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EFFECT OF ETHYLENEDIAMINE TETRAACETIC ACID CONCENTRATION ON THE PHOTOLUMINESCENCE BEHAVIOR OF CdZnS THIN FILMS

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Application of ethylenediamine tetraacetic acid (EDTA) in the chemical bath solution to enhance the photoluminescence (PL) behavior of chemical bath deposited CdZnS thin film was realized. The observed beneficial effect on the luminescence properties of CdZnS crystallites in the bath solution followed by deposition on glass substrates reduces the defect emission characteristics and enhances the quality of the PL emission. Also, the observed intensity of the characteristic room temperature photoluminescence emission was found to be dependent on the concentration of EDTA in the bath solution. PL spectra show quantum confinement effect and the peak is shifted towards blue wavelength when the concentration of EDTA was changed from 0.001mol to 0.2 mol concentration. Addition of EDTA with Zn^{2+} and Cd^{2+} is found to enhance the PL intensity. PL band shows blue-shift with intense emission on combine the EDTA with Zn^{2+} and Cd^{2+}, respectively.

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1. Introduction

Cadmium Sulfide (CdS) thin film is an important semiconductor material with direct band gap of 2.48 eV at room temperature and can be utilized for many important devices. However, control on composition, size and shape is much easier via chemical route [1-3]. Chemical bath deposition is one such method, becoming popular as a room temperature technique because of the simplicity and ease for fabrication [4, 5]. Semiconductor nanocrystals have received more attentions for both fundamental research and technical application, owing to their strong size-dependent properties and excellent chemical processibility. As CdS, $Zn_xCd_{1-x}Se$ are the most important II–VI group semiconductors, having vital optoelectronic applications for laser light-emitting diodes and optical devices based on nonlinear properties [6-9], many routes have been exploited to synthesize CdS semiconductor particles and particle arrays. The effects of four critical factors including temperature ramping-up rate, hydrothermal temperature, capping molecules, and sulfur source on the shape of CdS nanostructure formed by hydrothermal process was reported [10-12].

The control of the composition of $Cd_xZn_{1-x}S$ nano particles may lead to the development of ideal materials for short wavelength diode laser applications. Semiconducting CdZnS materials and also the related ternary compounds are promising materials for high density optical recording and for blue or even UV laser diodes. These applications are based on the structure of $Cd_xZn_{1-x}S$ which exhibit fundamental absorption edges that can varied from green to UV [13-18]. In solar cell systems, where

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CdS films have been demonstrated to be effective; the replacement of CdS with the higher band gap $Cd_xZn_{1-x}S$ alloys has led to a decrease in window absorption loss and an increase in the short circuit current [18-21].

2. Experimental

The cadmium chloride ($CdCl_2$), zinc chloride ($ZnCl_2$) and thiourea (NH_2-CS-NH_2) were used as the source materials for Cd^{2+}, Zn^{2+} and S^{2-} ions, respectively. A catalyst mixture was prepared by dissolving the appropriate amount of $CdCl_2$ and $ZnCl_2$ in distilled water. The CdZnS ternary thin film was co-precipitated by slowly adding aqueous solution of NH_4OH and EDTA to the mixture of $CdCl_2$ and $ZnCl_2$ aqueous solution, which was kept stirring with constant 60 rpm through out the reaction. Before making the final solution for the preparation of the films, each of the elemental solutions was stirred for 30 min to obtain homogeneity among the constituents of the solution for uniform coating. For the preparation of good quality films, the concentration of (0.32M) $CdCl_2$, (0.32M) $ZnCl_2$, (0.34M) NH_4Cl and (0.34 M) NH_2-CS-NH_2 were optimized and used as stock solution. The appropriate amount of $CdCl_2$, $ZnCl_2$, NH_2-CS-NH_2 and EDTA (0.001 – 0.02 mol concentration) solutions were mixed in a 100 ml beaker, and made alkaline by the addition of NH_4OH solution. The mixture was again stirred to form a homogeneous mixture. An appropriate amount of water was added to control the growth kinetics on the formation of CdZnS thin films. The glass substrates having a size of 1x1 cm^2 are cleaned by using hydrofluoric (HF) acid and water having the ratio 1:3 volume ratio for 3 min at room temperature and placed vertically inside the chemical bath with the help of a circular teflon disc. The disc was attached with the constant rotator rotating at 60 rpm and was kept immersed inside the chemical bath.

The deposition was carried out for 1 hour at a bath temperature of 80ºC. The NH_4OH solution controlled the precipitation of metal ions to reduce the free metal ion concentration. The deposition of a thin film takes place through the condensation of the metals and sulfur ions on the initial layer, which acts as a catalytic surface. The reaction mechanism for the fabrication of CdZnS ternary thin films can be described as follows. Ammonia solution is added to the Cd and Zn salt solution to form the cadmium tetraamine ions $[Cd(NH_3)_4^{2+}]$ and zinc tetraamine ions $[Zn(NH_3)_4^{2+}]$, respectively.

