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PHOTOLUMINESCENCE IN Er-IMPLANTED AMORPHOUS Ge-S-Ga THIN FILMS

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The photoluminescence (PL) properties of Er-doped amorphous layers have been investigated. The Er^{3+} ions with fluences of 10^{15}, 2×10^{15}, 5×10^{15} and 10^{16} ions cm^{-2} have been embedded by a subsequent ion implantation into freshly deposited films. The Rutherford backscattering spectrometry (RBS) has been used to investigate the film structure and depth distribution of the constituents. A strong broad PL band centered at 1540 nm, corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions, has been found under excitations at 809, 791, 662 and 532 nm. Annealing at 230 ^oC leads to an improvement of the PL intensity by ~ 50 %. The observed effects are discussed in terms of the glass structure becoming damaged during ion implantation, and the partial restoration of the structure by subsequent annealing.

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1. Introduction

Chalcogenide glasses are of great interest for a variety of photonic applications such as optical amplifiers and frequency converters due to their low phonon energy, high refractive index, extended infrared transparency, etc [1-3]. In particular, Er^{3+}-doped chalcogenide thin films can be used to fabricate planar optical amplifiers or lasers in order to be integrated with other devices on the same chip [4]. However, the large difference in the evaporation rates of chalcogenide and rare-earth atoms excludes the deposition of Er^{3+}-doped films by thermal evaporation since nearly undoped films are obtained by this method. Ion implantation is a convenient way to incorporate Er^{3+} ions into thin films, as the Er^{3+} concentration depth profile can be tailored by varying the ion energy and fluence [4,5].

It has been found that Ge-S-Ga glasses may dissolve relatively large amounts of erbium which leads to a strong Er^{3+} intra-4f emission at the standard telecommunications wavelength of 1.54 μm [6]. Recently we have studied photoluminescence and structural properties of bulk GeS_2-Ga_2S_3-Er_2S_3 glasses [7,8]. In particular, the effect of broadening and narrowing in the PL emission cross-section has been evaluated depending on the excitation wavelength [9]. This report presents recent results on the role of the ion fluence, excitation wavelength and thermal annealing on the photoluminescence of Er^{3+}-implanted amorphous $(GeS_2)_{67}(Ga_2S_3)_{33}$ thin films.

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2. Experimental

Thin films were deposited by electron beam heating onto quartz substrates from bulk glass with a composition of $(GeS_2)_{67}(Ga_2S_3)_{33}$. They were consequently implanted by 320 keV Er^{3+} ions with fluences of 10^{15}, 2×10^{15}, 5×10^{15} and 10^{16} ions cm^{-2}, corresponding to concentrations at a mean ion range of 0.27, 0.54, 1.3 and 2.6 %, respectively. The electron diffraction investigation of the microstructure confirms the amorphous nature of the films. The film composition and the dopant concentration were determined by Rutherford backscattering spectrometry. The annealing was carried out at 230°C in vacuum for 2 hr.

Steady state photoluminescence spectra were measured using an ORIEL Cornerstone 1/8m monochromator and an ORIEL cooled InGaAs photodiode. The PL signal was excited using laser diodes operating at wavelengths of 809, 791, 662 and 532 nm.

3. Results

The Fig. 1 compares the theoretical and experimental RBS spectra for the layers studied. The best fit achieved using an SRM program corresponds to a 400 nm thin film containing 21 ± 1 % Ge, 21 ± 1 % Ga and 57.5± 0.5 % S (atomic density $N_{at} = 4.14\times10^{22}$ cm^{-3}). The depth profile of Er^{3+} is found to be roughly Gaussian with the maximum peaking at 85 nm and a straggling of 36 nm. The following specific features can be identified from Fig. 1: (i) the small peak between channels 440 and 420 is assigned to ion implanted erbium; (ii) the channels between 390 and 300 correspond to scattering from Ge and Ga which cannot be distinguished due to closeness of their atomic radii; (iii) the channels between 290 and 210 are related to S and (iv) those below 205 are attributed to scattering on Si at the interface between the substrate and the layer.

