

Nanopatterning of silica with mask-assisted ion implantation

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ABSTRACT

In the present paper we combined ion implantation and nanosphere lithography to regularly dope, by a mask-assisted process, a SiO₂ substrate with rare earth ions (Er) by ion implantation and to fabricate by sputtering a plasmonic 2D periodic array of Au nanostructures on the silica surface spatially coupled to the implanted Er³⁺ ions. The aim of this work is to study how Er³⁺ emission at 1.5 μm can be affected by the interaction with a plasmonic nanostructure. In particular we have found a variation of the radiative lifetime of the Er³⁺ emission and a change from single exponential to bi-exponential of the luminescence intensity decay.

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1. Introduction

Mask-assisted ion beam processing of insulating substrates is a versatile tool for achieving nanopatterning of a material through the formation of ordered nanostructures. The possibility of producing self-assembled monolayers of silica or polystyrene nanospheres (NSs) with size in the 100–1000 nm range on the substrate to be patterned can be considered a much simpler and cheaper alternative to conventional lithographic techniques for the synthesis of 2D ordered arrays of nanostructures, exploiting the so-called NanoSphere Lithography (NSL) [1,2]. Indeed after the nanosphere mask deposition, ion implantation can be used to selectively modify the substrate through the triangular holes left among adjacent NSs, providing that these are thick enough to stop incoming ions before reaching the substrate. The exposed area amounts to about 10% of the original surface and its honeycomb-like periodical structure can be scaled continuously by simply changing the NS size.

In this work we used ion implantation through self-assembled NS mask to directly and regularly dope the subsurface layer of a silica substrate with rare earth ions (Er) and to couple these ions with metallic nanostructures deposited by sputtering within the holes of the NS mask to form a plasmonic 2D nano-array, whose optical properties can be tuned by controlling the NS size.

2. Experimental

A colloidal monolayer (ML) of polystyrene (PS) spheres was made by self assembly according to the method proposed by Gierzig et al. [3]. This preparation has many advantages with respect to

other methods like spin-coating or solvent evaporation: spin-coating is a relatively fast technique but it's quite difficult to obtain monolayers without defects. On the other hand solvent evaporation methods give better results but at the expenses of a much longer processing time.

The monolayers in the present work were prepared using commercial PS nanospheres with nominal diameter of 330 and 722 nm: they were purchased from Microparticles GmbH (Germany) as 10% vol water solutions. Their size has been checked by Transmission electron microscopy: a standard deviation in size of about 5% was found.

The substrates used were HSQ300 fused silica glass slides (from Heraeus). All substrates were cleaned with acetone in ultrasonic bath for 1 min and then in a "Piranha" solution (a 3:1 mixture of concentrated sulfuric acid with 30% hydrogen peroxide) for half an hour, rinsed with deionised water and dried in a stream of nitrogen.

According to our method the 10% vol water dispersion of nanospheres was diluted adding an equal volume of isopropanol, a drop (30 μL) of this solution was distributed over a substrate (typically a 2.5 × 2.5 cm² silica slide) and then this was slowly immersed in a doubly deionized water bath. At the meniscus between water and the solution the nanoparticles assembled together by capillary forces, making a 2D colloidal crystal floating at the water surface. We then collected the self assembled monolayer by lifting it off from the water surface with the silica slide. This self assembly method is very flexible allowing the deposition of the monolayer over any kind of substrate, even non hydrophilic ones. Double-layer masks can be also produced by immersing the dry, monolayer-covered substrates, into water and depositing a second layer.

The samples were then implanted with Er⁺ ions with a 200 kV high-current implanter (Danfysik 1090) at the Ion Implantation Laboratory (LNL, Legnaro, Italy). Two sequential implantations

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were made at two different energies, 50 and 100 keV, with a total fluence of 1.5×10^{15} at/cm². The ion flux was maintained at 0.1 μ A/cm². The projected range (R_p) of the two implantations was 30 and 45 nm, respectively. Erbium ions are stopped by the PS nanospheres (e.g., SRIM simulations show that the R_p in the PS is 78 nm for the 100 keV Er⁺) and penetrate into the substrate only through the holes in the monolayer, producing a selective doping the silica substrate with a honeycomb P_{6mm} pattern.

After ion implantation, the samples underwent a further processing using the same mask to fabricate a gold nanostructure to be coupled with the implanted erbium. Gold atoms were deposited over the masks by dc-magnetron sputtering at about 5×10^{-3} mbar Ar pressure with 20 W power for 270 s: the average thickness of the resulting Au nanodots is about 10 nm, as measured by atomic force microscopy. The expected size [1] of the resulting nanotriangles (defined as their perpendicular bisector) is about 80 and 170 nm, for the 330 nm and the 722 nm PS nanospheres respectively, whereas the corresponding center-to-center nanotriangles distance is 190 and 450 nm, respectively. Table 1 summarizes the synthesis conditions and the geometrical characteristics of the samples analyzed in the present paper.

