# **Optical and Dielectric Properties of Cadmium Sulphide Thin** Film Grown Using Chemical Bath Deposition Technique

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Abstract: The optical properties of CdS thin films deposited by the Chemical Bath Deposition (CBD) technique were investigated. Results of the Transmittance, absorbance, reflectance, refractive index, extinction coefficient, and dielectric constant in both real and imaginary were reported. The optical properties were obtained using single – beam UV-VIS Helios Omega Spectrophotometer in the wavelength range of 280 – 920 nm with the optical absorbance measured directly and other optical properties extrapolated and calculated. The optical transmittance of the CdS thin films formed at different dip times were in the range of 52 - 79%. The energy band gap was found to be in the range of 3.75eV to 3.88eV. The optical transmittance indicated that the filmswere transmitting within the visible range which make them good material for thermal control window coatings and also for optoelectronic devices. The high frequency dielectric constant show anomalous dispersion of the refractive index in the region of lower wavelengths which is an indication of the polarizability.

Keywords: CBD, transmittance, absorbance, reflectance, band-gap, dielectric constant, CdS. \_\_\_\_\_

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#### I. Introduction

Cadmium Sulphide(CdS), is an n - type semiconductor material. It has been observed that CdS is an excellent heterojunction solar cell partner of (p - type narrow band gap semiconductor material like CdTe or CuInSe). CdS is used as a window material for low cost solar cells, for energy conversion, light emitting diodes and laser materials. It is also used in optical wave guides and nonlinear optical devices [1 - 3]. CdS being deposited by CBD has demonstrated numerous beneficial attributes toCu(In, Ga)Se<sub>2</sub>(CIGS) device. The CdS buffer layer improves the lattice match at the heterojunction interface, increase excess carrier lifetime, and optimizes the band alignment of the device and the process of cleaning of the absorber (CIGS) surface [4 - 5]. CdS has two types of crystal structures, cubic Zinc blende and hexagonal Wurtzite [6]. It is a wide band gap semiconductor and has a band gap energy of 2.42eV [2] hence in Nano scale this band gap increases beyond the bulk value [7]. In the recent years, various properties such as morphological/structural, electrical, optical, dielectric and other properties have been investigated by several researchers [8 - 14]. CdS thin film have been fabricated using several deposition techniques such as Screen printing [15], Electro deposition [16], molecular beam epitaxy (MBE) [17], Physical vapour deposition (PVD) [18 - 19] Spray pyrolysis [20 - 22], Thermal evaporation [23 - 24], Sol - gel deposition [25], Dip coating [6, 26], and Chemical bath deposition (CBD) [1,9,13,14,15,27 – 29]. In all these techniques a lot of efforts have been channeled towards obtaining high quality CdS thin film by optimizing various parameters such as deposition time, temperature, pH, source of precursors [6, 7, 27]. In this paper, the CBD technique has been adopted, because it is found to be simple, convenient, cost effective and capable of producing uniform and homogeneous thin films for industrial scale [27]. The films were deposited on glass substrates and thereafter characterized for their optical and dielectric properties.

## **II.** Experimental Details

Thin films of cadmium sulphide were deposited onto commercial glass slides  $(25.4 \times 76.2 \times 1)mm^2$ using the chemical bath deposition (CBD) technique[30]. All the chemicals used were of analytical grades. Prior to the deposition, the glass slides were first washed with an alkali free detergent and a piece of gauze sponge, then rinsed with distilled water many times. The slides were ultrasonically cleansed using dilute HCl and rinsed many times with de - ionized water and then dried in air. This process was carried out to ensure clean surface essential for the formation of nucleation centers that is required for thin film deposition. The deposition was carried out when  $0.264gdm^{-3}$  cadmium acetate in 30ml was placed in a 250ml glass beaker, as a  $Cd^{2+}$  precursor, 0.158 $gdm^{-3}NH_4OH$ in 15ml was added with constant stirring, which reduced the concentration of  $Cd^{2+}$ , 0.153 gdm<sup>-3</sup> Thiourea in 30ml was added as a source of sulphur, while

 $1.542gdm^{-3}$ Ammonium Acetate in 20ml was added to the mixture as a complexing agent this brought the volume of the resulting solution to 95ml. The PH of the mixture was maintained at 11.18. Keeping the alkalinity of the bath constant. Clean glass slides were inserted into the bath vertically with plastic rubber clips attached to a cover. The bath temperature was maintained at 90°C using 78HW – 1 constant magnetic stirrer.

The deposition was allowed to take place at time intervals of 20, 30, 40, 50 and 60 minutes respectively after which the slides were withdrawn from the bath simultaneously and rinsed with de – ionized water and first dried in air and then annealed in an oven at a temperature of 400°C for 60minutes. The samples were characterized for optical properties using spectrophotometer (UV-VIS Helios Omega) by measuring the absorption within the wavelength range of 280nm – 920nm. The transmittance and other optical parameters were calculated.

