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Effect of Gd Concentration and Annealing Temperature on Structural, Optical and Morphological Properties of Chemically Deposited ZnSe: Gd Thin Films

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Abstract
The ZnSe:Gd thin films were deposited onto non-conducting glass substrate by chemical bath deposition (CBD) method in an aqueous alkaline medium at bath temperature 80ºC. The total Gd solution concentration wearied from 1, 3, 5, and 7 moles % were used to thin film deposition process. The as-deposited thin films were annealed about 300, 400 and 500ºC in open atmosphere. The effect of different mole concentration of Gd solution and annealed temperature on structural and morphological properties of films was investigated by X-ray diffractions (XRD), scanning electron microscopy (SEM), and photoluminescence spectroscopy (PL). From the structural studies, the as-deposited films obtained cubic zincbland structure, while film was annealed about 300ºC the peak intensity is increases and also appeared hexagonal peak. The film was annealed at 400ºC hexagonal peaks are appear. Se metal was present at annealed temperature increases about 500ºC. The excitonic range of photoluminescence spectroscopy is reported. Optical transmission of thin films was obtained with 80% and the band gap energy of films has been blue shift compare to the bulk ZnSe (2.7eV). FE-SEM image of as-deposited and different annealed films have different shape of spherical particles with the large number of voids.

Keywords
Non-conducting glass substrate, ZnSe:Gd thin films, XRD, SEM, optical transmission.

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INTRODUCTION
In the recant year have been increase interest in the development of II-VI semiconductor material because their useful potential application in optoelectronic devices such as red, blue and green light emitting diodes, photovoltaic, laser screen, thin film transistor and photoelectrochemical cells [1]. Most of the research in this area of thin film deposition techniques is very much important towards different type of material and doped compound that are used. The rare earth metal doped semiconducting materials have been much potential application, wide band gap and

suitable application in electroluminication. Luminescence efficiency and quantum size effect of metal doped semiconducting materials intensively studied. Rear earth metal doped zinc selenide (ZnSe) semiconducting material which was acceptable to predict size dependent properties [2-7]. In this size regime, the semiconductor energy level become more from each other, in this crystal size is smaller and the effective band gap is increases. The wide band gap value is 2.8 eV and large binding energy is 21 Mev for bulk ZnSe, it makes ideal choice of inorganic semiconductor shell and doped semiconducting nanoparticles. Rear earth (RE) elements has an effective luminescence property as well as RE element doped semiconducting materials has sharp and temperature stable luminescence properties, due to the incompletely field 4f shell. It's had well screening effect which slightly affected the crystalline size of semiconducting materials [8]. Therefore, rear earth element doping is very much effective approach to improve the particle size and potential application in an optoelectronic device such as optical switches, nonlinear optics and colour thin film electroluminescence devices [9].

Chemical bah deposition method (CBD) provide suitable method because, it's is low cost, easy processing method, good surface coverage, no requirement of sophisticate instrument, low processing temperature and non-polluting properties. The chemical bath deposition method performs under atmospheric pressure and ambient (room temperature) temperature as well as this method performed in an aqueous alkaline medium for thin film formations because, the cation and anion reaction species are directly reacting by nucleation growth process.

In the present communication for the first-time preparation of different mole concentration of Gd doped ZnSe thin films were deposited onto non conducting glass substrate by using the chemical bath deposition method at an alkaline medium. The as-deposited thin films were annealed at different temperature such as 300, 400 and 500 ºC. Finally, the effect of rear earth metal ion concentration and annealing temperature on optical, surface and structure properties of Gd doped ZnSe thin films were studied by using x-ray diffraction (XRD), scanning electron microscopy (SEM), UV-visible spectroscopy and photoluminescence spectroscopy.

EXPERIMENTAL SECTION

The chemical bath deposition method was performed in an aqueous alkaline medium, where using commercially available non-conducting glass substrate. The substrate cleaning is significant role in the thin film deposition process. The glass substrate first clean with mailed soup solution and successively washed by using acetone then boil in chromic acid for 1h and washed with double distilled water, finally substrate dry in an oven 60ºC for 30 minutes. The sodium selenosulfate (Na_2SeSO_3) solution was prepared by using 0.625g of selenium metal (99.99%) powder and 0.1875g sodium sulphite in 100 mL of double distilled water and the above solution reflex for an about 7 h at 90 ºC. Freshly prepared sodium selenosulphite solution was used in thin film deposition process because, this solution was relatively unstable.

