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Research Paper

Rear earth element (REE) Ce doped ZnSe thin films deposited on the ITO substrate using simple electrochemical deposition method

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Abstract

Rear earth element Ce doped ZnSe thin films were deposited on the ITO substrate using simple electrochemical deposition method with different concentration of Ce^{3+} such as 3 and 5 mole % respectively. These electrochemically deposited thin films were characterized as a function of various doping concentration using UV–vis spectra, electrochemical impedance spectroscopy (EIS) and PL spectroscopy. The calculated average band gap energy is found to increase to compare the band gap of ZnSe (3.2eV), while using dopant concentration about 4 mole %, the band gap values is lower than the other samples.

Keywords: Rear earth element; Substrate, EI spectroscopy, photoluminescence and optical properties.

1. Introduction

In general, thin films can be obtained by many deposition techniques use such as physical vapor deposition, metal organic chemical vapor deposition, vacuum deposition, molecular beam epitaxy, vacuum evaporation, chemical bath deposition, sputtering and electrochemical deposition method are some of the well explored method for the prearation of ZnSe thin films [1-10]. Among these methods, the electrochemical deposition (ECD) method is one of the most extensively accepted techniques for growing semiconductor films from aqueous solution for the photoelectrochemical application [11-15]. Recently, metal chalcogenides are significant class of compound semiconductor material, which can find a variety of application. In exacting zinc

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selenide (ZnSe) based materials shows unique optical properties demonstrating some potential applications like red, blue and green light emitting diods, high-density optical storage, laser, thin films solar cells, blue LED, full colour display and as a buffer/window layer for thin film solar cells due to the fact that ZnSe is a direct band gap photonic material with a wide energy band gap of 2.7 eV. Particularly large area films of compound semiconductors for use in solar cells and display devices have been grown by using simple electrochemical deposition method [16-20]. The electrodeposition is a low cost deposition technique, which is readily adjusted there is good control over film thickness, morphology and composition. ZnSe thin film formation can be easily controlled by various electrolyte parameters like temperature, solution concentration and also bath pH. However, to the best of our knowledge there are several repost on the electrochemical deposition of ZnSe from aqueous solution and from non-aqueous solution [21-25].

In general, rare-earth (RE) metals have effective luminescent center for rare earth metals doped semiconductors are due to their well temperature-stable luminescence and involved incompletely filled 4f shells that are well screened and slightly affected by the crystalline field [26-30]. Hence, doping of rare-earth element is one the effective approaches to improve the luminescence properties of semiconductor materials for the wide range of potential application in optoelectronics like nonlinear optics, color thin film electroluminescence screen devices and optical switches [31-35]. In this paper, we have examined the deposition of various concentrations of Ce^{3+} ions doped ZnSe thin films on ITO coated conducting glass substrate using electrochemical deposition technique in an aqueous electrolyte medium. The effect Ce^{3+} ions concentration on the structural, morphological, compositional and optical properties of ZnSe thin films were studied.

2. Experimental part

Pure ZnSe thin films were deposited using the electrochemical deposition (ECD) technique. The deposition procedure as similar to the previously reported literature. In Ce^{3+} ions was doped during the ZnSe thin film growth process by ECD technique. Linear sweep voltammetry (LSV) experiments were carried out using a potentiostat / galvaostat (CH Instrument USA, model 604E). All the chemicals were analytical reagent grade, purchased from Sigma-Alrich Company (USA) and used without further purification for the preparation of reaction solutions. The electrochemical measurements were performed in a conventional three electrode system with ITO coated glass substrate was used as working electrode.

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A platinum wire was used as the counter electrode and saturated calomel (Ag+ / AgCl /KCl) electrode served as the reference electrode. All the reaction solution was prepared by using double distilled water. In actual experimental procedure, 0.3M of $ZnSO_4$, concentration of solution varied from 1 to 5 mole % of $C_6H_9EuO_6.xH_2O$ and 0.003M of SeO_2, the pH of the reaction mixture was adjusted by adding sulfuric acid. The Ce^{3+} doped ZnSe thin films were successfully carried out at 50 °C by ECD with the potential of -700 mV for 10 min in the reaction bath. After the film formation the samples were subsequently removed from the bath, rinsed with double distilled water, dried in air and kept in a desiccators for further characterizations.

