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Synthesis and Characterization of Screen-Printed CdS Films

V. Kumar[1*)], D. K. Sharma[1], M.K. Bansal[2], D.K. Dwivedi[3], T.P. Sharma[4]

[1] Department of Physics, Krishna Institute of Engg. & Technology, Ghaziabad, India
[2] Department of Physics, B.I.T, Meerut, India
[3] Department of Physics, M.M.M.E.C, Gorakhpur, India
[4] Department of Physics, Rajasthan University, Jaipur, India

Abstract:

Cadmium sulphide films having energy band gap of 2.4 eV found applications in solar cells and electroluminescent devices. CdS polycrystalline films have been prepared on ultra-clean glass substrate by screen-printing technique and then sintered in air. Optimum conditions for preparing good quality screen-printed films have been found. The optical band gaps 'Eg' of the CdS films were determined from the UV transmission spectroscopy and were found to be 2.47eV. The Wurtzite structure of CdS films was confirmed by X-ray diffraction analysis. DC conductivity and activation energy of films was also measured in vacuum by two-probe technique.

Keywords: *CdS; Screen printing; Conductivity; X-ray diffraction; Band gap; Photoluminescence*

1. Introduction

The use of thin film polycrystalline semiconductors has attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices. The technological interest in polycrystalline-based devices is mainly caused by their very low production costs. CdS is an important II-VI group compounds semiconductor material. CdS films are regarded as one of the most promising materials for hetrojunction thin film solar cells. Wide band gap CdS has been used as the window material together with several semiconductors such as Cu_2S / CdS [1] and CdS / $CuInSe_2$ [2]. However due to high cost of such a material, studies were developed towards polycrystalline semiconductor and particularly thin polycrystalline films [3].

Several techniques have been used to produce CdS thin film such as chemical bath deposition [4, 5], thermal evaporation [6, 7], spray pyrolysis [8], screen printing followed by sintering [9] and chemical route using organic substances [10]. Generally in each of these methods, polycrystalline, stable, uniform, adherent and hard films are obtained. Screen-printing is an inexpensive and convenient technique for large area preparation of the films. This technique is suitable for coating surfaces of any morphology and geometry. In particular screen-printing is low cost and relatively simple technique for achieving good quality thick films [16-19].

CdS has been the subject of intensive research because of its intermediate band gap,

*) **Corresponding author**: vipinkumar28@yahoo.co.in

high absorption coefficient, reasonable conversion efficiency, stability & low cost [11, 12]. CdS thin films are well known for their extensive applications as an optoelectronic material in solar cells [13, 14] and photo detectors [15].

In the present paper optimum conditions for depositing good quality CdS screen printed films and optical, structural, electrical properties have been studied. To the best of our knowledge DC electrical conductivity of CdS screen printed films has not reported earlier.

2. Experimental details

In present investigation, CdS films were prepared by screen-printing followed by sintering process [16-19]. A commercially available CdS powder with 99.99% purity was used as the starting material. Slurry consisting of CdS powder, 10% wt. of $CdCl_2$ and an appropriate amount of ethylene glycol were thoroughly mixed. $CdCl_2$ was used as an adhesive and ethylene glycol as a binder. The paste thus prepared was screen printed on ultra clean glass substrates, which had been cleaned by embry powder and acetone and finally washed with distilled water. The samples thus prepared were dried at 120°C for 4 hour in open air. Reason of drying the sample at lower temperature was to avoid the cracks in the samples. Removal of organic materials took place at about 400°C, so sintering temperature cannot be less than 400°C. Cadmium chloride is hygroscopic and its melting point is 568°C. However, the evaporation of cadmium chloride starts above 400°C. So to get a stable sintered film, cadmium chloride and organic material should not remain in the sample. It was reported that $CdCl_2$ in CdS films enhances the sintering of CdS films [20] meaning that $CdCl_2$ served as a flux to promote particles fusion and granule regrowth at relatively low temperature and finally evaporated during sintering, and also reported that the sintering temperature between 620°C and 650°C was optimum for the sintering of CdS film with 9% wt of $CdCl_2$ in nitrogen atmosphere [20]. To obtain good quality CdS screen printed film we have optimized the sintering temperature and sintering time by performing the experimental process for different values of these two parameters and concluded that samples should be sintered in air atmosphere at 500°C for 10 min in a temperature controlled furnace. CdS films prepared in this way had a thickness of about 20μm (By Weighing). Adhesion of the films to the substrate was better and no pinholes or cracks were apparent. The X-ray diffraction pattern shows no peaks of CdS oxidation. No $CdCl_2$ phase has also been observed in XRD pattern. All the films were synthesized under the same experimental conditions.

