Direct laser writing of surface reliefs in dry, self-developing photopolymer films

Jens Neumann, Kay S. Wieking, and Detlef Kip

Fabrication of surface reliefs is achieved by raster scanning dry photopolymer films under a focused laser beam. The formation of the structure takes place subsequent to illumination without any chemical treatment or wet processing. Computer-generated optical elements can be recorded quickly, easily, and at low cost. The technology is particularly well suited for rapid prototyping and design purposes. These photopolymer films have potential in photonics applications, such as diffractive optical elements and waveguide structures. © 1999 Optical Society of America

OCIS codes: 220.4610, 050.1970, 230.7370.

1. Introduction

It is well known that photoresist can be used to fabricate surface reliefs.[1–3] The fabrication of those structures can also be done in chalkogenide glasses,[4] semiconductor-doped glasses[5] and in liquid[6] or dry self-developing photopolymer materials, e.g., in azobenzene polymer films,[7,8] in dichromated poly(acrylic acid) films,[9,10] and in dry photopolymerizable mixtures consisting of acrylamide, a sensitizing dye, triethanolamine and polyvinyl alcohol.[11,12] Because of the very large amplitudes (~10 μm) of the surface variations achieved in the latter material, Boiko *et al.*[13,14] were able to fabricate diffractive optical elements for applications in the middle-infrared spectrum, particularly for wavelengths of CO_2 lasers. The films are illuminated inhomogeneously with a halogen lamp and computer-generated amplitude masks (contact copying[15]). To avoid dye bleaching and distortions of the profiles, low light intensities less than 10 mW/cm^2 and illumination times of several minutes have been used. It has been shown that the increase in relief amplitude in this dry material is induced by a mass transport from the dark to the illuminated areas due to diffusion,[14] as previously demonstrated for liquid photopolymerizable layers.[6,16] Consequently, these films exhibit low surface scattering, compared, e.g., with direct laser writing in glass.[5]

In this paper, we report on the fabrication of surface-relief structures by raster scanning dry photopolymer films on an *xy* stage relative to the spot of a focused laser beam. To our knowledge, this technique has been never used before. This technical approach is also well suited for liquid photopolymerizable layers. From the physical point of view, the main difference to the technique of contact copying are relatively high intensities (~10 W/cm^2). Thus the illumination time for every pixel is low (approximately microseconds). Because the pixels are written sequentially, the overall exposure time is comparable with the case of contact copying. We show that with this technique, controlled fabrication of continuous-relief structures is possible. Furthermore, we can easily control the height and the form of the profiles by varying the scanning density and velocity. The introduced method offers significant advantages such as low cost and ease of realizability, because of the lack of masks and the good availability of high-precision computer-controlled *xy* stages, which are commercially sold by many companies.

2. Experimental Method

The surface-relief fabrication includes four stages[14]: (1) dry polymer film preparation, (2) inhomogeneous illumination, (3) relief self-development, and (4) fixing by uniform exposure. The photopolymer films are prepared as described by Calixto[11]: Acrylamide, methylene blue, triethanolamine, and polyvinyl alcohol are dissolved in ethanol and water. The solution is spread on glass substrates and is subjected to a

The authors are with Fachbereich Physik, Universität Osnabrück, D-49069 Osnabrück, Germany. J. Neumann's e-mail address is jens.neumann@uos.de.

Received 5 April 1999; revised manuscript received 15 June 1999.

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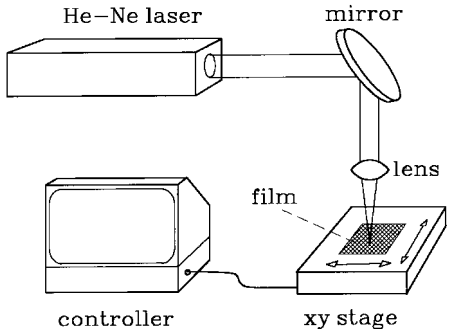

Fig. 1. Schematic of the experimental setup: The beam of a He–Ne laser is focused onto a polymer film, which is mounted on a computer-controlled *xy* stage.

