Micropatterning of Organic-Inorganic Nanocomposites for Micro-Optical Applications

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1 Introduction

Microoptic elements like gratings and strip waveguides can be produced by different patterning techniques. Organic polymers and inorganic SiO_2/TiO_2-based sol-gel materials can be used for low-cost mass production of such elements.

Organic polymers have good optical properties and can be easily patterned, but their thermal and mechanical stability is poor [GAL 90a, GAL 90b , ULR 72, WEB 75]. Strip-waveguides are generated by local photopolymerization and gratings are prepared by embossing the polymer heated near T_g. Molecules with non-linear optical properties can be incorporated but relaxation stability after poling is not yet satisfying.

Inorganic films made by sol-gel techniques combine good mechanical and thermal stability with low optical losses. The preparation of crackfree layers with a thickness of more than one micron is extremely difficult [LUK 83]. Densification temperatures near T_g make it impossible to incorporate optical active organic substances as these would be destroyed. Local densification by laser-treatment can generate carbon particles within the structure and thus increase the optical loss to more than 5 dB/cm. In case of embossing techniques,near-net shaping is not possible because of high shrinkage

to 70 Vol.% during the densification step. Shrinkage rates can be reduced by the incorporation of polymeric species like PEO, but values better than 30 Vol.% could not yet be obtained [RON 91, TOH 88, MAT 90].

Many of the problems listed above can be overcome by using inorganic-organic nanocomposites of the ORMOCER type. These materials are synthesized through the sol-gel route where the inorganic backbone is formed by a hydrolysis / condensation process and an organic network is built up by polymerization. Crosslinking of the inorganic backbone and the organic network is achieved by covalent or coordinative bonds. The inorganic component increases thermal stability and surface hardness in comparison to pure organic polymers. The organic component allows densification temperatures of less then 150 °C. By the variation of the synthesis parameters many properties can be tailored. For optical applications, the refractive index can be varied by composition. Reduction of mechanical stresses allows to deposit layers of more than 10 μm in thickness in one step by several coating techniques. Optical active compounds can be introduced either as guest-host systems or as network forming units. The low over-all shrinkage allows embossing with a near net shaping quality. The option of curing the materials by UV or VIS irradiation permits patterning by direct laser writing or maskaligner techniques.

2 Experimental and results

2.1 Synthesis and properties of the nanocomposite materials

A system based on methacryl oxypropyl trimethoxy silane (I), zirconium n-propoxide (II) complexed with methacrylic acid (III) was used in this work. The detailed procedure of the synthesis of this type of nanocomposite has been published elsewhere [NAS 90]. Molar compositions between 10:1:1 and 10:6:6 (I:II:III) were used to match

the refractive index in the range $1.509 < n < 1.540$ at 632.8 nm. For coating, the viscosity was varied in the range of 6 - 7 mP·s by solvent addition to the sol and 1 - 2 wt.-% of a photoinitiator (e.g. Irgacure 369, Ciba Geigy) was added.
Layers with thicknesses of more than 10 μm could be deposited in one step on glass or fused silica substrates by spin-, dip- and a modified flow-coating technique. Heating of the freshly deposited layers to 60°C for some minutes results in a smooth and homogenous surface required for patterning. Layers produced by spin-coating have surface roughness less than 5 nm.

2.2 Embossing procedure

Grating patterns were generated on layers deposited on fused silica using the in-house built device shown in fig. 2.1.

