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Recent Advances in Transition Metal Doped PbS Thin Films Prepared by Chemical Deposition Methods: A Comprehensive Review

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ABSTRACT

Lead sulphide (PbS) thin films doped with metals have attracted significant attention for use in next-generation photovoltaic and optoelectronic devices. This interest primarily arises from their tuneable bandgap, strong optical absorption, and quantum confinement effects associated with reduced crystallite size. This review presents recent developments in the synthesis and characterization of transition-metal doped PbS thin films prepared using solution-based methods. The review focuses on the influence of key deposition parameters, including precursor concentration, choice of complexing agent, bath temperature, solution pH, and dopant concentration on the structural, optical, morphological, and electrical properties of PbS thin films. The reports have shown that metal doping can significantly modify crystallite size, optical bandgap, carrier mobility, and surface morphology, thereby influencing the suitability of these films for solar cell absorber applications. However, several challenges still need to be addressed, including achieving uniform dopant distribution, preventing secondary phase formation, reducing defect density, and improving long-term stability. By bringing together recent findings, this review highlights the major material related factors that limit device performance and discusses possible processing strategies for developing more stable and efficient solution processed PbS based photovoltaic absorber layers.

1. Introduction

Bulk PbS is a narrow bandgap semiconductor with a direct bandgap of approximately 0.41 eV at room temperature and an exciton Bohr radius of about 18 nm [1, 2]. PbS nanocrystals with dimensions comparable to or smaller than the exciton Bohr radius exhibit pronounced quantum confinement effects, enabling size dependent tuning of the optical bandgap [3]. PbS nanoparticles with dimensions comparable to or smaller than the exciton Bohr radius (~18 nm) exhibit pronounced quantum confinement effects [4]. This allows one to control the bandgap simply by altering the particle size [5]. In addition to nanoparticles and quantum dots, PbS thin films have attracted considerable attention for applications in thin film solar cells, infrared detectors, and other optoelectronic devices [6]. They have a lot of potential for use in applications including thin film solar cells and infrared detectors [6-8]. The optical response of PbS thin films can extend from the visible to the near infrared region, depending on factors such as crystallite size, film thickness, stoichiometry, defects, and doping [6, 9, 10]. Their relatively long exciton lifetimes (0.2-0.8ms) make them promising candidates for optoelectronic applications [11]. If the right deposition procedures are used and the working conditions are optimized. The optoelectronic properties of PbS thin films can be tailored to meet the requirements of various applications [12]. Chemical bath deposition (CBD) [9, 13], sequential ionic layer adsorption and reaction (SILAR), electro deposition [14] and spray pyrolysis [15] are some of the more common chemical approaches used to deposit PbS thin films. For optimal optoelectronic performance, these deposition techniques allow for exact regulation of layer thickness, shape, and crystallinity [16]. Doping PbS thin films with transition metals may improve their electrical, optical, and structural properties. Transition metal doping is a technique used to improve PbS for solar cell applications by modifying its bandgap, carrier

concentration, and charge transport behaviour [3, 17]. Wet chemical methods, such as hydrothermal synthesis or hot injection of precursor solutions, are also employed, providing additional tunability through reaction parameters and solvent choice, though limited by achievable reaction temperatures and solubility constraints [18, 19].

The tunable bandgap, high absorption coefficient, and long exciton lifetimes of PbS thin films make them highly suitable as absorber layers in solar cells. When integrated into heterojunctions or quantum dot architectures, PbS films can efficiently harvest light from visible to near infrared wavelengths, thereby enhancing device performance. Transition metal doping further improves photovoltaic properties by increasing carrier mobility, reducing recombination losses, and enabling precise bandgap engineering to better match the solar spectrum [12, 20, 21]. As a result, optimized PbS thin films doped with transition metals show a lot of potential as next generation thin film solar cells that convert more energy efficiently [22]. PbS thin films doped with various transition metals have been investigated by numerous authors to modify their optoelectronic characteristics [23]. Dopant atoms can alter the electronic structure of PbS by occupying substitutional or interstitial sites, introducing defects, distorting the lattice, and changing the carrier concentration [24, 25]. These structural and electronic changes depend largely on the type and concentration of the dopant, which can, in turn, affect the performance of PbS based semiconductor devices [26, 27]. Using the SILAR technique, Gulen et al. [28] prepared Fe doped PbS thin films on glass substrates [28]. They observed that the optical bandgap decreased from 1.66 to 1.25 eV as the Fe concentration increased from 1% to 9%. similarly, Ag doping has been shown to alter the optical bandgap of PbS thin films, with the observed blue shift attributed to quantum confinement effects [29]. Doping is an effective approach for tuning the electronic properties of PbS by partially substituting Pb²⁺ ions with suitable dopants. By carefully selecting the dopant type and concentration, properties such as carrier density, electrical conductivity, and band structure can be tailored, potentially improving the performance of PbS in solar-cell applications [30, 31].

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2. Chemical Routes for the Synthesis of PbS Thin Films

A variety of chemical methods are available for fabricating PbS thin films. Among these, solution-based techniques such as chemical bath deposition, Spray Pyrolysis and SILAR are particularly popular because they are simple, cost-effective, and offer good control over the resulting film properties [32].

2.1 Chemical Bath Deposition (CBD) Technique

Chemical bath deposition (CBD) has gained considerable attention as a convenient technique for the preparation of thin films because it requires relatively simple equipment and can be carried out at low cost [32–37]. Thin films made by the chemical bath deposition process can be used to swiftly and economically create a wide range of materials [38–43]. The method is also suitable for depositing uniform films over comparatively large substrate areas [44–50]. In the case of PbS thin films, the characteristics of the deposited films are strongly influenced by the deposition conditions, including precursor concentration, bath temperature, deposition time, pH, and substrate properties [32], as illustrated in Fig. 1 [9].

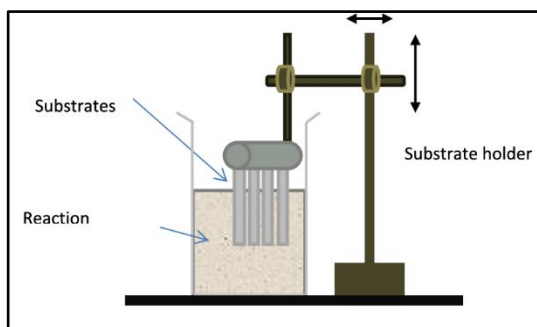


Fig. 1 Schematic illustration of the chemical bath deposition process used for the preparation of PbS thin films [9]

Several studies have investigated the deposition of PbS thin films by chemical bath deposition (CBD) using different complexing agents such as triethanolamine, diethanolamine and hexamine as complexing agent for PbS thin films [51, 52], precursor systems [53], bath temperatures [53] and solution pH values [54]. Achieving PbS films with large grains, good crystallinity, and favourable carrier mobility remains an important objective, although only a limited number of studies have reported substantial improvements in these properties [12, 55]. CBD grown PbS films have been widely investigated for infrared photodetector applications, where high crystallinity, favourable carrier transport, and an appropriate optical band gap are important material requirements [55, 56]. Carrier mobility is also influenced by crystallite size and grain boundaries, as smaller crystallites generally result in a greater density of grain boundaries, which may hinder charge transport [57]. Preetha and Remadevi investigated the effect of Al doping on the structural and electrical properties of PbS thin films prepared by CBD. The results showed that an appropriate amount of Al improved both the crystallinity and electrical conductivity of the films, with 3 at. % Al producing the most favourable results. All the films exhibited p-type conductivity, irrespective of the doping concentration. These findings suggest that Al doped PbS thin films could be promising for applications such as infrared detectors and sensor devices [26].

In another study, Siva Senthil et al. [58] investigated PbS thin films were deposited on glass substrates by CBD using $\text{Pb}(\text{NO}_3)_2$, NaOH, thiourea $[\text{SC}(\text{NH}_2)_2]$, and water under different deposition conditions. The structural properties of the films were examined using X-ray diffraction, which confirmed the formation of cubic PbS with a preferred orientation along the (111) plane. Optical measurements were carried out using UV-Vis. spectroscopy to evaluate the transmittance, reflectance, and absorption behaviour of the films. The deposited PbS films exhibited strong absorption in the ultraviolet and visible regions, while their transmittance increased in the infrared region. The estimated optical band gap ranged from 1.88 to 2.10 eV, indicating that the optical properties of the nanocrystalline PbS films were influenced by the deposition conditions and nanoscale effects [58].

In another study, Gosavi et al. [59] investigated the optoelectronic and physicochemical properties of low-cost PbS thin films deposited on glass substrates at room temperature were investigated at different deposition times for potential ammonia gas sensing applications. X-ray diffraction (XRD) analysis confirmed the cubic polycrystalline structure of the films, with crystallite sizes ranging from 18 to 22 nm. Raman spectroscopy revealed characteristic peaks at approximately 92 and 143 cm^{-1} , while

energy-dispersive X-ray (EDX) analysis confirmed the elemental composition of the prepared films. The films exhibited a flower-like grain morphology and strong optical absorption, with an estimated optical band gap of 1.48 eV [59].