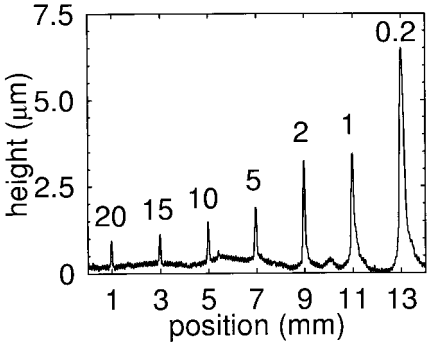

Fig. 2. Surface deformations induced on a photopolymer film by scanning it with different velocities v ranging from 0.2 to 20 mm/s relative to the spot of a focused laser beam ($P = 2$ μW).

drying period for 24 h in the dark and under normal room conditions.

We illuminate the light-sensitive, dry polymer films inhomogeneously with the laser writing system shown in Fig. 1. We recorded the surface reliefs by raster scanning the film under a focused laser beam. Because we choose methylene blue as the sensitizing dye, inexpensive laser diodes and He–Ne lasers can be used. In our setup, we employ a He–Ne laser with stable output power during usual illumination times of several minutes. The lens has a focal length of $f = 10$ cm and a numerical aperture of 0.1. The movement is done by an *xy* stage (resolution: 1 μm; accuracy: 5 μm; flatness: <0.8 μm; straightness: <0.3 μm) that has built-in encoders for position control. Since the stage works with a position and velocity control circuit, errors are minimized and are not accumulated over long distances. The stage does not allow movements in z direction. Although the films are not perfectly flat, the usage of an autofocus system is unnecessary because the focus depth is nearly the thickness of the film $d \sim 50$μm, which is much larger than the overall variation of the film thickness and the flatness of the stage.

Subsequent to the exposure the surface relief was permitted to develop in the dark without any chemical or thermal treatment or wet processing. After approximately 5 h we fixed the relief by uniform illumination for 1 h with the white light of a halogen lamp. The resulting surface profiles are analyzed with a confocal microscope.

3. Experimental Results

Figure 2 shows typical surface deformations on a photopolymer film induced by Gaussian-shape laser beams for different velocities v of the *xy* stage. The undulating trace is an artifact caused by the confocal microscope. The heights of these straight lines depend on the laser beam power P (Fig. 3). The maxima of relief structures are formed in the lit areas, but maximum surface profiles do not develop for highest laser beam powers because of dye bleaching (see, e.g., 14 and references therein). Since dye bleaching increases with increasing light intensity, the relief height decreases for $P > 5$ μW. This nonlinearity in Fig. 3 can be counteracted by a variation of the scanning velocity.

It should be mentioned that the heights and the widths of the reliefs also depend on the composition of the polymer mixture and the remaining water content of the films after drying, which may be controlled by weighting. Once a combination of these parameters is optimized, one can effectively and easily control the size of the relief features by varying the velocity v.

The resolution is limited by the necessary focal depth $DOF = 8\lambda f^2/\pi D^2$, which should be at least the film thickness d. Here f is the focal length of the lens; λ of 632.8 nm and D are the wavelength and the diameter of the recording laser beam, respectively. The limit of grating spacing possible with this process is the beam-waist diameter $W = (2\lambda DOF/\pi)^{1/2}$. The attainable relief height increases monotonically with the film thickness d in agreement with the mass-transport model of relief formation,[6,16] since the thickness linearly increases the mass of monomers to be transported. The lowest value suitable for the fabrication of CO_2-laser diffractive optical elements is $d \simeq 60$ μm.[14] Thus the limiting spot size $W_{min} \simeq 5$ μm is 1 order of magnitude smaller than the resolution limit (15 lines/mm) of 60-μm-thick films.[14]

The parameter W depends on the desired application. It may be smaller in thinner films, e.g., for the

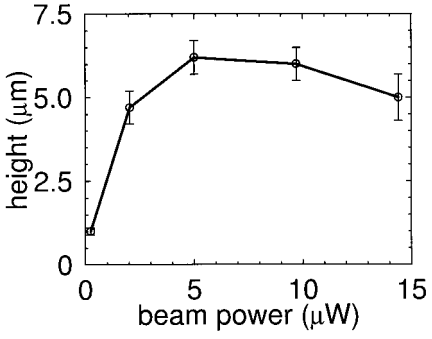

Fig. 3. Height of surface reliefs induced on photopolymer films as a function of the recording laser beam power (scanning velocity $v = 1$ mm/s).

