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# Optical investigation on zinc doped cadmium sulphide nanocrystalline thin films

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Optical investigation on blue shift behavior of zinc doped cadmium sulphide nano-crystalline thin films have been prepared by spray pyrolysis method at 375 ± 10 °C. The crystallinity and phase have been characterized by glancing angle X-ray diffraction. The XRD peaks confirm the hexagonal structure of cadmium sulphide. The crystallites sizes are found its range of 15–20 nm. The surface morphology is analyzed by using field emission scanning electron microscopy. The morphology of the film is seen as uniform distribution of homogeneous fine solid grains which are compact in nature. Optical absorption spectrum reveals an absorption peak at 475 nm. Indicating that blue shift due to quantum confinement effect, as a result the direct energy gap is increased and found its value is 2.91 eV. Raman spectrum reveals the longitudinal optical phonon peaks are at 302 $cm^{-1}$ and 603 $cm^{-1}$. The noticeable asymmetry and frequency shift confirm the decrease in particle size. X-ray photoelectron spectroscopy reveals the surface composition and binding energy of elements and it confirm the presence of zinc. The photo-luminescence spectrum reveals an emission peak at 728 nm is analyzed. Zn doped cadmium sulphide thin film is useful for window material in solar cells and luminescent red phosphor.



## 1. Introduction

Nowadays a line of research is focus towards the nano-science. Nanostructure materials attract for physical, chemical, optical and electrical properties, which are diverse from their bulk counter parts [1]. Significant and innovative physical and chemical properties are generated at nano-scale thin films due to the quantum confinement effect [2]. Quantum dot solar cells are promising sensitizing devices for photovoltaic applications in solar energy conversion [3].

The world is suffering from a serious pollution and future deplete of fossil fuels. Solar radiation is considered as one of the most abundant supply of free energy in nature. The solar energy is one of the hopeful solutions for the global energy crisis. Thus, solar cells have been extensively studied in order to increase the efficiency, and reduce the cost of converting solar energy into electricity. The thin film solar cells open up an exceptional potential in cost reduction. Polycrystalline nature of cadmium sulphide (CdS) thin film solar cells are the reason for low cost and high conversion efficiency [4].

Hexagonal wurtzite structure of bulk CdS has a melting point of 1600 °C and band gap energy is 2.42 eV at room temperature. Its refractive index is 2.52 at wavelength 600 nm. It has three phases in size reduction viz. wurtzite, zinc blend and rock salt. Wurtzite is the most stable phase and also easy to synthesize. Wurtzite phase is seen both in bulk and nano-scale, but not in cubic and rock salt phase. It exhibits size dependent behavior, at size 2.5 nm it has melting point ~400 °C. The phase changes from wurtzite to rock salt cubic phase at a very high pressure [5–13]. CdS nano films exhibits structural, electronic, optical, luminescence and photo conducting properties, which deviate from their bulk [14,15]. The probable application prospects are in photo detectors, LASER, LED, phosphor, sensors, address decoders, high density magnetic information storage and others [16]. The politenesses of ternary compounds have been much more attractive for the alteration of the band gap and the lattice parameters. In formation of solar cell a low dimension window layer material is necessary to avoid high current loss. High efficiency devices require a thin film window layer to

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increase the blue response [17]. Window layer absorbs the blue portion of solar spectrum. The blue absorption reduces the current density of the solar cell [18,19]. Zinc doped CdS (CdS:Zn) is necessary for tuning the band gap. It has a potential use in window materials which are used in solar cell device without lattice disparity [20]. Its high band gap makes it transparent to all wavelengths of solar spectrum. This transparency leads to decrease the window absorption losses and increases the short circuit current [21].

CdS thin films are prepared by various methods such as electro chemical [22,23], chemical bath deposition [24,25], thermal evaporation [26], chemical vapor deposition [27], vapor-liquid-solid growth [28], pulsed laser deposition [29], spray pyrolysis [30]. The equipment used in vacuum deposition method is not user friendly and relatively costly with the spray pyrolysis. 'Spray pyrolysis' is a conservative process, easy, economical, versatile and creative skill to prepare stoichiometric thin films over large areas on substrate [31].

In the present work, CdS:Zn ($Cd_{0.98}Zn_{0.02}S$) thin films have been prepared onto glass substrates through the spray pyrolysis. The approach involved to modify the composition of the spray solution by adding the organic additive to realize a better morphology of the film. The crystalline nature morphology of grains is a substantial blue shift and this leads to increase the band gap energy. The blue shift is essential for good window material in solar cells. Further, photoluminescence (PL) broad emission peak at 728 nm is due to the surface defect of 'S' (sulphur) vacancies and 'Zn' acts as a sensitizer. Here in we propose, CdS:Zn nano-crystalline thin films possibly useful for window material in solar cells and also the luminescent red phosphor.