In another study Banerjee and Mitra [60] investigated the effect of Ni doping on the particle size, optical band gap, dielectric properties, and electrical conductivity of PbS thin films. PbS films doped with 3%, 6%, and 9% Ni were deposited on glass substrates using the chemical bath deposition (CBD) method. X-ray diffraction (XRD) analysis confirmed the formation of cubic, single phase PbS. Ni incorporation influenced both the particle size and optical band gap of the films, with noticeable changes observed up to a doping concentration of 6%. The dielectric and electrical properties were further evaluated using complex impedance spectroscopy. Among the investigated samples, the PbS film containing 6% Ni exhibited the highest electrical conductivity [60].

2.2 Spray Pyrolysis Technique

The chemical spray pyrolysis method makes it easy to incorporate various components into thin films in different amounts by simply adding them to the spray solution. Spray pyrolysis does not require high-quality targets or substrates, and it does not require a vacuum at any stage, as illustrated in Fig. 2 [61]. Spray pyrolysis (SP) has several advantages for thin-film deposition, such as simple equipment, relatively low processing costs, and good potential for scale-up to industrial production. The technique is also versatile and can be used to deposit films of metals, semiconductors, and oxides, including dense and porous films as well as single- and multilayer structures. The composition and properties of the deposited films can be tailored by varying the precursor composition and deposition conditions. This flexibility allows better control over the morphology and composition of the resulting films. Owing to these advantages, SP is considered a promising technique for the large-scale fabrication of functional thin films and nanostructured materials [62].

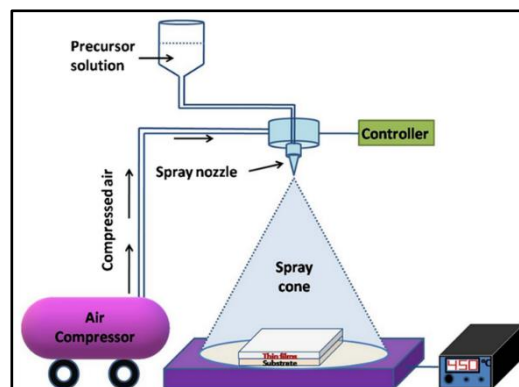


Fig. 2 Schematic representation of the experimental setup for heated plate spray pyrolysis [61]

It is generally believed that reliable fundamental kinetic data can be obtained from well-defined film surfaces, provided that the films are compact and homogeneous and free from substrate related effects [63]. Spray pyrolysis has been widely used to prepare thin films of various oxides and chalcogenides, including PbS and PbS based ternary alloys such as $\text{Pb}_x\text{Zn}_{1-x}\text{S}$ [64] and $\text{Zn}_x\text{Pb}_{1-x}\text{S}$ [65], as well as mixed CdS-PbS films [66]. Vidhya et al. [16] investigated the effect of Ce doping on PbS thin films prepared by the Jet Nebulizer Spray Pyrolysis (JNSP) technique for photosensor applications [16]. The films were doped with 0, 1, 3, and 5% Ce. XRD examination, the cubic structure of the films was verified; when the Ce concentration increases, the crystallite size decreased, suggesting that Ce was successfully incorporated into the PbS lattice. In FESEM analysis, the aggregated morphology was shown to be a result of doping. Doping with Ce increased optical absorbance, which in turn lowered the bandgap and resulted in a red shift in the absorption spectra, as verified by XPS.

2.3 The SILAR (Successive Ionic Layer Adsorption and Reaction) Process

Successive Ionic Layer Adsorption and Reaction (SILAR) is a simple and cost-effective solution-based method commonly used for depositing thin films. In this technique, a substrate is alternately immersed in cationic and anionic precursor solutions, with rinsing after each step to remove loosely attached ions. During repeated SILAR cycles, the adsorbed ions react on the substrate surface, gradually forming a thin film of the desired material. The thickness of the deposited film can be easily controlled by changing the number of deposition cycles. Since the process is carried out under relatively mild conditions and does not require complex or expensive

equipment, it is considered an attractive technique for thin-film fabrication. Due to its simplicity and good control over film thickness and composition, SILAR has been widely used to prepare various semiconductor thin films, including PbS [67, 68].

PbS thin films were deposited on indium tin oxide (ITO) substrates at room temperature (30 °C) using the successive ionic layer adsorption and reaction (SILAR) method, as shown in Fig. 3 [69]. Recent studies have examined SILAR deposited PbS thin films for use in PbS/CdS heterojunction solar cells [70]. The current density-voltage (J-V) characteristics of the fabricated devices were evaluated, with the device prepared using 40 SILAR cycles showing the highest conversion efficiency. However, no clear relationship between film thickness and device efficiency was observed [70]. Another study investigated a ZnTe/PbS structure, where ZnTe served as a buffer layer and PbS acted as the absorber layer [71]. This study investigated the use of lead sulphide (PbS) as an absorber layer and zinc telluride (ZnTe) as a buffer layer. Detailed structural and chemical analyses showed that growth parameters, such as temperature and reagent concentration, significantly influenced the interfacial morphology and properties. However, growing PbS thin films on ZnTe requires careful control because ZnTe can dissolve in the alkaline solution used during CBD. At higher temperatures, the substrate plays an important role in determining the orientation relationship, with PbS growing epitaxially on the textured ZnTe layer. At lower temperatures, the ZnTe layer tends to deteriorate because of the slow growth rate of the PbS film, preventing the epitaxial relationship from being transferred to the subsequent layers.

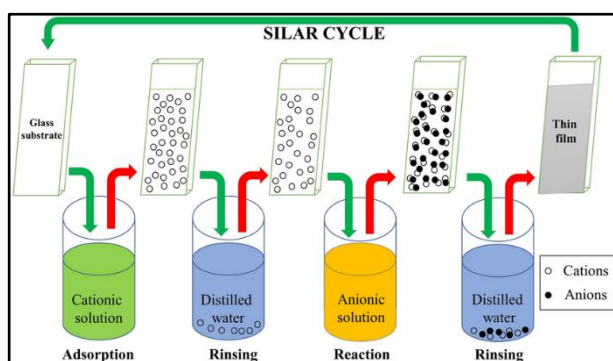


Fig. 3 Schematic representation of the SILAR technique [69]

3. Techniques for Characterizing PbS Based Thin Films

A variety of characterization techniques are used to investigate the properties of PbS thin films. X-ray diffraction (XRD) is commonly employed to determine the crystal structure, phase composition, and degree of crystallinity of the films. Surface morphology, grain structure, and particle distribution can be examined using scanning electron microscopy (SEM) and field-emission scanning electron microscopy (FESEM), while atomic force microscopy (AFM) provides detailed information about surface topography and roughness. The optical properties of PbS thin films, such as the absorption coefficient and optical band gap, are typically studied using UV-Vis. spectroscopy. Fourier-transform infrared spectroscopy (FTIR) is useful for identifying chemical bonds, functional groups, and possible impurities present in the films. In addition, electrical measurements are performed to determine important parameters such as resistivity, electrical conductivity, carrier concentration, and carrier type. Overall, these characterization techniques provide a comprehensive understanding of the structural, morphological, optical, chemical, and electrical properties of PbS thin films [72].

3.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used to examine the surface morphology of the undoped and Cr doped PbS thin films, as shown in Fig. 4. The images correspond to (A) pure PbS, (B) PbS-Cr (2%), (C) PbS-Cr (4%), and (D) PbS-Cr (6%) films. The magnified insets provide a clearer view of the surface features, while the cross-sectional images in Figs. 4(A) and 5(D) reveal the film thickness and overall layer structure.

The undoped PbS film exhibits a relatively smooth and continuous surface composed of small, closely packed grains. With the incorporation of Cr, noticeable changes in the surface morphology are observed, suggesting that the dopant influences the nucleation and growth process of the PbS films. At the lowest Cr concentration, the film still retains a comparatively uniform appearance, although the presence of some larger and irregularly shaped grains indicates localized variations in grain

growth. As the Cr concentration increases, changes in grain size, particle distribution, and surface texture become more pronounced. The higher Cr-doped films show a comparatively heterogeneous granular morphology, with variations in grain dimensions and a greater tendency for particle aggregation. These changes may be associated with the influence of Cr incorporation on the growth kinetics and nucleation behavior of the PbS films, leading to modifications in grain development and surface packing.