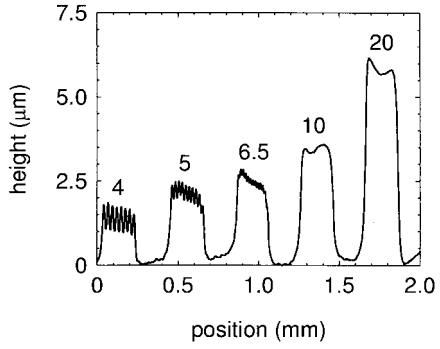

Fig. 4. Surface-relief profiles recorded with different scanning densities ranging from 4 to 20 lines/mm (v = 20 mm/s and P = 20 μW).

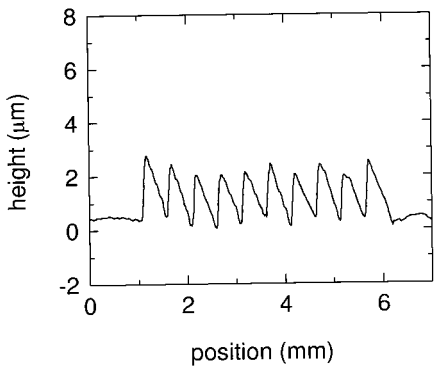

Fig. 5. Surface profile of a blazed grating.

fabrication of diffractive optical elements for shorter wavelength or for waveguiding structures. Additionally, it can be further improved by use of shorter wavelengths of the recording laser beam, e.g., the UV, blue, or green lines of an Ar^+ laser and an appropriate sensitizing dye, e.g., eosin Y.[12] In our experiment the beam-waist diameter is $W \simeq 40$ μm because of the focal length $f = 100$ mm and the diameter $D = 2$ mm of the recording beam.

Overlapping of individual lines permits profiles of complex structures. Figure 4 shows surface deformations induced by our raster scanning 2-mm-wide areas with constant scanning densities ρ ranging from 4 to 20 lines/mm. With smaller line spacing the single profiles merge into rectangular structures with nearly flat tops. The overlaid diffusionlike profile may be compensated by appropriate corrections in the velocity of the stage. The height of these plateau structures increases with the scanning density ρ, whereas the height of each single line decreases. Figures 2 and 3 demonstrate that the height of structures can be controlled additionally by the velocity of the *xy* stage and the power of the laser beam. Thus a desired relief depth, with or without the fine structures induced by single laser beam traces, can be obtained by variation of the above parameters as shown in Fig. 4 for $\rho \leq 6.5$ lines/mm and $\rho \geq 10$ lines/mm, respectively.

The ease and flexibility of controlling structure heights permit the fabrication of continuous-relief structures, e.g., blazed gratings (Fig. 5). The key factor here is the density of the merged lines. For the profile shown in Fig. 5 the scanning density in each period is continuously raised from 10 to 40 lines/mm. The velocity of the *xy* stage and the power of the laser beam are constant and chosen in a way that the desired profile height develops and the fine structure as well as an overlaid diffusion profile is suppressed.

4. Conclusions

We have described a new and simple technique that is suitable for the direct laser writing of surface reliefs in dry photopolymerizable films, e.g., diffractive optics for infrared wavelengths. It also can be applied to other materials, e.g., dry photocrosslinkable films[9,10] and liquid photopolymer layers.[6] The outstanding advantage is the absence of any chemical posttreatment and mask technology. The flexibility of controlling relief features by water content; mixture and thickness of the polymer films; scanning velocity and density of merged lines; as well as by the laser beam power, wavelength, and focal spot size permits the specific fabrication of complex surface structures.

Investigations of obtainable structure heights and resolution limits in films of different mixtures as well as the fabrication of prototype diffractive optical elements are in progress and will be the subject of a forthcoming paper. Furthermore, because of the low scattering surfaces we will focus our research on the application of the technique of laser beam writing to waveguiding structures, too.

This research was supported by the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (project 13N6926).

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