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Chemical Bath Deposition of Low-Cost Cadmium Sulfide Thin Films for Optoelectronic Devices

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Abstract

Cadmium sulfide thin films are highly valued for their versatile optical and electrical properties, making them essential in various technological applications. Composed of cadmium and sulphur, these films are typically deposited onto substrates using methods such as chemical vapor deposition, sputtering, or chemical bath deposition. This study focuses on the deposition of transparent Cadmium sulfide thin films on glass microslides using the low-cost Chemical Bath Deposition technique. Prior to deposition, thorough cleaning of the glass surfaces was conducted to avoid contamination. The deposition solution, consisting of a Cadmium Chloride and thiourea mixture in distilled water, utilized acetonitrile as a complexing agent. The pH was adjusted using ammonia solution. The deposition temperature ranged from 60° to 70°, with continuous stirring. This approach demonstrates an effective method for producing CdS thin films suitable for applications in optoelectronics and other technological fields. Bandgap of the films was also calculated with the help of Transmission Spectra. Surface Morphology studies were also carried out.

Keywords: Chemical bath deposition, CdS, thin films, thiourea, CH_3CN

Introduction

Cadmium Sulfide (CdS) is a semiconductor from the II-VI group which have garnered significant attention due to its many photoconductive properties [1, 3]. It has been extensively studied for both fundamental and practical purposes. Recently, there has been a surge in research focusing on the preparation and characterization of CdS thin films, which are highly valued for their wide energy gap, excellent transparency in visible light, high absorption coefficient, electron affinity, low resistivity, ease of forming ohmic contacts [4, 5]. These attributes make CdS an ideal material for use in solar cells, photoconductors, and diode lasers [6, 7].

CdS, an n-type semiconductor with a direct bandgap, has shown increasing importance due to its promising potential for cost-effective and reliable photovoltaic applications, especially when paired with traditional p-type partners like CdTe. The theoretical maximum efficiency of CdTe/CdS polycrystalline solar cells is nearly 30%, though practical efficiencies are around 16.5% in laboratory settings, indicating room for improvements [8].

CdS films have been prepared using various techniques such as Thermal Evaporation [9, 10], Molecular beam epitaxy[11], spray pyrolysis [12], Electrodeposition [13], chemical bath deposition (CBD), etc. Among these methods, CBD has been the most widely used for the deposition of CdS thin films since the 1960s due to its many advantages. Firstly, the chemicals required are commonly available and inexpensive. Secondly, there is no need for sophisticated instrumentation, making the synthesis process simple. For instance, a glass beaker can serve as the reactor, and substrates can be made from various materials in different shapes and sizes. Thirdly, the film thickness and deposition rate can be controlled by adjusting the pH, temperature, and relative concentrations of reactants in the bath solution. Additionally, the reaction occurs at low temperatures (27-80°) [14-21].

The development of thin films of CdS has evolved significantly since Russell and Richards first reported on vacuum evaporation in 1947. Subsequent breakthroughs included Neugebauer and Fahrenbruch's pioneering work on chemical deposition techniques such as chemical bath deposition (CBD) in 1966, which Braslavsky further advanced in 1972. Albano *et al*. explored electrodeposition in 1975, broadening the range of deposition methods. By 1978, Bube provided a comprehensive review of various techniques, while Chopra and Dutta summarized developments by 1983, underscoring the expanding applications of CdS thin films. Hodes' contributions from 2007 onward focused on refining chemical deposition methods, while Gao and Lu introduced spray pyrolysis in 2008. Park *et al*. advanced thin film growth with pulsed laser deposition (PLD) in 2011, followed by Zhang *et al*.'s exploration of atomic layer deposition (ALD) in 2015. Kumar *et al*. utilized chemical spray pyrolysis in 2018 for solar cell applications, and Chen *et al*. developed chemical vapour deposition (CVD) techniques for CdS films in 2020.

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Most recently, Xu *et al*. investigated magnetron sputtering in 2022, highlighting ongoing efforts to enhance film quality and functionality. As of 2023, research continues to advance in refining existing techniques and exploring new methods, aiming to optimize CdS thin films for diverse applications in electronics, optoelectronics, and beyond.