The precursors of Zinc sulphate ($ZnSO_4$), sodium selenosulfate (Na_2SeSO_3), Gadolinium (III) acetate hydrate ($Gd(CH_3CO_2)_3 \bullet xH_2O$),Hydrazine hydrate ($N_2H_4.H_2O$) and ammonia solution (25%) were purchased from Sigma-Aldrich and used without any purification. The 100 mL of reaction solution obtained by mixing 10 mL of 0.5M zinc sulphate, 13 mL of 80% hydrazine hydrate solution, 10mL of (1, 3, 5 and 7%) Gadolinium (III) acetate hydrate solution, 5 mL of 25% ammonia solution, 2M of sodium selenosulphate solution and sufficient amount of double distilled water. Then, the above reaction solution is stirred at ambient conditions for few minute. The well cleaned glass substrates were inclined at vertically in the reaction solution containing backer. The solution evaporation was avoided to the beaker was sealed. The Gadolinium metal doped thin films were achieved by chemical bath deposition at 80°C for 1h. The deposited substrates were subsequently removed from reaction solution. The obtained deposited film washed with double distilled water, dried in room temperature few minutes. Then, these thin films have been annealed at different temperature at 300°C, 400°C and 500°C for 30 minutes in an open atmosphere.

RESULT AND DISCUSSION

MORPHOLOGY STUDY

The surface morphology of thin films was studied by using scanning electron microscopy (SEM) is an excellent method to study the morphology of sample. The SEM image of Gd doped ZnSe thin films were deposited on non-conducting glass substrate with different mole concentrations of as-deposited thin films are shown in Fig. 1(a-d).

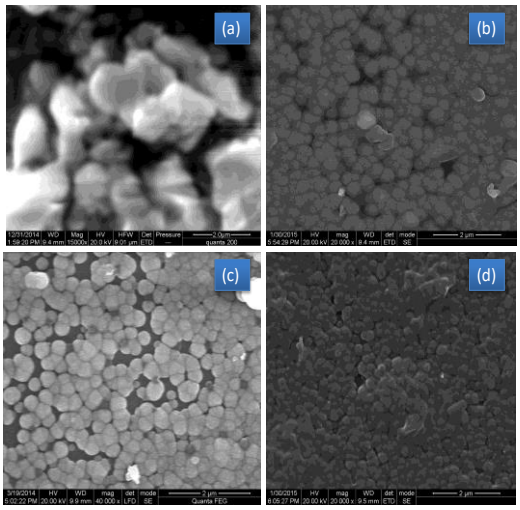

Figure 1(a-d) SEM images of Gd doped ZnSe thin film as-deposited with different mole concentrations at (a) 1 %, (b) 3 %, (c) 5 % and (d) 7 %.

The films were very well spherical particle, pinhole free and no voids are formed onto substrate surface. The ZnSe:Gd thin films consisting of different size and morphological of spherical particles are densely backed glass surface very nicely. As-deposited Gd doped thin film each particle is a well-formed particle and covered on substrate surface without pinhole and creak is shown in Fig. 1(a). Fig.1 (b) shows as-deposited 1 Mole % of Gd doped thin film is very nice and densely backed spherical shape of particle is presented and particle are aggregated it is clearly indicating cluster by cluster growth process was accord. If film the doping concentration increased about 5 moles % exhibit good coverage of substrate surface with the film composed large number spherical particle and the average particle size is decreased show in Fig. 1(c). Fig. 1(d) shows SEM pattern of 7 mole % of Gd doped ZnSe thin film aggregated to form a clusters and size of grain decreased and the film substrate surface roughness was increased it's clearly indicated increases doping concentration the Se loss and thickness of film decreased. Fig. 2 (a-d) shows EDAX patterns of 1 to 7 moles % of Gd doped ZnSe thin films on glass substrate.

