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LIGA Technology for the Synthesis of Diffractive Refractive Intraocular Lenses

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Abstract—The manufacturing of test diffractive refractive intraocular lenses is illustrated by means of LIGA (deep X-ray LIthography and GAlvanoplastics and polymer forming). Dynamic X-ray lithography used while rotating the substrate versus an X-ray mask fixed in a beam of synchrotron radiation (SR) yields smooth optical 3D surfaces with roughnesses of 10–30 nm rms in polymethylmethacrylate (PMMA) layers. The axisymmetric diffractive refractive profile of a lens is predetermined by the radial angular function of the X-ray mask topology. The quality of the optical surface is reproduced for the nickel master form, which is electroplated onto a gold layer atop the PMMA relief. The optical quality also remains high for replicated lenses synthesized in this manner during silicon polymerization.

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INTRODUCTION

Developing methods for the replication of polymeric microstructured articles is an important branch of science and engineering. Methods for lithography replication combined with galvanoplastics to create metal master forms with the subsequent multiple forming of polymeric articles is used extensively for manufacturing microstructures [1, 2]. The acronym LIGA will be used below to designate the set of these processes, similar to the familiar designation in [1] for such processes in Latin: LIGA is an acronym of the German words Röntgentiefenlithographie, Galvanoformung und Abformung. X-ray lithography combined with penetrating X-ray collimated radiation from a synchrotron source is used to reproduce the geometry of microstructures in the depth of a polymeric layer. The polymer is modified in the area of radiation with a greater accuracy and a higher aspect ratio [3] than in photo- or laser lithography.

A specialized automated LIGA X-ray lithography stand and technological complex [4] were created on the basis of the VEPP-3 electron and positron storage rings at the Siberian Center for Synchrotron and Terahertz Radiation (SCSTR) (http://ssrc.inp.nsk.su/CKP/stations/passport/0a/). Automatized programmed positioning of both the X-ray mask and a substrate with X-ray sensitive material in three coordinates ensures a high degree of flexibility in obtaining geometric variants during X-ray lithographic irradiation. In this work, we used the rotation of a plate made of X-ray sensitive organic glass versus a fixed X-ray mask during irradiation in order to study the possibility of applying LIGA technology to the manufacturing of diffractive lenses [5].

Bifocal intraocular lenses (IOLs) with both refractive and diffractive components are required in ophthalmology [6–7]. They enable the eye to see distant and nearby objects, due to there being two foci in the diffraction component (in the zero and first orders of diffraction). This effect, together with the readjusting of the brain to work with overlapping focused and defocused images, compensates for the inability of the muscle to accommodate the eye with an artificial lens. Such lenses are now manufactured from a flexible polymer and are introduced folded into the patient's eye by an injector through a one-millimeter incision, substantially reducing the post-operative distortion of the eye's cornea and hence increasing the predictability of the result from eyesight correction [8]. In order to form on the retina a color image with distant and nearby objects, without aberration under conditions of varying light intensity, a thin flexible lens must comprise refractive, diffractive and phase components. Developing new methods and technological processes for manufacturing polymer optics, and for creating the relief of a surface that requires the precise reproduction of a complicated function, is therefore an important task.

The IOL relief of the diffractive component can be created using dynamic X-ray lithography on a surface of organic glass made of polymethylmethacrilate (PMMA), irradiated with a dose of X-ray radiation varying in the radial direction and then developed in a solvent [5]. Since direct IOL forming in organic glass by means of dynamic X-ray lithography is not effi-

