COMPARATIVE STUDY OF THE OPTICAL PROPERTIES OF CdZnS DEPOSITED BY TWO METHODS

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Cadmium Sulphide thin films doped with zinc were prepared at room temperature ion using successive ionic layer adsorption and reaction (SILAR) and chemical bath (CBD) techniques. The bath consist of solution of cadmium sulphide (CdS) as a source of Cd^{2+}, Zinc Sulphate ($ZnSo_4$) as a source of Zn^{2+},thiourea $[CS(NH_2)_2]$ as a source of Sulphide ion and ammonia (NH_3) as the complexing agent. The deposited films were annealed at temperature of 473K,573K and 673K in each case in order to investigate the effect of annealing temperature on the deposited films .Films deposited by both techniques were investigated using X-ray Diffractometer (XPERT=PRO) and UV Spectrophotometer. The optical constants were evaluated using the straight forward analysis proposed by Swanepole. The X-ray diffraction patterns of these films show that films are polycrystalline in nature having preferential orientation along the (002) plane. Our result revealed that the optical properties of the films has a reasonable trend with deposition method and annealing temperature.

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1. Introduction

Cadmium sulphide (CdS) and Cadmium Zinc Sulphide ($Cd_{1-x}Zn_xS$) have properties in between CdS and ZnS.Introduction of Zn^{2+} to the CdS buffer layer promotes the electronic and optical properties of the film thereby opening new widows in the application of the films in device production. The large band gap of Cadmium Zinc Sulphide thin films makes the material much more attractive for the fabrication of solar cells. The thin film is widely used as a wide bandgap widow material in heterojunction photovoltaic solar cells and photoconductive devices. [2].

Sequel to the above qualities more attention is being given in producing good quality CdS thin films for various applications. There are many techniques which had been used to deposit CdS and CdZnS thin films such as electrodeposition, successive ionic layer adsorption and reaction ((SILAR)),vacuum evaporation, spray pyrolysis and chemical bath deposition (CBD) etc [3].

In this research, successive ionic adsorption and reaction ((SILAR)) and chemical bath deposition (CBD) method was used because they are relatively simpler and cheaper method and has emerged as one of the recent soft chemical solution methods. It is advantageous due to layer-by-layer growth comprises excellent material utilization efficiency, good control over deposition process along with film thickness and specifically convenient for large area deposition on virtually any type of substrate.

The (SILAR) deposited results in pin-hole free and uniform deposits since the basic building blocks are ions instead of atoms [4, 5]. In this research, we studied the optical properties of CdZnS thin films deposited on a glass slide using both techniques.

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2. Experimental

The chemical bath for the synthesis of CdZnS using the CBD consists of .5 mls,0.05M of $CdCl_2$, 20 mls 0.05 M NH_4Cl, 7.5 mls, 1M NH_2CSNH_2, 7.5 mls, 0.05 M of $ZnCl_2$ and 60 mls of distilled water. The glass slides were inserted into the beaker and deposition were allowed to take place for 1 hr. In the synthesis of CdZnS by successive ionic layer absorption and reaction (SILAR) on glass substrates, cadmium solution, zinc solution and ammonia solution were added together into one beaker 1while beakers 2 and 3 contains distilled water and thiourea solution [NH_2CSNH_2] respectively. Cadmium solution and zinc solution serves as source of Cadmium ion (Cd^{2+}) and zinc ion (Zn^{2+}) respectively while Thiourea was used as Sulphide ion (s^{2-}) source, Ammonia solution was used as complexing agent. The four beakers were place in water bath which was kept at a temperature of 343 K. The synthesis of CdZnS by this method involved the following steps.

(i)Four properly cleaned glass substrate were immersed in a cationic precursor solution that is contained in beaker (1) for 30sec. Cadmium and zinc ions were absorbed on the surface of the substrates.

(ii).The substrates were rinsed in high purity distilled water that is in beaker 2 for 5seconds to remove the non-adhered films.

(iii)The substrates were then immersed in the anionic precursor solution contained in beaker 3 for 30 seconds which provides the sulphide ions that react with the adsorbed $Cd^{2+}$to form the CdZnS thin films.

(iv) Finally, the substrates were rinsed again for 5seconds in distilled water to remove non-adhered thin films. This four steps above makes one complete cycle and it was optimized at thirty (30) cycles. The four synthesized thin films were thereafter dried in air. Thermal treatments were carried out on three of the synthesized thin films at 473 K,573 K and 673K respectively while one is kept as the control (as- deposited).