Experimental Details

Typically, to obtain CdS thin films via CBD in an aqueous solution, cadmium salt is used as the Cd ion source, thiourea as the sulphur source, a base to adjust the pH of the solution, and a ligand to control the precipitation of chalcogenides and hydroxides. Various ligands have been utilized in CdS deposition, including NH_3, triethanolamine, ethylenediamine, ethylenediaminetetraacetic acid, nitrilotriacetic acid (NTA), cyano-complex, citrato-complex, and more recently, tartaric acid.

Thin films of CdS were deposited with the help of low-cost Chemical Bath Deposition technique. The transparent films were deposited on glass microslides. To avoid contaminated areas on the glass surface, slides were thoroughly cleaned with liquid soap and distilled water followed by ultrasonic cleaning. 0.1 M solution of $CdCl_2$ and thiourea $SC(NH_2)$ with 200 ml distilled water as a starting material and Acetonitrile (CH_3CN) using as a complexing agent. $CdCl_2$ supplied by Qualigens (molecular weight 183.31) was used as 'Cd' source and thiourea supplied by C.D.H was used as 'S' source. 4.5623 gm $CdCl_2$ and 1.5224 gm thiourea was dissolved in Distilled water. Distilled water used was 200 ml. In the alkaline bath, the pH of the solution was maintained between 8 to 11 by using ammonia solution. Round about 10.30 ml ammonia solution was used. Acetonitrile used was 5 ml. The temperature was kept in the range of 60°-70°. The bath was continuous stirred during the growth of the films. A uniform growth was obtained after stirring the solution within 90 to 120 minutes.

Result and Discussions

Optical studies are among the most important methods of characterizing the material. Transmission spectra of thin films are essential for understanding their optical properties, such as refractive index, absorption coefficient, and bandgap. The transmission (T) is the ratio of transmitted light intensity to incident light intensity, while absorption (A) is the fraction of light absorbed, related to transmission and reflectance (R), $A(\lambda)=1-T(\lambda)-R(\lambda)$. According to the Beer-Lambert Law, absorption is proportional to the absorption coefficient (α) and the film thickness (d). The refractive index (n) and extinction coefficient (k) describe the phase velocity and attenuation of light in the material. The bandgap energy (Eg), critical for semiconductors, can be estimated from the transmission spectrum.

To obtain transmission spectra, one must first prepare a uniform thin film on a transparent substrate and measure the transmitted light across various wavelengths using a spectrophotometer. The transmission spectrum $T(\lambda)$ is calculated, and if reflectance is known, the absorption spectrum $A(\lambda)$ can be determined. The absorption coefficient $\alpha(\lambda)$ is then estimated, and spectral features are analysed to determine optical properties like the bandgap energy.

For example, to determine the bandgap energy, one might plot the transmission spectrum and convert it to absorbance using $A(\lambda) = -\log(T(\lambda))$. A Tauc plot, which involves plotting $(\alpha h\nu)^2$ versus photon energy ($h\nu$), can help to estimate the bandgap energy by identifying the x-intercept.

In this study, the optical transmission spectra of the films were analysed to understand the spectral nature of optical absorption and to determine both the nature and magnitude of the bandgap. Figures 1 and 2 present the transmission spectra and $(\alpha h\nu)^2$ versus $h\nu$ plots, respectively, for CdS films grown using the chemical bath deposition method under optimal conditions.

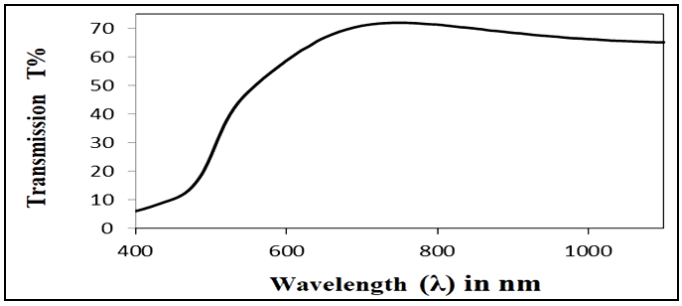

Fig 1: Plot between wavelength and T%

The absorption coefficient, derived from the transmission spectra using the formula in Equation. For all wavelengths, the reflection coefficient is assumed to be a constant 20%. The direct bandgap values for the various samples were obtained from the linear intercepts of the $(\alpha h\nu)^2$ versus $h\nu$ plots.