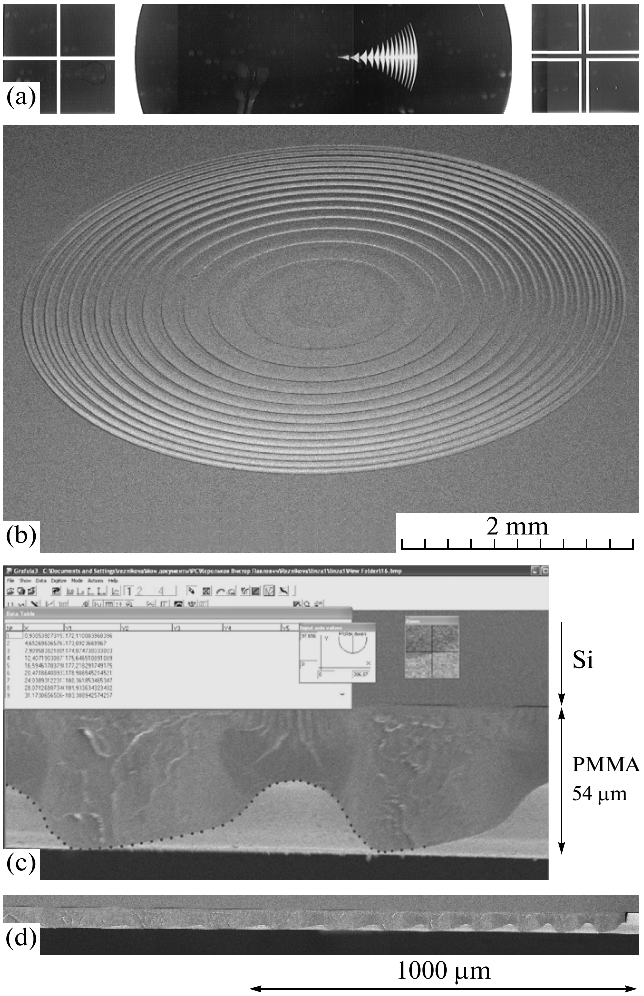

Fig. 1. (a) Fragment of a photomask with a structure of rotation and the signs of alignment registered during observations using an optical microscope. (b) Typical X-ray lithographic rotational replica of a hybrid diffractive refractive lens 5 mm in diameter in 950-PMMA layer with ~50 μm thickness on the substrate during observations using a scanning electron microscope (SEM). (c) Example of measuring the profile of a replica's flank diagonal shear on a SEM slide in the Grafula program; (d) result from stitching the slides.

cient, our work was aimed at developing a better method for manufacturing IOLs from biologically compatible polymer. Here, we present the results from developing a technique that includes the production of X-ray lithography rotation replicas and galvanoplastics for creating metal LIGA master forms, along with polymer forming for the multiple reproduction of polymer lenses with diffractive structures.

X-RAY LITHOGRAPHIC ROTATIONAL REPLICAS

An X-ray lithographic replica formed in the layer of an X-ray resist during the irradiation of a continuously rotating substrate through a mask fixed in a synchrotron radiation (SR) beam will be referred to below as rotational.

Figure 1 shows microscopic images of an initial photomask and the X-ray lithographic replicas obtained using an X-ray mask that corresponds to a photomask with the precision of contact photolithography. The photomask was manufactured by directly producing the topology in a resistive layer using a laser lithographer (Institute of Automation and Electrometry, Siberian Branch, Russian Academy of Sciences, Novosibirsk) and with the automatically controlled rotation and displacement of the substrate [7]. The sizes of the photomask and the corresponding X-ray mask are given in Fig. 2a.

During X-ray irradiation, the fir-tree structure of the X-ray mask is oriented vertically, as is shown in Fig. 1a, with respect to the center of the SR beam. The X-ray mask is held stationary while the substrate with the PMMA layer is rotated. SR intensity is constant in its horizontal cross sections, but it has a Gaussian distribution in the vertical direction. The power of radiation absorbed by the PMMA decreases from the middle of the fir tree to the ends of its branches by ~5%. The plane of the X-ray mask is about 20 m away from the SR source (the wiggler in the VEPP-3 storage ring), whose mean square divergence is 2.5 mrad. The rotating substrate with the PMMA is several millimeters away from the X-ray mask. Since the spectrum of radiation absorbed by the PMMA on the LIGA stand lies in the range of 1–3 Å, the effect of diffraction on the form of the X-ray resistive replica's profile is negligible. The axis of substrate rotation is aligned with the optical axis of the X-ray mask using the appropriate coordinate stages inside the radiation chamber, the test structures in the X-ray mask, and the optical system of the digital display, the X-ray scintillator of which is located near the plane of the irradiated substrate.

