Fabrication of GRIN-Materials by Photopolymerization of Diffusion-Controlled Organic-Inorganic Nanocomposite Materials

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ABSTRACT

New photopolymers have contributed significantly to the recent growth of holographic and lithographic applications. Photopolymerizable organic-inorganic hybrid materials, based on methacrylate functionalized silane and zirconia particles as holographic recording material, are presented. Thick films of this composite system were prepared and volume diffractive gratings were fabricated by a two laser beam interference technique. The formation of the gratings is based on the diffusion of high refractive index components (ZrO_2-nanoparticles) to areas with high irradiation intensity with subsequent immobilization by full irradiation of the film. The influence of the zirconia particles as the main component for obtaining highly efficient gratings is presented and the correlation between particle concentration and refractive index profile is shown.

INTRODUCTION

The sol-gel process allows the production of ceramic colloidal particles in the presence of organoalkoxysilanes, bearing various functions. The synthesis of multifunctional transparent inorganic-organic composites is possible, if the particle size can be kept in the lower nanometer range. Composites with a high refractive index generally require the incorporation of inorganic components such as ZrO_2 or TiO_2 as inorganic network formers [1]. A material system based on 3-methacryloxypropyl trimethoxysilane (MPTS) and zirconium propylate (Zr), chelated by methacrylic acid (MA) has shown to be suitable for index matching, by varying the Zr/MA-concentration [2]. As reported earlier, these materials have been developed for optical applications like gratings, waveguid [3,4] and microlenses [5]. The organic polymers can be photopolymerized and micropatterned using mask techniques. Those patterns can then be fixed using a subsequent development step. Without this development step, the refractive index difference between the polymerized and unpolymerized zones reduces during a full irradiation of the micropatterned area with a UV lamp, as already known from the study of organic polymers.

The question arises how far double bonds attached to inorganic high refractive index nanoparticles in a low viscosity polymerizable matrix are able to migrate into the irradiated area. In this case, after full area irradiation, differences in the refractive index n between preirradiated areas and the areas being exposed only to the full area treatment should exist. This would lead to a permanent gradient information in the films (holographic process).

In this paper, the possibility of fabricating high efficient gratings using this process was investigated. First evidence for the existence of such a diffusive process in case of the MPTS/Zr/MA system is described in [5]. A fundamental understanding of diffusion behaviour is necessary for the prediction of index profiles, in order to produce micro optical components with well defined optical properties [6,7].

EXPERIMENTAL

The inorganic-organic nanocomposite is based on 3-methacryloxypropyl trimethoxysilane (MPTS), and zircononium-n-propylate complexed with methacrylic acid (Zr/MA). The synthesis process is described elsewhere [1]. The compositions of the materials employed for holographic experiments were varied according to their mole ratios (MPTS/ZrMA) as follows 10:0:0, 10:1:1, 10:2:2, 10:4:4 and 10:10:10. Irgacure 369 was employed as a photoinitiator (0.4 mole %/C=C). Butanol was taken as a solvent to adjust the viscosity of the sols to the same value for all compositions. Films of 10 μm thickness were prepared between two glass plates as substrates [6]. The distance between the substrates was set using glass fibers of 10 μm thickness, and the sol was filled between the substrates by capillary forces.

The two-wave mixing experiment was carried out with a laser beam of wavelength 351 nm (from an Ar^+-laser), divided into two beams of exactly the same power by a beam splitter and directional mirrors. These two writing beams interact producing an interference wavefront with a periodic change of the irradiated intensity within the sample. A detailed description of the experimental set up is given in [3]. For the given angle of 2 degrees between the two writing beams, the energy density of 0.8 W/cm^2 is sinusoidal spatially modulated with a period of 10 μm. The width of the interference region is 1.5 mm. Concentration profiles of Zr/MA were detected by micro-Raman spectroscopy and energy dispersive X-ray analysis (EDX) in a scanning electron microscope (SEM).

