A novel photodefinable polymer containing rare-earth doped nanoparticles for optical amplification

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We report on neodymium doped LaF\textsubscript{3} nanoparticles dispersed in a photo definable polymer. Standard spin coating is used to deposit uniform thin films on a silicon dioxide buffer layer, which can be photocured and developed to produce monomode active optical waveguides. Optical properties of the film are obtained using a prism coupling setup, showing low losses of the photosensitive polymer host material in both the visible and infrared. In addition, the absorption and emission due to the neodymium doped LaF\textsubscript{3} nanoparticles have been determined for a range of particle concentrations.

Introduction

Optical waveguides based on photodefinable polymer materials attract a lot of attention, due to their low cost and ease of processing compared to inorganic waveguides. Functional devices are developed like powersplitters [1] and modulators [2] which demonstrate the wide range of possible applications. The availability of redispersable LaF\textsubscript{3} nanoparticles doped with rare-earth ions [3] offer the potential of optical amplification. The nanoparticles can be made soluble in polymers by adding organic ligands to the particle surface. Shielding of the rare-earth ions by the excellent host prevents quenching of the excited states by the organic matrix and the small size of the nanoparticles prevents scatter losses. We intend to use these benefits, i.e. the direct patterning of a photodefinable polymer and the optical active properties of the rare-earth ion, for the development of low cost optical amplification devices.

Neodymium doped nanoparticles

The choice for neodymium arises from the luminescent properties of the material with wavelength ranges that are of interest regarding telecom applications. Neodymium exhibits intense narrow-band luminescence in the near-infrared region around 880, 1060 and 1330 nm. The luminescent properties arises from transitions within the 4f subshell, which is shielded by the filled 5s and 5p shells. Figure 1, shows the energy levels of neodymium which are indicated by Russell Saunders notation. The electrons can be excited by photon absorption from the \( ^4I_9/2 \) groundstate to the \( ^4G_5/2 \) state. After a fast non-radiative decay to the \( ^4F_{3/2} \) state there are three radiative transitions of interest:
$^{4}F_{3/2} \rightarrow ^{4}I_{13/2}$ transition with emission around 1330 nm

$^{4}F_{3/2} \rightarrow ^{4}I_{11/2}$ transition with emission around 1060 nm

$^{4}F_{3/2} \rightarrow ^{4}I_{9/2}$ transition with emission around 880 nm

The host material in which the neodymium is present plays an important role regarding the lifetime of the excited state. The energy of the excited state can be absorbed by the surroundings in the form of phonon emission. This quenching process is dependent on the availability of high-energy vibrations in the host material. LaF$_3$ crystals are known for their low phonon energy (380 cm$^{-1}$) [4] and are therefore an attractive host for the neodymium. In order to use the LaF$_3$:Nd nanoparticles in an organic environment they have to be soluble in an organic solution. This has been achieved by changing the surface properties of the particles by adding organic groups (ligands) to the surface. For the synthesis and characterization of the nanoparticles see Stouwdam et al. [3]

**Polymer host material for the LaF$_3$:Nd nanoparticles**

Photo definable optical polymer materials, like the SU-8 an epoxy-based negative photoresist from MicroChem, have shown great potential for the application in polymer based optical waveguides. Thin films can easily be spin coated and directly patterned using standard I-line lithography [1]. The simplicity of this process and the wide range of available optical polymer materials makes this technology an attractive low-cost solution for complex planar photonic circuits.

