Optimization of Optical Properties of Annealed Cadmium Selenide (Cdse) Thin Films Grown by Chemical Bath Deposition Technique

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Abstract
Two groups of cadmium selenide thin films deposited at 25^0C and 74^0C respectively on glass substrates by chemical bath deposition method were studied. A moderately stable sodium selenosulphite (Na_2SeSo_3) was used as a source of Se^{2-} ions. To prevent spontaneous precipitation and ensure ion-by-ion deposition on the substrate, TEA was used as a complexing agent. The optical characterization was centered on transmittance, reflectance for the annealed and various annealing temperature of thin film. The structural nature was obtained from X-ray diffraction (XRD) analysis. The optical properties were obtained from absorption and transmittance data within the range of 200-to-1000nm. Some of the films were found to have a good transmittance and low reflectance hence suitable for window coatings for cold climates and antireflection coatings.
Key Words: - Characterization, Deposition and annealing temperature and time, optical, Chemical Bath Technique, Cadmium Selenide thin Films, annealing, transmittance, reflectance, band gap.

Introduction:
Due to the technological application of thin films in various devices, more thin films with a significant dielectric constant variation over a length of microns or even less are being realized, through modern thin film fabrication. Various thin films can be developed using different techniques like physical vapour deposition, chemical vapour deposition, chemical solution deposition etc. Using these techniques, different types of thin film could be developed such as semiconductor thin film, superconductor, metal thin film resistor, thin film capacitors, etc. (Blakemore, 1974, Rosenberg et al, 1980). Thin films with special applications such as ZnS ,CdSe or silicon nitride etc have been shown to provide broadband antireflection properties and hence are highly used (Pankove,1975). The grown CdSe thin films have been extensively studied due to their variety of applications in optoelectronic devices Owing to its optical and structural properties especially with reference to CdSe that can be used as an optical window. (Udeaja, 1996). However, poor absorption and reflectance characteristics has been reported to be peculiar and in an effort to discover the cause and overcome this problem, deposition was done at both room and higher temperatures, different annealing temperatures were also used in this work. The deposited CdSe are semiconductors.
Several methods such as: pyrolysis (Kosugi et al, 1998), Hot-wall epitaxy (HWE) (Huber, 1979 & Sitter et al, 1988). Cathodic sputtering (Grove, 1852), Electrochemical deposition (Nelkon, 1985 & Awe et al, 1984) has been used in deposition of thin films, but for good quality film suitable for use as selectively absorbing surfaces as those of cadmium selemide, high temperature techniques ($>900^0c$) are unsuitable since this can cause rapid oxidation and contamination by environmental gases. Information from literature showed that CdSe thin films with a band gap of 1.8ev has been grown using solution growth technique (Mondal et al, 1983) also a grown CdSe with a band gap range of 1.45 - 1.98ev has been reported (Osuji 1994).Categorically, good qualify CdSe should be reddish brown or yellowish brown in colour with high transmittance within visible (VIS) and near infra-red (NIR) ranges and low absorbance towards IR. This makes it suitable for solar cell application.
We present in this paper the procedure for preparing Cadmium selenide thin films using the chemical bath techniques, which is simple, less expensive in chemical and equipment and most suitable for control experiments. Since spontaneous precipitation affects both structural and optical qualities, a complexing agent and buffer solution that control the PH were used to ensure high quality thin films that enhance the study of effects of deposition and annealing temperatures on the properties of thin films.

Experimental Details
Cadmium Selenide thin films were produced using chemical bath deposition technique. In the deposition, the reaction bath was made up of solution of 5ml of 1M cadmium acetate ($(CH_3COO)_2Cd.2H_20$), 4ml of 1M sodium selenosulphite (Na_2SeSo_3), 5ml of 13.4M ammonia solution (NH_3), 10ml of 7.4M Triethanalomine (TEA)