RESULTS AND DISCUSSION

The illumination of the sample with an interference pattern produces a periodical variation of the optical thickness (refractive index -**n** multiplied to the film thickness -**d**). This leads to a diffraction effect, when the sample is illuminated with coherent light from a probe laser (He-Ne-laser 632,8 nm), and the variation of the optical thickness can be monitored in real time by following the diffraction efficiency as a function of illumination time. To complete the hologram-storage-process, the patterned region was illuminated with an UV light [5]. The preparation of the film between the two glass substrates (see experimental section) eliminates changes in thickness due to shrinkage and only changes in the index of refraction can be detected.

The grating formation was followed in real time with the probe laser. In figure 1 a the measured diffraction efficiency in dependence of time and Zr/MA concentration during the writing process is shown. For all concentrations, the illumination by the interference pattern was completed after 20 minutes and the behaviour of the diffraction efficiency was followed for an additionally 15 minutes, using only the reading beam of the experimental set-up during the fixing process (fig.1 b)

From figure 1a it is obvious that a maximum saturation of the diffraction efficiency exists for all MPTS/Zr/MA concentrations, which decreases with increasing Zr/MA concentration. For the pure prehydrolysed MPTS system, which contains no nanoparticles, the saturation diffraction is lower in comparison to the particulate systems. It is also obvious, that for this pure MPTS system with fastest kinetics of grating formation, the curve shows no irregularities and represents a one step process. A different behaviour can be observed in the presence of nanoparticles.

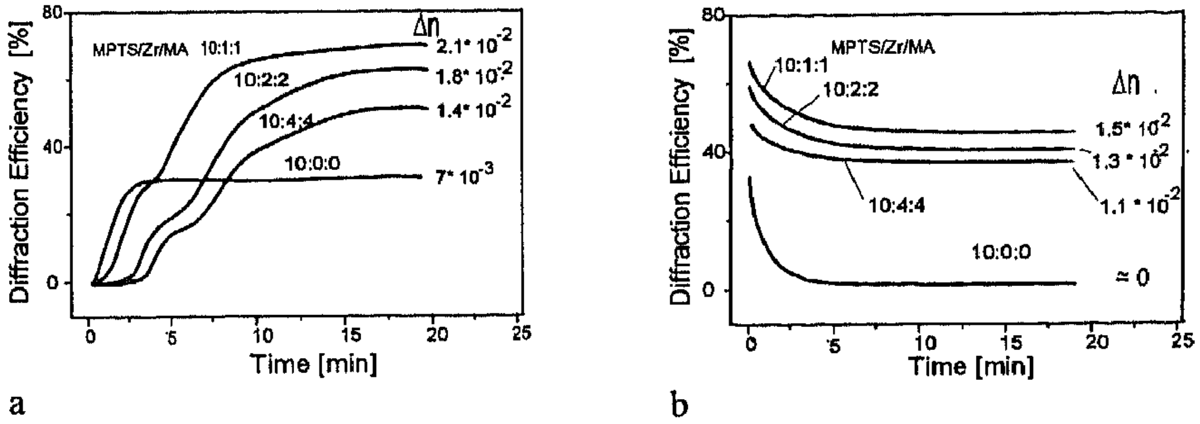

Fig 1 Real time diffraction efficiency measurement and Δn values of different nancomposite systems, a) Writing process b) fixing process. The Δn values are calculated by coupled wave theory (see text).

A two step process can be observed which is evidenced by a point of inflection in the diffraction efficiency curves. The position of each point of inflection is shifted to longer illumination times with increasing Zr/MA concentration. Absorption effects can be neglegted, as there is no interaction between the reading beam at 633 nm and the polymerizing systems.