3. Results and discussion

3.1. Optical Properties

The optical transmittance of the films was measured at room temperature in 300-800 nm wavelength range using a UV / VIS spectrophotometer. Almost all the II-VI Compounds are direct band gap semiconductors. According to Tauc relation [21], the absorption coefficient for direct band gap material is given by

$$\alpha h\nu = A\,(h\nu - E_g)^n\ ,$$

Where $h\nu$ is photon energy, A is constant which is different for different transitions and E_g is the band gap, and n is equal ½ for direct band gap material. It has been observed that plots of $(\alpha h\nu)^2$ Vs $(h\nu)$ are linear over a wide range of photon energies indicating the direct type transitions. The extrapolation of these plots on the energy axis gives energy band gaps. Fig. 1 represents the transmittance spectra of CdS screen-printed sintered film. For determination of band gap we have plotted a graph between $(\alpha h\nu)^2$ Vs $(h\nu)$ as shown in fig. 2. The extrapolation of straight line on the energy axis gives a band gap of 2.47eV for CdS screen printed sintered film, which is very close to values reported in other studies [8-10].

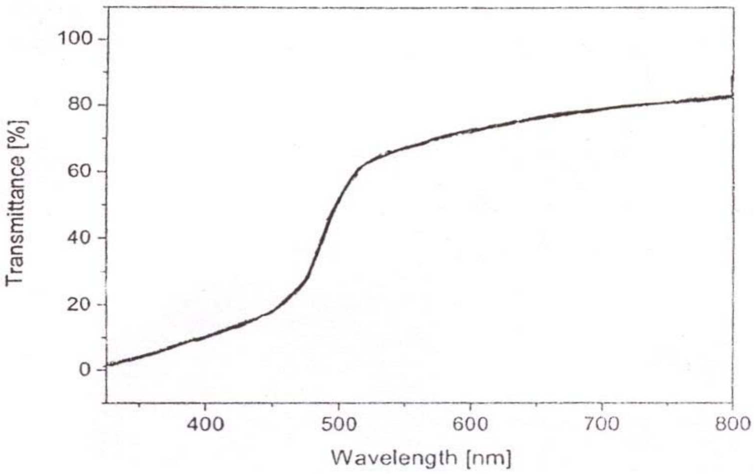

Fig. 1. Optical trasmission spectra of screen-printed sintered CdS film.

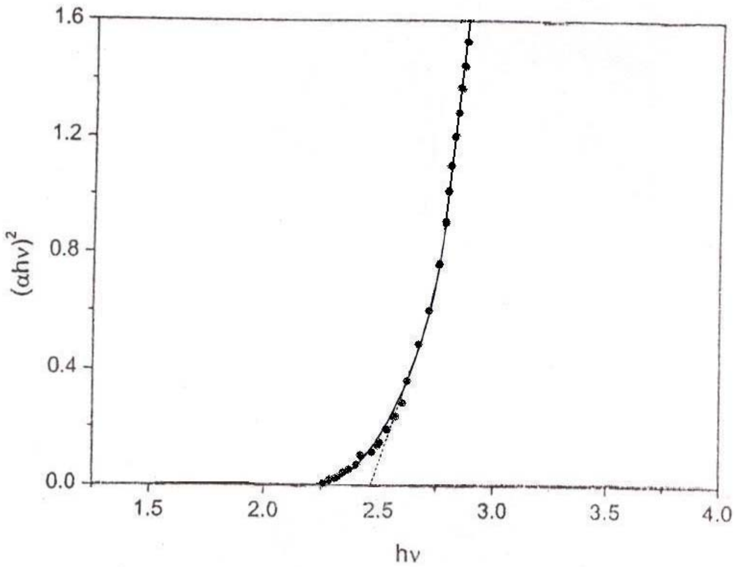

Fig. 2. Plot of $(\alpha h\nu)^2$ Vs. Photon Energy of the screen-printed sintered CdS film.

