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To cite this article: Tina Sabel, Gonzalo de Vicente Lucas & Marga C. Lensen (2019) Simultaneous formation of holographic surface relief gratings and volume phase gratings in photosensitive polymer, Materials Research Letters, 7:10, 405-411, DOI: [10.1080/21663831.2019.1621956](https://doi.org/10.1080/21663831.2019.1621956)

To link to this article: <https://doi.org/10.1080/21663831.2019.1621956>



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Published online: 30 May 2019.



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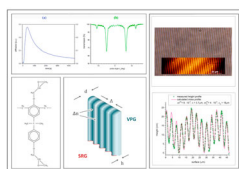
Simultaneous formation of holographic surface relief gratings and volume phase gratings in photosensitive polymer

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ABSTRACT

We report on secondary surface relief grating formation associated with holographic recording of volume phase gratings in epoxy-based, free-surface, volume holographic recording material, as well as in pure Epon SU-8 photoresist. Light-induced gratings are formed simultaneously by photo-triggered mass migration in the cause of component diffusion. Height profiles of surface relief gratings are compared with refractive index modulation profiles of corresponding volume phase gratings. Parasitic volume gratings and non-sinusoidal profiles are also investigated. Based on the correlation of volume and surface gratings, analysis of the height profiles allows conclusions to be drawn on the mechanisms of volume holographic grating formation.



IMPACT STATEMENT

This paper reports on correlated volume and surface gratings, offering novel analytical possibilities to contribute to a deeper understanding of the holographic grating formation process.

ARTICLE HISTORY

Received 12 November 2018

KEYWORDS

Photosensitive materials; polymerization–diffusion process; diffraction gratings; volume holographic gratings; surface relief gratings

Introduction

Diffraction structures can be found on the surface as well as in the volume of optical materials. Corresponding representatives are surface relief gratings (SRGs) and volume phase gratings (VPGs), respectively. Both can be light induced, e.g. by means of holographic recording, but they differ fundamentally in the mechanism of the diffraction of light, as well as regarding their particular characteristics such as achievable diffraction efficiency and, as a consequence, also with regard to their specific applications.

Most photosensitive materials are designed either for volume or for surface patterning. However, some systems have been described for hybrid volume/surface gratings, where a periodic modulation of the surface is observed in addition to a volume phase grating [1–3]. Such dual grating structures are of exceptional interest for many applications such as the fabrication of diffractive solar

concentrators [4], for protective technologies [3,5] or for multi-functional optical systems as tailor-made diffractive devices, for example, for enhanced multilevel security or integrated optics [6], as well as for biomaterials such as for novel intraocular lenses (IOLs) [7].

Double periodic structures can coexist independently of one another but may also be correlated. Correlated grating structures are formed where modulations of refractive index and thickness arise as a consequence of photopolymerization and mass transport processes [8,9]. This is the case for polymers where volume holographic grating formation can be attributed to an interplay of polymerization and diffusion, induced by the spatially modulated exposure: a light pattern is projected onto the photosensitive medium, inducing local polymerization, proportional to the light intensity. Thereupon, a chemical gradient is induced, resulting in monomer diffusion and subsequent polymerization. As a consequence, the

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Supplemental data for this article can be accessed here. <https://doi.org/10.1080/21663831.2019.1621956>

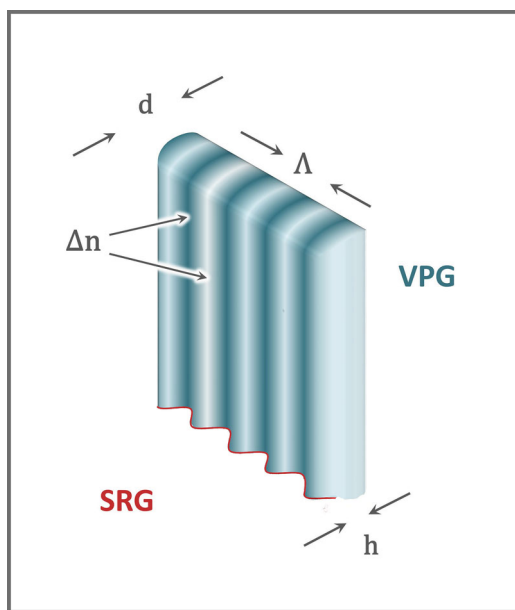


Figure 1. Scheme of hybrid volume/surface grating (VPG and SRG) with corresponding parameters: grating constant Λ , thickness d , refractive index contrast Δn and profile height h .

hologram is formed as a periodic modulation of optical properties, according to the recording light pattern [6]. It is known that diffusion plays a crucial role in photopolymer shrinkage [6,10]. Here, SRGs can be formed as a result of optical shrinkage of the photosensitive material in the course of photo-triggered mass migration.

