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Recent Advances in the Design of CdZnS Thin Films for Solar Cell Applications: Progress, Challenges and Future Prospects

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ABSTRACT: Cadmium zinc sulphide (CdZnS) thin films have emerged as promising window and buffer layer materials for thin-film solar cells owing to their tuneable band gap, high optical transparency, and favourable band alignment with common absorber layers. This review presents a comprehensive assessment of recent advances in the synthesis, deposition techniques, properties, and solar cell applications of CdZnS thin films. Particular emphasis is placed on solution-based chemical deposition methods, including Chemical Bath Deposition (CBD), Spray Pyrolysis, and the Successive Ionic Layer Adsorption and Reaction (SILAR) technique, which have been widely explored due to their low cost, simplicity, and scalability. The influence of deposition parameters and Zn incorporation on structural, morphological, optical, and electrical properties is critically analysed, highlighting the role of band gap engineering in enhancing photovoltaic performance. Furthermore, the application of Cd-doped ZnS and CdZnS thin films as buffer and window layers in solar cells is reviewed, demonstrating their potential to improve light transmission, interface quality, and device efficiency.

KEYWORDS: CdZnS thin films; Chemical bath deposition; Spray pyrolysis; SILAR method; Band gap engineering; Solar cells.

I. INTRODUCTION

Thin films are ultra-thin material layers deposited on suitable substrates, with thicknesses typically ranging from a few nanometres to several micrometres (Abou-Ras et al., 2016). Such films are widely employed to alter surface characteristics or to impart specific functionalities to materials and devices. At nanometre and micrometre length scales, the structural arrangement of thin films plays a decisive role in determining their mechanical strength, optical response, electrical conductivity, and thermal behaviour (Raut et al., 2011; McDonnell and Wallace, 2016). One of the defining features of thin-film materials is their rapidly expanding role in modern technologies, which has made them a central topic in materials science research encompassing both experimental and theoretical investigations. From a materials engineering perspective, thin films not only exhibit the intrinsic properties of bulk matter but also reveal strong correlations between synthesis routes, growth mechanisms, and material performance (Lee et al., 2014). The functional performance of thin films is highly sensitive to their elemental composition and growth conditions, as these factors directly influence the structural evolution and defect formation within the film. The method employed for thin-film fabrication, together with the inherent kinetics of film growth, significantly affects crystallinity, morphology, and phase stability. Moreover, the physical differences between thin films and bulk materials are largely governed by thickness, where even minor variations during deposition can lead to substantial changes in properties across the nano-to-microscale regime (Khan, 2015). Because of this pronounced thickness-dependent behaviour, thin films-particularly chalcogenide semiconductors-have attracted considerable scientific interest over the past decade. These materials have been extensively explored for optoelectronic applications due to their high conversion efficiency, tuneable physical properties, and increasing relevance in applied technologies.

Among chalcogenides, cadmium sulphide (CdS) remains one of the most thoroughly investigated materials since the initial observation of photovoltaic effects in CdS crystals with metallic contacts. CdS is an n-type II-VI binary semiconductor exhibiting a direct band gap of approximately 2.42 eV at room temperature, along with high carrier concentration (10^{16} - 10^{18} cm⁻³), moderate carrier mobility, a large absorption coefficient, and excellent electrochemical stability. These characteristics have enabled its widespread application in photovoltaic devices, light-emitting diodes, photodetectors, chemical and biological sensors, thin-film transistors, photocatalysis, optical storage technologies, and

hydrogen generation systems (Carrasco-Chavez et al., 2023). In comparison, zinc sulphide (ZnS) is another technologically significant II–VI semiconductor distinguished by its much wider direct band gap of around 3.7 eV at 300 K, which confers high transparency in the visible spectrum and superior chemical stability. ZnS also possesses a high refractive index, making it attractive for optical and optoelectronic applications. Polycrystalline and nanocrystalline ZnS thin films have received increasing attention due to their potential role in photovoltaic technologies and their extensive use in optoelectronic devices. Among various techniques, chemical bath deposition has been widely recognized as one of the most suitable approaches for producing ZnS thin films for photovoltaic applications because of its cost effectiveness, simplicity, and capability for large-area deposition (Eid et al., 2010). The adoption of such solution-based deposition methods has enabled the development of ternary $Cd_{1-x}Zn_xS$ thin films as alternatives to conventional CdS window layers. The introduction of Zn into CdS leads to a higher band gap material, thereby reducing optical absorption losses in the window layer and improving lattice compatibility with $Cu(In,Ga)Se_2$ chalcopyrite absorber layers (Jia et al., 2009). Beyond solar cell applications, CdZnS and related ternary semiconductor systems have gained significant attention for use in high-density optical data storage as well as blue and ultraviolet laser diode technologies. These applications stem from the tuneable electronic structure of $Cd_xZn_{1-x}S$, whose fundamental absorption edge can be continuously adjusted from the green to the ultraviolet region.