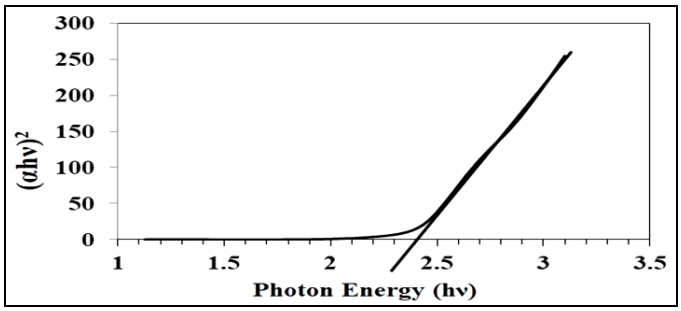

Fig 2: Plot between $(\alpha h\nu)^2$ and Photon Energy ($h\nu$)

As shown in Figure 1, the transmission percentage (T%) ranges from 0% to 75%, with the samples absorbing most of the radiation within the 400 nm to 800 nm wavelength range. Figure 2 indicates that the linear intercept intersects the x-axis at 2.4 eV, establishing the bandgap of the CdS thin film, grown by chemical bath deposition, as 2.4 eV.

Surface Morphology of the above grown films at different temperatures were also studied. Figure 3 shows the Scanning Electron Microscopy (SEM) image of the film grown at 60^0, While the Figure 4 Shows the SEM image of the film grown at the temperature at 70^0. We see that the grains are spherical in shape. There is not major change in the surface morphology in going from temperature 60^0 to 70^0. It may vary at higher temperature, but we have not studied it at higher temperature above 70^0. Studies are still going on.

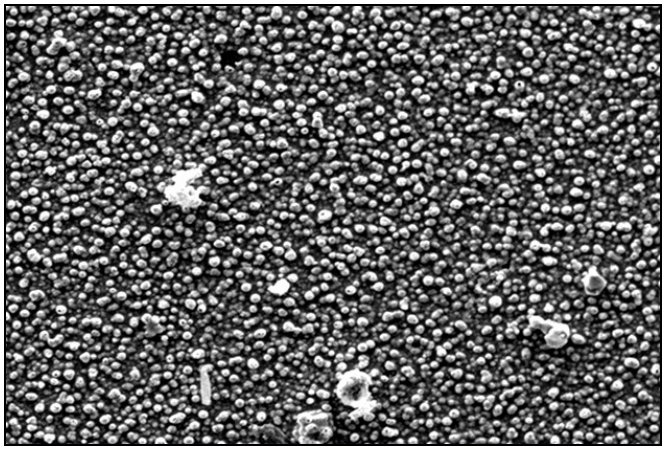

Fig 3: SEM image of CdS thin film grown at the temperature 60^0

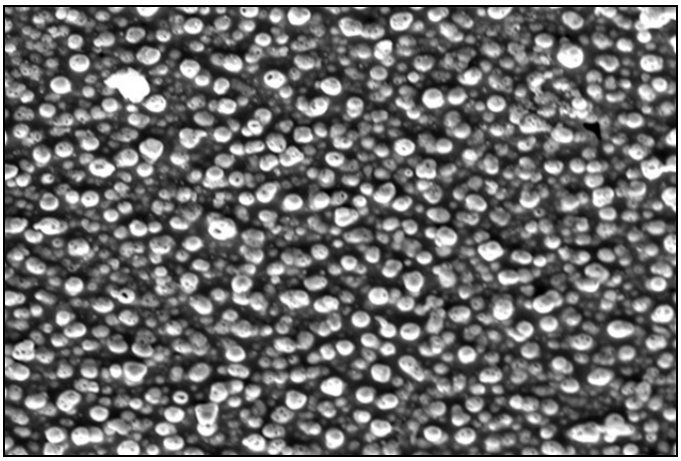

Fig 4: SEM image of CdS thin film grown at the temperature 70^0

Conclusion

In conclusion we have optimized the condition of chemical bath deposition of CdS thin films and have shown that Acetonitrile (CH_3CN) works as a complexing agent. Deposited thin films are cubic and bandgap is 2.4 eV.

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