Optical Properties of PMMA Polymer Doped with Er\(^{3+}\) and Er\(^{3+}/Yb\(^{3+}\) Ions

V Prajzler\(^1\), I Huttel\(^2\), O Lyutakov\(^2\), J Spirkova\(^2\), J Oswald\(^3\), Z Burian\(^1\) and V Jerabek\(^1\),

\(^1\) Department of Microelectronics, Faculty of Electrical Engineering, Czech Technical University, Technicka 2, 166 27 Prague 6, Czech Republic
\(^2\) Institute of Chemical Technology, Technicka 5, 166 28 Prague 6, Czech Republic
\(^3\) Institute of Physics of the ASCR, v.v.i. Cukrovarnicka 10, 162 53 Prague 6, Czech Republic

Abstract. In this paper we report about fabrication and properties of polymethylmethacrylate doped with Er\(^{3+}\) and Yb\(^{3+}\) ions. The reported layers were fabricated by spin coating onto Si, Si/SiO\(_2\) or onto glass substrates. For the Er and Yb doping ErCl\(_3\) and YbCl\(_3\) or ErF\(_3\) and YbF\(_3\) powder dissolved in C\(_5\)H\(_9\)NO or C\(_2\)H\(_6\)OS were used. The research was focused on investigation of the influence of the amount of the dopants on the photoluminescence spectra at 1.55 \(\mu\)m. It was found that the increasing Er\(^{3+}\) content increased the intensity of the luminescence and that co-doping with ytterbium ions increased the intensity of the luminescence as well.

1. Introduction

Erbium ions are the most interesting dopants because of the Er\(^{3+}\) emission at 1.55 \(\mu\)m, which corresponds to the wavelengths where absorption of silica optical fibers is minimal. Optical materials such as semiconductors, glass and optical crystals doped with erbium offer prospects for optical sources or amplifiers operating at 1.53 \(\mu\)m [1], [2], [3], [4], however the doping means to solve rather complex problems. Therefore new materials such as polymers have been investigated in the last decade as well.

Optical waveguides and devices based on polymer materials have attracted considerable interest because of their potential applications in optical communications and in integrated optics [5], [6]. Even though the usefulness of Er\(^{3+}\)-containing devices has been already proved one drawback, i.e., lacking of absorption bands where low cost pump sources can emit, remains. One way to overcome this problem is using co-doping with a Er\(^{3+}\) sensitizer, which has a broad absorption band and for that ytterbium is especially attractive [7], [8].

2. Experiment

2.1. Fabrication of the samples

The polymer layers were fabricated by a spin coating of Polymethylmethacrylate (PMMA) polymer (EXP 03051-9, Brewer Science Inc.) onto silicon, silica on silicon and glass substrates, or PMMA was poured into a bottomless mold placed on a glass substrate and let on to dry. For the doping the ErCl\(_3\) and YbCl\(_3\) or ErF\(_3\) and YbF\(_3\) were dissolved in C\(_5\)H\(_9\)NO or C\(_2\)H\(_6\)OS (Sigma-Aldrich) (the content of...
erbium in the solutions varied from 1.0 at.% to 10.0 at.%), and added to the PMMA. The samples containing 1.0 at.% of erbium were doped with ytterbium in the amounts that varied from 1.0 at.% to 10.0 at.%.

2.2. Measurement

Properties of the fabricated layers were analyzed by various methods. Refractive indices ($n$) of the samples were determined using refractometer at the wavelength ranging from 250 to 750 nm and by prism coupling method at 632.8 nm. The absorption spectra were taken at the wavelength range from 300 to 1000 nm using UV-VIS-NIR Spectrophotometer (Shimadzu UV-3600). The photoluminescence measurement was carried out at excitation wavelengths of 980 nm by using semiconductor laser P4300 operating at $\lambda_{ex} = 980$ nm with $E_{ex} = 500$ mW at room temperature.

3. Results and discussion

Number of propagating modes determined by prism coupling method varied from 1 to 6 depending on the thickness of the deposited layers. Refractive index of the virgin PMMA is 1.49 (as measured at 632.8 nm) and the Er$^{3+}$, as well as the Er$^{3+}$ + Yb$^{3+}$, doping made it to decrease. The refractive index of the sample that contained 1.0 at.% Er$^{3+}$ + 10.0 at.% Yb$^{3+}$ was 1.389. Similar decreasing of the refractive index value has been already observed [9], though the authors reported much smaller decrement of the $n$ (from 1.575 for the un-doped polymer to 1.573 found at the Er$^{3+}$ + Yb$^{3+}$ doped one, measured at 1550 nm). Explanation of that dramatic decrease of the $n$ observed in our samples may be associated with dilution of the PMMA with the above-mentioned solvents.

Transmission spectra at wavelength from 500 nm to 600 nm of the Er$^{3+}$ doped PMMA samples are given in Fig. 1. The figure shows that the band attributed to the $^2H_{11/2}$ transition is stronger in the samples with higher Er$^{3+}$ concentration. Transmission spectra of the Er$^{3+}$ + Yb$^{3+}$ doped PMMA (Fig. 2) show that in the contrary with the former, here the $^3F_{5/2}$ is stronger (For the assignment of the H and F bands see [10]).

![Figure 1. The transmission spectra of the Er$^{3+}$ doped PMMA layers.](image1)

![Figure 2. The transmission spectra of the Er$^{3+}$+Yb$^{3+}$ doped PMMA layers.](image2)

The photoluminescence spectra of the Er$^{3+}$ doped PMMA samples are given in Fig. 3. The figure shows the typical photoluminescence bands attributed to the erbium transition $^4I_{13/2} \rightarrow ^4I_{15/2}$. Fig. 3 also shows that the increasing content of Er$^{3+}$ ions increased also the photoluminescence intensity. The highest PL intensity so far observed had the sample containing 10.0 at.% of erbium. If that value is still below the highest critical concentration when the concentration quenching effect could occur is still a matter of further investigation.
Photoluminescence spectra of the $\text{Er}^{3+}$-doped PMMA layers are given in Fig. 3. Doping with ytterbium ions increased the intensity of the luminescence as well.

Photoluminescence spectra of the $\text{Er}^{3+} + \text{Yb}^{3+}$ doped PMMA samples are given in Fig. 4. Doping with ytterbium ions increased the intensity of the luminescence as well.
4. Conclusion
In conclusion, we found that the samples deposited onto the Si/SiO₂ substrate had waveguiding properties. The number of propagating modes varied from 1 to 6 depending on the thickness of the deposited layers. We observed photoluminescence emission at 1530 nm due to the transition \( {^4I_{13/2}} \rightarrow {^4I_{15/2}} \). Addition of ytterbium ions increased the intensity of the luminescence. Best results we obtained with the samples containing 1.0 at.% of Er and 10.0 at.% of Yb ions.

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6. References
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