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Deposition and Characterization of Spray Pyrolytic Cadmium Sulphide Thin Film

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Abstract: Precursor solutions of cadmium chloride (CdCl_2) and thiourea $[(\text{NH}_2)_2\text{CS}]$ were used to prepare Cadmium sulphide (CdS) thin film on glass substrate by chemical spray pyrolysis technique at the substrate temperature of 623 K. The structural properties of the film were investigated through the analysis of X-ray diffraction pattern (XRD), scanning Electron Microscope (SEM) and Energy Dispersive Analysis (EDAX). The growth of crystal became stronger and more oriented as seen in the X-ray diffraction pattern. This diffraction analysis revealed the polycrystalline nature and the preferential orientation growth of CdS compound having hexagonal structure along (002) plane. The size of the cadmium sulphide crystallite with nano dimension 27.73 nm was determined using the Full Width Half Maximum value of the Bragg peak. The surface morphology had been observed on the surface of this film using scanning electron microscope. The stoichiometric property was determined using Energy Dispersive Analysis X ray spectrum and the optical absorption and transmittance spectra have been recorded for this film in the wavelength range 300–1100 nm. The optical band gap energy is found to be 2.3 eV with direct allowed band-to-band transition for film deposited at 623 K.

Keywords: hexagonal; crystallite size ; stoichiometric ; transmittance; band gap.

1 Introduction

The yellow colored inorganic compound CdS and it occurs in nature with two different crystal structures as the rare minerals greenockite and hawleyite, but it is more prevalent as an impurity substituent in the similarly structured zinc ores sphalerite and wurtzite, which are the major economic sources of cadmium. The compound that is easy for isolation and purification is the key component for the chosen system [1]. Chalcogenide semiconductor thin films are being intensively investigated for low-cost photovoltaic and optoelectronic applications. Cadmium sulfide is commonly used as *n*-type semiconducting layer for hetero junction thin films solar cells. Multilayered CdS films can be employed in the manufacture of the optoelectronic devices [2]. Among the II–IV semiconductor compounds, cadmium sulphide belongs a special physical properties such as photoconductivity in visible and near ultraviolet spectral regions and high optical transparency has been extensively studied [3]. Thin films are well known for their applications in many technological based industries as materials for many semiconducting devices CdS and CdSe are suitable candidates used in manufacturing of light

dependent resistors sensitive to visible and near infrared light. It can be combined with other layers for use in certain types of solar cells in thin film form. Also it is the first semiconductor materials to be used for thin-film transistors [4]. The interest in compound semiconductors for thin-film transistors largely demanded after the emergence of amorphous in current technology. The films of Cadmium Sulfide has been used for piezoelectric and have been used as transducers which can operate at frequencies in the Giga Hertz region [5, 6]. It can also be used for electronic goods, displays of light emitting diodes, liquid crystal display, optical coating, luminance, magnetic and optical data storage, antistatic coatings, hard surface coatings, pigments. CdS thin films are regarded as one of the most promising materials for hetero junction thin film solar cells with optical band gap of 2.35 eV has been used as the window material together with several semiconductors such as Cadmium Telluride [7], Cu₂S [8], InP [9] and CuInSe₂ with 14 to 16% efficiency [10]. Chemical deposition of thin films has advantage as a low deposition cost technique to realize economic and large area devices on various aspects of chemically deposited thin films. The growth mechanism

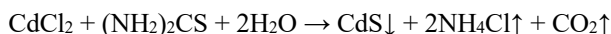
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has an experimental advantage of varying the parameter such as deposition rate, composition and temperature [11].

The deposition of CdS film has been explored by various techniques, such as thermal evaporation [12], sputtering [13], molecular beam epitaxy [14], spray pyrolysis [15], chemical bath deposition [16]. Chemical spray pyrolysis technique is a method of growing thin films of certain materials on a glass substrate and it has been identified as a low cost process suitable for the preparation of large area thin films. In this paper, it is intended to prepare and characterize cadmium sulphide thin film on glass substrate at suitable thermal energy and molarity concentration using the precursor's solutions consists of cadmium chloride and thiourea of 0.1 M and 0.2 M respectively.

2 Experimental details

The precursor solutions of cadmium chloride and thiourea were dissolved separately in a solution containing de-ionised water and isopropyl alcohol in proper ratio. The molarities of cadmium and thiourea solutions were 0.1 M and 0.2 M, respectively. A few drops of concentrated hydrochloric acid were added for complete dissolution. The precursor solutions were sprayed at the substrate temperature of 623 K. The other deposition parameters like solution flow rate, carrier gas pressure and nozzle to substrate distance were kept as 3 ml per minute, 0.7 kg/cm² and 20 cm respectively. After deposition of this film, it was allowed to cool to room temperature, cleaned with distilled water, dried and then stored in a dessicator. The atomization of the chemical solution into a spray of fine droplets is effected by the spray nozzle, with the help of compressed air as carrier gas. When the solution was sprayed the following reaction takes place at the surface of the heated substrate



The substrate is glass having 2.5 cm x 1.5 cm x 0.1 cm, and is placed in a fitted socket at the surface of a substrate heater when sprayed. The heater is a cylindrical stainless steel block furnace electrically controlled to an accuracy of $\pm 5^\circ\text{C}$. The colour of the deposited thin film is light yellow and adheres to the substrate. This yield is a uniform growth of CdS film on glass substrate and their structural and optical properties were characterized. The X-ray diffraction pattern of the film was recorded with a JEOL Pa Xray diffractometer operating with 0.15406 nm monochromatized Cu α radiation at 40 kV and 30 mA. Transmission and absorption coefficient spectra of the prepared sample were measured by normal incidence of light, using a double beam UV-3101 Shimadzu spectrophotometer in the wavelength range 300 to 1100 nm.

