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Formation of a Periodic Diffractive Structure Based on Poly(methyl methacrylate) with Ion-Implanted Silver Nanoparticles

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Abstract—We propose to form optical diffractive elements on the surface of poly(methyl methacrylate) (PMMA) by implanting the polymer with silver ions ($E = 30$ keV; $D = 5.0 \times 10^{14}$ to 1.5×10^{17} ion/cm^2; $I = 2$ μA/cm^2) through a nickel grid (mask). Ion implantation leads to the nucleation and growth of silver nanoparticles in unmasked regions of the polymer. The formation of periodic surface microstructures during local sputtering of the polymer by incident ions was monitored using an optical microscope. The diffraction efficiency of obtained gratings is demonstrated under conditions of their probing with semiconductor laser radiation in the visible spectral range.

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At present, microstructured composite materials based on optically transparent dielectrics containing nanosized elements are used as optical diffractive elements (gratings) and photonic crystals. The field of modern physics studying these systems and related phenomena is called diffraction nanophotonics [1]. In practice, these gratings can be used in optical communication systems for feeding laser radiation into thin-film waveguides and/or filtering optical signals in waveguides. Nanosized elements in these gratings can take the form of metal nanoparticles, in particular, particles of noble metals [2]. Collective excitation of conduction electrons in these nanoparticles (surface plasmon resonance, SPR) under the action of an electromagnetic wave and the resonant enhancement of local field significantly modifies dielectric constants of these effective media at special radiation frequencies [3, 4]. The interaction of light with these periodic structures, especially with metal–dielectric systems, has been extensively studied [1]. These structures can feature a broad spectrum of optical resonance effects, which account for the unique properties of the ordered composite medium. Diffraction gratings with metal nanoparticles featuring the SPR phenomenon are called plasmonic gratings.

In practice, dielectric-based plasmonic gratings have been prepared by various methods including mechanical cutting, imprinting with precut gratings, applying magnetic fluids, and using photolithographic and holographic techniques. Recently, we have proposed and experimentally implemented a method of obtaining plasmonic gratings based on inorganic glasses and crystals with metal nanoparticles formed by ion implantation through a surface mask [5, 6].

The present study was aimed at demonstrating the possibility of obtaining diffraction gratings for the visible spectral range based on polymer matrices, e.g., of poly(methyl methacrylate) (PMMA), with periodic regions containing nanoparticles of noble metals (in particular, silver) synthesized by ion implantation through a surface mask. Polymer materials have been widely used for creating waveguide structures of various types and optically controlled photonic elements such as prisms, lenses, etc. It should be noted that organic materials have been less profoundly studied (as compared to metals and semiconductors) with respect to ion irradiation effects and the possibility of micro- and nanostructuring under ion implantation conditions.

Polymer-based diffraction gratings were manufactured using 1-mm-thick transparent PMMA substrates, which were implanted with 30-keV Ag$^+$ ions to doses from 5×10^{14} to 1.5×10^{17} ion/cm^2 at an ion beam current density of 2 μA/cm^2. The ion irradiation was carried out at a residual gas pressure of 10^{-5} Pa on an ILU-3 particle accelerator as described previously

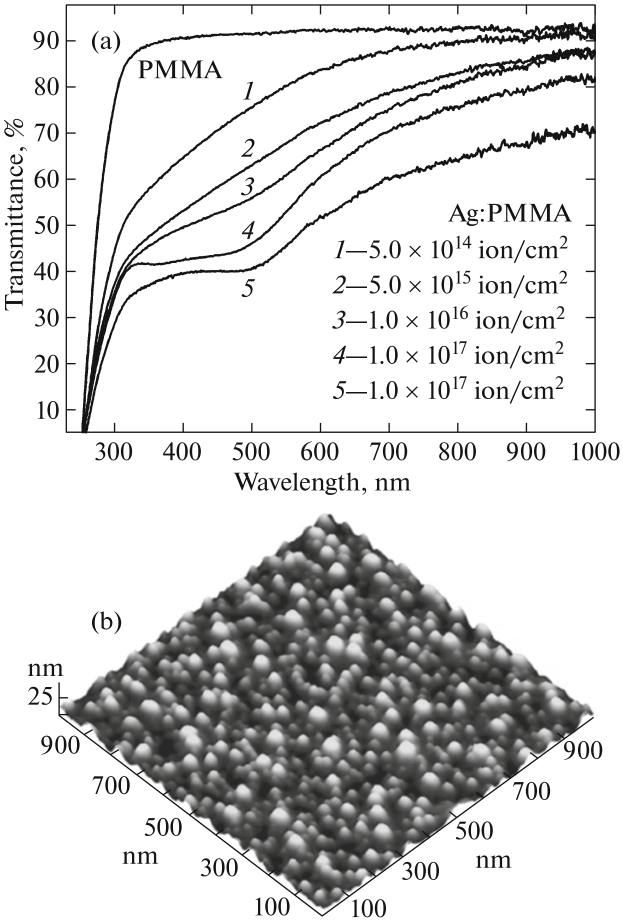

Fig. 1. (a) Optical transmission spectra of unirradiated PMMA and ion-irradiated Ag:PMMA samples (*1–5*) implanted to various doses; (b) AFM image of silver-implanted PMMA surface in unmasked polymer region.