Cadmium and Zinc ions first combined with EDTA and its formation is as follows

$$Cd^{2+} + EDTA \rightarrow Cd(EDTA)^{2+}$$
$$Zn^{2+} + EDTA \rightarrow Zn(EDTA)^{2+}$$

Again it releases the Zn and Cd ions slowly,

$$Cd(EDTA)^{2+} \rightarrow Cd^{2+} + EDTA$$
$$Zn(EDTA)^{2+} \rightarrow Zn^{2+} + EDTA$$

So the CdZnS formation reaction was controlled through EDTA. The overall reaction of the CdZnS formation is

$$[Cd(NH_3)_4^{2+}] + [Zn(NH_3)_4^{2+}] + S^{2-} + NH_3 \rightarrow CdZnS + \text{Remaining product.}$$

The deposition of the CdZnS thin films are based on the precipitation followed by condensation. After 50 minutes, the coated substrates are removed and washed with deionized water to remove loosely adhered CdZnS powder.

3. Results and discussion

Fig. 1 shows the PL emission spectra of as-grown CdZnS thin film. The spectral width of the PL spectrum is very broad because of the wide size distribution of CdZnS crystallites. In the PL spectrum, the band-edge PL is very weak, and a surface defect-related PL band with a large shift towards higher wavelength is dominant.

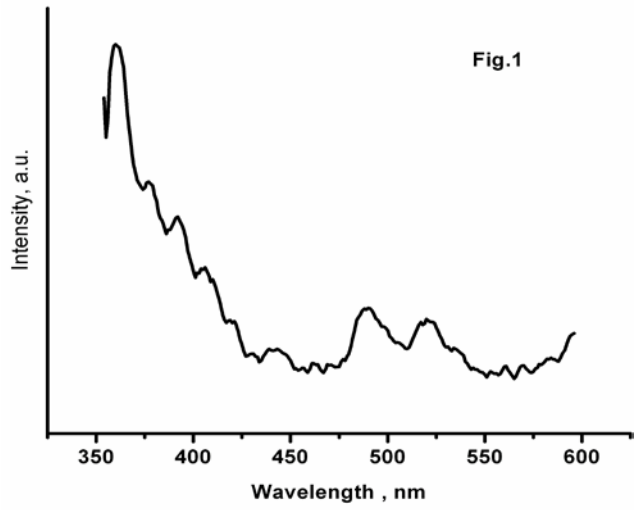

Fig. 1 The room temperature photoluminescence spectrum of the grown CdZnS thin film.

Fig. 2 (a-d) shows the PL emission spectra of the CdZnS thin films in addition with EDTA (0.002, 0.004, 0.006 and 0.008 mol concentration) in the chemical bath process. It is noted that the PL emission spectrum is completely different from that of the as-grown sample; namely, the emission peaks, which originate from the near band edge transition and from the defect surface states of CdZnS thin films, are observed clearly. The observation of the broad emission peak indicates that the size-distribution width of the CdZnS thin film is reasonably small.

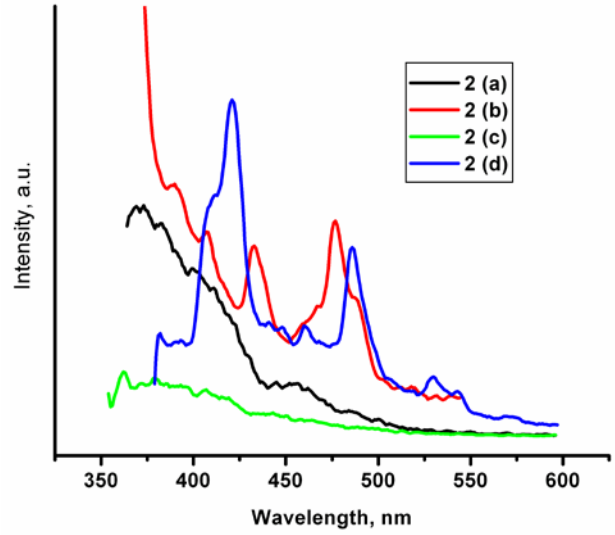

Fig. 2 (a-d) The room temperature photoluminescence emission spectrum of the CdZnS thin film fabricated under the influence of EDTA (a) 0.002, (b) 0.004, (c) 0.006 and (d) 0.008 mol concentration.

Fig. 3 (a-c) shows the PL emission spectra of the surface-modified CdZnS thin films after the EDTA added (0.01, 0.05 and 0.02 mol concentration) chemical bath process. The band-edge PL is strongly activated by the surface modification and is observed as the main PL band, while the defect-related PL is dominant before the addition of EDTA as shown in Fig. 1. It is noted that the addition of EDTA enhances the intense band-edge PL emission by three orders of magnitude. These results demonstrate the success of preparing the size- and surface-controlled CdZnS thin

films. The CdZnS thin films after the addition of higher EDTA concentration have an intense PL emission.

