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Plasmon mode excitation and photoluminescence enhancement on silver nanoring

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ABSTRACT

We demonstrate a simple and high-performance laser-assisted technique for silver nanoring fabrication, which includes the ablation of the Ag film by focused nanosecond pulses and subsequent reactive ion polishing. The nanoring diameter and thickness can be controlled by optimizing both the pulse energy and the metal film thickness at laser ablation step, while the subsequent reactive ion polishing provides the ability to fabricate the nanoring with desirable height. Scattering patterns of s-polarized collimated laser beam obliquely illuminating the nanoring demonstrate the focal spot inside the nanoring shifted from its center at a distance of $\sim 0.57R_{ring}$. Five-fold enhancement of the photoluminescence signal from the Rhodamine 6G organic dye near the Ag nanoring was demonstrated. This enhancement was attributed to the increase of the electromagnetic field amplitude near the nanoring surface arising from excitation of the multipole plasmon modes traveling along the nanoring. This assumption was confirmed by dark-field back-scattering spectrum of the nanoring measured under white-light illumination, as well as by supporting finite-difference time-domain simulations.

1. Introduction

Noble metal ring nanostructures are increasingly attracting great interest because they provide a significant enhancement of localized electromagnetic field due to surface plasmons excitation, and also allow for fine-tuning of plasmon resonances through variation of ring size and shape [1–4]. Such nanostructures have already found their way into many areas: surface enhanced spectroscopy (SERS, SEIRA) as highly effective antennas [5], optical data storage as recording marks to achieve super resolution [6], the optical telecommunications band as plasmonic waveguides [7] as well as in biological and chemical sensors [8]. To produce ring metal nanostructures, methods of colloidal [2], electron [3], and ion beam lithography [5] as well as chemical synthesis [4] are applied, which enables us to create single nanorings of various size, geometry, and form, as well as their periodic arrays. However, technologically much simpler laser surface modification techniques can be found having proved the ability to create a wide range of functional nanostructures [9–17].

This paper will discuss that using such methods in conjunction with subsequent reactive ion etching, which will allow us to produce individual ring Ag-nanostructures with controlled geometrical dimensions on a dielectric substrate. Also it will be shown that such nanorings can increase the electromagnetic field intensity near their surface similar to the structures made by other techniques. Application of the laser-produced nanorings as functional plasmonic nanostructure will be demonstrated for local enhancement of the photoluminescence signal.

2. Nanoring fabrication

Fabrication of submicron rings is revealed to be done in two stages. At the first stage the 35- and 50-nm-thick silver films deposited by e-beam evaporation (Ferrotec EV M-6) on the smooth quartz substrate are normally irradiated by single second-harmonic (532 nm) pulses (pulse duration ~7 ns, maximum pulse energy – 10 mJ) of a Nd:YAG laser system. An optical microscope (Nikon Eclipse lv100d) equipped with the lens (60×, NA=0.65) was used for laser light focusing onto the Ag film surface, as well as for visual inspection of the sample positioning relative to the laser focal spot with an accuracy of ~700 nm. To improve the quality of the laser beam used for nanostructuring each pulse was coupled to the section of the single-mode optical fiber (Thorlabs SM400), which acts as a spatial filter and provides almost perfect Gaussian-like energy distribution on its output. The sample was arranged onto the 3-axis linear motorized nanopositioning system

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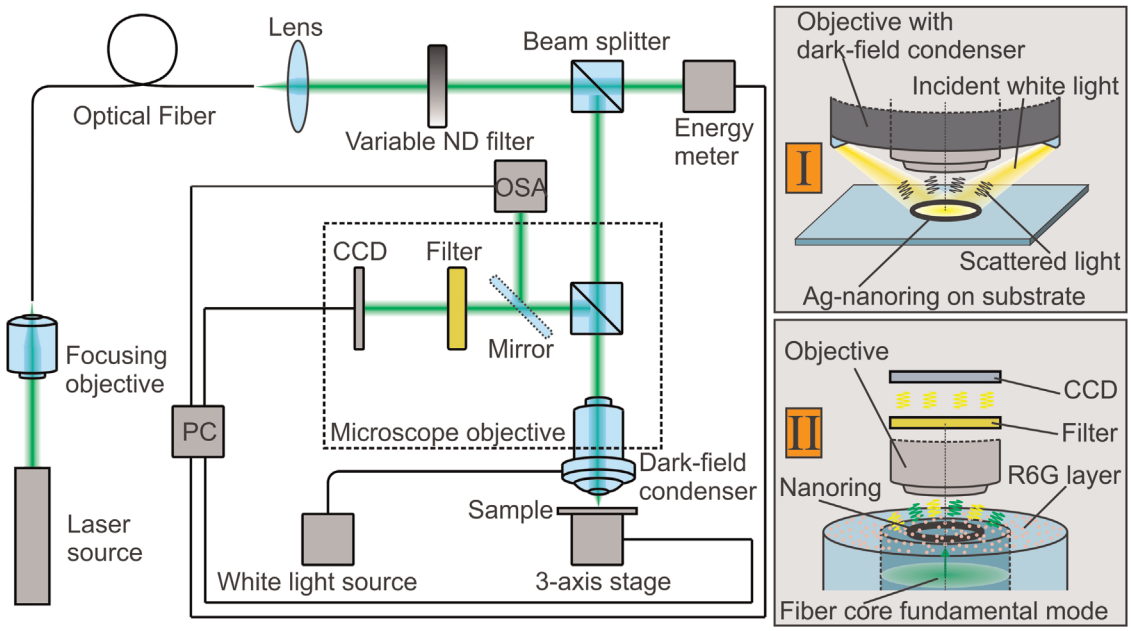