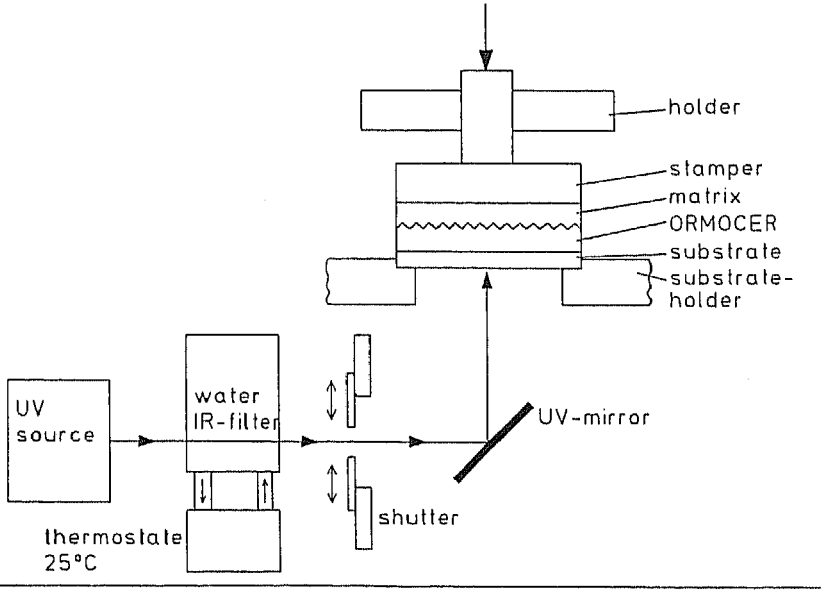

Fig. 2.1. Device for the embossing technique

A black glass stamper with a grating of 2400 parallel lines per millimeter (Fa. Zeiss) was used. It was placed onto the uncured layer and a defined pressure of 10 - 100 $N \cdot cm^{-2}$ was imposed. Photocuring was carried out by irradiation with UV-Light through the silica substrate for 10 minutes. After the curing step the stamper was removed and the layer was heat treated (130°C, 1 h) for final curing. In fig. 2.2 a SEM of a grating fabricated by this procedure is shown.

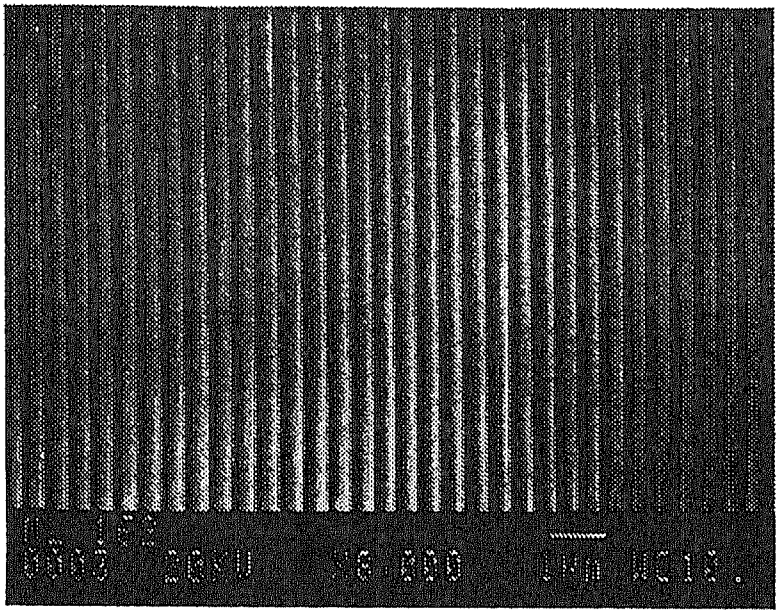

Fig. 2.2. Grating generated by the embossing technique, 2400 lines/mm

The overall shrinkage rate of less then 5 Vol.% results in a near-netshaping quality of the embossed patterns. This low shrinkage rate in combination with high film thickness generates grating amplitudes of several hundred nm, which is essential for high diffraction efficiencies.

Some problems concerning adherence of the material to the stamper still have to be overcome by improving the clean room technology and by insertion of separating thin layers.

2.3 Direct laser writing

Layers deposited in the same manner as described in 2.2. were used for direct laser writing [SCH 91]. The device for this procedure is shown in fig. 2.3.
The substrate is fixed on a unit which can be positioned in x- and y-direction under computer control allowing flexible sample movement. A laser beam focusing unit permits generation of patterns variable in size and geometry.