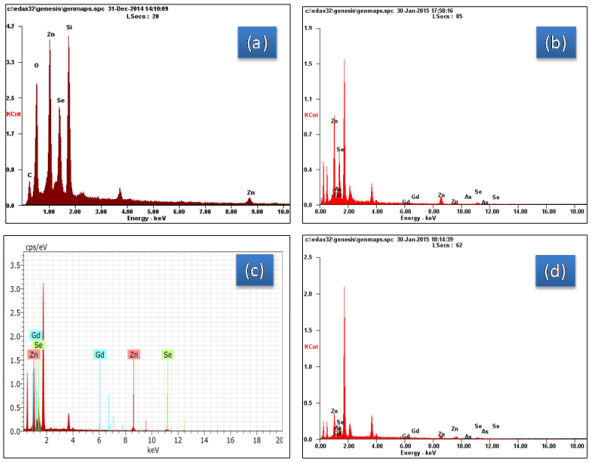

Figure 2(a-d) EDAX results of different mole concentration of Gd doped ZnSe as-deposited thin films at (a) (a) 1 %, (b) 3 %, (c) 5 % and (d) 7 %.

Fig. 2 (a) shows EDAX pattern of 1% of Gd doped thin film which exhibit only Zn and Se signals of as-deposited film. When increases Gd concentrations up to 7 % thin films were exhibit Zn and Se peak. In addition, the peak of the element Gd was presented it is shown Fig.2 (b-d), which is almost equal to stand value of ZnSe.

STRUCTURAL CHARACTERIZATION

The structure characterization of Gd doped ZnSe thin films were studied by using X-ray diffraction technique. Fig. 3-6 are shows the XRD patterns of Gd doped ZnSe thin films with four (300, 400 and 500°C) different annealed temperatures were sued. Fig. 3 shows the XRD pattern of as- deposited Gd;ZnSe thin films with different mole (1% to 7%) concentration of Gd solutions were used, these films are appeared poor and polycrystalline nature of diffraction peak about 5 mole%, while thin film doped with 7 mole% of Gd solution se metal phase was appeared.

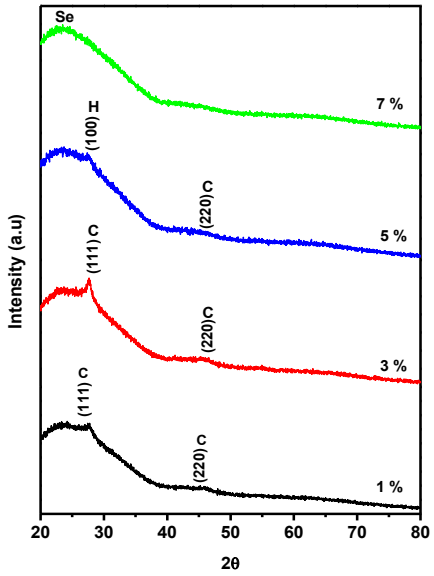

Figure 3(a-d) XRD patterns of Gd doped as-deposited ZnSe thin films with different mole concentration at (a) 1 %, (b) 3 %, (c) 5 %, (d) 7 %.

It's clearly indicated increase impurity level Se contribution is less to film deposition processes. The cubic zinc blend and hexagonal wurtzite structure of Gd doped ZnSe thin films were annealed with 300°C as shown in Fig. 4.

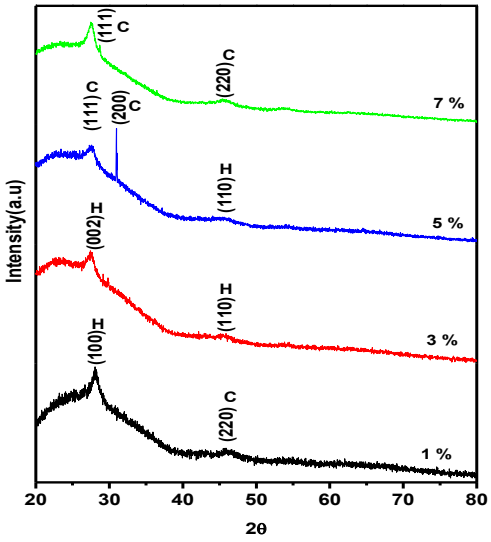

Figure 4(a-d) XRD patterns of Gd doped ZnSe thin films 300 °C annealed with different mole concentration at (a) 1 % , (b) 3 %, (c) 5 %, (d) 7 %.

