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Upconversion luminescence particles based on $NaYF_4$ matched with passive optical devices

I. M. Asharchuk [1]✉, N. A. Vovk [2], V. I. Sokolov [2],
I. O. Goryachuk [2], N. V. Minaev [2], M. A. Tarkhov [1]

[1] Institute of Nanotechnologies of Microelectronics of the RAS, Moscow, Russia;

[2] Federal Scientific Research Center "Crystallography and Photonics" RAS, Moscow, Russia

✉ ilyaasharchuk@gmail.com

Abstract. The work is aimed at creating matching passive elements with optical planar devices. A three-dimensional structure-interface was made to match the position of the center of the optical fiber with active optical elements. $NaYF_4$ microparticles doped with rare-earth ions Yb^{3+}, Tm^{3+}, Er^{3+} with a diameter of 2.2 μm and 1.65 um were synthesized. The formation of hemispherical lenses with radii from 0.75 to 25 um has been demonstrated for optical matching with optical fiber by IR (infrared) photopolymerization.

Keywords: upconversion, two-photon polymerysation, rare-earths

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Апконверсионные люминесцентные частицы на основе $NaYF_4$ совмещенные с пассивными оптическими устройствами

И. М. Ашарчук [1]✉, Н. А. Вовк [2], В. И. Соколов [2],
И. О. Горячук [2], Н. В. Минаев [2], М. А. Тархов [1]

[1] Институт нанотехнологий микроэлектроники РАН, Москва, Россия;

[2] Федеральный научно-исследовательский центр «Кристаллография и фотоника» РАН, Москва, Россия

✉ ilyaasharchuk@gmail.com

Аннотация. Работа направлена на создание согласования пассивных элементов с оптическими планарными устройствами. Создана трехмерная структура-интерфейс для согласования положения центра оптоволокна с активными оптическими элементами. Синтезированы микрочастицы $NaYF_4$, легированные редкоземельными ионами Yb^{3+}, Tm^{3+}, Er^{3+}, диаметром 2.2 мкм и 1.65 мкм. Было продемонстрировано формирование полусферических линз радиусом от 0.75 до 25 мкм при оптическом согласовании с оптическим волокном путем ИК (инфракрасной) фотополимеризации. Продемонстрирована зависимость сигнала от позиции ввода в согласующий элемент.

Ключевые слова: апконверсия, двухфотонная полимеризация, редкоземельные элементы

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Introduction

Today, the directions for creating single-photon radiation sources necessary for quantum computing, quantum cryptography, etc. are relevant [1]. However, an equally important problem is the manufacture of matching elements for detecting and delivering radiation to single-photon sources and detectors, respectively [2]. Upconversion nanoparticles (UCNPs) doped with Er^{3+}, Tm^{3+}, Yb^{3+} lanthanides can serve as single-photon emitters; they have anti-Stokes emission, manifested by the generation of high-energy photons through multiphoton absorption of low-energy photons [1]. Compared to traditional phosphors such as fluorescent dyes and quantum dots, UCNPs are resistant to photobleaching, they are photostable and have real intermediate energy levels [3–5]. Such features of UCNPs with matching technology become attractive for the development of single-photon radiation sources necessary for quantum computing.

Materials and techniques

To obtain fluoride microcrystals of the composition $NaY_{0.78}F_4$: $Yb_{0.2}$, $Er_{0.02}$, $NaY_{0.78}F_4$: $Yb_{0.2}$, $Tm_{0.006}$ with a hexagonal crystal lattice (β-form), commercial reagents were used: oxides of yttrium, ytterbium, erbium, sodium carbonate , oleic acid 90%, 1-octadecene 90% (Sigma-Aldrich), and trifluoroacetic acid 99% (PanReac). Synthesis was carried out by thermal decomposition of trifluoroacetates of rare earth elements and sodium in an oxygen-free environment in a mixture of oleic acid and 1-octadecene. To determine the phase of the crystals, X-ray diffraction analysis (XRD - X-Ray Diffractometry) was used. The electron microscopy (SEM) method was used to analyze the shape and size of the particles. To form polymer microlenses, we used an original approach, NIR photopolymerization [6] based on lanthanide-doped upconversion microparticles (UCMPs) $NaYF_4$:Yb, Tm. UCMPs convert NIR light into ultraviolet (UV) or visible (VIS) light, which in turn triggers the photopolymerization reaction in Dental Clear photopolymer (HARZLabs, Russia). The microparticles were deposited on the substrate by centrifugation at a speed of 1800 min-1 for 30 s. For the photopolymerization process, a continuous laser with a wavelength of 975 nm (PL980P330J, Thorlabs) and an incident power of 50 mW was used. The radiation was focused using an Olympus UPlanSApo 60x/1.2 NA objective. W.

