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RECENT ADVANCEMENTS IN CHEMICAL BATH DEPOSITED PRISTINE CdS THIN FILMS FOR PHOTOVOLTAIC APPLICATIONS

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Abstract

Cadmium sulfide (CdS) is (II–VI) group n-type semiconductor with appreciable physical and electronic properties. The wide band gap of about 2.42 eV, large absorption coefficient of 4×10^4 cm^{-1} and high mobility (440 cm^2 V^{-1} s^{-1}) make it applicable in photovoltaic energy conversion. Consequently, CdS is considered an excellent window material as well as a buffer layer for almost all chalcogenide thin film technologies, including copper zinc tin selenide (CZTSe), copper indium gallium selenide (CIGS) and CdTe-based solar cells. However, the defects present in the CdS thin films, such as inter-granular caves and pin holes, relaxation losses due to excess photon energy, and carrier recombination, can potentially affect the low light-to-current conversion efficiency with respect to the theoretical value of the above solar cells. Many studies have been carried out to produce CdS thin films with good optoelectronic properties suitable for photovoltaic applications. Among the numerous methods of depositing CdS, chemical bath deposition (CBD) stands out as a simple and low-cost method to prepare high-quality CdS thin films among those methods. However, the efficiency of resultant CBD-CdS thin films is strongly dependent on several parameters that should be very carefully adjusted: composition of the solution, especially sources, and concentration of sulfur and cadmium ions, pH and temperature of deposition bath, as well as the duration of the deposition on the morphology and quality of the CdS films. Additionally, doping, hydride methods, and surfactant-assisted deposition approaches are also performed to enhance the physical properties of the CdS. Regardless of the deposition technique, the post-deposited films' characterisation and deposition process optimisations are still an open subject. This review article describes the recent approaches to enhance the optoelectrical properties of the CBD CdS thin films and their recent advance in photovoltaic applications.

***Keywords*:** CBD, CdS, Chemical bath deposition, Photovoltaic, Thin film

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Introduction

Cadmium sulfide (CdS) thin films, especially those synthesised through chemical bath deposition (CBD), have drawn significant attention for their optimal band gap (~2.42 eV), superior optical properties, and straightforward fabrication process. In recent years, several techniques have been employed for the synthesis of CdS nanostructures, including aerosol-assisted chemical vapour deposition (AACVD), spray pyrolysis (Shaikh et al., 2019; Yadav et al., 2010); sputtering (Liang et al., 2013), and electrodeposition (Behar et al., 1999). Among these methods, CBD has garnered significant attention for its ability to produce uniform and pinhole-free thin films. Additionally, CBD is a favoured method for depositing high-quality, uniform CdS films with controlled thickness and composition due to its simplicity and cost-effectiveness. (Kumarage et al., 2016; Kumarage et al., 2016; Toma et al., 2021).

CdS thin films exhibit unique properties that make them highly suitable for a range of technological applications. In optoelectronics, CdS thin films are utilised in light-emitting diodes (LEDs) due to their superior luminescent properties (Hasanirokh et al., 2021). Furthermore, transparent semiconductive films are integral to touch screens and flat-panel displays, where transparency and conductivity are essential. CdS thin films find applications in photodetectors and sensors, where their wide bandgap and high electron mobility enable efficient detection of ultraviolet and visible light, as well as environmental pollutants and hazardous gases (Halge et al., 2021; An et al., 2021; Raj et al., 2020; Nawaz et al., 2021). CdS thin films are crucial in heterojunction solar cells, including cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) solar cells. In here, CdS thin films are employed as window layers in solar cells (Bouich et al., 2019). These thin layers exhibit transparency, thereby permitting the passage of light into the solar cell and simultaneously minimising reflection and absorption losses. The high optical transparency of CdS in the visible range ensures maximum light transmission to the absorber layer. At the same time, their wide bandgap minimises absorption losses, allowing most incident light to reach the absorber layer. Additionally, CdS is used as a buffer layer in many solar cells, including CdTe and copper zinc tin sulfide (CZTS) (Kumar et al., 2021), (Kauk-Kuusik et al., 2021), (Jena et al., 2024), (Hosen et al., 2023). These layers serve multiple essential purposes: they provide excellent interface passivation, reducing surface recombination and enhancing device efficiency by creating a smooth interface between the absorber and transparent conducting oxide (TCO) layers. CdS films also facilitate favourable band alignment with the absorber material due to their suitable bandgap (~2.42 eV), which aids in efficient charge carrier separation and collection. Furthermore, during the TCO layer deposition, the CdS buffer layer protects the absorber layer from potential damage (Wen et al., 2021; Leng et al., 2021; Ashok et al., 2020).

CdS thin films also contribute to the overall light-to-current conversion efficiency and stability of photovoltaic (PV) devices. Their excellent electrical properties, such as high carrier mobility and low resistivity, enhance charge carrier collection, reducing losses and improving the fill factor of the solar cell (Suazo et al., 2020; Qin et al., 2020; Nisika et al., 2020). Their thermal and chemical stability ensures that the performance of the solar cells is maintained under various environmental conditions. Furthermore, recent studies have focused on optimising and doping CdS thin films to enhance their optical and electrical properties for PV applications.