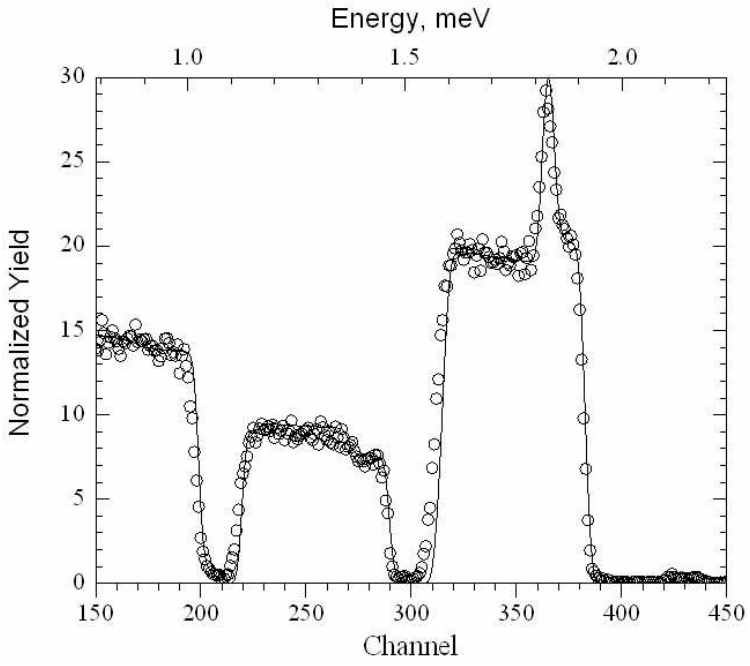

Fig. 1. RBS spectrum of studied films, experimental (points), simulated (line).

The photoluminescence spectra exhibit a broad emission band centered at 1540 nm (Fig. 2) which corresponds to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition in Er^{3+} ions in accordance with the energy level diagram of erbium [5]. Fig. 2 shows that the PL band appears to be broadened with increasing Er^{3+} fluence. This effect is hardly noticeable at low Er^{3+} fluences and it is apparent for the highest Er^{3+} fluence of 10^{16} ions cm^{-2}. A similar effect has been observed both in non-annealed and annealed

samples. The Fig. 3 shows that the increase in the fluence also leads to the reduction of PL efficiency of Er^{3+} ions, calculated as the ratio of PL intensity at 1540 nm to the erbium concentration (C_{Er}).

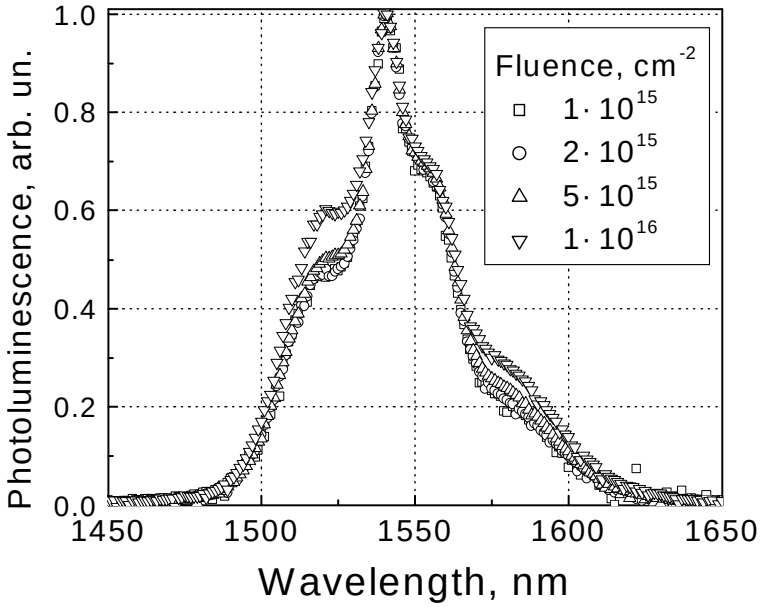

Fig. 2. PL spectra of non-annealed films at different fluence.

