SYNTHESIS AND CHARACTERIZATION OF CADMIUM CHALCOGENIDE CdX (X = S, Te) THIN FILMS

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ABSTRACT

Thin films of cadmium chalcogenides, CdS and CdTe, on glass substrates were prepared by chemical spray pyrolysis technique. The structural characterization of the films was performed by XRD, which confirmed that the films were of CdS and CdTe, respectively. XRD studies also showed that CdS crystallites were aligned with a preferred orientation along (002) plane whereas CdTe crystallites exhibited a preferred orientation along (111) plane. The optical characterization of these films was carried out using UV/visible spectroscopy. Both CdS and CdTe were found to behave as direct band gap semiconductors in these thin films. From the UV/Vis spectral data, the optical bang gap of both these thin film was determined.

Key words: Cadmium chalcogemide, Thin film, CdS, CdTe, Spray pyrolysis.

INTRODUCTION

In recent times, there has been a rapid development in the field of II–VI semiconductors for their immense use in thin film solar cells. With worldwide focus on alternative and green sources of energy, these thin film semiconductors have gained enormous importance in research for their potential applications as low cost, energy efficient and zero pollution solar cells. Thin films of cadmium sulphide (CdS) and cadmium telluride are one of the most important II-VI semiconductors which find very useful applications in optoelectronic and piezo-electronic devices. Because of their intermediate energy band gap, reasonable conversion efficiency and stability, it makes them one of the most widely used materials for CdS/CdTe heterojunction solar cells[1-9]. Thus, studies on the physical properties of the thin films are very pragmatic and useful, both for academic purpose as well as for commercial exploitation.

A number of techniques are available to prepare thin films of CdS and CdTe, such as

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physical vapour deposition (PVD), chemical vapour deposition (CVD), Successive Ionic Layer Adsorption and Reaction (SILAR), electro deposition, thermal evaporation etc.[1-11]. All these methods have sophisticated requirements in terms of high vacuum, precise temperature control and high cost of equipments. In contrast, the chemical spray pyrolysis technique is relatively simple and utilizes low-cost equipments, without requiring any stringent conditions of high vacuum or temperature for film preparation. The spray pyrolysis film deposition consists of spraying of a solution containing a soluble salt of the cation of interest onto a heated substrate[12,14]. It can conveniently be used for preparing thin films of any desired composition under controlled conditions. Further more, unlike closed vapour deposition methods, spray pyrolysis technique does not require high quality targets and/or substrates. In this method, the deposition rate and the thickness of the films can be easily controlled over a wide range by changing the spray parameters, thus eliminating the major drawbacks of chemical methods such as solgel, which produces films of limited thickness. All of these features are of great advantage in order to scale up the technique for industrial applications.

Further, the performance and efficiency of a thin film device depend strongly on the structural and optical properties of the films, which in turn are strongly influenced by the process parameters during film growth[15-19]. Thus, it becomes very important to carry out the structural and optical characterizations of the film. In this paper, we report the synthesis and Characterisation studies carried out on CdS and CdTe thin films prepared by chemical spray pyrolysis technique.

EXPERIMENTAL

The thin films of cadmium chalcogenides viz. cadmium sulphide (CdS) and cadmium telluride (CdTe) were prepared on glass substrates by the chemical spray pyrolysis technique. The thin films of CdS and CdTe are prepared in the same experimental setup in two different depositions by spraying aqueous solutions containing soluble salts of the cation of interest onto heated glass substrates, where the desired film of interest gets deposited due to pyrolytic decomposition of the solution .

All the glass substrates of dimensions 2.5 cm x 1cm x 0.1 cm were cleaned before deposition with freshly prepared chromic acid followed by detergent solution and distilled water. The cleaned glass substrates were placed on the surface of an electrically controlled substrate heater when sprayed. The substrate heater is actually an electrically controlled block furnace. The atomization of the solution into a spray of fine droplets was carried out by the spray nozzle, with the help of compressed air as carrier gas. The schematic

