The effects of Er/Al co-doping on the fluorescence of silica waveguide film

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In this research, Er/Al co-doped Si/SiO$_2$ optical waveguide films were fabricated for an optical amplifier application. The co-doping of Er and Al into silica soot deposited by FHD was successfully carried out by solution doping. The optimum conditions for sintering were 1330°C~1350°C. The fabricated waveguides showed a refractive index difference of 0.8~0.9%, which is appropriate for amplifier operation. According to the results of the fluorescence measurements, we could confirm the depression of the concentration quenching of Er ions by the co-doping with Al.

Key words: silica, wavequide, optical amplifier, co-doping, fluorescence.

Introduction

A PLC (Planar Lightwave Circuit) type optical amplifier is an integrated optical device applicable to access networks in optical communication. Because of its compact physical size, easy mass-production, and integratibility into monolithic multi-functional optical devices, this device is expected to be a key element in the next generation of optical communication network. However, to get reasonable amplification gain, a PLC type optical amplifier requires a high concentration of rare earth ions because of its short gain medium length. But a high concentration of rare earth ions causes the decrease of amplification efficiency by scattering loss, non-radiative emission, etc. Namely, if the concentration of Er^{3+} is high, Er ions form clusters and generate "concentration quenching", the reduction of stimulated emission lifetime in the meta-stable state. In a fiber amplifier, *to avoid such concentration quenching and to* increase the solubility of Er, co-doping of Al and Er into optical fibers is used. Al ions are dissolved into the silica network with a tetrahedral structure, $[AlO_{4/2}]^-$. These $[AlO_{4/2}]^-$ attract Er^{3+} ions to reduce free energy and prevent clustering of Er^{3+} ions [1-3]. In this study, we try to apply such a result from the fiber amplifier to the fabrication of waveguide by FHD.

In this study, the fabrication of a Si/SiO$_2$ optical waveguide amplifier by FHD (Flame Hydrolysis Deposition) and solution doping are mainly discussed. Underclad and core layer SiO$_2$ films were deposited by FHD and subsequently solution doping was carried out to add Er^{3+}/Al^{3+} *ions into the deposited core* layer film. The influences of pre-sintering and the solution doping process on the film were investigated to optimize the sintering process [4]. Measuring the thickness and refractive index of Er doped silica films was conducted by a Prism coupler method. In addition, as a basic characteristic of the amplifier, the fluorescence spectrum of Er^{3+}/Al^{3+}-doped silica films was measured to check if the films were properly doped with Er^{3+}.

Experiments

An underclad layer was deposited on a Si wafer by FHD in the form of a porous soot and subsequently sintered into optical grade dense glass film. Then, the core layer was deposited onto the underclad by the same method. The doping by Er was carried out after a pre-sintering processing at 950°C by a solution doping method with Al for 24 hours. The pre-sintering was intended to give some mechanical integrity to the soot particles in the core layer thus preventing physical dissociation of the layer during the solution doping process. After doping, the porous core layer was sintered into a dense silica glass film by heat treatment at 1330°C~1350°C. Since Al increases the sintering temperature and B lowers it, the sintering temperature was controlled by controlling the content of Al and B [5]. The content of B was proportionally doped to suppress the increase of the sintering temperature by the Al addition below 20°C to prevent the crystallization and mixing between the underclad and core layers [6-7]. The content of each constituent was controlled by the flow rate of source gases when fabricating the soot; the flow rates of SiCl$_4$ and POCl$_3$ were 44 sccm and 5 sccm respectively for both underclad and core layers, and GeCl$_4$ was 46 sccm for the core layer, BCl$_3$ was 3 sccm for the underclad layer and 17 sccm for the core layer.

An Er/Al solution for solution doping was prepared

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in different concentrations by dissolving reagent grade $ErCl_3 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ powder in ethanol. The solution concentrations of Er were 0.2 wt%, 0.35 wt%, 0.5 wt% and 0.65 wt% and those of Al were 0.25 wt% and 0.5 wt%.

