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Effect of cadmium ion source on the properties of CDS thin film grown by chemical bath deposition

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ABSTRACT

Cadmium sulphide (CdS) thin films were deposited from different cadmium salts by acidic chemical bath deposition (CBD) method. The effect of cadmium source on CdS thin films by thickness, optical properties, structural properties, functional groups and surface morphology with elemental composition were studied. Film growth rate and band gap were found to the sensitive to the Cd source used. The transmittance data analysis indicates that the optical band gap ranging from 2.37 eV to 2.43 eV was deduced. The XRD study reveals that the films were cubic in nature. SEM with EDS data shows that all the particles were spherical and average atomic ratio of Cd/S increases with the decrease in particle sizes.

Introduction

Cadmium sulphide is a group II – VI semiconductor having a wide bandgap around 2.4 eV that gained in many optoelectronic properties and applications [1, 2]. CdS has been used as an efficient window layer for the fabrication of supersaturates type solar cell structure due to its high transmitivity and low resistivity [3, 4]. Thin films of CdS hold promise in photovoltaic applications as window coatings in many types of solar cells with absorber materials such as Cu(In, Ga)Se [5], CdSTe [6] or $CuInSe_2$ [7] and for thin film transistors [8].

CdS thin films have been prepared by various deposition techniques such as sputtering [9], vacuum evaporation [10], spray pyrolysis [11], electrodeposition [12] and chemical bath deposition [13]. Among these various methods, chemical bath deposition technique is a simple, low cost, convenient and useful for large areas industrial applications. Another advantage of CBD method with respect to other methods is that the film can be deposited on different kinds, shapes and sizes of substrates [14].

In the present study, chemical bath deposition method has been employed for the deposition of CdS thin films by different cadmium salts (Cadmium acetate, Cadmium sulphate and Cadmium chloride) as a Cd^{2+} source on glass substrate. The aim of the present paper is to explore the effect of cadmium ion sources on the properties of CBD-CdS thin films. The thickness, structural, optical and morphological properties CdS films has been discussed.

Experimental Details

Materials

All reagents are analytically pure cadmium acetate, cadmium sulphate, cadmium chloride, thiourea, were of analytical grade and were used straightly. Other chemicals such as ammonia hydroxide solution, triethylamine and acetone were used without further purification and water used throughout was de-ionized double distilled water. CdS thin film was deposited on the commercial glass slides (75 mm x 25mm x 2mm) were used as substrate. Before deposition, the substrates were washed by soap solution and subsequently kept in diluted hydrochloric acid for 30 minutes and then cleaned with de-ionized water followed by rinsing in acetone and finally dried at 80°C in an oven.

Preparation of CdS thin film

Two concentrations of cadmium (0.1 and 0.5 M) and thiourea (0.2 and 1 M) sources were prepared. Typically, a 200 ml reaction solution was prepared at room temperature in a closed vessel. The pH value of the solution was adjusted to about 10.5 ± 1 by the ammonia solution. Three separate solutions were prepared at 0.1 M of $Cd(CH_3COO)_2.2H_2O$, $CdSO_4.8H_2O$ and $CdCl_2.2H_2O$ respectively was diluted by 40 ml of distilled water using a magnetic stirrer and 10 ml of triethylamine for complexing agent, which controls the precipitation of metal ions, So as to reduce the free metal ion concentration. The solutions reached at 75° C add 0.2 M thiourea, the solution to change like pale yellow color. The glass substrates were dipped into the solution and taken out from the reaction solution one by one with different time interval (30 min and 45 mins). The same procedure was adopted for the preparation of CdS film with 0.5 M Cd and 1 M thiourea.

Characterization method

Film Thickness was measured by gravimetric weight difference method using high precision digital sensitive microbalance (SHIMADZU –AY220). The optical transmission spectra were recorded at room temperature by using a double-beam Shimadzu UV 1800 Spectrophotometer in the wave length range 200 – 800 nm and the X-ray diffraction patterns were recorded using the computer controlled Rigaku D XRD unit is the scanning range as 2θ from 20 - 80° with Cu-Kα (λ = 1.5406

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Å) radiation. Fourier Transform Infrared spectra of samples were performed using a Perkin – Elmer FTIR spectrophotometer model RX1 in the region of 4000 – 400 cm^{-1} with a resolution ±4 cm^{-1}. Morphology and composition of the films were analyzed using by a Scanning electron microscope (JEOL JSM – 5610 LV), coupled to an Energy dispersive X-ray spectroscopy (OXFORD-EDS).

