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The Effect of Luminescence on Crystalline CdS Thin Films Prepared by Chemical Bath Route

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Abstract: ***The optical luminescence spectra were recorded in a wavelength range 300-600 nm with an excitation wavelength of 320 nm using PL spectrometer. From the spectra existence of stoke's shift, polycrystalline nature of the film and the presence of defects have been studied and presented in this paper in detail. Luminescence properties of CdS strongly depend upon the crystalline nature of the film. PL spectroscopy shows the emission peaks at 360, 495, 505, 520, 535 and 595 nm. Here, the peak at 520 nm corresponds to emission of near band edge excitonic peak, which exhibits green band emissions with different intensity on the time period. The emission wavelength is invariably shifted towards the red end of the spectrum compared to the peak of the excitation spectrum which finds commercial application in fluorescent lamps, such films can also be used as photovoltaic cells, and in photoconductive devices.***

Keywords: Thin Films, Excitons, Emission, Luminescence

I. INTRODUCTION

Cadmium sulphide thin film is a direct band gap (2.42 eV) metal chalcogenide II-VI semiconductor with high index of refraction (2.5) and n-type conductivity. CdS is a potential candidate for the application as window layer in solar cell [1-3], multilayer light emitting diodes [4], gas sensors [5] and transparent conducting semiconductor for optoelectronic devices [6]. It is also a best visible light active semiconductor photo catalyst. CdS thin films can be deposited either by physical or chemical methods such as vacuum evaporation [7], Spray pyrolysis [9], Pulsed laser deposition [8] and Chemical bath deposition [9]. Among the various methods the Chemical bath deposition is relatively reliable, simple, economic and cost effective route to synthesis CdS thin films [10]. In this paper the effect of luminescence on chemical bath deposited CdS thin film is presented.

II. EXPERIMENTAL DETAILS

The deposition of Cadmium Sulphide thin films is established on the reaction of Cd^{2+} and S^{2-} ions in deionized water solution. Chemical baths used for the deposition of Cadmium Sulphide thin films consist of cadmium chloride, thiourea, triethanolamine and ammonia. The pH of the solution can be adjusted by adding ammonia, thin film deposition were carried out at 70°C. Molar quantities of cadmium chloride and thiourea explicitly 1:1 are used. The deposition is implemented at many pH values of the bath from 6 to 14. The substrates positioned vertically in the bath for dissimilar deposition time changing from 30 to 120 min. It is detected that molar absorption of 1:1 has given worthy quality films. While depositing the films at temperature 70°C and with organized pH value 10 the surface of the film has become more uniform, was identical and compact.

III. RESULTS AND DISCUSSION

A. Photoluminescence Analysis

The photoluminescence process is a charge transfer process. The basic principle of PL analysis is to create charge carriers by optical excitation with photon energy above the band gap of the films (2.4 eV). Holes and electrons relax in their respective ground states in the valance and conduction band. They can then recombine radiatively as most free carrier. Hence the PL emission might have close relation with the luminescence of the recombination of photo induced electrons and holes, the free and self-trapped electron-hole pair or excitons. When the film is exposed to photon energy there is an electronic transition between two energy levels E_1 and E_2 with the emission of wavelength λ. Where $hc/\lambda = E_2 - E_1$. If the excitation energy is less than the energy difference between the ground state and the first excited state then no optical absorption will occur resulting in no PL. Photoluminescence analysis is a strong characterization strategy to study the optical emission of thin films. PL analysis of the cadmium sulphide deposited over glass substrate was performed to analyze the occurrence of the defects in the crystal. The optical luminescence spectra were recorded in a wavelength range 300-600 nm with an excitation wavelength of 320 nm using PL spectrometer. Fig 1-3 reveals the emission spectra of cadmium sulphide thin films prepared at pH 10 (60, 90 and 120 minutes) at 70°C respectively. The PL intensity is determined by the radiative recombination of excitons. The luminescence is found to increase, when the period of deposition increases, this is

attributed to the increase in crystalline size of the films hence the luminescence is found to be thickness dependent. The peak intensity in the case of higher deposition time period is found much higher compared to that of lower time period which is inferred in Fig 1-3. This could be due to shape effect of Cd atoms at S-site; the shape of the materials has an important effect on PL intensity. The emission peak occurs at higher wavelength than that of the excitation peak. In fact the peak emission wavelength is invariably shifted towards red end of the spectrum compared to the peak of the excitation spectrum. This phenomenon is known as the stokes shift, which finds commercial application in fluorescent lamps.