Chlorin, Zinc, Boron, and fluorine doping have improved carrier concentration, resistivity, conductivity, and transparency (Kumarage et al., 2020; Kumarage et al., 2018; Kumarage et al., 2018). The optimisation of deposition parameters, such as bath temperature and reactant concentration, has been critical in tailoring the structural, morphological, and optical properties of CdS films, with higher bath temperatures enhancing grain size and crystallinity (Rondiya et al., 2017; Kakhaki et al., 2016; A. Z. Shaikh et al., 2023). Additionally, innovative nanostructuring and surface engineering approaches have significantly improved the optoelectronic properties of CdS films (Dabhane et al., 2021; Rao et al., 2023; Hashim et al., 2023; Iqbal et al., 2019). Integrating CdS films with other semiconductor materials, such as CdS/ZnS bilayers, has shown improved efficiency and stability in solar cells (Hernández-Calderón et al., 2020; Abdalmageed et al., 2021; Castillo et al., 2017).

The advancements in chemical bath deposited CdS thin films over the past five years have been remarkable, driving forward the capabilities of photovoltaic technologies, from doping strategies and parameter optimisation to nanostructuring and material integration; these developments have collectively enhanced the performance and applicability of CdS thin films in solar cells (Hu et al., 2021; Chargui et al., 2023; Rahman et al., 2020). Fig. 1 (a) shows the number of worldwide publications in the last five years on CdS and Sri Lanka (Fig. 1 (b)). Accordingly, this review is focused on the recent advancement of the CBD CdS in their PV application.

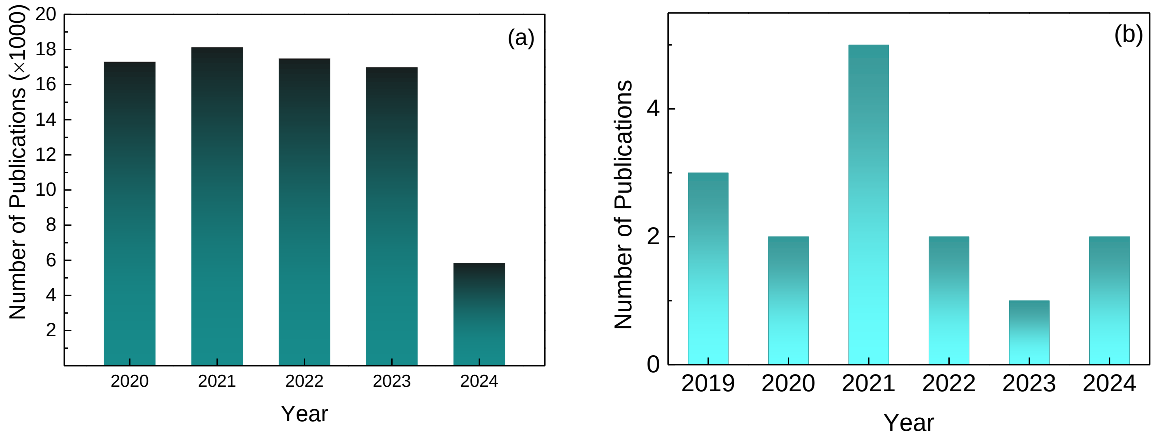

Figure 1: Number of Publications of CdS on PV Application, (a) Recent Five Years, (b) Sri Lanka (Source: Web of Science).

Due to their excellent characteristics for optoelectronic applications, CdS thin films produced via chemical bath deposition CBD have gained demand. Numerous research studies have been conducted to optimise these qualities and increase the efficiency of solar devices. However, there is still a need for a deeper understanding of how the deposition process parameters affect the performance of CdS films.

The article begins by providing an overview of CdS and introducing its essential properties. It then discusses how deposition parameters have been improved, explaining the changes made. After that, it examines how these improvements affect the properties of CdS itself, detailing any enhancements observed. Following this, the article explores how these advancements in CdS impact its usefulness in PV applications, describing the connection between the two. Lastly, it looks ahead to future directions for research on CBD-CdS, discussing potential focus areas. The article concludes by summarising the main points discussed.

Overview CdS

CdS is a compound semiconductor with a zinc blende (zb) crystal structure featuring a lattice composed of cadmium (Cd) and sulfur (S) atoms. In its crystalline form, CdS exhibits a cubic crystal structure with a lattice constant of approximately 0.56 nm. The bonding within CdS is predominantly ionic, with each cadmium atom surrounded by four sulfur atoms in a tetrahedral arrangement and each sulfur atom coordinated with four cadmium atoms (Fig. 2).

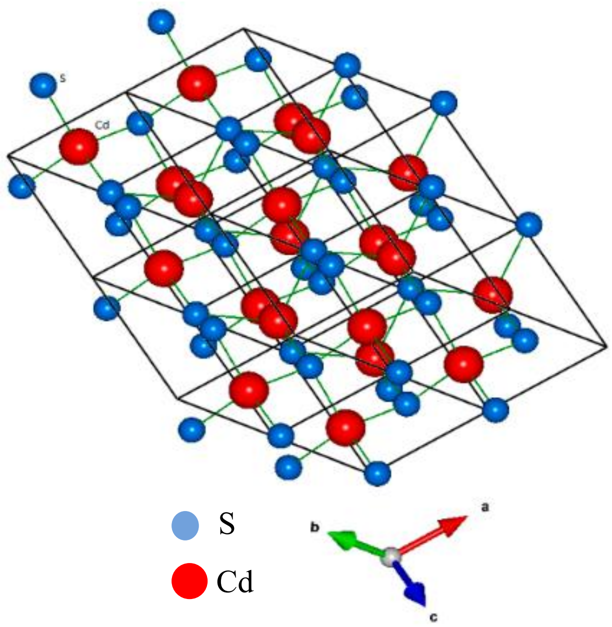

Figure 2: Zinc Blende Crystal Structure of CdS. Reprinted with the permission of (Güler & Güler, 2017).

