Efficient single-beam light manipulation of 3D microstructures in azobenzene-containing materials

Yuri Gritsai,1 Leonid M. Goldenberg,1,2,* and Joachim Stumpe3

1 Institute of Thin Film Technology and Microsensorics, Kantstr. 55, 14513 Teltow, Germany
2 Current address: University of Applied Science Wildau, Bahnhofstrasse, 15745 Wildau, Germany
3 Fraunhofer Institute for Applied Polymer Research, Science Campus Golm, Geiselbergstr. 69, 14476 Potsdam, Germany
*lengold@gmx.de

Abstract: Large aspect ratio 3D microstructures (arrays of square posts and linear rectangular gratings) fabricated in a number of azobenzene-containing materials by soft lithography were manipulated by a single beam of polarized light. The materials exhibited different response to the beam orientation and the direction of light polarization. An elongation of the square posts both along and perpendicular to the polarization plane was observed depending on material. Reversibility of the deformation has been demonstrated. Broadening of the hills, amplitude and shape changing were observed for linear gratings. A slanted expose led to the blazed asymmetric structures. Some aspects of light-induced deformation mechanisms in azobenzene-containing materials are discussed. The approach developed in the paper can be useful both for the understanding of mass transport mechanism in azobenzene-containing materials and for the fabrication of diffracted optical structures.

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1. Introduction

Azobenzene-containing materials are well known for the photo-induction of optical anisotropy and the generation of surface relief gratings (SRG) through photo-induced mass transport [1–4]. The phenomena are promising for the application in optics and photonics, such as diffractive optics, optical data storage and communications [3, 4]. The formation of SRG is advantageous for many applications due to its efficiency, all-optical nature and light reversibility. In the last decade a lot of different SRG types were realized in azobenzene-containing layers. Among them were one-dimensional gratings with sinusoidal and non-sinusoidal profiles and two-dimensional (rectangular, cubic, hexagonal etc.) gratings [2–4]. Recently a number of new types of materials appeared. E.g. we developed several types of effective easy made azobenzene-containing materials [4–11] different from traditional side-chain polymers. These new approaches led us to a record modulation depth of 1.8 µm [5] in supramolecular ionic materials [4], high thermal stability in polyelectrolyte material PAZO [6], a record inscription rate in oligomers obtained through epoxy ring opening [7, 10], colorless SRG in polyurea based oligomeric material [8], and an effective inscription (in addition with He-Ne laser) in extremely thin films in three-armed materials [9, 11].

Though the SRG inscription has been demonstrated in a plenty of azobenzene-containing materials there is still no clear understanding of the mechanism of the mass transport. The key to the photo-induced mass transport leading to SRG formation is the multiple isomerization between E and Z states of azobenzene moieties upon light irradiation. The multiple E-Z-E isomerization cycles in the steady state under polarized light exposure lead to orientation and movement in a molecular-scale level and can be consider as a driving force in an “elementary volume” (volume much smaller than SRG period but containing a sufficiently large number of molecular units; a description in terms of elementary volumes is widely used in electrodynamics and mechanics of continua). A deformation of elementary volume under multiple E-Z-E isomerization of azobenzene moieties can be studied e.g. by means of molecular mechanics [12]. But the understanding of a “bridge” between molecular level movement and micrometer scale deformation in SRG is quite complicated task because of cooperative nature of the SRG formation. One cannot consider pure elementary volume deformation but should take into account interactions between elementary volumes, stresses...
appearing as a result of such interactions, adhesion to substrates etc. Homogeneous thin films typically used for SRG inscription are not perfect objects from this point of view. High adhesion of azobenzene-containing layers to glass substrates, residual stresses as a result of micrometer scale deformations are factors limiting of SRG formation. E.g. one cannot typically record SRG of sub-micrometer period with sufficiently large amplitude or SRG with period of tenth and hundredth micrometers. The residual stresses restrict fine manipulations of already recorded structures even in reversible azobenzene-containing materials. From the other hand above mentioned reasons lead to difficulties of the SRG mechanistic studies.

