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Development of technological methods for fabrication high-density luminescent structures based on up-conversion $NaYF_4:Yb^{3+}$, Er^{3+} particles

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Abstract. In this paper, we present a technological method for creating high-density luminescent structures based on up-conversion $NaYF_4:Yb^{3+}$, Er^{3+} particles and experimentally demonstrate the possibility of their creation. This technology is applicable for large-scale fabrication of patterned media with a level of filling with microparticles of more than 96% for the fabrication of planar structures applicable in photonics and optoelectronics.

Keywords: up-conversion, luminescence, microparticles

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Материалы конференции
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Разработка технологических методов для создания высокоплотных люминесцентных структур на основе ап-конверсионных $NaYF_4:Yb^{3+}$, Er^{3+} частиц

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Аннотация. В данной работе представлен технологический метод создания высокоплотных люминесцентных структур на основе ап-конверсионных $NaYF_4:Yb^{3+}$, Er^{3+} частиц и экспериментально продемонстрирована возможность их создания. Данная технология применима для крупномасштабного изготовления патернированных сред с уровнем заполнения микрочастицами более 96% для изготовления планарных структур, применимых в фотонике и оптоэлектронике.

Ключевые слова: апконверсия, люминесценция, микрочастицы

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Introduction

Up-conversion nanoparticles doped with lanthanides are capable of converting excitation in the near infrared region into visible and ultraviolet radiation [1]. Their unique optical properties are a promising class of materials for a wide range of applications such as fluorescence microscopy, deep tissue bioimaging, nanomedicine, optogenetics, security labeling, and volumetric imaging. When microparticles are pumped with IR radiation at a wavelength of 980 nm, a pixel for a display can be obtained, the luminescence wavelength of which will depend on the chemical element with which $NaYF_4$ particles are doped [2]. In this work, methods have been developed that make it possible to deterministically place $NaYF_4:Yb^{3+}$, Er^{3+} microparticles in a patterned environment matrix with a high filling density. The small dispersion of microparticles by size allows filling the patterned environment with a high fill rate of > 96%.

Experimental technique

The method of forming high-density luminescent structures is based on the principle of filling with $NaYF_4:Yb^{3+}$, Er^{3+} particles pre-prepared arrays of holes on arbitrary substrates. To demonstrate the possibilities of creating luminescent structures, silicon wafers with thermal oxide 100 mm in diameter were chosen as substrates. At the first stage of creating a high-density luminescent structure, a pattern of the patterned environment was formed in the AZ4999 photoresist using a Heidelberg DWL 2000 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 during the process of applying the photoresist by spin coating. 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 wells formed in thermal silicon oxide, an aqueous suspension of $NaYF_4:Yb^{3+}$, Er^{3+} particles and hexane was formed. The weight ratio of particles to hexane was 1:10,000 times, respectively. The next step in the formation of a high-density luminescent structure was to place a 100 mm plate with holes formed in thermal oxide into the suspension and keep it there for several hours (Fig. 1). 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 [3]. Part of the $NaYF_4:Yb^{3+}$, Er^{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 holes due to surface forces were kept in them, and the rest of the particles are removed.

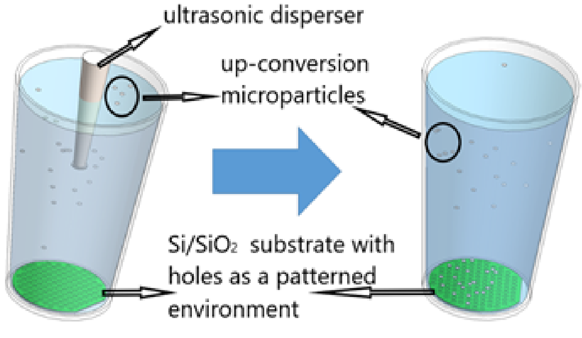

Fig. 1. Method of particle deposition in suspension by gravity on a 100 mm Si/SiO_2 substrate

To demonstrate the effect of luminescence of the structures, we used an installation consisting of a 20X magnification objective with a focal length of 20 mm. For quasi-dimensional luminescence of the obtained structures, the pump radiation was focused into the rear focal plane of the lens. A CMOS camera was used to detect particle radiation. To cut off the pump radiation, a filter was used to cut off the pump radiation at 980 nm 50 mW, which passes the radiation of up-conversion microparticles.

