Tailoring the optical properties of amorphous heavily Er³⁺-doped Ge-Ga-S thin films

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This study deals with the influence of Er-doping level and thermal annealing on the optical properties of amorphous Ge-Ga-S thin films. Nominal compositions of $(GeS_2)_{75}(Ga_2S_3)_{25}$ doped with high concentrations of 2.1 and 2.4 mol% Er_2S_3 (corresponding to 1.2 and 1.4 at% Er, respectively) have been chosen for this work. The results have been related to those obtained for the un-doped samples. The values of the refractive index, the absorption coefficient and optical band gap have been determined from the transmittance data. It has been found that the optical band gap of un-doped and 2.1 mol% Er_2S_3-doped films slightly increases with annealing temperature, whereas at 2.4 mol% Er_2S_3-doping level it is decreased. The dependences of the optical parameters on the erbium concentration and effect of annealing in the temperature range of 100-200 °C have been evaluated and discussed in relation to possible structural changes.

1. Introduction

Rare-earth (RE) doped luminescence materials have been extensively investigated due to their applications in integrated photonics. In particular, there has been a growing interest in erbium (Er) doped glasses because of the Er^{3+} intra-4f emission at the standard telecommunications wavelength at ~1540 nm [1-3]. Among the chalcogenide glasses, Ge-Ga-S (GGS) ones have been considered as good candidates for such optical devices as fibre lasers, light amplifiers and upconvertors [4]. It has also been established that especially Ge-Ga-S glasses are characterized by higher Er solubility in comparison with other chalcogenide glasses, which is mainly due to the structural modification by addition of Ga into Ge-S glass [4-6]. Besides, these glasses posses desirable characteristic optical properties such as low phonon energy, high refractive index and extended infrared transparency, resulting in enlarged spontaneous emission probabilities, lower non-radiative transition rates and higher quantum efficiencies of the optical transitions between Er^{3+} energy levels [1,2,4].

Recently, we have studied the influence of Ga content, excitation wavelength and temperature on the photoluminescence properties of heavily Er-doped $(GeS_2)_{100-x}(Ga_2S_3)_x$ (x=10, 20, 25 and 33 mol%) glasses. The observed decrease in both the optical energy gap and the host luminescence with Er doping confirms the suggestion that erbium may reduce the concentration of native defects and also improves the amorphous structure [7]. The considerable influence of GGS host composition on the efficiency of 4f-4f transitions of embedded Er^{3+} ions has been established with the outcome that the $(GeS_2)_{75}(Ga_2S_3)_{25}$ host appears near optimal for the emission efficiency of Er^{3+} ions [8]. Moreover, it has been found that with decreasing temperature down to 10 K the luminescence intensity at ~1540 nm is enhanced considerably with pronounced narrowing of the emission cross-section for $(GeS_2)_{75}(Ga_2S_3)_{25}$ glasses. The features in the emission cross-section of these glasses by doping with 2.1 and 2.4 mol% Er_2S_3 have been also specified [9]. Thus, studies on basic optical properties of these glasses in the form of thin films are reasonable from a practical point of view.

The purpose of this paper is to investigate basic optical parameters of thin layers, prepared from heavily doped with 2.1 and 2.4 mol% Er_2S_3 bulk $(GeS_2)_{75}(Ga_2S_3)_{25}$ samples, in particular the dependence of the optical gap (E_g) as a function of Er doping and annealing temperature and to correlate this behaviour with generation of defects in the amorphous structure. The measurements of transmission spectra on as-deposited and annealed samples in the temperature range of 100-200 °C have been performed.

2. Experimental

Starting compositions of $(GeS_2)_{75}(Ga_2S_3)_{25}$ doped with high concentrations of 2.1 and 2.4 mol% Er_2S_3 (1.2 and 1.4 at% Er, respectively) were chosen for this study (the un-doped host was used as comparison standard). Glassy ingots were prepared from previously synthesized GeS_2 and Ga_2S_3 (the procedures are described in Ref. [7]), and Er_2S_3 as a product of Alfa Aesar (Johnson Matthey Company, 99.9%). The mixtures were heated into evacuated quartz ampoules using a rocking furnace, melted up to ~1000 °C for ~12 h and then quenched in ice water. Thin films were thermally evaporated in vacuum

