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Effect of pH on the Optical Properties of Cadmium Sulphide (CdS) Thin Film Deposited Using Chemical Bath Method

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Abstract: Cadmium Sulphide (CdS) thin films have been deposited on glass substrates at room temperature by using Chemical bath deposition method. The bath composition included cadmium chloride hemidihydrate [$CdCl_2.2½H_2O$], thiourea [SC $(NH_2)2$] and Ammonia (NH_3) solution. The effects of the pH value on the optical properties of the films have been investigated. The as-deposited films have been characterized by the UV-VIS Spectrophotometer. The spectrum showed that absorbance was high in the UV and low in the VIS-NIR region. The optimum percentage transmittance and reflectance are 84.7% and 20.3% respectively within the same region. The band gap values of the films range from 2.4 to 2.6 eV. The optical properties of the films within the UV- VIS-NIR regions indicate that the films can find application in solar thermal technology, particularly in antireflection coating.

Keywords: CBD, Cadmium Sulphide, pH, Optical Properties

1. Introduction

Cadmium Sulphide and other metal chalcogenide semiconductor thin films have recently received a lot of attention due to their significant role in the photovoltaic industry and in the manufacture of optoelectronic devices [1].

Cadmium Sulphide, an inorganic compound with the chemical formula (CdS) belongs to the group II–VI family of semiconducting materials receiving increasing attention due to its wide variety of applications. It occurs in nature with two different crystal structures as the rare mineral greenodaite and hawleytic, but is more prevalent as an impurity substituent in the structure of zinc ore. It is a direct wide energy gap semiconductor with an optical band gap of 2.4eV at 300K, which is the reason why it appears colored [2]. Cadmium sulfide is commonly used as n-type semiconducting layer for heterojunction thin films solar cells based on CdTe and $Cu(In,Ga)Se_2$ (CIGS) [3]. It has also been used in other applications including electronic and optoelectronic devices, photoconductor, laser material, optical wave-guide, and non-linear integrated and optical device [4, 5, and 6]

The conductivity of CdS increases when it is irradiated with light, which is the reason why it is used as a photoresistor. When CdS is combined with a p-type semiconductor, it forms the core component of a photovoltaic (solar) cell. When fabricated into thin films, it can be used as a transistor [7, 8].

It also has properties of electroluminescence and cathodoluminescence. Cathodoluminescence means that when CdS is mixed with copper acting as the activator and aluminium acting as the coactivator, it luminesces under electron beam excitation. Thus, it is used as phosphor

Polymorph forms of CdS are piezoelectric while the hexagonal types are pyroelectric [9]. Different techniques both physical and chemical , have been used to deposit CdS thin film , such as successive ionic layer adsorption and reaction (SILAR) [10] , screen printing [11] thermal evaporation [12,13] sputtering [14,15] molecular beam epitaxy [16,17], spray pyrolysis [18], chemical bath deposition [19,20] , electrodeposition [21] , vacuum evaporation [22] and photo chemical deposition [23].

Amongst these methods, chemical bath deposition (CBD) is one of the cheapest methods to deposit thin films and nanomaterials as it does not depend on expensive equipment and can be employed for large area deposition. It has been severally used to prepare buffer layer in thin film solar cell based on copper indium gallium diselenide (CIGS). Deposition of CdS using CBD is based on the slow release of Cd^{2+} ions and S^{2-} ions in an aqueous alkaline bath and the subsequent condensation of these ions on substrates suitably mounted in the bath. The slow release of Cd^{2+} ions is achieved by adding a complexing agent (ligand) to the Cd salt to form some cadmium complex species which, upon dissociation, results in the release of small concentrations of Cd^{2+} ions.

However, the deposition condition such as bath composition, reagent composition, temperature, pH, deposition time, etc. strongly influences the film stoichiometry, microstructure and crystallinity, these characteristics determine the optical and electrical properties of CdS films.

Different cadmium sources have been used over the years to achieve this process, such as cadmium acetate [24], Cadmium sulfate [25], cadmium nitrate [26] and cadmium chloride [27].