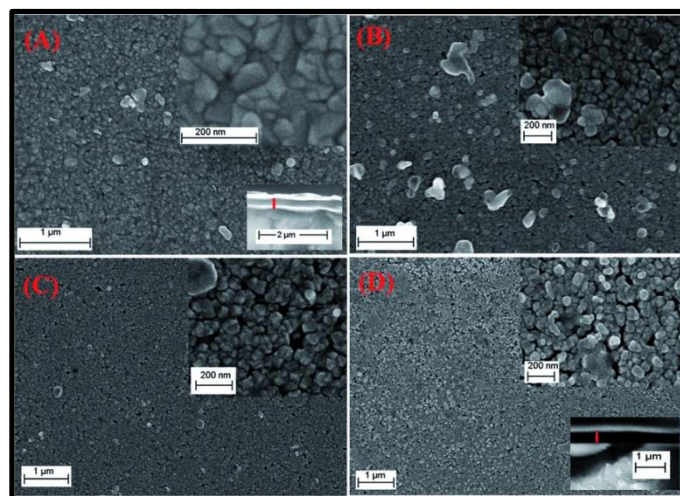


Fig. 4 SEM micrographs of (A) pure PbS, (B) PbS-Cr (2%), (C) PbS-Cr (4%), and (D) PbS-Cr (6%) thin films prepared by chemical bath deposition. The upper insets show the corresponding high-magnification surface morphologies, while the lower insets in (A) and (D) present the cross-sectional SEM images. Reproduced from Ahmed *et al.* [73]

The cross-sectional SEM images confirm the formation of continuous and compact films with good coverage over the substrate. No significant cracks, gaps, or voids are observed in the examined cross-sections, indicating good film integrity. Overall, the SEM results demonstrate that Cr incorporation significantly influences the microstructure of PbS thin films, particularly in terms of grain morphology, surface texture, and particle distribution. These morphological changes may subsequently influence the structural, optical, and electronic properties of the films [73]. A separate study employed field-emission scanning electron microscopy (FESEM) to examine the surface morphology of undoped and Cu doped PbS thin films. The FESEM images were recorded at an accelerating voltage of 10 kV. Figs. 5(a)-(d), obtained at a magnification of 100×10^3 with a scale bar of 500 nm, reveal the surface features of the films [73]. Fig. 5(a) shows the morphology of the undoped PbS film, while the Cu doped films exhibit noticeable changes in their surface structure with increasing Cu concentration.

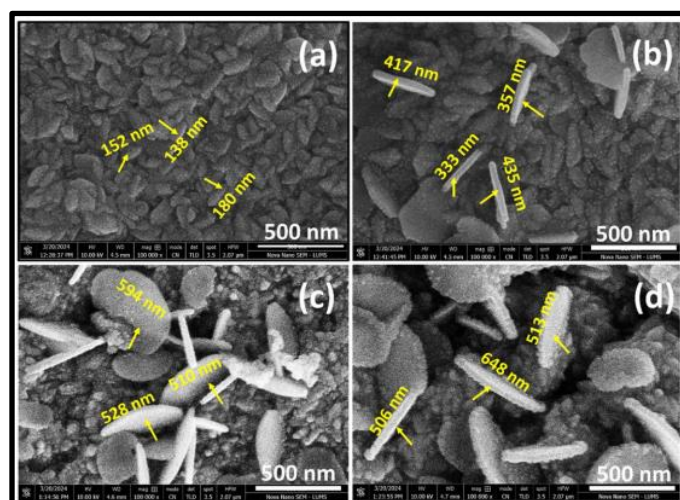


Fig. 5 FESEM micrographs of PbS thin films with different Cu doping concentrations: (a) undoped PbS, (b) 3.15% Cu doped PbS, (c) 6.25% Cu doped PbS, and (d) 12.5% Cu doped PbS. The measured dimensions of selected surface features are indicated in each micrograph. Adapted from Ramay and Aldosary [73]

The undoped PbS film in Fig. 5(a) exhibits a compact surface composed of irregularly shaped and closely packed grains. With Cu doping, noticeable changes in the surface morphology are observed. Figs. 5(b)-(d) show the formation of larger and more distinct grains with irregular, plate-

like, and elongated structures. The grain dimensions vary with Cu concentration, indicating that Cu incorporation significantly influences the nucleation and growth of the PbS films. The interconnected grains and relatively dense surface morphology suggest good film coverage [73].

Depending on the type and concentration of the dopant, PbS thin films may exhibit a wide range of surface morphologies, including fine or coarse granular structures [74], spherical, cubic [75, 76], plate-like, rod-like, and irregularly shaped particles [77, 78], as well as cauliflower-like [79], flower-like, dendritic, and porous features [80, 81]. In some cases, particle agglomeration, cracks, or pinholes may also be observed [82, 83]. The incorporation of transition metal dopants can significantly influence the nucleation and growth processes, leading to changes in grain size, particle shape, surface roughness, porosity, and the degree of agglomeration [84, 85]. As a result, the doped films may develop either a smoother and more uniform surface or a rougher and more porous morphology, which can subsequently affect their structural, optical, electrical, and photoelectrochemical properties [27, 86].

3.2 Fourier Transform Infrared (FTIR)

In order to determine the molecular interactions, chemical structure, vibrational bands, functional groups, and other characteristics of pure and transition metal doped PbS nanoparticles [87], Study reported that the spectra of pure PbS, 5% Cr doped PbS, 5% Sn doped PbS, and PbS films Co doped with 5% Cr and 5% Sn were largely similar [87].

FTIR spectroscopy was used as shown in Fig. 6. The FTIR spectra of pure PbS and the PbS–CdO composite show several characteristic absorption bands associated with different vibrational modes and chemical bonds. Following the incorporation of CdO, noticeable shifts in band positions and changes in their intensities are observed, suggesting modifications in the local chemical environment and possible interactions between PbS and CdO within the composite structure [88]. The Fourier transform infrared (FTIR) spectra of the films showed characteristic peaks associated with the PbS phase, along with additional peaks that may indicate the presence of impurities or functional groups. The absorption bands observed in the wavenumber range of 460–480 cm^{-1} were attributed to Pb–S bond stretching vibrations [88].

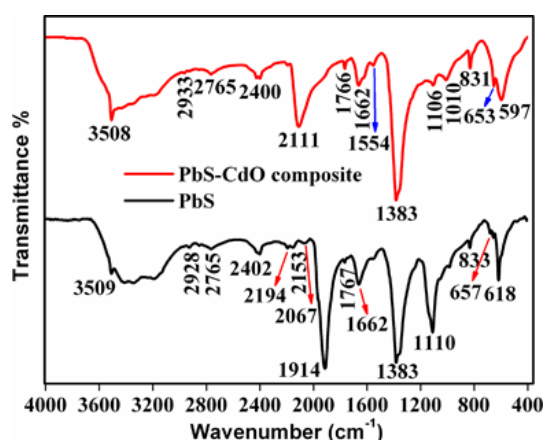


Fig. 6 FTIR spectra of PbS thin films Adapted from Suganya et al. [88]

3.3 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive technique commonly used to study the crystal structure and phase composition of materials [89]. According to Shokr et al. [90], the XRD patterns of $(\text{PbS})_{1-x}(\text{Zn})_x$ was shown for $x = 0, 0.01, 0.03, 0.05$ w.t.%. were examined All diffraction observed for the undoped film ($x = 0$) correspond to PbS, indicating high purity of the film [90]. In a similar way, in their study, Rajashree and Balu examined PbS films doped with varying Ni concentrations (0, 2, 4, 6, and 8 at.%) and found that the face-centered cubic (fcc) structure characteristic of PbS was maintained across all samples regardless of doping level. Interestingly, while the undoped sample exhibited a dominant orientation along the (200) plane, the introduction of Ni shifted this preference toward the (111) plane an observation suggesting that Ni doping influences the way crystallites form and grow within the film [86].

Cheraghizade et al. [91] used X-ray diffraction (XRD) to examine the structural properties of undoped, Zn doped, and Se doped PbS thin films. As shown in Fig. 7(a), all the films exhibited a polycrystalline structure with the characteristic cubic phase of PbS [91]. A closer look at the (311) diffraction peak in Fig. 7(b) showed a noticeable shift in its position after Zn and Se doping, indicating changes in the PbS lattice. These results suggest that both cationic and anionic dopants can influence the crystal

structure and introduce local lattice distortions without altering the fundamental cubic phase of PbS. Collective examination of the XRD patterns reveals that transition metal doping induces measurable modifications in the PbS crystal lattice, while the characteristic cubic rock-salt structure is generally retained. Dopant-dependent shifts in peak positions and variations in peak broadening indicate changes in lattice spacing, crystallite size, and microstrain, reflecting differences in the incorporation of metal ions into the PbS lattice. At higher dopant concentrations, the appearance of additional diffraction peaks may further suggest structural instability and the possible formation of secondary phases [92].

