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Original article

Single-step lithography-free fabrication of nanoscale broadband radiation sources

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ABSTRACT In this paper, we present a one-stage method for fabricating hybrid metal-dielectric nanostructures without the use of complex and expensive lithographic processes. The formation of arrays of nanoparticles occurs in the process of irradiation of a two-layer gold-silicon film with simultaneous mixing of materials. In this work, the internal structure of the obtained nanoparticles was studied using the methods of transmission scanning electron microscopy and energy-dispersive X-ray spectroscopy, and their broadband photoluminescence in the range of 450 – 900 nm was also demonstrated. These structures are promising as a source of radiation for optical measurements in lab-on-a-chip devices, which was shown by measuring the transmission spectrum of the Rhodamine B dye as an example.

KEYWORDS hybrid nanoparticles, broadband photoluminescence, laser-induced nanoparticles, dewetting, bilayer gold-silicon films

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1. Introduction

Hybrid nanostructures consisting of semiconductor materials with a high refractive index and low optical losses and noble metals, in which there are resonant oscillations of free electron plasma, have been actively studied in recent years for various applications in such areas as sensorics, optoelectronics, and nanophotonics [1–5].

Lab-on-a-chip devices [6] are currently being used to diagnose, monitor, and treat chronic diseases that require economically relevant and clinically accurate measurement of various biomarkers, such as IFN-γ-induced protein 10 (IP-10) for the diagnosis of rheumatoid arthritis, serum antibodies for the diagnosis of kidney disease, serum glucose concentrations for the diagnosis and monitoring of diabetes mellitus (type I and II). Currently, such measurements are carried out using enzyme immunoassay, chromatography, mass spectrometry, gel electrophoresis and polymerase chain reaction [8–10]. The disadvantages of such approaches are: a long time for the study, the need to transport the patient to the biomaterial collection point, the high cost of the study, and the need for special skills to conduct the study. The main advantages of lab-on-a-chip technology over traditional analytical detection methods include: lower liquid consumption, which reduces the cost of reagents and sample volume for analysis, faster analysis time due to better controlled liquid transfer and high surface to volume, more compact implementation and higher performance. However, to carry out efficient optical measurements in such devices, a miniature radiation source with characteristic dimensions less than 1 μm and emitting in the visible spectral range is required.

The creation of such a source based on silicon, due to its high compatibility with existing microelectronics technologies, is limited by the indirect gap structure of the material, which does not allow obtaining a quantum yield of emitters above 10^{-4} [11]. Nanoscale sources of gold or silver nanoparticles (NPs) also do not have high efficiency due to heating losses [12].

Obtaining emitters with high efficiency has become possible through the use of hybrid materials consisting of a mixture of gold and silicon. Silicon inclusions in metal structures lead to an increase in the spontaneous emission of a quantum system, which increases the efficiency of nanoscale light sources [13]. In particular, it has recently been demonstrated that optically resonant Au@Si hybrid nanostructures can be used as efficient nanoscale sources of white light and higher harmonics [2, 14, 15], as well as optical nanoantennas, which make it possible to enhance the photoluminescence (PL) of attached quantum emitters due to the Purcell effect [16, 17].

The fabrication of such nanoparticles (NPs) can be implemented using the methods of electron beam lithography [18], the formation of eutectic alloys [19,20], as well as laser printing methods [14,21], due to ablation in various media [22,23], irradiation of suspended particles in a liquid or combined methods, including an additional stage of chemical reduction using $HAuCl_4$ solution [4].

However, the methods listed above either have a high cost and labor intensiveness, or do not allow control over the size and location of the obtained NPs. In this paper, we present a method for fabricating metal-dielectric nanostructures, study their optical and material properties, and demonstrate the possibility of their use as a microsized emitter with an operating range of 450 – 900 nm.

2. Materials and methods

2.1. Fabrication of hybrid structures

For the fabrication of hybrid structures, two-layer films are used. The production of the film take place in two stages: a silicon layer of 100 nm thickness are deposited on a glass substrate by chemical vapor deposition, then 10 nm gold layer is deposited over the silicon by magnetron sputtering.

To form structures, the film surface was scanned by a laser beam with a wavelength of (790$\pm$5) nm, a pulse duration of 100 fs, and a pulse repetition rate of 80 MHz from the silicon side along a circular path with a radius of 1.3 μm. As a result, a hybrid structure is formed in the center of the irradiated region. The optimal regime for fabrication of ordered arrays was determined during preliminary experiments [15], and corresponds to a scanning speed of 30 mm/s and a laser fluence of 160 mJ/cm^2 for a two-layer Au (10 nm)/Si (100 nm) film, placed on a glass substrate.

