

Luminescence Properties of Er and Si Nanoparticles Co-doped Aluminum Silicate Thin Films

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The effects of Al doping on luminescence properties of Er ions (Er^{3+}) in Er and Si nanoparticles co-doped SiO_2 are studied. The purpose of Al doping is to improve concentration quenching of Er^{3+} luminescence and to realize higher concentration Er doping. We show that the concentration quenching is slightly improved by Al doping. However, the luminescence intensity is decreased. In order to clarify the mechanism of photoluminescence (PL) quenching by Al doping, the PL rise and decay time were analyzed. The result indicates that the number of optically active Er is decreased by Al doping.

Key words: Er, Si-nanoparticles, photoluminescence, concentration quenching.

1. INTRODUCTION

The Er-doped silica fiber has been widely used as an optical amplifier for long distance optical telecommunication [1]. There have been strong demands to miniaturize the device. However, a small absorption cross section of Er ions (Er^{3+}) prevents the miniaturization. There are two possible approaches to realize this. One of them is to employ photosensitizer that absorbs light and transfers its excitation energy efficiently to Er [2]. For example, Si nanoparticles act as an efficient photo-sensitizer for Er^{3+} due to large absorption cross section of Si nanoparticles and efficient energy transfer to Er^{3+} , if Er and Si nanoparticles are simultaneously doped into SiO_2 [3-7]. The advantage of the sensitized excitation is the broad excitation band covering the whole visible range and a part of the near infrared range because of the broad absorption band of Si nanoparticles.

The other approach is to increase Er concentration in SiO_2 . However, in pure SiO_2 , aggregation of Er, which quenches luminescence efficiency of Er^{3+} significantly, starts at relatively low Er concentration range (≈ 0.01 at.%). The solubility limit of Er in SiO_2 can be increased drastically when some kinds of impurities, such as Al, P and Bi, are doped simultaneously [8,9]. Especially Al doping is well known as an effective method to suppress the concentration quenching of Er in a SiO_2 matrix. By Al doping, Er concentration can be increased to 0.1 at.%, when the Al/Er ratio is higher than 10 [10].

These previous works suggest that the combination of these two approaches, i.e., doping of Si nanoparticles into impurity doped SiO_2 , results in further improvement of the performance of an Er doped SiO_2 optical amplifier. However, the research on Er and Si nanoparticles doped silica-based multi-component glasses is very limited [11-13]. Therefore, in this work, we investigate the effects of Al doping on luminescence properties of Er and Si nanoparticle co-doped SiO_2 thin films.

2. EXPERIMENT

SiO_2 thin films containing Er, Al and Si nanoparticles were prepared by a co-sputtering method. Small pieces of Si, Al_2O_3 chips and Er_2O_3 tablets were put on a SiO_2 sputtering target and were simultaneously sputter-deposited on a quartz substrate. Al and Er concentration of deposited films were estimated by electron probe microanalysis (EPMA). The Er concentration was changed from 0 to 1.3 at.% by changing the number of Er_2O_3 tablets during the sputtering. Excess Si concentration was fixed to about 7 at.% and Al concentration was about 6 at.%. After the deposition, the samples were annealed in N_2 gas atmosphere at temperatures above 900 °C. Photoluminescence (PL) measurements were performed by using a single grating monochromator and a liquid nitrogen cooled InGaAs diode array. The excitation source was a 488 nm line of an Ar ion laser. PL time transient, i.e., rise and decay curves, were measured by using a near infrared photomultiplier with an InP/InGaAs photocathode. All the measurements were performed at room temperature.

3. RESULTS AND DISCUSSIONS

Figure 1 compares PL spectra of the samples with and without Al doping. The Er concentration is 0.2 at.%. The peak corresponds to the intra-4f shell transition of Er^{3+} . The peak is broadened due to the Stark splitting of the 4f levels. We can see that the spectrum becomes broad by Al doping. This indicates that Al is coordinated around Er^{3+} and the crystal field is changed. Note that the spectra shape does not depend strongly on Er concentration. In the inset of Fig. 1, the PL peak intensity is plotted as a function of the Er concentration. Without Al doping, the PL intensity is proportional to the Er concentration up to the Er concentration of about 0.2 at.%, and then starts to decrease. This concentration quenching is due to the interaction between neighboring