Results and discussion

Kinetic study

CdS films deposited in an alkaline solution [15], an acidic CBD process involves the following steps

Cadmium dissociation

$Cd(CH_3COO)_2 \rightarrow Cd^{2+} + 2CH_3COO^-$ cadmium acetate dissociation → (1)

$CdSO_4 \rightarrow Cd^{2+} + SO_4^{2-}$ cadmium sulfate dissociation → (2)

$CdCl_2 \rightarrow Cd^{2+} + 2Cl^-$ cadmium chloride dissociation → (3)

Thiourea decomposition

$CS(NH_2)_2 + 2\ OH^- \rightarrow S^{2-} + CH_2N_2 + 2H_2O$ → (4)

Formation of CdS

$Cd^{2+} + S^{2-} \rightarrow CdS$ → (5)

CdS thin film formation is a thermally activated process, so thermal decomposition of metastable complex releases the metal ions while thiourea hydrolyzes is alkaline solution to yield S^{2-} ions. As the ionic product of Cd^{2+} and S^{2-} ions exceeds to solubility product of CdS then deposition of CdS film take place. The films are found to be homogeneous, well adherent to the glass substrate and dark yellow in color.

Thickness measurement

The film thickness was calculated by the weight gain method using the formula as t = M/AD, where thickness t, mass of film M, area A and density D. Fig. 1 shows the film thickness as a function of deposition time (30 and 45 mins), where bar A, B and C indicating the results using different cadmium salts [A= $Cd(CH_3COO)_2$, B= $CdSO_4$ and C= $CdCl_2$]. It is observed that the film thickness is increased with increase in molar concentration of ions, ie., 0.5 M concentration of each Cd salt film thickness are greater than 0.1 M concentration of respective Cd salt films and also the film thickness is increased with increase in the deposition time. So the lower value of molar concentration 0.1 M with 30 mins is kept constant throughout the characterization studies. The effect of cadmium salt on the growth rate of the film has been studied. The result shows that the $Cd[Cl]_4^{2-}$ complex has a much higher stability constant than $Cd[CH_3COO]_2$ or $Cd[SO_4]_3^{4-}$ complexes. This means much slower release of Cd ions and consequently a much thinner CdS film when $Cd[Cl]_4^{2-}$ was used. The same argument can be used to explain why the highest thickness was obtained when $CdSO_4$ was used. Actually, the order in which the stability constant decreased was exactly the same order the film thickness increased [16]. Therefore the highest thickness obtained in the case of $CdSO_4$ and the least thickness obtained in the case of $CdCl_2$ case.

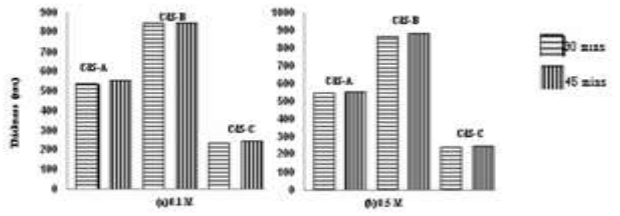

Figure 1. Variation of Film thickness with a) 0.1 M and b) 0.5 M concentration

Optical Properties

The optical transmittance spectra of all CdS films deposited from different cadmium salt in the wavelength 200 – 800 nm are shown in Fig. 2. It clears that, all films have high transmission, with the transmission in the CdS-C case being better than that of the other two films. The transmittance in the high-energy region extends up to 300 nm, and this is an indication of disorder effects or presence of amorphous component in the film based on XRD evidence. The average transmittance in the wavelength range 450 – 800 nm has values larger than 86 % as shown in figure, which is a good solar application [17].

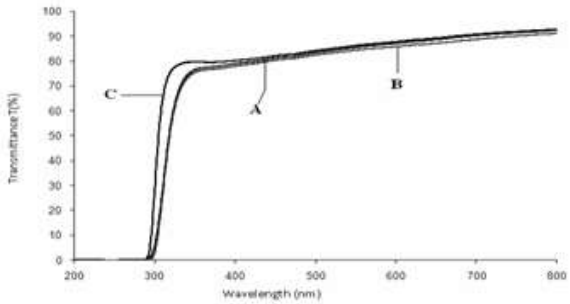

Figure 2. Optical transmittance of CdS thin films

The energy band gap (Eg) is determined by plotting a graph of $(\alpha h\nu)^2$ versus hν is shown in Fig.3 using the relation. $\alpha h\nu = A(h\nu - Eg)^n$, where A= constant hν = photon energy and α is the absorption coefficient. It shows that the optical band gap (Eg) of the CdS-C based film is the highest (2.43 eV) and the band gap of CdS-B based film is the lowest (2.37 eV). The CdS-A based film has an intermediate band gap (2.41 eV). These band gap dependence on Cd source, which is in good agreement with the reported values of band gap for CdS [18]. The linear nature of plot indicates the presence of the direct optical transition.