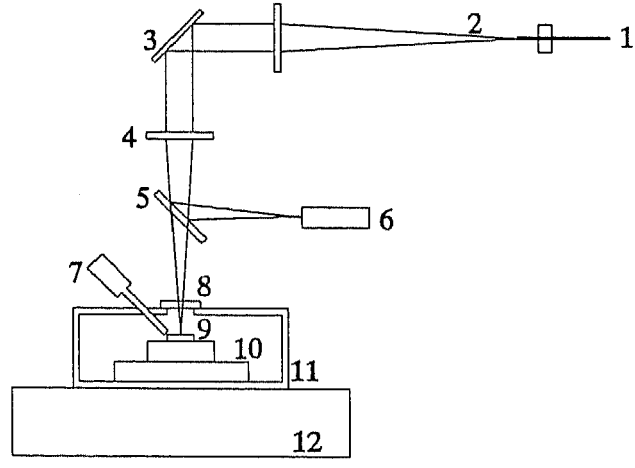

Fig. 2.3: Scheme of direct laser writing equipment. 1: laser beam, 2: beam expander unit, 3: flat mirror, 4: focusing lens (fused silica), 5: fused silica plate, 6: laser beam analyser, 7: TV-microprobe, 8: fused silica window, 9: sample, 10: motor driven xy-stage, 11: reactor housing, 12: optical table

In the areas irradiated by the laser beam, which can be focused down to 10 μm in diameter, the polymer network of the organic component is formed. The material of the non-polymerized areas is then removed by an adequate solvent, e.g. an alcohol or a ketone. The curing of the final patterns is accomplished by heat treatment (130°C, 1h).
A SEM of a strip waveguide which has been evocated by this procedure is shown in fig. 2.4. The optical loss of the waveguide has been determined to 3 dB/cm due to surface roughness and scattering by dust particles. Therefore the patterning process has to be optimized and clean room conditions have to be improved. But nevertheless this is a promising low starting value.

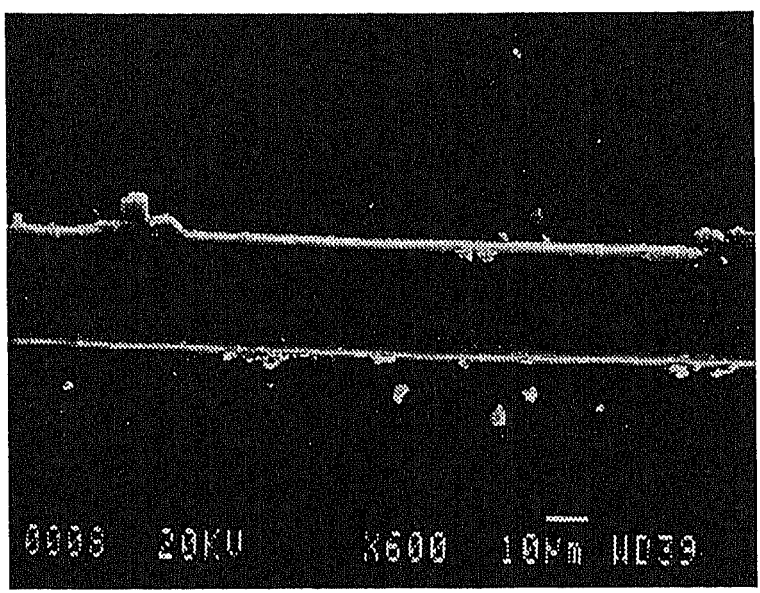

Fig. 2.4. Waveguide patterned by direct laser writing

2.4 Maskaligner technique

The same principle as described for laser writing is used for fabricating patterns by a maskaligner technique (fig. 2.5). The photocuring of a nanocomposite deposited on a substrate is carried out in a maskaligner apparatus providing a parallel arrangement with a defined distance of the coated substrate and a mask, which consists of a metal film deposited on a glass sheet. Through the transmissible areas of the mask irradiation and thus polymerization of the nanocomposite material is achieved. Typical values are 5 - 10 minutes irradiation time and 80 μm distance between mask and layer. The pattern is developed with a suitable solvent to remove the non-polymerized material according to 2.3. The standard heat treatment (130°C, 1h) accomplishes the curing of the nanocomposite and provides maximum hardness and stability.
In fig. 2.6 is shown a SEM of a pattern of parallel lines made by maskaligner technique.