3.2. Structural Properties

The X-ray diffraction pattern of CdS Screen printed sintered film for structural analysis is also reported in this work using CuKα radiation with the help of Philip X-ray diffractometer. The d-values were calculated by calculating θ values from the peaks of the X-ray spectrum by using Bragg's relation $2d\sin\theta = n\,\lambda$ (n=1 in present study and λ= 1.54045 for CuKα). These d values were compared with the standard ASTM data to confirm the structure of CdS. Fig. 3 is X-ray diffraction pattern of screen Printed CdS film with CuKα radiation. The experimental d-values of CdS screen-printed sintered film are in good agreement with the ASTM d-values of CdS having hexagonal (wurtzite) structure. Hence CdS screen-printed sintered films have hexagonal (wurtzite structure). The presence of sharp structural peaks in XRD confirmed the polycrystalline nature of CdS films.

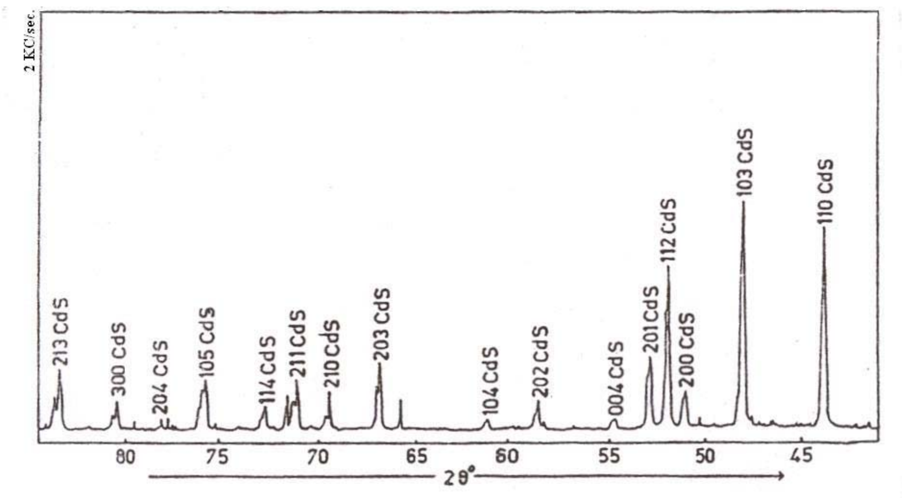

Fig. 3. XRD Pattern of CdS screen-printed sintered film.

3.3. Electrical Properties

The electrical transport properties of the materials are of great importance in determining whether material is congruent with our necessities or not [17, 18]. The electrical properties are dependent on various film and growth parameters such as film composition, thickness, and substrate temperature and deposition rate [17, 18]. For photovoltaic applications important characterization includes electrical conductivity.

Electrical Conductivity

The DC electrical conductivity of CdS screen-printed sintered films in dark in the range of temperature 300-400K was measured using two probe method in vacuum. The DC conductivity (σ_{DC}) of a semiconductor at a temperature T is given by (conventional Arrhenius relation for semiconductors)

$$\sigma_{DC} = \sigma_0 \exp\left(-\frac{\Delta E}{kT}\right)$$

Where σ_0 is pre-exponential factor depending on the sample, k is Boltzman's constant and ΔE is the conductivity activation energy measured from the bottom of the conduction band and T is the absolute temperature.

We may write $\ln\sigma_{DC} = \ln\sigma_0 - \left(\frac{\Delta E}{kT}\right)$

or $\ln\sigma_{DC} = -\left(\frac{\Delta E}{1000k}\right)\left(\frac{1000}{T}\right) + \ln\sigma_0$

When we plot a curve between $\ln\sigma_{DC}$ and $\frac{1000}{T}$, a straight line obtained having sloped $\left(\frac{\Delta E}{1000k}\right)$ and intercept $\ln\sigma_0$. Thus the activation energy ΔE can be calculated by using the slope of straight line.

