The production of Fresnel lenses in sol-gel derived Ormocers by holography

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ABSTRACT

Micro Fresnel lenses were prepared from photosensitive organic-inorganic nanocomposites of the Ormocer-type by irradiation of films of 10 μm in thickness with an interference pattern of two laser beams, mixing a planar reference wavefront and a spherical object wavefront. To monitor the polymerization behavior of the organic groups during irradiation under real time conditions, a characterization method was developed to study changes in optical thickness n·d by measuring changes of index of refraction and shrinkage during polymerization. Three-dimensional Fresnel structures were obtained by removing the unpolymerized areas by a solvent. Variation of index of refraction can also be obtained by diffusion of monomers in regions of higher light intensity. A model, similar to the Colburn-Haines model is presented.

1. INTRODUCTION

Composite materials based on methacryloxypropyl trimethoxysilan (MPTS), Zirkonium n-propoxide (ZR) and methacrylic acid (MA) are excellent model systems for the investigation of organic-inorganic nanocomposite materials.[1-3] Hydrolyzation and condensation behavior of the inorganic part already had been intensively investigated by Karl-Fischer titration, IR-spectroscopy and NMR.[4] Tailoring of the condensation rate of the MPTS component, and of Zirkonium-alkoxides by MA as complex forming agent was used to control rheological properties of the sol and thermal and mechanical properties of the final material. In addition to this, the polymerization behavior of the organic part of e.g. MPTS has to be controlled precisely to get high conversion rates without internal stresses and with high homogeneity. The conversion of C=C double bonds in case of organic-inorganic composite materials is far less investigated. In the MPTS/Zr/MA system, it was measured IR-spectroscopically and by Forced Rayleigh scattering (FRS).[4] In a FRS experiment, a diffraction grating is produced by superposition of two planar wavefronts leading to a periodical change of local light intensity. By different degrees of polymerization, a diffraction grating is built up and the diffraction efficiency, which is correlated to the optical thickness n·d, can be measured simultaneously. One disadvantage of the FRS experiment is given by the fact, that both n and d are changing during the polymerization process, and that these two processes can not be followed separately. From polymeric photoresists it is well known, that monomers will diffuse by the Colburn-Haines effect into region of higher light intensity.[5] The diffusion rates are responsible for the resulting profile of the index of refraction. Beside the knowledge of conversion rates in dependence on light intensity and exposure time, it is therefore essential to determine the gradients of index of refraction which are produced by "light trapping" of monomers.

These composite materials have a high potential for practical applications in integrated optics in combination with patterning techniques like embossing, mask-aligner techniques, direct laser writing and holography.[4]

2. THEORY

For a spherical refractive lens, focal length is only dependant on the index of refraction of the lens material and on the radius of curvature of the lens surface. The diffracting equivalent of such a spherical

0-8194-1612-6/94/$6.00

lens is a Fresnel zone plate (or Fresnel lens) which in case of phase modulation consists of concenmtric zones of different optical thickness.[6] The radii of these zones of different optical thickness are given by

$$r_m = (m\lambda f)^{1/2} \tag{1}$$

m are positive integer numbers, λ is the wavelength of the incident light and f is the principal focal length of the Fresnel lens.

From equation 1 it is evident, that a Fresnel lens has a wavelength dependent focal length which allows to tailor optical properties for a well defined wavelength and to reduce chromatic aberration. When a Fresnel lens is illuminated with a planar wavefront of monochromatic light, real and virtual foci result on the optical axis. The focal lengths on both sides of the lens are given by a^2/λ, $a^2/3\lambda$, $a^2/5\lambda$ (where a is the radius of the first zone, Fig. 1) The brightest (principal) image is at a/λ with images of lower brightness at smaller distances.[7,8] . As a result , higher order foci exist in addiction to the principal one. These are located at f/3,f/5, f/7, etc. on the optical axis.