From a theoretical perspective, the electronic structure of CdS is governed by its band structure, which determines its optical and electrical properties. The band structure of CdS consists of a valence band (VB) and a conduction band (CB), separated by an energy band gap (E_g). The valence band primarily comprises 3p orbitals of sulfur atoms, while the conduction band is formed by the 5s and 5p orbitals of cadmium atoms. The band gap of CdS, approximately 2.42 eV at room temperature, corresponds to the energy required to promote an electron from the valence band to the conduction band (Fig. 3) (Edossa et al., 2020). This optimal band gap makes CdS suitable for various optoelectronic applications.

After establishing the relevance of CBD-CdS thin films in photovoltaic applications, the next part discusses new studies on how differences in deposition parameters affect the structural, optical, electrical, and morphological aspects of CdS thin films. This detailed review emphasises the role of these elements in improving the performance of optoelectronic devices.

Results and Discussion

The structural, optical, electrical, and morphological features of CdS thin films play a critical role in determining their PV performance (Mohammed et al., 2020; Rahman et al., 2020; Kamble et al., 2020). The structural properties, precisely crystallographic orientation and grain size, are critical determinants of charge carrier dynamics. Enhanced crystallinity and larger grain sizes help reduce recombination at grain boundaries, improving charge collection and enhancing solar cells' overall efficiency. CdS's optical properties, notably its wide bandgap (~2.42 eV), are optimal for functioning as a transparent window layer in PV systems, facilitating maximum light transmission while minimising absorption losses. This characteristic allows more light to reach the absorber layer, boosting light-to-current conversion efficiency. In addition, the morphological features, including film smoothness and uniformity, enhance the interface quality between the CdS layer and the absorber, minimising leakage currents and contributing to improved stability and performance of PV devices (Kumar et al., 2020; Vakaliuk et al., 2022). Together, these properties underscore the importance of optimising CdS thin films for solar technology advancements.

However, it is important to note that the optical and electrical properties of CBD-CdS thin films are highly sensitive to the conditions under which they are grown. Parameters such as bath composition, temperature, and deposition duration critically influence the morphological and structural properties of CdS films (Sinha et al., 2019; Ashok et al., 2020; Chol et al., 2021). This, in turn, affects their optoelectrical characteristics. For instance, modifications in growth parameters can lead to crystallinity, grain size, and smoothness variations, which directly impact charge carrier mobility and optical transparency. Therefore, a comprehensive understanding of the relationship between these growth conditions and the resulting structural, optical, morphological, and electrical properties is essential for achieving the desired performance in CdS thin films, particularly for their application in optoelectronic and PV devices.

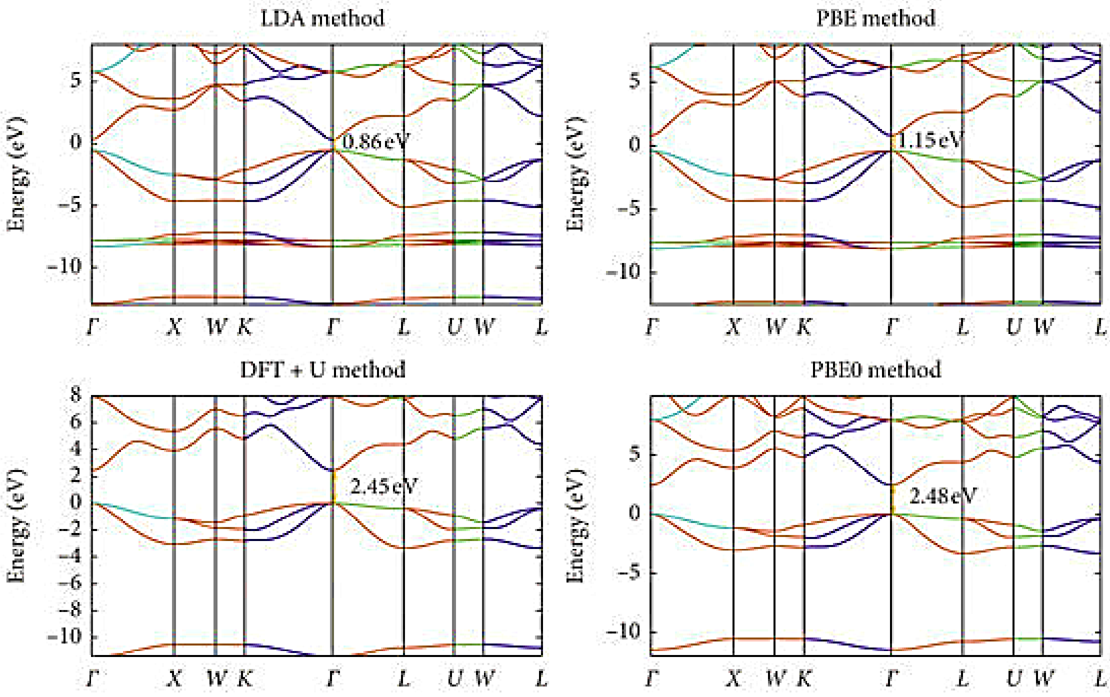

Figure 3: Band Structure of (a) zb-CdS Structure and (b) wz-CdS Structure along High Symmetry Points with Respect to LDA, PBE, PBE + U, and PBE0 Approximations. Reprinted with the permission of (Edossa et al., 2020).

