Journal of Nano- and Electronic Physics
Vol. **12** No 5, 05006(5pp) (2020)

Журнал нано- та електронної фізики
Том **12** № 5, 05006(5cc) (2020)

The Optical Properties of Europium-doped Zinc Selenide Films

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(Received 01 May 2020; revised manuscript received 15 October 2020; published online 25 October 2020)

Europium-doped ZnSe films were sprayed on glass substrates electrostatically. Keeping other deposition parameters such as flow rate of precursor solution, spray volume, voltage and distance of nozzle to substrate constant, temperature was varied from about 300 °C and 400 °C with an interval of 25 degrees. Optical studies at different temperatures are presented. Thickness of the films obtained by surface profile indicates nanosizes of 50, 100, 150, 75 and 60 nm in the considered temperature range. Optical studies reveal high transparency, very minimal absorption and reflection characteristics of ZnSe:Eu films in the visible region. Absorption peaks visible at 250 nm suggest the occurrence of defect state near the band edge. Large absorption coefficient suggesting evidence of high density of states for ZnSe:Eu is observed. High transmittance results suggest the films suitability in coating materials that are required to exhibit high transparency for laser applications, while low reflectance values and large refractive index reveal the films could be applicable in solar cell coatings that require high efficiency and in manufacturing optoelectronic devices. Higher optical conductivity at photon energies above 3 eV is evident. Steep increase in extinction coefficient with photon energy indicates the probability of raising the electron transfer across the mobility gap with high photon energy and greater attenuation of light. Band gap investigation of ZnSe:Eu films reveals a strong blue-shift (3.01 eV to 3.12 eV) from the bulk ZnSe (2.72 eV) band gap.

Keywords: Zinc selenide, Europium, Nanofilms, Spray pyrolysis, Optical studies.

DOI: 10.21272/jnep.12(5).05006 PACS numbers: 78.66.Hf, 73.50.Pz

1. INTRODUCTION

The bulk of devices in the electronics industries rely more on semiconductors as their raw materials for manufacturing purposes. II-VI semiconductors have been vastly researched possibly on account of their numerous applications in device manufacturing technology. It is very essential to explore the properties (optical) of materials in order to establish their energy (band) gap and process of transition so as to suggest suitable relevance of the films [1]. Zinc selenide is characterized by a wide energy (band) gap of about 2.7 eV. Due to the properties exhibited by this material, it has found applications in a range of devices such as optoelectronic devices, solar cell production and so on. ZnSe films have earlier been prepared by electrodeposition [2], solution growth [3, 4], spray pyrolysis [5], thermal evaporation [6], RF magnetron sputtering [7], etc. Some research articles on Eu-doped ZnO and ZnS films [8-9] exist. However, little report is available on Eu-doped ZnSe [10, 11] films by solvothermal and CSVC deposition techniques.

Spray pyrolysis (electrostatic) was considered to grow Eu-doped ZnSe nanofilms taking into account its novelty in this regard. When compared to conventional spray pyrolysis technique, electrostatic spray pyrolysis is capable of producing fine and extremely tiny droplets which is the desire of this research. Also, when compared with sophisticated techniques such as pulsed-laser deposition, molecular beam epitaxy, sputtering, vacuum evaporation, this technique was desired to dope the films because it proffers a clear-cut approach of doping films by the effortless insertion of the expected dopant to the spray mixture. This technique also comprises of an easy set-up and much technicality is not mandatory when using this process. The core motivation of this research is to examine only the properties (optical) of ZnSe:Eu films in detail and carefully suggest their suitable relevance based on the obtained results. Zinc selenide (ZnSe) has been studied extensively; hence we are of the view that doping ZnSe with europium could well improve the properties (optical) and possibly introduce new functions of the material. This assumption is so considering the luminescent property exhibited by europium which has the prospect of improving the properties (optical) of ZnSe, which of course may open novel sections of application of the material.

