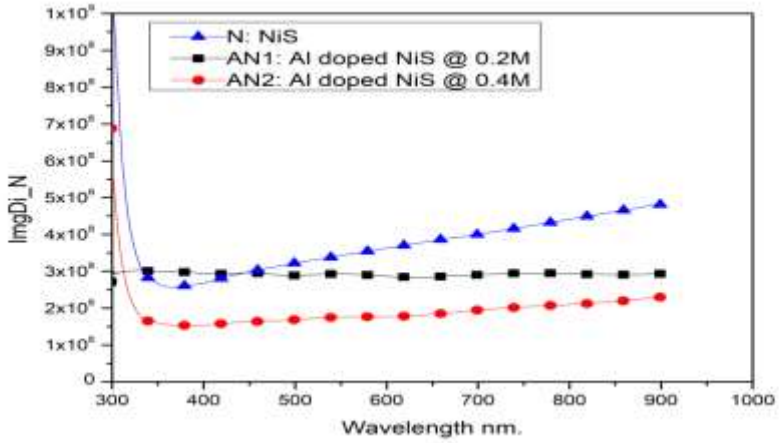

Figure 8(f): Complex dielectric constant of AlNiS thin film doped with various aluminum concentrations.

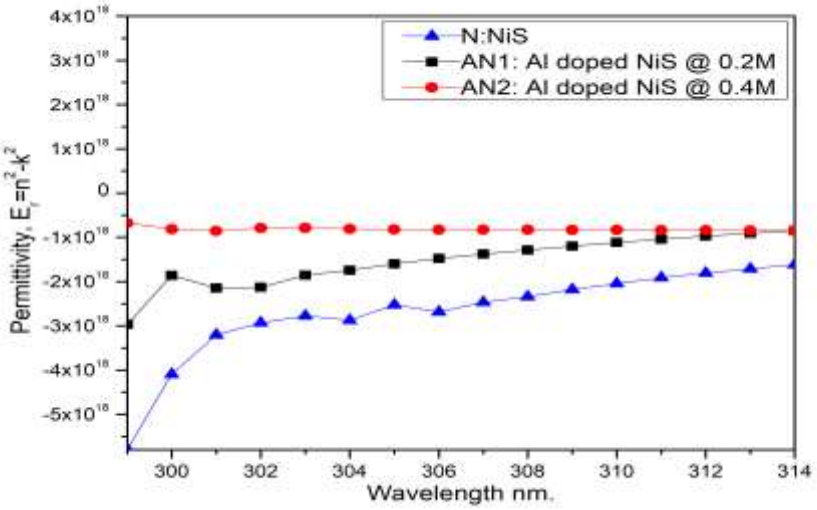

Figure 8(g): Relative permittivity of AlNiS thin film.

The results presented herein focus on the overall effects of the parameters under investigation—dopants, dip time, and ligand—on the properties of the thin films. The morphological characteristics, as observed from SEM images, are shown in Figure 1, which depicts the morphology of PbS grown with various ligand concentrations and slightly different dip times. The morphology of NiS thin films is shown in Figure 2a for as-deposited NiS, while Figures 2b and 2c represent AlNiS films doped with different aluminum concentrations, revealing variations in grain size for both as-deposited and Al-doped samples. Figures 3a, 3b, and 3c illustrate the morphology of PbS grown with different ligand concentrations. Figures 4 and 5 display the XRD characteristics of both films, each exhibiting peaks at similar orientation planes and within comparable angles, as is typical for sulphide-based chalcogenides.

The observed trends in morphological and X-ray diffraction characteristics clearly demonstrate the influence of the investigated parameters on morphology and crystallographic properties. Regarding solid-state properties, the logarithm of the absorption coefficient, as shown in Figure 6 for PbS, provides evidence of the effect of ligand variation on solid-state properties. This effect is also reflected in the energy band gap plots, where $(\alpha h\nu)^2$ is plotted as a function of photon energy, and it is observed that varying ligand concentration results in changes to the energy band gap of PbS thin films, as shown in Figure 7b. Similarly, the plot of $(\alpha h\nu)^2$ versus photon energy for NiS reveals that aluminum dopant concentration influences the energy band gap of NiS thin films, as seen in Figure 8a. Furthermore, all solid-state characteristics, including extinction coefficient, refractive index, and dielectric constants for both PbS and NiS thin films, clearly indicate that ligand variation (for PbS) and dopant concentration (for NiS) significantly affect their solid-state properties as outlined. Another noteworthy observation is that the source of

The anion originates from the same source, thiourea, in all cases, although the ligand used in each case differs. Furthermore, all chalcogenide-based thin films share a simple growth mechanism, whereby the cation from the electropositive metal element combines with chalcogen ions (S, Se, and Te) when the appropriate ligand is employed. However, in the case of MoS_3, which is produced by the treatment of tetrathiomolybdate with acid, it is known to be amorphous and typically forms glass [21]. This is due to its exceptional glass-forming ability, high refractive index, and lower photonic energy compared to standard materials. Consequently, MoS_3 exhibits high photosensitivity and excellent transmission across the infrared, visible, and UV regions of the electromagnetic spectrum. These properties arise from its high absorption coefficient, which influences its energy band gap, as is generally observed in nanomaterials. This characteristic enables the tuning of their energy band gap to optimize photon absorption from solar radiation, facilitating efficient conversion into electricity. The energy band gap of these materials can be manipulated by the parameters discussed in this work, making them suitable for numerous applications, as outlined in the literature. Therefore, due to these unique properties, sulphide-based chalcogenide thin films, and indeed other chalcogenide-based thin films, have attracted significant attention for decades and continue to do so, particularly because of their abundance on Earth and environmental friendliness.

4. SUMMARY

From the assessment of chemical bath-grown sulphide-based chalcogenide thin films, several salient but important points emerge, particularly regarding their growth mechanisms and characteristics. It is clearly demonstrated that these films exhibit similar nucleation processes, as shown in the two cases considered, with the source of their anion originating from the same precursor. Another notable observation is that their properties can be readily influenced by dip time, ligand, and doping. This is evident from the results, which show that morphological, structural, solid-state, and even energy band gap properties were modified and adjusted compared to the as-deposited state [22-24]. Based on these findings, it can be affirmed that sulphide-based chalcogenide and, more broadly, all chalcogenide-based thin films are useful in all the applications cited in the literature. This explains their continued prominence and demand among materials science researchers in recent times.

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