To remove the mask, the samples were then immersed in a 50:50 solution of Toluene and THF (purchased from Sigma Aldrich) for 2 min and then sonicated for 30 s to dissolve the PS nanospheres and remove them from the substrate, leaving only the gold nanostructures. A thermal treatment at 600 °C in air for one hour was done to recover the implantation damage and to activate the Er³⁺ ions.

The photoluminescence (PL) spectra of Erbium were measured by using the 488 nm wavelength of an argon laser as excitation, focusing the beam over the sample and collecting the emission in a 45° geometry with 2 lenses and with a R5509 NIR phototube cooled at 80 K with liquid nitrogen.

3. Results and discussion

Fig. 1 shows a SEM image of a typical self-assembled mask on silica made with 722 nm PS spheres. The monolayer has a good quality in term of long range order (as can be seen in the Fourier transform in the inset) and has only a small quantity of structural defects (mainly point defects like nanosphere vacancies).

After the implantation step we observed a partial coalescence of the PS spheres, as can be seen in the AFM images of Fig. 2, induced by the implantation mixing. This promotes a progressive fluence-dependent reduction of the pore size and therefore also of the size of the nanostructures made by metal sputtering through the mask. Fig. 3a shows an AFM 3D image of the triangular nanodots made by sputtering gold through a 722 nm PS colloidal monolayer. A well ordered array of quasi-triangular dots, reproducing the pores pattern of the PS mask, is found. The metallic nanotriangles have a side of about 300 nm and a maximum height of about 10 nm.

These gold nanodots exhibit peculiar plasmonic properties: their surface plasmon resonance (SPR) peak is red-shifted to the near infrared region of the spectrum, hundreds of nanometers away from the typical frequency of spherical gold nanoparticles, whose SPR band is in the 510–530 nm range. Fig. 3b shows the optical spectra of the Er–Au330 and Er–Au722 samples showing

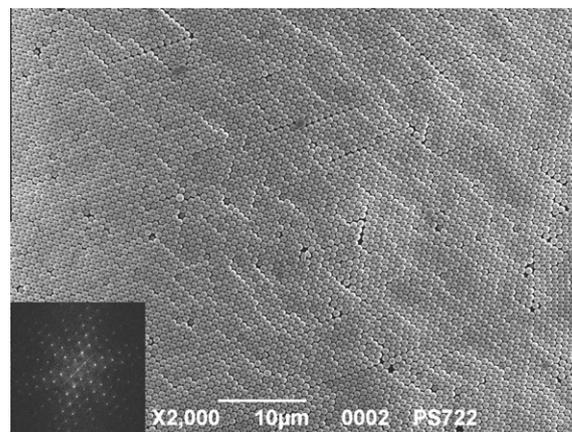


Fig. 1. SEM image of a self assembled monolayer made of PS nanospheres with size 722 nm. The inset shows the 2D Fourier transform of this image.

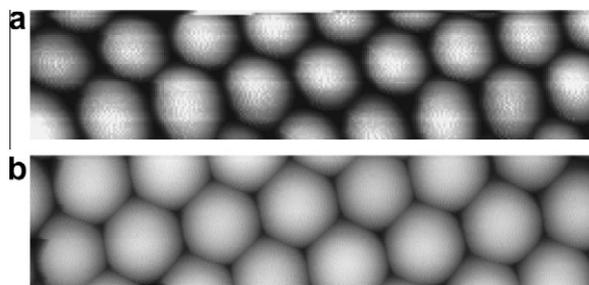


Fig. 2. AFM characterization of a 722 nm PS mask before (a) and after (b) Er⁺ implantation. A partial coalescence between adjacent nanospheres can be observed.

the size dependency of the resonance frequency: the wider the nanodots, the larger is the red-shift toward the IR spectrum. Moreover, the spectra exhibit two main bands which can be attributed to different multipolar contributions to the extinction cross section.

To optically activate the implanted erbium ions and to obtain room temperature photoluminescence, a high-temperature thermal treatment (around 900 °C in silica) is in general needed to recover the implantation damage and restore the erbium coordination site [4,5]. On the other hand, a so high temperature annealing can change the shape of the nanostructure from triangles to the thermodynamically more stable spheres: this evolution can be eventually used to finely tune the plasmon peak position in order to optimize the interaction between gold nano-array and erbium ions. Therefore, to better control the thermally-induced modifications of the metallic nanodots shapes, in the present study the samples were annealed at 600 °C for 1 h in a nitrogen atmosphere. After the annealing the optical absorption of the two nanostructures changes: the plasmon peak appears to be blue-shifted for both samples. For example the SPR band of Er–Au330 sample had a shift of about 400 nm after annealing, with a long tail in the NIR spectrum, indicating the occurrence of nanodots shape changes toward the spherical one (see Fig. 4).