2. MATERIALS AND SUBSTRATES PREPARATION

The preparatory materials for this communication are zinc acetate (source of zinc ion), hydrochloric acid (HCl) which served as a stabilizing agent, selenium dioxide (source of selenium ion) and europium (III) oxide (source of europium ion). Prior to deposition of ZnSe:Eu films, the glass slides which served as substrates were ultrasonically cleaned in a sonicator for 12 min and rinsed in water (distilled) and eventually refluxed (using a soxhlet apparatus). After refluxing, the glass substrates were left to dry and placed in a clean air-tight glass jar to avoid contamination of any kind.

3. EXPERIMENTAL PROCEDURE

A 0.4 M solution comprising zinc acetate (dehydrate) and selenium dioxide were mixed in equal proportions inside a beaker. The solution was stabilized by the simple addition of little drops of concentrated HCl. The spray mixture was stirred continuously by a mag-

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netic stirrer hot plate for 15 min to ensure uniformity of the solution. 10 wt. % of europium (III) oxide was simply added to the spray mixture and continuously stirred for 30 min before being sprayed directly onto the heated glass slides through a nozzle (syringe) at separate growth/deposition temperatures between 300 °C and 400 °C. On decomposition, light pinkish ZnSe:Eu films were formed on the glass substrates. The temperature attained by the glass slides was provided externally and measurement obtained with a *k*-thermocouple connected beneath the heating plate. During the process of growth, flow-rate was kept constant at 400 µl/spray, nozzle-substrate distance was optimized at 5.67 mm at a steady voltage of 3.5 kV.

The proposed reaction mechanism for growing ZnSe:Eu films is described as follows:

Adding HCl as a stabilizer to zinc acetate releases the Zn^{2+} ion as indicated in equation (1):

$$Zn(CH_3COO)_2.2H_2O + 2HCl \rightarrow Zn^{2+} + 2[CH_3COOH] + 2H_2O + 2Cl. \quad (1)$$

When selenium dioxide is included into the reaction bath, it dissociates forming the complex Se^{2-} as indicated in equation (2):

$$SeO_2 \rightarrow Se^{2-} + O_2. \quad (2)$$

Europium trioxide dissociates in the reaction bath forming Eu^{3+} complex according to equation (3):

$$Eu_2O_3 \rightarrow 4Eu^{3+} + 3O_2. \quad (3)$$

The combined reaction of the ions in equations (1), (2) and (3) undergoes pyrolytic decomposition, resulting in ZnSe:Eu films according to equation (4):

$$Zn^{2+} + Se^{2-} + Eu^{3+} \rightarrow ZnSe:Eu \downarrow \quad (4)$$

4. RESULTS AND ANALYSIS

4.1 Thickness Measurement

ZnSe:Eu film thicknesses were acquired from a stylus profiler (Model: Veeko Dektak 150) at room temperature. For deposition temperatures of 300, 325, 350, 375 and 400 °C, the corresponding thicknesses are 50, 100, 150, 75 and 60 nm, respectively. The reduction in film thickness at increased temperatures might be as a result of the reduction in mass transfer of the precursor to the substrate due to gas convection from the chamber, pushing several of the droplets away from the substrate [12].

4.2 Optical Studies

The optical absorption spectra of ZnSe:Eu films in this research were determined from a UV-Vis spectrophotometer (Cary Model) in the wavelength region of 200 nm to 800 nm. The absorption spectra of ZnSe:Eu films determined at various temperatures are displayed in Fig. 1.

ZnSe:Eu films exhibited extremely poor absorption in the entire visible region (Fig. 1). ZnSe:Eu films displayed absorption peaks around 250 nm. These peaks may be associated with the absorption of SeO_2 since selenium is unstable in air and therefore reacts with oxygen in air [5] and also due to some defect states that may have occurred within the band edge [13]. All the absorption curves recorded a sharp decrease at wavelengths slightly below 400 nm which agrees with the reports of [14] for ZnSe films. The sharp decrease observed in the absorption spectra of ZnSe:Eu films at wavelengths less than 400 nm can be attributed to the onset of inter-band transitions at the fundamental band edge [15].