In photovoltaic devices where CdS has traditionally served as an effective window layer, substituting CdS with higher band gap $Cd_{1-x}Zn_xS$ alloys has been shown to reduce window absorption losses and enhance short-circuit current density (Kumar and Sankaranayanan, 2009). The energy band gap of the $Cd_xZn_{1-x}S$ II–VI semiconductor system can be precisely tailored by adjusting the Cd and Zn composition, spanning from about 2.42 eV for CdS to nearly 3.70 eV for ZnS. As a result, CdZnS nanoparticles synthesized with optimized Cd:Zn ratios have been widely recognized as promising wide band gap materials for heterojunction thin-film solar cell fabrication (Hussein et al., 2022). Apart from photovoltaic uses, CdZnS (CZS) thin films exhibit broad applicability in optical, electronic, and optoelectronic devices. These films have been prepared using various deposition techniques such as electrodeposition, close-spaced sublimation, thermal evaporation, spray pyrolysis, chemical bath deposition, dip coating, and chemical vapor deposition. Among these methods, close-spaced sublimation is known for producing reproducible, mechanically robust, adherent, and stable films through a relatively simple processing route (Mahmood and Shah, 2014). In recent years, II–VI semiconductor thin films have continued to attract extensive research attention due to their versatility in solar cell and optoelectronic device fabrication. Although CdS has been widely employed as a window layer, its absorption of the blue portion of the solar spectrum limits current density and overall device efficiency. Consequently, the selection of an appropriate window material is critical for achieving high-performance solar cells. In this context, ternary CdZnS thin films, with their enhanced chemical stability, improved structural quality, and superior optical transparency, have emerged as promising window layer candidates (Asogwa, 2010). Therefore, in view of this, the paper aims to comprehensively review the various synthesis methods, properties, and applications of CdZnS thin films.

II. CDZNS THIN FILMS: SYNTHESIS, DEPOSITION TECHNIQUES, AND PROPERTIES

The synthesis and deposition technique employed for the fabrication of CdZnS thin films plays a crucial role in determining their properties. Since CdZnS is a ternary II–VI semiconductor alloy, precise control over composition, film thickness, crystallinity, and surface uniformity is essential to achieve the desired band gap and functional performance, particularly for optoelectronic and photovoltaic applications. Different chemical deposition techniques have been extensively explored in the literature owing to their simplicity, low cost, and suitability for large-area coating, making them highly attractive for solar cell technologies. Among the various approaches reported, solution-based chemical techniques such as CBD, Spray Pyrolysis, and the SILAR method have received significant attention. These methods enable controlled incorporation of Zn and Cd ions into the host lattice, allowing effective band gap engineering and tailoring of film properties through adjustment of deposition parameters such as precursor concentration, temperature, pH, and deposition time. Moreover, these techniques offer advantages such as low processing temperature, compatibility with different substrates, and ease of scalability. The choice of deposition method strongly influences the nucleation and growth mechanisms of CdZnS thin films, which in turn affects grain size, surface morphology, defect density, and optoelectronic behaviour. Therefore, a comparative understanding of these techniques is essential for optimizing film quality and enhancing device performance. In this section, a comprehensive review of the widely used CBD, Spray Pyrolysis Technique, and SILAR Method is presented, with emphasis on their growth mechanisms, process parameters, and their impact on the resulting properties of CdZnS thin films.