The replicas were characterized optically using a HITACHI S 3400N tip II electron scanning microscope, WLI and MI-4 interferential microscopes, MBS-10 and MBI-15 optical microscopes, a photocamera, and visual observation. When polymer with a more uniform molecular mass composition (relative to, e.g., organic glass) is used, an X-ray lithographic replica of a diffractive refractive lens with a 5–26 μm depth of relief is seen by the naked eye as a 3D mirror drop on a surface. The roughness, measured on the replica's surface in a uniform PMMA as the mean square deviation of the profile, lies in the range of 10–30 nm.

To obtain a hard uniform layer of PMMA, we used 950 PMMA A11 X-ray resist produced by MicroChem Corporation (http://www.microchem.com), which is an 11% solution of a polymer with a molecular mass of about 950000 a.u. in anisol. To reach thicknesses of 20–60 μm, the resist must be plated several times by centrifuging and exposed to a low temperature drying process that yields a residual concentration of anisol in layers of less than 10%. Replicas were developed in a so-called GG solution [2].

DESIGN OF THE MASK

The topology of the photomask's rotational figure (an open field for radiation; see Figs. 1a and 2) is characterized by a radial angle function with a division into m zones with radii $r_m = (m\lambda F_m/n_e)^{1/2}$, where λ is the length of a wave of visible light, F_m is the focal length, and n_e is the index of medium refraction. The fractions of the angle function at the boundaries between the neighboring zones are close to perpendicular to radial axis r in the radial system of coordinates. The angle function in the limits of each zone is the linear $\varphi_m(r) = (r - a_m)/b_m$. The lines of the zones differ by the coefficient of inclination to the x-axis and the zero ordinate, since the angle maxima $\varphi_m(r_m) = \frac{r_m}{\text{const}}$ are located on a straight line that crosses the mask's axis of rotation. The optical design thus includes diffractive and refractive components, and the test topology allows us to find the parameters of nonlinear deviation for the LIGA processes.

The photolithography and electrochemical gold plating that we used in [4] to produce an absorbing 20 μm-thick layer on the glassy carbon plate of the X-ray mask introduce a systematic error into the topologic polar angle function of rotation element $\varphi_0(r)$. The reasons for deviations $\varphi(r) = \varphi_0(r) + \Delta\varphi_0(r)$ are diffractive photolithographic distortions and modifications in the topological geometry of materials with different coefficients of thermal expansion during heating and cooling in the gold galvanic process. The photomask's topological profile measured using the Grafula digital program for microphotos differs from the fir-tree profile of the X-ray mask (Fig. 2a) by a value of less than $\Delta\varphi_0(r)/\varphi_0(r) < 5\%$. During static X-ray lithography, the change in the geometry of the resistive replica compared to the topology of the X-ray mask is negligible.

Spatial distribution (1) of the SR dose absorbed in the X-ray sensitive layer is proportional to the radial angle function of the photomask's fir tree and is independent of the rate of rotation:

$$D(r) = k\varphi(r), \tag{1}$$

Coefficient of proportionality k (2) is calculated using the Mathcard program, allowing for the geometric and spectral features of the photon source on the VEPP-3:

$$k = It\iiint\prod e^{-\mu_i(\lambda)d_i}\mu(\lambda)e^{-\mu(\lambda)z}d\lambda dz. \tag{2}$$

where It is an exposure dose that includes the parameters of the synchrotron radiation source and the time of exposure; $\mu_i(\lambda)$ and $\mu(\lambda)$ are the table spectral linear coefficients of absorption for the materials and media with thicknesses of d_i, located in the SR beam in front