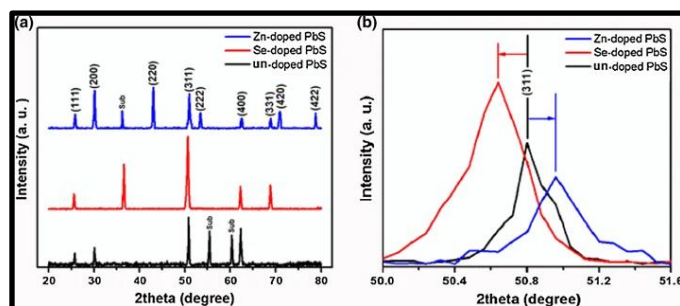


Fig. 7 X-ray diffraction (XRD) patterns of undoped, Se doped, and Zn doped PbS thin films: (a) full diffraction patterns showing the characteristic crystallographic reflections and (b) enlarged view of the (311) diffraction peak, illustrating the variation in peak position with dopant incorporation. Reproduced from Cheraghizade et al. [91]

3.4 Optical Characterization of Pure and Doped PbS Thin Films

The optical properties of the films were evaluated by measuring their absorbance and transmittance to investigate the effect of doping. With increasing Sb doping concentration, the absorption edge shifted toward longer wavelengths (red shift), accompanied by a decrease in the optical band gap from 1.69 eV to 1.59 eV [93]. The absorption spectra of materials can vary significantly depending on their optical properties and energy band gaps. Mn doped nanocrystalline PbS thin films exhibited strong absorption in the UV-visible region. The optical band gap increased from 1.90 eV to 2.28 eV as the crystallite size decreased from 21 nm to 11 nm. These band gap values are considerably higher than the bulk PbS band gap of approximately 0.40 eV, which may be attributed to quantum confinement effects [94]. As the crystallite size decreased from 21 nm to 11 nm, the optical band gap increased and exceeded the bulk PbS band gap value of approximately 0.41 eV. The linear relationship between $(\alpha h\nu)^2$ and $(h\nu)$ confirmed the direct allowed transition in the PbS thin films. The study reported that the optical band gap of PbS films increased with increasing Mn dopant concentration [94]. In another study the energy band gap of Ni doped PbS thin films increased from 1.4 to 2.4 eV, whereas that of Cd doped PbS thin films increased from 0.5 to 1.5 eV [95].

4. Comparison of Different Transition Metal Dopants in PbS Thin Films

In a study by Nazir et al. [96] $\text{Pb}_{1-x}\text{Mn}_x\text{S}$ nanoparticles with Mn concentrations ranging from $x=0$ to 0.06 were synthesized using a chemical co-precipitation method. The effects of Mn doping on the structural, morphological, optical, electrical, and vibrational properties of the nanoparticles were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy. The crystallite size ranged from 11.93 to 14.33 nm, while XRD analysis confirmed the formation of a single-phase face-centered cubic (FCC) structure without detectable impurities. SEM images revealed distinct morphological changes with Mn doping, showing flower-like structures for pure PbS, stone-like structures for 4% Mn-doped PbS, and rod-like structures for 6% Mn doped PbS. Raman spectroscopy showed an increase in peak intensity for the 6% Mn doped sample. As the Mn concentration increased, the optical band gap decreased from 1.48 eV for pure PbS to 1.42 eV [96].

Electrical measurements indicated a drop in resistivity from 1.3×10^6 to $2.1 \times 10^3 \Omega\text{-cm}$ and an increase in conductivity from 7.69×10^{-7} to $4.76 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ with greater Mn content, indicating the potential of both pure and Mn doped PbS nanoparticles for low-temperature electronic applications [96]. Chemical growth onto glass substrates at 80 °C produced nanocrystalline thin films of PbS and Cd doped PbS, as described by AUTHOR et al. [95]. Morphological measurements showed that Cd doping changed the substrate granules random orientation to irregular.

Table 1 Different metal dopants in the PbS thin film and different synthesis methods

Dopant	Doping Concentration	Synthesis Method	Effects on Properties	Ref.
Zn	0-6 wt. %	Chemical spray pyrolysis	Bandgap tuned from 0.53 to 1.65 eV increased carrier concentration	[97]
Cu	0-5 wt. %	Microwave-assisted chemical synthesis	bandgap 1.02 ± 0.01 eV to 1.37 ± 0.01 eV; Cu doping improves dielectric and electrical properties, making doped PbS samples valuable in optoelectronics.	[98]
Ni	0-8 wt. %	Chemical Spray pyrolysis	Face-centered cubic with (111) orientation shift; red-shifted bandgap (2.26 to 2.06 eV); increased transparency and conductivity; smaller crystallite size	[86]
Mn	0-6 wt. %	Co-precipitation Technique	band gap decreased from 1.48 to 1.42 eV; and conductivity increased from 7.69×10^{-7} to $4.76 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$ with Mn content.	[96]
Cd	-	Chemical Bath Deposition method	Band gap value of the PbS thin films increased from 2.12 eV to 2.65 eV; The crystallite size of the films decreased from 74 nm to 64 nm	[95]

5. PbS Based Solar Cell Applications

PbS thin films have attracted considerable interest since the early development of chemical deposition techniques, which were established for PbS film preparation in the late 1940s. Later, PbS thin films were investigated for solar energy applications, including photothermal conversion, either as single layers deposited on metallic substrates or as multilayer structures such as PbS-CdS-PbS and $(\text{PbS})_{1-x}(\text{CdS})_x$ composites. PbS thin films have also been explored for solar-control and other optoelectronic applications. Yeon et al. [99] developed depleted multi junction solar cells using PbS thin films, in which two band-aligned absorber layers were stacked and fabricated by chemical bath deposition method [99]. The structure of the suggested device is shown in Fig. 8(a). It consists of several layers of PbS with bandgaps of 1.61 eV and 0.92 eV, respectively. Light of longer wavelengths is absorbed by PbS with a small bandgap, as shown in Fig. 8(b), while light of shorter wavelengths is absorbed primarily by PbS with a high bandgap. A broader absorption spectrum led to an improvement in the device's power conversion efficiency (PCE), as shown in Fig. 8(c), from 3.10 to 4.03%.

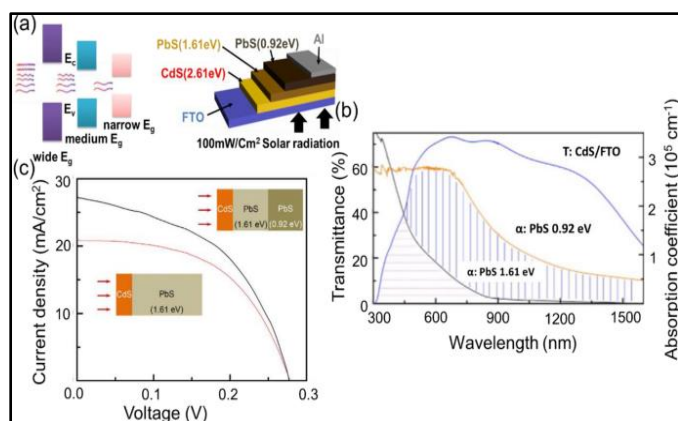


Fig. 8 (a) A schematic depicting the final device's layers and their respective bandgap diagrams. (b) Transmittance spectra of CdS/FTO/Glass show distinct values, whereas PbS thin films with band gaps of 1.61 eV exhibit absorption coefficients with varied values. (c) Graphs showing the potential energy output of solar cells with and without stacked layers of PbS Adapted from Yeon et al. [99].

Tables 1-3 summarize how different doping approaches, transport layers, and interface-engineering strategies influence the structural, optical, electrical, and photovoltaic properties of PbS based materials and devices. Overall, the results show that careful selection of dopants and appropriate device or interface engineering can significantly affect charge transport, energy band alignment, and ultimately the overall performance of PbS based optoelectronic devices.

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Table 2 Photovoltaic performance of pure and doped PbS absorber layers

PbS absorber layer	Dopant /modification	Window / ETL layer	Device structure	(V)	J _{sc} (mA/c m²)	FF	PCE (%)	Ref.
PbS thin film	Pure PbS	CdS	Glass/ITO/CdS/PbS/graphite	0.2 90	14.00	0.36	1.63	[100]
PbS thin film	Pure PbS	PbS	Glass/SnO ₂ /CdS/PbS/HgTe	-	-	-	1.668	[5]
PbS thin film	Pure PbS	CdS	TO/CdS/PbS/Ag	1.0 0	12.44	0.39	4.85	[101]
PbS/CdS heterojunction	PbS/CdS double absorber	ZnO s/CdS	ZnO-based PbS/CdS heterojunction	-	-	-	5.59	[102]
PbS thin film	Cd ²⁺ -doped PbS	In ₂ O ₃	FTO/In ₂ O ₃ (n)/Cd:PbS (p)/Al	0.6 35	12.36	0.32	2.50	[29]

Table 3 Photovoltaic performance of PbS quantum dot solar cells with ETL and interface modifications