2.1 Chemical Bath Deposition (CBD):

Chemical Bath Deposition (CBD) is one of the most widely employed solution-based techniques for the preparation of CdZnS thin films due to its simplicity, low processing temperature, cost-effectiveness, and suitability for large-area coatings. Owing to these advantages, CBD has been extensively used for fabricating CdZnS thin films intended for photovoltaic and optoelectronic applications, where band gap tunability and optical transparency are critical. Kumar and Sankaranarayanan (2009) reported the successful deposition of CdZnS thin films using a short-duration microwave-assisted CBD technique. Optical absorption, transmittance behaviour, and band gap tunability as a function of Zn^{2+} concentration were analysed using UV–VIS–NIR spectroscopy, while photoluminescence (PL) characteristics were recorded at an excitation wavelength of 370 nm. The study demonstrated that ternary CdZnS thin films with varying Zn^{2+} content could be fabricated efficiently within a reduced deposition time using microwave assistance. Crystallographic analysis confirmed that the films possessed a hexagonal structure. Surface morphology studies revealed that films prepared with lower Zn^{2+} concentrations exhibited superior surface quality compared to those with intermediate and higher Zn^{2+} contents. The work clearly illustrated that surface texture and self-organization of CdZnS thin films can be effectively tailored by adjusting the Zn^{2+} concentration in the chemical bath. All deposited films exhibited low absorption and a direct optical transition. A systematic increase in the optical band gap from 2.92 eV to 3.26 eV was observed with increasing Zn^{2+} concentration, confirming that band gap modulation is primarily governed by Zn incorporation. Additionally, films with lower Zn^{2+} content showed higher transmittance, a more compact and less dissociated surface morphology, and stronger PL emission intensity compared to films with higher Zn^{2+} concentrations.

Jia et al. (2009) synthesized ternary CdZnS thin films via the conventional CBD technique and studied the influence of Zn^{2+} concentration and deposition duration on film formation using optical transmission measurements. Their results emphasized the competitive complexation behaviour of Cd^{2+} and Zn^{2+} ions with ammonia, which plays a crucial role in determining film composition, particularly at lower Zn^{2+} concentrations. While Zn incorporation into the film increased with increasing Zn^{2+} concentration, the rate of Cd^{2+} incorporation was found to be faster than that of Zn^{2+} during prolonged deposition, indicating a composition-dependent growth mechanism.

McPeak et al. (2013) introduced a continuous-flow microreactor-based CBD approach as an advanced technique for rapidly screening deposition conditions across a single substrate. Along the substrate length, an increase in the Zn:Cd ratio, amorphous phase content, and quantum confinement effects was observed, resulting in a monotonic increase in the band gap from 2.42 eV to 2.75 eV. This CBD method was shown to be effective for identifying optimal CdZnS compositions and deposition parameters for thin-film photovoltaic applications.

Shrivastava et al. (2015) conducted a comparative study on CdZnS nanocrystalline films deposited by CBD using two different capping agents, cetyltrimethylammonium bromide (CTAB) and trisodium citrate (TSC). Structural and morphological analyses were performed using XRD, SEM, TEM, and AFM. The films exhibited both hexagonal and cubic crystal phases. SEM images revealed cabbage-like surface features, while AFM analysis indicated the presence of nanorod structures. TEM diffraction patterns confirmed the nanocrystalline nature of the films with multiple crystallographic planes. Elemental analysis further verified the absence of impurities, demonstrating the effectiveness of capping agents in controlling film morphology and purity.

Akhanda et al. (2017) synthesized CdZnS thin films on glass substrates by CBD at 82°C using cadmium chloride, zinc acetate, and thiourea as precursors. By systematically varying the ratio of zinc acetate to cadmium chloride, the authors studied the resulting changes in structural, optical, and electrical properties through XRD, SEM, and UV–VIS spectroscopy. The results indicated that increasing Zn content led to a deterioration in crystalline quality. Optical studies showed high transmittance values of 85–90% beyond 700 nm, with band gaps increasing gradually with Zn concentration. Electrical measurements revealed that film resistance increased as Zn content increased.

Mosiori et al. (2017) prepared ternary CdZnS thin films via CBD by introducing different Zn^{2+} concentrations into CdS films. The bath chemistry involved cadmium nitrate, zinc nitrate, thiourea, and ammonia. The study highlighted the role of competitive complex formation between Cd^{2+} and Zn^{2+} ions with ammonia during film growth. The films exhibited optical transmittance above 80%, tuneable band gaps between 2.47 and 2.72 eV, refractive index values ranging from 2.58 to 2.39, and sheet resistivity on the order of $10^2 \Omega \cdot cm$, confirming effective band gap engineering through Zn incorporation.

Zellagui et al. (2020) deposited $Cd_xZn_{1-x}S$ thin films on glass substrates using a simple and cost-effective CBD approach for photovoltaic applications. Comprehensive characterization showed that the films possessed mixed cubic and hexagonal phases with grain sizes between 6 and 25 nm. The films exhibited visible-range transmittance of 50–80% and band gap values spanning from 2.6 to 3.6 eV, underscoring their suitability for optoelectronic and solar cell devices.