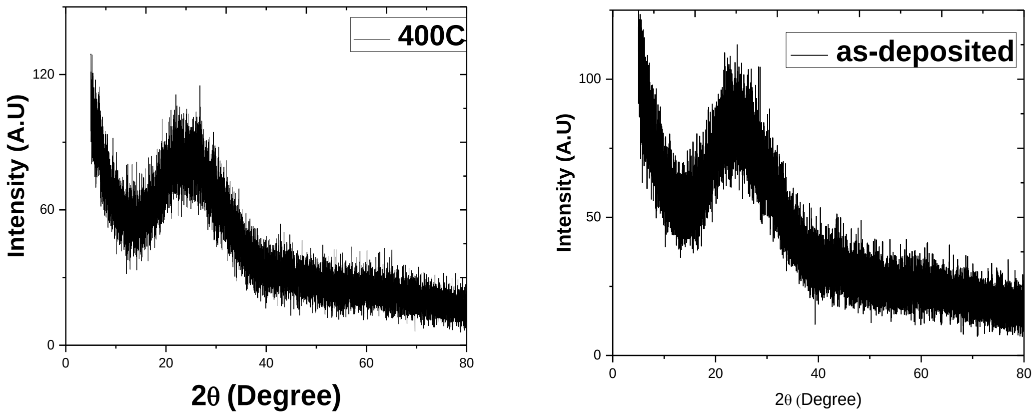


Fig.1: XRD pattern of CdZnS thin films deposited by CBD technique

3. Results and discussion

3.1 Structural Analysis

The films adherences were good with high cadmium content and the colours were white-yellowish showing the present of Zn in the sample. The thicknesses of the films were measured with Nano indenter and ranges from 350nm -420nm with average of 380nm. The crystal structure and orientation of cadmium zinc sulfide CdZnS thin films synthesized by CBD and SILAR which were thermal treated and as deposited were examined by X-ray diffraction (XRD) using a PANanalytical (XPERT-PRO), 45Kv, 4OmA, D8 advance X-Ray Diffractometer using Cu-kα radiation ($\lambda K\alpha_1$ = 1.5406 Å) with 2theta range of 5.004-79.996 degrees. The lattice parameter (a) of a unit cell was calculated from the peak position using the formula of cubic system [9].

$$h_{hkl} = \frac{a}{\left(h^2 + k^2 + l^2\right)^{1/2}} \tag{1}$$

The average crystallite size ($D_{h\,k\,l}$) of the CdZnS thin films were estimated from the X-Ray Diffraction patterns using Debye Scherer formula [5, 7].

$$D_{hkl} = K \frac{\lambda}{\beta h\,k\,l \cos(\theta_{hkl})} \tag{2}$$

Where λ is the wavelength of the incident radiation (λ = 1 .54060 Å), k is a dimensionless constant often called the shape factor with a value of 0.9, $\beta_{h\,k\,l}$ is the full with at half maximum (FWHM) of the privileged orientation diffraction peak and θ_{hkl} is the Bragg's diffraction angle. Figure 1 Shows XRD patterns of synthesized cadmium zinc sulfide (CdZnS) thin films by CBD method representing as deposited (CAS), thermal treated at (200C) and (400C) respectively. It was found that (CdZnS) thin film is poly crystalline consisting of CdZnS cubic and hexagonal phase which is agreement with work of Ezekoye, Ighodalo , Ezekoye , Emeakaroha , Ezema and Offor [7]. Study of XRD pattern of CdZnS thin films of figure 2 (CAS) shows that thin film synthesized had preferential normal spinel orientation along the (JCPDS: 03-065-2887, a = 5.8320Å). The orientation of CdS thin films located around two theta 26.450 are with reflection of (002); other peaks located are around two theta 30.434, 44.324 and 51.961 corresponding to the reflections of (200), (110) and (112) with low intensities.as in the same figure 1B (JCPDS: 00-043-1127, a = 5.9680Å). This had orientation located around two theta = 29.952 and 30.132 with reflection of (110) and (012) respectively.