~10^{-6} Torr with rate maintained as ~10 Å/s at room temperature ??? onto Corning 7059 glass substrates from a molybdenum (100 amps) boat. A constant voltage of 30 V with a current of 65 amps was applied and the distance between the source and substrate was fixed as ~14 cm. The thickness of deposited films was ~200 nm. The layers were annealed at 100, 150, and 200°C for 1 hour under a vacuum of 10^{-5} Torr using a homebuilt setup. The amorphous structure of the films was checked with the help of X-ray diffractometer (Model: Phillips X'Pert Pro). The optical transmission spectra were recorded by a FTIR spectrometer (Model: Bruker IFS 66V/S) in the wavelength range of 350-900 nm.

3. Results

The amorphous nature and homogeneity of the prepared layers is confirmed by X-ray diffraction analysis, both for as-grown and annealed ones, as shown in Fig. 1. The films posses a good adherence to the substrate surface, even though they were deposited at room temperature. This is enhanced with increasing annealing temperature and is accompanied by changing their colour from yellow to lighter one, i.e. a bleaching effect occurs.

The optical transmission spectra of both as-grown and annealed at 200 °C films are presented in Fig. 2. It turns out that Er-doping leads to lower transmittance in comparison to that of the host material, which is ~80% at $\lambda = 500$ nm. Note that upon annealing, the transmittance of the 2.1 mol% Er_2S_3-doped GGS films increases, while in the case of higher (2.4 mol% Er_2S_3) or no doping the transmittance is decreased.
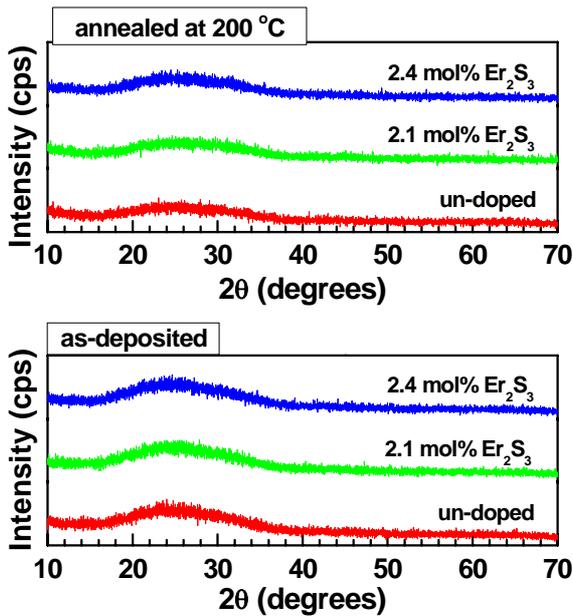

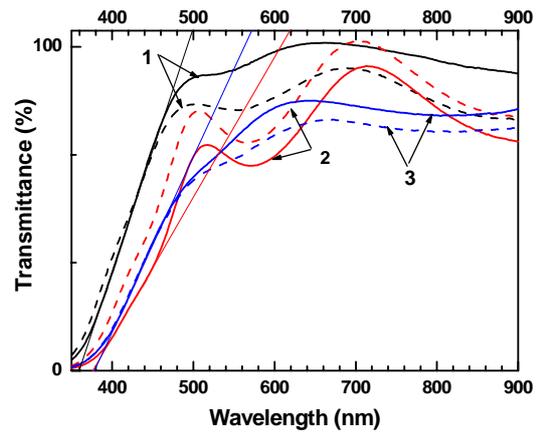*Fig.2. Transmission spectra of the studied films: as-grown (solid line), annealed (dash line); un-doped (1), at 2.1 mol% Er_2S_3 (2), at 2.4 mol% Er_2S_3 (3).*

The spectra are clearly consisting of two distinguishable regions separated by a wavelength, treated as characteristic wavelength (λ_c) [10], which corresponds to the onset of electron excitation from the valence band to conduction band [10]. This parameter can be used to determine the optical parameters and value of the optical energy band gap of the materials. For all the films, sharp fall in transmittance at below λ_c and clear interferences patterns along with high transmittance for wavelengths exceeding λ_c are observed (Fig. 2). The λ_c values for as-deposited un-doped, 2.1, and 2.4 mol% Er_2S_3-doped films, obtained by a linear-fit of sharp-transmittance region of optical spectrum, are thus estimated as 488, 609 and 557 nm, respectively. With increasing annealing temperature, the λ_c position of the un-doped and 2.1 mol% Er_2S_3-doped samples is slightly shifted towards lower wavelengths, while at the higher Er doping the shift is towards higher wavelengths. This indicates that upon annealing the light absorption range of 2.4 mol% Er_2S_3-doped sample increases as compared to the other ones.