A deeper understanding of the underlying grating formation mechanisms is most important for the development of advanced materials and the corresponding opening of novel applications [6,11]. With regard to the analysis of the structures, surface gratings are much more easily accessible, compared to volume gratings [12]. In the case of correlated volume and surface gratings, this leads to the unique opportunity to derive information on the volume grating, based on investigations of the surface profile.

To illustrate the correlation of hybrid volume/surface gratings, Figure 1 shows a scheme of such dual gratings with their respective descriptive parameters. The volume phase grating is specifically characterized by its thickness d and the refractive index contrast Δn ; the surface relief grating by its height h . Shared parameters are the grating constant Λ and the shape of the profile.

The shape of the profile for both, surface and volume gratings, can be characterized by means of their surface and refractive index profiles, $h(x)$ and $n(x)$, respectively. In the case of correlated gratings, those profiles are correlated as well. Beyond a certain functionality, the surface grating can provide information on the corresponding volume grating. If the surface relief grating formation

is concomitant of the holographic recording of volume phase gratings, the shape of the SRG height profile $h(x)$ should be determined by the refractive index profile $n(x)$ of the volume grating. As a consequence, we can compare the surface profile—which is much more easily accessible—with the refractive index profile to derive information on the volume grating.

In general, the refractive index profile can be calculated as follows [13]:

$$n(x) = n_0 + \Delta n^{(0)} \cos(|\vec{K}|x) + \Delta n^{(1)} \cos(2|\vec{K}|x) + \Delta n^{(2)} \cos(3|\vec{K}|x) + \dots \quad (1)$$

with $\vec{K}$ the grating vector and $\Delta n^{(i)}$ the i -th order of refractive index modulation. If the refractive index profile is sinusoidal, only the first order of refractive index modulation in Equation (1) is different from zero. However, especially non-sinusoidal surface profiles allow us to draw conclusions on the special grating formation mechanisms of the corresponding VPG.

Those mechanisms can be described by the parameter R , or rather the ratio of monomer diffusion rate and polymerization rate:

$$R = \frac{D}{F_0} |\vec{K}|^2 = \frac{4\pi^2 D}{\Lambda^2 F_0} \quad (2)$$

with the grating period Λ , the diffusion coefficient D and half the maximum polymerization rate F_0 .

R controls how polymerization distributes to the i orders in Equation (1). Non-sinusoidal refractive index profiles may result from saturation effects [14,15]. This is particularly the case when diffusion proceeds very slowly, and polymerization is predominant, corresponding to a small value of R ($R \ll 1$) [16]. Therefore, a large value of R is usually desired. However, higher harmonics may also emerge for large R in the case of insufficient monomer supply.

Thus, investigating the shape of the SRG profile can be used to derive information on the volume grating and contribute to a deeper understanding of the grating formation mechanisms.

In general, the light-induced grating formation mechanisms differ depending on the type of photosensitive material. The development of SGRs in a photoresist material, such as SU-8, all optically, i.e. without wet chemistry, would combine the benefits of excellent applicability of a commonly used negative photoresist with the advantages of holographic recording, such as high precision, a fast process and easy control over grating parameters [4].

Here we report on direct light-induced secondary surface relief grating formation, correlated with holographic

recording of volume phase gratings in epoxy-based polymer films without any post-exposure treatment and in free-surface samples. For most materials, layer formation requires to use covered samples between two surfaces, with the result that no surface relief grating formation can be observed [3]. However, epoxy-based material composition allows to fabricate free-surface samples without a protective layer [14]. We investigate two material compositions. The first material is based on doped SU-8, which has proven to be particularly suitable and well-characterized for volume holographic recording [14]. It exhibits high refractive index contrast (in the order of $5 \cdot 10^{-3}$) at exposure energy densities of about 0.5 J/cm^2 with good dimensional stability. Diffraction efficiency close to 100% is achieved with $200 \mu\text{m}$ thick layers. Sharp angular selectivity better than 1° is obtained. Second, the pure Epon SU-8 is investigated. Although the pure SU-8 without dopant as the diffusing component is not qualified for holographic grating formation, it has recently been shown that it forms transient absorption as well as phase gratings [17]. For more details on the doped and undoped system, in terms of composition as well as performance, see [14].