RBS (Rutherford Backscattering Spectrometry) and EPMA (Electro Probe Micro Analysis) were employed to measure the concentration of Er/Al in the silica films. In RBS, He ions were used as the ion beam source, and there were accelerated by a Pelltro (NEC 6SDH2) in the Tandem mode. The accelerating voltage was 2 MeV, and the charge of the He ions, incident angle and scattered angle were 20 uC, 0° and 10°, respectively. The measured spectrum from RBS was made to fit a theoretical spectrum using the rump program. The data fitting was quantitatively conducted by dividing the sample into 16 layers. However, B, P, and Al were not detected by RBS due to their light atomic mass or low content. Instead, ICP-AES and EPMA were employed to measure the concentration of these elements. In EPMA, the beam current, accelerating voltage and probe diameter were 1×10^{-8}A, 20 kV, and 200 µm, respectively. In ICP-AES, JOBIN YVONJY 138 ULTRACE model was employed. The thicknesses and refractive indice of the Er/Al doped silica films were measured by the Prism coupler (Metricon Model 2010) at a wavelength of 633 nm [8].

The fluorescence spectra were measured as a basic optical characteristic for the optical amplifier and to clarify the effect of Al co-doping. The fluorescence spectrum was measured by launching the pumping laser light into the polished edge of the silica films and collecting the light emitting from the surface of the film. Er^{+3} in the $^4I_{15/2}$ ground state was pumped to the $^4I_{11/2}$ by a Ti-sapphire tunable laser (CW, 980 nm, 460 mW). The fluorescent light emitted by the transition from $^4I_{15/2}$ to $^4I_{11/2}$ was selected by a 1/4 m monochromater (Oriel Co.), amplified by a lock-in-amplifier, and detected by an InGaAs PIN detector (Hamamatsu Co.).

Results and Discussion

The measured concentrations of Si, Ge, B, P and O in the core layer were 27.4 wt%, 2.5 wt%, 1.4 wt%, 0.1 wt% and 68.4 wt%, respectively. Since the process parameters such as the source flow rates of Si, Ge, B and P and the sintering temperature were fixed for all the films, no variation in the concentrations was observed for the various samples. Fig. 1 and Fig. 2 show the variation of dopant concentration as a function of the Er/Al solution concentration used during the solution doping process. These results show that the Er concentration in the sintered silica films increased linearly with the concentration of Er in solution even though the absolute concentration of Er is lower in the sintered films compared to the solution. Al also appears to exhibit a similar doping behavior. At least, it has been
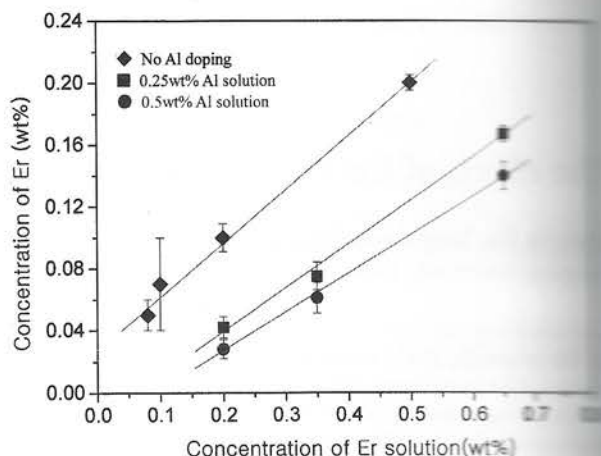

Fig. 1. The variation of Er concentration in the silica film as a function of Er solution concentration.
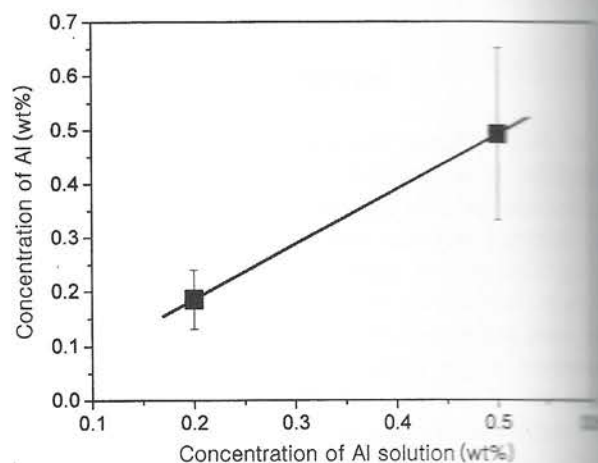

Fig. 2. The variation of Al concentration in the silica film as a function of Al solution concentration.

shown that the concentration of Er/Al doped into the sintered film could be controlled predictably by changing the concentration of in the solution. The maximum concentration of Er doped into the glass film was measured to be 0.2 wt% for the 0.5 wt% Er solution.