representation of the spray system is given in Figure 1.
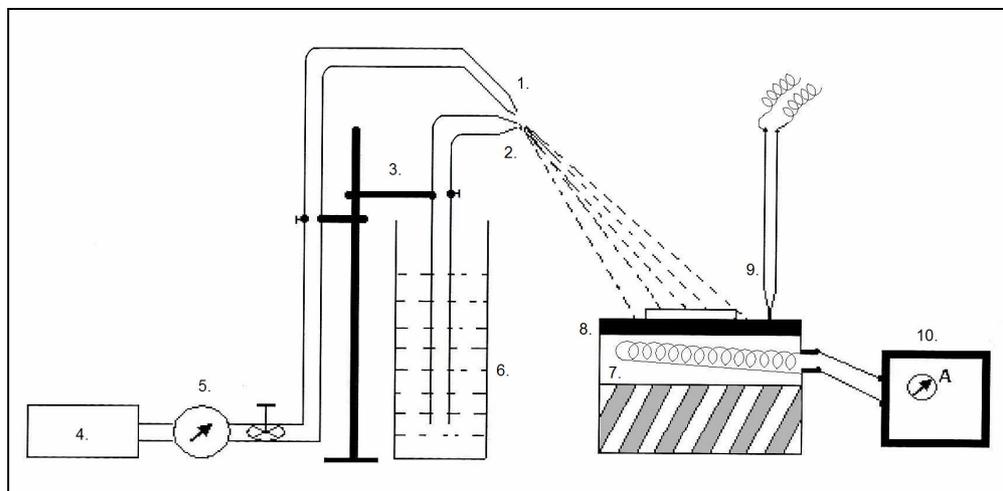
Fig. 1: Schematic representation of the spray system [(1) Air output nozzle; (2) Spray nozzle; (3) Iron stand; (4) Air compressor; (5) Pressure regulator and gauge; (6) Spray solution container; (7) Block furnace; (8) Substrate; (9) Thermocouple; (10) Temperature control unit]

The various process parameters used in the film deposition are listed in Table 1.

Table 1. Spray parameters for film deposition

Spray parameter	Value/Name
Precursor solution for CdTe thin films	Aqueous solution of $CdCl_2$, TeO_2, hydrazine, NH_4OH, HCl
Precursor solution for CdS thin films	Aqueous solution of cadmium chloride ($CdCl_2$) and thiourea [$(NH_2)_2CS$]
Nozzle-substrate distance	50 cm
Solution flow rate	5 mL/min
Gas pressure	3 kg/ cm^2
Substrate temperature	$410 \pm 10\ ^0C$

During the course of spray, the substrate temperature was monitored using a precalibrated chromel-alumel thermocouple with the help of a Motwane digital multimeter (Model: 454).

The CdS thin films were prepared by spraying an aqueous solution of cadmium chloride ($CdCl_2$) (Merck, India) and thiourea $[(NH_2)_2CS]$ (Merck, India) on glass substrate kept at 400^0C. The starting solutions for deposition were taken as 0.5 M aqueous solution of thiourea and 0.5 M aqueous solution of cadmium chloride. The solutions were mixed thoroughly and then the final solution was sprayed onto heated substrates kept at temperature ranging from $410 \pm 10°C$. The following chemical reaction takes place at the surface of the heated substrate, leading to the formation of CdS

$$CdCl_2 + (NH_2)_2\,CS + 2\,H_2O \rightarrow CdS + 2\,NH_4Cl + CO_2$$

This reaction yields a uniform growth of CdS films on the glass substrates. The CdS films obtained were found to be transparent but slightly yellowish in physical appearance.

The CdTe thin films were prepared using the spray solution as a mixture of water, ammonium hydroxide, hydrazine hydrate and hydrochloric acid. As a source of cadmium and tellurium, cadmium chloride ($CdCl_2$) and tellurium oxide (TeO_2) are added in the solution with concentration of ~ 0.02 M. Hydrazine hydrate is used as a reducing agent. Ethylenediamine tetraacetic acid (EDTA) is added as a complexing agent for the spray solution with the concentration of 0.02 M and 0.05 M. The pH value of the solution was adjusted to 11.2 by the addition of hydrochloric acid and monitored using a Metler Toledo pH meter (seven Easy pH). Flow rate of the solution was maintained at $\sim 3\text{-}5$ mL/min. The deposition was carried out on glass substrates kept at $400 \pm 10°C$

In case of the thin film formation of CdTe, hydrazine supplies energy to reduce Te valency Te^{4+} to Te^{2-}, that creates a favourable condition for forming CdTe in the presence of Cd^{2+} ions. The chemical reaction for the process is given as –

$$TeO_3{}^{2-} + 2\,OH^- \rightarrow Te\downarrow + 2\,O_2 + H_2O + 4\,e^-$$
$$Cd^{2+} + Te + 2e^- \rightarrow CdTe$$
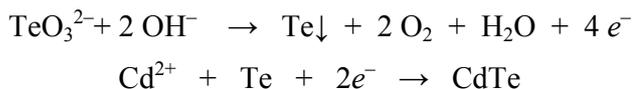
It is worth mentioning that adding hydrazine hydrate to the solution improves the precipitation of CdTe on glass. The CdTe films obtained were found to relatively less transparent as compared to that of CdS films and slightly brownish in physical appearance.