We used a setup [7], based on a submicron three-dimensional positioning system ABL1000 (Aerotech, USA) air-bearing direct-drive linear stage and high-speed galvano-scanner 'HurrySCAN II 14' (ScanLab). The second harmonic of the TEMA-100 femtosecond laser (Avesta-Proekt, Russia), with $\lambda = 525$ nm, 70 MHz, 200 fs and power up to 200 mW, was used as the light source. An acousto-optic modulator at operational frequencies up to 1 MHz was used as the optical shutter. The NFOL process was used to create the microadapter. Polymethyl methacrylate (PMMA) 495K A2 is used as a spin-coated resistive material. The typical average power of femtosecond laser radiation for the implementation of the NFOL process on PMMA with a thickness of 800 microns was 18–22 mW [8]. Determination of the morphology of microlenses with a radius of 1.55 um was carried out using atomic force microscopy in the contact mode of the probe.

For hollows formation were applied are next technological procesess. The first step of creating a pattern of was formed in the photoresist (AZ4999) using a laser lithograph, followed by development in a 0.7% KOH solution. When applying the photoresist, the thermal oxide plate was processed in GMDS to improve the adhesion characteristics. The thickness of the photoresist was 600 nm. Next, the thermal oxide was etched through the formed mask by plasma-chemical etching in C_4F_8 gas. To further fill the hollows formed in thermal silicon oxide, an aqueous suspension of $NaYF_4$: Yb^{3+}, Tm^{3+} particles and hexane was formed. The weight ratio of particles to hexane

was 1:10,000 times, respectively. The next step was to place a 4” mm plate with formed hollows into the suspension and keep it there for several hours. Due to the natural settling of particles on the surface, a uniform layer was formed, the technology is similar to the deposition of carbon nanotubes [8]. Part of the $NaYF_4$: Yb^{3+}, Tm^{3+} particles also fell into pre-prepared wells. The final technological step in the formation of the final structure was the removal of “extra” particles by the method of hydrodynamic cleaning under the action of a high-pressure water jet. Particles that got into the hollows due to surface forces are kept in them, and the rest of the particles are removed.

To determine the response when combining the fiber through a microoptical adapter, an installation was assembled where the signal from the detector arrived at a UCMPs located on planar detector. The input signal at a wavelength of 975 nm with a power of 500 uW was fed through a fiber to fiber U-bench system (Thorlabs) for a single-mode fiber with a core of 7 um and a core diameter of 125 um. A chopper was inserted into the fiber to fiber U-bench system to modulate the signal at a frequency of 7 Hz. The electrical signal from the detector was sent to the lock-in amplifier. Alignment before insertion of a single-mode fiber was performed using a 3-axis micrometric shift.

Results and discussion

As a demonstration, the process of supplying an optical fiber to a hemispherical microlens made by IR photopolymerization was implemented. The principle of formation of microlenses is shown in Fig. 1 (I, II-*a*), UCMPs are re-emit absorbed quanta from a wavelength of 975 nm to the visible and UV wavelengths (345.360, 450.475, 645 nm), and the photoinitiator dissolved in the monomer has an absorption spectrum in the short wavelength range (Fig. 1(I), blue line). This starts the IR photopolymerization reaction. Microstructures in the form of microlenses were formed on a cover glass substrate. By varying the exposure time, several sizes of microlenses of different diameters were obtained (Fig. 1(II-*c*)). At an exposure of 30 s under the action of laser radiation with a wavelength of 975 nm, the diameter of the hemispherical microlenses was ~ 50 μm. Since spincoating was used at the initial stage in the deposition of UCMPs, their ordered distribution over the substrate was not achieved. A deterministic particle arrangement process has been proposed and described in Materials and Methods above. Next, a microadapter was fabricated over the formed microlenses with UCMPs (Fig. 1(III)). Figure 1 (II-*b*) shows an electron photograph of the synthesized particles. Synthesized microparticles with a hexagonal crystal lattice and low dispersion of diameter $d = 1.65 \pm 0.1$ and 2.2 ± 0.13 um for $NaYF_4$:$Yb^{3+}Er^{3+}$ and $NaYF_4$:Yb^{3+}, Tm^{3+}, respectively. Hemispherical microlenses with radii from 0.75 to 25 um were obtained.

