JOURNAL OF NANO- AND ELECTRONIC PHYSICS | *ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ*
Vol. **10** No 3, 03006(5pp) (2018) | Том **10** № 3, 03006(5cc) (2018)

Optical Analytical Studies of Electrostatic-Sprayed Eu-doped Cadmium Selenide Nanofilms at Different Temperatures

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(Received 27 February 2018; revised manuscript received 07 June 2018; published online 25 June 2018)

Electrostatic spray pyrolysis was utilized to grow nanofilms of Eu-doped cadmium selenide at different temperatures. Optical analysis performed on the grown films reveals extremely poor reflection and absorption of light throughout the visible spectrum. However, high transmission was determined at higher wavelengths (visible spectrum) for the films. Other optical constants such as absorption coefficient, optical conductivity, refractive index, extinction coefficient, dielectric constants (imaginary and real), sum of both dielectric constants (imaginary and real) are analyzed. Optical band gap studies disclosed the band gaps of CdSe:Eu films were blue-shifted from CdSe bulk value (1.75 eV); from 2.4 eV to 2.84 eV.

Keywords: Photon Energy, Optical Constants, Band gap, Substrate temperature, Blue-shift, Electromagnetic spectrum.

DOI: 10.21272/jnep.10(3).03006 PACS numbers: 78.20.Ci, 78.40.Fy, 78.66.Hf

1. INTRODUCTION

CdSe belong to the group of semiconductors (II-VI) with a direct wide band gap greater than 1.70 eV. Cadmium selenide (CdSe) is one of the semiconductor materials which have been constantly investigated during recent years for both fundamental and practical aims [1]. Owing to its characteristic properties, CdSe has diverse applications as regards manufacturing of optoelectronic devices, photovoltaic devices, etc. In the form of thin films, cadmium selenide has been deposited by means of chemical growth process [2-4], spray pyrolysis [5-6], electrodeposition [1], etc. In our research, the growth of CdSe:Eu nanofilms using field-supported spray pyrolysis at different temperatures is reported. This method was preferred because it offers an easy way of doping semiconductors by simply adding the dopant inside the spray solution and can also be relied upon to grow uniform and adherent films at the nanoscale. An in-depth analysis of the optical constants of Eu-doped cadmium selenide films is thereafter presented.

The motivation for this report arises from the fact that very little report [7-8] is available in the literature on Eu-doped CdSe while an in-depth study on the optical constants of Europium-doped CdSe nanofilms has not been considered in previous submissions.

2. EXPERIMENTAL

Nanofilms of CdSe:Eu were deposited on ultrasonically clean microscopic glass substrates by electrostatic field-supported spray pyrolysis. The spray solution contains 0.4 M of cadmium acetate dehydrate, 0.4 M of SeO_2 (selenium dioxide) and 0.1 M (15 %) of europium trioxide respectively. The spray solution was agitated with a stirrer (magnetic) for 30 minutes. The resulting harmonized mixture was sprayed via a syringe pump connected to a spray nozzle onto the already hot glass substrates at different temperature (300 °C, 320 °C, 340 °C, 360 °C and 380 °C) respectively. Nozzle-substrate distance, voltage and flow rate were optimized at 5.82 mm, 7 kV and 400 μL/hr respectively. The temperatures of the hot plate was provided by an external heater and measured by a thermocouple attached to the bottom of the hot plate. Surface profile analysis was used to determine the film thickness.

3. RESULTS AND DISCUSSIONS

3.1 Optical Constants

The absorbance values were obtained directly from a Cary UV-VIS spectrophotometer from 200 nm-800 nm. Other optical constants were estimated from the relevant equations.

The absorbance curves (Fig. 1) at different temperatures for the deposited CdSe:Eu films are shown. All the CdSe:Eu films exhibited low absorption of radiation inside the visible spectrum. The highest absorbance for each deposited films occurred in the ultraviolet (UV) region. A downward trend (abrupt decrease) towards the visible (VIS) region of the electromagnetic spectrum was obvious for all films. The abrupt decrease observed