The mixture phase of cubic and hexagonal structure of 1mole % Gd doped thin film show Fig. 4 (1%). The increasing impurity level about 3% hexagonal wurtzite phase only presented. When film was doped with 5% mole concentration of Gd solution the cubic zinc bland with hexagonal wurtzite nature of diffraction peaks are appeared it's shown in Fig. 4 (5%). The Gd solution concentration increased about 7 mole%, where cubic zinc bland phase was return as well as crystalline nature of film was increased it is shown in figure 4 (7%). The thin films were annealed at 400°C the crystalline nature of film is increased with cubic zinc bland and hexagonal nature of peak are appear and ZnO phase, it is shown in Fig. 5 (1-7%).

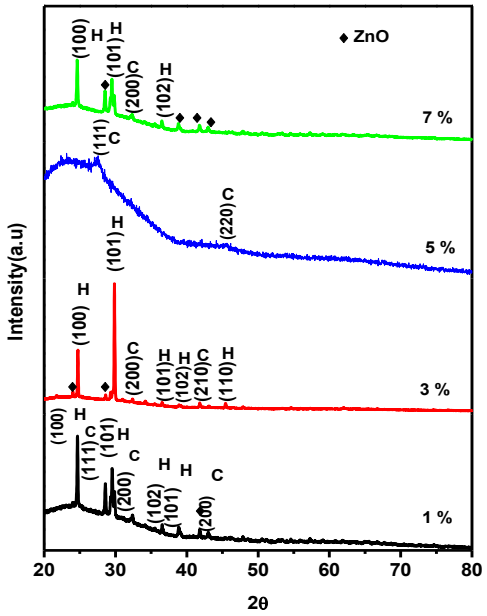

Figure 5(a-d) XRD patterns of Gd doped ZnSe thin films 400 °C annealed with different mole concentration at (a) 1 %, (b) 3 %, (c) 5 %, (d) 7 %.

From the Fig. 6 (1-7%) shows XRD pattern of 500°C annealed thin film with different mole concentration of Gd solution it is shown cubic and hexagonal nature of thin film and Se metal where presented it's clearly indicate about 400°C annealed films were appeared Se metal, it is already studied.

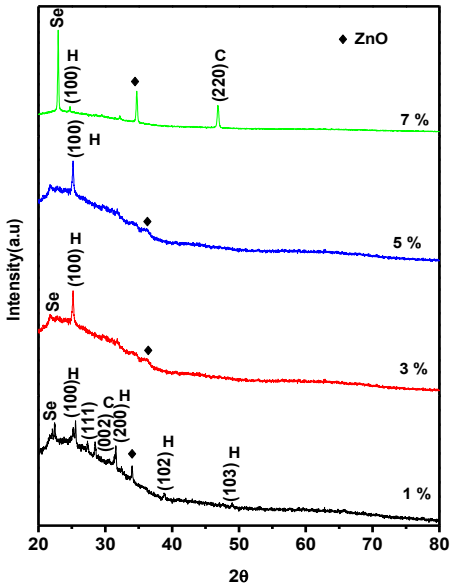

Figure 6(a-d) XRD patterns of Gd doped ZnSe thin films 500 °C annealed with different mole concentration at (a) 1 % , (b) 3 %, (c) 5 %, (d) 7 %.

The lattice constant "a" determine for all prepare sample from high intense diffraction peak of (hkl) plane using the following Bragg's equation.

$$\text{Lattice constant (a)} = d\,(h^2 + k^2 + l^2)^{1/2} \quad (1)$$

where hkl is the miller indices and d is the inter plane spacing of the atomic planes. The calculated lattice constant values are agreement with the sanded values. The lattices constant determined using calculated d-spacing values and these values are present in Table 1. The crystalline size and lattice constants were investigated by using the Hall-Williamson method; hence it is a very simple method [10]. The size and strain induce broadening of XRD peaks is investigated using this method for considering the peak width as a function of 2θ values.

Table: 1: Representation of the FWHM, d(exp)Å, dislocation density, number of the crystallites/unit area, and Lattices constant of the as-deposited and annealed Gd doped ZnSe films.