In principle the coupling between an emitter and the plasmonic nanostructure (sketched in Fig. 5a) should modify the intensity and/or the lifetime of the photoluminescence signal [6]. The measured PL spectrum in the present study is the typical emission spectrum of Er³⁺ in silica centered at 1.5 μ m. The main difference is in the lifetime of the PL emission, as it can be seen in Table 2. The measured lifetime of PL emission in the reference sample is 1.7 ± 0.1 ms to be compared with the typical value of the lifetime

Table 1
Summary of the samples analyzed.

Sample label	Mask type	Sputtering conditions	Nanotriangles distance
Er ref	No mask	–	
Er–Au330	PS, 330 nm	Au, 20 W, 270 s	190 nm
Er–Au722	PS, 722 nm	Au, 20 W, 270 s	420 nm

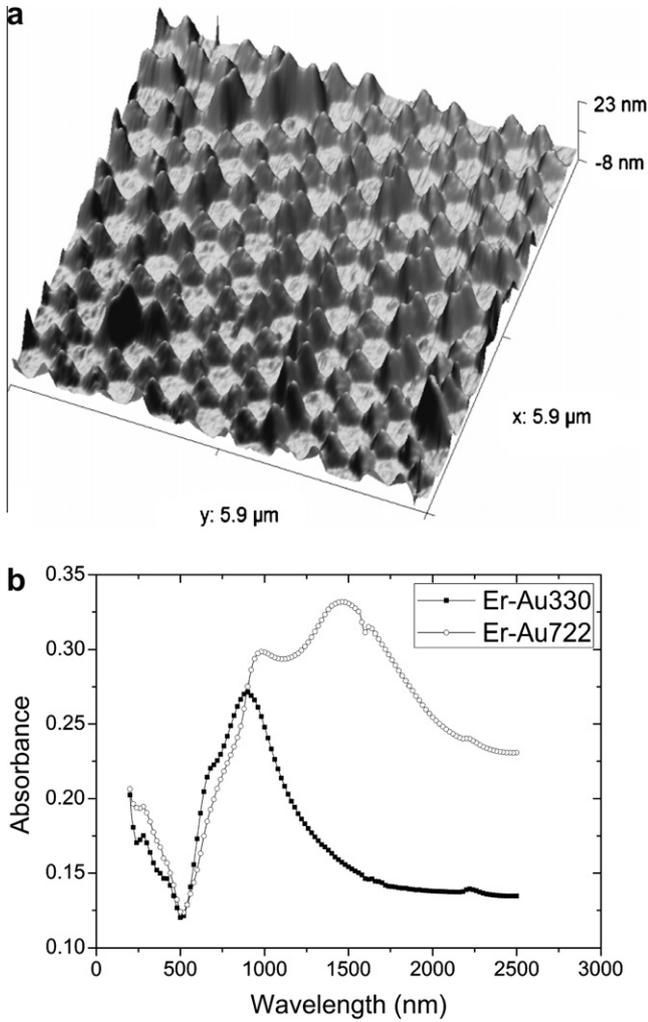


Fig. 3. (a) 3D AFM image of Au nanodots in the Er-Au722 sample; (b) optical spectra of the two samples with gold nanostructures.

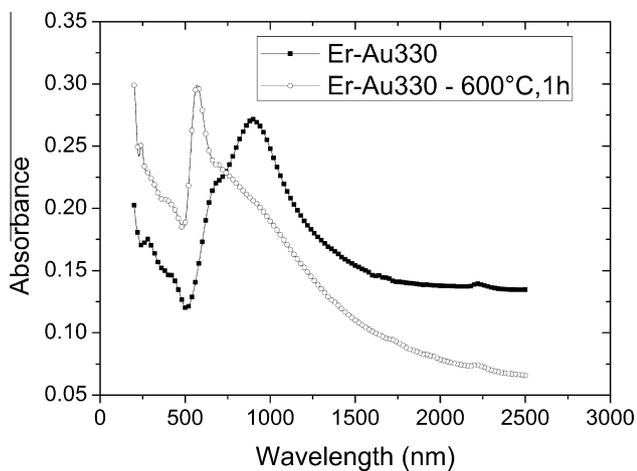


Fig. 4. Comparison of the optical absorption spectra of the ash deposited and annealed Er-Au330 sample. A large blue shift of the main plasmon resonance peak caused by the thermal annealing is clearly visible.

in silica of about 10–12 ms [4]. This difference indicates that the annealing at 600 °C was not sufficient to completely recover the Er site, as expected, therefore leaving efficient nonradiative channels.

