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Optical and Electrical Properties of CdS thin films prepared by spray pyrolysis

KEYWORDS : Spray pyrolysis, Reflectance and Transmittance spectra and Energy band gap

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ABSTRACT

A thin film of CdS is a semiconducting material for the use in the fabrication of hetero-junction solar cell. Spray pyrolysis is a simple, cheap and inexpensive method of depositing thin films of large area. We have deposited thin films of CdS on glass substrate at 300 0c by this method, using aqueous solutions of cadmium chloride and thiourea and from the reflectance and transmittance studies the band gap energy (Eg) is calculated 2.47 eV and has a very high absorption coefficient near the band edge which shows the direct allowed transition of CdS thin films. The resistivity of the films was measured for temperature ranging from 313 0K to 573 0K. The activation energy values were calculated from Arrhenius plot; Shallows levels arising from internationals cadmium or sulphur vacancies are found to extrinsic conductivity near room temperature where as deep trap states influence at higher temperature.

INTRODUCTION

CdS is an important II-VI group compound semiconductor material. A CdS film has a wide band window material in hetero-junction solar cells due to their greater open-circuit voltage and short-circuits current [1]. As ZnS and CdS have high melting points, direct synthesis of such phosphors from the melt is not possible. However, due to high cost of such material are must understand its optical, electrical and photo-conducting properties in the form of thin polycrystalline films. There are various techniques for the preparation of thin films. Screen-printing [2], Chemical bath deposition [3] and [4], Vacuum evaporation [5] and Spray Pyrolysis [6-10] are well known for the preparation of thin films.

We have deposited polycrystalline thin films of CdS by spray pyrolysis. This method is simple, inexpensive and suitable for water soluble salts and films are so produced have good adherence to moderately heated substrates. In this paper result obtained from optical transmittance, reflectance and electrical property studies of spray pyrolytically deposited CdS thin films are discussed.

EXPERIMENTAL DETAILS

Aqueous solutions 0.1M of $CdCl_2$ and thio-urea were used for spraying the films. The chemical used was of AR grade. The solutions were prepared in double distilled water. Proportion of $CdCl_2$ and thio-urea was adjusted in the ratio 1:2.2 by volume in the spraying mixture so as to obtain the CdS thin films. Excess sulphur was necessary to obtain CdS films. The deposited films showed sulphur deficiency, when the ratio of solutions was taken 1:1 by volume. Excess (in the form of thiourea) were used to remove this deficiency [11].The temperature of the substrate measured by pre-calibrated thermocouple was maintained at 300 ± 5^0C which was the most suitable for production of CdS thin films. The substrates used were cleaned in hot distilled water and then in dilute phosphoric acid repeatedly. The distance between the sprayer and substrate was kept at 30 cm. The sprayer was mechanically moved to and fro during spraying to avoid the formation of droplets on the hot glass substrate and to ensure instant evaporation. The solution was sprayed at a pressure of 12 Kg/cm^2 .The rate of flow was maintained at 3.5 ml/min. The thickness so obtained was of the order of 0.16 μm. The colour of the films was deep-yellow.

OPTICAL STUDY

Transmittance (T) and Reflectance (R) v/s wavelength of the films was measured at room temperature using Double-beam Spectrophotometer (UV-Visible Varian Spectrophotometer). The spectrophotometer is generally used to study the transmittance of solutions. In our experiment we used spectrophotometer for measuring the Transmittance and Reflectance of the films deposited on glass substrate. Glass plate identical to substrate used was placed in path of the reference beam and substrate with deposited film was placed in the path of the reference beam and substrate with deposited films was placed in the path of the sample beam for recording transmittance. While recording the Reflectance BaO was used as a standard (i.e.100% reflectance), the range of wavelength used was 350-700 nm. For calculation of absorption coefficient (α) at various wavelengths, the method used [12] was adopted.

The absorption coefficient (α) at various wavelengths for thickness (t) is given by the relation,

$\alpha t=\ln(I_o/I)$ (1)

Where, I_o and I are the intensities of incident and transmitted radiation respectively.

Transmittance (T), Reflectance(R) and α are related to each other by the relation,

$T=$ (2)

Equation (2) is valid in the vicinity of the fundamental absorption edge when

$R^2 \exp(-2\alpha t) <<1$.

The equation (2) is used to calculate α, the value of T and R are taken from spectrophotometric curves for the sample (fig.1 and 2.).

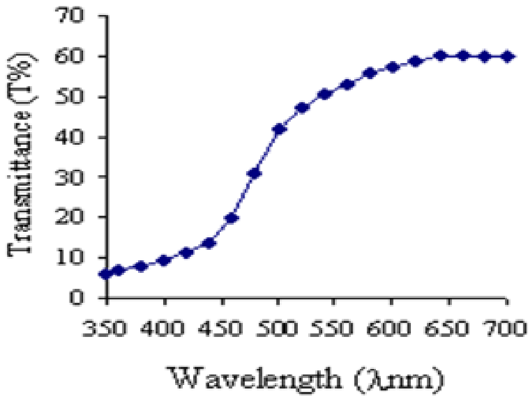

Figure 1: Transmittance vs wavelength as deposited CdS thin films

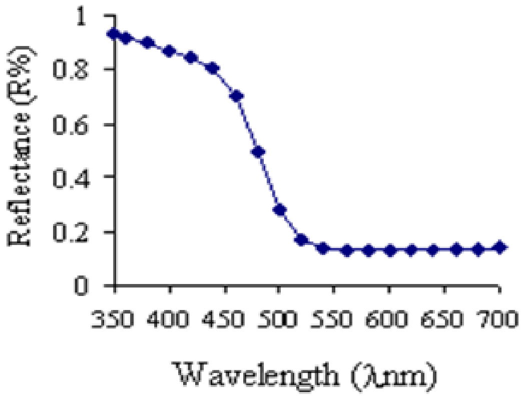

Figure: 2 Reflectance vs wavelength as deposited CdS thin Films

STUDY OF REFLECTANCE

The diffuse reflectance for normal incidence in the wavelength range of 350 nm to 700 nm (fig.2.). As the wavelength increases there is a sharp decrease in the reflectance. The onset of decrease of reflectance gives the approximate value of band gap [13]. The lack of steepness in the diffuse reflectance curve can be attributed to the small grain size.

