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SHORT COMMUNICATION

Photoluminescence of Nanocrystalline ZnS Thin Film Grown by Sol–Gel Method

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Abstract Nano and polycrystalline ZnS thin films play a crucial role in photovoltaic technology and optoelectronic devices. In this work, we report the photoluminescence (PL) characterization of nanocrystalline ZnS thin films synthesized by dip coating method. The PL spectra exhibit broad nature with multiple emission peaks which are due to the different defect levels in the prepared film.

Keywords Photoluminescence · Thin film · CIE coordinates · Dip coating

Introduction

ZnS is a commercially important II–VI semiconductor having a wide optical band gap, rendering it a very attractive material for optical applications, especially in nano crystalline form [1]. Due to their lower toxicity, high transparency and cost effectiveness, they are used as buffer layers in thin film solar cells [2, 3]. They are highly used in electroluminescent devices, light emitting diodes [4–6], antireflection coatings [7], lasers [8], low voltage cathodoluminescent display devices [9], bio sensors [10], DNA markers [11], multilayer dielectric filters [12], and also it is an efficient phosphor in flat panel displays [13]. ZnS has also been used as a passivation layer in the preparation of quantum dots [14] and can be used in diodes, field effect transistors, electro–optic modulators etc. [15–17].

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Nanostructured thin films have been prepared by various methods like pulsed laser deposition, ultrasonic spray pyrolysis, chemical bath deposition, hydrothermal method, anodisation, spin coating etc. Chemical bath deposition is one of the cheapest methods for synthesizing nanostuctured thin films and ZnS thin films have been developed in this method by various researchers [18–20]. Characterisation of these thin films by photoluminescence plays a key role in the study of their application in display devices, imaging etc.

Experimental

Synthesis and structural characterization of the ZnS thin films in this work is reported elsewhere [21]. Here ZnS thin films were prepared using wet chemical method on glass substrate. The chemical bath were prepared by dropwise addition of 1 M Sodium sulphide [$Na_2S.9H_2O$, 98 %, Merck] solution to 0.5 M Zinc acetate [$(CH_3COO)_2 Zn.2H_2O$), 98 %, Merck] solution with continuous stirring. The well cleaned substrates were immersed in the bath kept at a temperature of 80 °C. Six dips of 30 min duration were given to the substrate. After each dip the substrate is taken out and washed with distilled water and dried.

The photoluminescence emission spectrum of synthesized ZnS thin film sample was taken using Shimadzu RFTC 5301spectrophotofluorimeter with 150 W xenon lamp as the light source.

Results and Discussion

The x ray diffraction pattern of nanostructured ZnS thin film is depicted in Fig. 1 with major refletion from (200) plane according to JCPDS database No. 77–2100 [21]. The minor diffraction peak at 42.2^0 corresponds to ZnO phase present

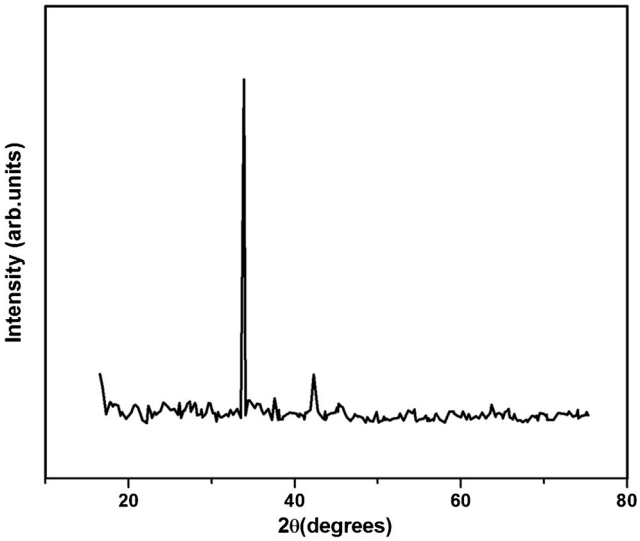

Fig. 1 X ray diffraction pattern of nanostructured ZnS thin film

in the sample. The grain size of the ZnS phase was evaluated to be 27 nm by means of Debye–Scherrer's formula

$$t = \frac{0.9\lambda}{\beta Cos\theta}$$

where t, λ, β and θ are the grain size, wavelength of x-ray (Cu K_α), full width at half maximum of the diffraction peak and glancing angle respectively.

Figures 2 and 3 show the PL spectra monitored at two excitation wavelengths 356 nm and 245 nm respectively. Gaussian fitting was applied to deconvolute the emission curves. The unsymmetric nature of the PL spectra with multiple peaks is due to the various native defect levels that may be present in the prepared ZnS thin film.

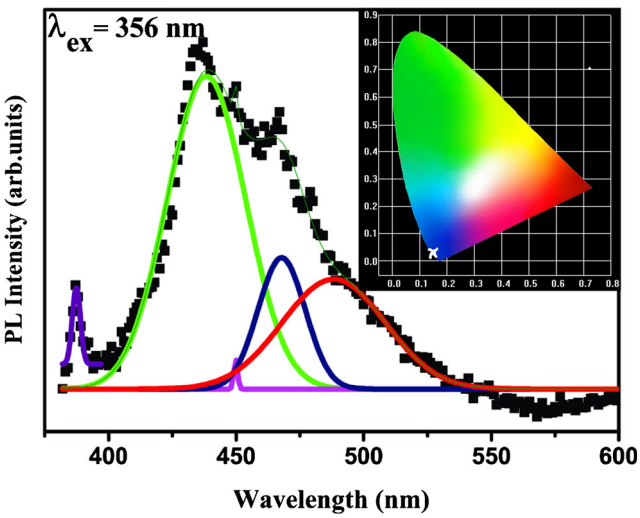

Fig. 2 Photoluminescence spectrum of ZnS thin film monitored at λ_{ex}= 356 nm [Inset: CIE Diagram]