Bath and annealed temperature(ºC)	FWHM Value	d(exp)(Å)	Dislocation density (10^{16} line/m^2)	Number of particle in unity area($10^4/m^2$)	Lattice constant
80	0.0066	3.2190	2.13×10^{15}	3.18	5.5754
300	0.0178	3.1741	1.93×10^{15}	61.30	5.4977
400	0.0026	3.6188	3.35×10^{14}	0.22	-
500	0.0143	3.4956	1.01×10^{16}	35.59	-
80	0.0106	3.2190	5.56×10^{14}	13.37	5.5754
300	0.0143	3.2547	1.00×10^{16}	32.74	5.6373
400	0.0024	3.5829	2.85×10^{14}	0.17	-
500	0.0039	3.5270	7.53×10^{14}	0.72	-
80	0.4165	3.2178	8.65×10^{18}	81.87	5.5733
300	0.0161	3.2304	1.27×10^{16}	46.44	5.5952
400	0.0115	3.2454	6.49×10^{15}	18.13	-
500	0.0038	3.5270	7.15×10^{14}	0.67	-
80	0.1587	3.7095	1.26×10^{18}	5.26	6.4250
300	0.0168	3.2547	1.38×10^{16}	53.18	5.6373
400	0.0030	3.5943	4.46×10^{14}	0.33	-
500	0.0027	3.9056	3.64×10^{14}	0.27	-

The high intense diffraction peaks are used to calculate the strain and crystalline size of prepared sample. The considered integral line with is given by following equation.

$\beta_{obs} = \beta_{inst} + \beta_{size} + \beta_{strain}$ (2)

$\beta = \beta_{size} + \beta_{strain}$, (3)

Where, β_{obs} is the experimental full width at half maximum (FWHM) of high intense diffraction peak from XRD pattern, ($\beta_{obs} - \beta_{inst}$) is give the instrumental broadening of corrected FWHM) (β), β_{size} and β_{strain} are the line broadening contributions due to crystallite size and strain respectively. The crystalline size of all prepared samples was calculated by following Scherrer equation.

$\beta_{size} = K\lambda / D\cos\theta$, (4)

Where D is the average crystalline size, λ is the wavelength of (1.5405 Å) X-ray diffraction, β is the FWHM of high intensity diffraction peak. Also, the strain of broadening is given by the Wilson relation as,

$\beta_{strain} = 4\varepsilon \tan\theta$, (5)

Where ε is the microstrain of root mean square value therefore (4) becomes

$\beta = K\lambda / D\cos\theta + 4\varepsilon \tan\theta$, (6)

The above equation rearranging, we get

$\beta \cos\theta = K\lambda / D + 4\varepsilon \sin\theta$. (7)

This is the Hall- Williamson equation. It is used for determining the strain and crystalline size of the all prepared samples.

$D = 0.9\,K\lambda / \cos\theta$ (8)

The obtained values of crystalline size, strain and band gap for all prepared sample are shown in Table 2. The lattice constant is determined by using d-spacing value of high instance diffraction peak and these values are present in the Table 1. The average FWHM value is decreases with increase annealed temperature and

this effect may be responsible for increases of strain values.

Table: 2 Representation of the strain, particle size and optical band gap of Gd doped ZnSe thin films as-deposited and different annealing temperature.

Annealing Temperature (°C)	Bath Temperature (°C)	Particle size(nm)	Strain	Band Gap value
80	80	21.63	1.6019 x 10^{-3}	3.88
300	80	8.03	4.3169 x 10^{-3}	3.52
400	80	54.57	6.3511 x 10^{-4}	3.72
500	80	9.94	3.4870 x 10^{-3}	3.80
80	80	13.4	2.5720 x 10^{-3}	3.85
300	80	9.98	473 x 10^{-3}	3.80
400	80	59.15	5.859 x 10^{-4}	3.60
500	80	36.43	9.514 x 10^{-4}	3.59
90	80	0.34	0.1011	3.81
300	80	8.86	3.9086 x10^{-3}	3.71
400	80	12.41	2.7927 x 10^{-3}	3.81
500	80	37.39	9.270 x 10^{-4}	3.52
80	80	0.89	0.0388	3.60
300	80	8.49	4.0803 x 10^{-3}	3.71
400	80	47.31	7.3252 x 10^{-4}	3.16
500	80	52.38	6.6170 x 10^{-4}	3.50

The micro strain value is decreases with increased crystalline size when annealed temperature was increased.

$\delta = 15\varepsilon/aD$ (9)

$N = t/D^3$ (10)

The dislocation density and number of particles in the unit area of thin films are shown in table 1. When the annealed temperature is increased the dislocation density and number of particles in the unite area values are gradually decreased. The reason may be annealed temperatures affect the surface of all prepared thin films. The variation of $(\alpha h\nu)^2$ Vs $h\nu$ of Gd doped ZnSe thin film absorption edges which conformed direct band gap transition is shown in Fig. 7-10.