Najm et al. (2022) focused on understanding the formation mechanisms of CdS thin films, which remain widely used as buffer layers in polycrystalline solar cells. Through combined experimental and numerical studies, the influence of thiourea concentration on film properties was examined. Optical band gaps ranged from 2.32 to 2.43 eV, and XRD confirmed polycrystalline behaviour under most conditions. Electrical characterization indicated that films with a Cd/S molar ratio of unity exhibited the highest carrier concentration and lowest resistivity. The study concluded that ion-by-ion growth plays a dominant role in CdS formation and that buffer layer optoelectronic properties critically influence CIGS solar cell performance.

Soni et al. (2023) deposited ternary CdZnS thin films on glass substrates using a low-cost CBD technique, employing cadmium acetate and zinc acetate as precursors. The films exhibited polycrystalline nature with both cubic and hexagonal phases. Band gap values increased systematically from 2.52 eV for CdS to 2.75 eV for multilayer CdZnS structures. PL spectra showed distinct excitation peaks, confirming the optical activity of the films.

Borah et al. (2024) synthesized $Cd_{1-x}Zn_xS$ nanocrystalline thin films on glass substrates using CBD by varying deposition time while keeping other parameters constant. Films deposited for 30 minutes exhibited optimal characteristics suitable for solar cell buffer layers, combining high optical transparency with good structural quality. Empirical models were also developed to quantitatively correlate deposition time with film properties.

Salem et al. (2024) fabricated Fe-doped CdZnS thin films using CBD and investigated their structural and optical behaviour. XRD analysis revealed nanocrystalline cubic structure, while EDS confirmed the incorporation of Fe ions at approximately 30% of total elemental content. SEM images showed a distinctive leafy and fibrous surface morphology. Optical analysis indicated both direct and indirect band gaps of 2.8 eV and 2.3 eV, respectively.

Shrivastava and Shrivastava (2025) reported the fabrication of CdZnS thin films using the chemical bath deposition technique under optimized experimental conditions. The deposited films exhibited good adhesion to microscopic glass substrates and were found to be thin, continuous, and uniform in thickness across the surface. Detailed characterization of the films was carried out using XRD, TEM, and EDAX. Both selected area electron diffraction (SAED) and XRD patterns were examined and compared to confirm the structural features of the films. TEM observations revealed a granular surface morphology with an average grain size of approximately 140 nm. The interplanar spacing values obtained from the SAED patterns were consistent with those determined from XRD analysis, thereby confirming the crystalline nature of the CdZnS thin films.

2.2 Spray Pyrolysis Technique:

Spray pyrolysis is a versatile and scalable thin-film deposition technique that involves the thermal decomposition of precursor solutions sprayed onto heated substrates. This method is particularly attractive for the fabrication of CdZnS thin films due to its ability to produce uniform coatings with good crystallinity, precise compositional control, and compatibility with large-area substrates. The relatively high substrate temperatures used in spray pyrolysis promote enhanced grain growth and improved structural quality, making it suitable for optoelectronic and photovoltaic applications where crystallinity and charge transport are critical. Rajathi et al. (2013) synthesized CdZnS thin films on mineral glass substrates by spray pyrolysis at different deposition temperatures using optimized coating conditions. The direct optical band gap values, estimated from transmittance measurements, ranged between 2.82 eV and 3.4 eV. Electrical measurements revealed a relatively low resistivity of approximately $50 \times 10^3 \Omega \cdot \text{cm}$ for films deposited at 450 °C. SEM images showed uniformly distributed surface features with densely packed fine grains, with grain sizes ranging from 100 nm to 350 nm.

Karadeniz et al. (2015) carried out a comparative study by depositing CdS, CdZnS, and CdSnS thin films on glass substrates using chemical spray pyrolysis under identical experimental conditions. The films were subsequently annealed at 400 °C for two hours. Morphological analysis revealed that CdSnS films exhibited nanoplate-like

structures, CdZnS films showed pinhole-rich surfaces, and CdS films were composed of nanosized grains. All films displayed hexagonal crystal structures, though with varying preferred orientations. Optical analysis demonstrated that the energy band gap varied depending on Zn or Sn incorporation.