Structural Properties

CBD-CdS thin films exhibit a distinctive structural composition, manifesting cubic phase orientations in the (111), (200), and (220) planes, complemented by reflection peaks corresponding to hexagonal CdS (100), (002), and (102) planes. This dual-phase characteristic signifies their polycrystalline nature, comprising a blend of hexagonal and cubic grains (Kumarage et al., 2016). Recent studies show CBD-CdS films predominantly adopt a hexagonal structure with a preferred orientation along the (002) direction when increasing the bath temperatures with a consistent deposition time (Fig. 4 (a, b)) (Ouachtari et al., 2011). This preferential growth is ascribed to heightened crystallinity facilitated by enhanced reactant decomposition and ion production. Moreover, studies by El-Shaer et al. (El-Shaer et al., 2023), Mohammad et al. (Mohammed et al., 2014), and Hariech et al. (Hariech et al., 2022) report an increment in the intensity of the dominant peak with prolonged deposition durations, correlating with larger crystallite sizes. However, prolonged deposition exceeding 75 minutes at 55 °C has also been linked to the emergence of a CdO phase peak at 15.07° in the X-ray diffractogram (XRD) patterns (Hariech et al., 2022).

Furthermore, the concentration of Cd^{2+} in the solution plays a crucial role in film formation. XRD patterns of CdS thin films exhibit a preferred orientation along the (002) plane, with the sharpest peak observed at 0.006 mol L^{-1}, indicating hexagonal structure and enhanced CdS crystal growth at this concentration (De Fang et al., 2013). Beyond this concentration, increased Cd^{2+} levels lead to more acute ion-ion reactions, promoting homogeneous CdS particle formation while inhibiting complexation and reducing precursor availability for film growth.

The pH value of the reaction solution also significantly impacts film growth dynamics. Studies have shown that films display cubic phases with significant peaks at 26.7° and 44.2°, respectively, across different pH values (Zhang et al., 2018). While pH does not alter the crystal structure significantly, lower pH values enhance peak intensities, which is attributed to thicker CdS films formed under acidic conditions. High-resolution transmission electron microscope (TEM) images further reveal nanocrystalline structures with grain sizes ranging from 8 to 15 nm, indicating the composition of nanocrystals.

Annealing temperature emerges as another critical determinant of the structural evolution of CdS thin films. For instance, the CdS films have demonstrated prominent peaks corresponding to hexagonal (110) and (202) planes when annealed at a temperature of 374 K (Ouachtari et al., 2011). However, the coexistence of hexagonal (002) and cubic (111) planes at the annealing temperature between 473 and 573 K and exclusive peaks associated with hexagonal CdS planes when temperatures exceed 673 K. Consequently, the dominance of the hexagonal structure under higher annealing temperature is suggested. Additionally, several studies have reported the increment in grain sizes from 45 to 55 nm with rising annealing temperatures (Fekri & Eshghi et al., 2021; Zhan et al., 2015).

Additionally, deposition and annealing environments have influenced the structural properties of CBD-CdS (Diaz-Grijalva et al., 2019; Ashok et al., 2020). For instance, Sankalpa et al. illustrate the detrimental impact of N_2 purging during both deposition and annealing stages on crystallite size, highlighting the environmental sensitivity of CdS thin film growth (Fig. 4 (c)) (Sankalpa et al., 2024). Meanwhile, the effect of the annealing duration on grain growth has been extensively discussed by Enríquez et al. (Enriquez et al., 2013; Metin et al., 2010).
Accordingly, the annealing process initiates grain growth within the first 15 minutes, followed by a reduction between 15 and 30 minutes and a slight subsequent increase beyond 30 minutes. Furthermore, grain size evolution is intricately linked to annealing temperature and duration, influenced by recrystallisation dynamics and material loss during post-deposition treatment. Lower annealing temperatures promote recrystallisation, whereas higher temperatures lead to substantial material loss. Apart from the annealing and bath temperature, recent studies have explored several other parameters that influence the crystal orientation and overall quality of CBD-CdS. For instance, comparative investigations using magnetic and oscillating agitation methods reveal distinct outcomes in terms of crystallographic orientation. Oscillating agitation consistently enhances the predominant (111) diffraction peak, characteristic of a wurtzite-type cubic structure, with supplementary peaks such as (220) and (311) confirming the crystal phase integrity (Tec-Yam et al., 2011).

Moreover, substrate positioning within the reaction beaker has become a pivotal parameter affecting CdS film crystallinity. Horizontal and inclined positions tend to trap colloidal precipitates, potentially compromising crystal orientation (Tec-Yam et al., 2011). Experimental findings further illustrate that substrate location influences crystallite size, as evidenced by larger dimensions observed when the Fluorine doped tin oxide (FTO) glass side faces downward, contrasting with varying sizes observed using the Williamson and Hall (W-H) method across different positions (Kumarasinghe et al., 2017). Additionally, the thickness uniformity of CdS samples correlates with their placement within the reaction beaker, with films positioned at the bottom exhibiting greater thickness than those near the top. Moreover, substrate rotation techniques demonstrate a practical approach to achieving uniform, transparent, and adherent CdS films. Film thickness increases linearly with rotation speed at 150, 300, and 450 rpm, although speeds exceeding 600 rpm may interrupt the growth process due to material detachment (Zhang et al., 2018). These insights underscore the intricate interplay between deposition techniques, substrate positioning, and resultant CdS thin film properties, offering valuable considerations for optimising film quality in practical applications.

Optical Properties

Enhancing the optical properties of CdS is crucial for advancing PV technology. CdS thin films, with a favourable bandgap of approximately 2.4 eV, are integral to thin-film solar cells, enabling efficient light absorption aligned with the solar spectrum. Improving these films' transparency, crystallinity, and bandgap engineering can significantly enhance photon capture and electron extraction efficiencies in PV devices. (Kumarage et al., 2016).