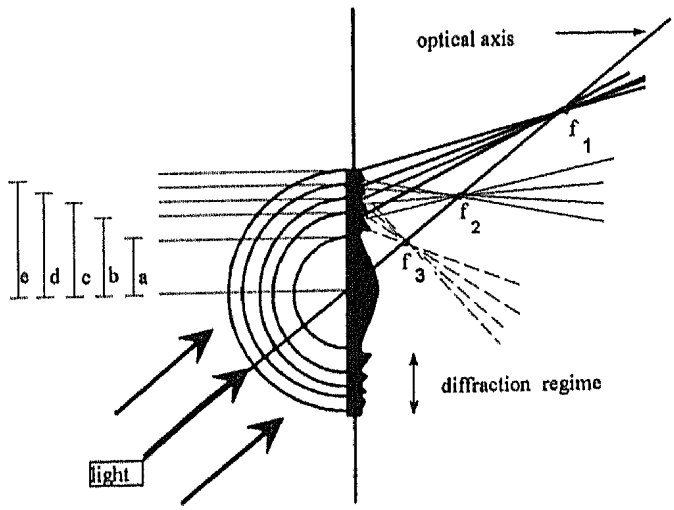


Figure 1: Fresnel lens with locus of foci. The radii from the zones are given by eq. (1) $a=f\lambda$, $b=\sqrt{2f\lambda}$, $c=\sqrt{3f\lambda}$, $d=2f\lambda$ $e=\sqrt{5f\lambda}$.

In case of diffraction, the resulting phase shift Φ is giving by:

$$\phi = \frac{2\pi nd}{\lambda} \tag{2}$$

where d is the depth of the relief profile, and λ the wavelength of the incident light.
The diffraction efficiency η is generally given by a Bessel function j_i of the form

$$\eta = \left| j_i(\phi_i) \right|^2 \tag{3}$$

where i is an integer that describes the diffraction order. The Fresnel lens works on the basis of diffraction because the zone periods at the outside of center (see Fig.1) are close to the optical

wavelength. The optical properties including focal length and focal spot size are essentially the same as those of refractice type lenses such as ordinary convex and graded index lenses.

The generation of refractive index differences in polymerizable materials can be explained by the Colburn-Haines model,[5] assuming that in irradiated areas a decrease of the monomer concentration takes place by photopolymerization. The resulting chemical potential gradient then is responsible for the diffusion of unreacted monomers from dark into irradiated areas. The resulting local change of composition causes local variations of the refractive index, which, by use of suitable slit geometries of the mask (or intensity of the light beam) can be used for the fabrication of desired patterns. Diffusion of monomers is influenced by various parameters like increasing viscosity. The refractive indices obtained by these processes depend on the obtained composition, the polymerization shrinkage and hence the degree of conversion. The obtained pattern can be stabilized either by removing the unpolymerized areas by solvent or by polymerization after removing of the mask in a second step. Since the Colburn-Haines model has been developed for photoresists patterned by mask techniques, the slidwidth of the has to be taken into consideration. (Fig. 2). Figure 2 d shows the expected index modulation for an "over sized" slidwidth and Figure 2 b the expected effect when the slidwidth is small enough for the monomer diffusion from edge to center during the recording process.

