Development of optical wave guides by sol-gel techniques for laser patterning

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ABSTRACT

ORMOCER's with high optical performance and chemical stability are synthesized via the sol-gel process. Methacrylate group substituated silanes are copolymerized with methacrylic acid which acts as a chemical link between Zr as second inorganic network former. Chemical stable complex formation is proved by IR analysis and ^{13}C NMR investigations. This material is laser patternable by the addition of a suitable photoinitiator and is characterized by high dielectric strength and low optical loss for applications in optics and non-linear optics.

1. INTRODUCTION

Sol-gel derived layers are of high interest for optical applications, especially for optical waveguides. A variety of glass compositions can be synthesized by sol-gel techniques[1] and dopants with interesting optical properties can be introduced[2]. The process is of special interest for the preparation of coatings, since sols with viscosities suitable for coating techniques can be prepared. The fabrication of channel waveguides requires further processing steps as etching or laser ablation. Therefore, the state of the art is relatively low. Fabes[3] reported on a laser densification process followed by an etching step, but the optical loss in these layers is extremely high. Another patterning process for sol-gel materials is reported by Popall et al.[4-6], using organically modified ceramics. Laser radiation is used in this investigations to photopolymerize active groups. The irratiated parts become insoluble and remain after a development step patterns are obtained. The patterning process was developed for microelectronic materials and the optical properties had been of no interest in these developments. The question arises whether laser patternable organically modified sol-gel materials can be prepared with homogeneities suitable for optical applications. Therefore, special synthesis techniques had to be applied to obtain sufficient homogeneity.

2. EXPERIMENTAL

The coating materials were prepared by reacting one mole 3-methacryloxypropyltrimethoxysilane (purified by vacuumdestillation), dissolved in methanol with 1.5 mol H_2O at 50 °C for one hour. Subsequently the reaction mixture was cooled down to -10 °C, and a

solution of 0.1 mole zirconium-n-propoxide in 1-propanol, complexed with 0.1 mole methacrylic acid was added. The mixture was stirred for 90 minutes followed by the addition of water (0.15 mol). After a reaction time of 24 hours at room temperature, one weight percent of a photoinitiator (Irgacure 184, Ciby Geigy) was added.

After the solution was filtered with a 0.2 μm membran filter, the carefully cleaned fused silica substrates were coated by a flow-coating technique[7]. The films were then dried at 40 °C for half an hour.

The fabrication of planar waveguides was carried out by UV-exposure in a Beltron UV curing apparatus with 2400 W UV-power and a coveyor band speed of 3 m/min. For laser writing, a frequency doubled Ar ion laser was used. The power of the frequency doubled beam was 10 mW at 257 nm. In fig. 1, the laser patterning device is shown.

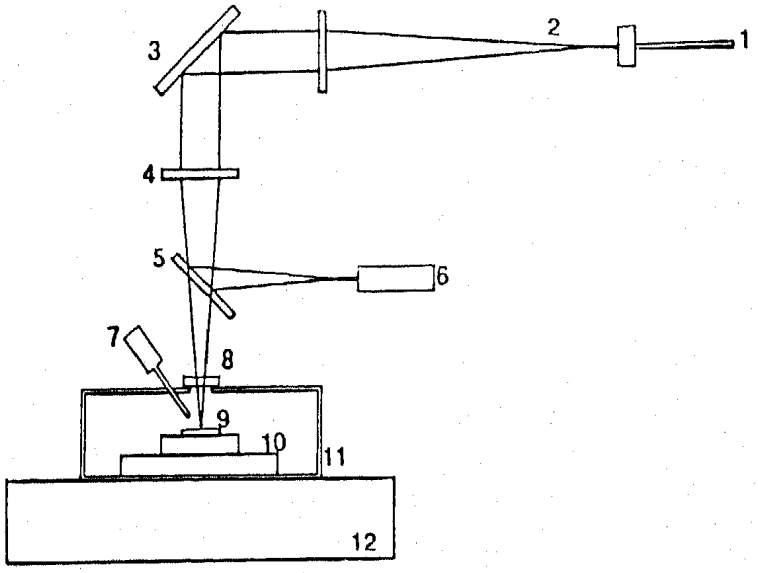

Fig. 1. Scheme of a direct laser writing equipment. 1: laser beam, 2: beam expander unit, 3: flat mirror, 4: focusing lense (fused silica), 5: fused silica plate, 6: laser beam analyser, 7: TV-microprobe, 8: fused silica window, 9: sample, 10: motor driven x-y-stage, 11: reactor housing, 12: optical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

The spot size of the writing beam can be adjusted by a beam expanding gallilean telescope and a focussing quartz lens. The quality and shape of the focused beam is controlled by a video-setup in combination with a TV-microprobe. The intensity profile is measured by a two dimensional laser beam profilanalyser. By the combination of the TV-microprobe and the beam analyser an exact process controlling is possible. The film on a substrate is placed onto two motor driven stages providing horizontal xy-movement. The

spatial resolution of the system is 100 nm at a maximum velocity of 0.5 mm/sec.
Optical losses of the planar waveguides were measured by prism film coupler technique[8]. The incident laser beam of a 1 mW HeNe laser at 633 nm was coupled into the waveguiding film by a right angle prism. The intensity of the guided wave was measured at different distances from the incoupling point by a digital image analysis system, and the optical loss was calculated.
For dielectric strength measurements, a 90 μm thick film of the uncured material with different solution content was slot coated on a copper block. A metal ball, which was movable by a micrometer screw was brought into contact with the copper block and then returned for 70 μm. High voltage was then applied and the breakdown voltage was registrated.