PbS absorber layer	Dopant /modification	Window / ETL layer	Device Structure	(V)	J _{sc} (mA/cm²)	FF	PCE (%)	Ref.
PbS CQD	Pure PbS CQD	ZnO	ITO/ZnO/PbS CQDs/Au	0.55	24.20	0.61	8.20	[103]
PbS CQD	Mg doped ZnO ETL	Mg:ZnO	PbS CQD/Mg:ZnO ETL device	-	-	-	9.46	[104]
PbS CQD	Mg:ZnO + ZnO NC interface layer	Mg:ZnO / ZnO NC	ITO/Mg ZnO/ZnO NC/PbS CQDs/Au	0.56	26.72	0.471 2	7.09	[105]
PbS CQD	CsMg-doped ZnO ETL	CsMg:ZnO	PbS CQD device with CsMg ZnO ETL	0.61	23.25	0.578	8.40	[106]
PbS CQD	PbS-TBAI/PbS-EDT ligand engineering	ZnO	ITO/ZnO/PbS-TBAI/PbS-EDT/Cr/Ag	-	-	-	6.50	[107]

6. Challenges and Future Recommendations

One of the main challenges in the chemical doping of PbS thin films is achieving precise control over dopant incorporation, distribution, and reproducibility. Several studies have reported a reduction in the crystallite size of PbS following the incorporation of transition-metal dopants. For example, the crystallite size of Cr doped PbS films decreased significantly with increasing dopant concentration [108]. This reduction in crystallite size is often associated with increased lattice strain and dislocation density, indicating lattice distortion and structural defects. Such defects may include dislocations, grain boundary defects, and possible non-uniform dopant distribution. These defects can act as recombination centres or charge-carrier scattering sites, thereby hindering charge transport and reducing the potential benefits of doping [85]. Another challenge associated with transition metal doped PbS thin film solar cells is their long-term stability. Further research is required to address the stability issues of solid-state quantum dot-based solar cells. Additionally, significant challenges remain in developing low-cost, environmentally friendly, stable, and high-efficiency PbS-based solar cells [109, 110]. The stability of solar cells is compromised when lead sulphide (PbS) quantum dots are exposed to ambient conditions because they are easily oxidized [111]. How stable PbS quantum dot (QD) solar cells are during oxygenated, continuous light exposure depends on the ligands used [112]. According to PbS colloidal quantum dot (CQD) solar cells, achieving the required efficiency in very stable devices has been an ongoing issue in the development of solution-processed photovoltaic technology [112]. Additionally, there is a relation between band-gap and charge transport. Many dopants that broaden or shift the absorption also make it harder for carriers to move around (by increasing scattering or making deep traps), which may lower the device's current and fill factor even when the absorbance improves. The chemical methods may create secondary phases or uneven (surface vs. bulk) dopant distributions that make it hard to understand spectrum data and photovoltaic metrics unless they are backed up by rigorous depth profiling using TEM/EDS/XPS. When it comes to using solar cells in real life, there are issues with stability, scalability, and the environment. Transition metal dopants have the potential to accelerate surface oxidation or corrosion when exposed to

light or air, which may oxidize PbS. Long term device stability must be shown on a large scale, and lead is hazardous, so it has to be encapsulated and handled properly at the end of its life. Given these challenges, the development of transition-metal doped PbS films for photovoltaic applications requires careful optimization of the chemical bath deposition conditions, detailed structural and electronic characterisation, effective trap passivation, and accelerated ageing studies to assess their long-term stability and reliability. Addressing these factors is essential for developing photovoltaic devices with improved efficiency and sustained operational stability. Future investigations into transition metal doped PbS thin films produced using chemical techniques should emphasise improved control, repeatability, and optimization for practical applications. Important methods include setting precise doping windows for uniform doping without secondary phase formation by methodically optimizing chemical bath parameters. These factors include precursor concentration, complexing agents, pH, and deposition temperature. Technically advanced characterization methods such as time resolved photoluminescence (TRPL), high-resolution transmission electron microscopy (HRTEM), and depth-resolved X-ray photoelectron spectroscopy (XPS) are required to comprehend the effects of dopants on a material's microstructure and optoelectronic characteristics and to accurately measure the distribution of dopants, defect states, and carrier lifetimes. To further reduce trap states and enhance charge transfer, post deposition procedures such surface passivation and thermal annealing in controlled environments could be considered. For thin film technologies to be sustainable, it is important to find scalable deposition methods, such as continuous flow chemical bath deposition or spray assisted chemical deposition.

7. Conclusion

Transition metal doped PbS thin films prepared by chemical deposition methods have significant potential for photovoltaic and optoelectronic applications due to their tunable structural, optical, and electrical properties. The reviewed studies demonstrate that dopants such as Cu, Ni, Cd, Mn, Zn, and Co can modify crystallite size, lattice parameters, morphology, optical band gap, carrier concentration, and electrical conductivity, thereby influencing light absorption and charge-carrier transport.

CBD and SILAR methods provide simple, low-cost, and versatile routes for controlling film properties through parameters such as precursor concentration, pH, temperature, deposition time, and deposition cycles. However, excessive doping may lead to dopant inhomogeneity, secondary-phase formation, lattice distortion, strain, and defect states, which can increase carrier trapping and recombination. In addition, the oxidation and environmental instability of PbS remain important challenges for long-term device applications.

Future research should focus on optimizing dopant concentration and deposition conditions while establishing clear relationships between dopant incorporation, defect chemistry, material properties, and photovoltaic performance. Surface passivation, interface engineering, suitable charge-transport layers, and effective encapsulation can further improve carrier extraction and device stability. Overall, controlled transition-metal doping offers a promising strategy for developing low-cost and tunable PbS thin films for future photovoltaic and optoelectronic technologies.