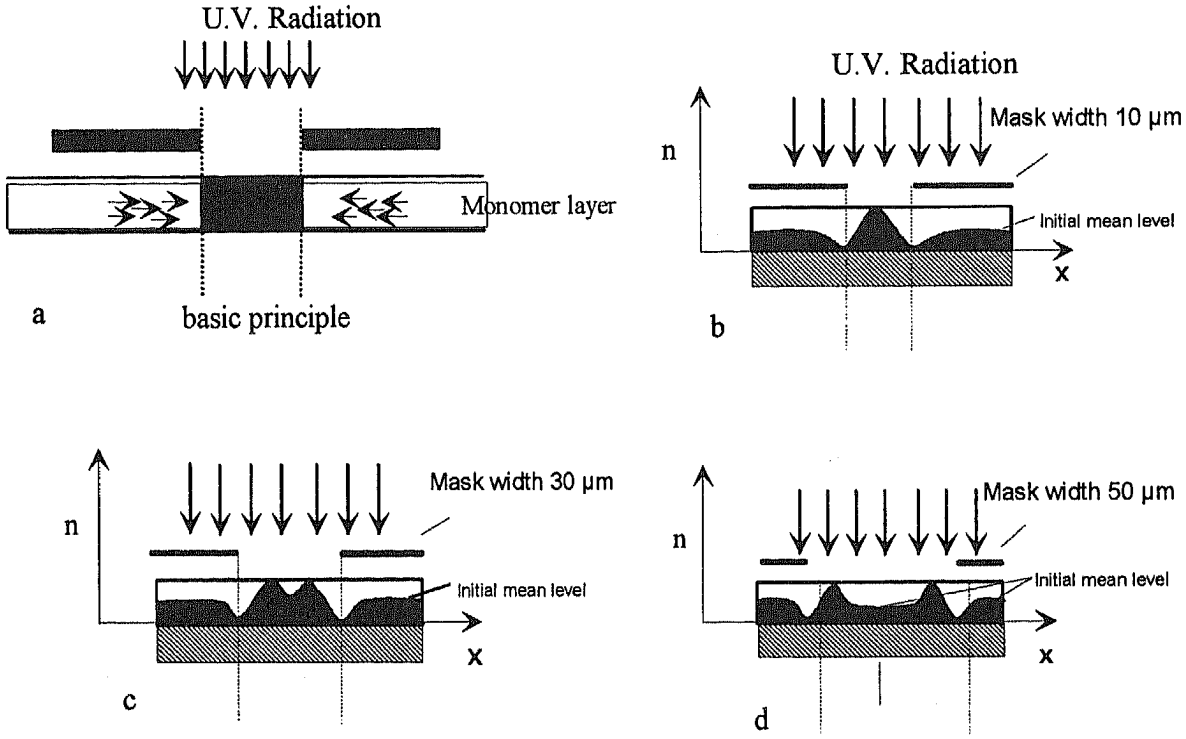


Figure 2. Colburn-Haines model describing the development of a refractive index profile obtained by diffusion of monomers for several slit widths

The produced index profile acts as a phase grating for a second probe beam of monochromatic light if the grating period is large enough. The considerations show that diffraction effects given by the index profiles are dependent on different slidwidths. This model was used to determine diffusion profiles by measuring diffraction efficiences of the formed phase grating during photopolymerization. However it has to be mentioned, that in the investigated composite system, the situation is more complicated than in organic monomer systems, since two polymerizable species are present, one of them bound to ZrO_2

particles and the other bound to an inorganic backbone (MPTS). The question arises, whether the Colburn-Haines model can be used for the investigated composite system patterned by interfering light beams.

3. EXPERIMENTAL PART AND RESULTS

The inorganic Si-O-Si backbone of the investigated composite is formed by controlled hydrolysis and condensation of MPTS. Methacrylic acid (MA) was used to stabilize ZrO_2 nanoparticles with an average diameter of 5 nm obtained after hydrolysis in presence of MA. Different MPTS/Zr/MA x/y/z molar ratio compositions were prepared ranging from 10:1:1 to 10:4:4 and 1 weight % of a photosensitive initiator (Irgacure 369 from CIBA-Geigy) was used to cure the nanocomposite by UV-sensitive polymerization of the methacrylate groups. More experimental details were described elsewhere[3,4]

Photopolymerization of C=C double bonds is directly correlated to polymerization shrinkage, because the distance between monomers of about 3-4 Å determined by van der Waals forces is reduced to 1.54 A which corresponds to the distance of a C-C single bond. In order to monitor changes in film thickness during polymerization, a March-Zehnder interferometer with a light source was used, which is not effective for photopolymerization. In Fig. 3 the shrinkage (decay of film thickness corresponds to the volume shrinkage) is shown.