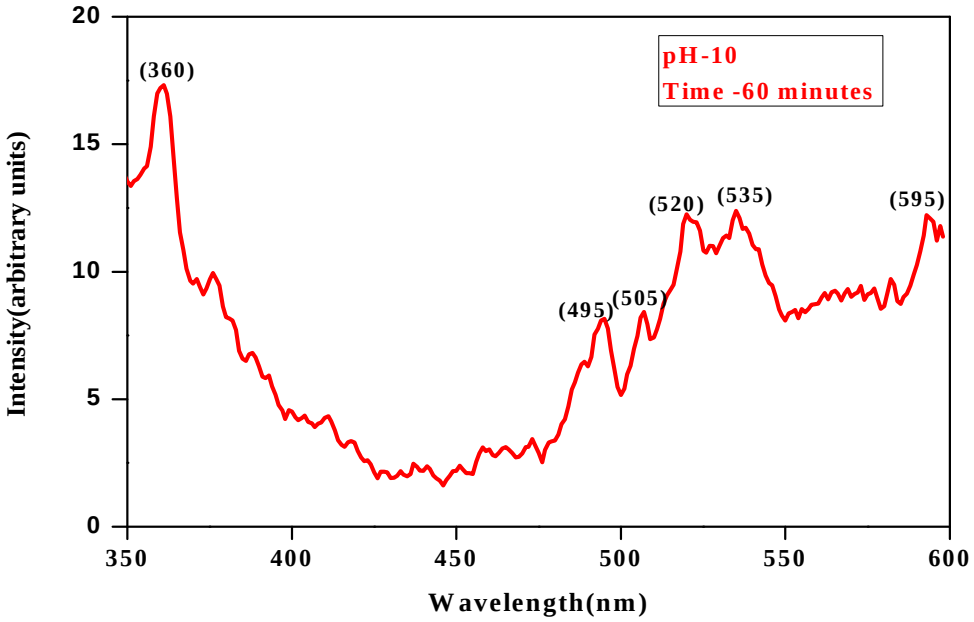

Fig.1 Photoluminescence Spectra of CdS thin films prepared at pH-10 (60 minutes)

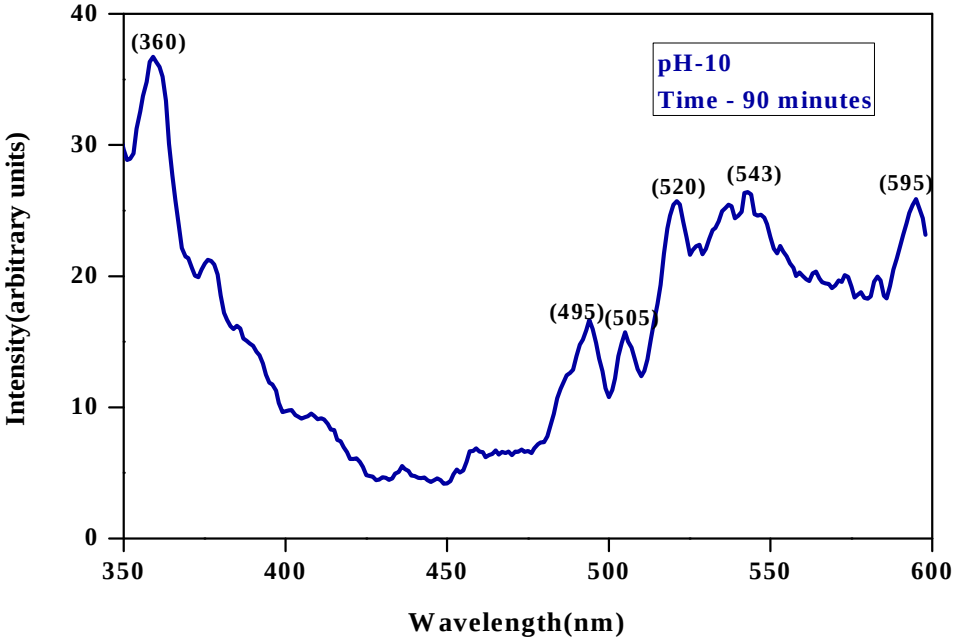

Fig.2 Photoluminescence Spectra of CdS thin films prepared at pH-10 (90 minutes)