Materials and methods

Sample preparation

The photosensitive polymers under investigation are based on the negative photoresist SU-8. It consists of epoxy resin, organic solvent, and photoinitiator [18]. A single SU-8 unit is shown in Figure S1 (Supplemental Material). Compositional details are listed in Table S1 (Supplemental Material).

Free-surface, ultraviolet curable epoxy-based samples, prepared by *micro resist technology GmbH*, are spin-coated on glass substrates with a rotation speed of 800 min^{-1} resulting in a layer thickness of approximately $200 \mu\text{m}$. Subsequent pre-exposure bake is carried out on a hotplate (80°C) for 30 min, driving out the remaining solvent in order to receive a tack-free film.

Holographic exposure

Holographic exposure is performed by two freely propagating recording beams with 1 mm beam diameter. The holographic exposure setup is shown in Supplementary Figure S2 (Supplemental Material). Light source is a linearly s-polarized 405 nm diode laser. Holograms are recorded with a dose of 1000 mJ/cm^2 . One-dimensional, plane-wave, transmission-type volume holographic gratings are created with symmetric recording geometry, resulting in unslanted gratings with a periodicity of $\Lambda = 2.7 \mu\text{m}$ (approximately 400 lines per mm).

After completion of holographic grating formation, the samples are fixed by UV flood cure with a dose of 350 mJ/cm^2 . The remaining photoinitiator is used up during this curing step, resulting in a sample which is no longer light-sensitive. No postbake, hardbake or any additional developing was applied.

Results

The formation of volume phase gratings

Figure 2 shows experimental evidence of the formation of volume phase gratings in doped as well as undoped material.

Permanent volume gratings with high diffraction efficiency are formed in the epoxy-based volume holographic recording material (doped material), while only transient volume gratings are formed in the pure SU-8 (undoped material), with very low permanent diffraction efficiency [17]. However, permanent surface relief gratings can be found on both systems, as shown below.

Corresponding surface relief gratings

The doped material

Figure 3 shows the height profile that was found in the case of the doped system. The surface relief grating has a groove depth of $h_{\text{max}} = 20 \text{ nm}$.

The measured height profile, shown in Figure 3, corresponds to a sinusoidal profile. It fits well to the calculated refractive index profile, which was calculated according to Equation (1), with refractive index contrast $\Delta n^{(0)} = 9.3 \cdot 10^{-3}$ and grating period $\Lambda = 2.7 \mu\text{m}$.

The undoped material

In contrast to the doped material, the undoped system shows non-sinusoidal SRGs with higher harmonics, as shown in Figure 4. The SRG exhibits a groove depth of $h_{\text{max}} = 10 \text{ nm}$.

The measured height profile for the undoped system shown in Figure 4 fits well to a calculated refractive index profile (using Equation (1)) with three orders of refractive index contrast: $\Delta n^{(0)} = 4.5 \cdot 10^{-3}$, $\Delta n^{(1)} = 1.5 \cdot 10^{-3}$, $\Delta n^{(2)} = 0.5 \cdot 10^{-3}$ and grating period $\Lambda = 2.9 \mu\text{m}$.

Secondary gratings

SRGs were also found on the doped system in the presence of secondary gratings. Secondary gratings, also called parasitic gratings, are unintentionally recorded structures that may arise if the recording beam is reflected on the back surface of the sample. Interference of the incident reference beam and the reflected signal beam induces the secondary grating [12]. It appears highly interesting to study such parasitic gratings in view of