[$N(CH_2CH_2OH)_3$] as complexing agent and 40ml of distilled water. Seven reaction baths of these films were prepared. The disassociation relation and the equation for the chemical reactions are:

$$[CH_3C00]_2\,Cd.2H_20+TEA \longrightarrow Cd(TEA)^{2+} + 2\,(CH_3\,C00)^{2-}.\,H_20$$
$$Cd\,(TEA)^{2+} \longrightarrow Cd^{2+} + TEA$$
$$Na_2\,SeS0_3 + OH \longrightarrow NaS0_4 + HSe^-$$
$$Cd^{2+} + OH^- + HSe^- \longrightarrow CdSe \downarrow + H_20. \quad (1)$$

Seven reaction baths of this films were prepared and the detail of the molar and volume concentration of the reagents as well as the times and temperature of the various reaction baths are displayed in table 1 below.
The reaction baths were thoroughly stirred with glass rod instead of the magnetic stirrers to ensure uniform deposition since it was observed that constant stirring with magnetic stirrers during the process of deposition did not allow films to deposit. Glass slides of 76mm x 26mm x1mm were used as substrates and synthetic foam covers were used not only to protect the reaction bath from environmental impunities but also to support the substrate instead of clamping them into open baths. The experiments were carried out under both room temperature (25^{o}C) and at (74^{o}C) respectively.
The thin films were annealed at different temperatures for one hour each. The optical characterization of the thin films was done using the single beam scanning spectrophotometer from the ultraviolet (UV), through the visible (VIS) to the near infrared (NIR) region of the electromagnetic spectrum. The surface structural analysis was undertaken with a photomicroscope attached to a camera set an objective magnification of X200. The composition analysis of the samples was done using X-ray photoelectron spectroscopy. The optical parameters were estimated from the absorbance and transmittance data while the thickness and band gap were obtained using optical techniques.
Fig1a,1b& 1c are the plotted graph of absorbance, transmittance and reflectance versus wavelength of the film samples. Fig2a shows the plot of (α hv)^2 Vs (hv) for CdSe. Considering the absorption edges, which are characteristics of the crystalline state of the films, the fundamental absorption which corresponds to the electron excitation from the valence band to the conduction band, was used to determine the value of the optical band gap. The relationship between the absorption coefficient (α) and the incident photon energy (hv) can be written as:

$$(a\,hn)^2 = \text{[illegible]}n - E_g \quad (2)$$

Where A = constant, E_g = band gap, n = transition type whose value may be $^1/2$, 2 and $^3/2$ for direct allowed, indirect allowed and direct forbidden transition respectively. However, using Tanc's plot of (α hv)^2 Vs (hv),the photon energy at the point where (α hv)^2 is zero represents Eg, which is determined by extrapolation shown in Figure 2a (with the value of 'α' determined from transmittance spectral) [Pankove 1975, (Tauc, 1970]. The grain sizes of the films were obtained using Debye Scherer relation:

$$D = \frac{K\gamma}{\beta\cos\phi} \quad (3)$$

Where k = 0.94, λ = X–ray wavelength = 1.54Å, β is the full width half maximum of the obtained pulse of XRD diffractograms. ϕ is the Bragg's angle.

Results and Discussion

The spectral absorbance and optical transmittance, reflectance and band gap of Cadmium selenide films are displaced in figure: 1, 2 and 3. Fig.1 presents the samples: Cd(7) showed peak absorbance at UV regions of 340 – 400 with peak value of 0.9 and 0.85 while sample Cd(2) and Cd(5) showed a uniform absorbance of about 0.80 and 0.70 in the rage of 340 – 640nm after which absorbance decreased uniformly. The poorest absorbance was exhibited by sample Cd(1). Transmittance was shown in Fig.2 to be the inverse of absorbance with the sample Cd(1) having the highest transmittance of about 92% transmittance in the range of 540 – 1000nm. All the thin films had relatively low reflectance of approximately 20% shown in Fig.3. It was equally shown that increase in the annealing temperature increases reflectance and absorbance but decreases transmittance. With the above properties of low reflectance and high transmittance the films are good materials for thermal control window which is coatings for cold climates and antireflection coatings. Generally, those deposited at room temperature (25^{o}C) have higher band gap value when compared with those at 74^{o}C. It was observed that minimum band gaps of the two groups occurred at annealing temperature of 100^{o}C while the maximum band gaps (2.12 &2.55) of the groups were observed on unannealed (as-deposited) samples of Cd(4) and Cd(1). Finally, table 1 shows that as the annealing temperature increases above 100^{o}C, the band gap increases. This may be attributed to possible reaction with some gases in the annealing oven (or sintering chamber). The average crystal size of the film was 2.6Å or 26nm. The band edge sharpness reduces with annealing temperature due to the reorganization of the films and filling of the voids as water contents evaporates (Erat, et al, 2007). Results from literature showed that the band gaps of CdSe ranges from 2.10eV – 2.55eV for the thin film produced using CBD, while that obtained by Erat, Pujari and Udeaja respectively ranged between 1.70eV and 1.8-3.3eV (Erat, 2007; Pujari, 2001; Udeaja, 1996). With this obtained value, when compared with the one obtained earlier using other methods of deposition (Rincon, 1998), the results are in compliance.