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References

- [1] A. Encinas-Terán, H.A. Pineda-León, M.R. Gómez-Colín, L.R. Márquez-Alvarez, R. Ochoa-Landín, et al., Synthesis and characterization of a semiconductor diodic bilayer PbS/CdS made by the chemical bath deposition technique, *ACS Omega* 9 (2024) 24321-24332.
- [2] Z. Mamiyev, N.O. Balayeva, PbS nanostructures: A review of recent advances, *Mater. Today Sustain.* 21 (2023) 100305.
- [3] X. Zheng, F. Gao, F. Ji, H. Wu, J. Zhang, X. Hu, Y. Xiang, Cu-doped PbS thin films with low resistivity prepared via chemical bath deposition, *Mater. Lett.* 167 (2016) 128-130.
- [4] C. Rajashree, A.R. Balu, V.S. Nagarethinam, Properties of Cd-doped PbS thin films: doping concentration effect, *Surf. Eng.* 31 (2015) 316-321.
- [5] D. Saikia, P. Phukan, Fabrication and evaluation of CdS/PbS thin film solar cell by chemical bath deposition technique, *TSF.* 562 (2014) 239-243.
- [6] M. Cheraghizade, F. Jamali-Sheini, R. Yousefi, Optical, electrical, and photovoltaic properties of PbS thin films by anionic and cationic dopants, *Appl. Phys. A* 123 (2017) 390.
- [7] D.G. Moon, S. Rehan, D.H. Yeon, S.M. Lee, S.J. Park, S. Ahn, Y.S. Cho, A review on binary metal sulfide heterojunction solar cells, *Sol. Energy Mater. Sol. Cells* 200 (2019) 109963.
- [8] R. Sakthi Sudar Saravanan, M. Meena, D. Pukazhselvan, C.K. Mahadevan, Structural, optical and electrical characterization of Mn²⁺ and Cd²⁺ doped/co-doped PbS nanocrystals, *J. Alloys Compd.* 627 (2015) 69-77.
- [9] S. Hassan, R.S. Hassan, G.A. Fattah, Effect of film thickness and microstructure on the optical and photoconductive performance of PbS thin films prepared by chemical bath deposition, *J. Mater. Sci.: Mater. Electron.* 37 (2026) 190.
- [10] D. Vankhade, T.K. Chaudhuri, Effect of thickness on structural and optical properties of spin-coated nanocrystalline PbS thin films, *Opt. Mater.* 98 (2019) 109491.
- [11] J. Wang, A. Mandelis, A. Melnikov, S. Hoogland, E.H. Sargent, Exciton lifetime broadening and distribution profiles of PbS colloidal quantum dot thin films using frequency- and temperature-scanned photocurrent radiometry, *J. Phys. Chem. C* 117 (2013) 23333-23348.
- [12] X. Zhang, H. Wu, Y. Pei, Y. Zhou, S. Gong, J. He, L.-D. Zhao, Investigation on thermal transport and structural properties of InFeO₃(ZnO)_m with modulated layer structures, *Acta Mater.* 136 (2017) 235-241.
- [13] I. Alghoraibi, Influence of the DEA concentration on structural and optical properties of nanodot PbS thin films growth by chemical solution deposition: unveiling dual optical absorption edges, *J. Nanomater.* 2024 (2024) 9504522.
- [14] M. Alanyalıoğlu, F. Bayrakçeken, Ü. Demir, Preparation of PbS thin films: a new electrochemical route for underpotential deposition, *Electrochim.* 54 (2009) 6554-6559.
- [15] B. Thangaraju, P. Kaliannan, Spray pyrolytically deposited PbS thin films, *Semicond. Sci. Technol.* 15 (2000) 849.
- [16] P. Vidhya, K. Shanmugasundaram, T. Govindaraj, T. Sasikala, V. Balasubramani, N.S. Kumar, Fabrication of crack-free PbS thin films by jet nebulizer spray pyrolysis technique for enhancing optoelectronic applications: an effect of Ce³⁺ doping concentrations, *Surf. Interfaces* 42 (2023) 103292.
- [17] M. Liu, Q. Zhan, W. Li, R. Li, Q. He, Y. Wang, Effect of Zn doping concentration on optical band gap of PbS thin films, *J. Alloys Compd.* 792 (2019) 1000-1007.
- [18] S. Wang, A. Pan, H. Yin, Y. He, Y. Lei, Z. Xu, B. Zou, Synthesis of PbS microcrystals via a hydrothermal process, *Mater. Lett.* 60 (2006) 1242-1246.
- [19] J. Zhang, R.W. Crisp, J. Gao, D.M. Kroupa, M.C. Beard, J.M. Luther, Synthetic conditions for high-accuracy size control of PbS quantum dots, *J. Phys. Chem. Lett.* 6 (2015) 1830-1833.
- [20] G.M.G. Khalaf, F. Fang, Y. Zou, P. Müller-Buschbaum, W. Chen, Emerging hole transport layers for PbS quantum dot solar cells and photodetectors, *J. Mater. Chem. A* 14 (2026) 8537-8559.
- [21] S.M. Chintapalli, L. Li, S.M. Thon, PbS colloidal quantum dot photovoltaics: progress towards infrared and flexible applications, *Chem. Commun.* 61 (2025) 14073-14086.
- [22] S. Rex Rosario, I. Kulandaisamy, K. Deva Arun Kumar, A.M.S. Arulanantham, S. Valanarasu, M.A. Youssef, N.S. Awwad, Deposition of p-type Al-doped PbS thin films for heterostructure solar cell device using feasible nebulizer spray pyrolysis technique, *Phys. B: Condens.* 575 (2019) 411704.
- [23] E.V. Mostovshchikova, V.I. Voronin, L.N. Maskaeva, I.V. Vaganova, N.A. Chufarova, V.P. Glazkov, Lead sulfide films with low iron doping: correlation between iron position and optical properties evolution, *J. Alloys Compd.* 852 (2021) 156932.
- [24] N. Zhang, X. Zou, Y. Gao, Heterovalent cation substitutional and interstitial doping in semiconductor sensitizers for quantum dot cosensitized solar cell, *Int. J. Photoenergy* 2015 (2015) 326850.
- [25] N. Mishra, S. Moskvich, M. Shandalov, E. Yabel, Y. Golan, G. Makov, Unusual defect chemistry of thorium doping of PbS, *Inorg. Chem.* 63 (2024) 20462-20469.
- [26] K.C. Preetha, T.L. Remadevi, Effect of Al incorporation on the structural, morphological, optoelectronic and transport properties of PbS thin films, *Phys. B: Condens.* 407 (2012) 4173-4181.
- [27] B. Touati, A. Gassoumi, S. Alfaifi, N. Kamoun-Turki, Optical, morphological and electrical studies of Zn:PbS thin films, *Mater. Sci. Semicond. Process.* 34 (2015) 82-87.
- [28] Y. Gülen, Synthesis and characterization of iron-doped lead sulfide thin films, *Metall. Mater. Trans. A* 46 (2015) 4698-4704.
- [29] B. Touati, A. Gassoumi, N. Kamoun Turki, Structural, optical and electrical properties of Ag-doped PbS thin films: role of Ag concentration, *J. Mater. Sci.: Mater. Electron.* 28 (2017) 18387-18395.
- [30] B. Touati, A. Gassoumi, C. Guasch, N.K. Turki, Cd²⁺-doped PbS thin films for photovoltaic applications: novel low-cost perspective, *Mater. Sci. Semicond. Process.* 67 (2017) 20-27.
- [31] S.K. Saha, A. Bera, A.J. Pal, Improvement in PbS-based hybrid bulk-heterojunction solar cells through band alignment via bismuth doping in the nanocrystals, *ACS Appl. Mater. Interf.* 7 (2015) 8886-8893.
- [32] T. Tohid, K. Jamshidi-Ghaleh, A. Namdar, R. Abdi-Ghaleh, Comparative studies on the structural, morphological, optical, and electrical properties of nanocrystalline PbS thin films grown by chemical bath deposition using two different bath compositions, *Mater. Sci. Semicond. Process.* 25 (2014) 197-206.
- [33] I.M.S. Mohammed, G.M.M. Gubari, N.P. Huse, A.S. Dive, S.H. Han, R. Sharma, Effect of Cd/S ratio on growth and physical properties of CdS thin films for photosensor application, *J. Mater. Sci.: Mater. Electron.* 31 (2020) 9989-9996.
- [34] N.P. Huse, A.S. Dive, S.V. Mahajan, R. Sharma, Facile, one step synthesis of non-toxic kesterite Cu₂ZnSnS₄ nanoflakes thin film by chemical bath deposition for solar cell application, *J. Mater. Sci.: Mater. Electron.* 29 (2018) 5649-5658.