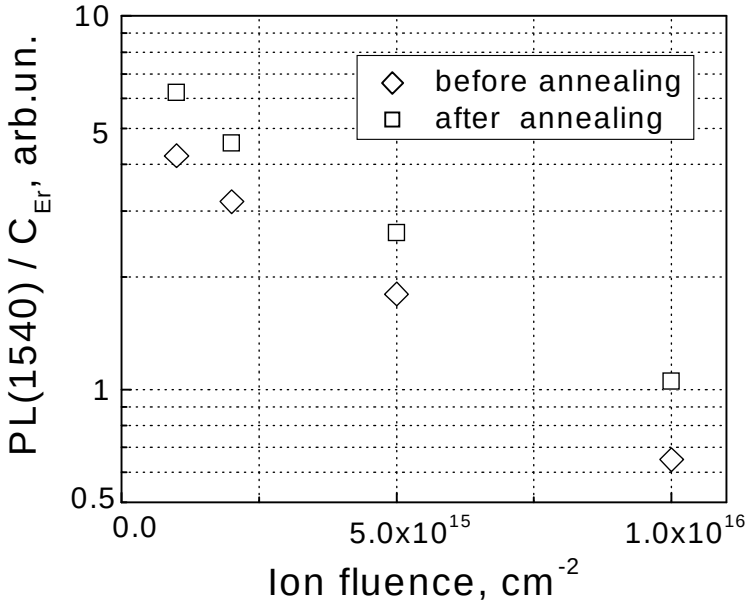

Fig. 3. The effect of Er^{3+} fluence and annealing on PL efficiency (calculated as the ratio of PL intensity at 1540 nm to the C_{Er}).

Fig. 4 shows that changes in the excitation wavelength does not modify the PL band of the Er^{3+}-doped films in contrast to results reported on bulk GeS_2-Ga_2S_3-Er_2S_3 glasses [9].

The influence of thermal annealing in vacuum at 230 °C, carried out after the ion implantation, is illustrated by Figs. 3 and 5. Fig. 3 shows that the annealing improves the PL efficiency by approximately 50 % in all samples and seems to reduce slightly the width of PL spectrum (Fig. 5).

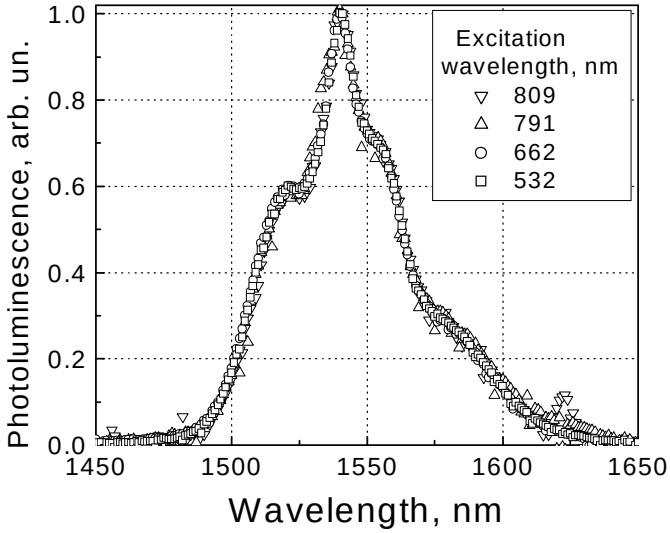

Fig. 4. PL spectra of non-annealed films at different excitation wavelengths (fluence of 10^{16} ions cm^{-2}).