Film thickness of the deposited films was determined by the weight-difference method using an electronic high precision balance (Citizen, Model: CY 204). All the film thicknesses were found to be in the range 1000 Å to 1050 Å for both CdTe and CdS thin films. The temperature was monitored during the entire deposition process using a pre-calibrated chromel-alumel thermocouple with the help of Motwane digital multimeter

(Model: 545)

The structural characterization of the films was performed using X-ray diffraction (XRD) analysis for phase identification using PANalytical X'Pert Pro X-ray Diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ A^0) X-ray source at 40 kV and 30 mA in the scanning angle (2θ) from 20^0 to 70^0 with scan speed 0.001 ^{0}/s. The optical transmission and absorbance spectra for as-deposited CdS and CdTe thin films were obtained in the ultraviolet (UV)/ Visible/ near infrared (NIR) region up to 1100 nm using Perkin–Elmer UV-VIS spectrophotometer (Model: Lambda 35) with normal incidence taking an uncoated glass as the reference.

RESULTS AND DISCUSSION

Structural studies

The XRD pattern of the CdS and CdTe thin films are as shown in Fig. 2 and Fig. 3, respectively.
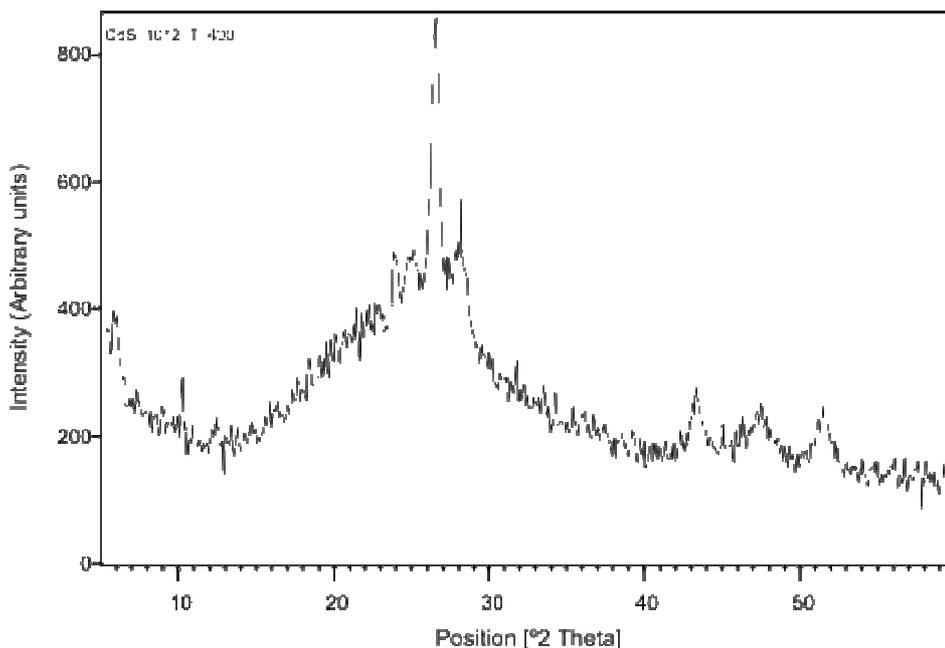
Fig. 2: XRD pattern of CdS thin films
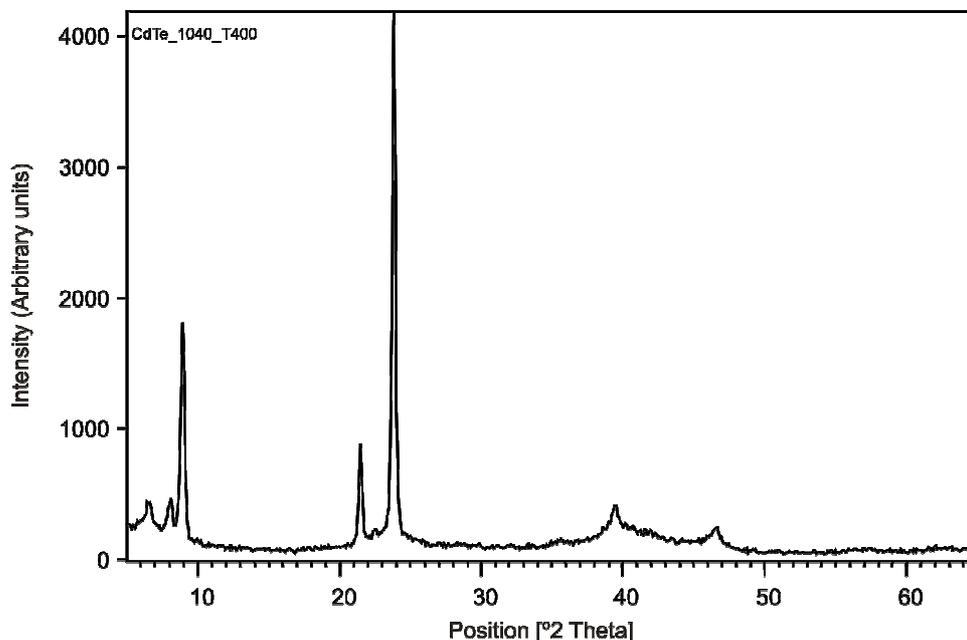
Fig. 3: XRD pattern of CdTe thin films