- [35] A.S. Dive, K.P. Gattu, N.P. Huse, D.R. Upadhyay, D.M. Phase, R.B. Sharma, Single step chemical growth of ZnMgS nanorod thin film and its DFT study, *Mater. Sci. Eng. B*. 228 (2018) 91–95.
- [36] N.P. Huse, R.M. Patil, R. Sharma, Characterization of economic and non-toxic copper-doped zinc sulfide thin film grown by facile chemical bath deposition method, *ES Mater. Manuf.* 20 (2023) 839.
- [37] G.M.M. Gubari, S.M. Ibrahim Mohammed, N.P. Huse, A.S. Dive, R. Sharma, An experimental and theoretical study of $\text{Cu}_{0.2}\text{Zn}_{0.8}\text{S}$ thin film grown by facile chemical bath deposition as an efficient photosensor, *J. Electron. Mater.* 47 (2018) 6128–6135.
- [38] S. Sengupta, R. Aggarwal, M. Raula, A review on chemical bath deposition of metal chalcogenide thin films for heterojunction solar cells, *J. Mater. Res.* 38 (2023) 142–153.
- [39] A.S. Dive, N.P. Huse, K.P. Gattu, R. Sharma, Soft chemical growth of $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{S}$ one dimensional nanorod thin films for efficient visible light photosensor, *Sens. Actuators A Phys.* 266 (2017) 36–45.
- [40] N.P. Huse, A.S. Dive, K.P. Gattu, R. Sharma, One step synthesis of kesterite $\text{Cu}_2\text{ZnSnS}_4$ thin film by simple and economic chemical bath deposition method, *AIP Conf. Proc.* 1832 (2017) 080082.
- [41] N.P. Huse, A.S. Dive, K.P. Gattu, R. Sharma, An experimental and theoretical study on soft chemically grown CuS thin film for photosensor application, *Mater. Sci. Semicond. Process.* 67 (2017) 62–68.
- [42] G.M.M. Gubari, I.M.S. M, N.P. Huse, A.S. Dive, R. Sharma, Synthesis and photosensor study of as-grown CuZnO thin film by facile chemical bath deposition, *AIP Conf. Proc.* 1953 (2018) 100072.
- [43] N.P. Chaware, H.P. Borse, M.R. Patil, N.P. Huse, Technology, experimental and numerical investigation of CZFS thin film absorbers for photovoltaic applications, *J. Nanosci. Tech.* 11 (2026) 1185–1188.
- [44] N.P. Huse, H.P. Borse, G. Roymahapatra, R. Sharma, Study of optoelectronic properties and density functional theory of kesterite $\text{Cu}_2\text{ZnSnS}_4$ thin film grown by facile solution growth technique, *ES Energy Environ.* 25 (2024) 1206.
- [45] H.P. Borse, N.P. Chaware, M.R. Patil, A.V. Patil, N.P. Huse, Comprehensive analysis of structural, optical, topographical, and photosensing characteristics of CuZnO thin films synthesized via facile chemical route, *J. Opt. Photonics Res.* 3 (2026) 241–247.
- [46] N.M. Patil, S.G. Nilange, V.A. Jundale, P.B. Kadam, R. Chandrashekhar, A.A. Yadav, Structural, optical and electrical properties of spray-deposited Fe-doped nanocrystalline $\text{ZnS}_{0.2}\text{Se}_{0.8}$ thin films, *Phase Trans.* 94 (2021) 493–510.
- [47] G.M.M. Gubari, I.M.S. M, N.P. Huse, A.S. Dive, R. Sharma, Synthesis and characterization of structural, morphological and photosensor properties of $\text{Cu}_{0.1}\text{Zn}_{0.9}\text{S}$ thin film prepared by a facile chemical method, *AIP Conf. Proc.* 1953 (2018) 100014.
- [48] A.S. Dive, N.P. Huse, D.S. Upadhye, S.B. Bagul, K.P. Gattu, R. Sharma, Growth of nanocrystalline $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{S}$ thin film by solution growth technique and their characterization as a window layer for solar cell, *Ferroelectr.* 518 (2017) 196–203.
- [49] A.S. Dive, N.P. Huse, K.P. Gattu, R.B. Birajdar, D.R. Upadhyay, R. Sharma, Theoretical and experimental investigations of intermediate bands in ZnS – Mg nanocrystalline thin film photosensor, *J. Mater. Sci.: Mater. Electron.* 28 (2017) 15161–15167.
- [50] N.P. Huse, A.S. Dive, D.S. Upadhye, S.B. Bagul, K.P. Gattu, R. Sharma, Effect of quantum confinement on photosensitivity in ZnS thin film grown by facile chemical bath deposition, *Ferroelectr.* 519 (2017) 170–177.
- [51] K.C. Preetha, K. Deepa, A.C. Dhanya, T.L. Remadevi, Role of complexing agents on chemical bath deposited PbS thin film characterization, *IOP Conf. Ser. Mater. Sci. Eng.* 73 (2015) 012086.
- [52] F.G. Hone, F.B. Dejene, Six complexing agents and their effects on optical, structural, morphological and photoluminescence properties of lead sulphide thin films prepared by chemical route, *J. Lumin.* 201 (2018) 321–328.
- [53] A. Osherov, V. Ezersky, Y. Golan, The role of solution composition in chemical bath deposition of epitaxial thin films of PbS on GaAs(100), *J. Cryst. Growth* 308 (2007) 334–339.
- [54] A.N. Chattarkar, S.S. Kamble, L.P. Deshmukh, Role of pH in aqueous alkaline chemical bath deposition of lead sulfide thin films, *Mater. Lett.* 67 (2012) 39–41.
- [55] M.M. Abbas, A.A.-M. Shehab, A.K. Al-Samuraee, N.A. Hassan, Effect of deposition time on the optical characteristics of chemically deposited nanostructure PbS thin films, *Energy Procedia* 6 (2011) 241–250.
- [56] U. Chalapathi, S.H. Park, W.J. Choi, Chemically deposited Sn-doped PbS thin films for infrared photodetector applications, *Appl. Phys. A* 127 (2021) 645.
- [57] K. Kushnir, K. Chen, L. Zhou, B. Giri, R.L. Grimm, P.M. Rao, L.V. Titova, Dynamics of photoexcited carriers in polycrystalline PbS and at PbS/ZnO heterojunctions: influence of grain boundaries and interfaces, *J. Phys. Chem. C*. 122 (2018) 11682–11688.
- [58] E.S. Senthil, R. Sangeetha, C. Nirmala, R. Sumathi, K. Mohanasudha, Studies on lead sulphide (PbS) thin film prepared by chemical bath deposition method, *SSP*. 350 (2023) 65–73.
- [59] N.M. Gosavi, K.R. Sali, R.A. Joshi, S.R. Gosavi, Study of synthesis dependent physicochemical and optoelectronic properties of nanocrystalline lead sulfide (PbS) thin films deposited using chemical bath deposition method, *Prog. phys. appl. mater.* 5 (2025) 137–152.
- [60] A. Banerjee, P. Mitra, Influence of nickel incorporation on electrical and dielectric properties of PbS thin films synthesized by chemical bath deposition, *Phys. Solid State*. 67 (2025) 499–507.
- [61] S.R. Sriram, S.R. Parne, N. Pothukanuri, D.R. Edla, Prospects of spray pyrolysis technique for gas sensor applications – a comprehensive review, *J. Anal. Appl. Pyrolysis* 164 (2022) 105527.
- [62] A.B. Workie, H.S. Ningsih, S.J. Shih, An comprehensive review on the spray pyrolysis technique: historical context, operational factors, classifications, and product applications, *J. Anal. Appl. Pyrolysis* 170 (2023) 105915.
- [63] T. Abzieher, T. Feeney, F. Schackmar, Y.J. Donie, I.M. Hossain, J.A. Schwenzer, T. Hellmann, T. Mayer, M. Powalla, U.W. Paetzold, From groundwork to efficient solar cells: on the importance of the substrate material in co-evaporated perovskite solar cells, *Adv. Funct. Mater.* 31 (2021) 2104482.
- [64] S. Çelik, M. Temiz, Effect of lead and zinc composition on the optical and structural characteristics of PbZnS thin films fabricated by spray pyrolysis, *Chalcogenide Lett.* 22 (2025) 89–96.
- [65] A.E. Adeoye, E. Ajenifuja, B.A. Taleatu, A.Y. Fasasi, Rutherford backscattering spectrometry analysis and structural properties of $\text{Zn}_x\text{Pb}_{1-x}\text{S}$ thin films deposited by chemical spray pyrolysis, *J. Mater.* 2015 (2015) 215210.
- [66] V.K. Kumar, K. Ramamurthi, E. Elangovan, Preparation of $(\text{CdO})_{1-x}(\text{PbO})_x$ and $(\text{CdS})_{1-x}(\text{PbS})_x$ thin films by spray pyrolysis technique and their characterization, *Solid State Commun.* 132 (2004) 673–677.
- [67] S.P. Ratnayake, J. Ren, E. Colusso, M. Guglielmi, A. Martucci, E. Della Gaspera, SILAR deposition of metal oxide nanostructured films, *Small*. 17 (2021) 2101666.
- [68] H. Soonmin, Recent advances in the growth and characterizations of SILAR-deposited thin films, *Appl. Sci.* 12 (2022) 8184.
- [69] E. Güneri, F. Göde, S. Çevik, Influence of grain size on structural and optic properties of PbS thin films produced by SILAR method, *TSE*. 589 (2015) 578–583.
- [70] C.E. Pérez-García, S. Meraz-Dávila, G. Arreola-Jardón, F. de Moure-Flores, R. Ramírez-Bon, Y.V. Vorobiev, Characterization of PbS films deposited by successive ionic layer adsorption and reaction (SILAR) for CdS/PbS solar cells application, *Mater. Res. Express* 7 (2020) 015530.
- [71] S. Sengupta, T. Templeman, C. Chen, E. Moon, M. Shandalov, V. Ezersky, J. Phillips, Y. Golan, Chemical epitaxy and interfacial reactivity in solution deposited PbS on ZnTe, *J. Phys. Chem. C*. 4 (2016) 1996–2002.
- [72] O. Makhlof, M. Khadraoui, A. Aissat, K. Sahraoui, R. Miloua, Structural, optical and electrical properties of mixed PbS–SnS thin films deposited by spray pyrolysis, *Mater. Today Commun.* 46 (2025) 112923.
- [73] A. Ahmed, M. Rabia, M. Shaban, The structure and photoelectrochemical activity of Cr-doped PbS thin films grown by chemical bath deposition, *RSC Adv.* 10 (2020) 14458–14470.
- [74] S. Gozalzadeh, F. Nasirpour, S.I. Seok, Towards environmental friendly multi-step processing of efficient mixed-cation mixed halide perovskite solar cells from chemically bath deposited lead sulphide, *Sci. Rep.* 11 (2021) 18561.
- [75] H. Li, D. Chen, L. Li, F. Tang, L. Zhang, J. Ren, Size- and shape-controlled synthesis of PbSe and PbS nanocrystals via a facile method, *Cryst. Eng. Comm.* 12 (2010) 1127–1133.
- [76] R. Bai, D. Kumar, S. Chaudhary, D.K. Pandya, Highly crystalline p-PbS thin films with tunable optical and hole transport parameters by chemical bath deposition, *Acta Mater.* 131 (2017) 11–21.
- [77] M.D. Khan, S. Hameed, N. Haider, A. Afzal, M.C. Sportelli, N. Cioffi, M.A. Malik, J. Akhtar, Deposition of morphology-tailored PbS thin films by surfactant-enhanced aerosol assisted chemical vapor deposition, *Mater. Sci. Semicond. Process.* 46 (2016) 39–45.
- [78] N. Pendyala, K. Rao, Temperature and capping dependence of NIR emission from PbS nano-microcrystallites with different morphologies, *Mater. Chem. Phys.* 113 (2009) 456–461.
- [79] H. Jumaa, Preparation and study of structural and optical properties of PbS:Cu nanostructured thin films, *EMJMS*. 26 (2024) 22–31.
- [80] L. Dong, Y. Chu, Y. Liu, M. Li, F. Yang, L. Li, Surfactant-assisted fabrication PbS nanorods, nanobelts, nanovelvet-flowers and dendritic nanostructures at lower temperature in aqueous solution, *J. Colloid Interf. Sci.* 301 (2006) 503–510.
- [81] K. Sali, N. Gosavi, R. Joshi, S. Gosavi, Study of synthesis dependent physicochemical and optoelectronic properties of nanocrystalline lead sulfide (PbS) thin films deposited using chemical bath deposition method, *Prog. Phys. Appl. Mater.* 5 (2025) 137–152.
- [82] H. Yildizay, Pinhole-free PbS thin films obtained by chemical bath deposition method, *BSEU Jour. Sci.* 8 (2021) 1017–1023.
- [83] B. Altuokka, M.C. Baykul, M.R. Altuokka, Some physical effects of reaction rate on PbS thin films obtained by chemical bath deposition, *J. Cryst. Growth* 384 (2013) 50–54.
- [84] A.M. Ahmed, M. Rabia, M. Shaban, The structure and photoelectrochemical activity of Cr-doped PbS thin films grown by chemical bath deposition, *RSC Adv.* 10 (2020) 14458–14470.
- [85] I. Dobryden, B. Touati, A. Gassoumi, A. Vomiero, N. Kamoun, N. Almqvist, Morphological and electrical characterization of Cu-doped PbS thin films with AFM, *Adv. Mater. Lett.* 8 (2017) 1029–1037.
- [86] C. Rajashree, A.R. Balu, Tuning the physical properties of PbS thin films towards optoelectronic applications through Ni doping, *Optik* 127 (2016) 8892–8898.
- [87] A. Javed, M.A. Wahab, M. Bashir, M. Ahmad, S.H.H. Sherazi, Shanza, Low-cost synthesis and comprehensive characterization of Cr^{3+} and Sn^{2+} co-doped lead sulfide thin films for optoelectronic applications, *Mater. Adv.* 6 (2025) 8586–8601.
- [88] M. Suganya, D. Prabha, S. Anitha, J. Srivind, S. Balamurugan, V.S. Nagarethinam, A.R. Balu, Thermal behavior, magnetic and antimicrobial properties of PbS–CdO nanocomposite synthesized by a simple soft chemical route, *J. Mater. Sci.: Mater. Electron.* 28 (2017) 12348–12355.
- [89] A.A. Bunaciu, E.g. Udristoiu, H.Y. Aboul-Enein, X-ray diffraction: instrumentation and applications, *Crit. Rev. Anal. Chem.* 45 (2015) 289–299.
- [90] E.K. Shokr, W.S. Mohamed, A.G. Adam, H.M. Ali, Optical characterizations of lightly doped $(\text{PbS})_{1-x}\text{Zn}_x$ thin films influenced by film thickness and annealing temperature for applications in highly intensive radiation systems, *J. Mater. Sci.: Mater. Electron.* 34 (2023) 1929.
- [91] M. Cheraghizade, F. Jamali Sheini, R. Yousefi, Optical, electrical, and photovoltaic properties of PbS thin films by anionic and cationic dopants, *Appl. Phys. A* 123 (2017) 390.