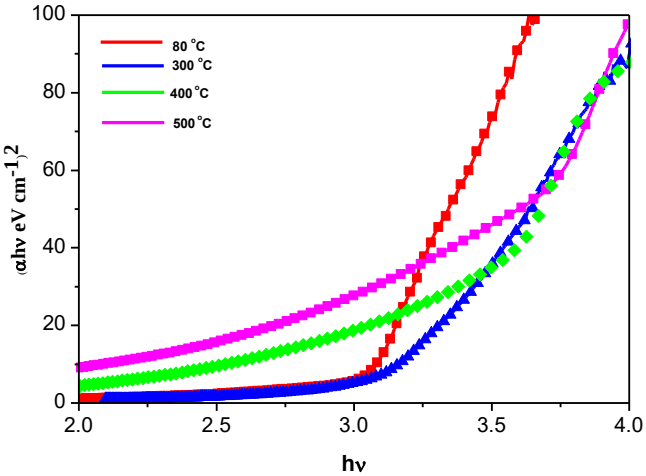

Figure 7(a-d) Absorption coefficient Vs photon energy patterns of 1% Gd doped ZnSe thin films with different annealing temperatures at (a) as-deposited, (b) 300 ºC annealed, (c) 400 ºC, (d) 500 ºC annealed.

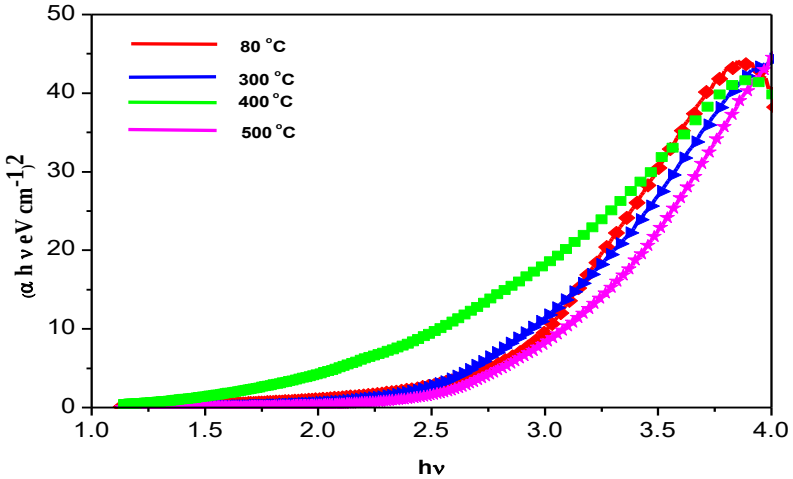

Figure 8(a-d) Absorption coefficient vs photon energy patterns of 3 % Gd doped ZnSe thin films with different annealing temperatures at (a) as-deposited, (b) 300 ºC annealed, (c) 400 ºC, (d) 500 ºC annealed.

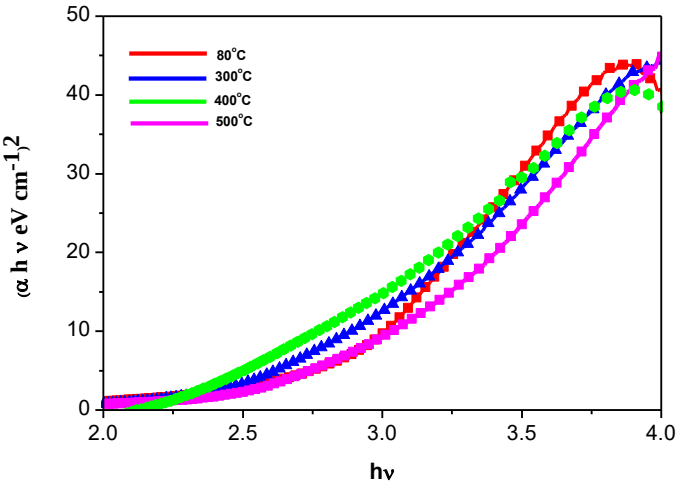

Figure 9(a-d) Absorption coefficient vs photons energy pattern of 5 % Gd doped ZnSe thin films with different annealing temperatures at (a) As-deposited, (b) 300 ºC annealed, (c) 400 ºC, (d) 500 ºC annealed.