The illumination of the sample with an interference pattern induces a polymerization of the regions corresponding to the bright fringes. This photochemical reaction produces a conversion of the monomer to polymer and additional monomer molecules containing zirconia diffuse to these regions from non illuminated areas. Due to the progressive formation of the polymer network, large molecules are prevented from migrating into the recording layer, hence a one-way diffusion process occurs, which only affects the unreacted monomers. This effect has as a consequence the increasing of the optical thickness of the polymerizing regions. This goes along with an increase in concentration of the monomer-derived polymer and a decrease in binder concentration in the irradiated regions

The hypothesis of a two step process, characterized by two different kinetics, was checked by calculating the photosensitivity ε. The kinetics of grating formation are directly correlated to the sensitivity, ε, of a photosensitive material. ε is defined as the slope of the linear region of the diffraction efficiency curve plotted against the incident light energy. The calculated sensitivities for the different compositions, shown in figure 2 are summarized in table I.The results indicate that the addition of Zr/MA reduces the sensitivity and hence the grating formation kinetics of the material. But there are differences in the sensitivity before and after the inclination points. Therefore a two step process can be postulated and is attributed in a first hypothesis to the MPTS and Zr/MA species. The sencitivity reduction process due the which has to be confirmed in future.

Table I Calculated holographic sensitivity ε in dependence of Zr/MA concentration, ε_1 before inclination point and ε_2 after the inclination point in curves shown in fig. 1a.

MPTS/ZR/MA	10:0:0	10:1:1	10:2:2	10:4:4
ε_1 [J/cm^2]	89.5	11.,8	7.5	1.5
ε_2 [J/cm^2]		10.22	7.12	1.43

The reduction of the sensitivity ε_1 and ε_2 during the grating writing process can be explained through the grating formation kinetics processes, photopolymerization and diffusion. In the first case, the increasing of the Zr/MA concentration in the MPTS/Zr/MA increases the light absorption of the sol and less UV-light energy will be used to induce a photochemical process. Whereas in the Second case, the increasing of Zr/MA concentration in the MPTS/Zr/MA leads to a increase of the Zr-particle radius, which decreases the mobility and consequently the diffusion of the Zr-particles.

The Δn values indicated in figure 1 for each particle concentration were obtained by the so called coupled wave theory. The refractive index modulation Δn is calculated by the diffraction theory described by Kogelnik [6]. As predicted by the coupled wave theory, the diffraction efficiency of gratings produced by two wave mixing techniques, exhibits a $\sin^2$ behaviour as a function of the incident angle of the reading beam. The holographic information can be reconstructed only under a narrow viewing angle on both sides of the Bragg incidence. The diffraction efficiency of such holographic elements depends on the following relationship:

$$\eta = \sin\left(\left(\nu^2 + \xi^2\right)^{\frac{1}{2}}\right)^2 \left(1 + \frac{\xi^2}{\nu^2}\right)^{-1} \text{ with } \nu = \frac{\pi \Delta n d}{\lambda \cos\psi} \qquad \text{and } \xi = \frac{\Delta\psi \pi d}{\Lambda}$$

(η: the diffraction efficiency, d: the film thickness, Δn: the variation of refractive index, ψ: the Bragg angle, $\Delta\psi$: difference between the Bragg incidence and the playback angle in the recording medium, Λ: grating periodicity and λ: wavelength of the probe laser). A typical angular response of the diffraction efficiency measurement of the 1st diffracted order of a grating stored in MPTS/Zr/MA is shown in figure 2

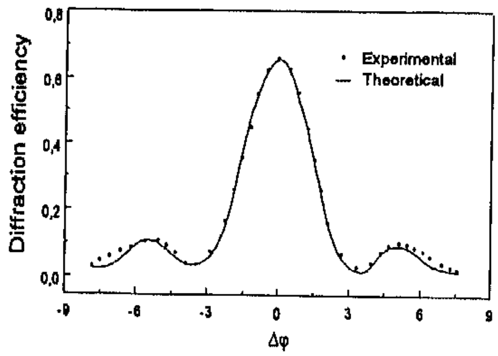

Fig.2. Diffraction efficiency in dependence of $\Delta\psi$, Λ=10 μm, d=10μm and λ=0.633 μm.