The refractive index (n) and reflectance (R) of the films are determined using the interference pattern envelope theory at above λ_c [10-12] since the absorption of the films in this region is negligible:

$$n = [N + (N^2 - n_0^2 n_1^2)^{1/2}]^{1/2} \qquad (1)$$

$$R = [(n-1)^2]/[(n+1)^2] \qquad (2)$$

where, $N = (n_0^2 + n_1^2)/2 + 2n_0 n_1 [(T_{max} - T_{min})/(T_{max} T_{min})]$, where n_0 is the refractive index of the air $\cong 1$, n_1 - the refractive index of the substrate $\cong 1.5$, T_{max} and T_{min} - the transmittance maximum and minimum, respectively. Upon annealing, the evaluated average refractive index of un-doped GGS films is increased from 1.59 to 1.75, while higher and nearly constant (~2.11 and 1.89) values are obtained for both as-grown and annealed samples doped by 2.1 and 2.4 mol% Er_2S_3. Further, the evaluated

Fig.1. XRD spectra of as-deposited and annealed at 200 °C films.

reflectance of the un-doped GGS films using equation (2) increases from 5% to 7.4% with the increase of annealing temperature, whereas 2.1 and 2.4 mol% Er_2S_3 doped GGS films is found to be about 13% and 9%, respectively. It reveals that the GGS films doped with 2.1 mol% Er_2S_3 have slightly higher reflectance than that of other GGS films.

The absorption coefficient (α) of the films for wavelengths below λ_c is calculated using the equation:

$$\alpha(\lambda) = [\ln(1/T)]/t \qquad (3)$$

where T is the transmittance, t - the thickness of the film since the films exhibit negligible reflectance in this range due to their strong absorption. At $\lambda < \lambda_c$, all the films have a high absorption coefficient (α) of the order of 10^5 cm^{-1}. The dependence of absorption coefficient α at λ_c as a function of annealing temperature is plotted in Fig. 3.
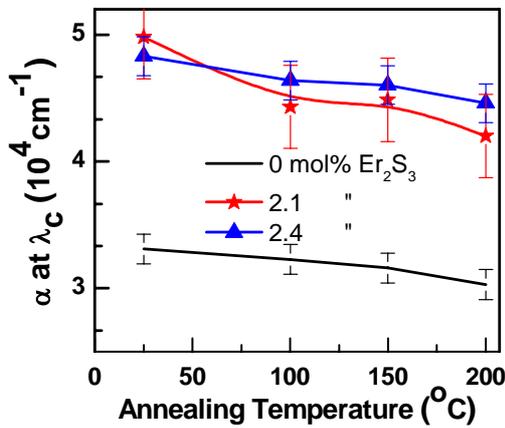

Fig. 3. Absorption coefficient at the characteristic wavelength λ_c is plotted versus annealing temperature

At higher Er concentration the overall absorption coefficient of the as-grown GGS films increases by a factor of 1.5, which can be seen in Fig. 4 (a). On the other hand, the absorption coefficient of the studied films slightly decreases with the increase of annealing temperature (Fig. 4 (b)), which is in good correlation with the results in Fig. 3, representing the variation of α at $\lambda = \lambda_c$ with annealing temperature.

In order to determine the optical band gap of the films, the obtained $\alpha(\lambda)$ dependence can be effectively approximated by α dependence versus hν [13,14] in the range of inter-band transitions corresponding to wavelengths at below λ_c:

