

Effects of Chloride Doping on Optical Absorption in Spray-Pyrolyzed CdS Thin Films

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ABSTRACT

Cadmium sulfide (CdS) thin films, vital window layers in optoelectronic devices like solar cells, face performance challenges from chloride impurities introduced via common spray pyrolysis precursors. This study investigates these impurities' effects on absorption properties by depositing undoped and chloride-doped CdS films on glass substrates at 303 K, 333 K, and 363 K using cadmium nitrate tetrahydrate and thiourea precursors. UV-Vis spectrophotometry revealed chloride-doped films exhibiting peak UV absorbance of 1.96 at 303 K surpassing undoped films' maximum of 1.90 at 333 K with progressive decrease across wavelengths (285-500 nm), indicating defect-mediated enhancements. SEM analysis confirmed superior compact, crack-free morphologies with uniform grains and reduced pinholes in 363 K doped films versus undoped counterparts. These findings demonstrate controlled chloride doping maximizes absorption and microstructural integrity, providing key insights for impurity-tailored deposition to elevate photovoltaic efficiency.

Keywords:

Cadmium Films,
Chloride Impurities,
Absorption Edge,
Spray Pyrolysis.

INTRODUCTION

The escalating global energy demand and finite nature of fossil fuels have accelerated the development of renewable sources like solar energy, which photovoltaic devices convert into electricity with high efficiency (Christian *et al.*, 2023). Cadmium sulfide (CdS), an n-type II-VI semiconductor with a direct bandgap of ~2.42 eV at room temperature, excels in optoelectronic applications such as solar cells, photodetectors, and sensors due to its high photosensitivity and stability (Korotcenkov, 2023). As a window layer in CdTe and Cu(In,Ga)Se₂ solar cells, CdS thin films' optical properties including absorbance, refractive index, and bandgap critically influence device performance (Powalla *et al.*, 2018, Nworie *et al.*, 2024). Among all thin film deposition techniques, Spray pyrolysis offers a simple, cost-effective, scalable method for depositing uniform, large-area CdS films with controllable thickness and doping through precursor solutions (Ishiwu *et al.*, 2024). Studies confirm these films typically exhibit polycrystalline hexagonal structures, n-type conductivity, and bandgaps of 2.4–2.5 eV. Yadav *et al.* (2010) reported optimal properties at 300°C substrate temperature,

including a 2.44 eV bandgap and low resistivity. Yadav & Masumdar (2011) achieved photovoltaic efficiency of 0.17% under similar conditions. Acosta *et al.* (2004) observed temperature-dependent orientations and bandgap shifts in indium-doped films. Abouelkhir *et al.* (2024), Faraj *et al.* (2017), and Yuksel *et al.* (2013) further demonstrated tunable crystallite size, morphology, and optoelectronic performance across deposition parameters. Alam *et al.* (2022) highlighted CdS's suitability through structural and compositional analyses.

In this study, CdS thin films were intentionally doped with chloride ions using common precursors in spray pyrolysis to systematically investigate how the impurity could affect absorption properties through defect states, lattice distortions, or stoichiometry shifts, which could degrade optoelectronic device performance.

MATERIALS AND METHODS

Spray pyrolysis was used in the preparation of the cadmium sulfide (CdS) thin films. 0.274 g of Cadmium nitrate tetrahydrate was dissolved in 100 mL of distilled water to form the cadmium ion solution, while 1.22 g of thiourea was dissolved separately in 100 mL of distilled

water to serve as the sulfur source. These aqueous solutions were mixed and stirred to ensure homogeneity before being loaded into the spray chamber. 0.3g of NaCl was added to the mixed precursor and stirred for homogeneity before spraying. During deposition, glass substrates were pre-cleaned by thorough washing and ultrasonication for 30 minutes, thereafter, oven dried at 60°C to ensure cleanliness and promote film adhesion. The spray nozzle was used to atomize the precursor solution into fine droplets. These droplets were transported through compressed air onto the pre cleaned glass substrates heated to controlled temperatures of 303 K, 333 K, and 363 K. The substrate temperature was maintained to facilitate thermal decomposition of the sprayed droplets, leading to the formation of uniform CdS thin films. The spray was carried out in timed cycles with the solution sprayed intermittently, allowing solvent evaporation and chemical reaction on the hot substrate surface to deposit the CdS film progressively. At completion of the spraying cycles, the films were dried using hot air. The deposited films were subjected to optical characterization using UV-Vis

spectrophotometry which revealed the films' transmittance and absorbance properties from which other parameters were determined. Morphological and grain structure analyses were performed through scanning electron microscopy (SEM) to assess temperature-dependent changes.

RESULTS AND DISCUSSION

The absorption results are as presented in figures 1 and 2 while the figure 3 and 4 is the SEM micrograph. Figures 1 and 2 present the absorbance spectra of undoped CdS and chloride-doped CdS thin films deposited via spray pyrolysis at substrate temperatures of 303 K, 333 K, and 363 K as a function of wavelength. The optical absorption coefficient (α) was determined using the Beer-Lambert law: $\alpha = 2.303 \times (A/T)$, where A is absorbance and T is film thickness. For undoped films, absorbance peaked at 1.90 for the 333 K sample, followed by 363 K and lowest at 303 K; chloride-doped films showed maximum absorbance of 1.96 at 303 K, decreasing to 1.72 at 363 K and 1.47 at 333 K.

