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REPLICATION OF PERIODIC STRUCTURES IN POLYMER MATERIALS

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Periodic structures of Si(001) and quartz glass master-matrices with the period of 4 μm and the polymer replicas fabricated by imprint lithography and UV light hardening techniques were investigated. The profile of the structures was examined by atomic force microscopy. Diffraction efficiency of the periodic structures was measured experimentally and calculated theoretically employing the integral technique. The results obtained show the diffraction efficiency to be an efficient tool for the control of surface relief formation during etching of master-matrix and its replication. It is shown that the quartz glass master-matrix is more efficient both for the imprint and UV hardening polymer replication as compared to the silicon one.

Keywords: polymerization, rheology of polymers, diffraction gratings, nanolithography, polymers as optical materials

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1. Introduction

Interest in diffractive optical elements (DOEs) for optical interconnects, optical imaging, optical data storage, laser machining, and optical sensors has grown rapidly in recent years [1]. DOEs are smaller in size and lower in weight than conventional optical elements and allow for integration of several functionally different optical components into a single combined element reducing the system complexity. Various types of DOEs in a form of Fresnel zone lenses, phase correcting elements, beam deflection elements, the zero-order gratings, and polarization elements have been implemented for optical interconnects [2, 3].

Here we present a study of the diffraction efficiency of replicated polymer-based periodic structures. Polymers are receiving global attention due to their wide-scale applications in planar photonics and optoelectronics including optical interconnects [4], switches [5], splitters [6], and surface relief structures [7]. This is a direct result of the relative ease and cost effectiveness with which planar polymeric structures can be fabricated as compared to semiconductor and oxide analogues, while maintaining the required performance levels. Polymers at the temperature above their glass transition are liquids, but with a rather high viscosity. These technological aspects are extremely important in polymer-based microtechnology [8, 9].

Diffraction efficiency of visible light is known as one of the most flexible methods for evaluation of geometrical parameters of diffraction gratings [10] as well as for control of the surface relief formation during fabrication of the master-matrix (see, e. g., [11]) and replication of the structures. The correlation between diffraction spectra and the surface relief parameters for the silicon master-matrix as well as for the polymer films has been demonstrated [12]. It has been shown that the diffraction efficiency of periodic structures can be controlled by changing the geometrical dimensions of a groove, i. e. the ratio of the ridge width and depth.

In the present study we examine the diffraction efficiency of the planar periodic structures of the crystalline Si(100) and quartz glass master-matrices and their polymer replicas fabricated by the imprint lithography and UV light hardening techniques.

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2. Experimental

2.1. Master-matrix

Two different master-matrices, the crystalline silicon (100) matrix and the quartz glass one, were investigated.

The crystalline Si(100) master-matrix was fabricated by the standard contact-optical lithography technique and reactive ion etching (RIE) using the plasma-etching set-up PK-2420RIE. The periodic trapezoidal profile structures with the period $d = 4$ μm and the depth $h = 0.5$ μm (see Fig. 1 and Table 1) were produced by RIE in the SF_6/N_2 gas mixture plasma at the RF power density of 0.6 W/cm^2 varying the etching exposure time (and keeping fixed other RIE parameters).

The quartz glass master-matrix was fabricated by RIE in $CF_4 + O_2$ plasma at the RF power density of 0.6 W/cm^2 using an aluminum mask, which after etching was removed in Cr_2O_3:NH_4F:H_2O solution. The profile of the matrix obtained was the same as that of the Si(100) matrix (Fig. 1 and Table 1).

The linear dimensions of surface areas of the master-matrices obtained were much larger than the He–Ne laser light wavelength, 0.6328 μm, used in the optical analysis.

2.2. Polymer replicas

The polymer replicas were fabricated using two different commercially available acrylic polymers, PMMA (polymethylmethacrylate) and photopolymer (acrylic trimethylolpropane ethoxylate). Respectively, two different replication techniques for a fabrication of periodic structures in the acrylic polymer films were used: the imprint lithography for photopolymer on PMMA and the UV light hardening for photopolymer on the master-matrix [14].