The co-doping of Al with Er has proved to reduce the doping concentration of Er in the glass film. As shown in Fig. 1, the glass film doped in the solution containing 0.65 wt% Er and 0.5 wt% Al was observed to contain a lower concentration of Er, which is 0.25 wt%. That is, although the Er concentration in the solution used for Er/Al co-doping was higher than that of the solution used for Er doping, the actual doping concentration in the co-doped film was lower than that of the single doped film. This means that co-doping with Al decreased the absolute doping quantity of Er. Furthermore, the proportionality between the Er concentration in solution and the actual concentration of Er in the sintered films decreased with the increasing Al concentration. On the other hand, the actual concentration of Al in the sintered films was close to the concentration
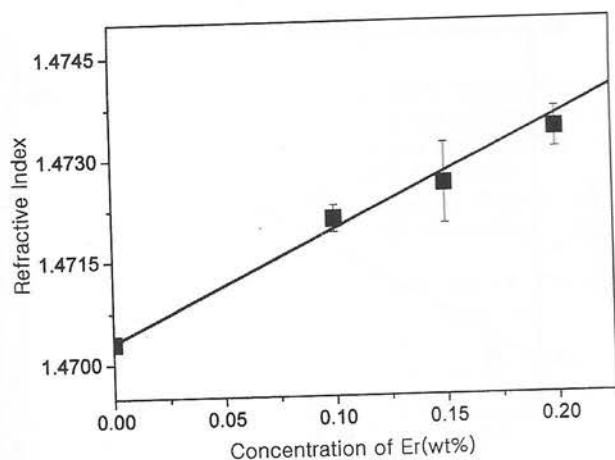
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Fig. 3. Refractive indices of Er doped silica waveguide films as a function of Er concentration (No Al doping).

oxygen increase and hence refractive index increase [10, 11]. As shown in the results, the addition of 0.2 wt% Er produced an increase of the refractive index by 0.0031, and the addition of 0.5 wt% Al produced an increase of 0.0015, smaller than the case of Er [12]. On the other hand, the refractive index of the underclad layer was about 1.46, which makes a suitable index difference $[= (n_{core} - n_{under})/n_{under}]$ of 0.8~0.9% for the fabricated waveguide amplifying medium. The thickness of the silica film was 14.6 μm for the underclad and 4.9 μm for the core layer in average.

Fig. 5 shows the fluorescence spectrum of Er/Al co-doped silica films. The maximum fluorescence inten-

in the solution and not affected by the Er concentration. This result suggests that Al is selectively adsorbed on the surface of the silica soot first and then Er is absorbed. It is known that the ion in the solution containing OH forms the hydrated ion and the hydrated ionic radius determines the adsorption behavior on the solid surface [9]. Since the ionic radius of Er^{+3} is larger than that of Al^{+3}, the ionic field strength (charge/ionic radius) of Al^{+3} is higher than Er^{+3}, which means that the tendency to form a hydrated ion is higher for Al^{+3} compared to Er^{+3}. Therefore, the OH species on the surface of a silica soot particle attracts Al^{+3} more strongly than Er^{+3} and this tendency is believed to produce the preferred adsorption of Al^{+3} over Er^{+3}.

