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Temperature sensor based on a polymer diffraction grating with silver nanoparticles

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Abstract. **The method is suggested for producing an optical temperature noncontact sensor on a polymer polymethylmethacrylate (PMMA) substrate with a diffraction optical element formed by implanting low-energy high-dose silver ions through a surface mask. Ion implantation is performed at an energy of 30 keV, a radiation dose of 5.0×10^{16} ion cm^{-2} and an ion beam current density of 2 μA cm^{-2} through a surface metal mask having the form of grid with square periodical holes (cells) of size 25 μm. In the course of implantation, silver nanoparticles are produced in periodical unmasked domains of irradiated PMMA. Operation of the temperature sensor on diffraction microstructures made of polymer with silver nanoparticles is demonstrated in the range from 20 °C to 95 °C by testing it with a probe radiation of a He–Ne laser.**

Keywords: *laser thermometry, temperature sensor, silver nanoparticles, plasmon absorption, optical diffraction, optical polymer materials.*

1. Introduction

Temperature measurement is very important in studying physical processes involved in substance heating or cooling. This problem can be solved contactlessly by measuring some other physical parameter dependent on temperature according to known physical laws. Actually, various methods are used, such as pyrometry [1], Raman scattering [2], nonlinear-optical diagnosis [3] etc. Among optical remote methods for temperature measurements there is laser diffraction thermometry, which uses various optical diffraction microstructures, for example, Bragg gratings [4] embedded or deposited onto the material surface. Devices comprising materials with embedded diffraction optical elements (DOEs) are called temperature sensors and are distinct in the range of measured temperatures for various materials.

Periodic DOEs on surfaces of various materials are formed by using various technological methods, such as electron lithography [5], deposition of colloidal microspheres [6], selective annealing in gas atmosphere [4], two-photon polymerisation by femtosecond laser pulses [7], etc. In producing DOEs, of particular interest is the technology based on ion implantation through a surface mask. This method was successfully realised in irradiating silica by phosphorus ions [8] and diamond by boron ions [9]. It was also used with a glass substrate (SiO_2) implanted with copper and silver ions [10, 11]. In the latter case, the periodic structures were domains comprising ion-synthesised copper and silver nanoparticles. Collective excitation of conduction electrons in such nanoparticles under an action of a light wave [surface plasmon resonance (SPR)] and induced resonance amplification of a local field substantially modify the dielectric functions of effective media at specific light frequencies, which results in an enhanced phase contrast in DOEs [10].

The method of silica substrate implantation through a mask (thin metal grid) was successfully used for designing an optical thermometry sensor device, which provides temperature measurements in reflection [8]. Amorphous cells limited to the lattice of monocrystal silica were formed on surfaces of such substrates. The implantation energy (40 eV), dose (3.12×10^{15} ion cm^{-2}) and ion type were chosen in such a way that an amorphous layer was formed starting from the irradiated silica surface. When such a periodic diffraction structure is probed by a beam of a cw He–Ne laser (λ = 632.8 nm), a diffraction pattern is observed. The sensor based on periodic silica microstructures (grating) measures temperature of material by detecting the variation of the Fraunhofer diffraction pattern in optical reflection from the grating due to thermal expansion or contraction of a semiconductor substrate. For this purpose, angular redistribution of diffraction maxima is observed, which occurs due to changing geometrical dimensions of the grating in the process of heating or cooling. From the value of diffraction beam deviation one can determine the corresponding variation of sample temperature and find the temperature by known formulae.

For fabricating a more sensitive optical temperature sensor than the silica sensor [8] that was characterised by a rather small coefficient of heat expansion, in the present work we suggest forming a DOE on a polymer matrix – polymethylmethacrylate (PMMA), which comprises silver nanoparticles in periodic micro-domains. Presently, this polymer material is actively used for creating various optical waveguides and light-controlled photonic elements such as prisms, lenses, and so on. The choice of silver is explained by that SPR for this type of nanoparticles in the visible range and, hence, the contribution into dielectric functions of PMMA in a composed material, are mostly revealed for noble metals [12]. A potential

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possibility of synthesising silver nanoparticles in PMMA by ion implantation was demonstrated earlier in [13, 14].