To effectively use the interesting properties of the LaF$_3$:Nd nanoparticles a host polymer which is transparent from the UV/VIS to the near-IR wavelength regions is required. In addition, to avoid scatter losses, the refractive index of the host must be matched to the refractive index of the nanoparticles. Transparency in the UV/VIS is required to define the waveguides by UV-exposure and for efficient excitation of the neodymium. SU-8 shows strong absorption in the VIS region after waveguide definition, which prevents efficient neodymium excitation. Therefore a lot of effort has been put into the development of a suitable photosensitive epoxy polymer. It was found that a material based on the most widely used epoxy monomer, bisphenol-A diglycidyl ether, meets these requirements. Figure 2(a) shows the loss spectrum of the developed material. For comparison the loss spectrum of SU-8 determined by S. Musa [5] is added. Low losses from the UV to VIS wavelength regions are observed. In the near-IR two windows appear, which are conveniently centered around two of the characteristic neodymium emission wavelengths, i.e. 1060 nm and 1330 nm. The loss measurements on the bisphenol-A epoxy are performed using a prism coupling setup [6]. Uniform thin films are spincoated on a silicon wafer with a silic Conrad oxide buffer layer and characterized by recording the transmission spectra of a white light source at several distances between the prisms. The
The refractive index of the host material has been determined using a spectroscopic ellipsometer and was found to be $n_d = 1.59$ which matches the index of the nanoparticles. The nanoparticles are dissolved in the polymer host material for a variety of concentrations and spincoated on a silicon wafer with a 5 $\mu$m silicon dioxide buffer layer. Moving prism coupler measurements clearly indicate the absorption lines of the neodymium, which appear at 520, 580, 740, 795 and 865 nm as can be seen in Figure 2(b). The absorption line around 580 nm is the most promising wavelength at which the neodymium can be efficiently excited. An increase in the UV-absorption tail is observed at higher nanoparticle concentrations, which is caused by impurities in the ligands and can be avoided by using ultra pure starting materials during the ligand synthesization.

**Waveguide fabrication and spontaneous emission measurement**

The processing steps for the newly developed photodefinable polymer doped with various concentrations of the LaF$_3$ nanoparticles as mentioned before are straightforward. A thin layer of the polymer solution is spincoated on a silicon wafer with silicon dioxide buffer layer, followed by a pre-bake step at 95°C for 5 minutes to evaporate the solvents. The coated film is brought in direct contact with a darkfield mask for I-line lithography. After exposure the 1.3 $\mu$m thick film was post-baked for 2 minutes at 95°C. During this heat treatment the crosslinking of the polymer takes place. The exposed film was developed using RER 600 (PGMEA) and rinsed with isopropyl alcohol. A typical SEM-image of the fabricated waveguide is shown in Figure 3. The neodymium has shown good absorption characteristics around 580 nm. Therefore a Rhodamine-6G dye laser, tunable around this wavelength is used to excite the neodymium for experiments on spontaneous emission. The emission spectra for LaF$_3$:Nd in a thin film are very similar to the spectra measured from pure nanoparticles as measured by Stouwdam et al. [3].

![Figure 2: Loss spectra of the host polymer for the nanoparticles compared to SU-8 (a) and loss spectrum of the host polymer with various nanoparticle concentrations (b) (a)](image)

![Figure 3: SEM picture of a waveguide fabricated using the low loss photodefinable polymer.](image)
Figure 4: Spontaneous emission from a polymer waveguide dispersed with 10 wt.% LaF$_3$:Nd nanoparticles. (a) emission around 880 nm. Resolution bandwidth 1 nm, measured using a PMT-detector. (b) emission around 1060 nm and 1330 nm. Resolution bandwidth 10 nm, measured using a InGaAs.

**Conclusion**

The properties of a novel photodefinable polymer are discussed. The photosensitive epoxy polymer exhibits low losses over a broad wavelength region, which makes the polymer an attractive host for the LaF$_3$:Nd nanoparticles. Absorption of light due to the nanoparticles reveal the excitation wavelengths of the neodymium in the VIS wavelength region. According to the absorption spectra the excitation of neodymium is most effective at 580 nm. The straightforward processing steps of waveguide fabrication using this photodefinable polymer are explained and a fabricated straight waveguide is used to measure the spontaneous emission. For the near-future we plan pump-probe experiments to determine the small signal gain of this compound material.

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**References**