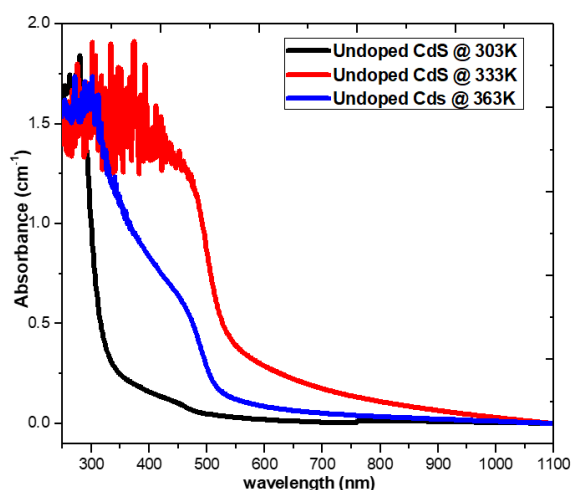


Figure 1: Absorbance curve for undoped CdS thin films deposited at 303K, 333K and 363K

Across all samples, absorbance decreased progressively with increasing wavelength, with spectra overlapping in the far-UV region and extending into the IR, exhibiting strong UV absorption (285–500 nm) that underscores their potential in optoelectronic devices a trend consistent with Hernandez-Calderon (2018);

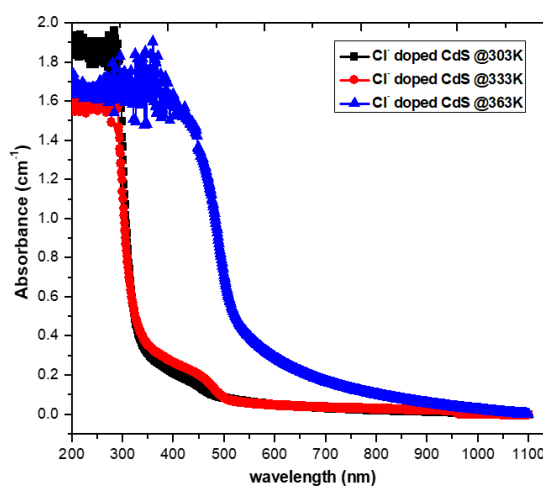


Figure 2: Absorbance curve for Cl⁻ doped CdS thin films deposited at 303K, 333K and 363K

Abouelkhir *et al.* (2024) and Nworie *et al.*, 2024. These chloride-induced variations suggest impurity-related defect states or lattice modifications that modulate absorption properties, with lower-temperature doping (303 K) enhancing UV response potentially through increased chloride incorporation.

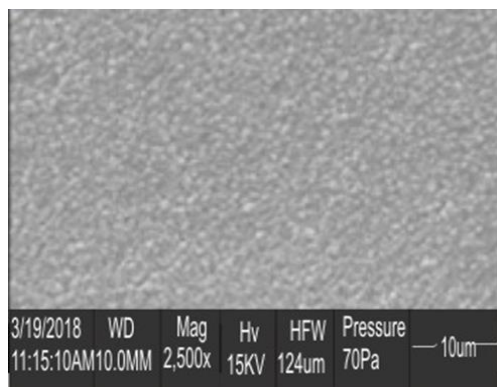


Figure 3: SEM image of Undoped CdS

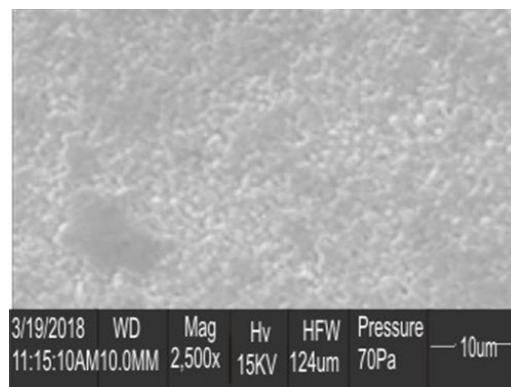


Figure 4: SEM image of Cl- doped CdS

Scanning electron microscopy (SEM) analysis reveals that electrons interacting with sample atoms generate signals detailing surface morphology, chemical composition, and crystallite orientation, achieved through raster scanning for sub-nanometer resolution (Pfanmüller *et al.*, 2013). As shown in Figures 3 and 4, chloride-doped CdS films deposited at 363 K display compact, crack-free morphologies with uniform grains and fewer pinholes compared to undoped counterparts, indicating that controlled chloride impurities refine microstructure and reduce defects. This improved uniformity enhances charge carrier transport and interface stability, critical for optimizing absorption efficiency and performance in photovoltaic window layers.

CONCLUSION

This study has demonstrated that controlled chloride doping in spray pyrolysis-deposited CdS thin films enhances UV absorbance and refines compact, crack-free morphologies with uniform grains, thereby maximizing absorption properties for superior optoelectronic device performance.

Declaration of Data Availability

Data are available upon request from the corresponding author.

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