Figure 2 Show typical XRD patterns of synthesized cadmium zinc sulfide (CdZnS) thin films by SILAR method representing as- deposited and thermally annealed at 673 K respectively. The CdZnS thermally treated at 400C showed a significant peak shift which indicated that thermal treatment have effect on the deposited films and as well the diffraction peaks indicate the presence of ternary CdZnS compounds. These were also in agreement with work of (Dzhafarov, *et al.*) [8]

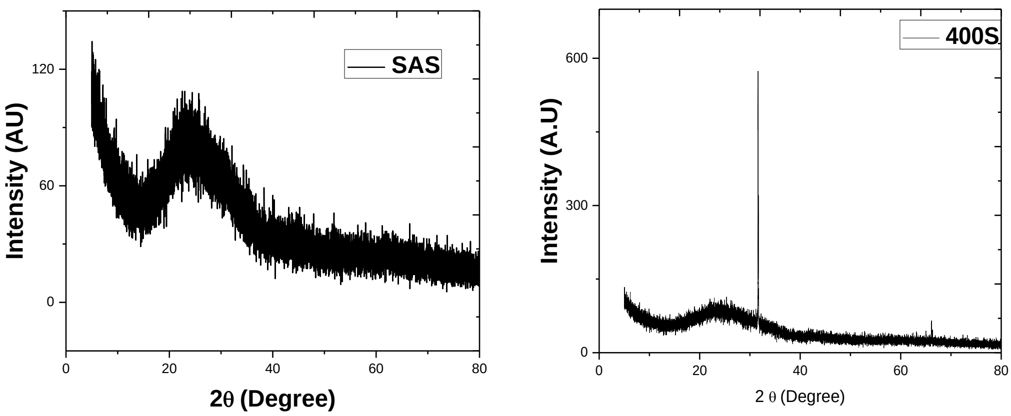


Fig. 2: XRD pattern of SILAR deposited CDZnS thin films or as-deposited and thermally annealed at 673K

3.2 Optical Properties

The plot of absorbance against wavelength is displayed in fig.3 (A and B). The plot indicates that all the deposited films are absorbing in the visible region of the spectrum. The plot also show that the absorbance decreased with increasing wavelength. However the trend is less pronounced in the films deposited using the SILAR technique. The difference could be attributed to the procedures involved in each technique. The highest absorbance value recorded in the CBD deposited film is 0.9 while the highest value of absorbance recorded in the SILAR deposited film is 0.38. Generally, the absorbance of CdZnS thin films decreases continuously with increase in wavelength from visible region to near infrared (NIR) region. The properties of high absorbance in the UV region make the films good materials for the construction of poultry roofs and walls and coating for eyeglasses for the protection of young chicks and the skin around the eyes respectively. This protects the skin from the sun's burning due to UV radiation while the admittance of infrared radiation helps to warm the inside of the poultry house, which is needed for young chicks [4, 8]. These films are useful as a photo catalyst only when the wavelength of light is shorter than 387nm.

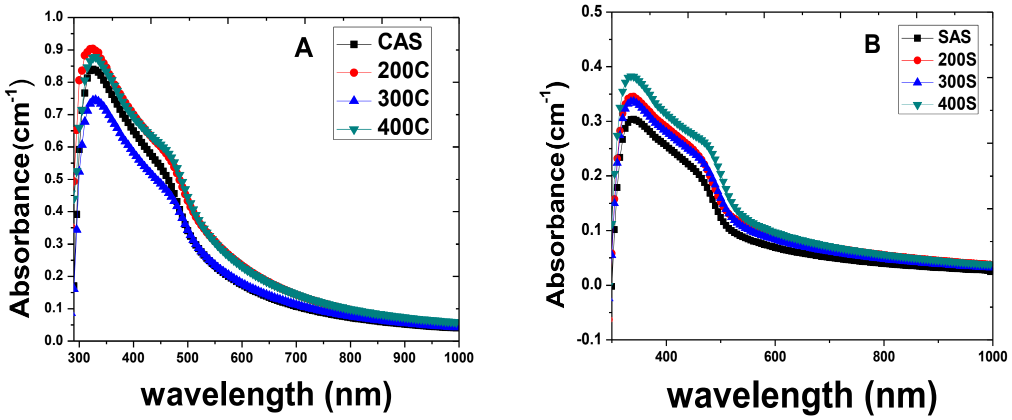
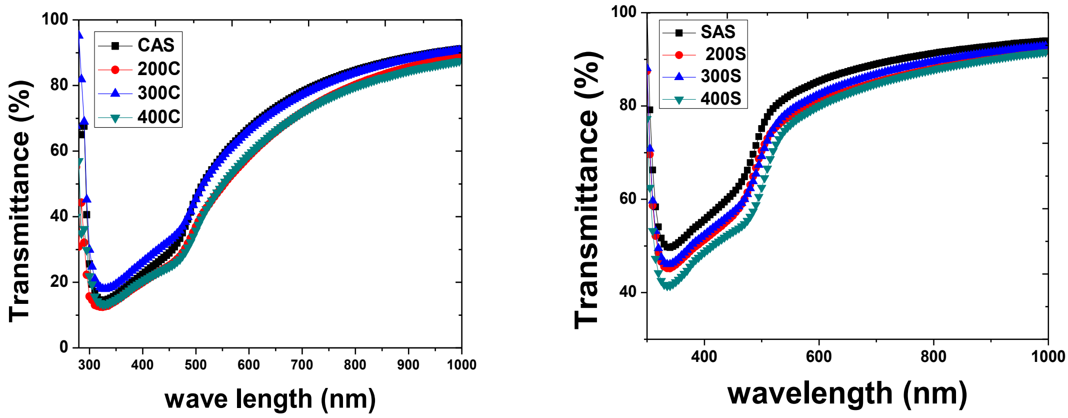