The imprint was carried out using the flat thermal pressure device of original design controlling the pressure, $p = 5$–10 MPa, the temperature, $T = 80-120\,^{\circ}$C, and the exposure, $t = 20-60$ s.

The UV light hardening replication was carried out with the photopolymer (the layer thickness of 2 μm, the area of 3 cm^2) on the quartz glass or crystalline silicon substrates using an original technological device ($T = 20\,^{\circ}$C, the irradiation distance of 10 cm, UV light source DRT-230, $\lambda = 360$ nm, $I = 10^4$ lx). The polymerization kinetics was controlled using a polarization microscope. The photopolymer layer was repeatedly scanned in a 5 s time interval and a uniform layer was observed after the exposure of 50 s. It should be mentioned that the photopolymer for UV light hardening is usually a complex mixture of the polymer, monomer, binders, photoinitiators, and sensitizers. The full conversion of the photopolymer can be ensured by monitoring the light source, photoinitiator package, and exposure conditions.

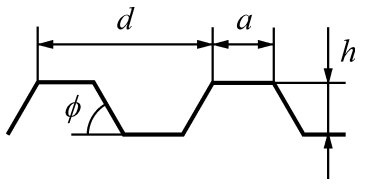


Fig. 1. Profile of the periodic structures investigated.

Table 1. Geometrical parameters of the periodic structures investigated (see Fig. 1): the ridge width a, the side wall angle ϕ, and the depth h. The period of master-matrices is $d = 4$ μm.

	a (μm)	a/d	ϕ	h (μm)
Master-matrix				
crystalline Si(100)	1.9	0.48	82°	0.5
quartz glass	1.4	0.35	82°	0.5
Photopolymer replica (UV hardening)				
from Si	2.1	0.49	82.5°	0.25
from quartz glass	2.63	0.66	78°	0.44
Imprint replica				
from quartz glass	2.46	0.67	78°	0.43

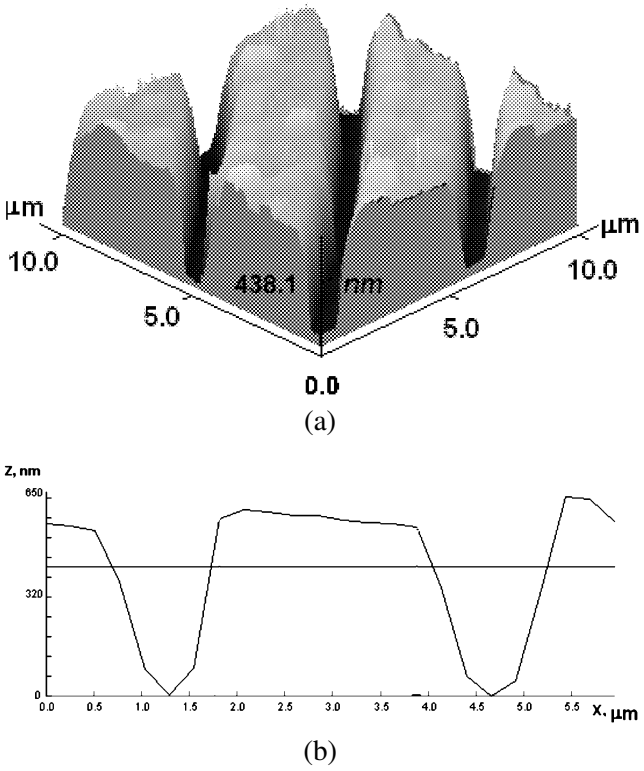
2.3. Analysis techniques

The profile of the periodic structures fabricated was examined by the atomic force microscope NANOTOP-206 operating in a contact mode. The silicon cantilever with the force constant 0.35 N/m was used. The optical response of the structures was investigated by the optical diffraction set-up (equipped with He–Ne laser, $\lambda = 632.8$ nm, and a photodiode as a detector) and the laser ellipsometer GAERTNER L115 ($\lambda = 632.8$ nm).