3. SYNTHESIS

In order to obtain ORMOCERs with high optical performance (optical loss of the waveguide should not exceed 1 dB/cm for short distance applications), a system was chosen which seemed promising for synthesizing homogeneous distribution of inorganic and organic components. The role of the inorganic components was focussed on providing mechanically stable (hard) surfaces and a Tg high enough to obtain sufficient thermomechanical stability. This is of importance if dopants like organic dyes have to be used to incorporate non-liniear effects. For photopolymerization based crosslinking, methacrylate double bonds were chosen from several reasons. First, methacrylate group substituted silanes ($RO_3Si(CH_2)_3OCOC(CH_3)CH=CH_2$, MS) are commercially available, acting as a bridge between the organic and the inorganic phase, and second, they can be copolymerized with methacrylic acid (MA) used as achemical link between additional inorganic units and MS. Zr was chosen as a second inorganic network former, since it is already known that Zr increases the refractive index in ORMOCERs[9,10] and mechanical properties of the systems are interesting[11,12]. The refractive index should be established at values $n_D > 1.5$ since SiO_2 was used as substrates. As shown in [4], methacrylic acid can be

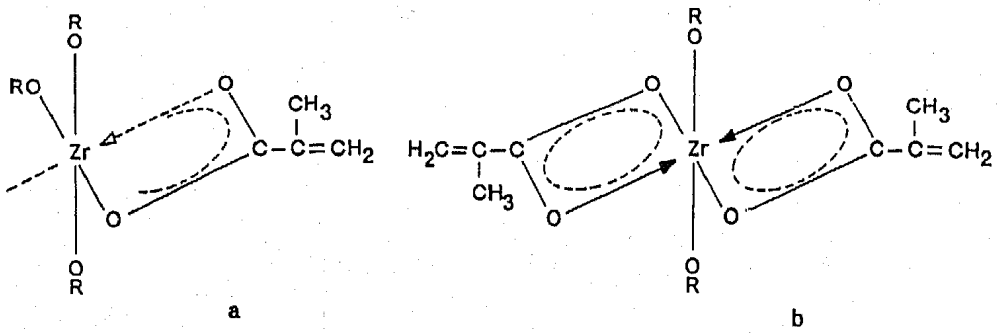

Fig. 2. Models for the "chelating" type of bonds between Zr and methacrylic acid. a: Zr: MA = 1 : 1; b: Zr: MA = 1 : 2.

reacted with Zr alkoxides up to the ratio Zr : MA = 1 : 2. IR analysis [4] shows a shift of the $m_{C=O}$ frequency of MA to lower wave numbers, as found in carboxylate anions. Another model is the formation of chelate type of complexes (fig. 2). How far this type of "link" between organic and inorganic units can be used for material tailoring mainly depends on the chemical stability of the bonds. The simple "salt formation" resulting in a pure ionic bond, for example, in $Na^{+}CH_3COO^{-}$, should lead to partial hydrolysis under wet conditions according to the pK values of organic acids. Experiments to hydrolyse the Zr acrylic acid compound, however, do not lead to any recovery of the free acid $m_{C=O}$ vibration, as shown by IR analysis (fig. 3). This supports the probability of the existance of structures suggested in fig. 2, which, as shown in fig. 3 also, can be maintained throughout a subsequent polymerization step. ^{13}C NMR investigations support the hypothesis of complex formation.