### **III.** Theoretical Considerations

#### 3.1 Growth Mechanism

The chemical process for the formation of the CdS can be described through this simple reaction; The deposition of CdS thin films occur when the ionic products of  $Cd^{2+}$  and  $S^{2-}$  exceeds the solubility product of CdS ( $K_{sp} = 1.4 \times 10^{-27}$ ). At this point CdS precipitate is obtained either in the bulk of the solution with the formation of colloids or at the surface of the substrate immersed in the solution leading to the formation of the layer. The chemical reaction leading to the layer formation may be represented as follows [31]; A). decomposition of the tetramine complex ion;

$$Cd(NH_3)_4]^{2+} \leftrightarrows Cd^{2+} + 4NH_3 \tag{1}$$

The instability constant of  $[Cd(NH_3)_4]^{2+}$  is given as  $K_i = 7.56 \times 10^{-8}$ B) Hydrolysis of thiourea in alkaline solution with  $S^{2-}$  ions generation:

 $(NH_2)_2CS + 2OH^- \rightarrow CH_2N_2 + 2H_2O + S^{2-}$  (2) This reaction consumes hydroxide ions tending to decrease the starting pH value of the reaction mixture. C) The CdS synthesis:

$$Cd^{2+} + S^{2-} \to CdS \tag{3}$$

### 3.2. Optical

The transmittance (T) can be calculated from the relationship [32, 33]  $T = \frac{1}{10^{A}}$ (4) Where A is the absorbance. From(4) above  $A = \log_{10} T$ (5) The absorption coefficient ( $\alpha$ ) can be calculated from the observed absorbance data using Beer Lamberts law  $\alpha = 2.303 \left(\frac{A}{d}\right)$ (6)

Where d is the thickness of the film.

The reflectance (R), is calculated from the relation [15, 32, 33]

$$A + R + T = 1$$
 (7)  
Or  $R = 1 - (A + T)$  (8)

For semiconductors, where  $(K^2 << n^2)$ , then the relationship between R and n [33, 34] is given by;  $R = \frac{(n+1)^2}{(n-1)^2}$ (9)

Where R is the reflectance, and n is the refractive index.  $\sum_{n=1}^{\infty} (n) = 1$ 

From (9) above, it is found that the refractive index n is given as;

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \tag{10}$$

Also the relationship between the extinction coefficient K and the absorption coefficient  $\alpha$  [34] is given as;

$$k = \frac{\alpha\lambda}{4\pi} \tag{11}$$

#### **3.3Dielectric Constants**

The high frequency dielectric ( $\varepsilon_{\infty}$ ) constant of the material can be determined using the relation [35]

$$n^{2} = \varepsilon_{\infty} - \frac{1}{4\pi^{2}\varepsilon_{o}} \left(\frac{e^{2}}{c^{2}}\right) \left(\frac{N_{opt}}{M^{*}}\right) \lambda^{2}$$
(12)

Where n is the refractive index, e is the electronic charge, c is the speed of light waves,  $N_{opt}$  is the number of carrier concentration, M\* is the effective mass of the charge carrier and  $\varepsilon_0$  is the electric permittivity of the free space or air. Consequently plotting a graph of  $n^2$  on y axis and square of the incident wavelength on the abscissa leads to obtain a straight line on extrapolation of this line will intercept the y – axis at  $\lambda^2 = 0$  in a certain value. This value gives the high frequency dielectric constant  $\varepsilon_{\infty}$ . While the ratio  $\left(\frac{N_{opt}}{M^*}\right)$  can be calculated from the

slope of the straight line. Another important dielectric property is the complex dielectric constant ( $\varepsilon^*$ ) which is related to the real and imaginary dielectric constant as [34]

$$\varepsilon^* = \varepsilon_1 + i\varepsilon_2 \tag{13}$$

Where  $\varepsilon_1$  is the real dielectric constant and  $i\varepsilon_2$  is the imaginary dielectric constant. The real and imaginary parts of the dielectric constants are related to the refractive index n, and extinction coefficient k, by the following equations [34]

$$\varepsilon_1 = n^2 - k^2 \tag{14a}$$

#### **IV. Results And Discussion**

#### **4.1 Optical Properties**

Determination of the optical band gap of the CdS thin films

The values of the energy gap,  $(E_g)$  were extrapolated from the plot of  $(\alpha h\nu)^2$  versus  $h\nu$  (Figure 1).  $\alpha, h and \nu$ ,

are absorption coefficient, Planck constant, and frequency, respectively. As can be seen  $(\alpha h\nu)^2$  varies linearly with  $h\nu$  beyond the energy gap which shows a direct transition [12, 36]. Accordingly, the energy gap is obtained by extrapolating the straight portion of the curve to zero absorption coefficients. CdS thin films grown here have the energy gap in the range of 3.75 to 3.89 eV. These values are somewhat larger than the typical value of the bulk CdS. The variation may be due to the quantum size effect as expected from the nanocrystalline nature of the CdS thin films and also from the loss of stoichiometry [4, 28, 36, 37].

