Optoelectronic properties of Zn-doped and air- annealed CdS thin film for Photovoltaic applications

Lakshmy. K[1], Rincy. E B [1], Jithu Michael [1] Dr.T.V.Vimalkumar[2]

[1]MSc Scholar, PG Department of Physics St. Thomas College (Autonomous), Thrissur-680001, Kerala, India

[2]PG Department of Physics, St. Thomas College (Autonomous), Thrissur-680001, Kerala, India

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Abstract: Thin films of Cadmium Sulphide on soda lime glass substrate were deposited by Chemical Bath Deposition Method (CBD). The CdS films were annealed in air at various temperatures. Zn-doped CdS thin films were deposited onto glass substrates by the chemical bath technique. The effect of the doping concentration on the physical properties of CdS films was investigated. The thickness, band gap energy, photosensitive and crystalline structure of the Zn- doped CdS films were investigated and compared to the undoped CdS films properties. It has been observed from XRD that the deposited layers are mainly consisting of CdS phase.The XRD pattern of CdS prepared by varying the pH of the precursor revealed that the CdS films grown in this process are polycrystalline in nature. The XRD pattern of CdS prepared by varying the molarity of thiourea reveals that the use of lower molarity of thiourea during the preparation of Cds thin film gives the sharp curves of (111) and (220) at the angles 26.5 and 44.1 respectively. After annealing, meta stable cubic phase was transformed into stable hexagonal phase. Zn- doped CdS films presented a cubic crystalline structure with (111) as the preferential orientation. The intensity of the (111) film decreases as the doping percentage increases The variation of optical absorption spectra CdS thin films and transmittance depends on the pH value. The direct optical energy gap (E_g) decrease from 2.35 to 2.29 eV for the pH value in the range 8-10.5. The manuscripts showed that the structural, optical and electrical properties of CdS depend on the post-deposition annealing temperatures and doping concentrations.

Key Words: *CdS, Chemical bath deposition, Air annealing, Doping, , Polycrystalline thin films, optical and Electrical properties …*

1. INTRODUCTION

The potential applications of chalcogenide based materials in electronic and optoelectronic devices are vast, but has received little attention until recently due to the cheap and wide availability of silicon based alternatives [1]. Chalcogenide II-VI, compound semiconductors, such as cadmium sulphide (CdS) has generated a lot of interest among scientists because of its extensive use in the fabrication of solid state devices such as solar cells, thin film transistors and electroluminescent displays. The excellent optical properties of CdS make it suitable for use in solar cells, photoconductor and diode laser [2, 3]. Being an n-type semiconductor material it has been observed that CdS is an excellent hetero junction solar cell partner of p-type narrow band gap semiconductor material like CdTe or $CuInSe_2$, where CdS layer is used as the window material. There exists a huge variety of thin film deposition processes and technologies which originate from purely physical or purely chemical processes such as chemical bath deposition (CBD) [4-16], electro deposition, laser ablation [17], sputtering [18],vacuum evaporation [19] .

Chemical bath deposition is currently attracting a great deal of attention as the techniques is relatively simple and cost effective, has minimum material wastage, does not need sophisticated instrument and vacuum, and can be applied in large area deposition at low temperature. Furthermore, doping the CdS films with other chemical elements during the CBD process has shown to affect the resulting physicochemical properties of the doped CdS films, such as the electrical resistivity, band gap energy, and crystalline structure. [20] reported a decrease on the CdS band gap energy, as low as 2.0 eV, by using Cu as a doping element during the CBD process. Similar results for the band gap energy were reported by [21], but using different chemical reagents when doping CdS with Cu. [22] used boron as CdS doping element and reported an increase on the boron-doped CdS electrical resistance. Thus, the capability of controlling the CdS physical properties by the doping process becomes an important issue to address in order to optimize the CdS performance on the wide range of potential optical and solar applications. Here, we report on the physical properties of doped CdS thin films fabricated by the CBD technique when Zn is used as doping element. The thickness, band gap energy, crystalline structure and elemental composition of Zn- doped CdS thin films are investigated and correlated to the Zn concentration.