Siouane et al. (2021) deposited $Cd_{0.5}Zn_{0.5}S$ thin films on glass substrates using spray pyrolysis and studied the effects of sulphide ion (S^{2-}) concentration on their properties. XRD analysis showed low polycrystallinity, with crystallite sizes ranging from 16 to 32 nm depending on S^{2-} concentration. SEM images revealed non-uniform nanostructured surfaces. Optical studies indicated that film transparency strongly depended on sulphide concentration in the precursor solution, while the optical band gap and refractive index varied inversely with S^{2-} concentration. Furthermore, a correlation between increased photoluminescence intensity associated with sulphur vacancies and reduced electrical resistivity confirmed the donor-like behaviour of sulphur vacancies.

Wang et al. (2023) investigated the deposition of $CdxZn_{1-x}S$ thin films on glass substrates using chemical bath deposition, focusing on the effects of low Cd^{2+} concentrations. By optimizing precursor concentration ratios through combined experimental and simulation approaches, films with enhanced homogeneity and density were obtained. SEM analysis showed optimal surface morphology at a Cd^{2+} concentration of 0.007 M. Optical characterization revealed high transmittance values approaching 90% in the 500–800 nm wavelength range, with tuneable band gap energies varying from 3.05 eV to 3.72 eV as Cd^{2+} concentration changed from 0.001 to 0.009 M.

Kariuki et al. (2026) presented a comprehensive review of several thin-film deposition methods, highlighting the key merits and limitations associated with each technique. It was found that film quality and optoelectronic properties such as band-gap tunability, optical transparency, and absorption strongly depend on the deposition method. Techniques like ALD provide excellent thickness control but suffer from high cost, slow processing, and toxic precursors. Spray pyrolysis and PVD enable large-area and high-quality films but require high temperatures and complex infrastructure. Spin coating offers morphological control but lacks scalability, while CVD produces uniform films at the expense of high processing temperatures and safety concerns. Among these methods, CBD stands out due to its low operating temperature, simple setup, and ability to produce uniform, high-quality thin films through parameter optimization. Its cost-effectiveness and scalability make CBD particularly suitable for industrial and photovoltaic applications, provided that chemical waste is properly managed.

2.3 SILAR Method:

SILAR method is a solution-based deposition technique that enables stepwise growth of thin films through alternate adsorption of cations and anions at the substrate surface. This technique offers excellent control over film thickness, composition, and nanostructure at relatively low processing temperatures, making it particularly suitable for fabricating multilayer and nanocrystalline semiconductor thin films. Due to its simplicity, low equipment requirement, and ability to tailor material properties through the number of deposition cycles, SILAR has been widely explored for CdZnS and related chalcogenide systems intended for photovoltaic and optoelectronic applications. Valkonen et al. (1997) demonstrated the growth of multilayer ZnS/CdS thin films using the SILAR technique. In the multilayer architecture, individual layers had nominal thicknesses in the range of 1–6 nm, while the total film thickness was controlled between 100 and 120 nm by varying the number of deposition cycles. XRD and SEM analyses confirmed the polycrystalline nature of the deposited films. The interfaces between individual CdS and ZnS layers were found to be diffuse rather than sharply defined, as thin intermediate $CdxZn_{1-x}S$ solid-solution regions formed at the interfaces. Post-deposition annealing promoted further interdiffusion between the layers, and after prolonged annealing at 300 °C for 50 hours, distinct CdS and ZnS diffraction peaks were no longer observable. SEM imaging indicated that layers with thicknesses of approximately 20 nm could still be distinguished as separate regions.

Laukaitis et al. (2000) reported the deposition of $CdxZn_{1-x}S$ thin films on GaAs substrates using the SILAR method from dilute aqueous precursor solutions. The study focused on examining the influence of composition and film thickness on crystallinity, refractive index, and surface morphology. The deposited films were polycrystalline with a predominantly cubic structure. An increase in both film thickness and cadmium content resulted in larger crystallite sizes and higher refractive index values. Stress analysis revealed that tensile stress dominated when the Cd concentration was relatively low ($x \leq 0.54$), whereas a transition to compressive residual stress occurred at higher Cd concentrations. The authors also established a clear relationship between growth mode and the evolution of residual stress within the films.

Agbo et al. (2016) synthesized zinc-doped cadmium sulphide thin films at room temperature using both SILAR and chemical bath deposition (CBD) techniques. The deposition bath consisted of cadmium sulphide as the Cd^{2+} source, zinc sulphate as the Zn^{2+} source, thiourea as the sulphur precursor, and ammonia as the complexing agent. The optical constants were evaluated using the Swanepoel method. The results indicated that both deposition technique and annealing temperature significantly affected the optical behaviour of the films, showing systematic and consistent trends.