The XRD pattern of CdS thin films consists of a few smaller peaks at the positions $2\theta =$ 23.872, $2\theta = 28.237$ with the largest peak centered at approximately at $2\theta = 26.608^{0}$, which corresponds to the (002)-reflection of the CdS lattice growing in a hexagonal phase, with the *c* axis perpendicular to the substrate surface. This confirms the formation of CdS thin film. However, other peaks at $2\theta = 43.652^{0}$ and $2\theta= 51.950^{0}$ corresponding to (110) and a(004) were also found to be present with relatively lower intensities. The relative intensities of the different peaks show that the CdS films have grown with a strongly preferential orientation along the c-axis (002). Also, we matched the obtained XRD spectra for CdS with the standard ICDD data base using the X'pert HiScore software and confirmed that the films are of CdS.

The XRD spectra of CdTe thin films consists of a few sharp peaks at 2θ positions 8.948^{0}, 21.452^{0}, 23.851^{0}, 39.499^{0} and 46.669^{0} with the largest peak centered at approximately at $2\theta = 23.851^{0}$, which corresponds to the (111) plane of the CdTe lattice growing parallel to the substrate. This confirms the formation of CdTe thin film, with (111) as the strongest preferred plane of orientation. Similarly to CdS thin films, we matched the obtained XRD spectra of CdTe with ICDD data base using X'pert high score software and confirmed the composition of the film to be CdTe.