3. Results

3.1. AFM analysis

The profiles of the silicon and quartz glass master-matrices, determined by the atomic force microscopy (AFM), are presented in Figs. 2 and 3. The geometrical parameters both of the matrices and of the replicated structures are summarized in Table 1.



(a)

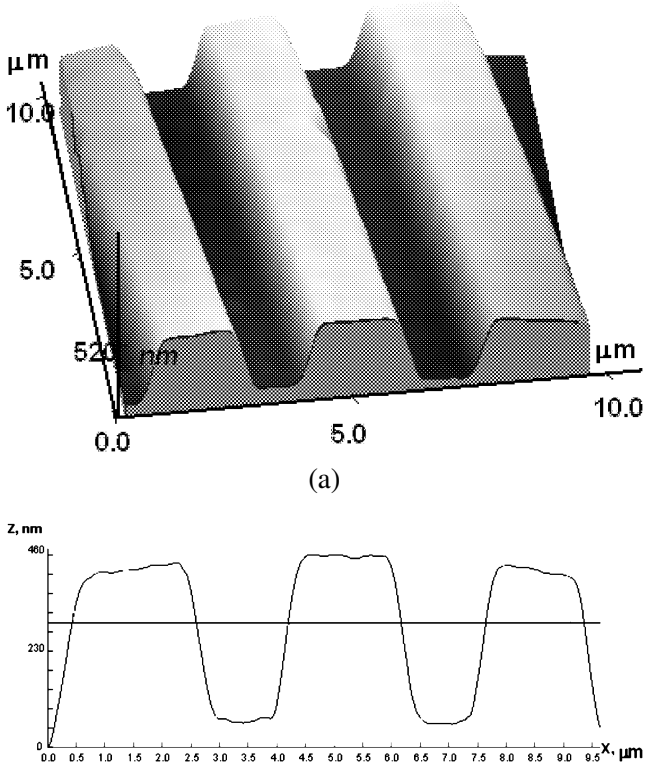
(b)

Fig. 2. (a) The 3D AFM image and (b) topography profile of the Si(100) master-matrix structure (of the depth $h = 0.5$ μm and the period $d = 4$ μm).

Figure 4 presents the AFM 3D image of the quartz glass master-matrix imprint replica in photopolymer on PMMA with the layer thickness of 1.8 μm. The imprint replica was fabricated at $p = 10$ MPa, $T = 112\,^{\circ}$C, and $t = 30$ s. As seen from Figs. 3 and 4, the geometrical parameters of the replica are distorted as compared with those of the reverse master-matrix. The depth of grooves decreases by about 20 nm and the period increases by about 200 nm during replication. The distortion is due to the plastic flow of the polymer during replication and the elastic macroscopic expansion of the structure. The resulting 2D structure, produced by an imprint, expands macroscopically by about 5%. To reveal an underlying mechanism of the period variation, additional experiments are required, which would enable for control of the imprint kinetics.

Unfortunately, the imprint technique used has not allowed us to fabricate the imprint replicas of the silicon master-matrices, contrary to the earlier successful replication of the shallow periodic Si structures [12].