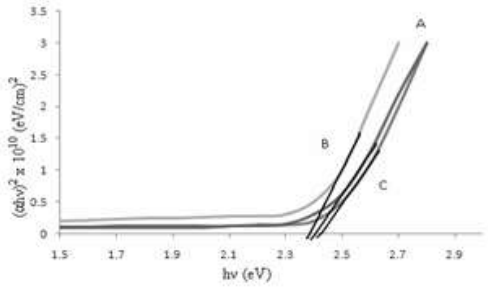

Figure 3. Plot of $(\alpha h\nu)^2$ Vs hν of CdS thin films

Structural analysis

The XRD patterns of "as-deposited" CdS thin film A, B and C are shown in Fig. 4. XRD results give the relative low crystal quality of the as-deposited CdS thin films. All films are cubic in structure. The film CdS-A is cubic with a main reflection (1 1 1) appeared at 26.580° peak is confirmed that cubic structure. Simillarly in CdS-B (1 1 1) at 26.640° and in the sample CdS-C (1 1 1) at 26.800° peaks are confirmed the all CdS films are cubic structure. However, when the relative intensities are carefully investigated, it's obvious that the degree of texture along the (1 1 1) orientation increases in order C, A and B based CdS film. The broad background is due to the amorphous glass substrate and also possibly due to some amorphous phase in CdS thin films. The average crystallites sizes of the films are calculated using the Scherrer formula

$D = K\lambda / (\beta \cos \theta)$

Where k is the Scherrer's constant (~ 0.9), λ is the wavelength of X-ray used, β is full-width at half-maximum and θ is the Bragg's

angle. The crystalline sizes in films of different thickness are of the order 90 – 400 nm and are in good agreement with the reported values [19].

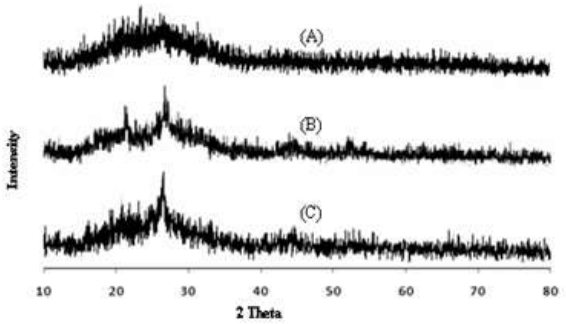

Figure 4. XRD pattern of CdS thin films

Fig.5 shows the FTIR spectra of CdS sources A, B and C. The broad band at 3429 cm^{-1} in A, B, C is due the stretching vibrations of O-H bond and bending mode of water molecules appeared at 1645 cm^{-1}. These band are due to the strong interactions of water with CdS is reflected. The band in the range 1090 – 1070 cm^{-1} is due to the asymmetric stretching vibration of SO_4^- group. The absorption band near 1400 cm^{-1} resulting from an NH_4^+ bending vibration. A strong and broad band at 730 – 736 cm^{-1} in all spectra is due to the stretching vibration of the Cd-S molecules [20]. There is a band at 614 cm^{-1} is due to the stretching frequency of Cd-S bond.

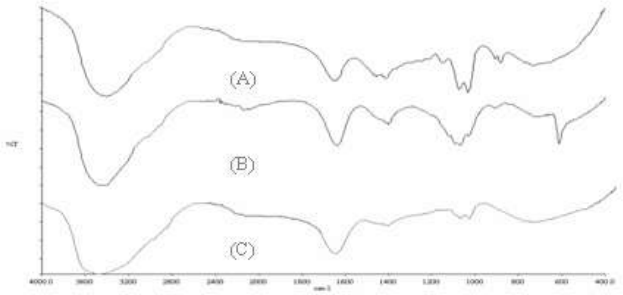

Figure 5. FTIR spectra of CdS A, B and C

Morphology and Elemental analysis

Scanning electron microscopy is convenient technique to study the microstructure of thin films. Fig. 6 shows the surface morphology of CdS thin films A, B and C at x 2000 and x 10000 magnification deposited from different cadmium ion source. It is observed that the "as – deposited" films are uniform throughout all the regions and without any void, pinhole or cracks and that they cover the substrates well. CdS films A, B and C have spherical particles of around 500, 800 and 200 nm in size respectively. The surface of the CdS-C films deposition is compact and smooth, showing a granular structure with well defined grain boundaries. It indicates that the CdS-C (cadmium chloride salt) is to diminish voids on the CdS films. The CdS-B thin films have the highest growth rate and thus the largest particle size when compared the CdS-A and CdS-C. The voids with different sizes ranging from 50 nm to 300 nm are observed in CdS - B, indicating low packing density of the films. The uniformity of the films can be controlled by using parameters such as variation of substrate, deposition time, and reactant concentration and deposition temperature. However, the particles in the CdS-C thin films are more compact than the other samples [21].