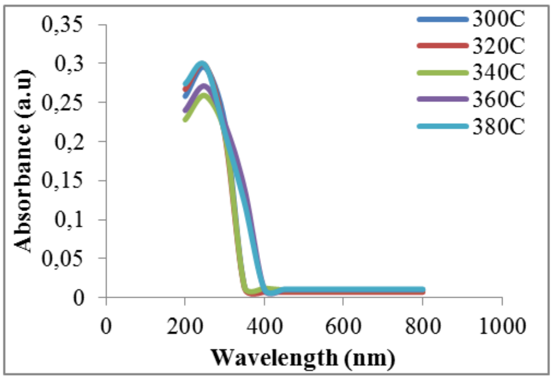

Fig. 1 – Absorbance curves for CdSe:Eu films deposited at different temperatures

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in the absorbance of the films at wavelengths under 400 nm suggests the onset of band-band transitions at the fundamental band edge [9]. Absorption peaks observed for the films at approximately 250 nm and 260 nm are possibly due to defect states present in the crystal.

Fig. 2 displays the transmittance spectra (at different temperatures) of CdSe:Eu films. High transparency is evident for CdSe:Eu films at longer wavelengths (visible region). For all the films deposited at different temperatures, the average transmittance in the UV region is in the range of 50.35 % to 61.52 %. In the VIS region, the deposited films show steep transparency (96.85 % to 98.33 %).

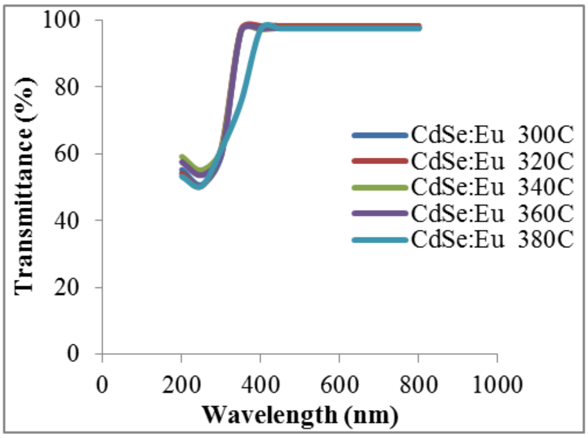

Fig. 2 – Transmittance curves for CdSe:Eu films deposited at different temperatures

The steep transmittance of the CdSe:Eu films in the VIS region signifies that the material will be valuable in coating of glasses, windows, vehicle windscreens, optoelectronic devices and optical lenses. Our results follow the same trend as those reported by [5] for spray deposited CdSe films and is in agreement with that of [4] for chemical bath deposited CdSe films.

The reflectance curves of the CdSe:Eu films for the different deposition conditions are shown in Fig. 3.

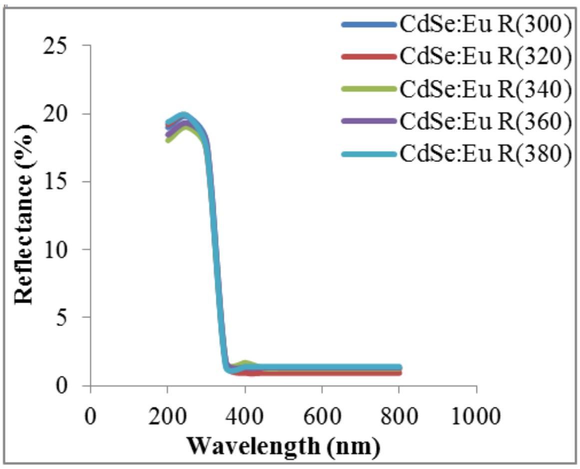

Fig. 3 – Reflectance curves of CdSe:Eu films deposited at different temperatures

The films show very weak reflection of radiation with regards to temperature variation. Reflectance within the range of 0.94 % to 1.33 % in the VIS region and 1.4 % to 19.85 % in the UV region were recorded. The weak reflectance behaviour exhibited by the Eu-doped cadmium selenide films makes the material a very important one for use as an anti-reflective coating on solar cells fabrication in order to attain high efficiency.

The graph of refractive index (R.I) of the Eu-doped CdSe films and photon energy are shown in Fig. 4.