Fig. 1. Schematic of the experimental setup used for laser nanostructuring of Ag films and studying the optical properties of the structures obtained. Inset I schematically shows the dark-field illumination and scattering signal detection from the Ag nanoring. Inset II shows the optical scheme of the experiment on the photoluminescence enhancement of organic dye Rhodamine 6G.

(Newport XM series), which provides 50-nm movement precision along all three axes. The pulse energy was modulated by a variable filter and controlled using high sensitive photodetector (J-10SI-HE Energy Sensor, Coherent EPM2000).

Laser pulse impact on the surface of metal films with thicknesses $h_{film}=35$ nm and $h_{film}=50$ nm at variable pulse energies E results in formation of the ring-shaped structures representing through holes surrounded by a resolidified melt rim (Fig. 2a and c, respectively). It should be noted that such structures appear only under ns-pulse irradiation, while femtosecond pulse irradiation does not provide resolidified melt rings surrounded the through holes (in this case femtosecond Ti:Sapphire-laser system is used as a radiation source in Fig. 1). Apparently, in the latter case Ag film detaches from the substrate due to thermoelastic tensions caused by the temperature-driven gradients [15,18], which results in formation of the microhole surrounded by the hemispherical cupola-like walls (Fig. 2e). On the contrary, nanosecond pulses initiate other thermodynamic processes caused by subsurface boiling in the film–substrate interface, which results in spreading of the melted metal and its solidification in the form of the ring with a smooth uniform edge at the through hole border [19,20]. Fig. 2a and c also shows that additional crown-like nanospikes at the nanoring edge appear under ns-pulse irradiation ($E>41$ nJ for $h_{film}=35$ nm and $E>52$ nJ for $h_{film}=50$ nm), which is an undesired effect in terms of achieving the regular geometrical shape of the nanoring.

Appearance of these periodically modulated nanospikes in the molten rim turns out to be associated with the initiation of the hydrodynamic (Rayleigh-Plateau) instability [16,21] appearing at increased pulse energies when the rim diameter and wall thickness reach some threshold values.

However, at lower pulse energies E ($E<37$ nJ for $h_{film}=35$ nm and $E<45$ nJ for $h_{film}=50$ nm) the nanorings demonstrate regular, nearly annular, shape with the radii of the structures R_{ring} ranging from 0.33 to 1.10 μm for the 35-nm-thick film and from 0.30 to 0.75 μm for 50-nm-thick film. As seen, the minimal diameter of the fabricated nanorings at such film thicknesses determining the minimum possible distance between adjacent nanoelements arranged into the array can achieve 0.3 μm. At pulse energies lower than 5 nJ for 35-nm-thick film and 6 nJ for 35-nm-thick film the through microholes and, as a consequence, the nanoring do not form. Instead, structures representing well-known resolidified nanojets (Fig. 2f) appear under ns-pulse irradiation [9]. In accordance with atomic force microscope, the height of all regular-shaped rings exceeds 200 nm, which is significantly higher than the initial Ag film thickness providing the ability to fabricate separately lying nanorings on the dielectric substrate via layer-by-layer polishing of the surrounded Ag film. Reactive ion polishing (RIP, Hitachi I4000) providing an average polishing rate ~0.33 nm/s is used for this purpose. In order to minimize the possible melting of the metal film under the action of the heating Ar^+ beam, the RIP procedure was performed for several consecutive polishing cycles each of which does not exceed 15 s followed by metal film cooling during 1 min after each cycle.

Fig. 2b and d demonstrates the result of thinning the nanostructures previously presented in Fig. 2a and c for the total ion beam exposure times 110 and 155 s, respectively. As seen, such polishing removes the metal film in the vicinity of the nanorings without any significant distortions of the regular ring shape. The height h of the obtained rings can be varied by optimizing the RIP exposure time. In this work the height of the nanorings was chosen to be 200 nm and 250 nm for structures fabricated in the 35- and 50-nm-thick Ag films, respectively. Likewise, the ring thickness t was found to be increased with initial film thickness. The resulting nanoring thicknesses were 150 nm and 200 nm for 35- and 50-nm-thick films, respectively. To demonstrate the reproducibility of the developed fabrication technique, square regular arrays of nanorings with $R_{ring}=350$ nm, $t=80$ nm, $h=100$ nm (Fig. 2g) and $R_{ring}=550$ nm, $t=200$ nm, $h=200$ nm (Fig. 2h), respectively, were fabricated on the 50-nm-thick Ag film. The observed variation of ring diameter ΔR_{ring} in these arrays can be explained by the pulse energy fluctuation at the 5-% level and does not exceed 70 nm and 100 nm for 35- and 50-nm-thick films, respectively. Apparently, ΔR_{ring} value can be reduced by improving the laser source stability.