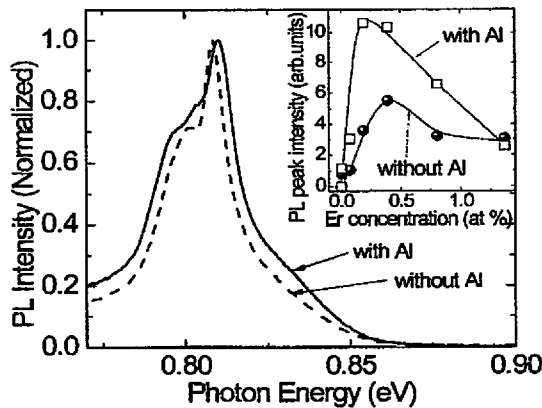


Fig. 1 PL spectra of Er in Er and Si nanoparticles doped SiO₂ with (solid curve) and without (dashed curve) Al doping. The inset shows PL peak intensity as a function of Er concentration for the samples with (filled circle) and without (open square) Al doping.

Er ions and the formation of Er clusters. On the other hand, for the sample with Al doping, the PL intensity continues to rise up to about 0.4 at.%, suggesting that the concentration quenching of Er can be suppressed by Al doping.

Although Fig. 1 suggests possible suppression of the concentration quenching by Al doping, the PL intensity of Al doped samples is lower than that of Al undoped ones when Er concentration is low. In order to improve the PL intensity of Al doped samples, we try to clarify the mechanism of the PL quenching by Al doping.

To estimate PL lifetime, excitation cross section, and the number of optically active Er³⁺, we measured the PL rise and decay curves. In the simplest model assuming a two level system, the rate equation of the number of excited Er (N^*) is expressed as

$$\frac{dN^*}{dt} = \sigma \phi (N - N^*) - \frac{1}{\tau} N^*, \quad (1)$$

where N , σ , ϕ and τ are the number of optically active Er, excitation cross section, photon flux of excitation laser and the lifetime of Er, respectively. The excitation by energy transfer from Si nanoparticles and direct excitation by light are included in σ . If Er³⁺ is excited by continuous wave light at $t = 0$, the PL intensity is

$$I(t) = I_0 [1 - \exp\{-(\sigma \phi + \frac{1}{\tau})t\}], \quad (2)$$

where I_0 is the steady state PL intensity, and $1/(\sigma \phi + 1/\tau)$ corresponds to the rise time (τ_{rise}).

Figure 2 shows the correlation between the PL rise time and the excitation photon flux. The excitation cross section and the lifetime can be estimated by the slope and the y-intercept of the line, respectively. The values of lifetime estimated by this method are close to those estimated by exponential fitting of decay curves. This result indicates that the estimated values are reasonable.

The steady state solution of Eq. (1) is

$$N^* = \frac{\sigma \phi \tau}{\sigma \phi \tau + 1} N. \quad (3)$$

If the excitation intensity is very low, $\sigma \phi \tau \ll 1$, Eq. (3) can be approximated to $N^* = \sigma \phi \tau N$ and the steady state PL intensity I_0 becomes proportional to $N^*/\tau_{radiative}$, where $\tau_{radiative}$ is the spontaneous emission time. Therefore, the ratio of the PL intensity between Al doped and Al un-doped samples is expressed as

$$\frac{I_{withAl}}{I_{withoutAl}} = \frac{\sigma_{withAl} \tau_{withAl} / \tau_{radiative_withAl} N_{withAl}}{\sigma_{withoutAl} \tau_{withoutAl} / \tau_{radiative_withoutAl} N_{withoutAl}}, \quad (4)$$

where the subscripts "withAl" and "withoutAl" refer to Al doped samples and Al undoped samples, respectively.

The spontaneous emission rate of Er is considered not to be strongly modified by Al doping. Therefore, the intensity ratio in Eq. (4) is determined by the excitation cross section σ , the PL lifetime τ and the number of optical active Er N . σ and τ can be estimated from the procedure discussed above, and from the experimentally obtained intensity ratio, $N_{withAl}/N_{withoutAl}$ can be estimated by using Eq. (4) under the assumption that the spontaneous emission rate is not modified by Al doping.