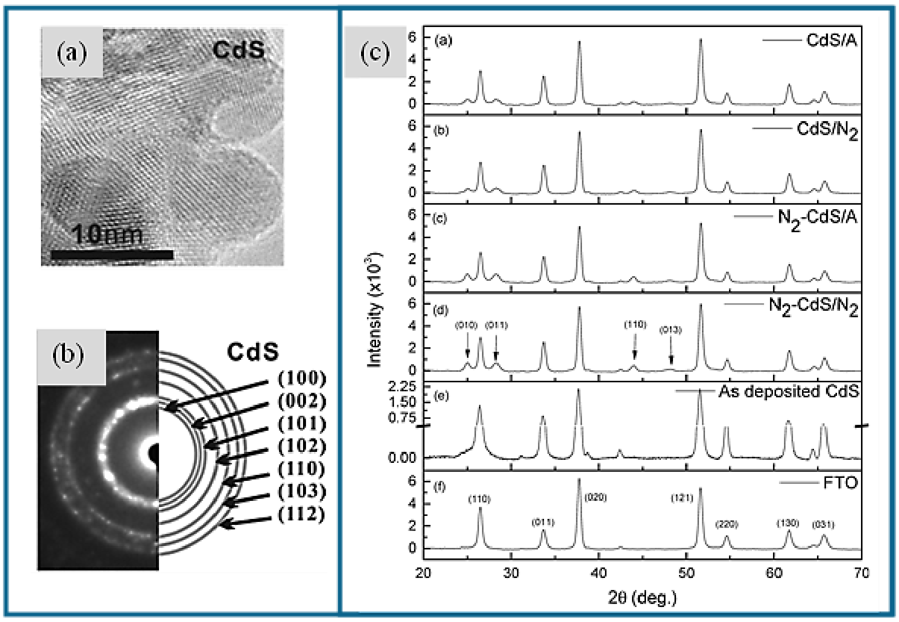

Figure 4: (a) HR-TEM, (b) Selected Area Diffraction (SAED), (c) XRD diffractogram of the Pure CdS and reprinted with the permission of (Zhao et al., 2017; Sankalpa et al., 2024).

For instance, Zhou and coworkers have investigated that the highest transmittance, peaking above 500 nm and exceeding 65% at wavelengths over 600 nm, occurs at a bath temperature of 40 °C (Zhou et al., 2013). Also, the transmittance rapidly increases with wavelength up to a maximum point, after which it decreases. Additionally, the CdS thin films deposited at 40 °C exhibit the highest E_g of 2.57 eV, indicative of wider optical bandgaps, whereas films deposited at 60 °C show the lowest E_g value of 2.27 eV (Fig. 5). The adjustment of deposition temperature influences E_g values, attributed to thermal effects affecting ion dispersion mechanisms. Lower temperatures favour ion-by-ion growth, whereas higher temperatures promote cluster-by-cluster formation, resulting in thicker films due to cluster-wise aggregation (L. Zhou et al., 2013). The ion-by-ion mechanism is less thermally activated than the cluster-by-cluster mechanism. The cluster-by-cluster mechanism results in higher film thickness due to cluster-wise aggregation compared to ion-by-ion mechanisms (Kumarage et al., 2016). The deposition kinetics are governed by ion mobility in the solution, increasing with temperature.

The variation in E_g values is attributed to sample thickness, with similar thicknesses deposited at 40 and 80 °C. This variation is crucial in manufacturing CdS-based PV devices, as it governs the photoactive properties of PV materials (Kumarage et al., 2016; Maghouli & Eshghi, 2019). However, as deposition time increases, the transmission spectra decrease due to crystallite size variations and structural defects. This can lead to more light-scattering events. As well as the deposition time increases, the band gap of the layers gradually increases while the corresponding band tails decrease (Maghouli & Eshghi, 2019).

The annealing temperature significantly influences the optical evolution of CdS thin films (Enríquez et al., 2013). The films in optimal conditions are highly transparent, with less light scattering (Ouachtari et al., 2011). It realises that the average transmittance of CdS thin films increases with the annealing temperature to reach the maximum value and decreases at the annealing temperature of 450 °C. Moreover, the average transmittance increases with the annealing duration. On the other hand, the absorption increases with the annealing temperature between wavelength 300 to 500 nm (Ouachtari et al., 2011). The annealing process led to a decrease in defect density, improving the average transmittance compared to as-deposited CdS thin films. Filling voids in CdS thin films leads to denser films and reduced energy gaps, primarily because sulfur tends to leave the film at annealing temperatures above 375 °C. At annealing temperatures exceeding 400 °C, oxidation may occur due to water adsorption from the bath solution (Metin & Esen, 2003). The band gap variation with respect to annealing conditions shows a decrease in band gap from the as-deposited state up to 350 °C, followed by an increase as temperatures reach 400 °C.

Additionally, the band gap decreases with an annealing time of up to 30 minutes, then increases with further annealing, assuming a constant temperature. However, it is crucial to note that material loss becomes a significant factor at higher temperatures or longer annealing durations. (Enríquez, 2013). Optical transmittance spectra of CdS thin films have been applied with different pH and Cd^{2+} concentrations (De Fang et al., 2013). According to Zhang et al., high transmittance over 81% in the long wavelength range can be achieved at a pH of 11.9 (Zhang et al., 2018). However, the E_g values decreased with increasing pH (11.7 - 11.9) values, ranging from 2.42 - 2.31 eV, possibly due to grain size variation. The film's transmittance increases rapidly with wavelengths less than 550 nm but becomes gentle as wavelengths increase. The film's transmittance decreases when wavelengths are less than 500 nm, meeting the requirement of CdS thin film as a window layer and improving solar cell efficiency (Zhou et al., 2012).