Bhattacharjee [24] synthesized and deposited CdS using a mixture of cadmium acetate ($Cd(OOCCH_3)_2$). $3H_2O$, thiourea (H_2NCNH_2) and Ammonium Hydroxide (NH_4OH). He studied the effect of annealing on the structural and electrical properties of the films. The result shows that the crystallite size was found to increase upon annealing and the resistivity decreases upon annealing.

Be Xuan et al., [25] studied the structural, morphological and optical properties of CBD deposited CdS thin films by varying the processing parameters and the Cd/S ratio of the starting precursors in order to better understand the growth conditions. The reagents used for the deposition include cadmium sulfate CdSO4, ammonia water NH_4OH and thiourea CS (NH_2)2. The results showed that the as deposited CdS films were polycrystalline and homogeneous. The grain size increased with increasing the Cd/S ratio and/or the deposition time.

The effect of Cd source on the film properties has been studied by Khallaf et al., [28]. They reported that films were found to be highly stoichiometric when cadmium chloride and cadmium iodide were used. The lowest resistivity and highest mobility and band gap obtained were in the case of cadmium sulfate. All films were found to be cubic, regardless of the Cd salt used.

It is necessary to eliminate spontaneous precipitation in order to form a thin film by a controlled ion-by-ion reaction. This can be achieved by using a fairly stable complex of the metal ions. The concentration of the metal ions is controlled by adding an appropriate complexing agent in correct concentration. For producing CdS, ammonia solution acts as the complexing agent. If a high concentration of S^{2-} ions exists locally, such that the solubility product is exceeded, localized spontaneous precipitation of a sulphide can occur.

This problem can be overcome by generating chalcogen ions slowly and uniformly throughout the volume of the solution. This is achieved by having thiourea in an alkaline aqueous solution.

The kinetics of growth of a thin film in ts process is determined by the ion-by—ion deposition of the chalcogenide on the nucleating sites of the immersed surfaces.

In this study, we report the preparation of CdS thin films onto microscope glass slides by CBD method and the effect of pH on the optical properties of the as-prepared CdS thin films are investigated.

2. Materials and Methods

Chemical bath deposition technique was used to deposit Cadmium sulphide thin films on glass substrates which had been previously degreased in concentrated HCl for 24 hours, washed in cold water with detergent, rinsed with distilled water and dried in air.

The cadmium sulphide thin films were prepared from an alkaline bath using aqueous solutions of cadmium chloride hemidihydrate [$CdCl_2.2½H_2O$] and thiourea [$SC(NH_2)2$] which acted as a source of Cd^{2+} and S^{2-} ions, respectively. The complexing agent used was NH_3. The complexing agent slows down the reaction so that fast precipitation is avoided.

In this experiment, four reaction baths were used. 4mls of 0.02M cadmium chloride hemidihydrate [$CdCl_2$**.2½**H_2O] was measured into a 50ml beaker using burette; 8mls of 1.0M thiourea [$SC(NH_2)2$] was then added. On addition of thiourea, solution remained yellow. Various volume of ammonia solution (ligand) was then added in order to vary their pH value. The mixture was then topped to 50mls level by addition of various volume of distilled water. It was thereafter stirred using the glass rod stirrerd gently to ensure uniformity of the mixture. A glass substrate was dipped vertically into all of the four reaction baths with the aid of a synthetic foam cover. Each bath was allowed to stand for twenty four hours, after deposition, the films were rinsed with copious amounts of distilled water, dried in air and kept in an air tight container to avoid contamination. The films were prepared for different pH (8, 9, 10, and 11) values of the solution. The approximate values of the pH of the solutions were determined by the use of a pH paper.

A summary of the preparative conditions for the deposition is shown in table 1.

Table 1. *A summary of the preparative conditions for the deposition of CdS film.*

Slide no.	Vol.of $CdCl_2.2½H_2O$ (ml)	Vol. of $SC(NH_2)2$ (ml)	Vol. of NH_3 (ml)	Vol.of Dist.H_2O (ml)	pH	Deposition time (hrs)
1.	4	8	5	33	8	24
2.	4	8	6	32	9	24
3.	4	8	7	31	10	24
4.	4	8	9	29	11	24

After the films were deposited, they were characterized using a 752N England UV-VIS spectrophotometer in the UV-VIS-NIR regions with blank glass slide as reference.