A temperature sensor in the present work was formed by using the low-energy high-dose implantation by silver ions through a surface mask, which resulted in synthesis of metal nanoparticles in periodic cells of the DOE.

2. Experiment

Optically transparent substrates of thickness 1 mm were chosen for forming and demonstrating DOEs on PMMA. Implantation was performed by Ag^+ ions at an energy of 30 keV, radiation dose of 5.0×10^{16} ion cm^{-2} at a current density in the ion beam of 2 μA cm^{-2} in residual vacuum of 10^{-5} Pa on an ILU-3 ion accelerator by the method described in [13] but through a surface mask, namely, a copper-nickel grid with square cells of size 25 μm. The dimensions of the implanted domain of the sample (temperature sensor) were 1×1 cm. Spectra of optical transmission of PMMA and Ag:PMMA samples were recorded with an AvaSpec-2048 waveguide spectrophotometer (Avantes, Netherland). Local morphology of the surface was investigated by a FastScan atomic-force microscope (AFM) (Bruker Corp.). Operation of the optical temperature sensor on a polymer DOE was analysed by probing it with a beam of a He–Ne laser (λ = 632.8 nm).

3. Results and discussion

The depth concentration profile of implanted silver at an energy of 30 keV in PMMA was simulated by the SRIM-2013 computer algorithm. It was shown that silver atoms are accumulated in the near-surface implanted layer, which leads to origin and growing of silver nanoparticles. The penetration depth of implanted silver ions in PMMA, as was shown earlier by spectra of Rutherford backward scattering [13], and, hence, the thickness of the active layer with nanoparticles formed by the DOE in PMMA, are ~100 nm for given implantation conditions.

Spectra of optical transmission are shown in Fig. 1 for non-irradiated PMMA and for silver-ion-implanted Ag:PMMA. One can see that, in contrast to the initial PMMA matrix, the Ag:PMMA sample is characterised in the visible range by a selective absorption band with a maximum near ~500 nm. This band testifies that silver nanoparticles are formed in PMMA and is related to manifestation of the SPR effect in metallic nanoparticles [12–15]. In addition, during the process of polymer implantation, the transmission of the latter reduces, which is caused by breakdown of a polymer chain structure and production of carbon fragments (carbonisation) [16].

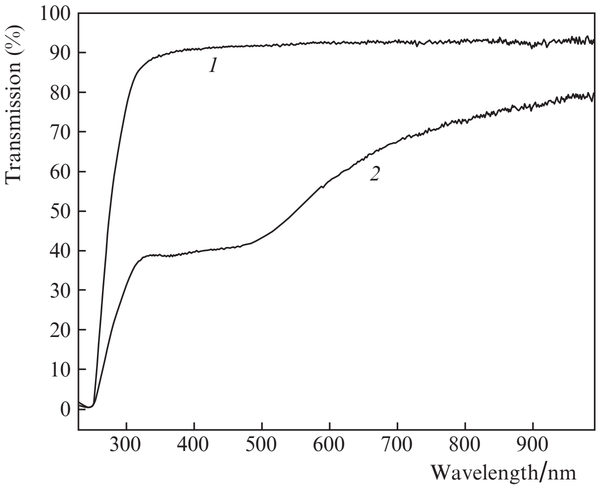

Figure 1. Optical transmission spectra of (*1*) non-irradiated PMMA and (*2*) PMMA with ion-synthesised silver nanoparticles.

It is thoroughly described in [15] that in direct collisions of accelerated metal ions with atoms of irradiated material and in crossing their electron orbits, the implanted atoms actually instantaneously capture released matrix electrons and are neutralised to atoms. An excess of silver atom concentration over a solubility limit in the polymer leads to origin of seeds (which comprise at least three atoms) of metal nanoparticles. Successive arrival of implanted silver ions to polymer, their neutralisation and attachment to temporary seeds results in growing and final formation of stable silver nanoparticles. The process of nanoparticle growing is simultaneously determined by the diffusion coefficient and local concentration of silver atoms, just as it occurs with metals in oversaturated colloid solutions.