2 EXPERIMENTAL METHODS

2.1 Materials and methods

CdS thin films were deposited on soda lime glass substrates using CBD technique. and substrate was pre-cleaned before CdS film deposition process, in order to obtain good adherence and uniformity for the deposited CdS films. The experimental setup for CdS film preparation involves a chemical bath containing $CdCl_2$ (0.1M), Ammonia (28 to 30%) and thiourea solution (0.1 M) was added to the chemical bath. The bath temperature was maintained at 65^0 C in a constant temperature water bath under constant magnetic stirring until the film deposited over the glass slide. The CdS films were annealed in air at various temperatures (100, 200, 300 and 400 °C) for 60 minutes. Zn-doped (1%,2%, 3%) CdS thin films were deposited onto glass substrates by the chemical bath technique. $ZnSO_4$ was incorporated as dopant agent into the conventional CdS chemical bath in order to promote the CdS doping process.

The CdS films grown on glass substrates via chemical bath deposition followed by heat treatment (annealing), doping were subjected to be taken for structural and opto-electrical characterization. The thickness measurement was done using stylus profilometer Dektak 32 and it is approximately 200-800 nm. The annealing effects were studied for a film thickness of about 800 nm. The X Ray diffraction (XRD) technique was performed for studying the bulk structure of the film using RINGAKU X- Ray diffractometer of CuKα radiation.=1.54056 A^0). In order to study optical properties optical absorption spectra was recorded in the wavelength range 200 to 2500 nm using UV visible NIR spectrophotometer UV JASCO-V-570. The electrical resistance of the film in dark/Light was measured using a two probe method viz. KEITHLY SMU 236 in the temperature range 100 to 300 ^{0}C.

3 RESULTS AND DISCUSSIONS

3.1 Structural characterization

The films were subjected to XRD technique for the information on the crystal lattice of material and to characterize the crystalline phase. The XRD pattern of CdS prepared by varying the pH of the precursor revealed that the CdS films grown in this process are polycrystalline in nature and the peaks corresponding to angles (in degree) at 26.5 and 44.1 can be indexed to (111) and (220) of cubic CdS phase. When the pH increases sharp peaks of (111) was obtained. The XRD pattern of CdS prepared by varying the molarity of thiourea reveals that the use of lower molarity of thiourea during the preparation of Cds thin film gives the sharp curves of (111) and (220) at the angles 26.5 and 44.1 respectively.

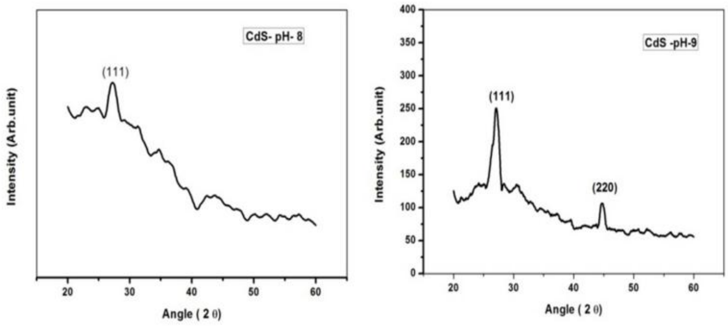

Fig 1 XRD analysis of CdS with pH Variations

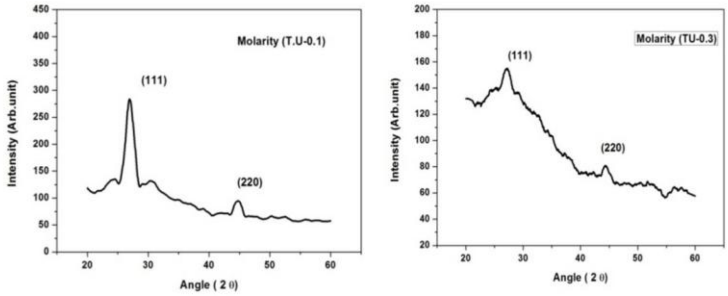

Fig 2 XRD analysis of CdS with Molarity variation of Thiourea

The XRD patterns of as deposited, annealed at 200^{0}C and annealed at 300^{0}C are shown in figures below. It can be seen from the diffraction patterns that the peak intensity changes with the annealing temperature indicating structural changes of material. We have observed that an intense peak appears at approximately 26.5°, which corresponds to the CdS hexagonal plane (002), or cubic plane (111)[23].