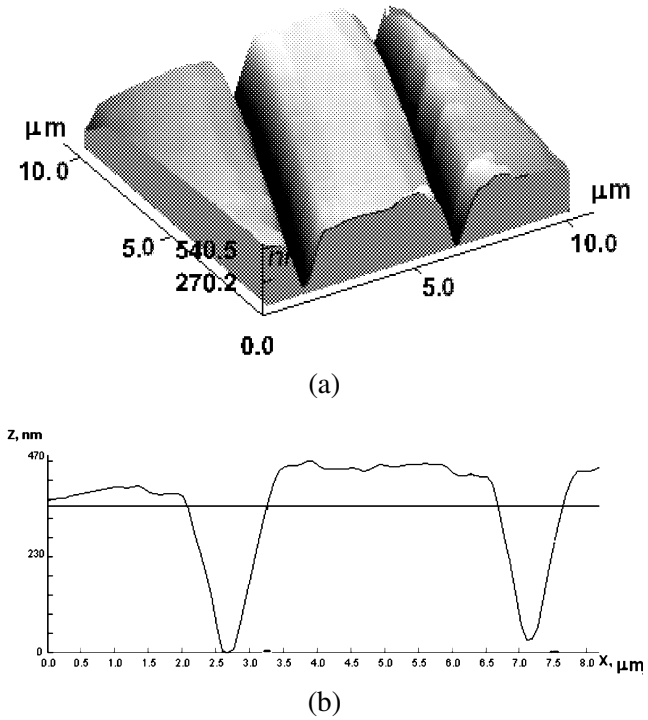
The technological imprint parameters were out of the range of the necessary conditions for an efficient relief transfer from the silicon matrix to the polymer which could be considered as a noncompressible Newtonian liquid [9]. An increase in the groove depth of the



(a)

(b)

Fig. 3. (a) The 3D AFM image and (b) topography profile of the quartz glass master-matrix structure (of the depth $h = 0.5$ μm and the period $d = 4$ μm).



(a)

(b)

Fig. 4. (a) The 3D AFM image and (b) topography profile of the imprinted quartz glass master-matrix structure shown in Fig. 3.

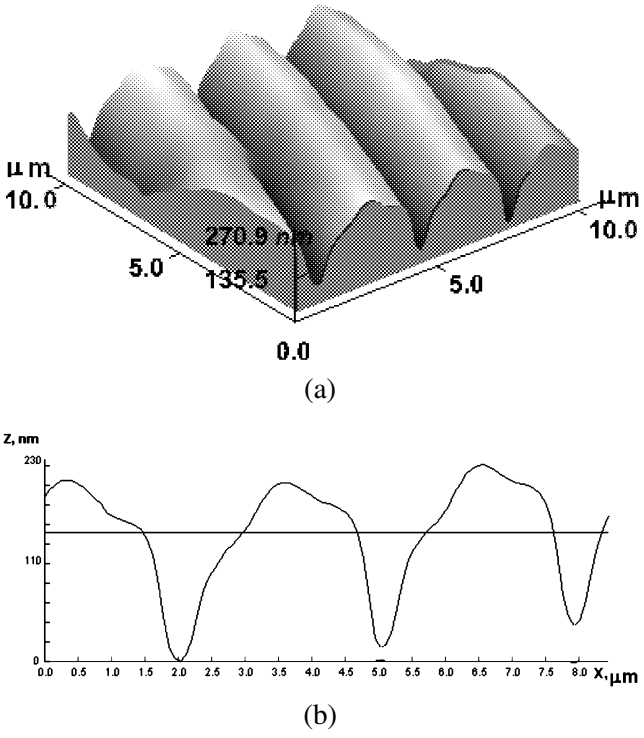


Fig. 5. (a) The 3D AFM image and (b) topography profile of the photopolymer replica of the Si master-matrix structure shown in Fig. 2.

