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Optical properties of ErFOD-doped polymers and fabrication of channel waveguides

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ABSTRACT

ErFOD-doped P(MMA-co-GMA) (poly-methyl-methacrylate-co-glycidyl-methacrylate) polymer film was synthesized. The NIR photoluminescence (PL) spectrum of the material showed strong characteristic emission of Er^{3+} ions with broad full width at half-maximum (FWHM) of 55 nm. The rib channel waveguide using ErFOD-doped P(MMA-co-GMA) was designed and fabricated. The loss and gain measurements of the waveguides were also characterized. Further theoretical analysis on Er^{3+} ions in P(MMA-co-GMA) was performed using Judd–Ofelt theory. The results showed that it is a promising material for the elaboration of laser or optical amplifier.

1. Introduction

Erbium-doped waveguide amplifiers (EDWAs) have received increasing attention in the past few years due to the small size and potential applications to integrate with other optical devices. Usually, inorganic host materials, such as glasses and crystals are used to fabricate EDWA [1–3]. Compared to inorganic hosts, polymeric optical waveguide devices have excellent properties: high bandwidth, simple processing, low cost and compatible with silicon substrate. Various techniques such as photobleaching [4,5], ion-implantation [6], direct write electron beam [7–9], and reactive ion beam etching (RIE) [10] have been used to fabricate polymeric channel waveguide. Using RIE technique, we can avoid some destroying processes in other techniques that may degrade the optical activity of the core material [11]. Besides, the RIE is compatible with conventional semiconductor process. Many successful Er-doped polymer active waveguide devices have been demonstrated using RIE [12–14]. So polymer host is a good choice which can also be used to fabricate EDWAs.

In this work, ErFOD-doped P(MMA-co-GMA) polymer film was synthesized. The NIR photoluminescence (PL) spectrum of the material showed strong characteristic emission of Er^{3+} ions with broad full width at half-maximum (FWHM) of 55 nm. P(MMA-co-GMA) polymer was used as the host matrix, because of its good complex solubility, good transparency and resistance to lase damage. ErFOD including C–F bonds was selected as the dopant because of good solubility in many polymers, and fairly long lifetime. The rib channel waveguide using ErFOD-doped P(MMA-co-GMA) was fabricated. The loss and gain measurements of the waveguides were also characterized by fiber coupling. Using Judd–Ofelt theory, many factors, such as absorption cross-section, metastable state lifetime, and spontaneous transition probability which affected the performance of waveguide amplifiers were calculated.

2. Experimental

2.1. Materials and reagents

Tris(6,6,7,7,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) Erbium (ErFOD, 99.99%) was obtained from Sigma–Aldrich (St. Louis, USA). Methyl-methacrylate, 2,2,2-trifluoroethyl methacrylate and glycidyl-methacrylate were purchased from ACROS organics. The solvent toluene and cyclopentanone were dried with anhydrous $MgSO_4$ and redistilled.

2.2. Preparation of P(MMA-co-GMA)

The solution of methyl-methacrylate monomer and glycidyl-methacrylate monomer in toluene was stirred vigorously with 2 wt.‰ AIBN and heated at 70 °C for 24 h under N_2. The resulting solution was cooled to room temperature and dipped into ether. The white precipitate was collected by vacuum filtration. The purified polymer was dried in vacuo.

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2.3. Preparation of P(F-MMA-co-GMA) (poly-2,2,2-trifluoroethyl methacrylate-co-glycidyl-methacrylate)

The preparation is similar with P(MMA-co-GMA), and 2,2,2-trifluoroethyl methacrylate replace methyl-methacrylate. 2,2,2-Trifluoroethyl methacrylate and glycidyl-methacrylate are used for this polymer preparation. The P(F-MMA-co-GMA) was diluted with cyclopentanone, and phthalic anhydride was added as cross-linking agent. The cross-linked polymer is resistant to some common chemical reagents.

2.4. Preparation of doped P(MMA-co-GMA)

The P(MMA-co-GMA) was diluted with cyclopentanone, and phthalic anhydride was added as cross-linking agent. ErFOD were mixed into polymer solution under agitation. The concentration of Er^{3+} ions is 0.5375×10^{20} ions/cm^3. The compound solution can be spin-coated as the core layer. The compound solution is also gradually heated from 70 °C to 120 °C during 10 h. Then a transparent disc was obtained used for the absorption spectrum.

2.5. Waveguide fabrication

For the material system ErFOD-P(MMA-co-GMA), no aggregation occurred after solvents removal bake, so the film was appropriate for the waveguide fabrications. The configuration of channel waveguide was used in the study [15], and structure is shown in Fig. 1.