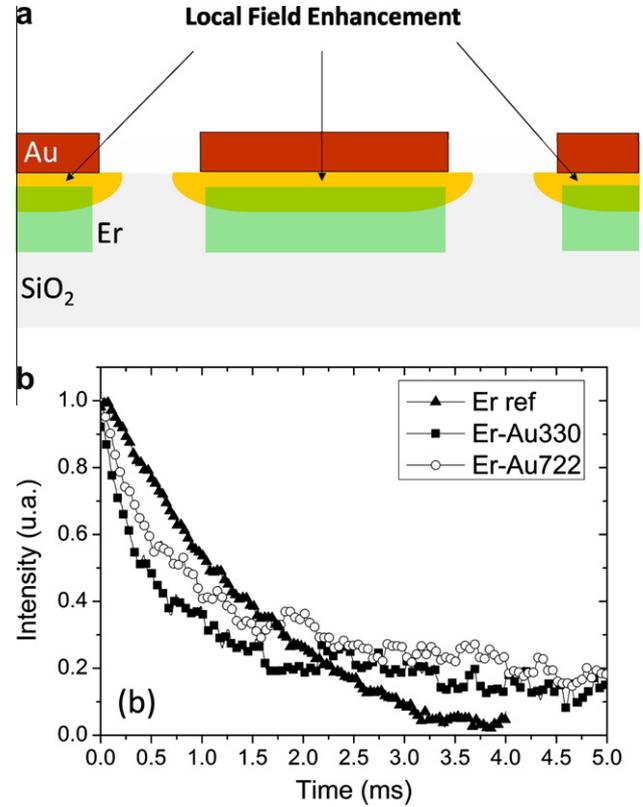


Fig. 5. (a) Sketch of the local field interaction between the gold nanostructures and the implanted erbium; (b) PL intensity decay measured at 1540 nm for a reference sample of Erbium in silica and for the two samples with gold nanostructures.

Table 2

Measured lifetimes of the Er³⁺ PL emission intensity for the reference sample and the two samples with gold nanostructures of different size. For bi-exponential decays, two lifetimes τ_1 and τ_2 are reported.

Sample	Lifetime τ_1 (ms)	Lifetime τ_2 (ms)
Er ref	1.7 ± 0.1	–
Er-Au330	1.7^*	0.26 ± 0.02
Er-Au722	1.7^*	0.20 ± 0.02

* For Er-Au330 and Er-Au722 samples the τ_1 value has been fixed to the same value of the reference sample.

Fig. 5b shows the normalized photoluminescence intensity for the reference sample, and two samples with Au nanostructures. Whilst in the Er reference the PL intensity follows a single exponential decay, in the samples Er-Au330 and Er-Au722 it exhibits a more complex bi-exponential decay described by Eq. (1).

$$I(t) = I_1 \cdot e^{-(t/\tau_1)} + I_2 \cdot e^{-(t/\tau_2)} \quad (1)$$

This kind of decay suggests the occurrence of two different Er populations that do not interact in the same way with the gold nanostructures. One possible interaction between plasmonic nanostructures and fluorophores is mediated by the strong electromagnetic field that is located near the metal surface. This field enhancement exponentially decays over typical lengths of few tens of nanometers inside the silica matrix, while the Er concentration ranges from 20 to 70 nm. A good fit of the experimental time decays has been obtained by fixing τ_1 to the lifetime value of the reference sample while allowing the faster component τ_2 to vary. This interpretation scheme is suggested by the idea that some Er ions could be too far from the surface to efficiently interact with the gold nanodots: therefore they behave as if the nanodots were not

present, i.e., as in the reference sample. On the other hand, Er ions implanted closer to the surface are more sensitive to the enhanced near field and this can account for the shorter lifetime. Further investigations are in progress to better clarify this point, which indicates that by a suitable tuning of the nanostructure-emitter distance a variation of the emission lifetimes can be achieved, therefore affecting and possibly increasing the quantum efficiency of the emitter [7]. It is worth underlining that Er excitation is performed in the present experiment under resonant conditions: indeed, out of resonance excitation does not produce detectable PL signal indicating that the main effect is correlated to a plasmonic interaction and not to a standard energy transfer process mediated by the nanostructures [5].

4. Conclusions

We used a self assembled monolayer of PS nanospheres as a mask for ion implantation and for gold deposition in order to build a system in which a fluorophore (Er) and a plasmonic nanostructure both patterned in regular arrays are spatially coupled. A modification of the Er^{3+} lifetime is found in the samples with the plasmonic nanostructures indicating an electromagnetic coupling

with the emitters. This structure still needs to be optimized in two steps: (i) Er ions should be closer to the plasmonic nanostructures and (ii) the metallic nanostructures could be further optimized by tailoring their SPR band to better match the excitation wavelength.

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