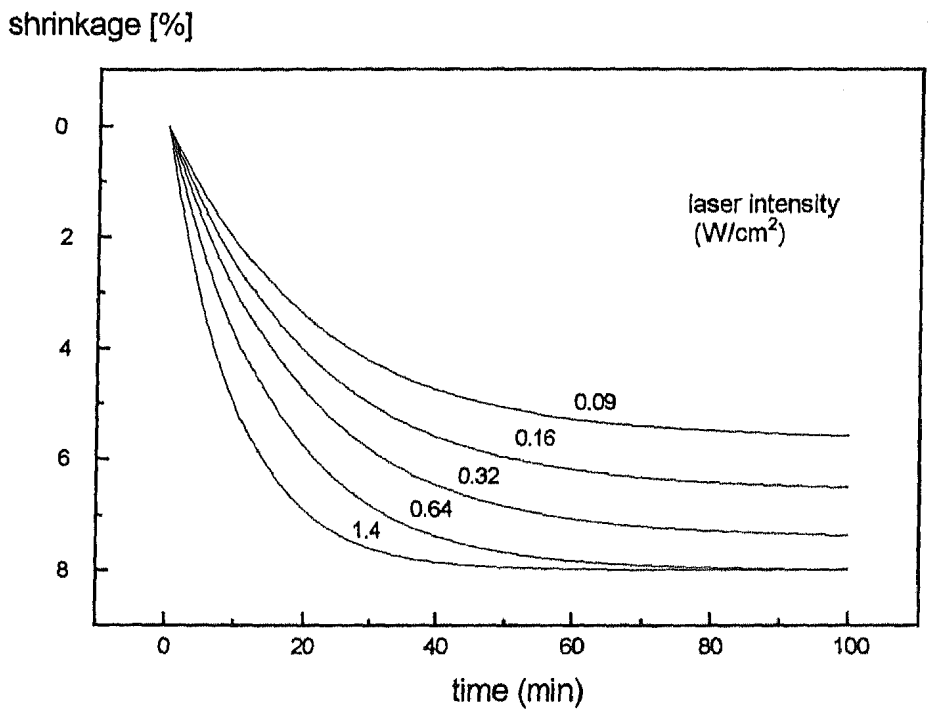


Figure 3: Shrinkage of a thin gel film of the system MPTS/ZR/MA measured in real-time during photopolymerization for different laser intensities.

The shrinkage follows an exponential function for all laser intensities. In all cases a plateau is obtained for decreasing intensities and the time for reaching the plateau is increasing. With intensities > 0.6 W/cm^2 the plateau remains at 8% shrinkage without further increase. Measurement of the density of the polymerized

material by the Archimedes principle and calculation of the shrinkage results in 7 % volume reduction, which is in good agreement with the data obtained by the Mach-Zehnder setup. For organic acrylate photoresists, the shrinkage was theoretically estimated to be 22.5 cm^3/mol due to reduction of free volume by the conversion of van der Waals distances and a double bond into two single bonds.[16] This considerations can be used to calculate theoretically the shrinkage by using the following equation:

$$S(\%) = \frac{\rho(g/cm^3) * 22.5(g/mol) * conversion(\%)}{M/D} \qquad (4)$$

S=shrinkage, ρ=density of the monomer, M= molecular weight of the monomer, D= number of double bonds per monomer units

Results obtained from equation (4) are in good agreement with measured shrinkage rates from methacrylates. In case of tetraethylenglycoldimethacrylate, e.g. a theoretical shrinkage of 14.4 % for 100% conversion is calculated compared to a measured shrinkage of 14.2 %. For organic-inorganic composites shrinkage is additionally influenced by condensation reaction forming the inorganic backbone. Assuming complete hydrolyzation for MPTS and $Zr(OProp)_4$, resulting in a mean molecular weight of 187g/mole for a composition of 10:1:1 (MPTS:ZR:MA), a shrinkage of about 7.5 % is ontained by using equation (4) for a conversion of 60 % (as measured by IR-spectroscopy), which is also in very good agreement with the data obtained experimentally by the Mach-Zehnder setup. This shows that even for the more complex Ormocer system the presented approach can be used to correlate directly shrinkage to conversion of the organic part of the Ormocer material. Investigations to determine the total shrinkage which is given by the conversion and a thermally induced post condensation process are in progress.

For the determination of the diffusion of the unpolymerized species into the irradiated areas, an experimental setup according to Fig. 4 was built up. Different slidwidths between 10 and 50 µm were used according to the Colburn-Haines evaluation. (Fig. 2)