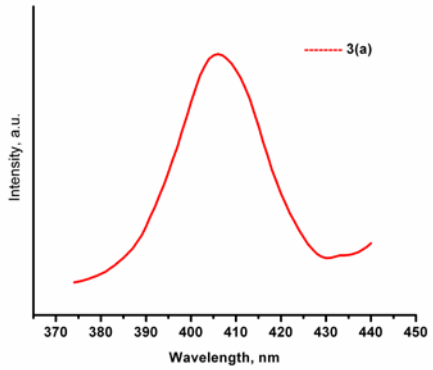

Fig. 3 (a) The room temperature photoluminescence emission spectrum of the CdZnS thin film fabricated under the influence of EDTA 0.01 mol concentration.

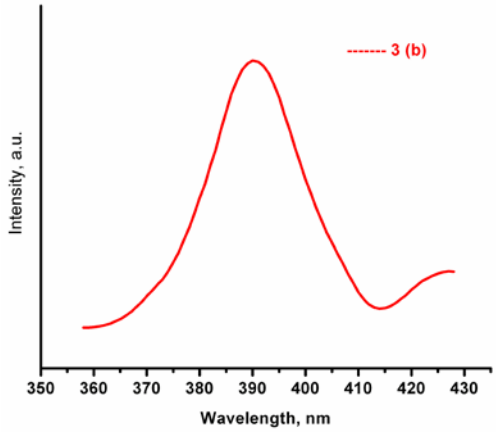

Fig. 3 (b) The room temperature photoluminescence emission spectrum of the CdZnS thin film fabricated under the influence of EDTA 0.05 mol concentration.

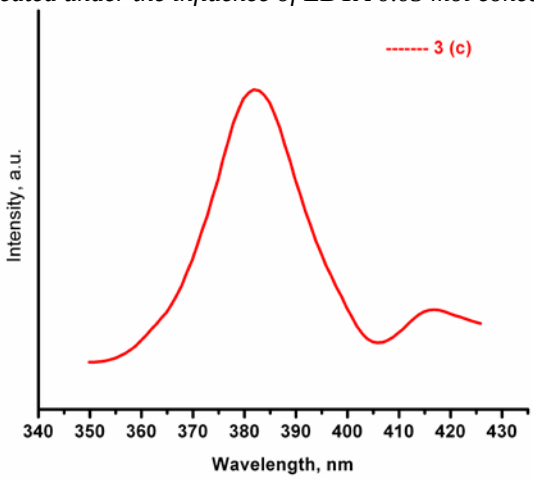

Fig. 3 (c) The room temperature photoluminescence emission spectrum of the CdZnS thin film fabricated under the influence of EDTA 0.02 mol concentration.

The PL intensity is maximum for CdZnS thin film prepared with 0.02 mol concentrations of EDTA. This is because at this concentration the surface trap states responsible for PL emission are very large. At higher concentrations the PL is blue-shifted indicating the formation of deeper trap levels. The weak shoulder observed at ~ 415 nm is due to excitonic emission of CdZnS thin films. The broad low energy PL spectrum is due to trap state emissions arising from surface defect states. In CdZnS thin films, defects consist of cadmium, zinc and sulfur vacancies, and interstitial sulfur, cadmium and zinc atoms adsorbed on the surface. The decrease in intensity of PL in the

deposited CdZnS thin film is due to the decrease in the sulfur vacancy caused by an increase in additive action of EDTA releasing more S^- ions. Conversely, at higher mol concentrations of EDTA, the additive action of EDTA is favored. It may also be mentioned here that corresponding to blue-shift in the CdZnS thin film prepared with higher EDTA concentration yield a blue-shift of PL maximum. The observed dependence of emission wavelength maximum and bandwidth on concentration of EDTA is given in the Table 1.

Table 1 The observed dependence of emission wavelength maximum and bandwidth on concentration of EDTA.

S.No	EDTA mol concentration	Emission wavelength, nm
1	0	486 and 525
2	0.002	Poor emission
3	0.004	Poor emission
4	0.006	430 and 475
5	0.008	420 and 485
6	0.01	390.2
7	0.05	381.9
8	0.02	405.8

The action of EDTA as additive agent and is evident from Fig. 3. The PL band width is minimum and emission wavelength is maximum for CdZnS thin film Fig 3 (d) indicating a transition at 0.02 mol concentration of EDTA. The nucleation and growth can be controlled by adjusting the concentration of EDTA in the chemical bath solution. It is also found that the tunability becomes effective at EDTA mol concentrations above 0.01. The defects due to S^{--} vacancies also decrease at higher concentrations due to the increased additive action of EDTA releasing controllable S^{--} ions, thereby causing a decrease in defects due to sulfur vacancies, which in turn results in increase in the intensity of PL emission.

4. Conclusions

CdZnS thin films showing a broad and intense PL spectrum and has been synthesized by chemical bath deposition technique in presence of different concentrations of EDTA. The prepared CdZnS thin films characterized by room temperature photoluminescence emission spectroscopic study as a function of EDTA concentration. The optical properties of these CdZnS thin films were investigated, showing an intense band edge luminescence emission at higher EDTA concentration. Spectral features of CdZnS thin film depend on the EDTA concentration in the chemical bath. Considerable enhancement of PL emission was obtained for higher EDTA added CdZnS thin films, suggesting an effective route to enhance the luminescence.

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