The transmittance values for all the deposited films were evaluated from the absorbance values from the relation [16]:

$$T = 10^{-A}. \quad (5)$$

In equation (5), T is the transmittance of the material under investigation while A represents the absorbance. The transmission spectra for ZnSe:Eu films are presented in Fig. 2.

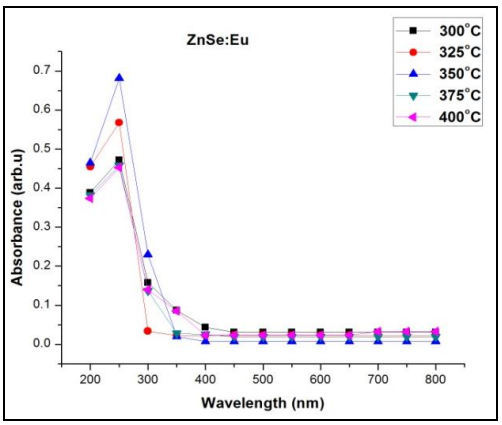

Fig. 1 – ZnSe:Eu films absorption spectra at different deposition temperatures

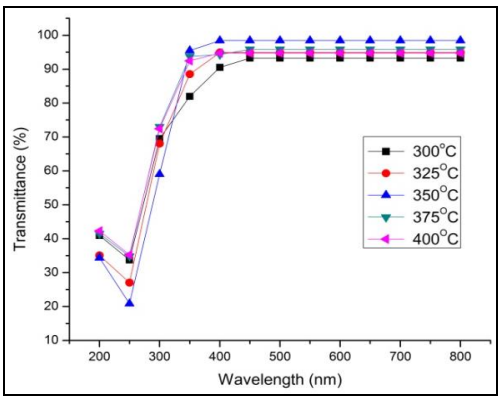

Fig. 2 – Transmission spectra of Eu-doped ZnSe films at various temperatures

From Fig. 2, the transmission spectra of all ZnSe:Eu films were between 59 % and 72 % in the UV region, while the films exhibited very high transparency (91 % to 98 %) in the visible region at different deposition conditions (temperature), which suggests the material's suitability for fabricating transparent products. Airplane windows need to be extremely free from ice and also need to be highly transparent particularly in cold air and all flying conditions. This condition is very crucial for safe take-off and flying in cold air, as well as

shielding planes from electromagnetic interference and maintaining transparency in demanding conditions [17]. This high transmittance exhibited by Eu-doped ZnSe films indicates that ZnSe:Eu will prove absolutely useful in coating airplane windows to help maintain transparency at all weather conditions and to maintain a safe flight.

The reflectance values for all europium-doped ZnSe films being studied were calculated from the absorbance and transmittance values from the relation [1]:

$$A + T + R = 1, \tag{6}$$

$$R = 1 - [A + T]. \tag{7}$$

The reflection spectra of Eu-doped ZnSe films are presented in Fig. 3.

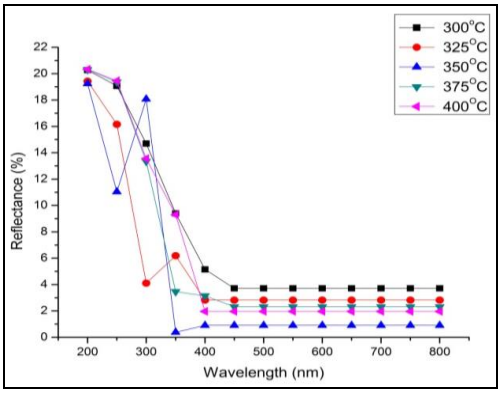

Fig. 3 – Reflection spectra of Eu-doped ZnSe films at different deposition temperatures

Fig. 3 is suggestive that ZnSe:Eu films are poorly reflective in the ultra-violet and visible regions. Previous researchers [5, 13] have also reported low reflectance values for ZnSe films. Reflectance values of ZnSe:Eu films obtained for different deposition temperatures are between 0.9 % and 20.33 %. The low values of reflection in all cases of the investigated films at overall spectral ranges testify their probability of usage as an anti-reflective coating in high efficiency solar cells [11].