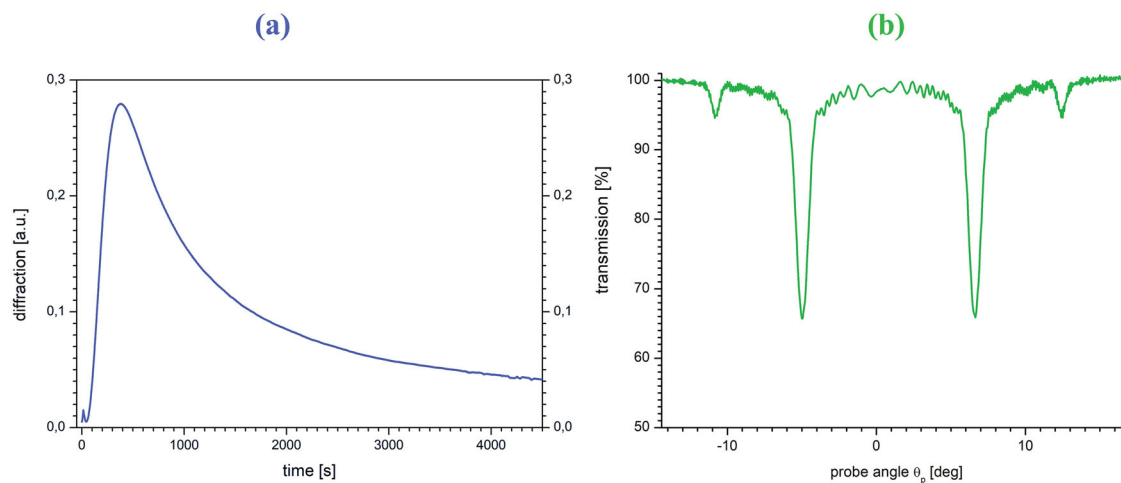


Figure 2. Experimental evidence of volume phase gratings: (a) Real-time growth curve of a volume grating in undoped SU8. (b) Bragg selectivity curve in the form of angular resolved transmission for a volume grating in the doped material.

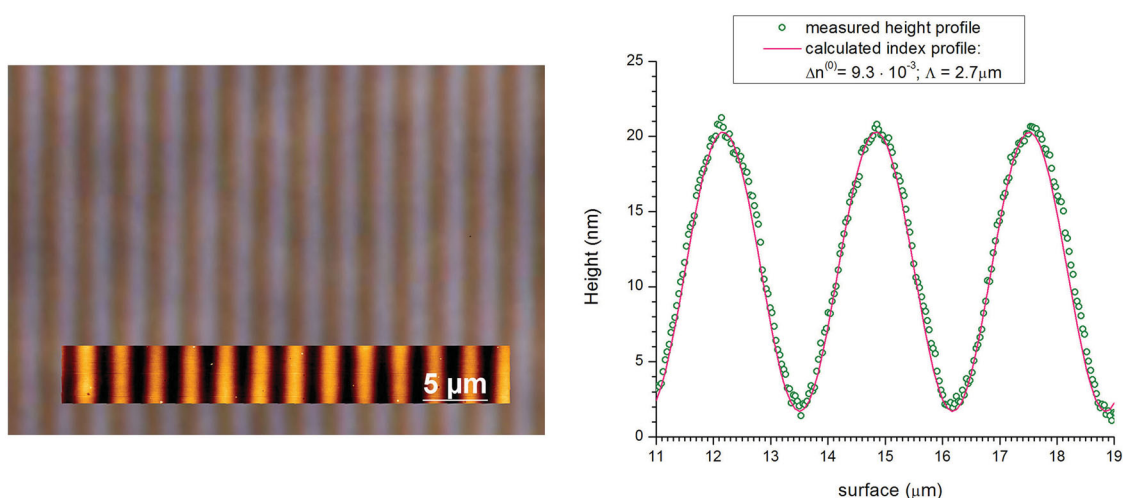


Figure 3. SRG on the doped system: AFM image with optical overlay (left) and height profile (right). The calculated sinusoidal index profile (line) fits the AFM measurement (dots).

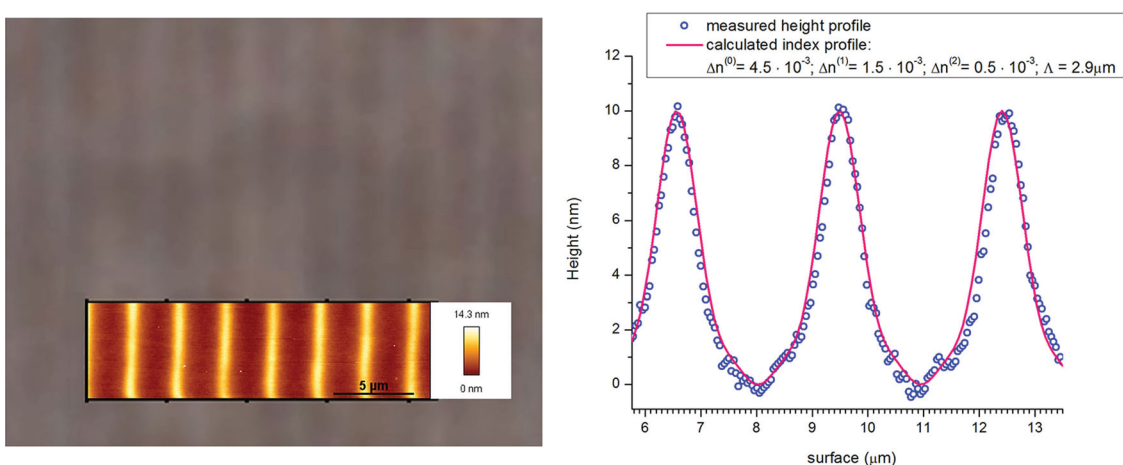


Figure 4. SRG on the undoped SU-8: AFM image with optical overlay (left) and height profile (right). The calculated index profile with higher harmonics (line) fits the AFM measurement (dots).