Additionally, magnetic agitation produces more compact films with minor time, possibly due to mechanical energy infringement, while oscillating agitation moves the solution slowly and locally (Tec-Yam et al., 2011). The higher transmittance value occurs at the bottom when the substrate is in the rack system. The absorption above the wavelength of 500 nm indicates good crystalline quality. Additionally, stirring speed significantly impacts the thickness and optical properties of CdS films. Meanwhile, the influence of rotation velocity (150, 300, 450, and 600 rpm) was investigated during the chemical deposition of CdS films at 75 °C (Oliva-Avilés et al., 2010). The results indicate that while the variation in rotation speed had no significant effect on the band gap energy or surface roughness, it did lead to a linear increase in the deposition rate. Furthermore, stoichiometry was notably affected, with higher rotation speeds producing a more favourable Cd/S ratio of 1:1. These findings suggest that optimising rotation speed could enhance deposition efficiency and improve the scalability of CdTe/CdS solar cell production for industrial applications.

Meanwhile, Kong and coworkers reported a redshift in the optical absorption spectra due to particle size and quantum confinement effect (Kong et al., 2013). The optical properties of CBD-CdS thin films, such as transmittance and band gap, change with the NH_3 concentration in the solution (Zhao et al., 2012; Xue et al., 2015; Jaber et al., 2012).

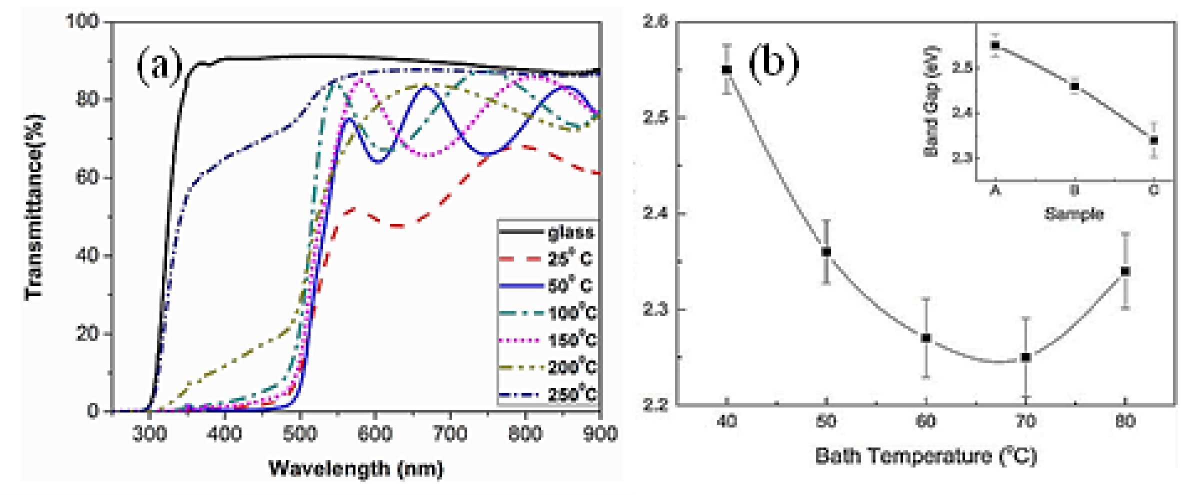

Figure 5: Variation of (a) Optical transmittance, (b) Band gap of CBD-CdS. Reprinted with the permission of (Memarian et al., 2017; Kumarage et al., 2016).

Electrical Properties

The electrical properties of CBD-CdS thin films exhibit significant variation with changes in annealing temperature, primarily driven by phase transitions, grain size alterations, and the evaporation of sulfur and cadmium (Quiñonez-Urias et al., 2014). These factors significantly influence film stoichiometry, leading to voids, dislocations, imperfections, and oxidation at elevated temperatures (Enríquez et al., 2013). A detailed study by Metin et al. (2010) demonstrated that electrical conductivity increases with rising annealing temperatures. This enhancement is attributed to reduced lattice defects, which scatter electrons at grain boundaries. With fewer defects, the Arrhenius-type conductivity increases, peaking at 423 K and decreasing at 723 K due to grain contact discontinuities.

Further studies have reported higher open-circuit voltage (V_{OC}) values for CdS films in photoelectrochemical cells (PEC) when annealed at 373 K (Mustafa et al., 2012). Sankalpa and colleagues (2024) highlighted significant advancements in the PEC performance of CdS films (Sankalpa et al., 2024). Their experiments revealed substantial improvements in short-circuit current (I_{SC}) and V_{OC} for films subjected to nitrogen (N_2) purging and annealing. Films annealed at 300 °C achieved the highest I_{SC}, V_{OC}, and flat-band voltage (V_{FB}) values, measuring 55 μA, 0.475 V, and −675 mV, respectively. These improvements are attributed to a well-packed structure, increased interconnectivity, and an elevated sulfur-to-cadmium ratio of 0.76.

Post-deposition activation using a saturated $CdCl_2$ bath via dip coating has been shown to enhance the electrical properties of CdS thin films (Dharmadasa, 2014; Shah et al., 2017; Z-b et al., 2019; Wang et al., 2015). Improved electrical properties are due to structural changes caused by the treatment, as Kumarage et al. (2020) demonstrated. The presence of Cl^- as a fluxing agent supports grain growth, reducing grain boundaries and charge carrier scattering. However, the toxicity of $CdCl_2$ raises environmental concerns, prompting the exploration of $MgCl_2$ as an eco-friendly alternative (Mis-Fernández et al., 2017). $MgCl_2$ treatment enhances PEC cell performance by increasing carrier concentration, improving the effective surface area, and providing grain boundary passivation (Kumarage et al., 2018).