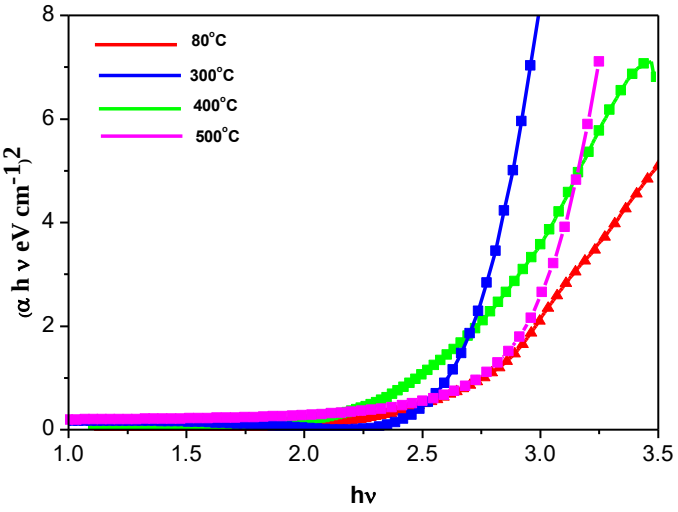

Figure 10(a-d) Absorption coefficient vs photons energy pattern of 7% Gd doped ZnSe thin films with different annealing temperatures at (a) As-deposited, (b) 300°C annealed, (c) 400°C, (d) 500°C annealed.

PHOTOLUMINESCENCE STUDY

Fig. 11-14 shows typical room temperature photoluminescence (PL) spectrum of Gd doped ZnSe thin films. Electron and holes can generate by absorption of photon energy, the generate electron trapped in a different interstitial site and vacancies. Fig, 11 (a-d) shows PL pattern of as-deposited Gd doped ZnSe thin film obtain at four (1-7%) different mole concentrations of Gd solution which shows strong broad emission peak inside at 408 nm (3.03eV). This emission generally considers near band edge emission (NBE) of ZnSe. The NBE emission is due to the bound excitons and donor-acceptor pairs. The week and brad emission of two peaks are appeared. A broad strong emission obtains at 478 nm (2.54 eV), one broad week emission peak centre at 518 nm (2.39eV).

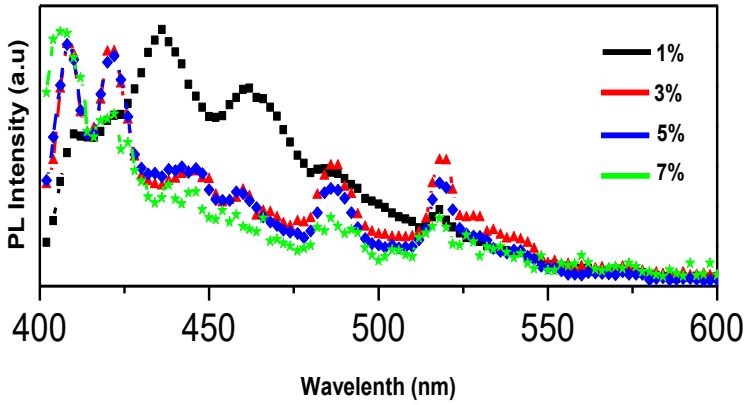

Figure 11(a-d) Photoluminescence patterns of Gd doped ZnSe as-deposited thin films with different mole concentration at (a) 1%, (b) 3%, (c) 5%, and (d) 7%.

Fig. 12 shows different mole concentration and 300°C annealed Gd doped ZnSe thin films PL emission of 408 nm wavelength indicates the band to band transition in ZnSe host matrix. This less wavelength 408 nm of thin film clearly suggested the transfer of excitons to deep trap level of Gd ions. While the emission peak 421 nm is related to surface defect emission. The strong blue emission peak canter around 487 nm (2.5 eV) and the broad green emission peak extending around 518 nm (2.4 eV) is a typical deep defect related emission.