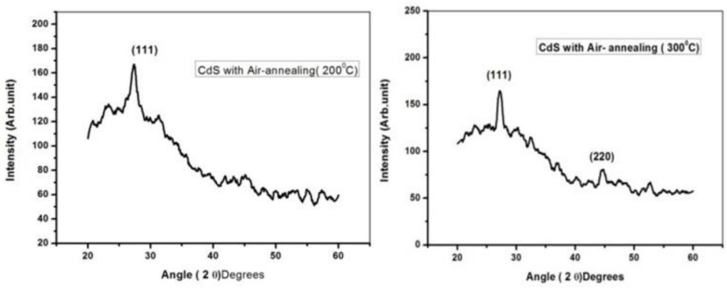

Fig 3 XRD pattern of CdS with air annealed

The XRD spectra of the Zn doped thin films are shown below. The intensity of the (111) film decreases as the doping percentage increases. The intensity of the plane (220) is more for 2% Zn doping and it is not visible in 3% doping. The (3 1 1) plane is only significant for 1% Zn doping. The diffraction peak is observed at about 26.5^0.The interplanar distance increases with increase in doping concentration

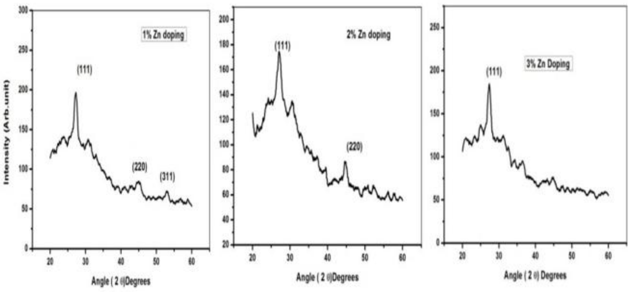

Fig 4 CdS sample with 1, 2, 3% Zn Doping

3.2 OPTICAL CHARACTERIZATION

The value of the optical energy band gap was estimated from the plots of $(\alpha h\upsilon)^2$ vs $h\upsilon$ where α .is the absorption coefficient and υ is the frequency of radiation. It is observed that absorbance is lower for the pH value 8 and higher for the pH value 10.5. The linear nature of the plots indicates that CdS is a direct band gap material and confirms the direct nature of the optical transmission. The extrapolation of straight line to $h\upsilon= 0$ axis gives the value of the band gap. The direct optical energy gap (E_g) decrease from 2.35 to 2.29 eV for the pH value in the range 8-10.5.

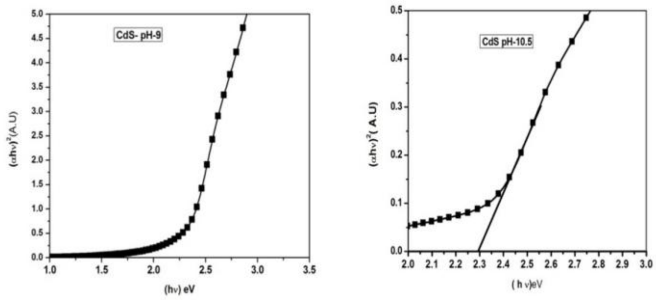

Fig 5$(\boldsymbol{\alpha} h\boldsymbol{\nu})^2$ **vs hυ** graph of variation of pH of the precursor solution

The variation of the square of optical absorption spectra as a function of the photon energy was recorded for both as-deposited and annealed CdS layers. The linear nature of the plot indicates that CdS is a direct band gap material. The band gap energy of the as-deposited thin film was found to be 2.37 eV. The annealed samples show a relative decrease in band gap with annealing temperature. After annealing the sample at 300^{0}C for 1 hour in air caused a decrease in band gap to be 2.18 eV. Decrease in the band gap could be attributed o the phase transition from cubic to hexagonal phase[24] or more likely a reduction in strain within the film. Annealing the sample at 200^{0}C further decreased the band gap energy to about 1.85 eV.

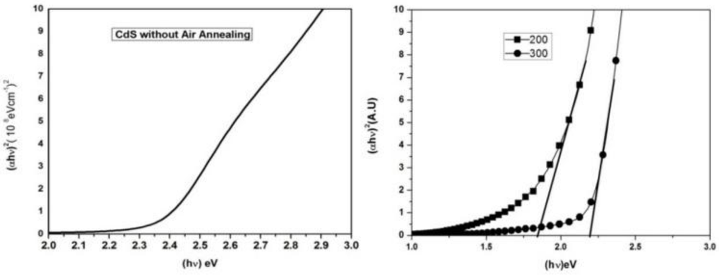

Fig 6 $(\alpha h\nu)^2$ vs $h\nu$ curve of CdS without Air Annealing, air annealed