The temperature dependence of the dark conductivity of screen-printed CdS film is shown in Fig.4.

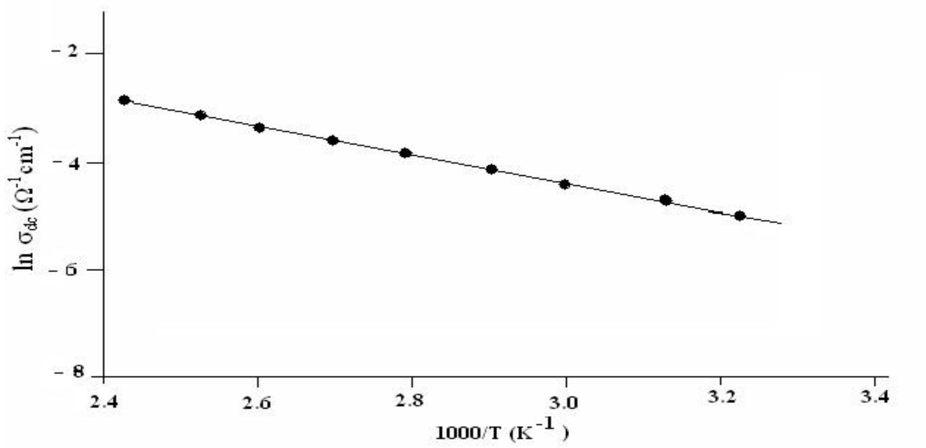

Fig. 4. Temperature dependence of DC conductivity of CdS screen-printed sintered film.

The conductivity of CdS samples increase with the increase in temperature. The plot of $\ln\sigma_{DC}$ against $\frac{1000}{T}$ for CdS films is a straight line indicating that conduction in CdS film is through thermally activated process. Obviously, the straight line nature of this plot suggests that grain boundary limited conduction is the dominant conduction mechanism. We would like to state that the grain boundaries are consequence of imperfections associated with the poly crystalline films. Seto [22] explains the high temperature conduction mechanism in semi conductors. In present investigation, the dark conductivity of CdS film comes out of the order of $10^{-3}\ \Omega^{-1}cm^{-1}$ and value of activation energy comes out about 0.16 eV, which is in good agreement with earlier reports [23].

4. Conclusions

The optical, structural and electrical properties of screen-printed sintered CdS films were investigated. The band gap of CdS screen-printed sintered film comes out to be 2.47 eV. Films of CdS were found to be polycrystalline in nature and have hexagonal wurtzite structure. It has been observed that the dark DC conductivity of CdS film comes out of the order of $10^{-3}ohm^{-1}cm^{-1}$ and value of activation energy comes out about 0.16eV. The conduction in CdS films is through a thermal- activated process. Due to optimum band gap, polycrystalline nature, stable material, fairly high DC conductivity and activation energy, CdS screen printed sintered film may be suitable for solar cells, Wide band gap window material and other photovoltaic devices. Screen-printing technique is simple, inexpensive, viable and attractive means of obtaining films of II-VI semiconductors.

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Садржај: *Кадмијум сулфидни (CdS) филмови са енергијом процепа од 2,4 eV налазе примену у соларним ћелијама и електролуминесцентним апаратима. CdS поликристални филмови су припремљени на ултра-чистом стакленом субстрату техником сито-штампе и синтеровањем у атмосфери ваздуха. Аутори су нашли*

оптималне услове за припрему квалитетних филмова. Оптички енергетски процеп 'Eg' CdS филмова одређен је УВ трансмисионом спектроскопијом и износи 2,47 eV. Рендгенска дифракција потврдила је структуру Вурцита. ДЦ кондуктивност и енергија активације филмова такође су мерени у вакууму методом две пробе.
Кључне речи: *CdS; сито штампа; кондуктивност; рендгенска дифракција; енергетски процеп; фотолуминесценција*