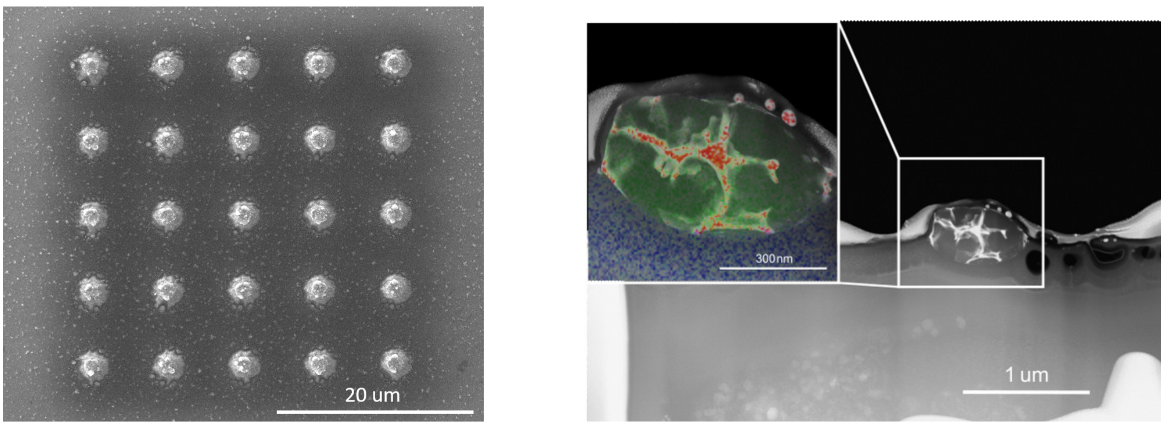
2.2. Characterization of obtained structures

The fabricated structures are characterized using scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), and energy dispersive X-ray spectroscopy (EDS). SEM images are obtained using an Inspect microscope (FEI Company, USA) in the secondary electron recording mode with an accelerating voltage of 20 kV. STEM and EDS studies are carried out on a Libra200FE microscope (Zeiss, Germany) with an accelerating voltage of 200 kV. To study and analyze the resulting hybrid structures using STEM, lamellae is fabricated using a focused ion beam of gallium ions using a Zeiss Auriga Laser dual-beam workstation.

The optical properties of hybrid nanoparticles are also studied by photoluminescent spectroscopy. To excite and record optical responses, we use an experimental setup including a TEMA-150 femtosecond ytterbium laser (Avesta, Russia) and a Horiba LabRAM HR confocal spectrometer with a CCD detector DU 420A-OE 325 (Andor, Great Britain). Thorlabs optical filters are inserted in the optical path of the measuring setup to separate laser radiation from radiation of pump diode (FELH1000) and to block residual laser radiation before the detector (FESH1000). The radiation is focused and the signal was collected using a Mitutoyo NIR M Plan Apo M 50x objective, NA = 0.65.

3. Results and discussion

Figure 1a shows an ordered array of spherical NPs with a characteristic size of about 1 μm. The results of the analysis of the elemental composition in Fig.1b show that silicon spheroids coated with a gold network and smaller gold NPs with diameters of about 20 – 40 nm appear during fabrication.



(a) (b)

FIG. 1. (a) – SEM image of the array of obtained NPs. (b) – STEM image of a NP cross section; the inset shows a map of the elemental composition of a hybrid NP: red areas correspond to gold, green areas to silicon, blue areas to oxygen, and light gray areas to platinum and gold. Dark cavities in the near-surface region are voids.

The appearance of such hybrid structures presumably occurs when a thin film breaks up into particles as a result of heating in an oven or local exposure to laser radiation [24] with simultaneous mixing of gold and silicon Fig. 1b. Previously, silicon [26] and gold [25] nanoparticles were obtained by this method.

Figure 2 shows the photoluminescence spectrum of a single particle, showing the photoluminescence (PL) in the range from 450 to 900 nm, as well as the spectrum of the original film for comparison. To determine the PL mechanism, we plot the dependence of the PL intensity on the pump fluence (inset in Fig. 2 on a log-log scale. From the slope of the line, one can say that PL occurs as a result of two-photon absorption. Amplification of radiation in hybrid nanostructures consisting of silicon bound to the plasmonic part mainly occurs due to multiphoton absorption in the silicon part, while "hot" charge carriers generated in gold located on the surface of the silicon spheroid can be injected into silicon due to the tunneling effect, providing an increase in the efficiency of PL [27].