3. Result and discussion

3.1 XRD studies

The crystalline size and crystal structure of chemically deposited Cde:ZnSe thin film were determined by using x-ray diffraction technique. Ce:ZnSe film is recognized to occur in either cubic (zinc blended type) or hexagonal (quartzite type) structure shape or sometimes a mixture of both phases present. The calculate average crystalline size of as deposited and annealed Ce:ZnSe thin films, was calculated from full width half maximum value of the more intensive diffraction peak. Using Scherrer formula.

$$D = \frac{k\lambda}{\beta\cos\theta}$$

Where D is the crystalline size, λ is wavelength of x-ray radiation, β is the full width half maximum of high intensity daniffraction peak, k is the constant and θ is angle of diffraction maximum [36-40]. Figure 1 shows X-ray diffraction image of chemically deposited and annealed ZnSe thin films onto non-conducting glass substrate. Figure 1 show the as-deposited films, while as deposited film is poor crystallinity and did not existing well resolved peaks are detected of these films from XRD pattern over a broad hump of as deposited film which is corresponds to the cubic nature of ZnSe film.

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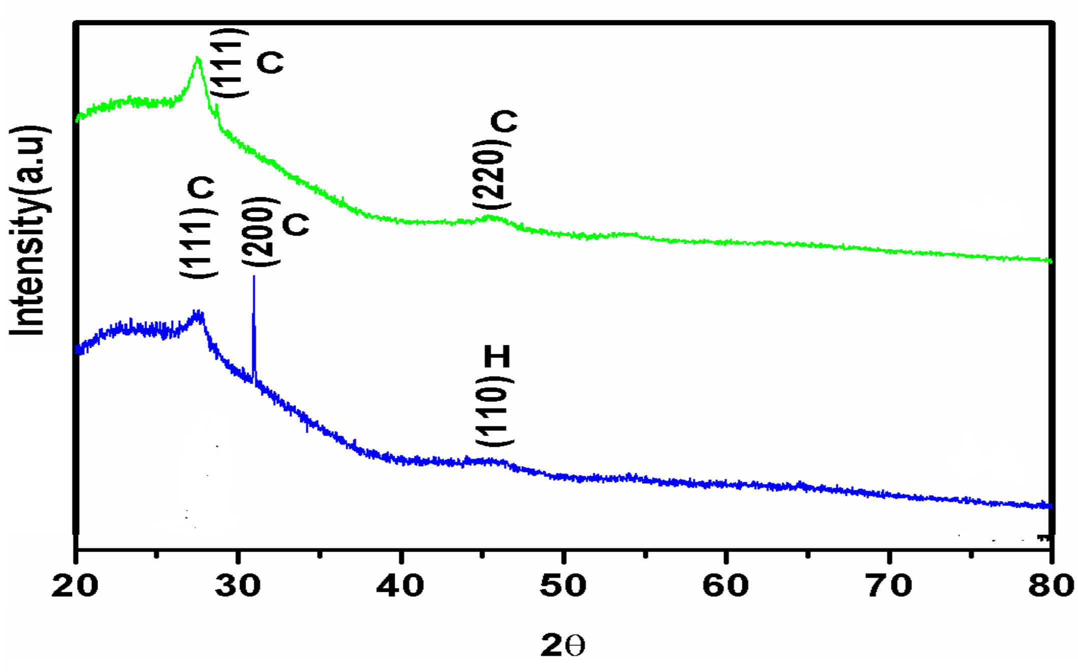

Fig. 1. XRD analysis of chemically deposited Ce:ZnSe thin film.

3.2 SEM studies

The FESEM photograph of the Ce:ZnSe thin films used different complexing agents are shown in Fig.2. The substrate is fully covered without uniform films with particles on it in the as-deposited Ce:ZnSe thin films. We observed that the significant changes in the surface morphology of as-deposited ZnSe thin films used different complexing agents. When complexing agents such as ammonia, hydrazine hydrate and polyvinyl alcohol used, the FESEM image exhibits different sizes of spherical shape of well adhere a grains and crack free, respectively.