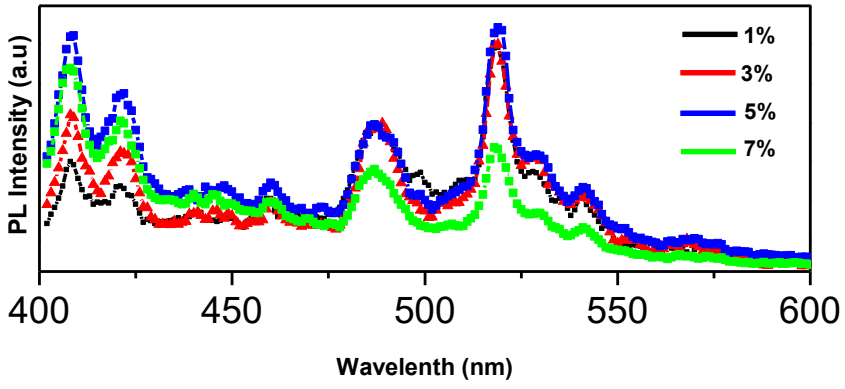

Figure 12(a-d) Photoluminescence patterns of Gd doped ZnSe thin films 300 °C with different mole concentration at (a) 1%, (b) 3%, (c) 5%, and (d) 7%.

In the typical PL spectra of the different mole concentration films were shows (Fig. 13) and the same annealed at 400°C, the emissions are very weak in intensity and the emission peaks are centered at 408 nm (3.03 eV), 421 nm (2.94 eV), 487 nm (2.54 eV) and 518 nm (3.39 eV). From Fig. 14 also shows same emission peaks are appear about 500°C annealed thin films.

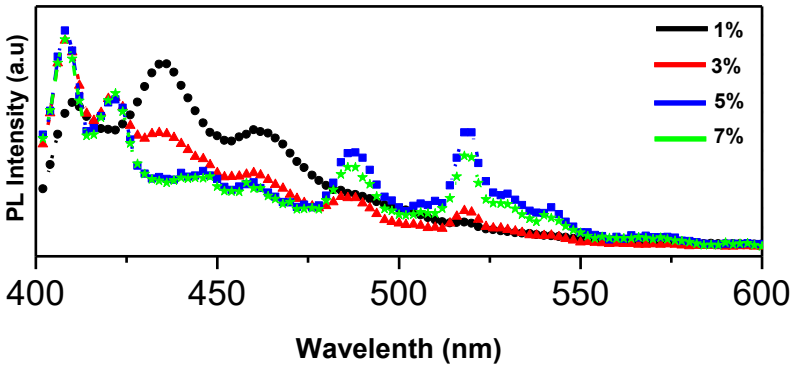

Figure 13(a-d) Photoluminescence patterns of Gd doped ZnSe thin films 400 °C with different mole concentration at (a) 1%, (b) 3%, (c) 5%, and (d) 7%.

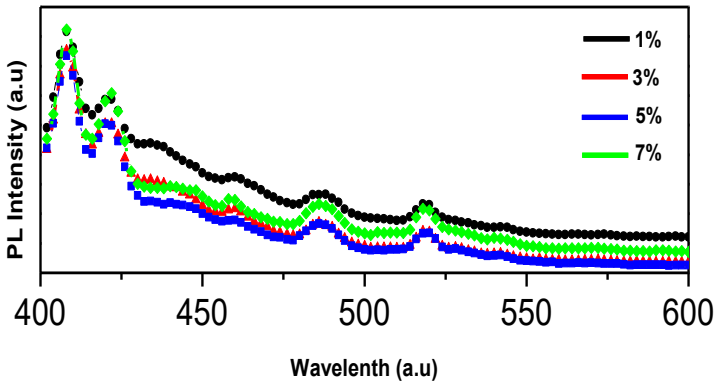

Figure 14(a-d) Photoluminescence patterns of Gd doped ZnSe thin films 500 °C with different mole concentration at (a) 1%, (b) 3%, (c) 5%, and (d) 7%.

CONCLUSION

The Gd doped ZnSe thin films were deposited onto non-conducting glass substrate by chemical bath deposition method. The effected of Gd solution concentration and different annealed temperature of deposited thin film on optical, structural and morphological properties were studied. From the scanning electron microscopy study, the prepared thin films have been achieved large number of uniform spherical particles. The XRD studies reveal that the crystalline nature of thin films has cubic and hexagonal structure. The average band gap value of Gd doped thin film from 3.16 to 3.88 eV which exhibit corresponding blue shift value for bulk ZnSe is confirmed by UV-visible spectroscopy studies. PL measurement shows a strong near band edge emission peak with one broad strong peak for blue emission and weak broad peak of green emissions indicate the Gd doped ZnSe thin films with few defects.

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