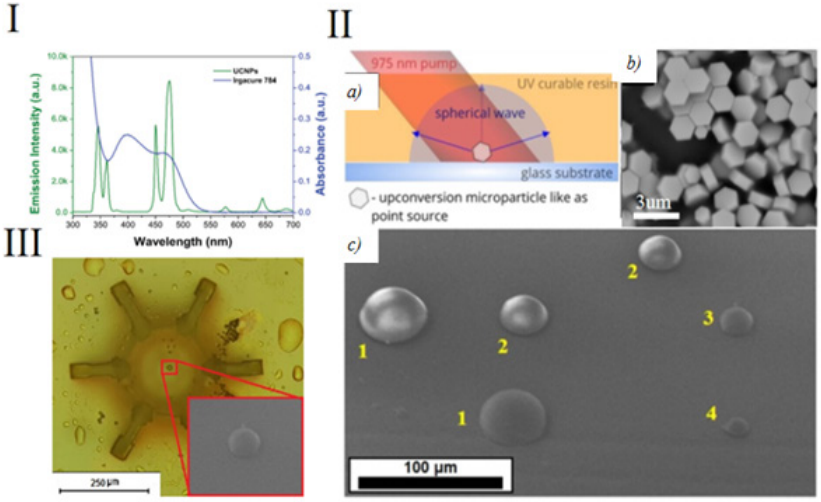

Fig. 1. I Luminescence spectra of an upconversion $NaYF_4$ microparticle: Yb^{3+}, Tm^{3+} (green curve) and absorption spectra of the Irgacure 784 photoinitiator (blue curve). II (*a*) schematic representation of the principle of IR photopolymerization, (*b*) SEM image $NaYF_4$: Yb^{3+}, Tm^{3+} particles, (*c*) SEM photograph of hemispherical microlenses formed by IR photopolymerization with different exposure times by 975 nm radiation pump power 50 mW (1) 30 s (2) 20 s (3) 10 s (4) 5 s III Three-dimensional structure of the optical fiber interface formed above the microlens, top view

It can be seen that the passive optical device, consisting of a microparticle and a particle formed on top of it, is located in the center of the microadapter. The Fig. 2, *a* shows a schematic representation of signal acquisition from a microparticle located above a planar detector. Point -350 is taken as the position when the fiber is near the front plane of the adapter. Point 0 was determined by the position of the fiber close to the microparticle.

The Fig. 2, *b* shows the dependence of the detector signal on the position of the injected fiber. It can be seen that as the fiber approaches the detector, the signal level increases and, reaching a certain level, does not change – it reaches a plateau. This happens at around – 150 microns. The relative plateau level is 1.4 micro volts.

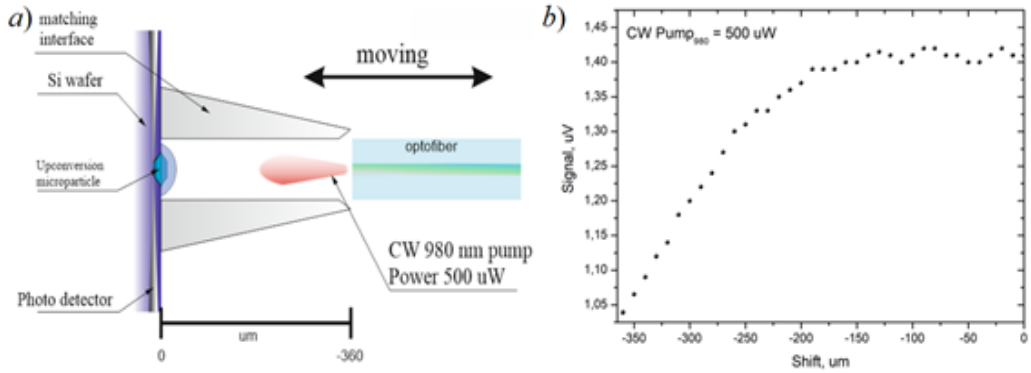

Fig. 2. Scheme describing the process of introducing an optical fiber into the optofiber matching interface (*a*); dependence of the signal from the photodetector on the depth of fiber insertion (*b*)

Fluctuations in the signal from the detector are visible. The authors hypothesized that these fluctuations are related to the temperature instability of the detector associated with its heating. Since the calculated intensity at the output of a fiber with a thickness of 7 microns and a radiation power of 500 microwatts is 1.2 kW/cm^2. However, further experiments are expected to confirm or refute this hypothesis.

Conclusion

The hemispherical microlenses formed by IR photopolymerization with different exposure times by 975 nm radiation pump power 50 mW , minimal microlensese diameter were reached 1.5 um. The developed technological approach to the creation of a microoptical holder for standard single-mode and multimode fibers is demonstrated. This type of holder can be used to manufacture an optical matching unit for optical fibers with sensitive optical elements. Which allows you to combine the position of the center of the optical fiber with active optical elements. The resulting interface unit can be used in planar integrated optical microdevices.

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THE AUTHORS

ASHARCHUK Ilya M.
ilyaasharchuk@gmail.com
ORCID: 0000-0001-6445-0009

VOVK Nikolay A.
vovkolg2011@gmail.com

SOKOLOV Viktor I.
visokol@rambler.ru

GORYACHUK Ivan O.
ivolgor@yandex.ru

MINAEV Nikita V.
minaevn@gmail.com

TARKHOV Michael A.
tmafuz@mail.ru

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