The refractive indices of ZnSe:Eu films were analyzed at different deposition temperatures from reflectance values from the relation [1, 16]:

$$n = \frac{1 + R^{1/2}}{1 - R^{1/2}}. \tag{8}$$

Fig. 4 reveals the plot of refractive index versus photon energy at different deposition temperatures for ZnSe:Eu films.

From Fig. 4, the refractive index of ZnSe:Eu films at different deposition temperatures reveals a constant value of about 1.06 to 1.88 at photon energies below 4 eV. However, at high photon energies, the films recorded high refractive index between 2.24 and 2.64 for the range of temperatures (300 °C to 400 °C) under investigation. This property of high refractive index exhibited by the films at high photon energies suggests that they will be useful in the manufacture of optoelectronic devices.

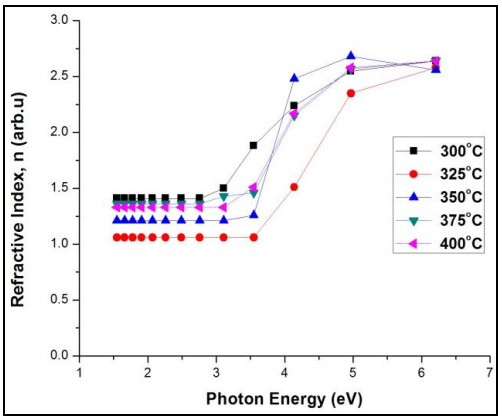

Fig. 4 – Variation of the refractive index of ZnSe:Eu films with temperature

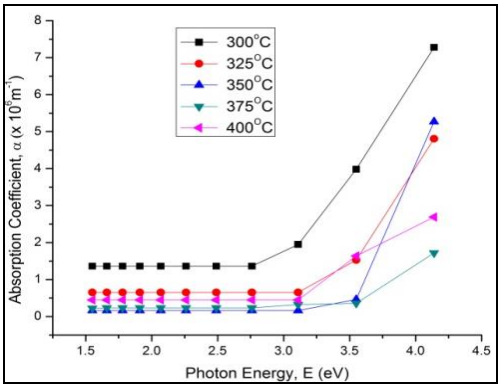

Fig. 5 – Absorption coefficient of ZnSe:Eu films at different deposition temperatures

The absorption coefficient values of ZnSe:Eu films at different deposition temperatures were calculated from the relation [1]:

$$\alpha = \frac{-(\ln T)}{t}, \tag{9}$$

where t and T represent thickness and transmittance.

A similar trend is observed for all ZnSe:Eu films. An almost steady value is observed at photon energies below 3 eV and increases afterwards. This behavior simply implies that the material possesses high absorbance at short wavelengths and low absorbance values at longer wavelengths. The values of absorption coefficient are very large, which is a consequence of the very large density of states in the solid phase [18].

The optical conductivity of ZnSe:Eu films under study was calculated for different deposition temperatures.

ZnSe:Eu films at different deposition temperatures exhibited a steady high optical conductivity at small photon energies (corresponding to the visible region) and thereafter, the films exhibited some form of sudden increment at photon energy over 3 eV (about 3.5 eV), except for the film deposited at substrate temperature of 300 °C which increased at a photon energy of about 2.8 eV. For semiconductors, the optical conductivity increases sharply for higher photon energy which satisfactorily agrees with the results reported in this research.

Extinction coefficient plot of ZnSe:Eu films is seen in Fig. 7.