Fig.3 (A and B): Plot of Absorbance against Wavelength for CBD and SILAR deposited films respectively

Optical transmittance is generally complex and depends on the coefficient of absorption [4,9]. The variation of the transmittance against wavelength for the CdZnS thin films deposited by the CBD and SILAR methods is shown in figures 4 A and B. From the Swanepole's method which is based on the Manfacer theory, the envelope of the interference maxima and minima occurs in the spectrum [5, 10, 13]. The plots indicates that within the lower wavelength, the films displayed low values of transmittance. The plots equally show that the transmittance increased with lower energy. It can also be deduced from the graphs that all the films were transparent in the longer wavelength region irrespective of the annealing temperature and deposition method. However, the range of transmittance for the CBD deposited film is 18-90 % while the range of transmittance for the SILAR deposited is 40- 95%. The values of transmittance in each case is close agreement with the works of other authors [3,11].



A B

Fig. 4 (A and B): Plot of Transmittance against Wavelength for CBD and SILAR deposited films respectively

It is evident from the plot that the transmittance varies with annealing temperature. This could be attributed to the increase in grain size associated with thermal treatment.

The index of refraction n at transmittance region where the coefficient of absorption is zero is given by

$$n = \sqrt{[N + (N^2 - S^2)^{1/2}} \quad (3)$$

$$\text{Where } N = \left(\frac{2s}{T_m}\right) - 0.5(s^2 + 1) \quad (4)$$

In equation 4, T_m is the envelope function of the transmittance minima and ,s, is the refractive index of the substrate in this case glass.

The plot of refractive index against wavelength is shown in fig.5 (A and B) for the CdZnS thin film deposited by CBD and SILAR method .The index of refraction was found to be in the range of 1.05 – 1.15 for CBD deposited film and 1.5 – 2.65 for SILAR deposited film. The plot equally showed that as the annealing temperature increases the index of refraction increases. However, the SILAR deposited film displayed a lot of slopes and steps in the curves when compared to the CBD deposited film. The range of n obtained were in close agreement with that obtained by Agbo, Nweke, and Nwofe. [11]

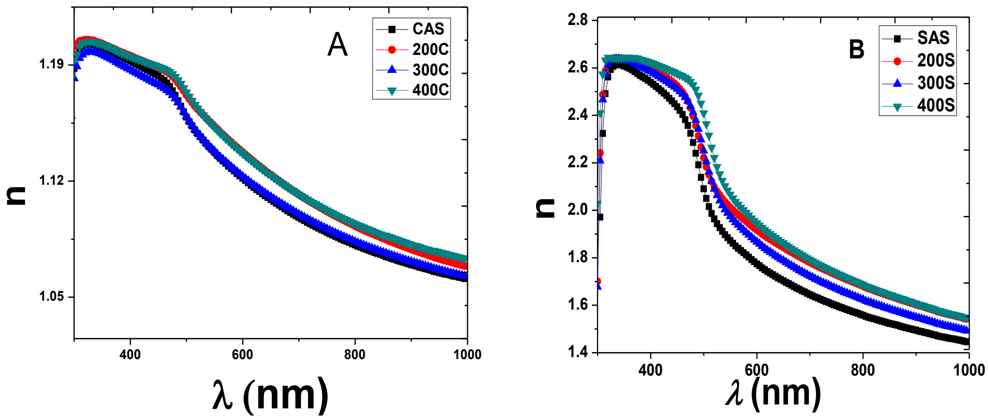


Fig. 5 (A and B): Plot of Refractive index against Wavelength for CBD and SILAR deposited films respectively