the possible avoidance of unintentionally recorded secondary structures as well as to draw conclusions on the material response.

Figure 5 shows the results of SRGs in the case of secondary gratings. The groove depths of the surface relief grating are $h_{\max} = 17$ nm for the regular grating and $h_{\max,S} = 8$ nm for the secondary grating.

The measured height profile shown in Figure 5 can be described as a superposition of two sinusoidal profiles, corresponding to the regular and to the secondary grating, respectively. The calculated refractive index profile (using Equation (1)) fits the AFM measurement with $\Delta n^{(0)} = 8 \cdot 10^{-3}$ and $\Lambda = 3.7$ μm for the regular grating and $\Delta n_S^{(0)} = 4 \cdot 10^{-3}$ and $\Lambda_S = 18$ μm for the secondary grating.

Discussion

Grating formation mechanisms

We have found light-induced surface relief gratings on doped as well as undoped SU-8 material. The simultaneous formation of surface relief gratings and volume holographic phase gratings by holographic interference exposure can be explained based on photo-triggered mass migration, resulting from the light-induced polymerization–diffusion process in the course of volume hologram formation. In accordance with investigations on other photosensitive polymers [1,8,19], it can be concluded that the diffusion of material plays a substantial role in the surface relief formation.

With reference to the well-known issue of mechanical stability for photosensitive materials, it can be concluded that optical shrinkage also has implications on the free surface of uncovered samples. Photocuring is always linked to shrinkage, as a result of the shortened particle distance in the covalent bond, compared with the individual van der Waals radii prior to the curing [20]. From other studies, analysing how the shrinkage affects the grating shape, it was concluded that shrinkage does not increase the deformations in the sinusoidal profile significantly [21].

Quantitative analysis

For surface modulation induced by two linearly polarized interfering beams, in the case of s-polarization, typically very weak surface amplitudes are obtained (in the order of several nanometres) [22]. For symmetrical, sinusoidal surface relief gratings, the first order diffraction efficiency can be calculated as a function of the groove depth to period ratio $\eta(h_{\max}/\Lambda)$ [23]. The periodicity of SRGs reported here is $\Lambda \approx 3$ μm . To obtain diffraction efficiency above 1% in this case, a groove depth of $h_{\max}$

> 300 nm would be required. In fact, we have found $h_{\max}$ in the order of several nanometres. As a result, the SRGs reported here do not show any optical functionality at all. To obtain secondary surface relief grating formation with optical functionality, increased groove depth would be required. For acrylamide—as well as acrylate-based photopolymer systems, a distinct dependence of the surface relief amplitude on the spatial frequency of recording was observed [1,3]. If such a relation would also exist for epoxy-based systems, this could be exploited to increase the SRG groove depth to obtain additional optical functionality. This could lead to multi-functional optical systems with hybrid volume/surface structures.

Apart from that, it appears highly interesting to study surface relief gratings without optical functionality to draw conclusions on the corresponding volume phase grating. However, in-depth investigation of secondary SRGs under variation of material and recording parameters, such as layer thickness and spatial period, should be applied for a detailed quantitative analysis. A result that indicates this is the differences in the spatial period of the gratings reported here, that can be explained based on the influence of the recording intensity and exposure duration on the Bragg selectivity [10]. For acrylate—as well as epoxy-based material, it has been demonstrated that internal as well as external accessible parameters, such as material viscosity, recording intensity and exposure duration strongly influence the grating formation and could provide a tool for an inherent control of optical shrinkage [3,10,24]. Therefore, those parameters could also be used to control and adjust the corresponding SRGs.

Qualitative analysis

The measured height profiles allow us to draw conclusions on the respective mechanisms of volume holographic grating formation.