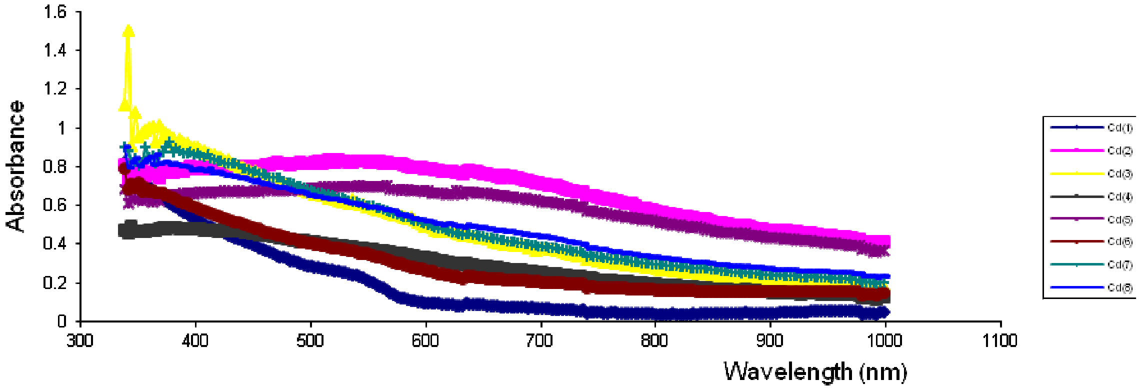

Fig 1: Absorbance vs wavelength for CdSe

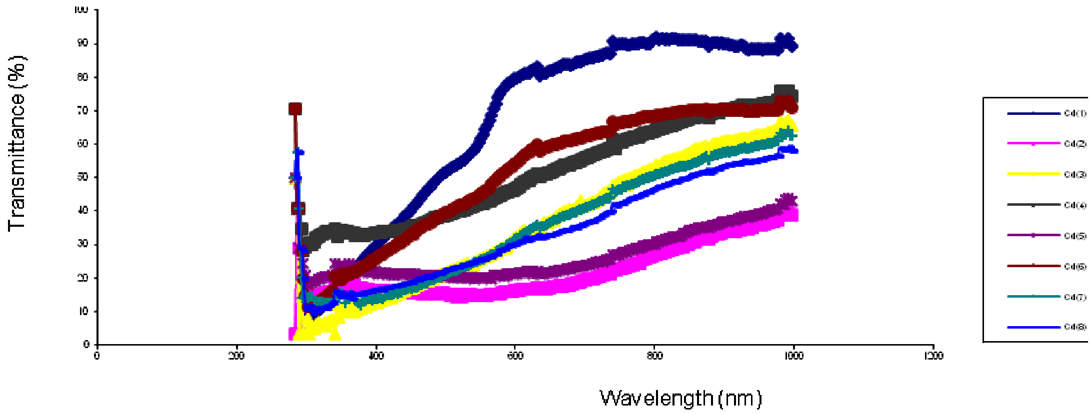

Figure 2: Transmittance vs. wavelength for CdSe

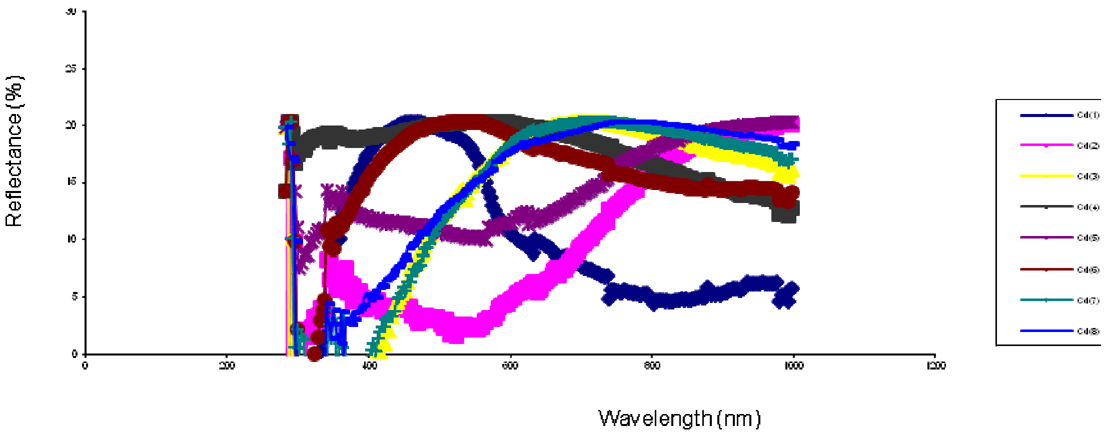

Figure 3: Reflectance vs. wavelength for CdSe

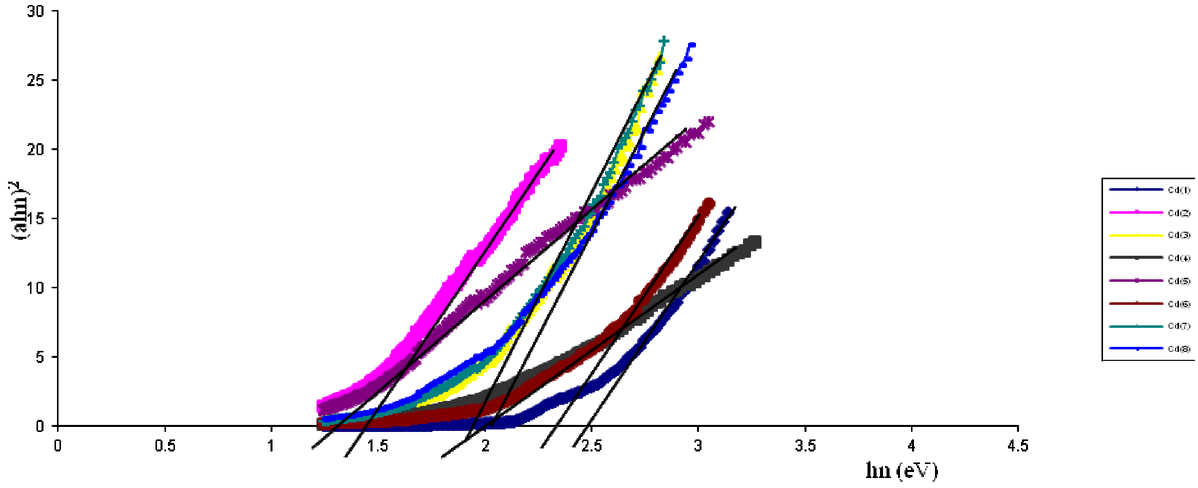

Figure 3b: Plot of (ahn)^2 vs. hn for CdSe

Table 1: Summary of the Band Gaps of the grown films.

S/NO	CdSe Film	Band gap hv (ev)	Annealing Tempt.(^{o}C)	Diptime (hrs)	Deposition Tempt.(^{o}c)
1.	Cd (1)	2.55	0	24	25
2.	Cd (2)	1.35	100	4	74
3.	Cd (3)	2.10	300	4	74
4.	Cd (4)	2.12	0	4	74
5.	Cd (5)	1.28	100	24	25
6.	Cd (6)	2.28	300	24	25
7.	Cd (7)	2.10	200	4	74

It was found that the deposition temperature had no effect on the optical properties of these films through they were affected by deposition time (diptime), as it increases the thickness. The band gap was not strongly affected by annealing.