The dielectric constant (real and imaginary) can be evaluated with the help of the refractive index n and the extinction coefficient k. The real part of the dielectric constant is evaluated using the relation

$$\varepsilon_r = n^2 - k^2 \quad (5)$$

While the imaginary dielectric constant can be calculated using the relation

$$\varepsilon_i = 2nk \quad (6)$$

The spectrum of real dielectric constant for the CBD and SILAR deposited CdZnS thin film is shown in fig 6 A and B. The plot indicates, that the real dielectric constant ϵ_r for CBD film ranges from 0 .50 to 0 and were almost independent of the annealing temperature. However in the SILAR films, the range of ϵ_r is between0.5 to 0.6. Here, the ϵ_r, varied with annealing temperature such that as the annealing temperature increases, the ϵ_r increases. It is also evident from fig 7A and B that the CBD film displayed better filtered property. The plot of imaginary part of the dielectric constant is displayed in figures 7A and B. The plot indicates that the dielectric constant (imaginary) were inversely proportional to the wavelength. The highest value of ϵ_i recorded for the CBD deposited film is -5.8 while the highest value recorded for the SILAR deposited film is -6. Films having such value of imaginary dielectric constant will tend to have low value of loss factor (Azizar, Rahman and Khan , 2010), Thus are good candidate for photonic applications.

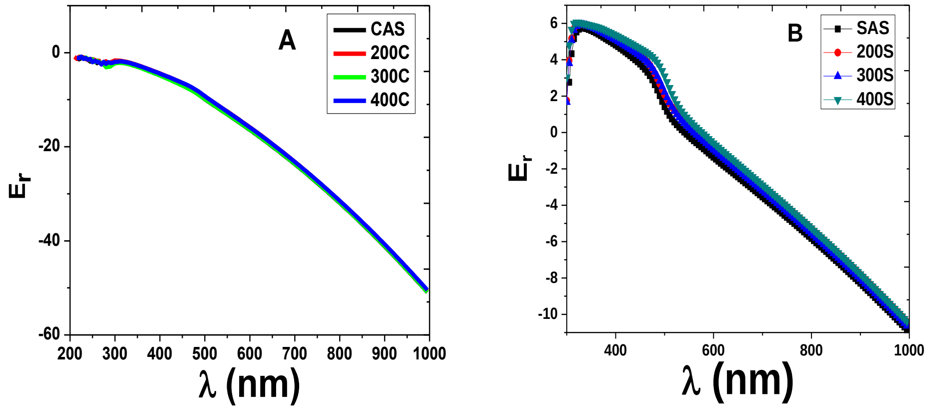


Fig. 6 (A and B): Real dielectric constant against Wavelength for CBD and SILAR deposited films

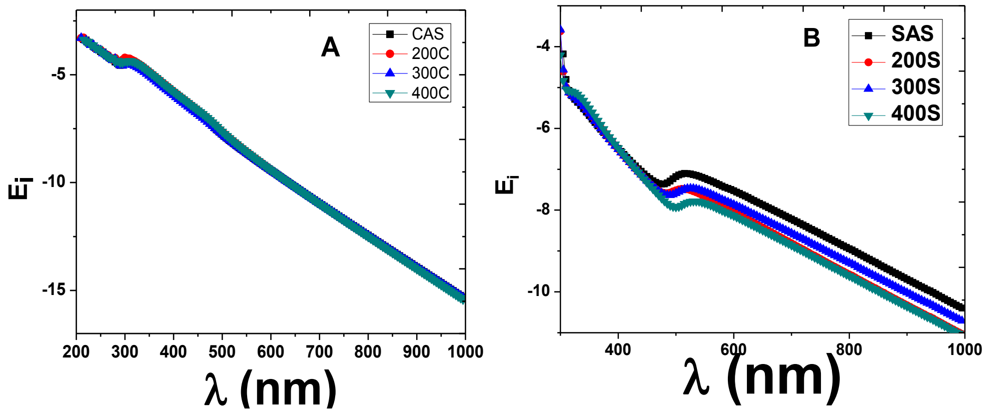


Fig. 7 (A and B): Imaginary dielectric constant against Wavelength for CBD and SILAR deposited films

4. Conclusion

High absorbance along the UV, visible region, especially for the films deposited by CBD with higher absorbance magnitude than that deposited by SILAR method which decreases as wavelength of the spectra increases. This property makes the films a good material for coating eyeglasses for safeguard from sunburn produced by UV radiations and electro chromic materials in smart windows devices. These films also show high reflectance in visible region which decrease as the wavelength increases, especially that deposited by CBD. This shows that deposition method and thermal treatment have effect on the properties of the deposited film. The characteristics of the deposited films shows that they are good materials for applications in laser diodes and Photovoltaic applications. The properties of films synthesized possess the same quality as films reported by other scholars.

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