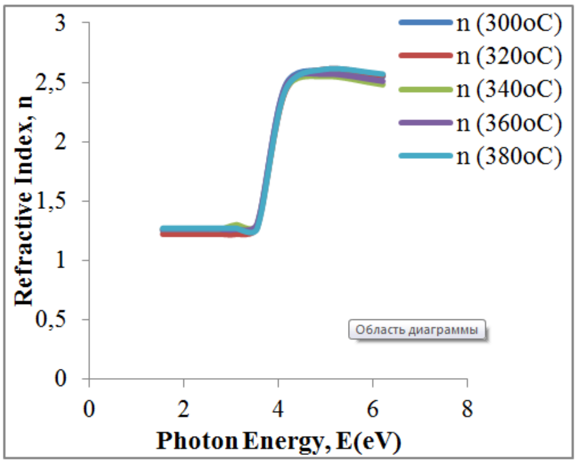

Figure 4 – Plot of R.I. of CdSe:Eu films at different temperatures

R.I. values between 1.22 and 1.31 at lower photon energies (below 4 eV) were observed for the CdSe:Eu films. However, at higher photon energies (above 4 eV), the CdSe:Eu films has high refractive index values between 2.42 and 2.61 with regards to the varied temperatures. The high R.I. exhibited by the CdSe:Eu films suggests the material will be valuable for fabricating devices based on optoelectronic effect.

The absorption coefficient (A.C.) values of the CdSe:Eu films under investigation were estimated from transmittance and thickness values using the expression:

$$\alpha = -\frac{\ln T}{t}, \tag{1}$$

where α, T and t represents absorption coefficient, transmittance and thickness in that order.

The values of A.C. of the CdSe:Eu films (at separate substrate temperatures) are plotted as seen in Fig. 5.

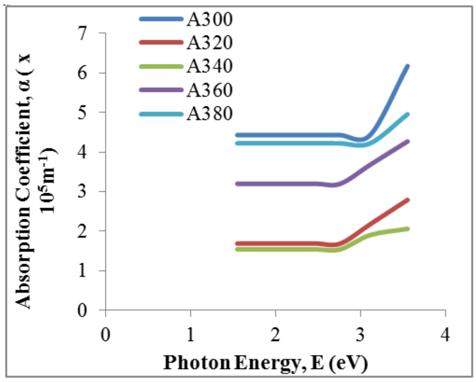

Fig. 5 – Plot of absorption coefficient of CdSe:Eu films at different temperatures

A.C. within the range of about $1.538 \times 10^5 \text{ m}^{-1}$ to $6.174 \times 10^5 \text{ m}^{-1}$ was noticed for the CdSe:Eu films in the temperature range of 300 °C to 380 °C.

The optical conductivity (O.C.) of the deposited CdSe:Eu films at different temperatures was estimated from A.C. and R.I. values using the expression:

$$\sigma = \frac{\alpha n c}{4\pi}, \qquad (2)$$

where σ, α, n, c and π represent optical conductivity, absorption coefficient, refractive index, speed of light and pie (a constant) respectively.

O.C. values (Fig. 6) appear constant at lower photon energies but increases sharply at about 2.76 eV (for films deposited at 320 °C, 340 °C and 360 °C) and about 3.11 eV (for films deposited at 300 °C and 380 °C) indicating the semiconducting nature of the films.

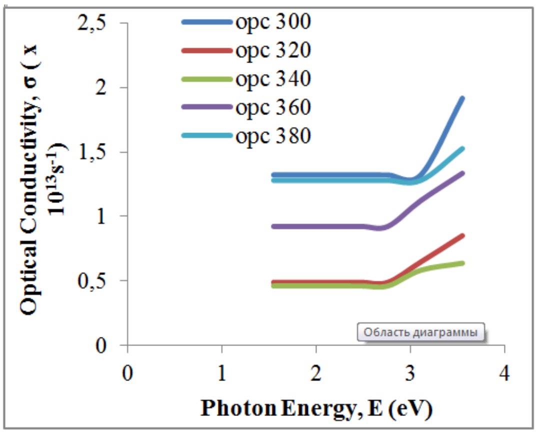

Fig. 6 – Graph of optical conductivity of CdSe:Eu films at different temperatures

The extinction coefficient (E.C.) of the CdSe:Eu films obtained at different temperatures was estimated from absorption coefficient and wavelength values using the expression:

$$k = \frac{\alpha \lambda}{4\pi} \qquad (3)$$

where k, α, λ and π represent values of E.C, absorption coefficient, wavelength and pie (a constant) respectively.