From this point of view objects made from azobenzene-containing polymers but with reduced influence of adhesion and stresses are fascinating. Among them one can mention free standing films without glass substrates [13] and colloidal particles [14, 15]. A new approach in this direction can be an application of preliminary shaped structures of azobenzene-containing polymer (e.g. like pillar, cube, and parallelepiped) on the glass substrate. Fabrication of the structures on the substrates is advantageous for the application as optical devices. From the other hand one can expect deformations of such isolated structures during light irradiation to be under strongly reduced influence of adhesion and stresses. Moreover deformations of isolated structures can be easier interpreted because they can be implemented by means of one polarized beam irradiation. A new insight in this direction contributed recent studies on transformation of structures in azobenzene-containing materials with single beam [14–18]. The last investigations [17, 18] explored a fabrication of array of microspherical caps. These can be used as microlens arrays to mimic the function of the compound eyes of insects, in organic light-emitting diodes, charge-coupled device cameras, and other microoptical systems [17]. However, the deformation ability of the microspherical caps is rather restricted due to reasons above mentioned. For effective manipulation one needs microstructures of large aspect ratio (microstructure height ratio to its base size).

In this report, we exploited single polarized beam manipulation of high aspect ratio microstructures produced in azobenzene-containing materials by soft lithography. For this task we used the deep structures fabricated in a number of materials with different properties. It is a first investigation of a light post-manipulation of soft-lithographically produced structures in azobenzene-containing films. We have shown that response of the structures to the light polarization depends on material and that complicated structures useful for diffraction optical elements e.g. blazed grating can be produced in this way.

2. Experimental

The materials used were as following: statistical methacrylate copolymer with side chains of 3-[4-(4-trifluoromethyl-phenylazo)-phenoxy]-butoxycarbonyl and 4-cyanobiphenoxetoxycarbonyl made in house (Dr. D. Prescher, Institute of Thin Film Technology and Microsensorsics), material A; epoxy based oligomer based on 4-aminobenzene and bisphenol A diglycidyl ether as described earlier [7, 10], material B; epoxy based three-armed material based on 4-aminobenzene and tris(4-hydroxyphenyl)methane triglycidyl ether as described earlier [10], material C; polyurea based oligomer as described in [8], material D; polyelectrolyte material PAZO as described in [6, 19–22], material E; and polysiloxane based supramolecular ionic material as described in [23–25], material F.

As masters for soft-lithography AFM calibration gratings from MikroMasch (Estonia) TGZ04, TGZ11 and TGX01 (Fig. 1) have been used. Silgard PDMS was used to fabricate PDMS stamps from calibration gratings. Depending on material the film were spin coated on the glass substrate followed by application of PDMS stamp and heating at 70° C from 3 min to 1 h (conditions for heating were used according to previous research [6–10, 19–25]). Conditions of spin-coating were also similar to previously published and film thickness was at least 1.5µm. All mentioned materials exhibited good replication ability of deep structures which was proved by comparison of AFM measurement of original calibration gratings and replicas.
Fig. 1. AFM calibration grating structures: for TGZ step height 1µm (TGZ04) and 1.5µm (TGZ11) (according to the manufacturer Mikromasch).

AFM measurements were performed using Nanoscope III (Veeco Instruments Inc., USA) in taping mode. Single beam exposure was performed using linearly polarized expanded beam of Ar⁺ laser at 488 nm with intensity 200-900 mW/cm². Diffraction was imaged by diffraction microscopy with Bertrand lens using Axiocam 2 (Carl Zeiss, Germany) microscope.

3 Results and discussion

As it was mentioned above previous researchers used mostly colloidal particles made of azobenzene-containing materials or array of semi-spheres made through replication of particle arrays or by laser ablation [14–18]. Such objects exhibit relatively low aspect ratio. The microwire fabricated by soft lithography [16] had high x:y aspect ratio but low z:x-y aspect ratio (z is direction perpendicular to the layer plane). An application of the structure with high z:x-y aspect ratio should lead to better developed effect and consequently to larger impact on the understanding of the process of photo-induced mass transport. On the other hand fine manipulation of deep structures might lead to the structures useful for the application in diffractive optical elements. Different materials can be easily elucidated using this more general approach and a difference in behavior related to possibly different mechanism can be identified.

3.1 Array of square posts

In all azobenzene-containing materials a crucial question concerning a correspondence between interference pattern (light, dark area, polarization) and hills and valleys in surface microstructure arises [3, 4]. The question is important either for mechanism understanding or from application viewpoint. The later, namely a possibility of the structure manipulation, was main interest in current work.

The response of materials to the light exposure changes from the valleys in bright areas for amorphous materials to hills in the case of LC materials [4], while polyelectrolyte based supramolecular material [26] did not correspond to this trend. When in addition one considers that typically the photo-induced mass transport is most efficient in the interference field without intensity pattern, but with polarization pattern, the matter becomes even more complex as the light polarization has to be taken into account.