Study of the PMMA surface by transmission electron microscope shows that the average dimension of an ion-synthesised silver nanoparticle in the domain not covered by a grid mask is ~10 nm at the implantation dose specified [13]. Micro-diffraction analysis shows that spherical nanoparticles have a face-centred cubic lattice with the lattice constant, corresponding to metal silver. No chemical compounds with silver ions are produced during ion implantation.

An AFM-image of the Ag:PMMA sample surface is shown in Fig. 2 for a domain not protected by the mask. In contrast to the relatively flat surface of non-irradiated PMMA, which roughness was below 1.5 nm, morphology of the implanted domain of Ag:PMMA is characterised by the presence of hemispherical formations – silver nanoparticles. The surface density N of silver nanoparticles is $\sim25\times10^9$ cm^{-2}. The growth of silver nanoparticles in the implanted layer and exposure of a part of them on a PMMA surface (Fig. 2) agrees with the SPR absorption in the optical spectrum (Fig. 1). The exposure

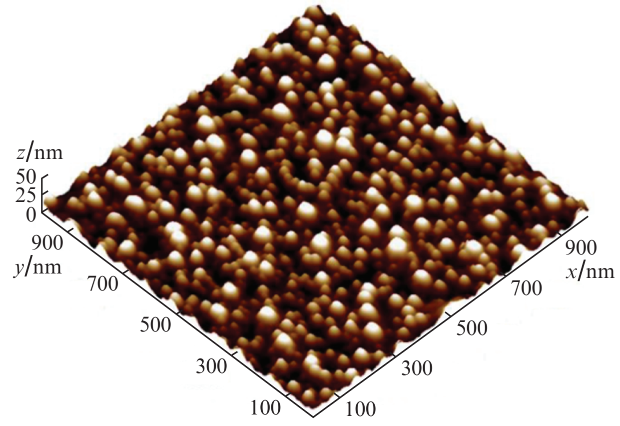

Figure 2. AFM-image of PMMA surface after implantation by silver ions in the domain of polymer not covered by the grid.

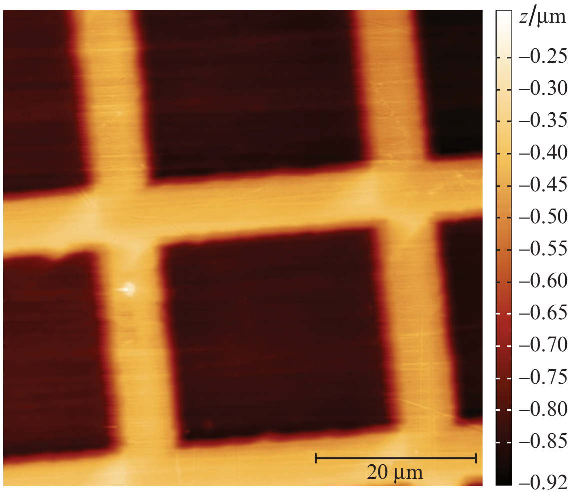

Figure 3. AFM-image of PMMA surface (a fragment of a periodical structure) implanted with silver ions through a surface mask.

is explained by enhanced PMMA sputtering as compared to silver nanoparticles.

An AFM-image of a periodic microstructure surface of PMMA with silver ions implanted though the mask is shown in Fig. 3. One can see that the surface of the irradiated sample looks like an ordered lattice with cells of size 25 µm limited by strips of unimplanted polymer. The ion-irradiated square domain of cells is a polymer with silver nanoparticles shown in Fig. 2, which are characterised by selective SPR absorption (Fig. 1).

It is known that implantation of silver ions into a dielectric and formation of metal nanoparticles in the latter increases its refractive index up to ∼1.7–1.9 in the visible spectral range (especially at the frequencies of plasmon resonance) [17]. Obviously, in the result of ion implantation of PMMA through the mask, a microstructure is formed with a periodically varied phase-contrast distribution of medium optical constants between the cells of grating with silver nanoparticles and cell walls from PMMA ($n_{\mathrm{PMMA}} = 1.5$). Hence, the microsrtusture formed with synthesised silver nanoparticles can be used in practice as a DOE integrated into a structure of an optical temperature contactless sensor.