3 Results and Discussions

Figure 1 shows the XRD diffraction profile of the spray pyrolysed CdS thin film with the substrate temperature of 623 K. The diffracted peak was obtained with the crystallinity with the preferential orientation growth of film having hexagonal structure along (002) plane diffracted with prominent Bragg peak at the 2θ position is 26.52° . The interplanar spacing corresponding to this peak is determined to be 3.40 \AA on the substrate plane with standard X-ray diffraction data, (JCPDS file no. 96-901-1664) obtained a single phase of hexagonal phase of CdS thin film. Authors Mary pradeepa et al. [17], Sundus M A Aldujayli et al. [18] observed the crystalline plane of CdS was present in prominent peak of XRD which could be indexed hexagonal structure of CdS and it had a good agreement values. The crystallite size can be determined from the (002) diffraction line using the Scherrer formula [19]:

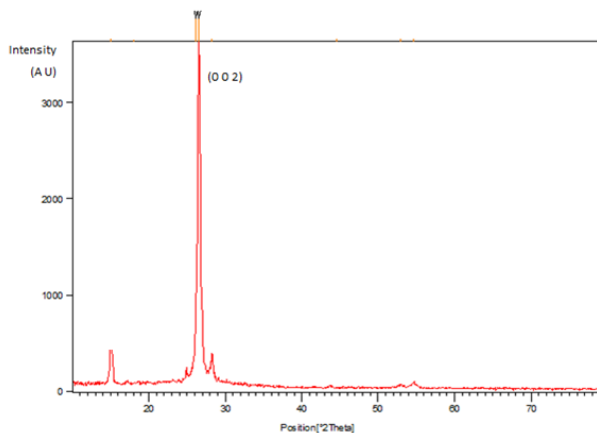


Fig. 1: XRD pattern of CdS thin film at 623 K.

Crystallite size was determined using $K\lambda/\beta \cos \theta$, where β is the full width at half maximum (FWHM) of the peak corrected for instrumental broadening; λ is the wavelength of the X-ray, and K is the Scherrer constant (0.9), which generally depends on the crystallite shape. The crystallite size was calculated in this spray pyrolysed film for the prominent peak is 27.73 nm. These crystallite size are similar to those obtained by Sundus M A Aldujayli et al.

The SEM photograph of the spray pyrolysed CdS thin film deposited with the temperature 623 K is shown in fig 2. It reveals that the average size of grain is 55 nm. Agglomeration of grain is not uniform throughout the film. As a result, grains with different dimensions are seen on the surface. The bright spots indicate more number of secondary electron being emitted from the surface. In contradiction dark area correspond to very less number of secondary electron emissions. In the study of particle morphology it was understood that it is several particles that are not perfect sphere. The crust forms around the droplet the trapped solution within the particle continuous

to evaporate. Once the particle exits the hot reactor, the trapper vapor condenses inside the particle.

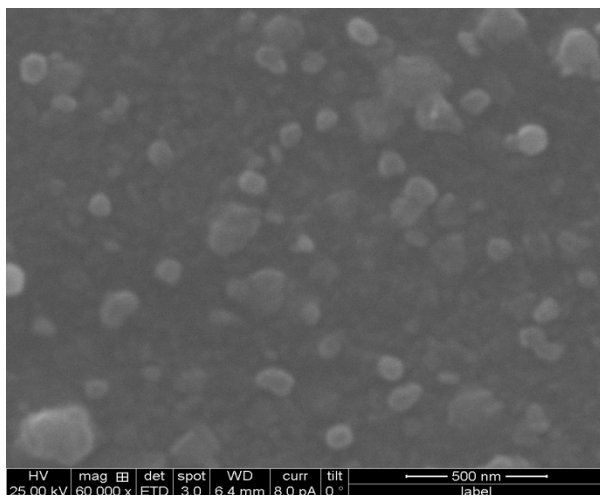


Fig.2: SEM image of CdS thin film with 60 k magnification at 623 K.

EDAX analysis was performed for the elemental compositional analysis of the CdS film.

The EDAX spectrum observes the characteristic peak corresponding to the binding energy of the elements. Figure 3 shows the EDAX spectrum showing strong peaks for Cd and S. From the observed EDAX analysis, the average atomic percentage of Cd : S was found to be almost stoichiometric in nature with the Cd% of 52 and S% of 48 which is in agreement with reported values [20].