Ashith and Rao (2018) prepared CdZnS thin films on glass substrates by the SILAR technique while varying the Cd/Zn composition. Crystallite sizes were estimated using the Williamson–Hall method, and variations in bond length were observed as a function of composition. Additionally, Urbach energy values were determined from optical absorbance data, providing insight into the degree of structural disorder and localized states within the films.

Muradov et al. (2020) fabricated $\text{Cd}_x\text{Zn}_{1-x}\text{S}/\text{PVA}$ nanocomposites by growing CdZnS nanoparticles within a polyvinyl alcohol (PVA) matrix using the SILAR technique based on cation sorption. The study investigated the influence of Cd^{2+} and Zn^{2+} concentrations, number of SILAR cycles, precursor sources, and reaction conditions on the formation mechanism and resulting properties. Comprehensive characterization was carried out using XRD, UV–visible spectroscopy, SEM, EDX, and optical microscopy. SEM analysis showed that particle size increased with the number of deposition cycles, with sizes ranging from 6.63–9.66 nm after two cycles and 8.89–22.7 nm after five cycles. Optical microscopy revealed non-uniform elemental distribution across the film thickness, attributed to differences in volume and surface energy. An increase in Cd^{2+} concentration led to larger particle sizes and a corresponding decrease in band gap energy, highlighting the strong dependence of optical properties on nanoparticle growth. These nanocomposite systems were identified as promising for applications in photovoltaics, solar cells, and optical markers.

Cabrera-German et al. (2023) provided a detailed chemical formulation and growth mechanism for SILAR-processed $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ thin films, demonstrating that copper concentration plays a critical role in determining optoelectronic behaviour. Through extensive chemical, structural, and optoelectronic characterization, including quantitative X-ray photoelectron spectroscopy, it was shown that films with low copper content consist of a mixture of ZnS, metastable $\text{Cu}_x\text{Zn}_{1-x}\text{S}$, and CuS phases. Evidence of a depth-dependent compositional gradient was observed, differing from the homogeneous films often reported in earlier studies. Analysis of copper and sulphur oxidation states suggested that film growth is governed by ionic exchange and diffusion processes. At higher copper concentrations, covellite CuS films formed on a ZnS seed layer. The study emphasized that precise control and analysis of depth-resolved compositional and structural characteristics are essential for optimizing conductivity and transparency in future device applications.

Gahramanli et al. (2025) reported synthesized of $\text{Cd}_{0.4}\text{Zn}_{0.6}\text{S}$ in the sonochemical route, using three different stabilizing agents—polyvinyl alcohol (PVA), 3-mercaptopropionic acid (3-MPA), and styrene—in order to examine the influence of stabilizers on the structural and optical properties of the nanoparticles. Parallel to this, the SILAR technique was used to fabricate $\text{Cd}_x\text{Zn}_{1-x}\text{S}/\text{PVA}$ nanocomposites with compositions of $x = 0.1, 0.2,$ and $1,$ along with $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$ nanocomposites synthesized at different temperatures ($25\text{ }^\circ\text{C}, 45\text{ }^\circ\text{C},$ and $65\text{ }^\circ\text{C}$) to study the effect of temperature on material properties. A comparative analysis of nanocomposites with identical stoichiometric compositions synthesized by both approaches revealed that ternary $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ compounds predominantly formed in the hexagonal phase, irrespective of the stabilizer type or particle size. However, in the case of binary compositions, a hexagonal phase was obtained through the SILAR process, whereas the sonochemical method favored the formation of a cubic phase. Significant variations in the optical band gap (E_g) were observed for $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ -based nanocomposites synthesized via the two different techniques. A red shift in the band gap was predominantly associated with the sonochemical approach, while a blue shift was more prominent in samples prepared using the SILAR method.

Overall, a comparative assessment of Chemical Bath Deposition (CBD), Spray Pyrolysis, and the SILAR method clearly demonstrates that each technique uniquely influences the growth behaviour and resulting properties of CdZnS thin films. CBD remains the most widely employed approach due to its low cost, effective control over composition and band gap, making it highly suitable for large-area photovoltaic applications, although excessive Zn incorporation may adversely affect crystallinity. Spray pyrolysis generally produces films with superior crystallinity and larger grain size as a result of elevated substrate temperatures, leading to improved electrical properties, but often at the expense of surface uniformity and substrate compatibility. In contrast, the SILAR technique offers exceptional control over film

thickness and composition at room temperature and is particularly effective for fabricating nanocrystalline structures; however, challenges related to film uniformity and large-scale scalability remain. Consequently, CBD is most suitable for photovoltaic device fabrication, spray pyrolysis is advantageous when high crystalline quality is required, and SILAR is ideal for controlled nanostructured film growth.