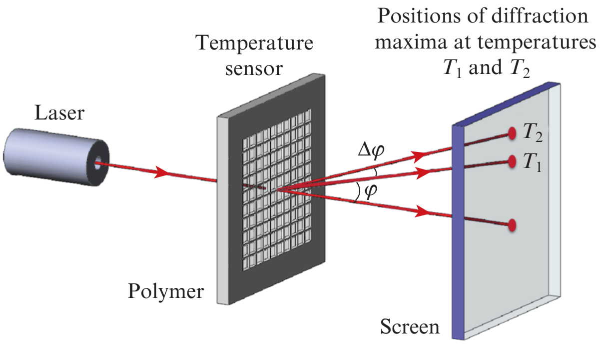

Figure 4. Scheme demonstrating the principle of measuring temperature T by the angle distribution of diffraction maxima $\Delta\varphi$ on a screen, which arises due to variation of lattice geometrical dimensions under heating or cooling.

The fabricated DOE sensor measures the sample temperature by a change of the Fraunhofer diffraction pattern (Fig. 4). An increase or decrease in the period (dimension) of the grating caused by thermal expansion or contraction under a temperature variation leads to redistribution of maxima in the diffraction pattern on a control screen. A current sample temperature T is determined from the value of the deflection angle φ of a diffraction probe laser beam and from the redistribution of diffraction maxima by angle $\Delta\varphi$ on the screen (Fig. 4).

The variation of the diffraction angle $\Delta\varphi$ as a function of temperature ΔT is expressed by the formula [8]:

$$\Delta\varphi = \frac{k\lambda\alpha\Delta T}{\sqrt{d^2 - k^2\lambda^2}}, \tag{1}$$

where k is the order of the diffraction maximum; λ is the wavelength; α is the thermal expansion coefficient; and d is the grating period.

As one can see from formula (1) the coefficient α is proportional to $\Delta\varphi$. Obviously other conditions being equal (k, λ, d), a thermometric device based on a material with a high value of α has a higher sensitivity. In the considered case, the PMMA substrate has $\alpha_{\mathrm{PMMA}} = 5\times10^{-5}\ \mathrm{K}^{-1}$ which is greater than that of silica by more than on order of magnitude $\alpha_{\mathrm{Si}} = 4\times10^{-6}\ \mathrm{K}^{-1}$ [8]. Hence, a temperature sensor based on PMMA has a higher sensitivity (in the temperatures range of operation for this polymer) than a silica DOE. Note that for PMMA the upper limit of operation temperature is below 120 °C, which corresponds to a destruction temperature of the polymer. This value determines the temperature range of practical employment of the polymer DOE.

The thermometric device on the basis of implanted PMMA comprising a DOE was subjected to a sight check by probing the polymer with a He–Ne laser beam ($\lambda = 632.8$ nm). In Fig. 5 one can see a schematic of an experimental setup for studying operation of the optical temperature sensor in the regime of stationary heating or cooling by measuring deviations of diffraction maxima on a control screen while varying the PMMA temperature.

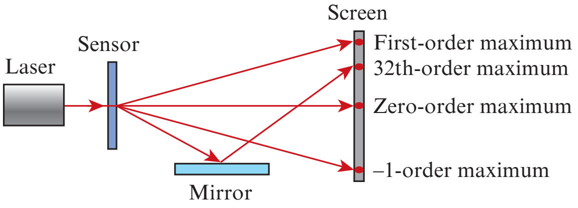

Figure 5. Schematic of the setup for observing the operation of an optical thermometric device in the transmission regime through a polymer sample with a periodic diffraction microstructure.

The diffraction maxima were observed on the screen at a distance of 65 cm from the sample. For better viewing the operation of the temperature sensor, the position of the particular 32th-order diffraction maximum was estimated on the screen relative to the central zero-order maximum. For this purpose, the 32th-order diffraction beam was redirected by a mirror to the screen near the image of the zero-order maximum. Images of shifted diffraction maxima on the screen during sample heating or cooling were recorded by a digital camera. The sample placed on a copper substrate was heated by an electrical coil in the temperature range from 20 °C to 95 °C. The sample temperature was controlled by a thermocouple.