Bath temperature significantly influences the electrical properties of CBD-CdS thin films by altering crystallisation dynamics and film morphology (Dissanayake et al., 2024; Smairi et al., 2022; Kumarage et al., 2016). Elevated bath temperatures increase the rate of reactant decomposition, promoting improved crystallinity and larger grain sizes, which facilitate enhanced electron mobility (Rondiya et al., 2017). However, excessively high temperatures can cause phase instability and secondary phase emergence, such as CdO, adversely affecting conductivity. Optimal bath temperatures around 75 °C strike a balance between crystallinity and structural integrity, maximising electrical performance. The V_{OC} and I_{SC} values vary with bath temperature, with smaller clusters leading to lower ISC values due to diminished light absorption and charge carrier generation. In comparison, larger clusters at higher temperatures enhance I_{SC} values.

The sheet resistance of CBD-CdS thin films increases with deposition time, with higher conductance occurring at lower deposition times at a bath temperature of 90 °C (Maghouli & Eshghi, 2019). The initial formation of CdS thin films involves discontinuous voids, which affect solar cell performance by decreasing shunt resistance. These voids disappear after 30 minutes, forming compact, continuous films through incubation and saturation stages (Chol et al., 2021). Additionally, pH buffer affects the electrical properties of CBD-CdS thin films by varying thickness, with resistivity tending to increase with pH (Zhou et al., 2012).

Treatments with Ethylenediaminetetraacetic acid (EDTA) and Triton X-100 (TX-100) have also impacted the electrical properties of CBD-CdS thin films, enhancing V_{OC}, I_{SC} values, and effective surface area at lower concentrations (Kumarage et al., 2017; Adikaram et al., 2019). This indicates a greater exposure area to semiconductors or electrolytes, leading to higher I_{SC} values.

Morphological Properties

Annealing temperature plays a crucial role in determining the morphological properties of CdS thin films produced by CBD. Studies have shown that CdS films effectively cover substrates without voids, pinholes, or cracks across a range of annealing temperatures. However, at 823 K, the film's morphology disappears, indicating a coarsening effect, a phenomenon not observed at lower temperatures (Metin et al., 2010). This suggests that higher annealing temperatures may enhance certain properties but can also lead to structural deterioration.

Before annealing, the particle size of CdS thin films is generally smaller compared to post-annealing (Zhou et al., 2013). This increase in particle size with annealing indicates grain growth, which can improve the film's crystallinity and reduce defect density. Annealing under a nitrogen atmosphere explicitly affects the composition of CdS deposits, transitioning from $Cd_{0.6}S_{0.4}$ to $Cd_{0.55}$S0.45 as the temperature reaches 250 °C. This compositional change highlights the sensitivity of CdS to annealing conditions, which can alter its stoichiometry and potentially its optoelectronic properties.

Research has demonstrated that CdS thin films exhibit a granular microstructure at an annealing temperature of 100 °C, with a surface chemical composition of 45.48% cadmium and 54.52% sulfur (Quiñonez-Urias et al., 2014). Additionally, in the same study, it has been revealed that annealing under a nitrogen atmosphere explicitly affects the composition of CdS deposits, transitioning from Cd0.6S0.4 to Cd0.55S0.45 as the temperature reaches 250 °C. This compositional change highlights the sensitivity of CdS to annealing conditions, which can alter its stoichiometry and potentially its optoelectronic properties.

A significant transformation in the crystalline structure of CdS nanofilm occurs when subjected to air-$CdCl_2$-annealing compared to simple air annealing (Kong et al., 2013). $CdCl_2$ acts as a catalyst, promoting enhanced grain growth and densification, resulting in a densely packed structure characterised by large polyhedron grains. This modification can significantly influence the film's electronic and optical properties, enhancing the performance of CdS-based devices.

The growth rate of CdS thin films is positively correlated with bath temperature, enhancing film density (Zhou et al., 2013). Additionally, it is important to note that the deposition rate is influenced by temperature and the addition of complexing agents, which play a significant role. However, higher bath temperatures (> 80 °C) can lead to the formation of coarser surface grains and decreased uniformity due to the reduced complexing ability of the agent at higher temperatures, which accelerates reaction rates. Consequently, this can result in surface roughness, making achieving high-quality CdS thin films challenging. Additionally, the potential of growing CdS nanostructures by altering the deposition duration has been reported (El-Shaer et al., 2023).

The optimising bath temperature is critical for ensuring dense, uniform, and smooth CdS thin films, which are essential for superior performance in practical applications. Different cluster sizes result in films with varying practical surface areas, leading to higher I_{SC} values due to increased effective surface area (Kumarage et al., 2016). Surface roughness decreases with increasing bath temperature, enhancing film quality (Sinha & Khare, 2020). Atomic Force Microscopy (AFM) images reveal significant microstructural changes based on bath temperature, with notable pinholes appearing at 65 °C, adversely affecting electronic characteristics. Moreover, longer deposition times lead to more uniform and crack-free surfaces (Maghouli & Eshghi, 2019). Optimised deposition times result in high-quality CdS films, with uniformity influenced by stirrer speed during deposition. Furthermore, desorption of NH_3 is critical for achieving uniform films (Wenyi et al., 2005; Zhang et al., 2018).