[7], but with an additional surface mask representing a nickel 20-μm-square mesh grid. The optical transmission spectra of initial PMMA samples and silver-implanted Ag:PMMA samples upon ion irradiation to various doses were measured on an Avantes AvaSpec-2048 spectrophotometer. The local surface morphology was studied by atomic force microscopy (AFM) in a tapping mode on a Bruker FastScan instrument. The depth profiles of gratings formed as a result of PMMA sputtering during ion implantation were studied with the aid of a Bruker ContourGT-K profilometer and Micromed Polar-1 optical microscope. The optical diffraction patterns of obtained gratings were analyzed by probing with radiation of a semiconductor laser operating at a wavelength of 527 nm.

The ion depth–concentration profiles of 30-keV Ag^+ ions implanted in PMMA were simulated using an SRIM-2013 algorithm. The results showed that silver is accumulated in a near-surface layer of the polymer substrate. As will be considered below, metal accumulation in a local layer leads to its supersaturation with silver atoms and the nucleation and growth of silver nanoparticles. The total depth of ion implantation and, hence, the thickness of an active layer of the diffraction grating based on the PMMA with silver nanoparticles under the given ion implantation conditions did not exceed ~100 nm.

Figure 1a shows the typical linear optical transmission spectra of the initial PMMA and Ag:PMMA samples ion-implanted to various doses. As can be seen, the implantation process is accompanied by monotonic decrease in the optical transparency of samples (cf. curves *1* and *2*) that is related to degradation of the polymer structure, in particular, the formation of carbon-based fragments (carbonization) [8]. Beginning with a dose of 1.0×10^{16} ion/cm^2, the spectrum of Ag:PMMA shows the appearance of a selective absorption band peaked at ~500 nm (curve *3*), which is related to the formation of Ag nanoparticles and manifestation of the SPR effect. As the ion dose grows further, the SPR maximum shifts toward longer wavelengths, which corresponds to growing silver concentration in the implanted layer and increasing sizes of silver nanoparticles [9].

Analogous behavior was observed for ion-implantation synthesis of noble metal nanoparticles in various inorganic glasses and crystals and repeatedly demonstrated in the literature [4–6]. The results of computer simulations of the extinction coefficients of silver nanoparticles in a PMMA matrix according to the theory of Mie [4] also confirmed a long-wavelength shift of the plasmon resonance of these nanoparticles with increasing dimensions, in agreement with the experimentally observed spectra (Fig. 1a).

For the creation of plasmonic diffraction gratings in Ag:PMMA, we have selected an implantation dose of 2.5×10^{16} ion/cm^2, which ensured the formation of silver nanoparticles in the polymer [7]. Observations by transmission electron microscopy (TEM) [7] showed that the average size of silver nanoparticles formed under these conditions was ~10 nm. Figure 1b shows an AFM image of the surface of such Ag:PMMA sample in a region not covered by the mask. In contrast to a relatively even surface of unirradiated (masked) PMMA, where the surface roughness height did not exceed 1.5 nm, the morphology of ion-implanted regions in Ag:PMMA was characterized by the presence of hemispherical protrusions. These protrusions appeared as a result of the partial stripping of spherical Ag nanoparticles in the near-surface layer, by analogy with previously observed ion-implantation synthesized metal nanoparticles in silicate glasses and sapphire [4]. The observed growth of silver nanoparticles in the ion-implanted layer and their partial stripping at the PMMA surface (Fig. 1b) are consistent with the appearance of SPR peaks in the optical spectrum (Fig. 1a). This stripping is caused by enhanced