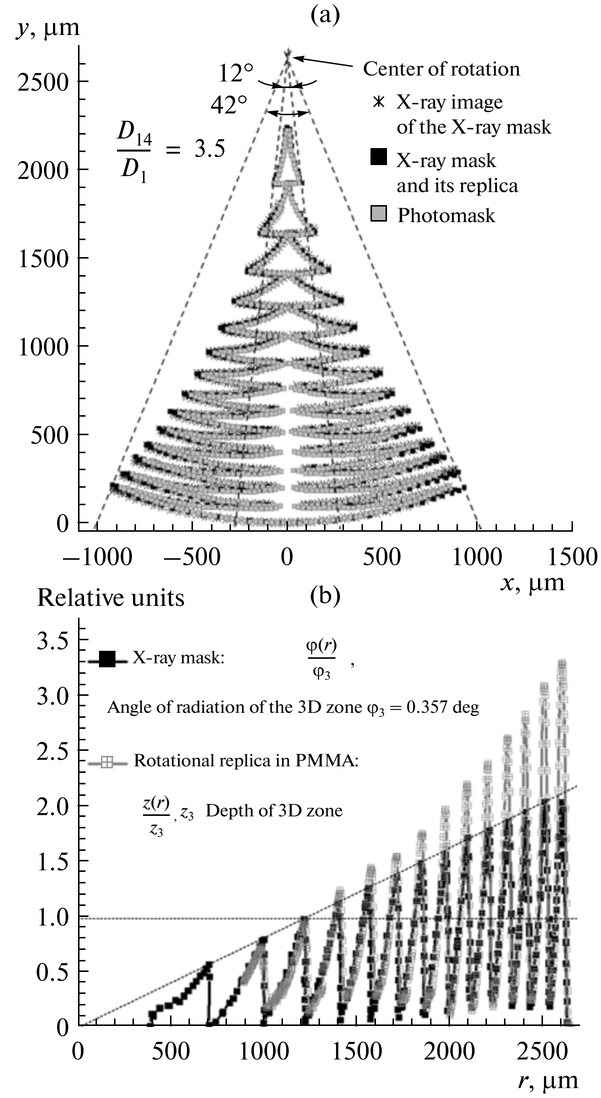

Fig. 2. (a) Measured coordinates of the boundaries of the masks' absorbing layers using their digital images and (b) the normalized angle function of the X-ray mask, relative to the normalized radial profiles of X-ray lithographic rotational replicas in PMMA.

and in back of the resist layer, respectively; and z is a coordinate in the depth of the resist.

The exposure dose of radiation is selected so that at a preset depth of development, the dose of the absorbed radiation is close to the threshold characteristics for the PMMA. The characteristic function of rate υ of the development (dilution) of the irradiated polymer and time τ determine depth z of the X-ray lithographic profile (3). Substituting (1) into (3), we obtain controllable dependence (4) of the radial function of the relief depth in PMMA on the geometry of the rotational figure in the plane of the x-ray mask:

$$z(r) = \upsilon\tau; \quad \upsilon = AD^B, \tag{3}$$

$$z(r) = \tau Ak^B(\varphi(r))^B = \tau w(\varphi(r))^B, \tag{4}$$

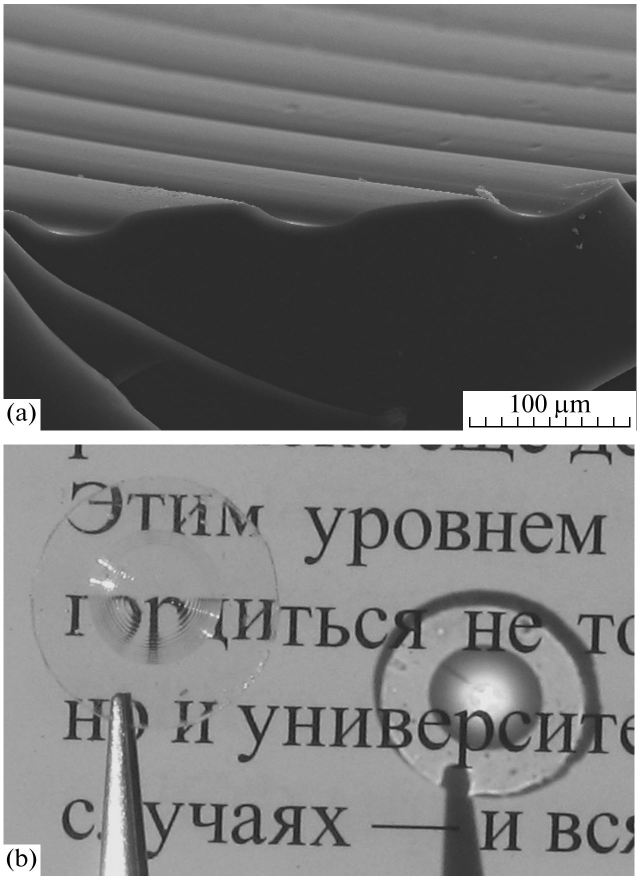

Fig. 3. (a) Flank of a cross section of a silicon LIGA replica obtained via polymerization of Sylgar-184 elastomer in a galvanic nickel master-form. (b) Photo of a transparent thin silicon diffractive refractive lens held with a pincette over a sheet of paper. The bright spot on the paper in the center of the shadow from the lens is a focusing of sunlight.

where A, B and w are empirical values with the technological working ranges $w = 0.3 \pm 0.1$ μm s^{-1} rad^{-B} and $B = 1.6 \pm 0.04$ for dimension [φ] = rad.