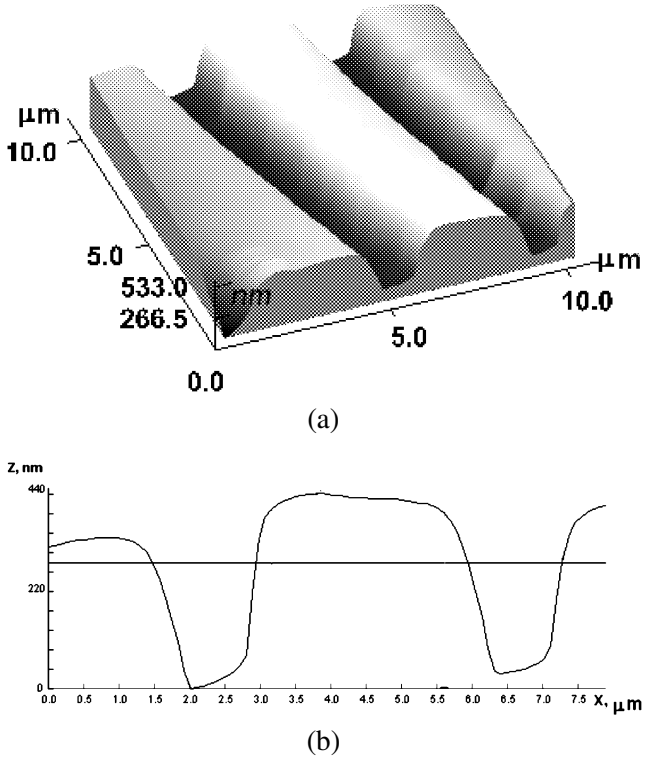


Fig. 6. (a) The 3D AFM image and (b) topography profile of the photopolymer replica of the quartz glass master-matrix structure shown in Fig. 3.

silicon matrices used in the present experiments was found to be crucial. An estimated pressure in the imprint press exceeded the strength of the silicon matrix and simply led to matrix breakdown.

Atomic force microscopy investigations have demonstrated that replication of the silicon master-matrix structure in the photopolymer layer using the UV hardening process is not efficient as well and leads to essential distortions of geometrical parameters (Fig. 5). During the UV hardening the trapezoidal profile of the silicon master-matrix is converted to the sinusoidal one and the height of the replicated structure decreases twice.

The quartz glass master-matrix structure replicated in the photopolymer layer using the UV hardening process is shown in Fig. 6. The depth decreases by about 20 nm and the period increases by about 200 nm as compared with the geometrical parameters of the reverse master-matrix, but the distortion is much smaller than that in the silicon master-matrix replicated structure.

3.2. Diffraction efficiency

The diffraction efficiency is defined as the ratio of the intensity of light reflected by a periodic structure in the given diffraction order $I(\theta)$ to the intensity of the incident light $I(0)$. The ratio $I(\theta)/I(0)$ for the linear diffraction grating is determined by the expression [10]

$$I(\theta) = I(0)\left(\frac{\sin\alpha}{\alpha}\right)^2\left(\frac{\sin N\beta}{\beta}\right)^2, \qquad (1)$$

where the coefficients $\alpha = (\pi a/\lambda)\sin\theta$ and $\beta = (\pi d/\lambda)\sin\theta$ are related with the main parameters of the diffraction grating, the ridge a and the period d, and with the angle of diffraction θ.

The diffraction efficiency for 2D structures investigated in the present work was measured experimentally and calculated theoretically employing the commercial computer program PCGrate 2000MLT based on the integral method [13]. The integral method is the only rigorous technique which enables one to examine the diffraction efficiency of the grating with a real groove profile in an arbitrary spectral range. In this method, integration of the surface current coincides with the real surface of the grating border and a groove profile can be represented not in a distorted form, unavoidable in Fourier expansions [13], but in an accurate form by means of the collocation points coinciding with points of the real groove profile. Thus, the technique allows for rigorous description of an ar-

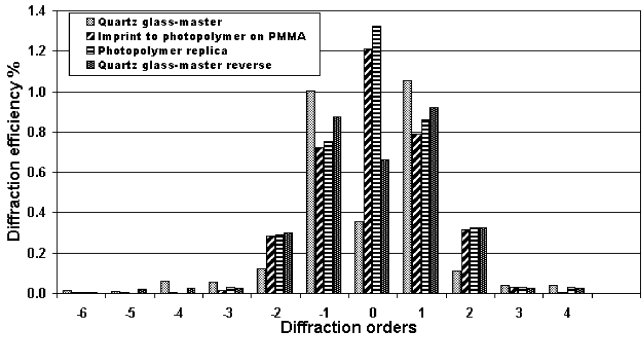


Fig. 7. Theoretical diffraction efficiency of different diffraction orders for the periodic structures of the quartz glass master-matrix, imprint replica, and photopolymer replica. The results were obtained with simulation code PCGrate.