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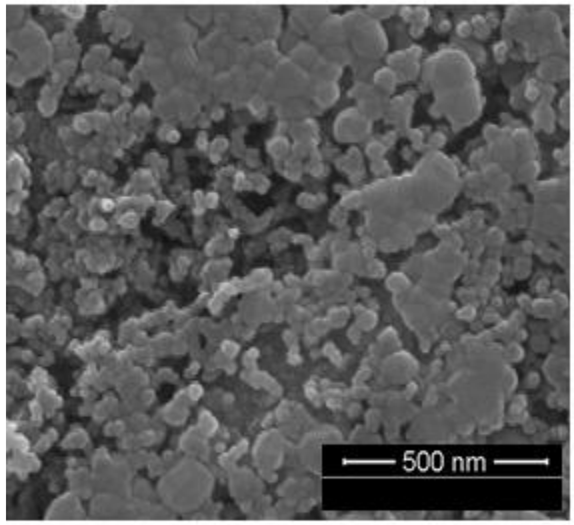

Fig. 2. FE-SEM images of Ce^{3+} doped ZnSe thin film.

3.3 Optical properties

Fig. 3 shows the absorption coefficient (αhν) Vs photon energy (hν) curve for different concentration of Ce^{3+} doped ZnSe thin films were examined by UV-visible spectroscopy. The absorption coefficient edge sharp for the 3 and 5 mole % of Ce^{3+} doped as-deposited ZnSe thin films are found to be 375and 365 nm, respectively and subsequent calculated band energy gap values are 2.55 and 3.25 eV. It is clearly indicated to the monophasic structure of ZnSe:Eu thin films. If the dopant concentration was increased significantly 3 and 5 mole% the absorption coefficient edge was not sharp for ZnSe:Ce thin films , which are observed at 355, 402 and 342 nm respectively and the calculated band gap value is found to be 2.97, 2.92 and 3.52 eV. The absorption edge was not sharper at this moment, it showed to the mixture of phases of cubic and hexagonal phase was presented [41-45].

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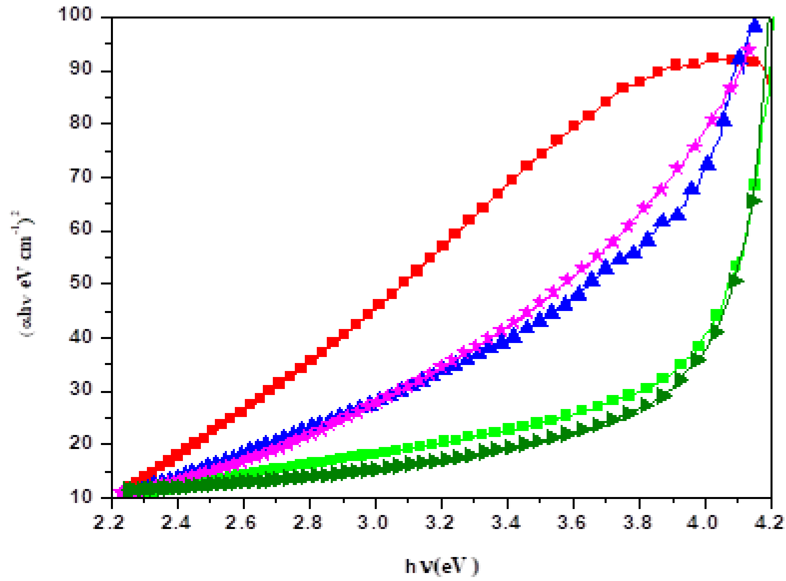

Fig. 3. Absorption coefficient vs photon energy spectra of as-deposited Ce:ZnSe thin film.

3.4 Electrochemical impedance spectroscopy (EIS)

The electrochemical impedance spectroscopy (EIS) was performed for semiconducting ZnSe thin films to resolve the current response to application of an ac voltage as function of the frequency. The Nyquist plot for Pure ZnSe and 3 and 5 mole % Ce^{3+} doped ZnSe thin films are shown in Figure 4. The measured charge transfer resistance is 8 (Ωcm^{-2}) for 5 mole % Ce^{3+} doped ZnSe thin film. From the observed results, the charge transfer resistance of 5 mole % Ce^{3+} doped ZnSe thin film is vary less compare to the others, this suggested that the addition of Ce^{3+} into ZnSe host lattice is favorable to the faster interfacial Ce-Ce charge transfer.