The E.C. values are observed to decrease steadily (Fig. 7) as photon energy increases and slightly increased further. The E.C. of CdSe:Eu films are very small ranging from 0.0055 to 0.0282 for all deposition conditions. The low extinction coefficient (k) confirms high transparency of the films [10].

The imaginary dielectric constant values of the CdSe:Eu films at different temperatures were obtained through the expression:

$$\varepsilon_2 = 2nk \qquad (5)$$

where n and k represents the refractive index and extinction coefficient respectively of the CdSe:Eu films.

From Fig. 9, the values of imaginary dielectric constant of the CdSe:Eu films are observed to decrease as photon energy increases and thereafter exhibited a slight increase at about 3.11 eV (for films deposited at300 °C and 380 °C) and 3.55 eV (for films deposited at 320 °C, 340 °C and 360 °C).

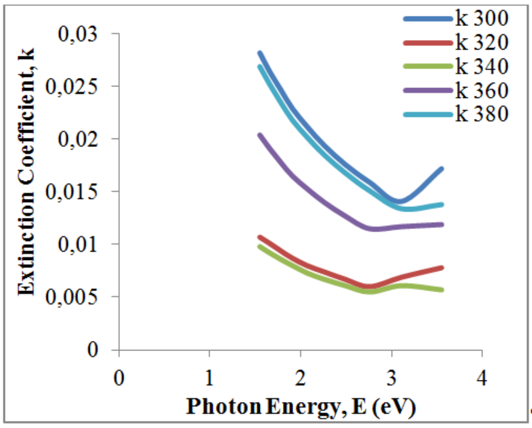

Fig. 7 – Plot of extinction coefficient of CdSe:Eu films at different temperatures

The real dielectric constant values of the CdSe:Eu films at different temperatures were obtained through the expression:

$$\varepsilon_1 = n^2 - k^2 \qquad (4)$$

where n and k represents the refractive index and extinction coefficient respectively of the CdSe:Eu films.

Real dielectric constant values of the CdSe:Eu films are observed to be constant at low photon energies and increases very sharply at high photon energies. This is in good agreement with the report of [11] for CdSe films obtained by chemical bath deposition technique. This behaviour arises as a result of the strong interaction occurring between the highly energetic photons and the charge carriers possessed by the material [11].

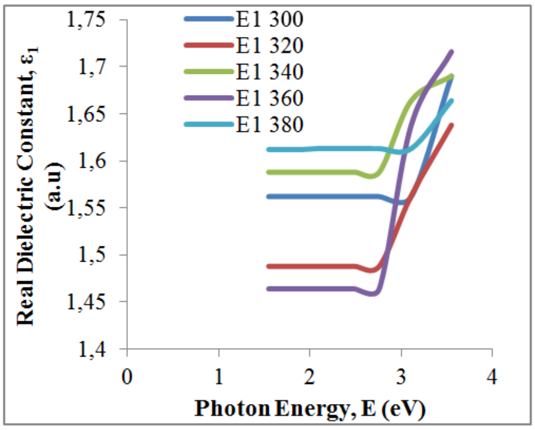

Fig. 8 – Graph of real dielectric constant of CdSe:Eu films at different temperatures

Variation of the sum of real and imaginary dielectric constant values of CdSe:Eu films with temperature is shown (Fig. 10). The values of the sum of real and imaginary dielectric constant of CdSe:Eu films are observed to decrease slightly at low photon energies (which corresponds to the VIS region) and increases very sharply at high photon energy (which corresponds to the near ultra-violet region). This behaviour can be attributed to the strong interaction existing between the highly energetic photons and the charge carriers of the deposited films [11].

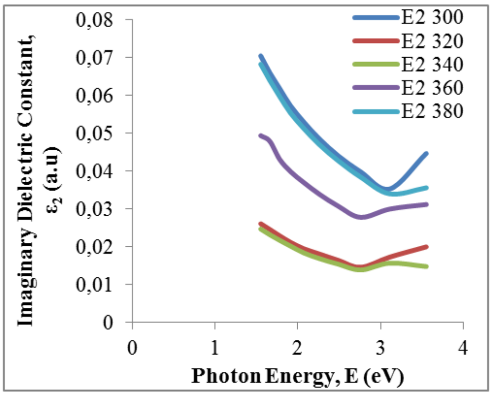

Fig. 9 – Graph of imaginary dielectric constant of CdSe:Eu films at different temperatures