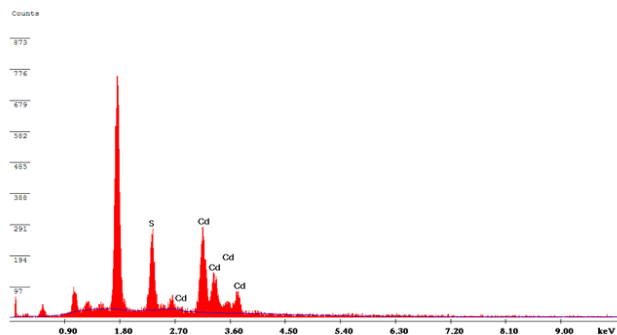


Fig.3: EDAX spectrum of CdS thin film at 623 K.

The surface morphological studies exhibited irregular structure in the film. The surface elemental compositional analysis of the film is carried out and shows near stoichiometry. The cation rich material shows (n-type) a good photocatalytic activity in the form of hetero junction [20].

To study the optical properties of the materials, the optical absorption spectra of this spray pyrolysed CdS thin film is recorded in the wavelength range 300 - 1100 nm at substrate temperature 623 K. From the absorbance spectrum the variation of the absorption coefficient α with respect to wavelength is calculated and plotted as shown in Fig.4.

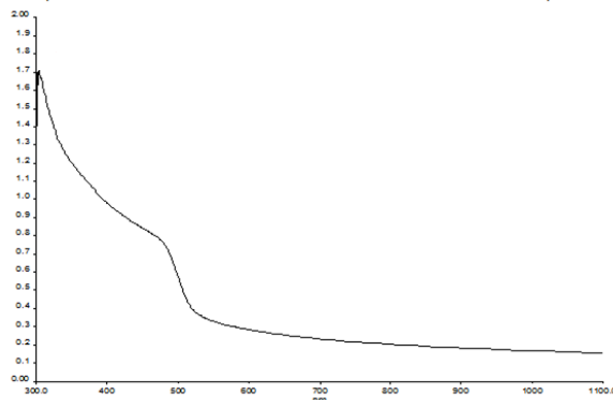


Fig. 4: Absorbance spectrum of CdS thin film at 623 K.

It shows that the value of absorption coefficient α decreases exponentially as the wavelength increases from 500 to 1100 nm. Hence the optical transmittance (T) with respect to wavelength of CdS thin film was observed that there was a considerable increase in transmittance nearly 70 percent is indicated in Fig 5, which may be due to increase in crystalline nature and this result is attributed by XRD analysis.

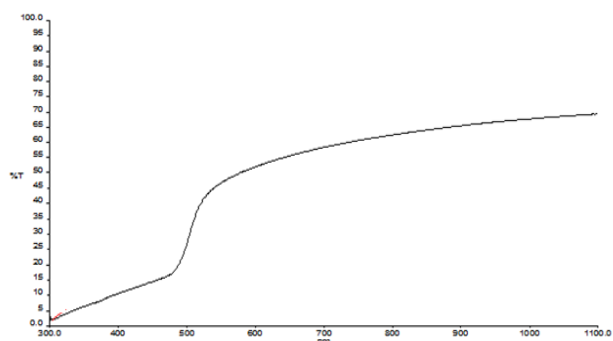


Fig.5: Transmittance spectrum of CdS thin film at 623 K.

In the high photon energy region, the energy dependence of the absorption coefficient 10^4 cm^{-1} suggests the occurrence of direct optical transition, which is investigated by the relation [21]. A graph is plotted between $(\alpha h\nu)^2$ and $(h\nu)$ is shown in fig 6, gives a direct allowed band gap of 2.3 eV for CdS. Previous workers [22-25] reported the wide optical direct band gap of CdS thin film as 2.3 eV.

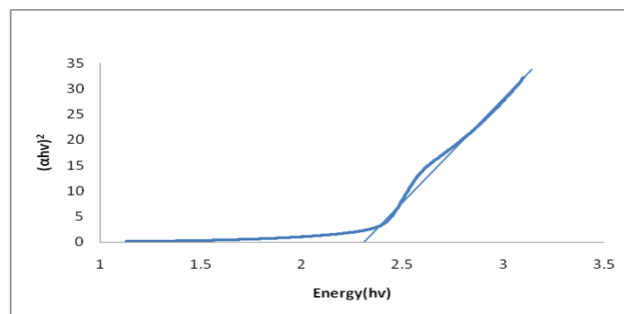


Fig. 6: Direct band gap plot of CdS thin film at 623 K.

4 Conclusions

The CdS thin film was prepared by spray pyrolysis technique on glass substrate using the precursor solutions of cadmium chloride and thiourea. Film has been characterized using structural and optical measurements. The film has hexagonal structure with a preferential orientation of (002) plane. The crystallite size measured by XRD studies was found to be 27.73 nm. Energy band gap was deduced from the optical absorption spectra; they show a direct transition in the range 2.3 eV, which suggest that this CdS thin film could be a potential candidate for opto-electronic as well as thin film solar cell devices.

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