$$\alpha E = A (E - E_g)^2 \qquad (4)$$

where E is the photon energy, E_p - the phonon energy, and E_g - the optical band gap.
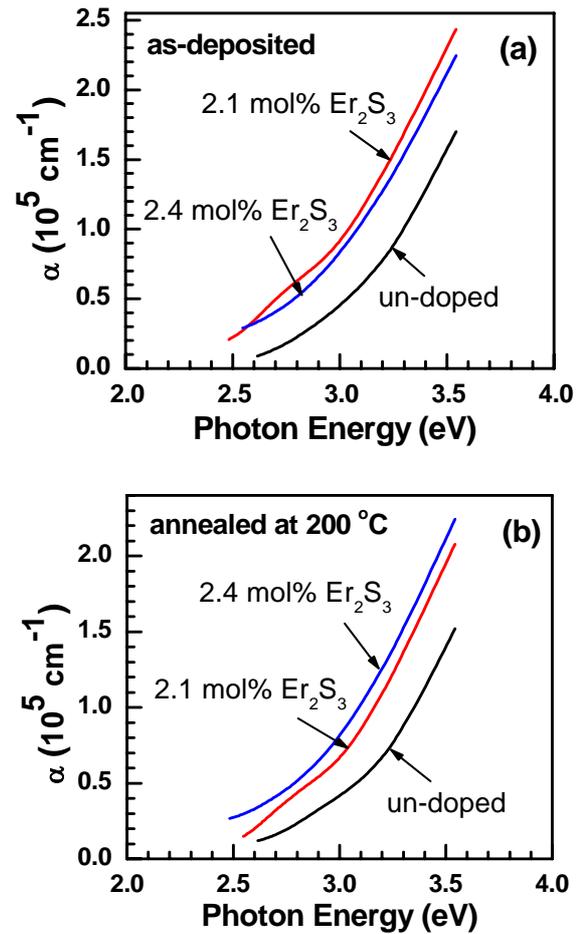

Fig. 4. (a) Dependence of α versus photon energy for as-deposited films; (b) for annealing at 200°C.

Expression (4) reflects the fact that the *k*-selection rule is relaxed in amorphous materials and at the same time the energy dependence of the transition probability is neglected. Power-law dependence with power 2 on the right hand side follows from the assumption of parabolic densities of states at both (valence and conduction) band edges [14, 15]. In the present case, the dependence of absorption coefficient on the incident photon energy is straight line at $\lambda < \lambda_c$. Consequently, we can attempt to evaluate the optical gap by using the plot of $(\alpha h\nu)^{1/2}$ versus photon energy $E = h\nu$ in Fig. 5 (a) and 5 (b) for as deposited and annealed films, respectively.

The variation of optical band gap E_g with annealing temperature is shown in Fig. 6. It turns out that E_g, corresponding to 2.1 mol% Er_2S_3 doping level, exhibits the lowest value of ~2.32 eV at room temperature among the studied films, i.e. as-grown and Er doped films. Besides, it should be noticed that the band gap is increasing with increasing annealing temperature for un-doped and 2.1 mol% Er_2S_3-doped GGS films, while it remains practically constant during annealing in case of 2.4 mol% Er_2S_3-doping.
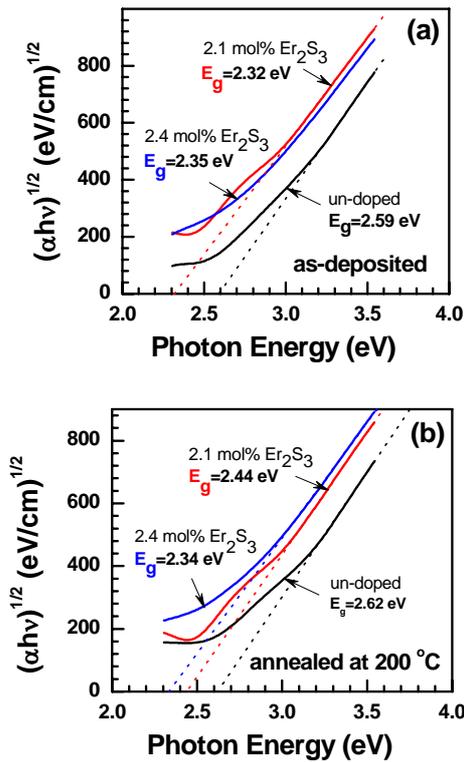
Fig .5. Dependence $(\alpha h\nu)^{1/2}$ on the photon energy for as deposited (a) and annealed (b) films.
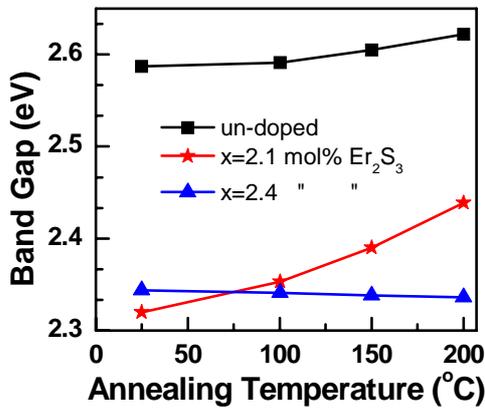

Fig. 6. Variation of optical band gap of GGS: Er³⁺ films with annealing temperature.