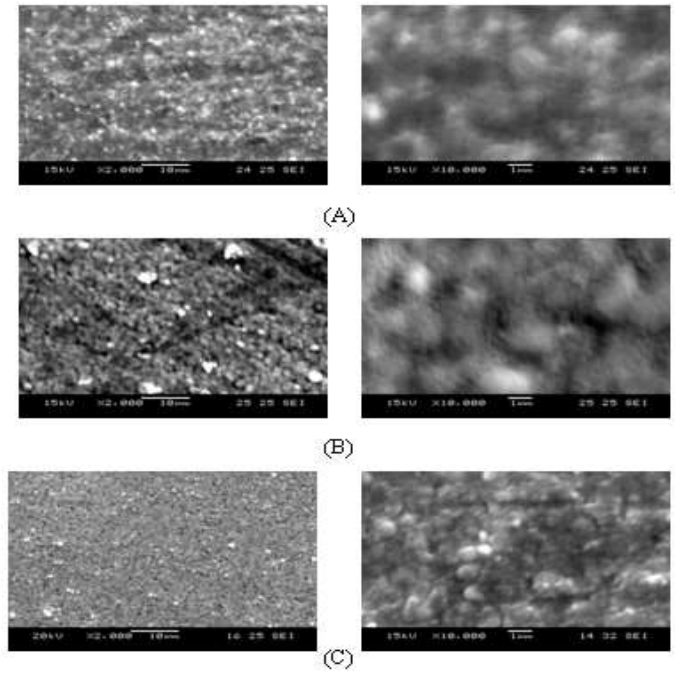

Figure 6. SEM images of CdS thin film.

Fig. 7 shows the EDS (Energy dispersive spectroscopy) result of the CdS thin film A, B and C. It has been used to determine the composition of CdS thin films. EDS analysis gives the presence of cadmium and sulphur in CdS film as Cd=54.90% and S=45.10% for CdS-A, Cd=53.84% and S=46.16% for CdS-B and Cd=56.46% and S=43.54% for CdS-C. It confirms that the films are cadmium rich. Besides the Cd and S peaks, line for Si and O that could come from the glass substrate. The atomic ratio Cd/S % of CdS samples A, B and C are 1.22, 1.17 and 1.30 respectively.

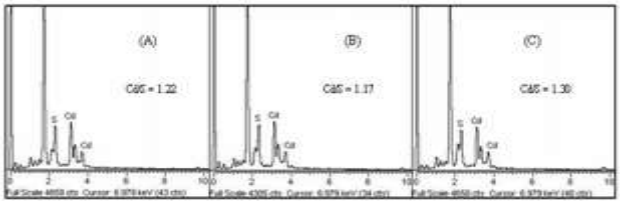

Figure 7. EDS spectra of CdS thin film

Conclusion

Cadmium Sulphide thin films were prepared by chemical bath deposition technique on glass substrates using three different cadmium ion sources with two concentrations (0.1 and 0.5 M). The film thickness dependence on the Cd source used in the deposition process. The least thickness obtained was in the $CdCl_2$ than other two films. All the films exhibit optical transmittance about 80% in the range of wavelength 400 – 800 nm. The band gap energy of the film was found to be in the range of 2.37 – 2.43. CdS-Cl thin film has relatively higher band gap and better quality. A slight increase in the band gap energy (CdS-C) due to cadmium chloride salt and this is also an advantage for solar cells. XRD studies showed that a cubic structure was present and grain size between 90 and 400 nm have been obtained. The FTIR spectral data supports the presence of a strong band at 735, 732 and 736 cm^{-1} has been assigned to Cd-S stretching. From the SEM study, all the particles are spherical and the different grains with in films are found to about few hundred nanometer. The crystallites sizes measured by XRD studies are found to be within 90 – 400 nm and are within 200- 800 nm from SEM. EDS data indicates the

presence of cadmium / sulfur for all the deposited films. The average atomic ratio of Cd/S increases with decrease in particle size.

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