III. CDZNS THIN FILMS IN PHOTOVOLTAIC APPLICATIONS: A REVIEW

The continuous demand for high-efficiency and cost-effective photovoltaic devices has driven extensive research into wide band gap semiconductor materials that can function effectively as window and buffer layers. In this context, CdZnS thin films have gained considerable attention due to their tuneable band gap, high optical transparency, favourable band alignment with common absorber materials, and improved charge transport characteristics. By adjusting the Cd-to-Zn ratio, the optical and electronic properties of CdZnS thin films can be precisely engineered, enabling enhanced light transmission in the short-wavelength region and reduced parasitic absorption losses in solar cell structures. These attributes make CdZnS a promising alternative to conventional CdS window layers in various thin-film solar cell technologies, including CdTe, CIGS, and kesterite-based devices. Lee et al. (2003) synthesized $Cd_{1-x}Zn_xS$ thin films ($0 \leq x \leq 1$) using a co-evaporation technique involving CdS and ZnS sources. Their results showed that when the ZnS molar fraction remained below 0.85, the $Cd_{1-x}Zn_xS$ films crystallized in a hexagonal phase with the *c*-axis oriented perpendicular to the substrate surface. In contrast, films prepared with ZnS molar fractions greater than 0.85 exhibited a cubic zincblende crystal structure. A systematic reduction in lattice constant was observed with increasing Zn content, reflecting the smaller ionic radius of Zn compared to Cd. Optical studies revealed that the band gap could be tuned from 2.41 eV for pure CdS to 3.48 eV for ZnS-rich compositions. When incorporated into $Cd_{1-x}Zn_xS/CdTe$ solar cells, the open-circuit voltage increased with Zn concentration due to a reduced electron affinity mismatch between the $Cd_{1-x}Zn_xS$ window layer and the CdTe absorber, reaching a maximum value of approximately 830 mV at $x = 0.35$.

Dongre et al. (2015) investigated the structural, morphological, and optical properties of CdS and CdZnS thin films. XRD patterns confirmed that both films crystallized in the zincblende structure, with grain sizes calculated as approximately 6.2 nm and 8 nm using Scherrer's formula. Optical band gap values of 2.58 eV for CdS and 2.69 eV for CdZnS were obtained from UV-Vis measurements. Photoelectrochemical (PEC) studies were carried out using an n-CdZnS/(1 M NaOH + 1 M Na₂S + 1 M S)/C configuration, and photovoltaic output characteristics were analysed to determine the fill factor and solar energy conversion efficiency.

Xu et al. (2017) conducted a detailed numerical investigation of $Cd_{1-x}Zn_xS/CdTe$ solar cells, validating their model through experimental data and established theoretical principles. The influence of Zn composition and buffer layer thickness on key photovoltaic parameters was systematically analysed. Simulation results indicated that a $Cd_{0.4}Zn_{0.6}S$ buffer layer with an optimal thickness of 30 nm yielded the best device performance. The incorporation of $Cd_{1-x}Zn_xS$ enhanced absorption in the blue region of the solar spectrum, thereby improving CdTe solar cell efficiency. Further simulations revealed that efficiency increased sharply for Zn compositions in the range $x = 0.05-0.3$ and stabilized at higher Zn concentrations, with an optimal Zn content of approximately 0.6. The study also emphasized the importance of buffer layer thickness, as excessively thin layers led to pinhole formation, while thicker layers increased photon transmission paths and affected device performance.

Munna et al. (2021) employed a dilute CBD technique to fabricate CdZnS thin films on soda-lime glass substrates. XRD analysis of CdS films showed a prominent (002) diffraction peak corresponding to a wurtzite structure, which shifted upon Zn incorporation during CdZnS formation. Morphological studies demonstrated that the dilute CBD approach enabled uniform film coverage even at low Zn^{2+} concentrations. Optical characterization revealed that film transparency was strongly dependent on Zn^{2+} content, with band gap values increasing from 2.42 eV to 3.90 eV as Zn^{2+} concentration was varied from 0 to 0.0256 M. Electrical measurements indicated an increase in resistivity with higher Zn concentrations. Numerical simulations further suggested that a CdZnS buffer layer prepared with a Zn^{2+} concentration of 0.0032 M could serve as an efficient buffer material for CIGS solar cells.