## 2. Experimental

To achieve a very fine small droplet, a simple steel nozzle is designed and the solution is straw through an air compressor [Model: VB Ceramics]. CdS:Zn thin films were deposited by spraying the solution of a known concentration on a heated glass substrate and compressed air being used as a carrier gas. An electric heater is made from the Kanthal wire and a preferred temperature can be achieved through a user friendly software tool. In order to maintain uniform temperature of the substrate, the substrate was placed on the cleaned metal plate, and it was kept 2.5 cm above the heating coils. The spraying arrangement was made in such a way that the sprayed solution directly fell on the substrate. Proper exhaust arrangement was made in order to outlet the surplus gas in the chamber. The various process parameters were optimized through trial and error process for the deposition of CdS:Zn thin films: Nozzle - substrate distance ~30 cm, Solution concentration ~0.05 M, Solution flow rate ~6.0 ml/min, Air tank pressure ~4.0 kg/$cm^2$ and Substrate temperature $375 \pm 10$ °C.

CdS:Zn thin films were deposited by taking 0.05 M concentration of solution by dissolving the stoichiometric amounts of Cadmium chloride ($CdCl_2H_2O$), Zinc nitrate ($Zn(NO_3)_2 6\ H_2O$) and Thiourea ($CH_4N_2S$) in double distilled water. Further, 0.02 M concentration of N, N-Dimethylformamide (DMF) was used as a supplement for drying control additive in order to modify the filled morphology of the films. CdS:Zn thin films were prepared by spraying the solution onto a well cleaned glass substrates and the deposition temperature was maintained at $375 \pm 10$ °C. The deposited films were annealed in air at 390 °C for 2 h using muffle furnace. To explore the structural characterization of annealed film by glancing angle X-ray diffraction (GAXRD) technique. X-ray beam irradiates the sample surface at a grazing angle slightly larger than the critical angle of total reflection. Rigaku's patented cross beam optics employing a scanning in diffraction angle 2θ and CuKα radiation (λ = 1.5405 Å). It helps in exposing large areas of the thin films (not substrate). The morphology of the film was studied by a field emission scanning electron microscope (FESEM) using FESEM ULTRA-55 (KARL ZEISS). The ULTRA 55 represents the latest development in GEMINI technology. The optical absorption spectrum of the thin film was recorded by Shimadzu UV-3600 Plus spectrophotometer. Shimadzu UV–VIS-NIR spectrophotometer with three detectors, consisting of a PMT (photomultiplier tube) for the ultraviolet and visible regions and InGaAs and cooled PbS detectors for the near-infrared region. Raman spectrum of the thin film was recorded by LabRAM HR. UV–Visible Raman with 325 nm LASER using CCD detector. LabRAM HR system provides ultra high spectroscopic resolution and a unique wavelength range capability that provides both great flexibility and high performance. X-ray photoelectron spectroscopy (XPS) data of the film was recorded using Multi-technique XPS with XPS-mapping capability. AXIS ULTRA-165, integrates the Kratos patented magnetic immersion lens and charge neutralization system with new spherical mirror analyzer. The PL measurement was performed using ROM version-4J14000 05, SL. No. 2526-002, (Model F-2700, FL-Spectrophotometer) (PMTvoltage-400 V) equipped with 150 W xenon lamp as an excitation source.

## 3. Results and discussion

Fig. 1 shows the glancing angle X-ray diffraction (GAXRD) patterns of CdS:Zn nano-crystalline thin film recorded in the range of 15–80°. The patterns are indexed as JCPDS no. 061–0314. The peaks are (100), (002), (101), (102), (110), (103), (200), (112), (201), (202), (203), (210), (211), (114) and (105) planes, these are well consistent with the JCPDS of CdS. The diffraction peaks depict that the film has a polycrystalline nature of hexagonal phase. The peaks (100) and (101) indicate wurtzite and peaks (102) and (103) are the characteristic of the hexagonal phase. The intensities of (100) and (103) lines are point out the unique hexagonal structure. The presences of sharp and well defined peaks are also confirm the polycrystalline hexagonal phase in nature. No other peak is in related with 'Zn' is seen in the patterns other than 'CdS'. It indicates that the incorporation of 'Zn' into the 'Cd' sites is more comfortable. There are several possibilities by which $Zn^{2+}$ ions incorporated into the host CdS crystalline structure '$Zn^{2+}$' ions may occupy interstitial positions in the CdS lattice and occupy empty locations of $Cd^{2+}$ ions [32–34].

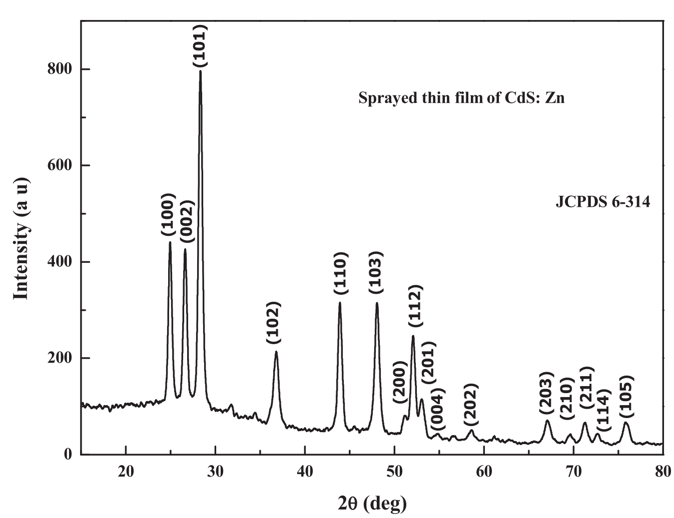


**Fig. 1.** GAXRD spectrum of CdS:Zn nano-crystalline thin film.