The optical properties investigated include the absorbance, transmittance, reflectance, band gap, refractive index, extinction coefficient and dielectric constant.

3. Results and Discussion

Data obtained from the optical characterization of the films in the wavelength range 200 to 1000 nm were used to plot the following graphs.

3.1. Absorbance

In spectroscopy, the absorbance (also called optical density) of a material is a logarithmic ratio of the amount of radiation falling upon a material to the amount of radiation transmitted through the material [29]. Optical absorption study of materials provides useful information to analyze some features concerning the band structure of materials.

The absorbance generally decreased with increase in wavelength and has relatively low values in the infrared region of the spectrum. The high absorbance in UV region makes the film good material for screening off UV portion of electromagnetic spectrum which is dangerous to human and animal health. It can also be used for eye glass coating for protection from sun-burn.

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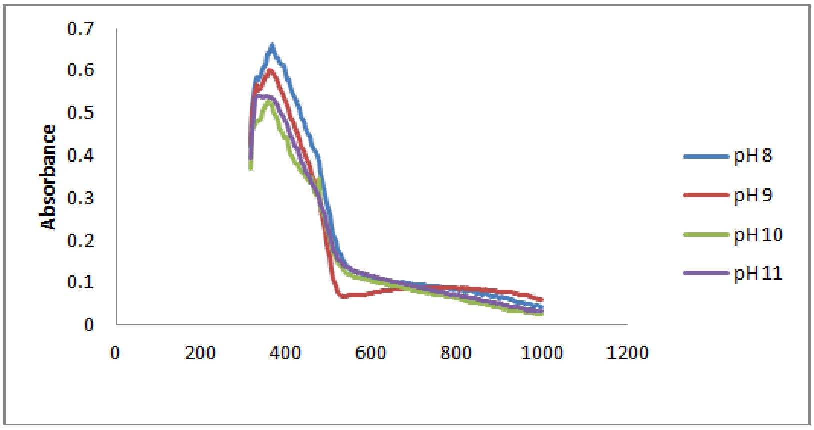

Fig. 1. *Absorption Spectra of CdS films with differnt pH value.*

Fig. 1 shows the optical absorption spectra of CdS film deposited at room temperature on glass substrate for pH values 8, 9, 10 and 11. The figure shows that absorbance decays exponentially with an increase in wavelength. The absorption peaks were centered at 365nm, for the four samples. The spectrum also showed that absorbance was high in the UV and low in VIS-NIR region.

3.2. Transmittance

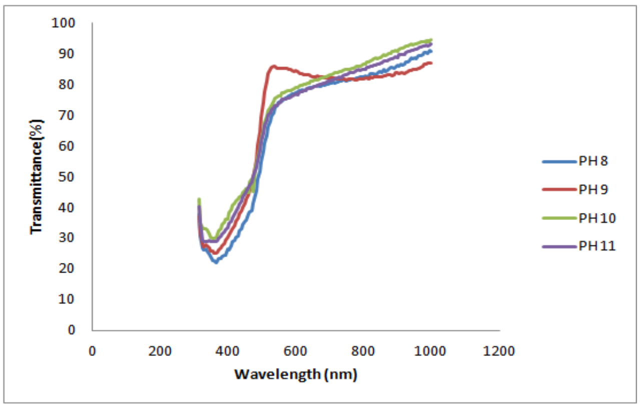

Fig. 2. *Transmittance Spectra of CdS films with varying pH value.*

Fig.2 shows the transmittance spectra of the CdS film. The optimum transmittance of 84.65% was obtained at pH 9, while the minimum transmittance of 22.8% was obtained at pH 8. It was also observed that the transmittance was low in the UV region which gradually increased in the visible and NIR regions. The high transmittance in VIS-NIR provides heat and visible light into the house. This high transmittance in the visible region makes cadmium sulphide films useful aesthetic window glaze materials. Also, the high transmittance of the film makes it suitable for solar energy collection because if coated on the surface of the collector, it will reduce reflection of solar radiation and transmits radiation to the collector fluid.