Figs. 3 and 4 show the change of refractive index at a wavelength 633 nm as a function of Er and Al concentrations. Here the concentrations of Er and Al are the actual values measured by RBS and EMPA as described in the previous section. It is reported that the addition of ions with a large radius such as Er^{+3} and Al^{+3} makes the dipole strength of the non-bridging
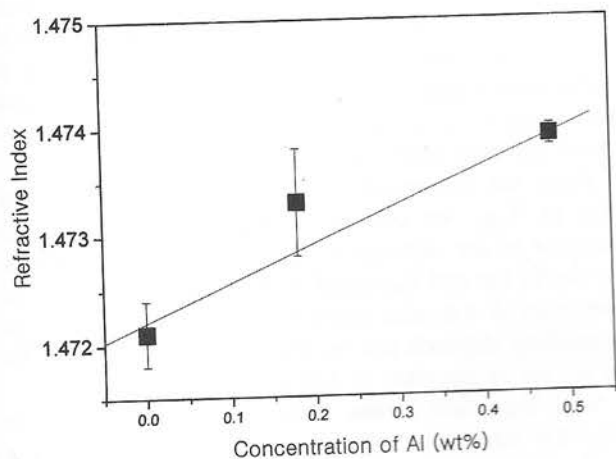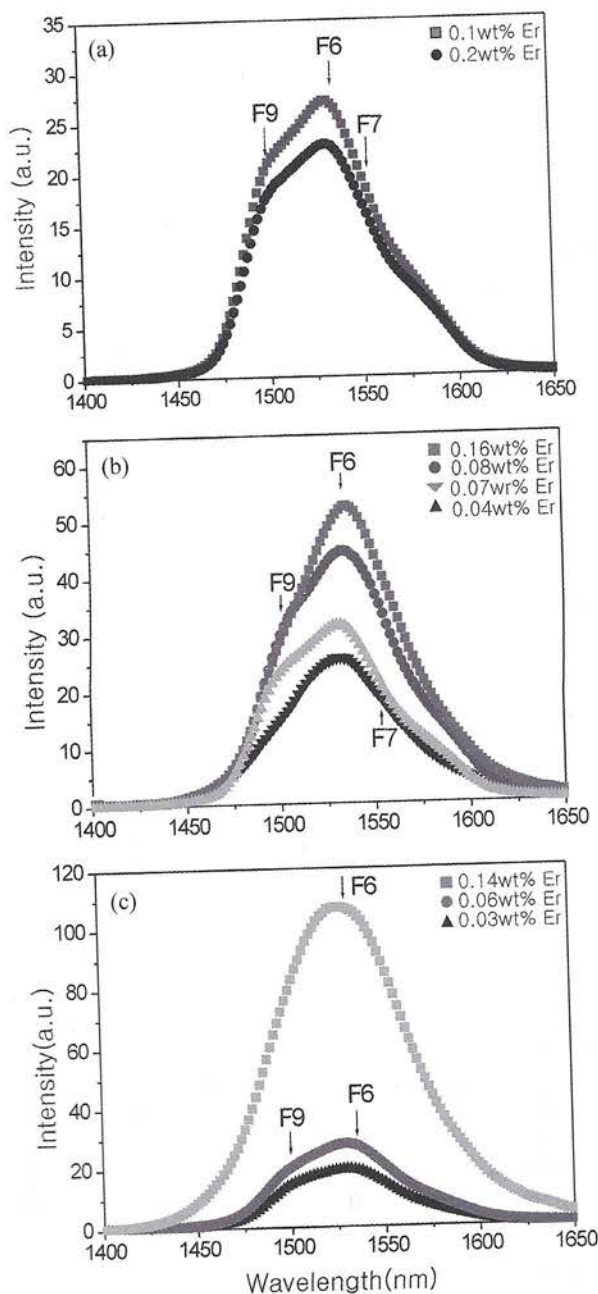

Fig. 4. Refractive indices of Er/Al co-doped silica waveguide films as a function of Al concentration at a fixed Er doping of 0.1 wt%.

Fig. 5. Fluorescence spectra of Er/Al codoped silica films with (a) no Al; (b) 0.18 wt% Al; 0.48 wt% Al.

sity showed at 1534 nm on average, and the main Stark levels were identified by F9, F6, F7 [13]. The spectrum is different from that of the SiO_2-Al_2O_3 host EDF in the location of the main peaks. This is due to the different crystal field around Er^{3+} originating from the different composition of host materials [13]. On increasing the doping level of Er/Al, a subtle change of the spectrum shape was observed, while the main Stark levels remained unchanged.