Typical XRD pattern displayed in fig.4b shows several peaks at 2Ɵ of 19.38 19.78, 34.36, 47.18 and 66.63. Cadmium sample Cd(2) presents one of the most outstanding peaks with almost a single peak at 2Ɵ around 20.36. This suggests a compound crystal whose over 90% volume is made of a single element leaving the rest of the elements as trace.

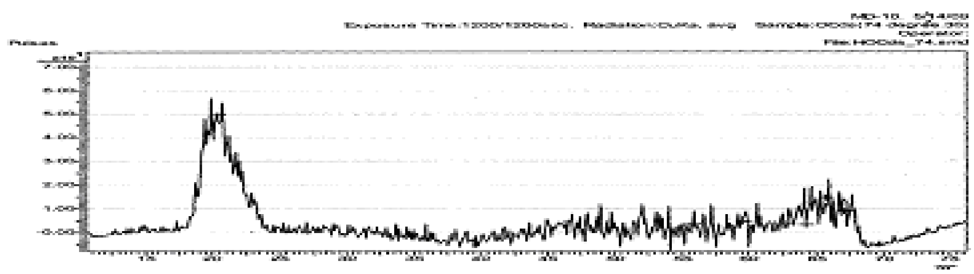

Figure 4a:XRD result of Cd(4)

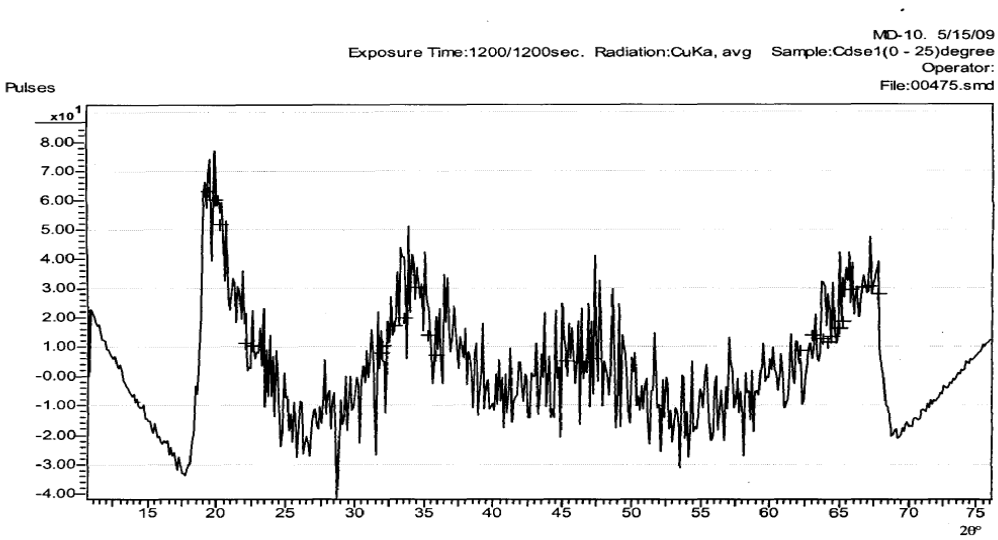

Figure4b:XRD result of Cd(1)

Conclusion

The deposition of CdSe thin films have been successfully carried out in alkaline medium using chemical bath deposition techniques. The deduction from the spectrophotometers shows that the peak values of "n" ranged between 1.10 and 2.35, the grain size of the films ranged between 1.14Å and 2.60Å, and the band gap ranged between 2.55eV and 1.28eV. The films were found to have a good transmittance of which, one reached, up to 92% in the VIS-NIR regions. These results show that the films could be used for window coatings for cold climates and antireflection coatings. It was found that the optical and solid state properties of CdSe thin films are functions of their deposition time and annealing temperatures but independent of the deposition temperature.

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