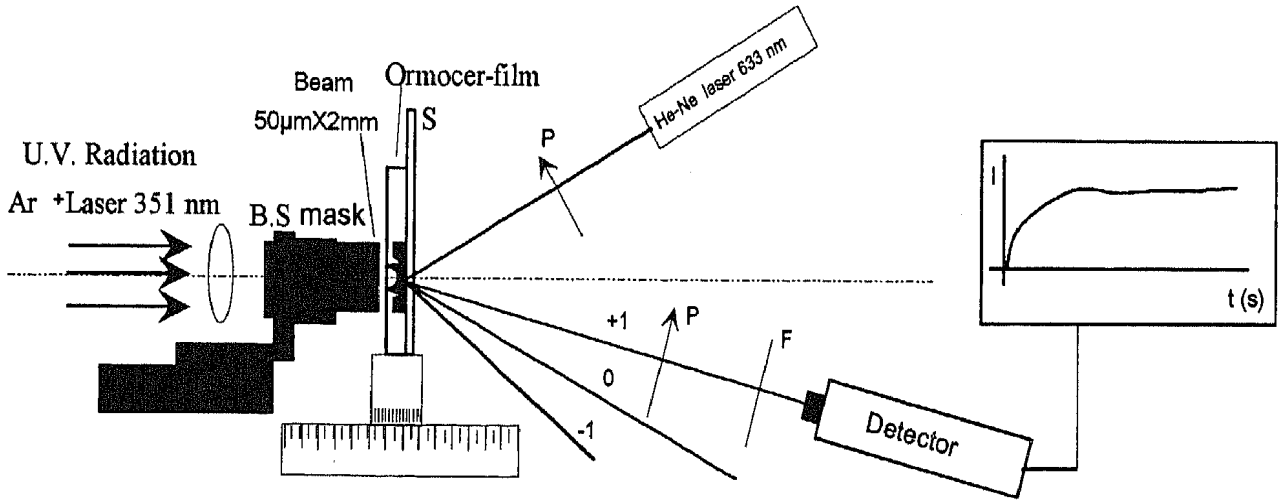


Fig. 4 Experimental setup to verify the formation of refractive index profiles given by Colburn-Haines mechanism in a real-time experiment (S: substrate, B.S.: beam expander, P: polarizer, F: filter, I: diffracted intensity, t(s): time)

The polymerization of a gel film was achieved by an Ar-Ionen laser operating at 351 nm with 200 mW laser power, a He Ne laser operating at 633 nm was used to probe the sample. A photomultiplier was used to detect phase gratings caused by diffusion processes into the polymerized sections according to the Colburn-Haines model in dependence on exposure time and mask size. For a 10 μm mask width, no diffraction efficiency could be detected; this was only possible for mask sizes of 30 and 50 μm. In Fig. 5 the diffraction efficiency η for a mask size of 50 μm in dependence of the exposure time for MPTS/Zr/MA 10:1:1 is shown.

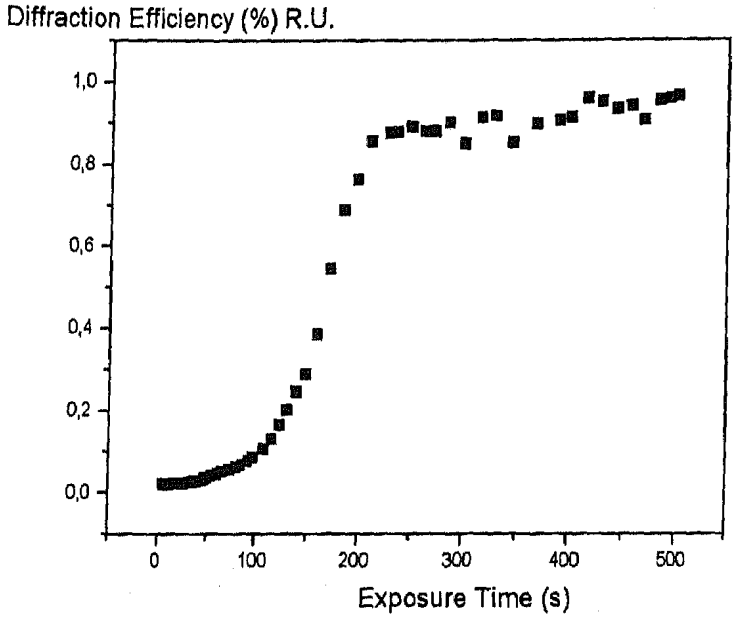


Fig. 5: Diffraction efficiency of phase gratings produced by exposing the composite film through a 50 μm mask. (laser intensity 8 mW/cm^2, 1 wt% initiator)

After about 200 sec the diffraction efficiency reaches a plateau by an increase of the viscosity and a very low increase of polymerization degree. The experiments indicate, that the Colburn-Haines model, which was developed for organic photoresist materials is also valid for photopolymerizable organic-inorganic composite materials. From these experiments however, it is not possible to decide which type of monomers (MA/ZrO_2, MPTS or both) are diffusing. This will be an objective of further investigations.