Optical studies

The optical transmittance spectra of the CdS and CdTe thin films are shown in Fig. 4 and Fig. 5, respectively.
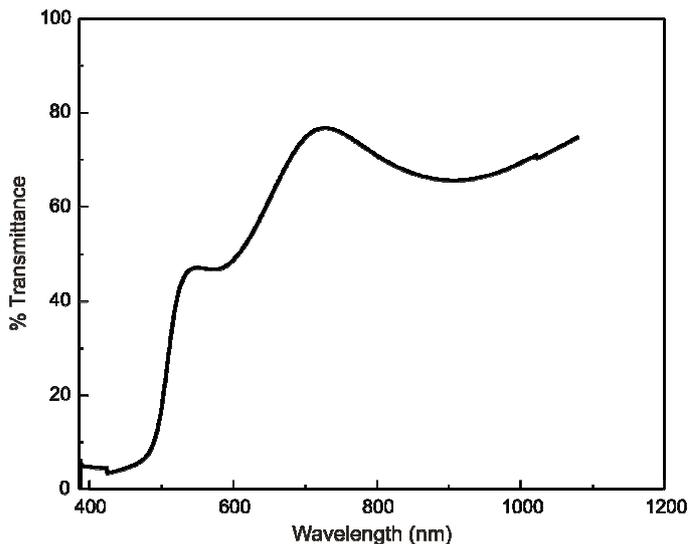
Fig. 4: Transmittance spectra of CdS thin films
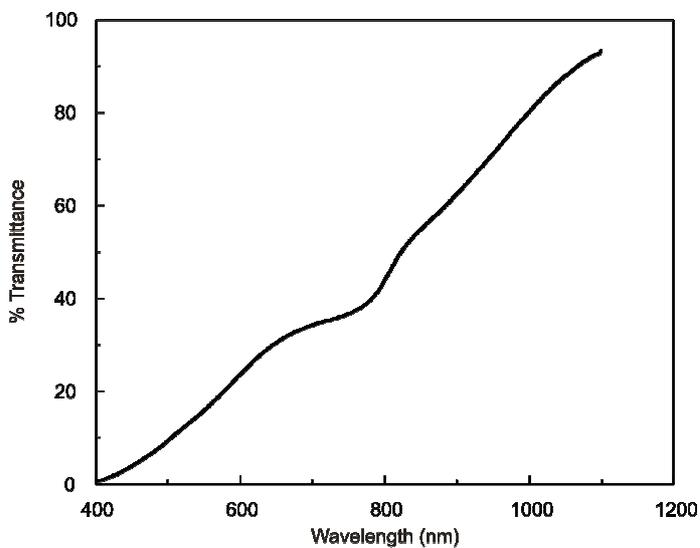
Fig. 5: Transmittance spectra of CdTe thin films
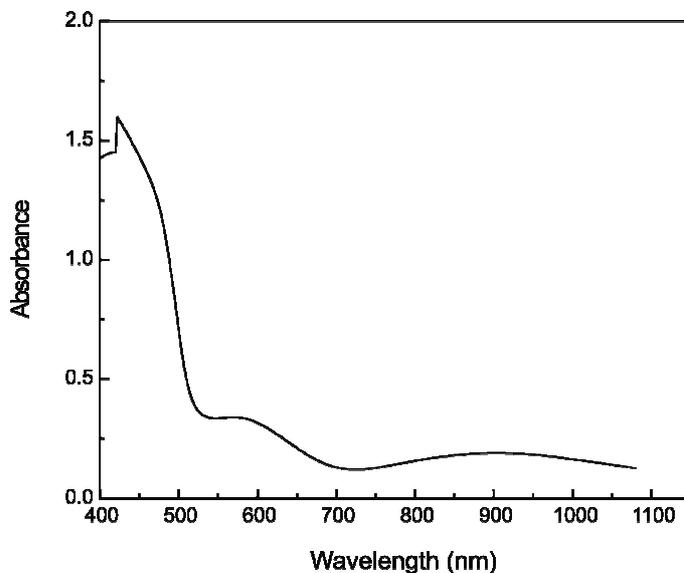
Fig. 6: Absorbance spectra of CdS thin films
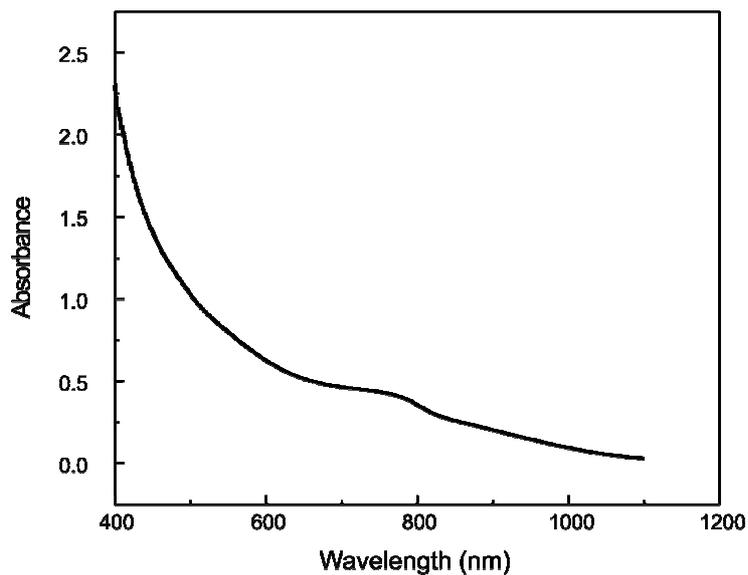
Fig. 7: Absorbance spectra of CdTe thin films

All the films show high transmission of more than 60 % for wavelengths longer than 500 nm and it keeps on increasing with the wavelength. However, in the visible and NIR

region, the transmittance of CdS thin films are more than that of CdTe thin films. The optical absorbance spectra of the CdS and CdTe thin films are shown in Fig. 6 and Fig. 7 respectively. In case of both the films, the absorbance is very low, which goes on decreasing with wavelength.