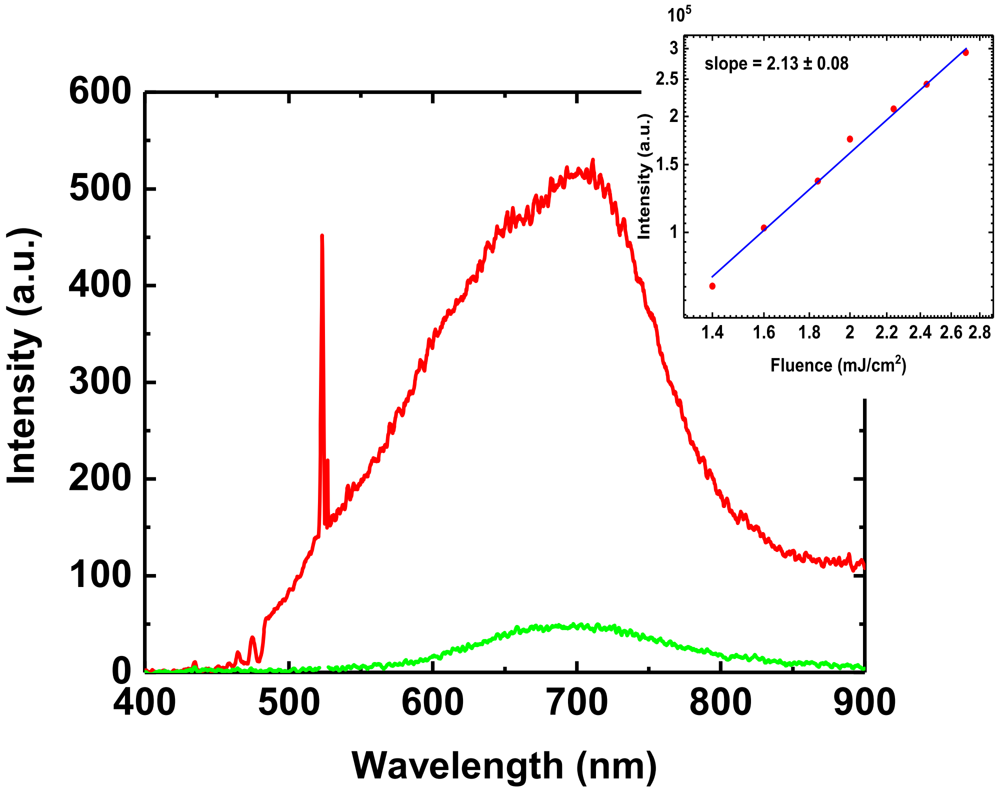


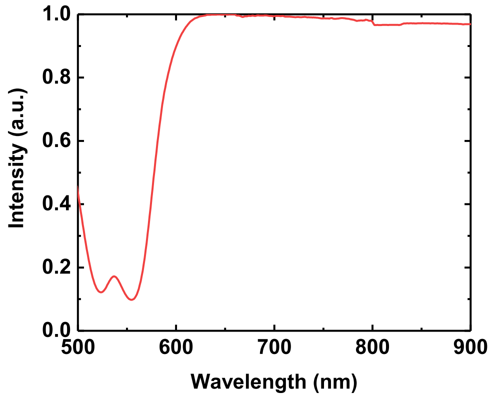
FIG. 2. PL spectra of the hybrid particle (red) and the original film (green). The inset shows the dependence of the broadband PL intensity on the pump fluence.

To demonstrate the possibility of using hybrid particles as a source of broadband radiation, the transmission spectrum of the Rhodamine B dye is measured. In the first case, a compact stabilized halogen light source with a fiber output (Avantes AvaLight-HAL-S-Mini) is used as a radiation source (Fig. 3a), and in the second, the PL emission of the hybrid particle (Fig. 3b). The radiation from the source passed through the cell with the dye and then was detected by the spectrometer.

As can be seen from Figure 3, the obtained transmission spectra are in good agreement, which proves the applicability of hybrid microstructures in the implementation of a nanospectrometer.

4. Conclusion

In this work, using femtosecond laser radiation, we experimentally demonstrate the creation of hybrid metal-dielectric nanostructures without the use of complex and expensive nanolithography methods. The formation of arrays of nanoparticles occurs in the process of irradiation of a two-layer gold-silicon film along a circular trajectory. Using the methods of transmission scanning electron microscopy and energy-dispersive X-ray spectroscopy, the internal structure of the obtained nanoparticles was studied. The obtained nanostructures consist of a mixture of gold and silicon and exhibit broadband photoluminescence in the range of 450 – 900 nm. It is also shown, using the example of measuring the transmission spectrum of the Rhodamine B dye, that such a structure can act as a radiation source for optical measurements in lab-on-a-chip devices.



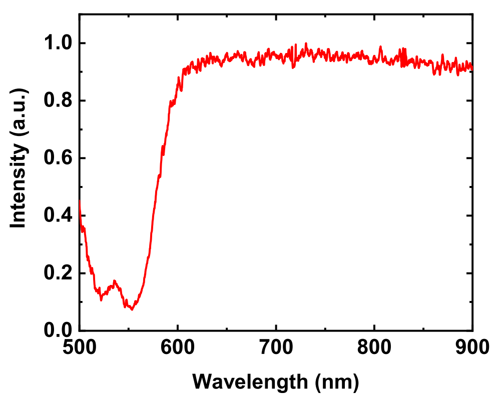


FIG. 3. Transmission spectra of the Rhodamine B dye obtained using a halogen lamp (a) and a hybrid particle (b)

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