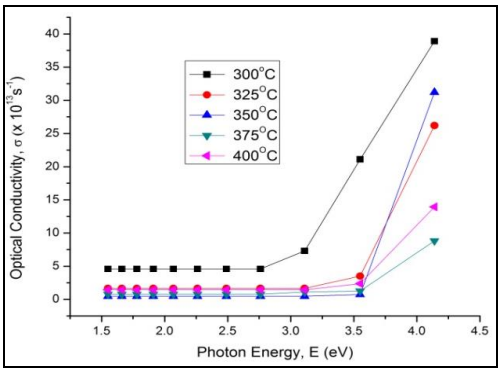

Fig. 6 – Optical conductivity variation of ZnSe:Eu films with temperature

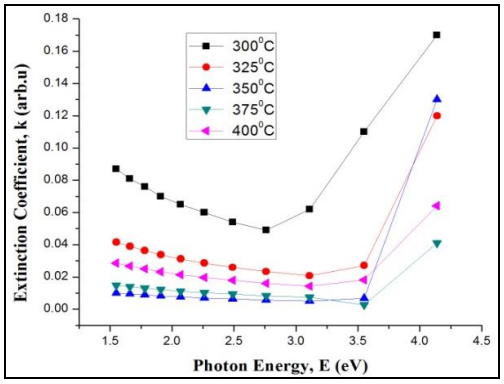

Fig. 7 – Extinction coefficient plot of ZnSe:Eu films at different deposition temperatures

By carefully examining Fig. 7, one discovers that the extinction coefficient of ZnSe:Eu films gradually decreased with an increase in photon energy before increasing spontaneously. The sharp increase of extinction coefficient with photon energy indicates the probability of raising the electron transfer across the mobility gap with high photon energy and greater attenuation of light [19].

Fig. 8 shows a plot of the real part of the dielectric constant for ZnSe:Eu films for different deposition temperatures.

For all deposited ZnSe:Eu films, the real dielectric constant assumes a constant value at low photon energy (visible region) and increases spontaneously above 2.5 eV near the UV region (Fig. 8).

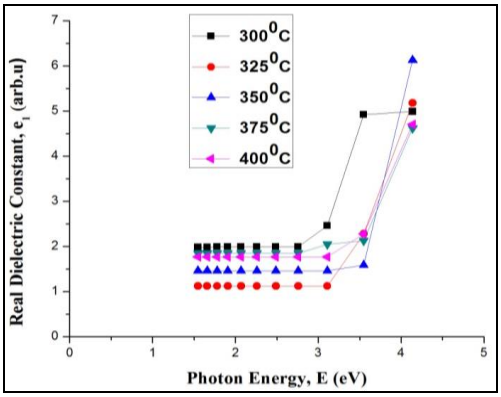

Fig. 8 – Real dielectric constant plot of ZnSe:Eu films at different temperature variations

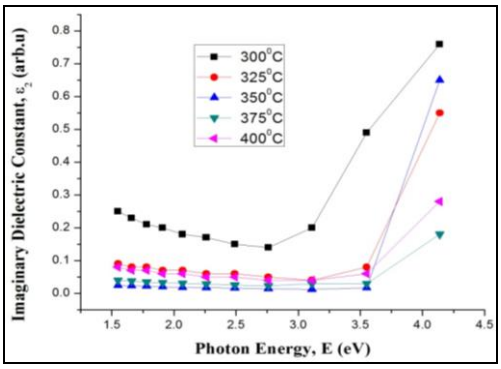

Fig. 9 – Imaginary dielectric constant plot of ZnSe:Eu films at different deposition temperatures

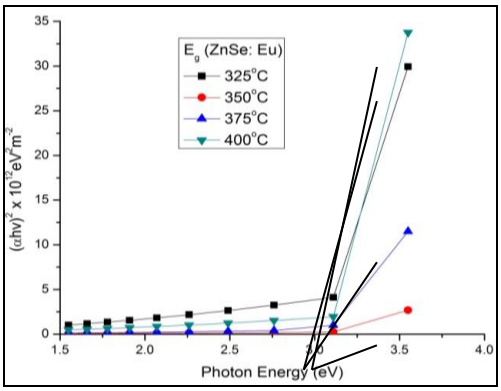

Fig. 10 – Plot of (αhν)2 versus photon energy for ZnSe:Eu films at different deposition temperatures

The imaginary dielectric constant of ZnSe:Eu films was analyzed and the plot is displayed in Fig. 9.

The imaginary dielectric constant values of ZnSe:Eu films assume a steady decline as the photon energy approaches higher values (UV region). Nevertheless, the films exhibited steep increase around 2.8 eV (for the film at 300 °C) and about 3.4 eV (for films at 325 to 400 °C).