Based on the experimental data from the Colburn-Haines experiment, an experimental setup was developed for the Fresnel lens fabrication by two wave mixing in a Mach-Zehnder interferometer set-up (Fig. 6)

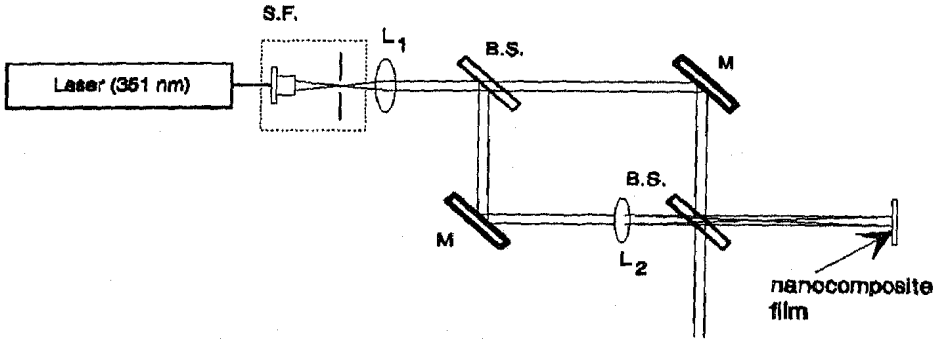


Fig. 6 Optical setup to produce micro Fresnel lenses by two wave mixing (S.F: spatial Filter, L_1, L_2 lenses, B.S:beam splitter, M: mirrors).

The interference pattern is built up with an Argon-laser operating at 351 nm and mixing an object wave with spherical wavefront (produced by L2) and a planar wavefront. These two beams interfere at the location of the sample and concentric rings of maximum interference intensity lead to degree of polymerization of almost sinusoidal form.

Different interference pattern and thereby different Fresnel lenses have been produced by changing the sample position or the length of the lens system L2.The theoretical maximum of diffraction efficiency of a thin phase zone is about 34%. The Fresnel lens presented here shows a maximum diffraction efficiency of 32% for the first order focus which is almost at the theoretical one.[9-11]Several Fresnel zone plates were generated under the same conditions and the reproducibility is excellent within ± 0.1 % of diffraction efficiency.In Fig. 7 a profilometer plot of a Fresnel lens produced by two wave mixing according to Fig. 6 and subsequent removement of unpolymerized material is shown.

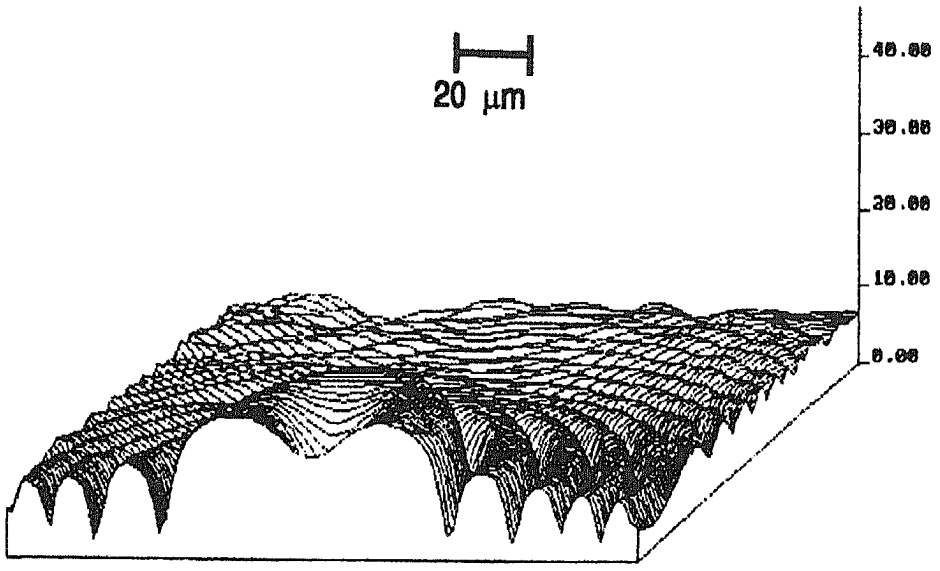


Fig. 7 Three dimensional plot of a Fresnel lens fabricated by two wave mixing experiment

The focal length has been determined by use of a microscope and measuring the distance necessary to move the stage between focusing on the surface of the lens and on the image of a point source at infinity.[12,13] By variation of the production parameters focal lengths between 0.5 and 2 mm could be realized.

The point spread function, which describes the light intensity distribution of an image produced by an optical system from a point light source[14,15] has been determined by an experimental device as shown in Fig. 8. A He-Ne laser in combination with an optical fiber (diameter 100 µm) was used as a point source because of the very large numerical aperture of the fabricated Fresnel lens. In order to increase the resolution for the measurement of point spread functions, a beam expander was installed in front of the camera of a Spiricon laser beam analyser.