STUDY OF TRANSMITTANCE

The transmittance curves for the wavelength range 350 to 700 nm (fig.1.). The transmittance increases with the wavelength. The rise in steep for the wavelength between 380 nm and 520

nm, above 520 nm the steepness decreases. This indicates that the region of absorption lies below 520 nm. Knowing the approximate region of band gap from reflectance curves, α is calculated by using equation (2), from the knowledge of T, R and t.

To calculate the exact value of band gap, a graph $(\alpha h\nu)^2$ against hν was plotted (Fig.3), for the region near and above the fundamental absorption edge, the extrapolated intercept on hν axis gave the value of band gap. The linearity of the graph indicated that the directly allowed transition described by the relation,

$\alpha=(h\nu-Eg)^{1/2}$(3)

he band gap values obtained as 2.47eV

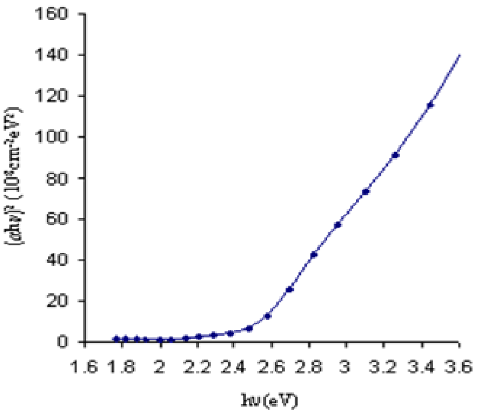

Figure: 3 Plot of $(\alpha h\nu)^2$ against incident photon energy (hν)

This agreed well with the results obtained by [1]. This result also agreed well [14], [15] was reported the value of band gap 2.42 eV of a single crystal CdS. While [2] reported energy band gap of CdS thick films was 2.57 eV by Sintering technique and they stated that the this value of band gap is in good agreement with the $Cd_{0.8}Zn_{0.2}S$ composition reported by other researchers [17] and they also confirmed from the X-ray diffraction study. This indicating that spray pyrolytically deposited films are of good quality.

ELECTRICAL PROPERTIES

The conductivity of the films, as determined by hot-probe method was n- type. The resistivity is determined for the temperature 313 ^{0}K to 573 ^{0}K at atmospheric pressure by Four-probe method [18].

The variation of conductivity with temperature is usually expressed as

$$\sigma = \sigma_0 \exp\left(-\frac{Ea}{KT}\right) \qquad (4)$$

where, E_a is the activation energy measured from the bottom of the conduction band, k-is the Boltzmann constant and T is the absolute temperature. Fig.4 shows the Arrhenius plot of conductivity vs inverse temperature for the above temperature range.

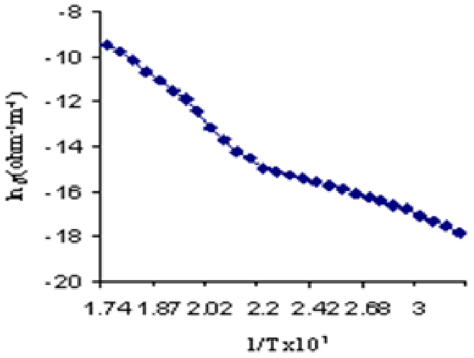

Figure: 4 Arrhenius plots of Conductivity of CdS thin films

Two distinct regions (I- 313 ^{0}K to 453 ^{0}K and II-453 ^{0}K to 573 ^{0}K) of conductivity are seen. The slope is less in the low temperature region (I), but increases with further increase of temperature (II). Activation energies calculated from these two regions are 0.045 eV and 0.94 eV, for the temperature ranges 313 ^{0}K- 453 ^{0}K and 453 ^{0}K to 573 ^{0}K respectively. Films are not doped intentionally and therefore the defects in the films do not possess the intrinsic conductivity strictly in this entire temperature range. Devi et al [4] has reported that the activation energy of cadmium or sulphur interstitials was between 0.06 eV and 0.82 eV for 308 ^{0}K to 448 ^{0}K and 448 ^{0}K to 523 ^{0}K for these temperature ranges respectively, which is in fairly good agreement with our 0.045 eV and 0.94 eV activation energies. The shallow trapping states preferably due to those interstitial cadmium or sulphur vacancies are dominate the extrinsic conductivity near room temperature whereas at high temperature those deep trap states influence.

CONCLUSIONS

Spray pyrolysis is a successful method for depositing CdS thin films on glass substrates by using cadmium chloride and thiourea solution of 0.1 M. optical study reveals that these films have direct allowed transition having energy band gap at 2.47 eV. Activation energy 0.045 eV and 0.94 eV are due to cadmium or sulphur interstitials was observed.

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