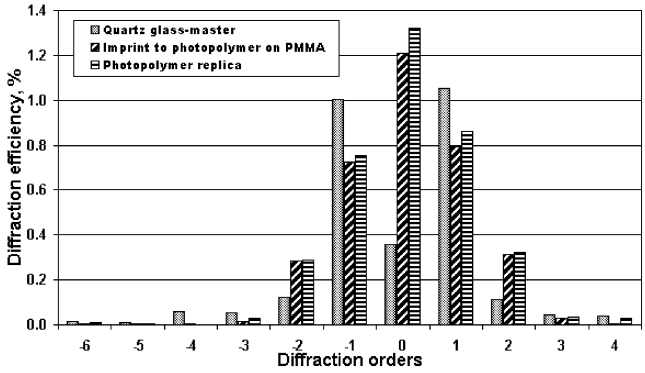


Fig. 8. Experimental diffraction efficiency of different diffraction orders for the periodic structures of the quartz glass master-matrix, imprint replica, and photopolymer replica.

bitrary profile function accounting for all its and its first derivative jumps. This is especially important for the modelling and fine tuning of the diffraction efficiency of the structures, the microroughness of which should be taken into account.

The simulated and experimentally measured diffraction efficiencies of different diffraction orders for the quartz glass and Si(001) master-matrices, the imprint replica to photopolymer on PMMA, and the photopolymer replica are presented in Figs. 7 and 8. The sets of parameters presented in Table 1 were used in theoretical calculations. As seen from the figures, the theoretical results nicely fit the experimental data.

Figure 9 illustrates the influence of the ridge width a on the diffracted efficiency of the -2, -1, 0, 1, 2 diffraction orders for the quartz glass master-matrix, the imprint to photopolymer on PMMA, the photopolymer replica, and the reverse quartz glass master-matrix.

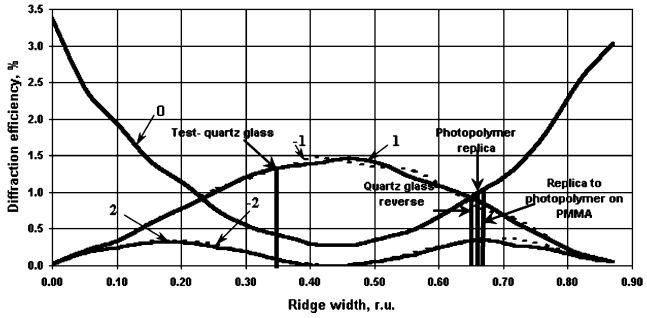


Fig. 9. The dependence of diffraction efficiency on the ridge width a for the periodic structures with the period $d = 4$ μm and the profile depth $h = 0.5$ μm. Numbers at the curves indicate the diffraction orders, and vertical lines indicate the ridge widths of experimentally investigated structures.

4. Discussion

The results of simulations presented in Figs. 7 and 9 demonstrate that variation of the groove depth contributes essentially to the diffraction efficiency of periodic structures. Keeping the depth of grooves constant and varying the width of the ridge, one can induce the wave intensity redistribution in different diffraction orders. Choosing the value of the ridge width within the interval of $0.22 < a/d < 0.64$, one can reduce significantly the intensity of the zero-order maximum increasing simultaneously the efficiency of the first-order maximum. This fact is extremely important in practical applications which implement periodic structures as the dispersion elements, because the central maximum does not contribute to the dispersion.

Summarizing the results of experimental measurements and mathematical simulations, one can conclude that the diffraction efficiency in different diffraction orders is an effective tool for determination of both the geometrical parameters of the periodic profile and efficiency of replication of the profile in polymer materials.