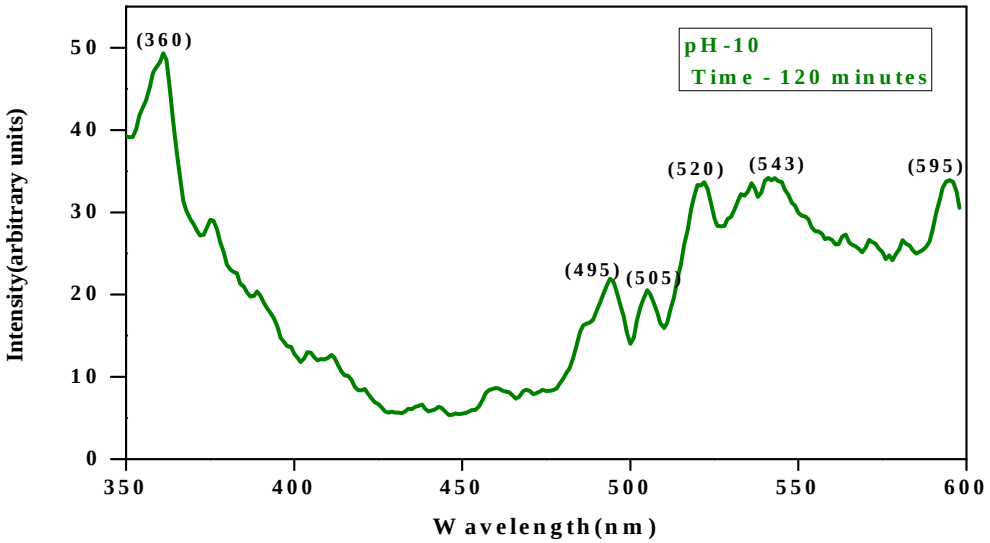

Fig.3 Photoluminescence Spectra of CdS thin films prepared at pH-10 (120 minutes)

The photoluminescence initiates from the recombination of surface states. Preliminary investigations show that photoluminescence (PL) spectra of the obtained CdS thin films have six distinct bands at 360, 495, 505, 520, 535, 543 and 595 nm respectively. The PL spectra of CdS thin films excited at 320 nm is to determine the band edge emissions of semiconductor in the visible region. Since the most common radiative transition is occurred in the semiconductor, the forbidden difference from the states of bottom of the conduction band and the top of the valence band both lie on the same energy axis versus wavelength (nm) also with some non radiative transitions from trapping states of vacancies and defects [11]. The peak at 520 nm corresponds to emission of near band edge excitonic peak. The peak positioned at 520 nm is close to the absorption edge for CdS and can be related to recombination. The other emission band can be attributed to defect luminescence. Photoluminescence spectroscopy can be used to determine the band gap of semiconductors since the most common radiative transition in the semiconductor occurs between states at the bottom of the conduction band and the top of the valence band [12]. All the films shows an intense peaks at 495 nm (2.51 eV), 520 nm (2.4 eV) and at 595 nm (2.09 eV) respectively. PL band appearing in the range of 2.18–2.54 eV are called green bands; band appearing between 2.07 - 2.18 eV are typically referred to as yellow bands; the orange band is located between 2 -2.07 eV, and luminescence observed around 1.54 – 2 eV is called the infrared / red band [16]. A donor level of 0.21 eV below the conduction band is suggested to be related to a cadmium interstitial Cd or to a sulfur vacancy V_S. The acceptor level located 0.29 - 0.30 eV above the valence band is believed to originate from an impurity rather than from a native defect in CdS. The recombination of a free hole with an electron from native donor level, Cd or v_S, 0.11 eV below the conduction band leads to a green emission observed at 2.4 eV. Luminescence in the green band (2.51 eV) is observed in all the samples. The green band described for CdS single crystals is divided into a series of equally spaced lines. Lines related to excitons bound to neutral acceptors or donors are found to appear at 2.54 and 2.55 eV. The peaks are due to emissions near the absorption edge that involves surface states or traps for electrons and also associated to Cd^{2+} and S^{2-} ion vacancies [13-17]. Thus the PL peak observed at 495 nm (2.51 eV) may be related to excitons bound to neutral acceptors or donors. Here, the peak at 520 nm resembles to emission of near band edge excitonic peak. This displays green band emissions corresponding to the defect linked luminescence emission. As reported in [15] the PL spectra of CdS thin films grown by spray pyrolysis method consisted of a characteristic red band centered at about 680 nm. The appreciation of this red band may be due to the excess of Cd^{2+}which leads to an increase in the defect level in the films. But in another report [20] the PL spectra of CdS thin films by CBD method the band was around 1.72 eV (red band) due to the sulphur vacancies [17]. In polycrystalline systems, the PL emission lines are not sharp peaks but are broad band's because of the presence of many recombination sites, the grains will have different impurity concentrations, surface areas and defect types (e.g. stacking faults) and concentrations. Hence, these results indicate that luminescence properties of CdS strongly depend on the crystalline nature of the film.