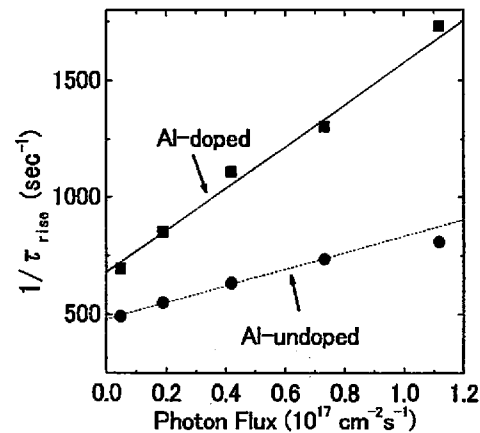


Fig. 2 Inverse of PL rise time as a function of photon flux for the samples with (solid squares) and without Al doping (6 at.%) (solid circles). Excitation cross sections are estimated from the slope of the lines.

In Figs. 3(a), 3(b) and 3(c), $\sigma_{withAl}/\sigma_{withoutAl}$, $\tau_{withAl}/\tau_{withoutAl}$ and $N_{withAl}/N_{withoutAl}$, respectively, are plotted as a function of Er concentration. We can see that $\sigma_{withAl}/\sigma_{withoutAl}$ is higher than 1 and also $\tau_{withAl}/\tau_{withoutAl}$ is close to 1. On the other hand, $N_{withAl}/N_{withoutAl}$ is about 0.5. These results indicate that the quenching of PL intensity shown in the inset of Fig. 1 originates mainly from the decrease of the number of optically active Er³⁺ in the samples.

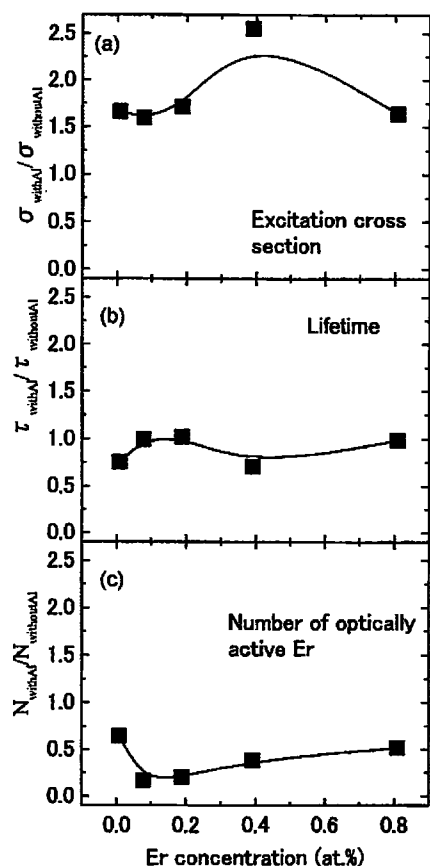


Fig. 3. The ratios of excitation cross section (a), lifetime (b) and the number of optically active Er^{3+} (c) between Al doped and Al un-doped samples are plotted as a function of Er concentration.

Although the mechanism of the decrease of optically active Er^{3+} is not clear, one of the possible reasons is as follows. The melting point and the viscosity coefficient of SiO_2 decrease by Al doping [14], which results in longer diffusion lengths of Si and Er during the annealing. The longer diffusion length increases the probabilities of forming Er clusters and also Er encountering to excess Si to form Er silicides. Since Er clusters and Er silicides are optically inactive, the number of optically active Er decreases by Al doping [15,16]. Therefore, in order to increase the PL intensity, a development of an annealing procedure which prevents clustering and silicidation of Er is indispensable. Furthermore, further optimization of Er, Al, and Si concentration is required to improve the PL properties.

5. CONCLUSION

We investigated the effects of Al doping on luminescence properties of Er and Si nanoparticles co-doped SiO_2 . PL spectra of Er were broadened due to the change of crystal field around Er by Al doping, suggesting that Er is coordinated by Al. We showed that the concentration quenching is slightly improved by Al

doping. However, the PL intensity was decreased. From the analysis of PL decay and rise curves, we estimated the ratio of excitation cross section, lifetime and the number of optically active Er between Al doped and Al un-doped samples. These results indicate that PL quenching by Al doping is mainly due to the decrease of the number of optically active Er^{3+} , probably due to the formation of Er clusters and Er silicides. An optimization of Er, Al, Si concentrations, and annealing conditions are required.

6. ACKNOWLEDGEMENT

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