The experimental and simulation results presented above illustrate that the replication process leads to a loss of diffraction efficiency. This is due both to the reverse of geometry (the reverse matrix is less efficient) and to profile distortions during imprint or UV hardening. Obviously, the physical factors determining distortions in the imprint or UV hardening techniques are different.

Despite the fact that the silicon-based technology is widespread and well documented [9], applications of silicon matrices are rather limited by a narrow range of the imprint replication technological parameters due to mechanical properties of Si matrices. The plastic

deformation of the polymers used in replication determines additional restrictions to the technological parameters. Considering the polymer during imprint as a noncompressible Newtonian liquid in the limit of low viscosity η, for a simple circular geometry one can obtain [9] the following relation between the actual polymer height $h(t)$, the stamp radius R, and the vertical imprint velocity $v(t)$:

$$v(t) \approx \frac{p_{\text{eff}} h^3(t)}{\eta R^2}. \qquad (2)$$

As seen, the geometrical parameters of the stamp and the elastic properties of the polymer dictate the value of the effective pressure p_{eff} to be used for the replication. This is the main reason for disadvantage of the silicon master-matrices as compared to the quartz glass ones.

The performed measurements of the diffraction efficiency of the quartz glass master-matrix replicas fabricated by UV hardening indicate that the diffraction efficiency decreases by about 20% as compared to the efficiency of the initial matrix. This is primarily due to the distortions of linear dimensions of the resulting polymer structure.

Unfortunately, the UV hardening method is not efficient for replication of the deep silicon master-matrix structures. Essential distortions of linear dimensions were revealed and the diffraction efficiency for the investigated geometry was too low for its experimental examination. To repeat the profile of the silicon master-matrix with a minimal distortion one has to change the concentration of photopolymer components taking into account adhesion properties of the silicon surface. The contact angle measurements reveal that the resultant profile is sensitive to the composition of polymer and to the surface properties of the matrix.

5. Conclusions

The acrylic polymer periodic structures for UV light diffraction gratings were fabricated as replicas of the Si(100) and quartz glass master-matrices with the period of 4 μm and the depth of 0.5 μm by the imprint lithography and UV light hardening techniques.

The replication induces distortions of the reverse master-matrix geometrical parameters. The depth of the initial profile decreases by about 20 nm and the period increases by about 200 nm, when the quartz glass master-matrix is used for replication.

Only the shallow gratings can by produced by the imprint on silicon matrices. The deep silicon master-matrix replicas can be obtained by the UV light hardening technique, but to avoid essential distortions of the resulting profile an optimization of the photopolymer components and of adhesion parameters of the silicon surface is required.

Investigations of the diffraction efficiency in different diffraction orders is an effective tool for determination of details of the periodic profile as well as of the replication efficiency in polymer materials.

Acknowledgement

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PERIODINIŲ DARINIŲ ANTRINIMAS POLIMERINĖSE MEDŽIAGOSE

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Santrauka

Naudojant standartinius litografinius ir cheminio bei plazminio ėsdinimo technologinius metodus, kristaliniame silicyje (100) ir kvarciniame stikle buvo suformuoti periodiniai dariniai, kurių periodas $d = 4$ μm, profilio gylis $h = 0{,}5$ μm. Dariniai buvo antrinami polimerinėse medžiagose (polimetilmetakrilate, akriliniame trimetilolpropanetoksilate), naudojant įspaudimo ir UV kietinimo metodus. Atlikti periodinių darinių difrakcinio efektyvumo eksperimentiniai ir teoriniai (naudojant PCGrate 2000MLT programą) tyrimai. Atlikta įvairių technologinių procesų įtakos periodinių darinių difrakciniam efektyvumui analizė. Darinių paviršiaus reljefo morfologijos tyrimai atlikti atominių jėgų mikroskopu NT-206, optinio atsako tyrimai – naudojantis lazeriniu ($\lambda = 632{,}8$ nm) difrakcijos stendu.