MANUFACTURING THE LIGA MASTER FORM

In developing the technology for the electrochemical plating of a metal master form atop a replica of a three-dimensional lens in PMMA, the optimal solutions had to be found for the material of the electrochemical underlayer and its electrical contact, plus the designs of the anode and cathode, the composition of the galvanic bath, and the process parameters. Among the electrochemical metals, nickel was selected as our material for electroplating the master form, as it is a hard and chemically resistant metal that can be fixed by a magnetic field. Nickel sulfamate ensures the highest concentrations of cations in water solutions. A galvanic bath with more than 30% concentrations of this salt has high chemical inertance and reproducibility of the parameters of the process during multiple plating. Surfactants, amphiphilic and anionactive compounds, and a weak acid about 1% each were added to the electrolyte solution to ensure the deposition of pure metal and reduce strains in the sediment. For this very purpose, the electrolyte was mechanically stirred, and the current density in it was adjusted to the rate of the process, i.e., 1 μm/min at the optimum temperature of ~55°C. The heat capacitive galvanic bath was covered with a lid, one half of which contained a fixed anode made of a bent 1 cm-thick nickel sheet; on the other half was a holder with a cathode. The cathode was a specimen with microstructures in the PMMA layer. The electroconductivity of the cathode surface was ensured by a 30–50 nm thick gold film, plated on the x-ray resistive relief in PMMA by physical electron sputtering. Electrical contact with the gold thin film on PMMA is made using a wire in the form of a small, soft multi-core copper brush. An adhesive band and/or frames made from organic glass with geometric packing are used for insulation.

Plasticity, the higher coefficient of thermal expansion of gold compared to nickel, the strong metallic gold–nickel linkage, chemical inertness, and weak adhesion to polymers facilitate the flawless replication of a 3D surface in galvanoplastics and the reproduction of its optical quality, both when separating the rotation replica of the PMMA layer and the multiple separation of thin polymer lenses.

LIGA SYNTHESIS OF 3D LENSES

Compared to the thermal pressurizing of ready-made polymers under low temperature polymerization, liquid prepolymers and elastomers fill in a form perfectly.

For the LIGA synthesis of polymer lenses, we used elastomer and the Sylgard-184 polymerization initiator (http://www.everbrightsolar.net/sylgard-184-silicone-elastomer-kit-encapsulation-184.html) produced by Dow Corning for coating solar electric batteries with a protective transparent polymeric cover. Optical silicon was polymerized in a LIGA master form for several days at room temperature, and for several hours under heating. A thin silicon lens is fairly flexible for twisting; it is solid, uniform, transparent in visible light, and tearproof. The chemical atomic composition was measured using an INGA ENERGY electron-probe energy-dispersive spectrometer. Except for hydrogen, the composition of Sylgard-184 polymer was (in at %) C : O : Si = 50.85 : 35.13 : 13.40. Figure 3 shows the flank of a cut/torn three-dimensional silicon lens, and a photo of it focusing the radiation from an external source.

CONCLUSIONS

Research was performed aimed at developing unique LIGA technology to manufacture IOLs. The optimum materials and process parameters for X-ray lithography, the electrochemical plating of a master form, and the multiple reproduction of polymer articles were determined. Thin diffractive refractive lenses synthesized in a LIGA master form by silicon polymerization were studied. Measurements of the geometry of the lithographic masks were adjusted to the 3D profiles of the lenses' surfaces at each stage of LIGA replication. The basic functions for technologically designing the topology of masks to create relief optical surfaces were determined using X-ray lithography during rotation. Continuation of our work will be aimed at determining the possibilities of LIGA technology for obtaining thin intraocular lenses with any degree of complexity of preset relief and depth functions for use in surgery.

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