3.3 ELECTRICAL CHARACTERIZATION

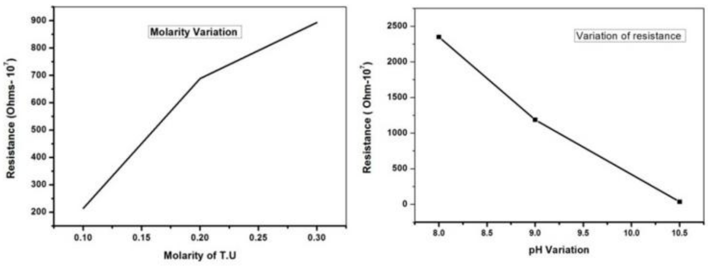

Fig 7 Variation of Resistance with pH of Solution & Molarity of Thiourea

The variation of resistance with pH of the solution shows a steady decrease in resistivity for higher pH values. The electrical resistance of the air-annealed CdS film was measured by two probe method. The variation of electrical resistance with annealing temperature is shown in Fig.8. Significant decrease in the electrical resistivity is observed in samples heated at 100°C. This is due to the partial conversion of CdS to CdO [25]. These results are consistent with other published results such as results of Danaher et al. [26] who attribute this decrease to O_2 desorption, while Ramaiah et al. [27] attribute similar results to the creation of number of sulfur vacancies in the films

Photosensitivity of a semiconductor material is defined as the measure of the minority carriers generated in the material under illumination, and is expressed as the ratio of difference between the dark current (I_d) and photocurrent (I_l)to the dark current.Photosensitivity is given by (I_L-I_D/I_D). Photosensitivity measurements were done using the Keithley 236 Source Measure Unit. Samples were illuminated using a tungsten halogen lamp of intensity 100 mW/ cm^2 for one minutes prior to photoconductivity measurement. An IR filter and a water column were used between sample and lamp to avoid heating of the sample. The Photosensitivity of the sample increased with the increase of the pH precursor.

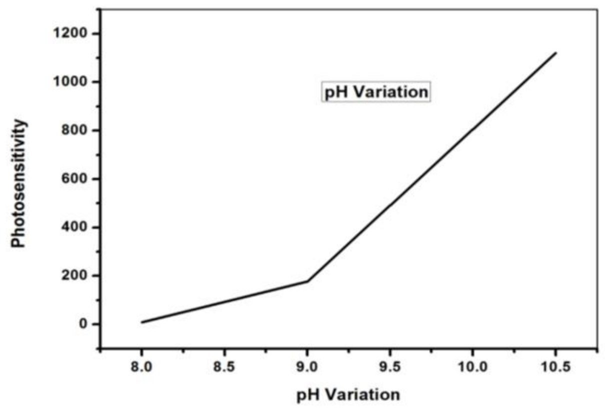

Fig 8. Variation of Photosensitivity with pH of the solution

4 CONCLUSIONS

The pH variations revealed that the CdS films grown in this process are polycrystalline in nature and the peaks corresponding to angles (in degree) at 26.5 and 44.1 can be indexed to (111) and (220) of cubic CdS phase. The peak intensity changes with the annealing temperature indicating structural changes of material. The intensity of the (111) film decreases as the doping percentage increases. The optical studies revealed that CdS have transmittance that depend on the pH value which allow direct transition of the optical band gap which decreases from 2.35 to 2.29 for the pH value of CdS thin films from 8-10.5. The band gap energy of the 2% Zn doped CdS film was observed to be about 2.3 eV. The as-deposited CdS films show near intrinsic conductivity. In general the results showed that the structural, optical and electrical properties of CdS depend on the doping and post-deposition annealing of the sample.

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BIOGRAPHIES

Dr.T.V.Vimalkumar[1] working as Assistant Professor, Department of Physics, St.Thomas College, Thrissur ,Kerala ,India, He has 10 year of research experience in National and International Research labs and he has published many research papers in International Journals

Lakshmy K[2]
MSc Scholar Department of Physics, St.Thomas College, Thrissur ,Kerala ,India

Rincy. E B[2]
MSc Scholar Department of Physics, St.Thomas College, Thrissur ,Kerala ,India

Jithu Michael[2]
MSc Scholar Department of Physics, St.Thomas College, Thrissur ,Kerala ,India