IV. CONCLUSION

PL analysis enabled us to disclose the evidence for good crystalline quality of CdS thin films. The existence of stoke's shift, polycrystalline nature of the film, emission peaks and the presence of defects have been investigated from the spectral analysis. The properties of luminescence of CdS strongly depend upon the thickness and crystalline nature of the film. Here, the peak at 520 nm corresponds to emission of near band edge excitonic peak, which exhibits green band emissions with different intensity on the time period. Hence these films find wide application in fluorescent lamps, photovoltaic cells, and in photoconductive devices. To verify the presence of red band, the analysis should be extended to higher wavelength.

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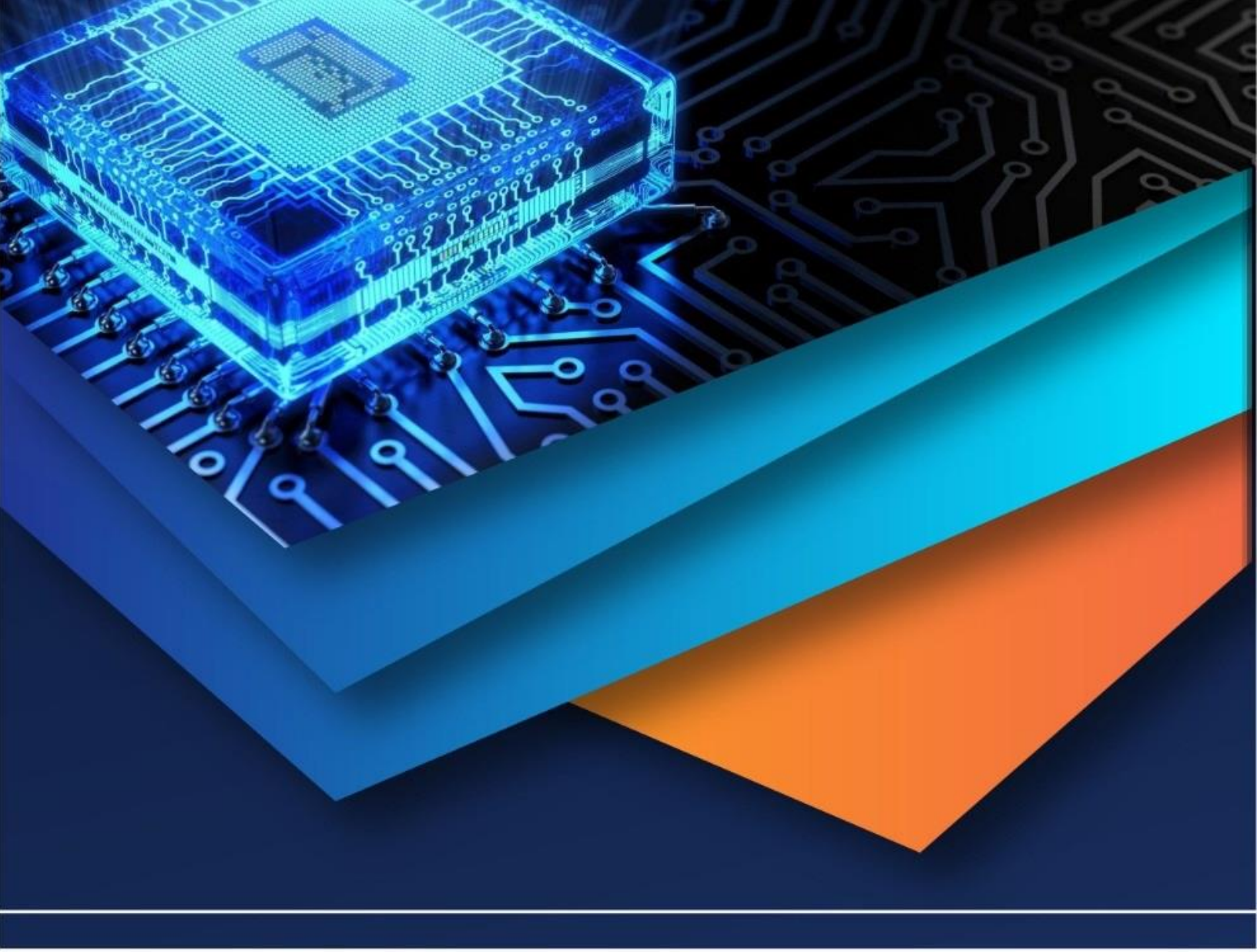

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