The calculated and measured curves exhibit a very good agreement. This is also the case for the calculated thickness of the film, which differs only 3% from the measured one. Unpolymerized C=C double bonds in the regions of lower intensities in the interference pattern are polymerized during the fixing process (figure. 1b). Diffraction efficiency drops to zero for the pure MPTS system, and the grating formed during the two wave mixing experiment is destroyed as a result of the homogeneous index of refraction over the whole illuminated area. For the particle-containing MPTS system, the diffraction efficiency does not fall to zero, which can only be explained by a fixed modulation of the index of refraction. The reduction of the index of refraction after the writing process up to the end of the fixing process for all Zr/MA concentrations can be explained by the conversion of C=C double bonds to C-C single bonds which reduces the mole refraction in the less illuminated areas during the writing process which are now postpolymerized during the fixing process. By this effect, the phase shift is lowered and the diffraction efficiency is decrease but does not drop to zero which can be only contributed by a concentration profile.

Raman spectra were recorded for different positions on the film, in order to elucidate the mechanism, which leads to a permanent modulation of the refractive index. In figure 3, the Raman spectra for the composite 10:2:2 is shown.

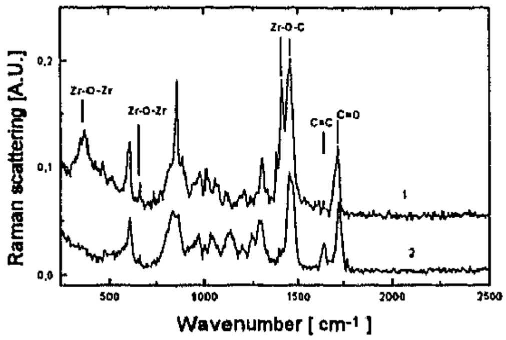

Fig.3 Raman spectra taken from irradiated (1) and unirradiated (2)

The Raman spectrum taken from irradiated (1) and unirradiated areas (2) shows that the signal intensity of the Zr-O-Zr bands (363 and 665 cm^{-1}) and Zr-O-C bands (1452 and 1576 cm^{-1}) increases in region 1. It can be conducted that the irradiated area (during the hologram storage) contains more zirconia than the non-illuminated areas. Furthermore, the C=C signal of region 2, shows that the conversion is not complete even after the fixing-process. To verify the results obtained by Raman-spectroscopy, films (10:2:2) and substrate were end-face polished and Zr-concentrations in the film plane was detected by energy dispersive X-ray (EDX) in a scanning electron microscope.

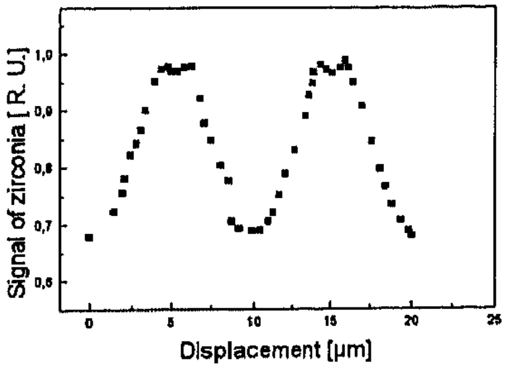

Fig.4: EDX signal of zirconia in a holographic micropatterned film of MPTS/Zr/MA (10:2:2)

From figure 4, it is evident that the maxima of the Zr-profile, as detected by EDX, coincides exactly with the grating period of 10 µm, which was set in the two wave mixing experiment. It follows that during the storage process an irreversible transport of the zirconia particles from the unirradiated to irradiated region is produced, which corresponds exactly with the refractive index modulation.

CONCLUSION

It could be conclusively demonstrated that, using organic-inorganic composite containing nanoscaled ceramic particles, a permanent gradient can be produced by applying a two laser beam interference technique. The gradient is caused by a modulation of the index of refraction, which is is derived from a concentration gradient of the complexed zirconia particles, as detected by micro-Raman-spectroscopy and EDX. The concentration gradient arises from diffusion of Zr/MA-nanoparticles into the (during the writing process) laser-illuminated sections of the film. The creation of phase gratings with a refractive index modulation up to $1.5*10^{-2}$ is obtainable by fixing this profile with a full area illumination step. This process has an enormous potential for producing GRIN (gradient refractive index)-materials. Future work will involve kinetic and mechanistic investigations of the diffusive process and the scope for producing even higher refractive index modulations.

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