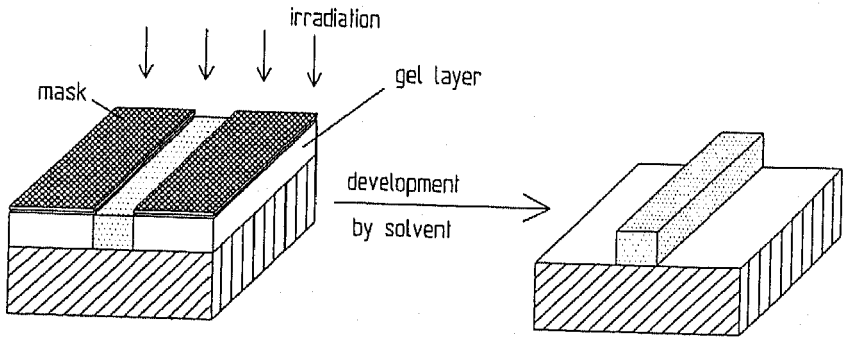

Fig. 2.5. Scheme of the maskaligner device

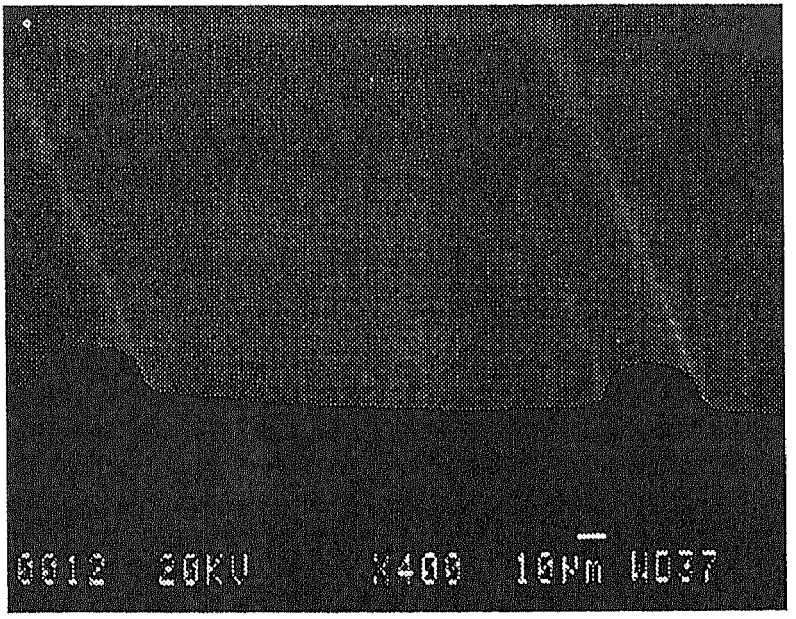

Fig. 2.6 SEM of a pattern of parallel lines made by maskaligner technique

3 Summary

Organic-inorganic nanocomposites for use in microoptics can be synthesized by the sol-gel process. Their properties can be taylored by variation of the materials and the synthesis parameters.
The inorganic backbone is formed during the hydrolysis and condensation reactions while the polymerization leading to the organic network is achieved by adding a proper photoinitiator and by light irradiatiation.

Layers of several μm thicknesses could be obtained showing good optical quality (opt. loss < 1 dB/cm). Their refractive index was adjusted by the appropriate composition.
Gratings were formed by an embossing step with near net shaping. Local photocuring allows micropatterning by flexible direkt laser writing or by maskaligner techniques for low cost mass production.
The special properties of the here presented organic-inorganic nanocomposites make them very interesting for many applications in the field of microoptics.

4 Acknowledgement

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5 Literature

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