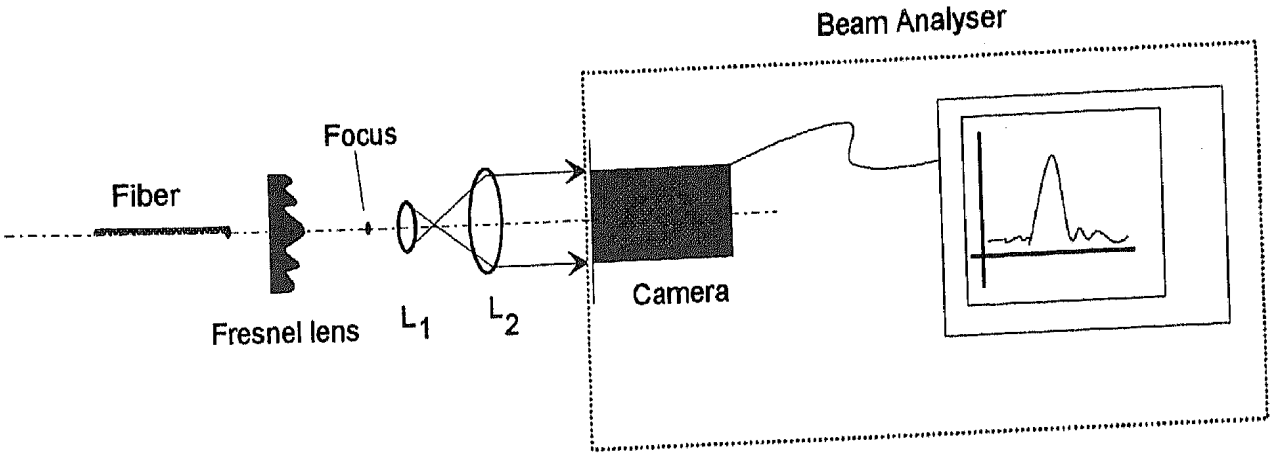
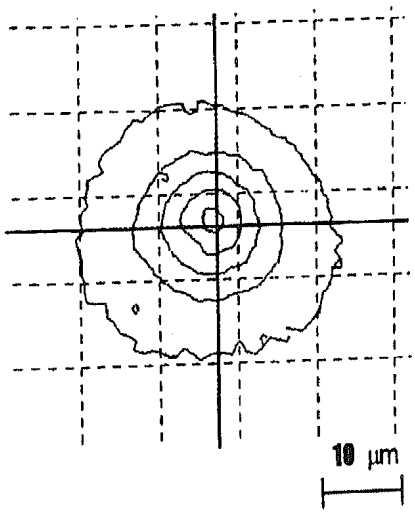
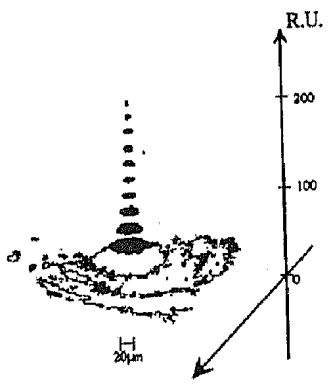


Fig. 8 The optical setup to measure the point spread function (L1,L2: lenses)

Figure 9a,b show the results of measured point spread function as a two-dimensional contour plot (Fig. 9a) and a three-dimensional intensity plot (Fig. 9b). The contour plot shows the good reproduction of the point source without distortions by the fabricated Fresnel lens. The focus diameter was determined from Fig. 9b at the half width of the intensity distribution to 20 µm. From Fig. 9b the very sharp and steep focus shape is evident.



a)



b)

Fig 9a-b Measurement of Point spread function with a Spiricon laserbeam analyzer
a) contour plot, b) three dimensional intensity profile of the focus

4. CONCLUSION

Nanocomposites of the Ormocer type are well suited for the requirements of holography. Micro Fresnel lenses can be prepared by dissolution of non-polymerized sections after mask illumination or by using the monomer diffusion into regions of higher light intensity according to the Colburn-Haines model as

desribed and used for organic photoresists. The quality of the lenses is represented by the point spread function which shows no deviation of the point source.

Further experiments have to be done to optimize the material by measuring the dependence of shrinkage on composition and double bond conversion and to evaluate quantitatively the monomer diffusion processes. Of high importance will be to find out what kind of species are able to diffuse and how this process can be controlled by changes in size of ZrO_2 nanoparticles, degree of condensation of the inorganic backbone and composition of the material.

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