The substrate was first fabricated using silicon wafer. Prior to use, 2 μm SiO_2 film as buffer layer was deposited on the silicon wafers. The optical amplifier multiplexer was fabricated using spin coating. P(F-MMA-co-GMA) was used as a bottom cladding and P(MMA-co-GMA) films doped ErFOD as a core. It is suitable that the refractive index of the core is 1.483 and the cladding is 1.443 at 1540 nm. Besides, P(MMA-co-GMA) and P(F-MMA-co-GMA) have the similar structure, so they have good adhesion. P(F-MMA-co-GMA) with 5–6 μm thickness is first spin-coated to form the bottom cladding, followed by thermal annealing at 120 °C for 3 h. Then we coated the core material. The complete films were baked at 125 °C to remove the solvent. A waveguide pattern on the core layer was formed by reactive ion etching (RIE) using oxygen. The upper cladding P(F-MMA) (poly-2,2,2-trifluoroethyl methacrylate) with 2 μm thick was finally spin-coated.

2.6. Spectroscopic measurements

Near-infrared (NIR) PL spectrum was recorded at room temperature on a Fluorolog®3-11(Jobin Yvon) instrument using a R5509-72 PMT Detector (Hamamatsu photonics k.k.) and Xe lamp as the excitation source. The thickness and the refractive index of the films were measured using a prism coupler (Metricon, model-2010) which employed the m-lines technique with TE mode at 1540 nm [16].

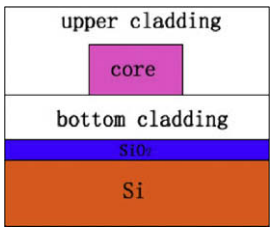

Fig. 1. The doped polymer channel waveguide structures.

3. Results and discussion

3.1. Optical properties of materials

Fig. 2 shows typical PL spectra of P(MMA-co-GMA) polymer film which is about 50 μm in thickness and doped with the ErFOD complex, respectively. The excitation wavelength of 980 nm was used for PL measurements of the doped film. Emission spectrum peaking at 1540 nm is assigned to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ translation of Er^{3+} ions with a band full width at half-maximum of 55 nm. As far as we know, the value is significantly larger than the corresponding one in Er-doped silica (11 nm FWHM), phosphosilicate glass (45 nm FWHM) [17].

With respect to the optical properties of the materials, refractive indices (n) of the P(F-MMA-co-GMA) bottom cladding and of undoped and doped P(MMA-co-GMA) polymers were determined at selected wavelengths using the m-line technique [16], and are tabulated in Table 1. The data indicated that inclusion of the ErFOD within the polymer matrices did not significantly alter the refractive index of the host at the dopant concentrations employed. Because there are some C–F bonds in ErFOD, the refractive indices of the doped polymers are lower than the undoped polymers.

3.2. Judd–Ofelt analysis of ErFOD-doped P(MMA-co-GMA)

Judd–Ofelt theory has been widely used to estimate the radiative properties of the rare earth containing materials because the model provides reasonable values on average [18,19]. Based on the Judd–Ofelt theory [20,21], the transition probabilities, fluorescence branching ratios and radiative lifetime of ErFOD-doped P(MMA-co-GMA) were calculated. Fig. 3 shows the typical absorption spectrum of the transparent disc of ErFOD-doped P(MMA-co-GMA). Five Er^{3+}-ion absorption bands corresponding to the absorptions from the ground state $^4I_{15/2}$ to the excited states $^4I_{11/2}$, $^4I_{9/2}$, $^2F_{9/2}$, $^4H_{11/2}$, $^4F_{7/2}$, respectively, are selected to account for Judd–Ofelt analysis.

The measured absorption line strength S_{meas} for the induced electric dipole transition of each band was determined experimentally from the area under the absorption band and can be expressed (1) [22,23]

$$S_{meas}(J \rightarrow J') = \frac{3ch}{8\pi^3 e^2} \frac{(2J+1)}{N_c} \frac{9n}{(n^2+2)^2} \frac{2.3}{\bar{\lambda} L} \times \int_{J \rightarrow J'} OD(\lambda) d\lambda \qquad (1)$$

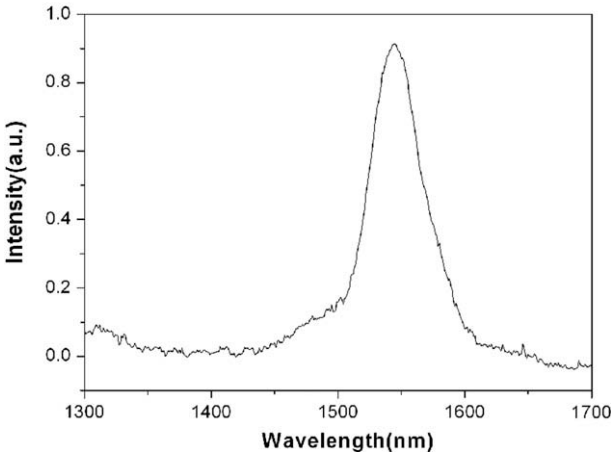

Fig. 2. Photoluminescence spectrum of ~50 μm thick ErFOD complex doped P(MMA-co-GMA) polymer film on glass.