The aim of this study is to form the visible range diffraction surface grids for optical plasmonic sensor applications based on transparent polymer matrix - PMMA, in which periodic areas with Ag-nanoparticles could be synthesized using mask ion implantation [1]. Earlier in our work [2] for the first time in practice it was experimentally demonstrated the principle possibility for the formation of Ag-nanoparticles in PMMA (Ag:PMMA) by Ag-ion implantation. Detailed modeling of optical extinction spectra of Ag-nanoparticles with different sizes in PMMA and carbon-PMMA surrounding were also realized [3].

The implantation of PMMA plates was performed by an ILU-3 ion implanter with doses from 5.0 \times 10^{14} to 1.5 \times 10^{17} ion/cm^2 and Ag^+-ion energy of 30 keV at a current density 2 \mu A/cm^2. For fabrication of a periodic diffraction structure on the PMMA a metal mask with a mesh size of 20 \mu m was used. Simulation of concentration depth profiles of implanted Ag-ions in PMMA using a computer algorithm SRIM-2013 for 30 keV, showed that most of Ag-atoms are collected near the polymer surface. Such accumulation of silver in the local layer leads to a supersaturation of the metal atoms, the nucleation and growth of Ag-nanoparticles [1]. The total thickness of the implanted layer with formed Ag nanoparticles in PMMA, for the given conditions of implantation does not exceed 100 nm.

Optical spectra of Ag:PMMA with different doses show that during of the irradiation the transmittance of the samples is monotonically decrease in the near-UV wavelength spectral range due to the destruction of the polymer structure, radical creation and the formation of carbon fragments (carbonization) as suggested in [3]. Formation of Ag-nanoparticles in the PMMA was evident by the optical transmittance showing an appearance of the characteristic plasmon absorption band with a maximum of about 500 nm for the sample created with a dose of 1.0 \times 10^{16} ion/cm^2. With increasing Ag-ion dose a shift of this maximum to longer wavelengths, which corresponds a raise of the silver concentration in the PMMA and an increase of the Ag-nanoparticle size, was observed.

For the formation of plasmonic diffraction grid the dose of 2.5 \times 10^{16} ion/cm^2 was selected. AFM image of the Ag:PMMA surface in areas which was not protected by the mask shows that in contrast to the relatively smooth surface of
the non-irradiated PMMA, the morphology of the Ag:PMMA region is characterized by the semi-spherical hillocks as a result of partial exposure of spherical Ag-nanoparticles at the surface.

Surface periodic microstructure on Ag:PMMA implanted through the mask PMMA was observed with an optical microscope. The entire surface of the sample was an ordered lattice with a mesh size of 20 \( \mu \text{m} \). The square areas are a cell of PMMA with Ag-nanoparticles exhibiting plasmon absorption. The walls between the square mesh lattice consist of a non-irradiated polymer. Details of the sample in the cell edge of a square mask were analysed by ContourGT profiler. As it was shown the periodic structure was formed by the surface sputtering of the polymer substrate.

It is known that implantation of the metal-ions of the dielectric increases its refractive index to \( \sim 1.7 - 1.9 \) in the visible region of the spectrum (especially at frequencies of nanoparticle plasmon resonance) [1]. Therefore, it is evident that by mask implantation of the PMMA a microstructure with periodically variable optical constants of the material (\( n_{\text{PMMA}} = 1.5 \)), i.e., between the cells of the lattice and its walls, was carried out. The imaging recorded by plasmonic grid by probing with the semiconductor laser at a wavelength of 527 nm demonstrates diffraction patterning from the samples. Note that the diffraction image was obtained in visible range wavelengths of plasmon absorption of Ag-nanoparticles. Therefore, it is obvious that by changing modes of ion implantation for synthesizing of nanoparticles of various sizes, thereby changing the effective refractive index of the individual elements in the diffraction grid, one can control the optical and diffraction characteristics for sensor applications in a sufficiently wide range.

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References