2D and 2.5D plasmonic metastructures for surface-enhanced infrared absorption applications: fabrication and properties

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Abstract. Metamaterials possess novel electromagnetic properties and have great potential for applications. Different type of nanosized plasmonic antennas considered to be effective functional materials in infrared spectrum. Still, strict requirements on dimensions and periodicity of nanostructures limits their practical implementation. Here, we have fabricated 2D and 2.5D different topology arrays of nanosized plasmonic antennas using e-beam and direct laser writing (DLW) lithography techniques. Applying the DLW method we created periodic polymer structures that act as a template for creating plasmonic nanoantennas with metallization and lift-off techniques. Improvement of the morphological parameters of such structures is possible due to STED-DLW (STimulated Emission Depletion assisted Direct Laser Writing) compatible photoresist. With e-beam lithography and lift-off techniques we obtained arrays of gold plasmonic nanoantennas. Using standard Fourier-transform microscopy we measure the spectral properties of fabricated nanostructures. We show that observed position, intensity and Q-factor of the collective surface plasmon resonance are directly conditioned by fabrication process. Thus, the studied structures can be applied as substrates for surface-enhanced infrared absorption (SEIRA). SEIRA antenna arrays in its turn possess considerable potential in real-world applications such as chemical and biological vibrational sensing.

1. Introduction
Special designs of metastructures, known as plasmonic antennas, are employed to overcome limitations of IR-spectroscopy. Such nanoantennas provide huge electromagnetic near fields, which can be used to enhance vibrational signals of molecules located in such hot spots [1]. Following this approach of surface-enhanced infrared absorption (SEIRA), one can increased the sensitivity by up to 5 orders of magnitude in comparison to conventional infrared transmittance spectroscopy. The development of new approach for creating SEIRA-active structures is a relevant scientific task.

2. STED-inspired direct laser writing
It was shown that optical lithography known as direct laser writing (DLW) competes (both in lithography speed and manufacturing cost) with e-beam lithography in usability efficiency for creation of the array of nanoantennas [2]. The DLW method is based on the phenomenon of photopolymerization...
as a result of two-photon absorption of light when the photoresist is exposed to focused femtosecond laser radiation. The subsequent raster scanning allows to create arbitrary 2D and 2.5D-structures. The resolution of a direct laser letter is limited by diffraction and is estimated by half the wavelength of the radiation used for writing. Thus, the DLW lithography allows to create large-sized antennas for a limited time, and hence increases the effective area for collective plasmonic excitations.

2.1. STED idea
The resolution of direct laser writing directly affects the roughness and other morphological defects of the obtained antennas. Accordingly, increasing the resolution of DLW makes it possible to improve the Q-factor of the plasmon resonance and, as a consequence, the selectivity and sensitivity of the IR-absorption.

The DLW resolution at a constant excitation wavelength can be increased applying the idea of STED (STimulated Emission Depletion) in order to reduce the axial and lateral dimensions of an effectively excited region. The essence of this method is to add a second depletion laser with a certain configuration of the electromagnetic field to stimulate radiative transitions along the edge of the focal spot, that is, to reduce the size of the excited region by using depletion field.

It should be noted that the use of the STED idea in luminescent microscopy was distinguished in 2014 by the Nobel Prize in chemistry [3]. A record resolution of 2.4 nm has been demonstrated in STED-nanoscopy with excitation wavelength of 775 nm. Thus, it is possible to create structures whose dimensions are less than the excitation wavelength by 2 orders of magnitude.

2.2. Experimental setup
We have created a setup for STED-DLW lithography based on a femtosecond Ti:Sapphire laser with a tunable excitation wavelength of 720-860 nm and a pulse duration of 50 fs. To realize the STED-idea we have used depletion CW-laser with a wavelength of 532 nm. The composition of the photoresist and the parameters were selected for reasons of suitable mode of laser writing [4].

With the help of improved technology of direct laser writing we fabricated 2D- (figure 1) and 2.5D-periodic structures with different spatial periods. The morphology of obtained structures was studied by scanning electron microscopy and atomic force microscopy.

![Figure 1. SEM-image of the periodic 2D "strokes" structure.](image)

3. E-beam lithography
One of the most common technologies for the production of metastructures is an electron-beam lithography. Further, the sample is metallized by the lift-off method to form a gold/silver plasmonic structure of the required thickness.

3.1. Results and discussion
We have chosen the optimal dimensional nanoantenna parameters and have fabricated arrays of periodic golden strokes with lengths of 2 µm and 2.3 µm with a height of approximately 100 nm. We constructed a physical model of such antennas with an absorbing medium to further perform computer simulations of the interaction of a single antenna with an incident plane wave. In addition, we have fabricated c-shaped structures with a characteristic radius of 0.5 µm that are split-ring resonators (figure 2). Morphological properties of the obtained nanoantennas were studied by SEM, AFM, and dark field
optical microscopy. Spectral properties of the fabricated structures were checked in mid-infrared spectral range. With standard Fourier-transform spectroscopic technique we measured the transmission spectra, as well as the dependence on the direction of polarization of the incident light.

Figure 3 shows typical transmission spectra of C-shape antenna array measured for different polarization of light. Reference spectra were taken on unstructured part of CaF$_2$ substrate. Minima in the spectra corresponds to collective plasmonic resonance of nanoantennas. Its position shows strong dependence on the relation between direction of polarization of electrical field and antenna gap. It shifts from 3.7 µm for E perpendicular to the gap of individual antenna to 7.7 µm for parallel orientation.

Thus, the fine-tuning of incident light polarization allows one to adjust the plasmon resonance of nanoantenna to the required vibrational frequency of chemical.

4. Conclusion

We considered two methods of lithography for the fabricating of plasmonic metastructures for SEIRA. The STED-DLW setup assembled and writing parameters for polymer structures selected. Both methods used to fabricate polymer templates and gold plasmonic nanoantennas for SEIRA applications. A physical model developed, the idea of which is the coincidence of the plasmonic resonance frequency of the antenna and the absorption line of the chemical to study. The PETTA (pentaerythritol tetraacrylate) oligomer, which used in the photoresist for DLW process, studied as a test chemical. The interaction of plasmons in nanoantennas and the absorbing medium can be discussed in the terms of the Fano effect. The interaction of nanoantennas with linearly polarized radiation studied experimentally and computer simulation of the interaction with IR radiation has carried out to determine the enhancement factor for such a system.

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