Zhang et al. (2022) deposited CdZnS thin films with low Zn content using a chemical bath deposition technique. Optical absorption studies showed that the CdZnS films possessed a wider band gap than pure CdS, which was attributed to a possible upward shift of the conduction band minimum. These characteristics suggest that CdZnS thin

films are well suited for kesterite-based solar cell applications. Device-level studies on CZTSSe solar cells incorporating CdZnS buffer layers yielded a PCE of 8.5%.

Sultana and Zubair (2023) numerically analysed the performance of single-heterojunction solar cells employing CZTS and CZTSe absorber layers with ZnS buffer layers and SnO₂ as the transparent conducting oxide. The study evaluated device performance under various operating conditions and structural parameters. Maximum efficiencies of 20.68% and 22.86% were achieved for CZTSe and CZTS solar cells, respectively, with optimized absorber and buffer layer thicknesses under standard illumination. Increasing the irradiance to three times the standard value resulted in efficiency enhancements of 1% for CZTS and 5% for CZTSe devices. Additional improvements were obtained through front-surface texturing at 90°, leading to efficiency gains of 39% for CZTS and 6.6% for CZTSe cells. Under optimized conditions, the textured devices exhibited efficiencies of 25.59% and 21.52%. The proposed device architecture highlights a viable pathway toward the development of high-efficiency, cost-effective next-generation solar cells.

Borah et al. (2025) reported the fabrication of nanostructured Cd_{1-x}Zn_xS thin films under optimized growth conditions using the CBD technique at a bath temperature of 60 °C with a deposition time of 30 minutes. During the synthesis, the sulfur concentration was kept constant, while the cadmium and zinc contents were systematically adjusted by varying the compositional ratio of Cd (1-x) and Zn (x) over the full range from 0 to 1. XRD analysis revealed that the Cd_{1-x}Zn_xS thin films crystallized in a hexagonal phase, with prominent diffraction peaks corresponding to the (002) and (101) planes. FESEM observations confirmed the uniform formation of crack-free Cd_{1-x}Zn_xS films across all Cd and Zn compositions. Film thickness, determined from FESEM cross-sectional images, was found to range between approximately 136 and 816 nm. Optical studies showed that the band gap energy of the films could be tuned from 2.4 to 3.75 eV by adjusting the Cd/Zn ratio. Overall, the results highlight the suitability of Cd_{1-x}Zn_xS thin films as promising semiconductor materials for optoelectronic applications and as effective window layers in solar energy devices.

Overall, the reviewed studies clearly demonstrate that CdZnS thin films offer significant advantages as window and buffer layers in thin-film photovoltaic devices. The ability to tailor structural, optical, and electrical properties through compositional engineering, deposition technique selection, and post-deposition treatments enables optimization of band alignment, optical transparency, and charge transport. Experimental and numerical investigations consistently indicate that appropriate control of Zn content and film thickness can effectively reduce optical losses, enhance short-wavelength response, and improve overall device performance. Furthermore, the compatibility of CdZnS thin films with various absorber materials highlights their versatility in next-generation solar cell architectures. Despite the promising progress, continued efforts toward interface optimization, defect minimization, and scalable low-temperature fabrication are essential to fully realize the potential of CdZnS-based photovoltaic devices.

IV. CONCLUSION

The present review consolidates recent progress in the design and development of CdZnS thin films for solar cell applications, with a focus on synthesis techniques, structure-property relationships, and device integration. Solution-based deposition methods, particularly Chemical Bath Deposition, Spray Pyrolysis, and SILAR, have been shown to offer effective control over film composition, thickness, and optoelectronic properties, enabling tuneable band gaps and high optical transparency. Among these, CBD stands out as the most suitable technique for large-area photovoltaic applications due to its low processing temperature, compositional flexibility, and compatibility with industrial solar cell architectures. Spray Pyrolysis provides improved crystallinity and electrical properties at elevated temperatures, while the SILAR method enables precise thickness and nanostructure control at room temperature. The incorporation of Cd into ZnS and the formation of CdZnS alloys significantly enhance the optical and electronic properties required for efficient buffer and window layers, leading to improved light harvesting and device performance in CdTe, CIGS, and CZTS solar cells. Despite these advantages, challenges remain in achieving uniform crystallinity at high Zn concentrations, minimizing defect density, and ensuring environmental and process scalability. Future research should focus on optimized compositional engineering, advanced deposition strategies, interface optimization, and low-cadmium or cadmium-reduced systems to fully exploit the potential of CdZnS thin films in next-generation, high-efficiency solar cell technologies.

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