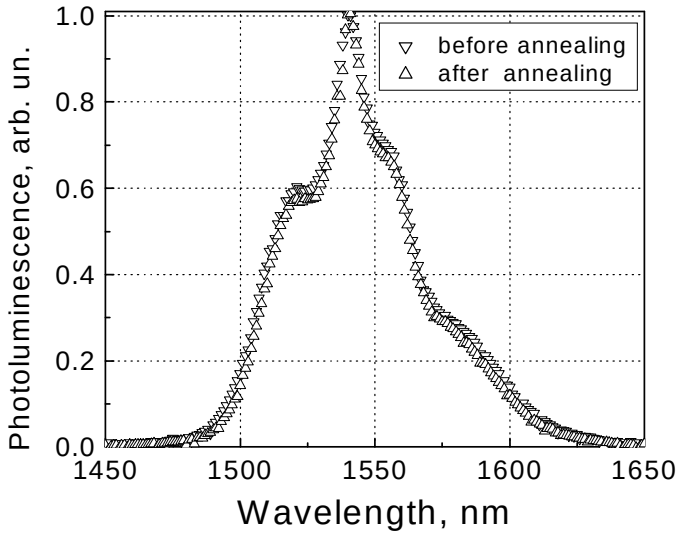

Fig. 5. Comparison of PL spectra of non-annealed and annealed films (fluence of 10^{16} ions cm^{-2}).

4. Discussion

Rare-earth ions, preferably in their trivalent bonding state, are of great interest in the development of optical communication technologies. In particular, erbium has an incomplete 4f electronic shell that provides for a rather sharp optical infra-4f transitions in Er^{3+}-doped materials. It is known that Er^{3+} emission occurs at an energy of 0.8 eV, corresponding to an important telecommunications wavelength of 1.54 μm. The Fig. 1 shows that considerable amount of Er can be

embedded in the studied chalcogenide $(GeS_2)_{67}(Ga_2S_3)_{33}$ thin films by ion implantation. Moreover, the detectable amount of Er^{3+} ions is optically active immediately after implantation, resulting in a broad PL emission cross-section at 1540 nm (Fig. 2). However, Fig. 3 shows that the increase of Er^{3+} fluence diminishes the PL efficiency per implanted Er atom. This effect may be is connected with two factors. First, the ion implantation process is known to damage the sample being implanted. Therefore, continuous implantation may destroy the optimal environment of active Er^{3+} complexes that have been already implanted. Second, the PL efficiency may be decreased by the cluster formation of Er^{3+} ions, and subsequent concentration quenching due to some energy migration between ions [10,11]. The width of the total PL band depends on the Stark splitting which in turn depends on the crystal field. The non-uniform glass structure appearing after ion implantation may lead to fluctuations of the crystal field and, hence, to a line-shape broadening. The crystal field may also be disturbed inside the Er^{3+} complexes. Both effects are reasonably consistent with the PL band broadening shown in the Fig. 2. Annealing increases the PL intensity (Fig. 3) and perhaps reduces the PL band width (Fig. 5). These results are in a good agreement with the expectation that annealing induces a partial "healing" of various defects in the glass structure that were created by implantation.

The Er-cluster formation may be the reason for the differences in PL bands obtained from bulk GeS_2-Ga_2S_3-Er_2S_3 glasses under different excitation wavelengths. In a previous paper [9], we have shown that the PL bands excited with laser diodes operating at 982 and 532 nm are practically identical in weakly doped bulk glasses with $C_{Er} \leq 0.4$ at %, meanwhile in heavily doped samples with $C_{Er} \geq 1$ at % they become rather broader at 982 nm excitation than that at 532 nm. This effect has been interpreted as an evidence of Er-clusterization and energy transfer within Er clusters. However, we have found that the effect of broadening is better pronounced in thicker samples. Therefore, the absence of broadening effect in the studied thin films (Fig. 4) may be due to their small thickness and cannot rule out the possibility of cluster formation and concentration quenching.

5. Conclusions

A broad PL emission band centered at 1540 nm in Er^{3+}-implanted $(GeS_2)_{67}(Ga_2S_3)_{33}$ thin films has been observed. Higher Er-ion fluences seem to lead to lower PL efficiency, which is defined as the PL intensity at 1540 nm per implanted Er^{3+}-ion. In addition, there may be some PL broadening with increasing Er^{3+}-ion fluence. The annealing of Er^{3+}-doped layers at 230 ^oC increases the PL efficiency by ~ 50 %. The line-shape of the emission cross-section does not change as the excitation wavelength is varied. The effects observed have been explained by the damage of glass structure during ion implantation and subsequent partial restoration of the structure due to annealing.

Acknowledgements

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