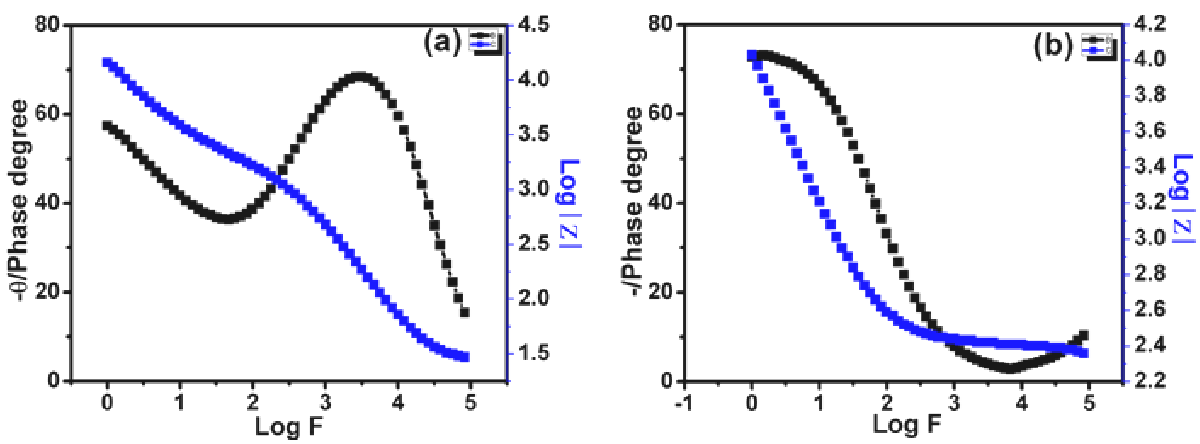

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Fig. 4. Electrochemical impedance spectroscopy (Nyquist plot) 3 and 5 mole % Ce^{3+} doped ZnSe thin film.

3.5 Photoluminescence (PL) spectroscopy

The photoluminescence (PL) spectroscopy is a further useful apparatus to discover the band gap position or band gap energy if it is an unknown semiconductor. Fig. 5 shows the PL spectra for Ce:ZnSe thin films were measured at excitation wavelength of 382 nm. The as-deposited thin films show broad band emission which may be due to deep level emission. From the results, the high intense emission peak shows by rear earth metal ion doped ZnSe thin film deposition process and it can be powerful study for the electrochemical properties.

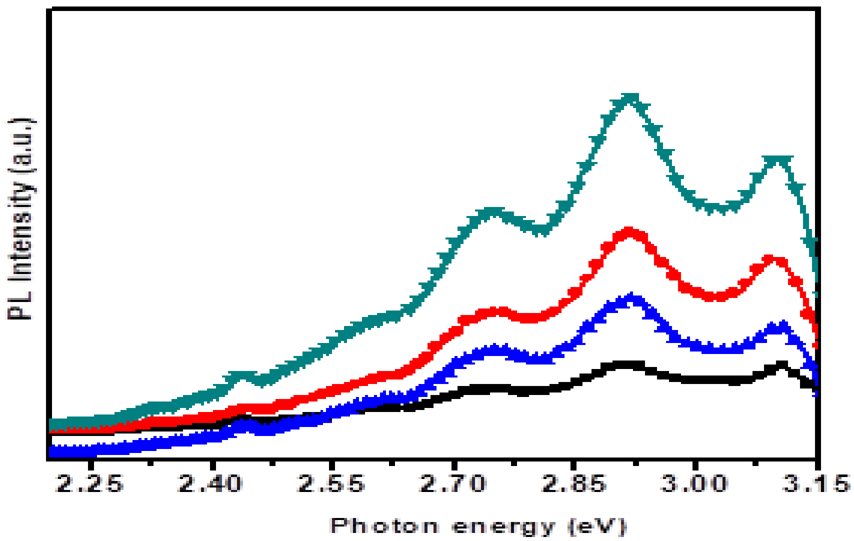

Figure. 5 Photoluminescence (PL) spectroscopy 3 and 5 mole % Ce^{3+} doped ZnSe thin film.

4. Conclusions

In summary, the Ce^{3+} doped ZnSe thin films were successfully deposited on ITO glass substrate by electrochemical deposition method (ECD). The observed band gap values are red shift when compare to the bulk band gap value of ZnSe (2.7 eV). The electrochemical impedance spectroscopy (EIS) indicates that the 5 mole % Ce^{3+} doped ZnSe thin film showed a less charge transfer efficiency with fine conductivity compare to the other samples. The PL studies demonstrate that the emission intensity of ZnSe thin film was found to be significant increased with respect to the pure ZnSe thin film. From the results of this present work, we can suggested that the ZnSe thin film are one of the better efficiency material for photoelectrochemical devise applications.

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