The energy gap (direct) of ZnSe:Eu films was analyzed from the equation [20]:

$$(\alpha h\nu) = C(h\nu - E_g)^n, \qquad (10)$$

where C is a constant, n represents the type of transition. For a direct transition, $n = ½$, while for an indirect transition n is 2, E_g is the band gap energy while $h\nu$ represents the photon energy in electron volts.

The energy band gap of ZnSe:Eu films at different deposition temperatures was obtained from the plot of $(\alpha h\nu)^2$ versus photon energy, and the band gap is obtained by extrapolating the linear section of the curve to the point where $(\alpha h\nu)^2$ equals zero.

Fig. 10 shows the plot of $(\alpha h\nu)^2$ versus photon energy for ZnSe:Eu films for different deposition temperatures.

As observed in Fig. 10, for all deposition temperatures, blue-shift (3.01 eV to 3.12 eV) is observed for the band gap of ZnSe:Eu when compared with that (about 2.72 eV) of bulk ZnSe. The strong blue-shift exhibited by the films is an indication of quantum confinement effect taking place at the nanoscale level which is responsible for the increment in energy band gap. The quantum size effect increases the energy of electrons and hence shifts the effective band gap to higher ener-

gy [18]. The values of energy gap for ZnSe:Eu obtained in this research are close to those reported in earlier studies [8] for ZnSe.

5. CONCLUSIONS

Eu-doped ZnSe nano/thin films were deposited on glass substrate using electrostatic spray pyrolysis technique at different deposition temperatures. Depending on the substrate temperature, energy band gap varied between 3.01 eV and 3.12 eV indicating a strong blue-shift from the bulk value (2.72 eV) of ZnSe. The strong blue-shift exhibited by the films is an indication of the presence of quantum confinement at the nanoscale level which is responsible for the increment in energy band gap. Optical study results (high refractive index) of nano/thin films reveals that ZnSe:Eu nano/thin films can be employed in the fabrication of optoelectronic devices including LEDs, LCDs, etc.

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Оптичні властивості плівок селеніду цинку, які леговані європієм

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Плівки ZnSe, які леговані європієм, електростатично розпилювались на скляні підкладки. Зберігаючи постійними інші параметри осадження, такі як швидкість потоку розчину прекурсора, об'єм розпилення, напруга та відстань сопла до основи, температура варіювалась приблизно від 300 °C та 400 °C з інтервалом 25 градусів. Оптичні дослідження представлені при різних температурах. Товщина плівок вказує на нанорозміри і складає 50, 100, 150, 75 і 60 нм у зазначеному діапазоні температур. Оптичні дослідження виявляють високу прозорість і дуже низькі характеристики поглинання та відбиття плівок ZnSe:Eu у видимому діапазоні. Піки поглинання, видимі при 250 нм, припускають появу дефектного стану біля краю смуги. Спостерігається високий коефіцієнт поглинання, який свідчить про високу густину станів у ZnSe:Eu. Високий коефіцієнт пропускання свідчить про придатність плівок в матеріалах покриттів, від яких вимагається висока прозорість для лазерних застосувань, тоді як низькі значення коефіцієнта відбиття та великий показник заломлення показують, що плівки можуть бути застосовані в покриттях сонячних елементів, що вимагає високої ефективності, та для виробництва оптоелектронних пристроїв. Є очевидною вища оптична провідність при енергіях фотонів більше 3 еВ. Різке збільшення коефіцієнта екстинкції з енергією фотонів вказує на збільшення ймовірності переносу електрона через зону рухливості з високою енергією фотонів і більшим ослабленням світла. Дослідження забороненої зони плівок ZnSe:Eu виявляє сильний синій зсув (з 3,01 еВ до 3,12 еВ) від положення забороненої зони об'ємного ZnSe (2,72 еВ).

Ключові слова: Селенід цинку, Європій, Наноплівки, Спрей-піроліз, Оптичні дослідження.