4. Discussion

The evaluation of the optical properties with respect to the high Er doping level of the studied GGS amorphous thin films are related to changes in the optical band gap. The observed peculiarities in the variation of optical parameters could be understood via the role of native defects and dopant concentration. These results also indicate that optical properties of Er³⁺-doped GGS films

can be tailored to some extent through annealing without disturbing their structure.

It has been found from our earlier studies on Er-doped Ge-S-Ga glasses that the strong photoluminescence band in the range of 1120-1460 nm from native defects of the host decreases at higher Er contents, which is a sign for a structural improvement in the host [7]. In particular for $(GeS_2)_{75}(Ga_2S_3)_{25}$ glasses, the intensity of the main emission band at 1540 nm increases with increasing Er content up to 2.1 mol% Er_2S_3 doping concentration and starts to decrease above 2.4 mol% Er_2S_3 (intensity quenching occurs) that is probably a sign for a non-uniform distribution of doping atoms in the glassy matrix [9].

It is well known that the Ge-S-Ga glassy network consists of GeS_4 and GaS_4 tetrahedral structural units (s. u.) connected through sulphur atoms [16], as essential building blocks. In particular, $[GaS_4]^{-1}$ tetrahedron generates one negative charge or defect because of the deficiency of sulphur since Ga is in a trivalent bonding sate. The number of such "defect" $[GaS_4]^{-1}$ s. u. in the glassy host network might be increased with the increase of annealing temperature due to possible re-evaporation of sulphur, having in mind the high vapor pressure of sulphur atoms [17,18], which may influence the optical band gap. In terms of the chemical bonding [19], the GGS glasses mainly contain metal-sulphur heteropolar bonds and metal–metal homopolar bonds [16]. Consequently, the increase of E_g values may reflect the decrease of the density of metal-sulphur bonds due to the possible re-evaporation of sulphur. Therefore, at high annealing temperatures the probability of the formation of heteropolar metal-sulphur bonds decreased and subsequently the E_g value increases. Thus, higher E_g value of as-grown undoped GGS film as compared to Er doped films is attributed to greater number of interstitial defects or formation of homopolar bonds. Increase of E_g in undoped and 2.1 mol% Er_2S_3-doped GGS films upon heat treatment is possibly due to eventual generation of more $[GaS_4]^{-1}$ s. u. or metal-metal bonds. On the other hand, the observed contraction in E_g at 2.4 mol% Er_2S_3-doping level with annealing temperature is probably due to the compensation/interstitial substitution of generated sulphur defects by excess of Er³⁺-dopant. Such compensation/interstitial substitution brings the structure to lower defect states that imply lower band gaps for 2.4 mol% Er_2S_3-doping at higher annealing temperature.

5. Conclusion

The impact of heat treatment on the structural and optical properties of Er³⁺-doped GGS glassy films has been studied. It follows from XDR analysis and optical transmission spectroscopy that all heat treated films, even at higher temperatures, retain their glassy nature whereas their optical properties are noticeably changed. Refractive indexes of prepared films are evaluated using the envelope of interference patterns superimposed on transmission spectra. Energy dependence of the absorption coefficient

has been deduced from measured transmission spectra that enabled evaluation of the optical band gap. Values of optical gap are determined as a function of doping concentration and annealing temperature. Un-doped GGS films exhibit higher band gap than that of Er^{3+}-doped GGS films due to the presence of native $[GaS_4]^{-1}$ defect states. Upon heat treatment, the band gap of un-doped and 2.1 mol% Er_2S_3-doped GGS films increases whereas it is decreased in case of 2.4 mol% Er_2S_3-doping. These variations in band gap of GGS:Er^{3+} films are mainly attributed to the generation and eradication of structural defects.

Acknowlegements

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