The observations were mostly made on the basis of single beam or mask exposure experiments with mechanistic interest. Concerning polarization issue the single beam experiments exhibited deformation along polarization direction [3]. It is generally accepted that the relief peaks are formed if the electric field vector in the light interference pattern is orthogonal to the grating vector and the valleys corresponds to the electric field vector parallel to the grating vector [21]. For one of the materials under this study (PAZO) [21] it was shown that the valleys corresponded to areas where the component of the electric field parallel to the grating vector is maximal. New insight in this direction contributed recent studies on transformation of structures in azobenzene-containing materials with single beam [14–18].

In this chapter we investigate the deformations of the square posts of azobenzene-containing materials with respect to polarization direction of driving light beam. The
deformations of such almost isolated objects are expected to be very informative because one avoids taking into account an influence of the opposite deformations of adjacent volumes which take place during holographic SRG recording. Moreover, one can expect the deformation of isolated square post with high aspect ratio to be similar to deformation of “elementary” volume mentioned in the introduction.

We tested different materials in respect to deformation: whether mass transport occurs along or perpendicular to polarization direction. For this purpose the array of square post (calibration grating TGX01) has been used as master. An AFM-image of original replica obtained in azobenzene-material is displayed in Fig. 2, left; the picture is symmetrical. Upon irradiation with linearly polarized light (polarization direction is indicated in Fig. 2) the elongation of the posts (Fig. 2 middle, right) has been observed. Remarkably, despite all material tested were amorphous, the direction of the elongation was different. A majority of studied materials exhibited the elongation along polarization direction (Fig. 2 middle). These were materials A, B, D, E; all of them are materials, where azobenzene moiety is covalently bound to the polymer chain or the central core. However one of the materials, F (Fig. 2 right), based on ionic non-covalent bounding of azobenzene to polymer backbone, shows the opposite behavior, where the elongation occurred perpendicular to the polarization direction (Fig. 2 right).

One can try to associate the elongation of the posts and SRG formation. The deformation of the post is expected to be in the same direction as in “elementary” volumes. The elongation of the “elementary” volume along grating vector should lead to the valley if specific volume is close to constant value. The elongation of the “elementary” volume in the direction normal to grating vector is more complicated for interpretation because macroscopic deformations of SRG in this direction are impossible due to symmetry. One should take into account both attempt to elongation of “elementary” volumes and impossibility of such elongation in macroscopic scale. As a result vertical deformations can take place i.e. hills of SRG. Of course this model is rather simple but it can explain some common features of the photo-induced deformation in azobenzene-containing materials (in particular SRG formation). For example, in well-studied material E (PAZO) the valleys correspond to the areas where polarization direction coincides with grating vector during SRG recording. At the same time the elongation of posts are observed to be parallel to polarization direction as predicted from above described simple model.

We have also tested a reversibility of the posts deformations. For this purpose we used the material E, because the material has been often used in our previous studies [6, 19–22] and exhibited excellent light reversibility. The change of the elongation direction upon rotation of polarization direction by 90 degree is shown in Fig. 3. Perfect reversibility of such
deformations open a prospect of fine adjustment of small 3D microstructures and make it possible to use such structures in optical applications (e.g. for adaptive optics).

As next step we have shown that upon slanted exposure with p-polarized light we were able to transform array of square posts in an egg-like asymmetrical structure (Fig. 4).

Both elongation along polarization direction and asymmetric deformation were observed. Asymmetry is also clearly observed in diffraction picture (Fig. 4e). A direction of the asymmetry testifies that electrical field vector determines mainly deformation direction of isolated microstructures in a case of arbitrary expose geometry as well. In the case of slanted exposure it means that the surface of the deformed microstructures tries to orient normally to the beam direction. These results show the opportunity for the fabrication of complicated diffraction elements which are not accessible by optical techniques alone.

3.2 Linear gratings

The arrays of deformed square posts described in 3.1 are mainly of interest as instruments to investigate the mechanism of light-induced mass transport in azobenzene-containing materials. In this chapter we investigate light-induced deformation in linear gratings. Such structures can be used in a number of optical applications although the deformations in this
case are more complicated for the interpretation. We have to note that the holographic formation of linear gratings in azobenzene-containing materials is the subject of a number of publications (see Introduction). However, further fine manipulation of holographically generated grating is restricted by residual stresses. Our approach is expected to overcome this restriction. Moreover, soft lithography makes it possible to create structures which cannot be recorded with holography (e.g. rectangular or tetragonal profile gratings).

Fig. 5. Transformation of deep (1.5 µm) tetragonal profile linear grating (a) in material B upon exposure with polarization perpendicular to grating lines (300 mW/cm², 30 (b), then 60 (c) min) and corresponding profiles (d).