- [92] Ö. Şahin, A. Ekinici, S. Horoz, Synthesis of PbS:Mo(3%) thin film and investigation of its properties, *J. Mater. Sci.: Mater. Electron.* 30 (2019) 7600-7605.
- [93] R. Kumar, R. Das, M. Gupta, V. Ganesan, Preparation of nanocrystalline Sb-doped PbS thin films and their structural, optical, and electrical characterization, *Superlatt. Microstruct.* 75 (2014) 601-612.
- [94] L.R. Singh, R.K.L. Singh, M.A. Hussain, Optical and photoconductivity properties of Mn-doped nanocrystalline PbS thin films deposited by chemical bath deposition method, *Chalcogenide Lett.* 20 (2023) 821-828.
- [95] S. Rajathi, K. Kirubavathi, K. Selvaraju, Preparation of nanocrystalline Cd-doped PbS thin films and their structural and optical properties, *J. Taibah Univ. Sci.* 11 (2017) 1296-1305.
- [96] S. Nazir, J.-M. Zhang, M.N. Akhtar, N. Abbas, S. Saleem, M. Nauman, A. Ali, Modification of physicochemical and electrical characteristics of lead sulfide (PbS) nanoparticles (NPs) by manganese (Mn) doping for electronic device and applications, *J. Sol-Gel Sci. Technol.* 108 (2023) 778-790.
- [97] A.E. Adeoye, E. Ajenifuja, S.O. Alayande, E.D. Ogunmola, O.A. Adeyemi, A.Y. Fasasi, Effects of Zn doping concentration on the optical and photovoltaic properties of $\text{Zn}_x\text{Pb}_{1-x}\text{S}$ thin film-based solar cell prepared by chemical spray pyrolysis, *SN Appl. Sci.* 2 (2020) 1560.
- [98] M. Shkir, B. Palanivel, K.V. Chandekar, A. Khan, A.M. El-Toni, A.A. Ansari, R. Ahmad Zargar, M.A. Sayed, S. AlFaify, Microwave-assisted synthesis of Cu-doped PbS nanostructures with enhanced dielectric and electrical properties for optoelectronic applications, *Mater. Sci. Eng. B.* 271 (2021) 115268.
- [99] D. Ho Yeon, B. Chandra Mohanty, S.M. Lee, Y. Soo Cho, Effect of band-aligned double absorber layers on photovoltaic characteristics of chemical bath deposited PbS/CdS thin film solar cells, *Sci. Rep.* 5 (2015) 14353.
- [100] J. Hernández-Borja, Y.V. Vorobiev, R. Ramírez-Bon, Thin film solar cells of CdS/PbS chemically deposited by an ammonia-free process, *Sol. Energy Mater. Sol. Cells* 95 (2011) 1882-1888.
- [101] F. Göde, S. Ünlü, Synthesis and characterization of CdS window layers for PbS thin film solar cells, *Mater. Sci. Semicond. Process.* 90 (2019) 92-100.
- [102] D.H. Yeon, B.C. Mohanty, C.Y. Lee, S.M. Lee, Y.S. Cho, High-efficiency double absorber PbS/CdS heterojunction solar cells by enhanced charge collection using a ZnO nanorod array, *ACS Omega* 2 (2017) 4894-4899.
- [103] X. Zhang, E.M.J. Johansson, Reduction of charge recombination in PbS colloidal quantum dot solar cells at the quantum dot/ZnO interface by inserting a MgZnO buffer layer, *J. Mater. Chem. A* 5 (2017) 303-310.
- [104] M. Xing, Y. Wei, D. Wang, Q. Shen, R. Wang, Mg-doped ZnO layer to enhance electron transporting for PbS quantum dot solar cells, *Curr. Appl. Phys.* 21 (2021) 14-19.
- [105] H. Ren, A. Xu, Y. Pan, D. Qin, L. Hou, D. Wang, Efficient PbS quantum dot solar cells with both Mg-doped ZnO window layer and ZnO nanocrystal interface passivation layer, *J. Nanomater.* 2021 (2021) 219.
- [106] R. Holfeuer, C. Maheu, H. Illner, R. Hoojier, H. Balakrishnan, B. März, S. Lotfi, H. Sezen, K. Müller-Caspary, T. Bein, J.P. Hofmann, T. Ameri, A. Hartschuh, A. Yousefi Amin, Printed CsMg-ZnO ETLs achieve over 9% efficiency in PbS quantum dot solar cells, *Mater. Today Energy* 48 (2025) 101813.
- [107] J.J. Khanam, S.Y. Foo, Z. Yu, T. Liu, P. Mao, Efficient, stable, and low-cost PbS quantum dot solar cells with Cr-Ag electrodes, *J. Nanomater.* 2019 (2019) 1205.
- [108] J. Huo, W. Li, T. Wang, Effect of Cr doping concentration on the structural, optical, and electrical properties of lead sulfide (PbS) nanofilms, *Coatings* 2019 (2019) 376.
- [109] H. Lee, H.C. Leventis, S.-J. Moon, P. Chen, S. Ito, S.A. Haque, T. Torres, F. Nüesch, T. Geiger, S.M. Zakeeruddin, M. Grätzel, M.K. Nazeeeruddin, PbS and CdS quantum dot-sensitized solid-state solar cells: "old concepts, new results", *Adv. Funct. Mater.* 19 (2009) 2735-2742.
- [110] K. Zeng, D.J. Xue, J. Tang, Antimony selenide thin-film solar cells, *Semicond. Sci. Technol.* 31 (2016) 063001.
- [111] J.P. Park, J.h. Heo, S.H. Im, S.-W. Kim, Exceptional stability of Mg-implemented PbS quantum dot solar cells realized by galvanic corrosion protection, *J. Mater. Chem. A* 3 (2015) 8433-8437.
- [112] D. Becker-Koch, M. Albaladejo-Siguan, V. Lami, F. Paulus, H. Xiang, Z. Chen, Y. Vaynzof, Ligand dependent oxidation dictates the performance evolution of high efficiency PbS quantum dot solar cells, *Sustain. Energy Fuels* 4 (2020) 108-115.