3.3. Reflectance

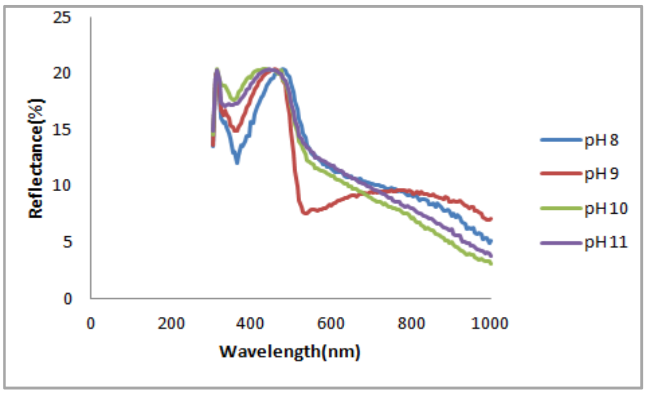

Fig. 3. *Reflectance Spectra of CdS films for different pH value.*

Fig. 3 shows a plot of reflectance index (R) versus wavelength of CdS films. Generally all the films show a very low reflectance throughout the UV/VIS/NIR region. The maximum reflectance of the film at VIS region is 20.3%.This low reflectance value makes cadmium sulphide thin film an important material for anti-reflection coating [30].

3.4. Bandgap

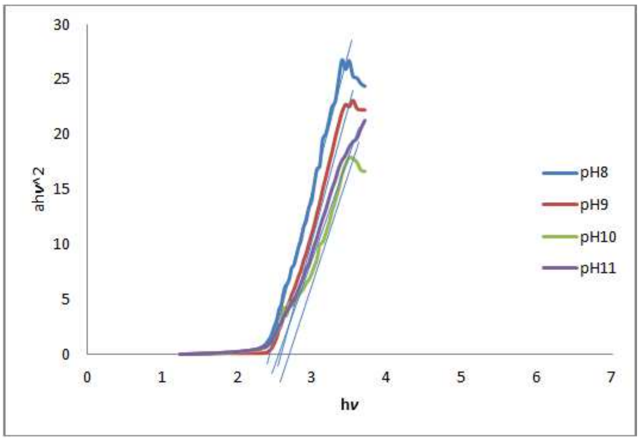

Fig. 4. *A plot of $(\alpha hv)^2$ as a function of energy (hv) for CdS.*

Fig. 4 shows the plot of $(\alpha hv)^2$ vs. hv for CdS for all the samples . The value of the optical band gap has been determined from the value of the intercept of the straight line at $(\alpha hv)^2 = 0$. The as-deposited CdS thin film optical band gap energy is calculated to be 2.4eV, 2.42eV, 2.5 eV and 2.6eV for pH8, pH 9, pH 10 and pH 11 respectively. These variations in energy band gap can be explained in terms of quantum confinement related with particle size. These bandgap values are in close agreement with the range obtained by Suresh et al., [26] and Lozada-Morales et al., [31]

3.5. Refractive Index

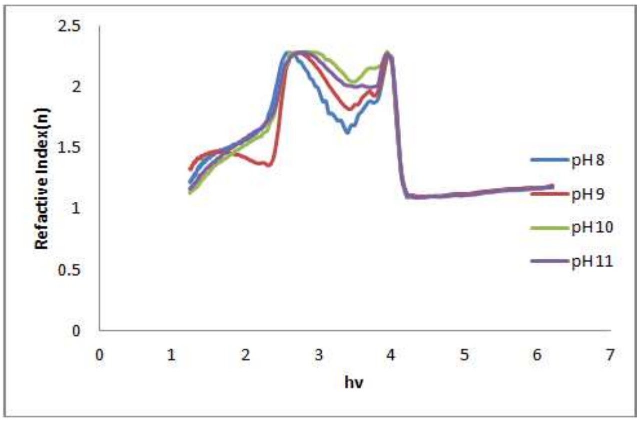

Fig. 5. *Graph of refractive index against photon energy.*

Fig. 5 shows the variation of refractive index against photon energy of the CdS film for all the four samples. The refractive index (n) is the range of frequencies in which films are weakly absorbing. The average values of n range between 1.25 and 2.21 with highest peak recorded at photon energy of 2.69 eV and 4.0eV. It was noted that the least value of n was recorded for the sample that had the highest pH value.