Based on these findings, it is evident that optimising deposition parameters plays a critical role in determining the quality and efficiency of CBD-CdS thin films. The concluding section will summarise the key insights gained from this study and outline potential future research directions to improve the performance of CdS-based photovoltaic applications further.

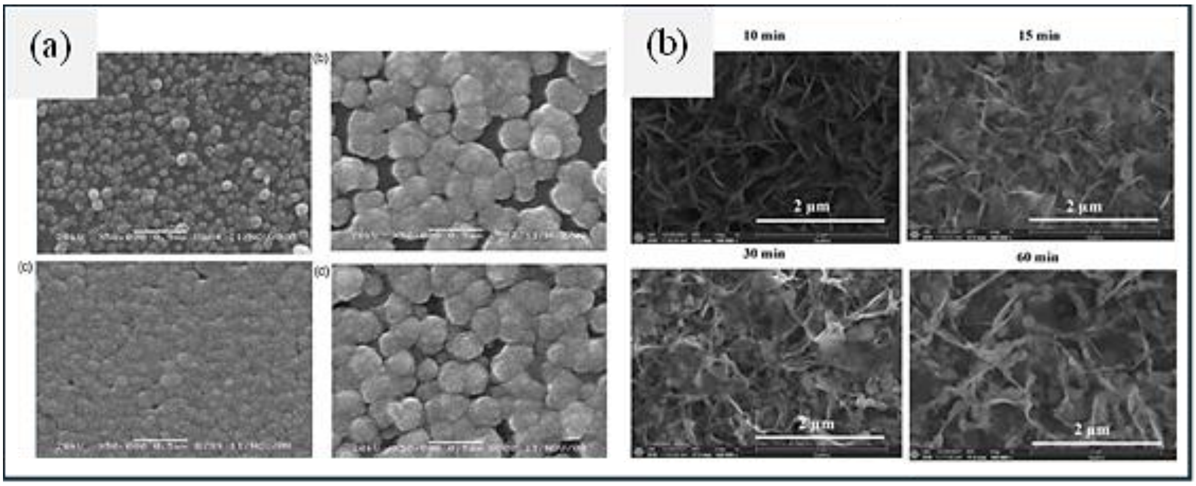

Fig. 6. (a) SEM Images for CBD-CdS Thin Films with Different Bath Temperatures; (b) formation nanostructures based on deposition duration. Reprinted with the permission of (Usoviene et al., 2023; El-Shaer et al., 2023)

Future Direction and Conclusion

Due to its unique properties, CdS remains a focal point in optoelectronic research. Despite extensive efforts employing various techniques such as doping, hybrid deposition approaches, post-deposition chlorine treatment, and surfactant-assisted deposition, CdS remains predominantly polycrystalline. This limitation underscores the need to investigate methods for enhancing the crystallinity of CdS, as higher crystallinity could significantly improve its optoelectrical performance.

An increased surface area is another crucial factor for improving CdS's electrical properties. A larger surface area can boost the electronic interface interface, enhancing the material's overall electrical performance. Additionally, optimising the optical band gap and engineering the Fermi level of CdS can further enhance its optoelectrical properties.

Recent advancements in nanostructures, including one-dimensional (1D) forms such as nanowires and nanorods, two-dimensional (2D) forms like nanosheets and nanoflakes, and zero-dimensional (0D) nanostructures, have shown considerable promise. These nanostructures exhibit high aspect ratios, surface-area-to-volume ratios, crystallinity, thermal stability, carrier charge transport, and chemical stability. Such attributes are critical for applications in solar cells and other optoelectronic devices.

Integrating nanostructures within thin films to create heterostructures with diverse morphologies offers a promising strategy for improving CdS's optoelectronic properties. The unique properties of nanostructures can address many challenges faced in enhancing CdS-based devices. For instance, the high surface-area-to-volume ratio of nanostructures can facilitate better light absorption and carrier transport, which is essential for efficient solar cells.

Moreover, high crystallinity in nanostructures can reduce grain boundaries, which typically act as recombination centres for charge carriers, thus enhancing the efficiency of optoelectronic devices. The high thermal and chemical stability of nanostructures ensures the material can withstand the demanding conditions often encountered during device fabrication and operation.

Engineering the optical band gap and the Fermi level of CdS through nanostructures can substantially improve optoelectrical properties. Tailoring the band gap optimises the absorption spectrum of CdS to match the solar spectrum better, thereby increasing solar cell efficiency. Similarly, engineering the Fermi level can improve the alignment of energy levels at interfaces, enhancing charge transfer and reducing losses.

This review also examines the synthesis of CdS via CBD, a technique notable for its simplicity and cost-effectiveness in preparing high-quality CdS thin films. The primary attributes affecting thin film performance are thickness and grain size, which influence conductance and grain-boundary resistance. Two growth mechanisms are identified: ion-by-ion at lower temperatures and cluster-by-cluster at higher temperatures. By controlling these processes, CdS thin films can achieve lower sheet resistance. Additionally, annealing at temperatures above 375°C reduces the optical band gap by reorganising the CdS film, making it more ordered and removing absorbed water and sulfur.

Critical factors in achieving uniform CdS films include the pH value and the cadmium-to-sulfur ratio in the deposition bath. Surface treatments such as EDTA and Triton X-100 can enhance the band gap, morphology, and Fermi-level engineering. Post-deposition chlorine treatment also improves CdS's physical properties through electrical passivation and enhancing electron states at grain boundaries.

This review concludes by presenting future trends in CdS thin film research, offering guidelines for novel approaches to enhance the optical, electrical, morphological, and structural properties of CdS. These insights aim to assist researchers in developing more efficient CdS-based optoelectronic devices.

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