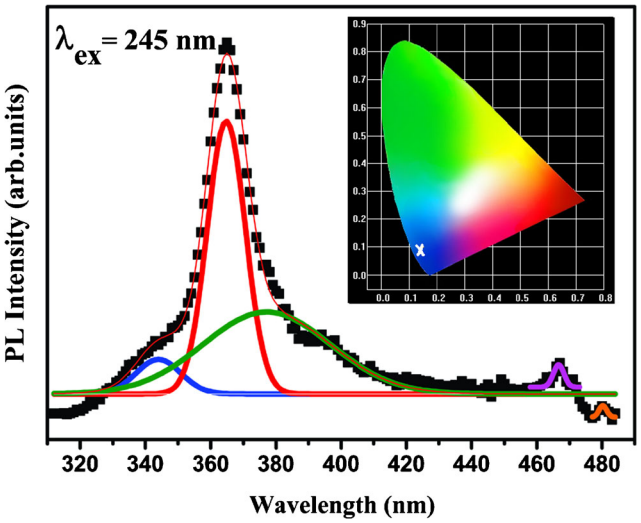

Fig. 3 Photoluminescence spectrum of ZnS thin film monitored at λ_{ex}= 245 nm [Inset: CIE Diagram]

Figure 2 exhibit peaks at 434, 468, 488, 387 and 449 nm. The highly intense peak at 434 nm is due to the sulphur vacancy (Vs) [22–24]. The emission band at 468 nm is due to the recombination of electrons in the sulphur vacancy level with the holes in the zinc vacancy [25–27]. The peak at 449 nm may be due to the recombination of sulphur vacancy related electrons and holes in the surface state near valance band. The band at 488 can be attributed to the zinc vacancies in ZnS film [28–30]. The small intense peak at 387 nm is from the trace amount of ZnO present in the prepared thin film [31–33]. The EDX and XRD of the ZnS thin film confirms the presence of ZnO phase [21]. From the CIE diagram the emission colour is found to be blue with CIE coordinates x=0.15 and y=0.026.

When excited with a wavelength of 245 nm (Fig 3), additional peaks are originated at 343 and 365 nm whereas the peak at 434 nm is suppressed and the resultant emission is bluish white in colour. The small peak at 343 nm is related to the red shifted free exciton band [34]. In undoped ZnS, the

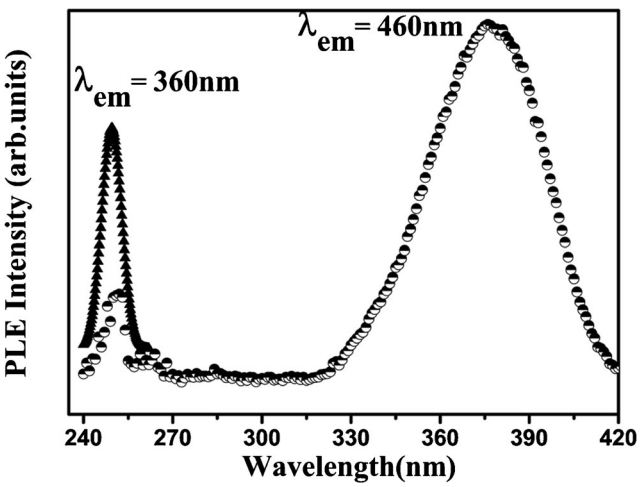

Fig. 4 Photoluminescence Excitation Spectrum of ZnS thin film

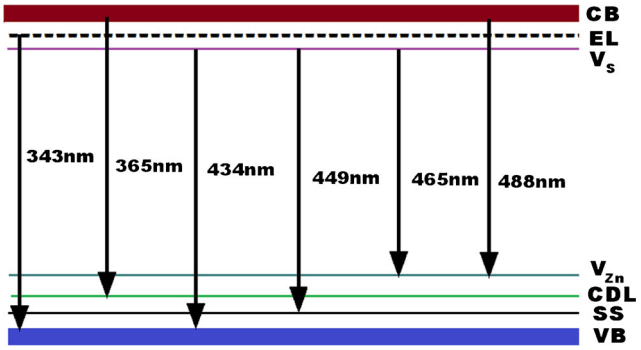

Fig. 5 Energy Band Diagram of ZnS thin film [VB-Valance Band, SS-Surface State, CDL-Complex Defect Level, V_{zn}- Zinc Vacancy, V_s-Sulphur Vacancy, EL-Free Exciton level, CB-Conduction Band]

presence of oxygen-related defect complexes introduces various luminescence centers [35]. Here the intense peak at 365 nm is due to one of such oxygen-related-acceptor defect complex [34]. The bluish white emission of the ZnS is confirmed from the CIE diagram with coordinates x=0.14, and y=0.088.

The photoluminescence excitation (PLE) spectra for the two emissions are shown in Fig. 4. While monitoring the PLE spectrum with emission wavelength at 360 nm the excitation was far above the band edge, at 245 nm. The excitation spectrum consisted of one intense peak at 365 nm and a less intense peak at 245 nm at an emission wavelength 460 nm.

The energy band diagram of the ZnS thin film prepared by sol–gel method is depicted in Fig. 5.

Conclusion

The photoluminescence emission and excitation spectra of ZnS thin film grown by sol–gel method were studied. The film exhibited bluish white and blue luminescence when excited at wavelengths 245 nm and 356 nm respectively. The different emission bands are from the various defect levels in the film. The prominent emission peaks at 365 nm and 434 nm are due to an oxygen related defect complex and sulphur vacancy respectively.

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