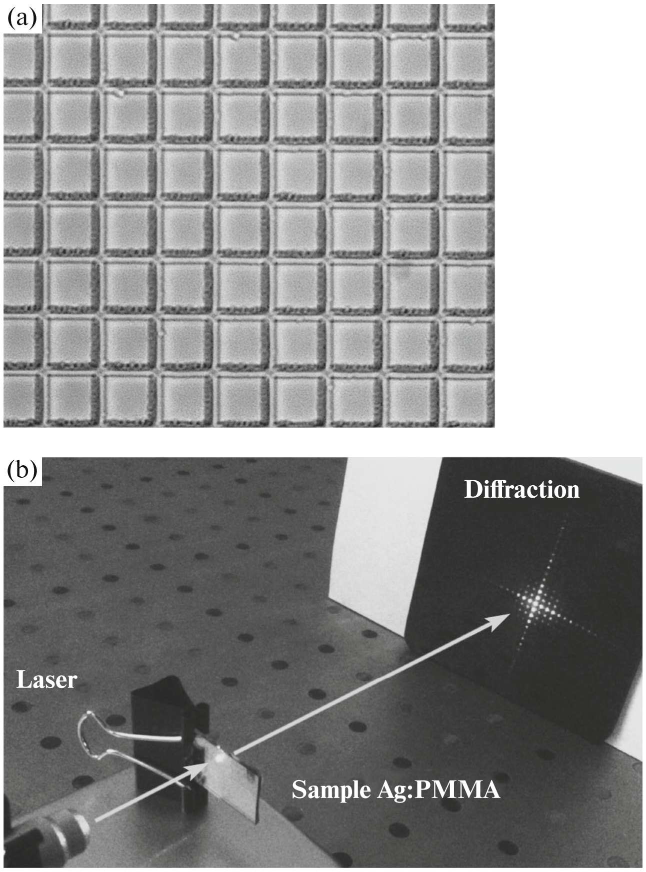

Fig. 2. (a) Image of the surface of a microstructured PMMA implanted with silver ions through a mask, as observed in the optical microscope (the square grating cell size is 20 μm). (b) Diffraction scattering pattern observed on the screen upon the transmission of light through a microstructured Ag:PMMA with ion-implantation synthesized silver nanoparticles probed by 527-nm laser radiation.

sputtering of PMMA as compared to that of silver particles.

The surface microstructures formed on the surface of PMMA ion-implanted through the mask were also observed in the optical microscope (Fig. 2a). As can be seen, the entire sample surface represents an ordered grating with 20-μm-square cells formed by the implantation of PMMA with silver ions in the indicated regime. The square areas of cells correspond to ion-irradiated PMMA, i.e., a polymer structure with silver nanoparticles exhibiting SPR absorption in the visible spectral range (Fig. 1a). The intermediate regions (spacers) between square cells consist of the unirradiated polymer.

Profilometric measurements performed at the boundaries between PMMA and Ag:PMMA regions unambiguously showed that the implantation of silver ions and formation of grating is accompanied by the effective sputtering of the PMMA substrate surface. As a result, the irradiated MMA regions appear as troughs (depressions) and the Ag:PMMA layer occurs several dozen nanometers deeper relative to the surface of unirradiated (masked) PMMA. Note that this result is the first experimental evidence of a practically sputtered PMMA surface upon the implantation of low-energy silver ions.

As is known, the implantation of a dielectric with metal ions leads to an increase in the refractive index up to ~1.7–1.9 in the visible spectral range (especially at SPR absorption frequencies of the metal nanoparticles) [10, 11]. Evidently, the PMMA irradiation through a mask leads to the formation of a microstructure with periodic variation of optical constants of the medium, i.e., with phase contrast between Ag:PMMA cells and pure PMMA spacers ($n_{\mathrm{PMMA}} = 1.5$). Therefore, the obtained microstructure with synthesized silver nanoparticles can be used in practice as a two-dimensional photonic crystal or an effective diffractive optical element. The microstructure formed by ion implantation in the indicated regimes is characterized by periodically varying the refractive index and represents a diffraction grating. This is illustrated in Fig. 2b by the pattern of diffraction scattering observed during probing of the grating in transmission mode by the light of a semiconductor laser operating at 527 nm. Note that this diffraction image is obtained in the visible range at a wavelength of the SPR absorption of silver nanoparticles. Thus, it is evident that, by selecting the regime of ion implantation so as to synthesize nanoparticles with various dimensions and, hence, desired variation of the effective refractive index of separate elements in the diffraction grating, it is possible to control its optical and diffraction characteristics.

In concluding, we have considered the process of ion-implantation synthesis of silver nanoparticles in PMMA matrix and demonstrated a method of creating two-dimensional plasmonic optical diffractive elements by low-energy ion implantation of a polymer through a metal mask. The proposed method provides microstructures with phase contrast ensured by the metal-implanted polymer regions containing silver nanoparticles possessing plasmonic resonance absorption. These experiments gave the first practical evidence of the effective sputtering of a polymer surface during its implantation with low-energy metal ions. The obtained results provide a basis of the patented technology [12] of diffraction gratings in thin PMMA layers with implanted silver nanoparticles. The main practical application of obtained results is related to the creation of new effective elements of plasmonic optics such as intellectual lenses, Bragg's gratings, plasmonic crystals, etc. [1].

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