One of the structures useful as diffractive optical element is a blazed linear grating widely employed in spectroscopic devices. Using azobenzene-containing materials such gratings have been fabricated using Fourier synthesis approach [3, 23]. Therefore, using the replicas of linear grating (Fig. 1) we exploited the ability to induce an asymmetry and tested the direction of the mass transport. As a first step deformations of deep linear grating with amplitude of 1.5 µm in material B have been investigated. An exposure of tetragonal profile structure (Fig. 5a) to a linearly polarized light with polarization direction along the grating vector led to the transformation of tetragonal profile into a cycloid profile structure (Fig. 5b). It resulted in the efficient mass transport along the polarization direction (Fig. 5b, c). It means that the distance between grating heels is decreased, particularly at longer exposure (Fig. 5c). Remarkably that in the same time the amplitude of the grating was decreased and the value of this decrease could not be explained by the change of the real shape. The only possible explanation is the mass transport of the material from the top of the grating to the bottom leading to rising of the bottom level (Fig. 5d shows the profiles of surface relief only and does not take into account the bottom level rising because the measurement of absolute height of the relief is quite complicate task). Longer exposure led to the same movement and eventually to practically sinusoidal grating.

The deformations of the linear gratings are in good agreement with the results obtained with the array of square posts. Taking into account that the elongation along the grooves is not possible one can expect the small transformation of the groove shape only in the case of

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polarization direction to be parallel to the grooves. In opposite, if driving light is polarized along grating vector broadening of the heels and decreasing of height are observed.

We have observed unexpected behavior in material C which is based on the same chemistry as material B. The directions of the deformations in material C are opposite to the ones observed in material B. In the case of polarization parallel to the grating vector (Fig. 6b) the grating only changes its shape; the top of the gratings loses its tetragonal shape, but the grating practically does not change the amplitude.

![Fig. 6. (a-c) Transformation of linear grating in material C upon exposure with polarization perpendicular (300 mW/cm², 30 min) and then along grating lines (300 mW/cm², 60 min) and corresponding cross-sections (d).](image)

On the opposite, an exposure with polarization along grating lines led to the mass transport along grating vector. This results in decrease of grating amplitude due to decrease in distance between grating ridges (it change practically from 1 µm to 0.1 µm, see cross-section in Fig. 6d). Note the last value is only an estimate as AFM measurements are prone to error in such cycloid structures. Unfortunately we have no results about deformations of square posts in material C because of difficulties in sample preparation procedure. This material (as well as other three-armed materials [9]) seems did not have enough elasticity, therefore, the posts in the replicas were not isolated and could not be used for our investigation described in 3.1. Nevertheless one can conclude that the mechanism of deformation in azobenzene-containing materials can depend even on small variations in chemical structure. Material C is three-armed and so the driving force is applied more symmetrically in comparison to side-chain polymer for example.

In addition we have subjected linear tetragonal profile grating to the slanted exposure with linearly polarized light (Fig. 7). The slanted exposure has been used before to produce blazed grating in bichromated gelatine [27] and azobenzene-containing polymer [28]. Here the fine manipulation of the square grating can be also considered as another approach for the manufacturing of blazed gratings. We have used material B and s-polarized light because it does not provoke significant broadening and height of the gratings in material B. We have obtained asymmetrical grating blazed depending on the light direction (Fig. 7). An asymmetrical orientation relative to the light direction is the same as in the case of slanted exposure of square posts (chapter 3.1). An advantage of this approach for the fabrication of
blazed grating is a possibility of fine manipulation of the grating profile depending on exposure conditions (orientation, intensity, polarization etc.) and reversibility of the deformation (total or partial, depending on the material). We have to note that full understanding of the light-induced deformations in such objects is quite complicated task and it is out of scope of this paper. Nevertheless the approach seems to be promising for the application in optics.

![Diagram of transformation of tetragonal profile linear grating](image)

**4 Summaries**

In conclusion, we demonstrated efficient single polarized beam manipulation of microstructures in azobenzene-containing materials using a number of materials with different properties and deep structures fabricated by soft lithography. We have shown that light-induced deformations (e.g. elongation of isolated cubic-like structures) could occur in both direction along and perpendicular to polarization depending on the material. We were able to produce complicated microstructures useful for optics which are not to achieve directly with holographic exposure. Moreover the approach developed in the paper can be useful both for understanding of the mass transport mechanism in azobenzene-containing materials and the fabrication of optical structures.

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