The transmittance as a function of wavelength is shown in figure (2). We have found that the films have high transmission at the VIS/NIR region of the spectra of about 55 - 79% and this makes it a good window layer material for solar cell [38]. The optical transmittance at longer wavelength region decreased more as the thickness is increasing. This may cause weak absorption when used as a buffer layer on CIGS solar cell [39, 40].



Fig. 2. The variation of Optical Transmittance against the wavelength of CdS Thin films at different Deposition time.

Fig.3 show the variation of Optical absorbance against the wavelength, the absorption spectra of all the samples indicates that at the UV region of the spectra, the absorption is high whereas near infrared domain is very low, which is a good property that makes the film suitable for optoelectronic devices such as window layer on solar cells [41, 42].



wavelength of CdS Thin films at different Deposition time

The reflectance spectra of all the samples is as shown in figure 4, the films exhibited low reflectance range of 10 - 20% throughout the VIS/NIR domain which is also a good property for window layer solar cells [43, 44]. Also this property of low reflectance throughout the visible range of the spectrum can be useful in antireflection coating [45].



Refractive index, n is a distinctive and an essential property for any optical material. It plays an important role in selecting the materials used for fabricating optical devices or in the optical applications. Consequently, the study of the refractive index behavior is very important, especially many optical phenomena are dependent upon its value. Refractive index, n is closely related to both the electronic polarization of ions and the local field inside the optical materials [24, 31, 43]. Figure 5 shows the variation of the refractive index with the photon energy, which indicate that some interactions take place between photon and electrons in the thin film. It is clearly evident thata peak appeared in the refractive index, which shifts to the higher energies and this shift confirms the increase in the optical band gap. This result is in agreement with the findings of Kariper et al [46].



Fig. 6. Variation of extinction coefficient with wavelength

The Extinction coefficient or the absorption index k, has an important role in the determination of several optical measurements, especially those related to the absorption of light waves in the medium and the dielectric constants. Where, k value measures the fraction of light lost due to the scattering and absorption per unit distance of the penetration medium [24]. As shown in figure 6, the wavelength range of 280 - 340nm show that the extinction coefficient was high and gradually decreases as the wavelength increases towards the VIS range of the spectrum. The lower values of extinction coefficient at the visible region is an indication that less light was lost by scattering which shows that the material is good for optical devices.

#### **4.2 Dielectric Constants**



Fig. 7a. ∀ariation of η<sup>2</sup> versus λ<sup>2</sup> to determine the high frequency dielectric constant

The dielectric constant of a material is determined by electronic, ionic, dipolar and space charge polarization. The high frequency dielectric constant of the materials is a very important parameter for calculating the physical or electronic properties of materials [24, 46]. Figure 7ashows the nature of the dispersion of the refractive index of the CdS thin film as a function of the square values of the incident wavelength. As it was observed, the dependence of  $n^2 \text{ upon } \lambda^2$  is almost linear at the longest wavelength region which leads to obtain a straight line. Upon extrapolation to the  $n^2 \text{at}\lambda^2 = 0$ , the values of the high frequency

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dielectric constant, ( $\varepsilon_{\infty}$ ) was estimated as shown in figure 7b which was plotted against the deposition time. Figure 7a shows anomalous dispersion of the refractive index in the region of lower wavelengths and, it rapidly decreased as the wavelength of the incident light increased which is an indication of high absorption in the UV region of the spectrum [24].



The real part of the dielectric constant,  $\varepsilon_1$  is related to the dispersion of the electromagnetic waves that travels within the material and it is also responsible for slowing down of the propagation speed of the electromagnetic waves through the material. It showed the electronic polarization and the local field within the material. On the other hand, the imaginary part,  $\varepsilon_2$  is responsible for the energy absorption from electric field due to dipole motion, so it provides a measure of the disruptive rate of the wave in the sample [24]. The real part of the dielectric decreases with the increase in the photon energy as can be seen from figure 8. Figure 9 is the imaginary part of the CdS thin films which increases with increase in photon energy.



#### V. Conclusion

CdS thin films was grown using Chemical Bath Deposition techniques and characterized. The optical properties were seen to be affected by the variation of deposition time. The optical transmittance was found to be high in the visible domain of the spectrum which is a property that makes the film good material for thermal coatings. The reflectance of the films were found to be very low in the visible region of the spectrum which is an indication that the films can be used for antireflecting purpose. The bandgap energy were in the range that is far above the bandgap of bulk CdS which could be attributed to quantum size effect. This difference in the bandgap makes the film good buffer material for solar cells. Result of the dielectric studyindicate goodpolarizability of the films.

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