Combined diffraction patterns of zero-, first-, and 32th-order maxima produced by the temperature sensor under PMMA heating are shown in Fig. 6. At an elevated PMMA temperature, one can clearly observe a shift of the 32th-order maximum towards the first-order maximum. In this experimental optical configuration (Fig. 5), the detected shift of the beam by 1 mm corresponds to a temperature change by 25 °C. In Fig. 7 one can see the experimental temperature shift dependence for the 32th-order maximum calculated from experimental data in Fig. 6. One can see that the dependence is linear, and the error of temperature measurement is 4%–5%, which determines sensitivity of the sensor.

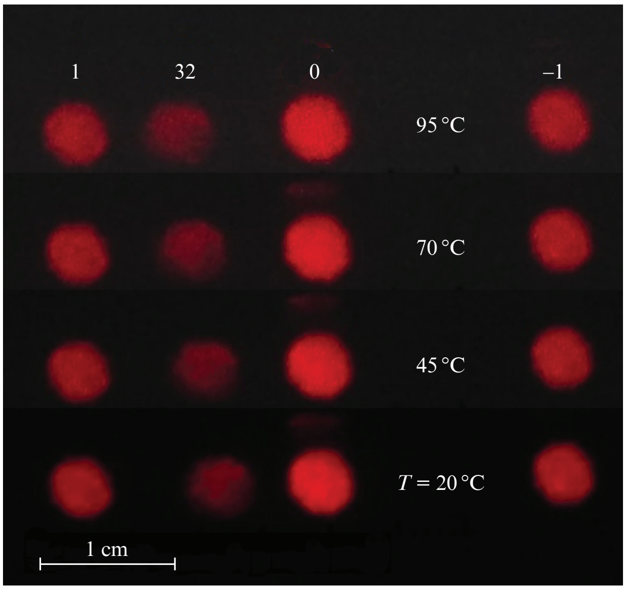

Figure 6. Diffraction patterns of positions of maxima of the orders –1, 0, 1 and 32 on a control screen detected under PMMA heating to temperatures 20 °C, 45 °C, 70 °C and 95 °C.

The microstructure formed at the prescribed implantation regimes with a refraction index periodically varying due to ion-synthesised silver nanoparticles presents a plasmon DOE, which can be used as an optical temperature sensor. Note that the diffraction pattern (Fig. 6) was obtained in a visible spectral range at the wavelengths corresponding to SPR absorption in silver nanoparticles.

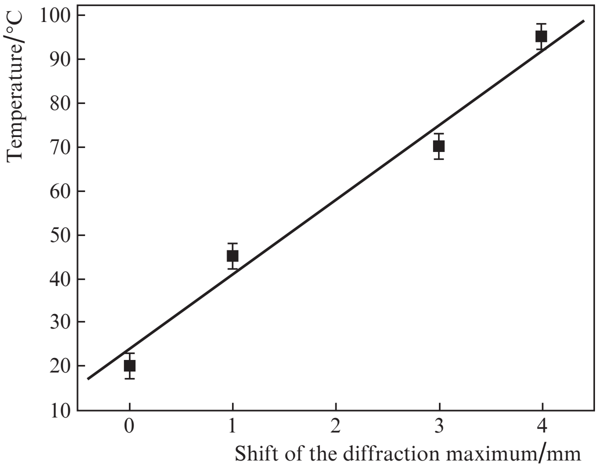

Figure 7. Temperature dependence of the shift of 32th-order diffraction maximum.

Thus, in the present work, the process of ion synthesis of silver nanoparticles in PMMA is considered and the method for designing a two-dimensional plasmon DOE is demonstrated in the case of low-intensity ion implantation of the polymer through a metallic mask. The microstructures are obtained, which have the phase contrast provided by the implanted domains of polymer comprising silver nanoparticles with plasmon resonance absorption. By varying the regimes of ion implantation, synthesising nanoparticles of various dimensions and, thus, changing the effective refraction index of separate elements in DOEs, one can control optical, diffraction, and, consequently, spectral characteristics of the temperature sensor. The design concept of the present work allowed us to receive a favourable decision for the patent for an invention concerning creation of a temperature-sensitive device based on PMMA with silver nanoparticles [18].

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