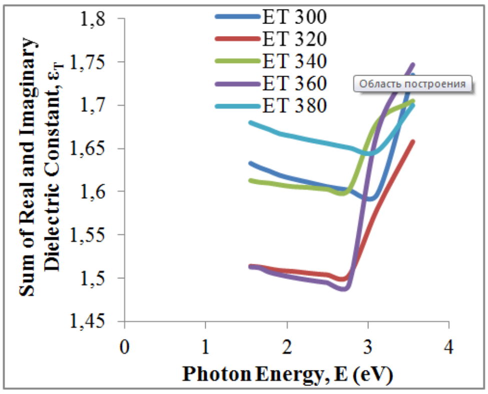

Fig. 10 – Graph of the sum of real and imaginary dielectric constants of CdSe:Eu films at different temperatures against photon energy

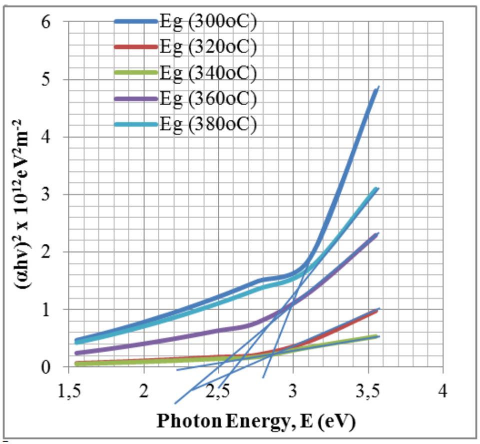

Fig. 11 – Graph of $(\alpha h\nu)^2$ of CdSe:Eu films at different temperatures against photon energy

The direct band gap of all the CdSe:Eu films was calculated from the equation:

$$(\alpha h\nu) = k(h\nu - E_g)^a, \tag{6}$$

where k represents a constant, a denotes the nature of transition, E_g signifies band gap while $h\nu$ symbolizes photon energy.

From Fig. 11, the band gap of CdSe:Eu films decreases from 2.84 eV to 2.40 eV as temperature increases from 300 °C to 340 °C. However, as the temperature increases further from 340 °C to 380 °C, a slight increment in band gap energy (2.4 eV to 2.61 eV) is observed for the CdSe:Eu films. The slight increase in band gap energy at higher temperature may be due to perceived imperfections or defects which may be present in the crystal. Table A gives a summary of the band gap energy of CdSe:Eu films obtained in this research at different temperatures.

Table A – Band gap energy of CdSe:Eu films at different temperature

Temperature (°C)	Band Gap Energy (eV)	Thickness (nm)
300	2.84	50
320	2.70	100
340	2.40	150
360	2.50	75
380	2.61	60

The band gap energy of CdSe:Eu films at different deposition conditions exhibited a strong increment (blue-shift) from the bulk value (1.75 eV). The strong increment (blue-shift) of band gap energy observed in this research from the bulk value of CdSe (1.75 eV) indicates quantum confinement effect taking place, which enhances and increases the band gap energy as the thickness approaches the nanoscale range.

4. CONCLUSION

Europium-doped cadmium selenide nanofilms were successfully deposited by electrostatic spray pyrolysis on ultrasonically cleaned microscopic glass slides at high temperatures between 300 °C and 380 °C at intervals of 20. Optical characterization performed on the samples at room temperature reveals low reflection and absorption together with high transparency in the VIS region. Band gap analysis show a decrease in band gap from 2.84 eV to 2.40 eV as temperature increases from 300 °C to 340 °C and further increases from 2.40 eV to 2.61 eV as temperature increases from 340 °C to 380 °C. All the obtained optical band gaps were however blue-shifted from the bulk value of CdSe which explains the quantum confinement effect occurring in the crystal at the nanoscale level.

ACKNOWLEDGEMENTS

The authors are indebted to the management and staff of NAMIROCH laboratory, Abuja-Nigeria for providing the spray system used for this research. The management and staff of chemical engineering department, Ahmadu Bello University, Zaria-Nigeria are highly appreciated for making available the UV-VIS-NIR spectrophotometer with which optical characterization was performed. Special thanks also go to the staff and management of Advance Physics Laboratory, Sheda Science and Technology Complex (SHESTCO), Abuja where the surface profile for obtaining film thickness was performed.

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