Results and Discussion

In the work, up-converting particles with a narrow size distribution were used (Fig. 2). It can be seen from the figure that the average particle size is 1.65 μm. The average deviation from the diameter is ± 0.1 nm. At instet shown SEM image of up-conversion microparticle. It have hexagonal form. Heigh microparticle is about 1 um.

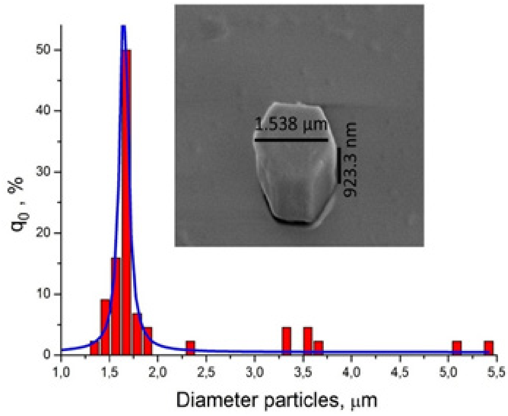

Fig. 2. Size distribution of $NaYF_4$:Yb^{3+}-Er^{3+} up-conversion particles

Fig. 3, *c* shows the photoluminescence map of $NaYF_4$:Yb^{3+}, Er^{3+} up-conversion microparticles in pre-prepared well arrays. The up-conversion luminescence was excited by a CW (continuous wave) laser with a wavelength of 980 nm power of ~ 50 mW. The number of particles that fell into the wells was also determined, depending on the diameters of the wells. The paper also shows that the method using plasma-chemical etching of thermal oxide as the creation of high-density luminescent structures has a significantly higher filling index with microparticles than the method using a photoresist mask with holes as a patterned environment. Our studies have shown that the filling density is at least 96% (Fig. 3, *a*).

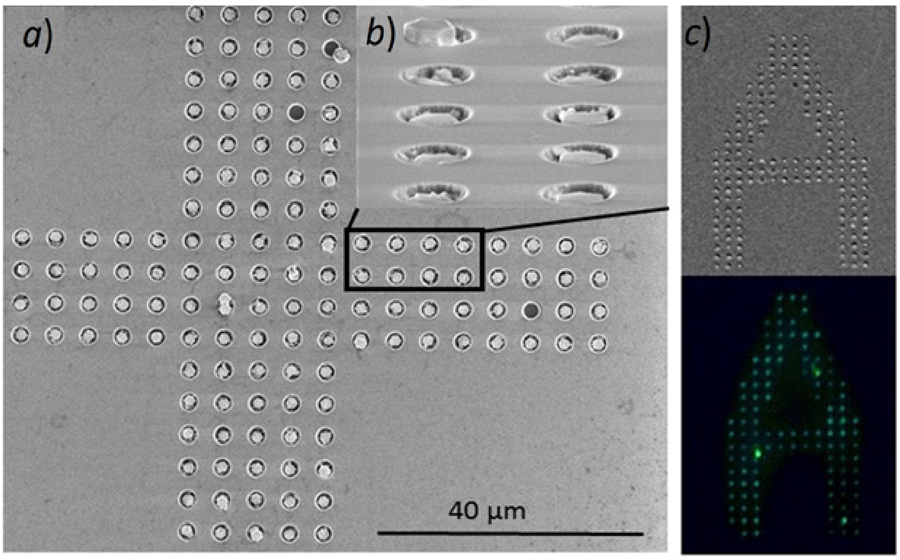

Fig. 3. Demonstration by scanning electron microscopy of the entry of microparticles into the patterned environment (*a*); magnified view of (*a*) the surface of the patterned environment at an angle (*b*); photoluminescence of up-conversion microparticles based on $NaYF_4$:Yb^{3+}, Er^{3+} at a laser wavelength of 980 nm (*c*)

The technique of creating an array of depressions by plasma-chemical etching allows to control the depth of particles in the hole, which is necessary for the creation of photonic integrated circuits. Fig. 3, *b* demonstrates that single particles do not escape from the upper plane of the SiO_2, except when two particles stick together.

Conclusion

The technology of particle deposition by suspension deposition into patterned media produced by plasma-chemical etching is a universal technology for deposition of particles of different sizes and geometries. This allows for scalable technology and the possibility of deterministic placement of different particles over a large area. Such possibilities are an advantage over technologies using a polymer as a layer for recesses [4], using probes of an atomic force microscope to create a patterned environment [5], or particle transfer technology using optical tweezers [6].

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