From the absorbance data, the absorption coefficient α was calculated using Lambert's law[20].

$$\ln (I_o / I) = 2.303 \, A = \alpha t \qquad \qquad …(1)$$

where I_o and I are the intensity of incident and transmitted light respectively, A is the optical absorbance and t is the film thickness. The absorption coefficient α was found to follow the relation[21].

$$\alpha = [A_o \, (h\nu - E_g)^{1/2}] / h\nu \qquad \qquad …(2)$$

where A_o is a constant, which is related to the effective masses associated with the bands and E_g is the band gap energy. Plots of $(\alpha h\nu)^2$ versus the photon energy $h\nu$ for films of CdS and CdTe are shown in Fig. 8 and Fig. 9, respectively.
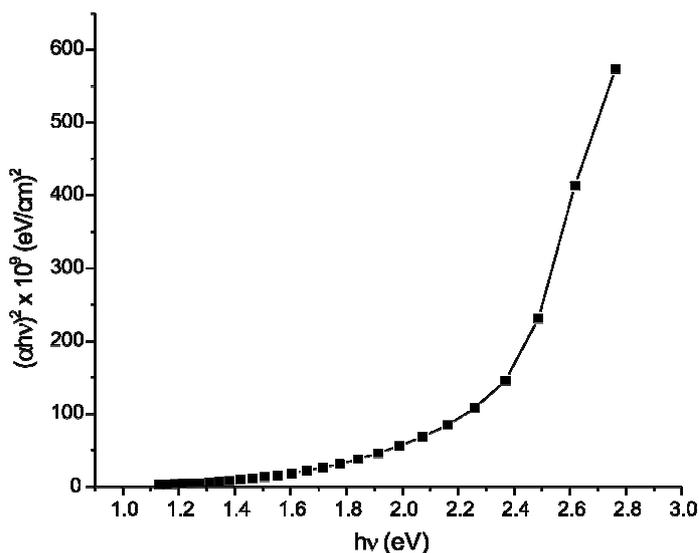
Fig. 8. Plot of $(\alpha h\nu)^2$ versus the photon energy $h\nu$ for CdS films

The linear nature of the plots indicates that the material is of direct band gap nature. Extrapolation of linear portion of the graph to the energy axis at α = 0 gives the band gap

energy E_g, which are found to be 2.3 eV for CdS and 2.9 eV for CdTe.
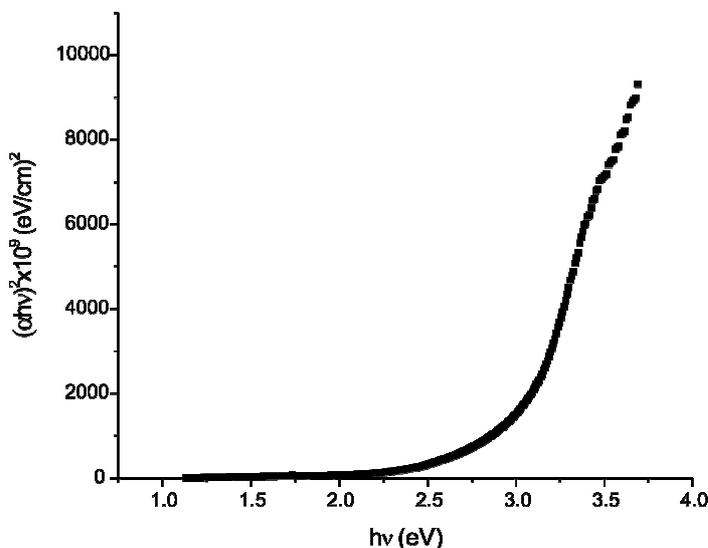
Fig. 9: Plot of $(\alpha h\nu)^2$ versus the photon energy hν for CdTe thin films

For single crystals, the band gap of CdS is 2.24 eV and that for CdTe is 1.5eV[22], the deviations in the energy band gap for single crystals and the cadmium chalcogenide thin films is explained by the fact that in polycrystalline phase, in the thin films, many defects are present, which lead to the creation of defect states. These defects states may be both deep or shallow, appearing in the vicinity of conduction band.

CONCLUSION

Thin films of II-VI cadmium chalcogenides viz. CdTe and CdS are prepared by chemical spray pyrolysis technique. The structural and optical characterisations of the prepared films are performed by XRD and uv/visible spectroscopy. The structural study confirms the prepared films to be of CdS and CdTe with strongest preferential plane of orientation as (002) for CdS and (111) for CdTe. The optical studies reveal the values of the band gaps for CdS to be 2.2 eV and that for CdTe to be 2.29 eV.

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