Fig. 5(a) shows spectra of the silica films doped with Er only. As the concentration of Er increased, the intensity of the spectrum decreased. Generally the fluorescence intensity is expected to increase if the quantity of the fluorescence source, Er, increases. However, at high concentrations of Er^{3+}, the clustering of Er ions occurs to reduce the energy by sharing non-bridging oxygens, and due to their close distance "concentration quenching" starts to appear, which results in the decrease of the fluorescence intensity and life time [14]. It is believed that this "concentration quenching" occurred in the samples in Fig. 5(a) and reduced the fluorescence intensity. On the other hand, silica films with 0.18 wt% Al (Fig. 5(b)) showed a reduction of fluorescence intensity at an Er concentration of 0.08 wt%, and silica films with 0.48 wt% Al (Fig. 5(c)) did not show this effect up to a Er concentration of 0.14 wt%. Namely, the Er concentration showing "concentration quenching" increased as the concentration of Al doped increased and this result is identical to the case of the Er/Al co-doped silica glass fiber. Therefore, it is believed that Al reduced the "concentration quenching" in the silica films and improved the emission efficiency by preventing Er ions from clustering. Using this principle, one could know that "concentration quenching" depends on not the absolute quantity of Er or Al but on the Al/Er ratio. [15] These results are summarized in Fig. 6 which shows the fluorescence intensity at a
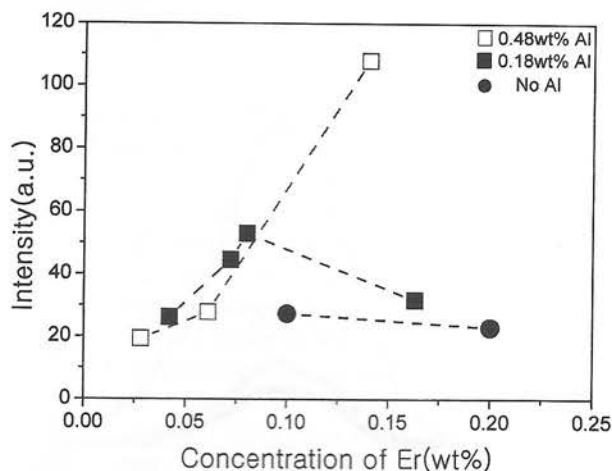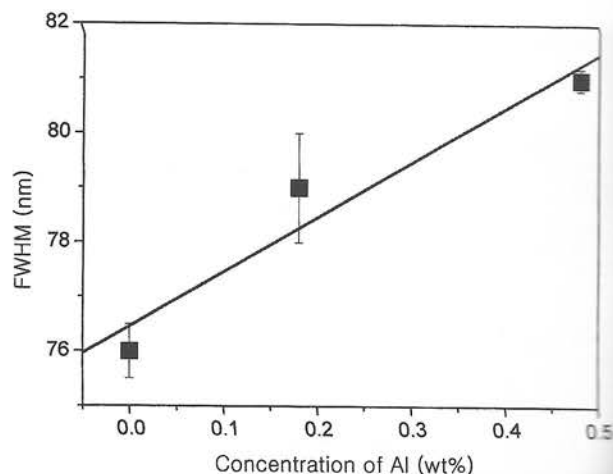

Fig. 7. FWHM of Er/Al doped silica film as a function of concentration of Al.

wavelength 1534 nm. This is clearly shows that the doping notably reduced the tendency of concentration quenching. Besides a reduction of concentration quenching, Al also is known to slightly increase the FWHM of the fluorescence spectrum at 1.5 μm [13]. This effect is confirmed in Fig. 7 from fluorescence spectra with normalized maximum intensity. The addition of 0.5 wt% Al produced an increase of FWHM by 5 nm, which is somewhat less than that reported in silica optical fibers [13].

Conclusions

In this research, the solution doping method was successfully applied to co-doping of Er and Al in silica waveguide films deposited by FHD. In the solution doping method, we could control the concentration of Er/Al in the film by changing the concentration of Er solution since the final concentrations of dopant exhibited a linear relationship with the concentration in solution. Even though, there was discrepancy in absolute concentration between final concentration and solution concentration due to different adsorption behavior of two dopants, the linear relationship made it possible to control the concentration of dopant in a predictable manner. The Er/Al doping concentration was controlled to give appropriate refractive index differences between underclad and core layer, 0.8~0.9%.

From the fluorescence emission by transition from $^4I_{6/2}$ to $^4I_{15/2}$, we confirmed that the addition of Al resulted in the depression of concentration quenching by the Er ion and increased the FWHM of fluorescence spectrum. It was also confirmed that the concentration quenching depends not on the absolute quantity of Er or Al but on the ratio of Al/Er.

With the result of this study, we could demonstrate that the fabrication of a waveguide amplifier with a high gain would be possible by co-doping technique.

Fig. 6. The variation of fluorescence intensity as a function of Er/Al concentration in silica film.

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