On the doped material, we found sinusoidal SRGs. Therefore, we can deduce that the parameter R , defined by Equation (2), has a large value. This implies, firstly, that diffusion proceeds very fast, compared to the speed of polymerization, and, secondly, that sufficient monomers are available. As a result, no higher harmonics emerge in the refractive index profile and only the first order of refractive index modulation in Equation (1) is different from zero.

This is also the case for secondary gratings. However, here it appears remarkable that the secondary grating amounts half the strength of the regular grating, considering the suboptimal visibility of the interference pattern in the case of the secondary grating [12]. A high sensitivity regarding the material response can be concluded from the large value of Δn_S .

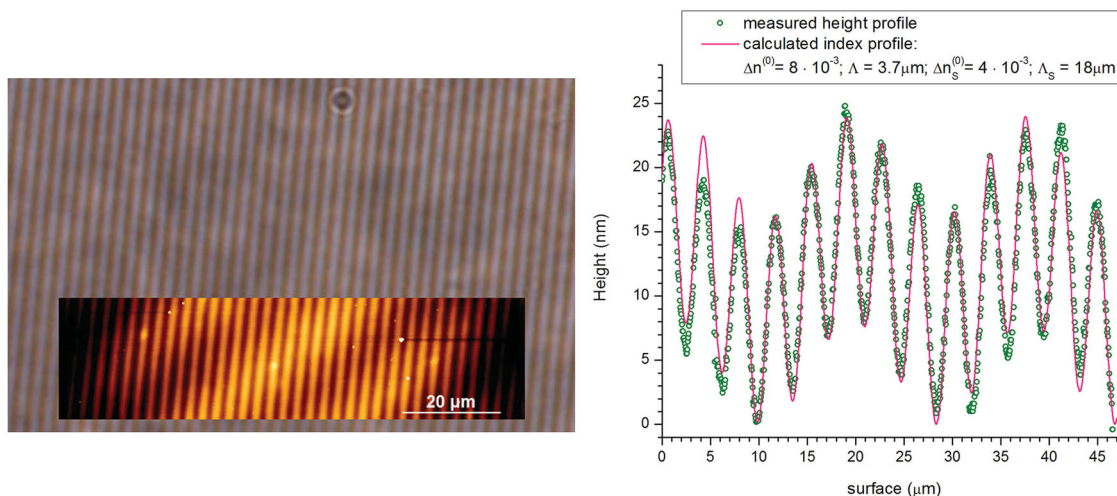


Figure 5. SRG for secondary gratings (doped system): AFM image with optical overlay (left) and height profile (right). The calculated index profile as a superposition of two sinusoidal profiles (line) fits the AFM measurement (dots).

For the undoped material, we found deviations from the sinusoidal case. They can be reduced to saturation effects. Here, the grating formation is characterized by the absence of the diffusing component [17]. In fact, the formation of a permanent grating in Epon SU-8 can only be explained by presumed diffusion of smaller molecules such as SU-1, SU-2, SU-4 and SU-6 [17]. In this context, it seems reasonable to assume that higher harmonics emerge due to a small R parameter, i.e. diffusion proceeds very slowly, and polymerization is predominant. This effect is further enhanced by an insufficient monomer supply. The small R and absence of dopant result in a refractive index profile with higher harmonics. As a result, the first three orders of refractive index modulation in Equation (1) are different from zero.

Conclusions

We found SRGs with sinusoidal height profiles as well as with higher harmonics on the doped and undoped SU-8 material, respectively. SRGs reported here do not feature optical functionality in terms of measurable diffraction efficiency. To obtain additional optical functionality and realize multi-functional optical systems with hybrid volume/surface structures, surface relief gratings with increased groove depth would be required. Apart from that, we analysed the SRGs to draw conclusions on the volume holographic grating formation mechanisms. A large R parameter, i.e. predominant diffusion was found in the case of the doped SU-8 material. In the case of the undoped SU-8, the R parameter is small, i.e. polymerization is predominant.

The pronounced formation of SRGs in the event of secondary gratings can be interpreted by a highly sensitive material response of the doped material.

Furthermore, results on light-induced SRGs in the negative photoresist SU-8 serve as a proof for the recently demonstrated presence of transient volume holographic gratings in SU-8 and corroboration of the corresponding explanation for the mechanism of their formation [17].

Acknowledgements

T. S. thanks micro resist technology GmbH for providing the photopolymer material and samples. T. S. and M. C. L. conceived and designed the experiments; T. S. and G. V. L. performed the experiments; T. S. analysed the data and wrote the paper.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) [SA 2990/1-1].

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