The high refractive index possessed by CdS films makes it suitable for use as anti-reflection coatings.

3.6. Extinction Coeffiecient

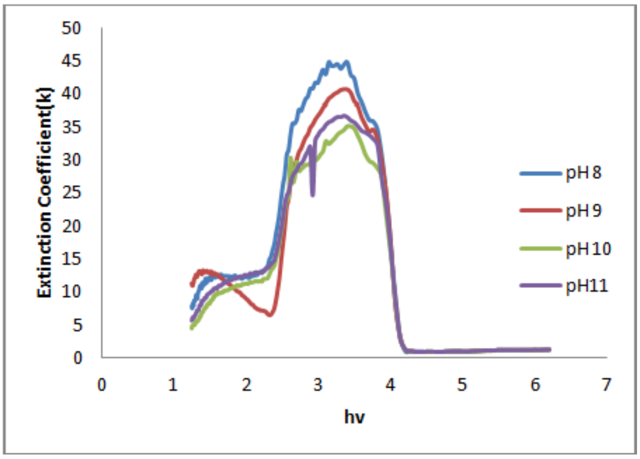

Fig. 6. *Graph of extinction coefficient against wavelength.*

Fig. 6 shows the variation of extinction coefficient of the CdS film against wavelength. The extinction coefficient allows for estimation of the molar concentration of a solution from its measured absorbance.

The extinction coefficient increases with increasing photon energy up to 3.4 eV, it then decreases slightly from 3.5eVto 4.0ev until it is almost zero at the boundary point.

3.7. Dielectric Constant

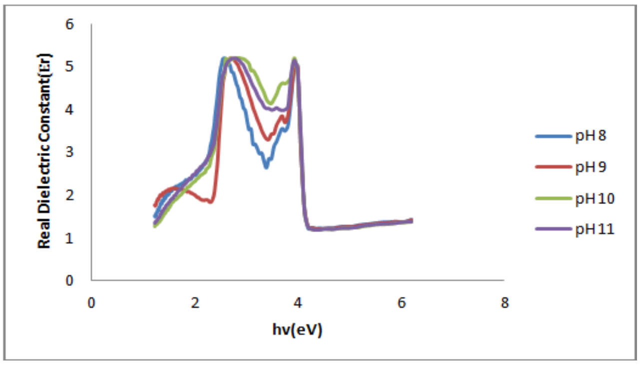

Fig. 7. *Graph of Real Dielectric constant against Photon energy.*

Fig. 7 shows the graph of the real part of the dielectric constant of the CdS film against photon energy. The dielectric constant increases with increasing photon energy up to 2.5eV, it then decreases from 2.7eV to 3.3eV and increases slowly with photon energy 4.00eV.The high-frequency dielectric constants was found to be 5.2.

4. Conclusion

Cadmium Sulphide (CdS) thin films have been deposited on glass substrates at room temperature by using Chemical bath deposition method. The films were prepared from an alkaline bath using aqueous solutions of cadmium chloride hemidihydrate, thiourea and Ammonia**.** The effects of the pH value on the optical properties of the films have been investigated. The as-deposited films have been characterized by the UV-VIS Spectrophotometer. The spectrum showed that absorbance was high in the UV and low in VIS-NIR region. The optimum transmittance in the VIS-NIR regions range from 72.2% --84.65%. The band gap values of films ranged from 2.4 to 2.6 eV depending on the pH value. Generally all the films show a very low reflectance throughout the UV/VIS/NIR regions.

The optical properties of the films within the UV- VIS-NIR indicate that the films can find application in solar thermal technology, particularly in antireflection coating.

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