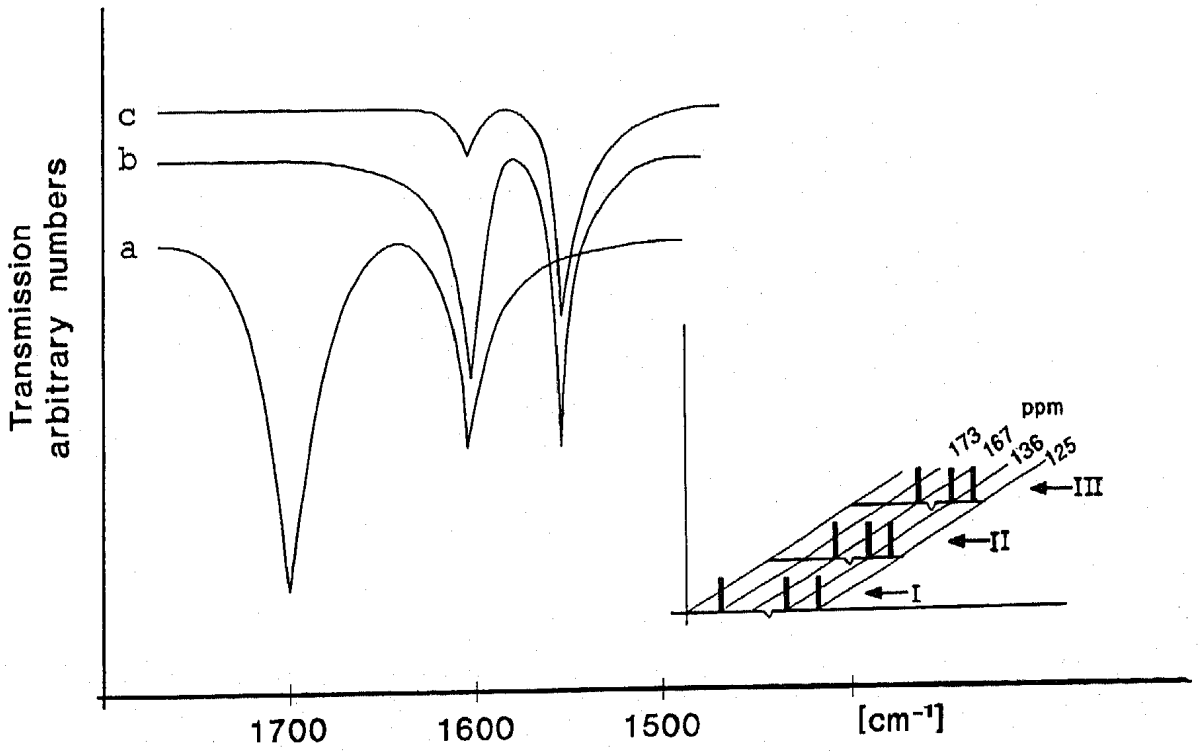

Fig. 3. IR and ^{13}C NMR analysis of Zr alkoxya methacrylic acid complexed. a: methacrylic acid; b: Zr/methacrylic acid complex (1 : 1); c: after polymerisation. I, II, III: same treatment, chemical shifts of -O-C- and C=C of methacrylic acid.

Based on these findings, the system Zr/MS, MA was considered to be the most promising composition suitable for patterning experiments,

especially with respect to immobilize the Zr for obtaining a molecular distribution and to end up with high homogeneities.

4.COATING AND PATTERNING RESULTS

For coating, the viscosity could be varied by solvent addition and for flow coating experiments, a viscosity of 6.6 mPa·sec was chosen. After UV-curing of the planar waveguides and after developments of the laser written patterns, the material was finally cured at 130 °C for 1 hour. This procedure gives a 12 µm film thickness for a one coating procedure.

Measured optical losses by coupling a HeNe laser beam into the film ranged from 3 dB/cm to 6 dB/cm. The photograph of a streak of guided light excited in an ORMOCER film is shown in Fig. 4

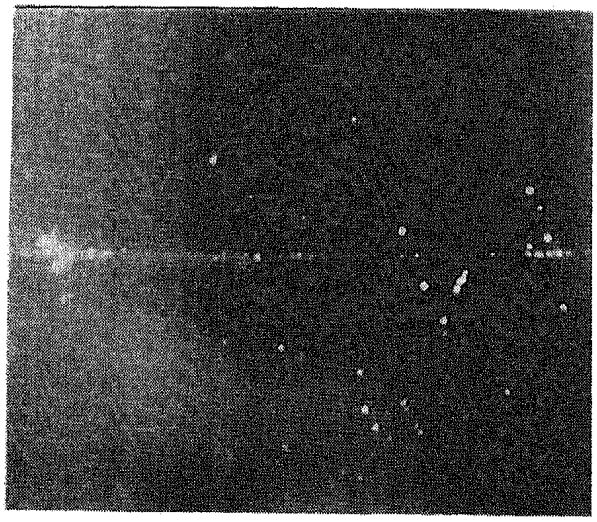

Fig. 4. Photograph of a streak of guided light excited in the ORMOCER film of Zr/MS/MA.

The scattering of the results mainly could be attributed to dust particles embedded in the coating or on top of the coating, which could be visualized by optical microscopy. These dust particles can also be seen in fig. 4 as randomly distributed white spots. It is expected to improve the loss remarkably by improving the clean room conditions. Anyway, the losses should be far higher, if phase separation had taken place during hydrolysis and condensation.

The laser written patterns were developed by treating the coating in propanol for 2 minutes, thereby the undeveloped regions are dissolved and washed out. In fig. 5 is shown a SEM micrograph of a strip waveguide of 30 µm width obtained by this process.

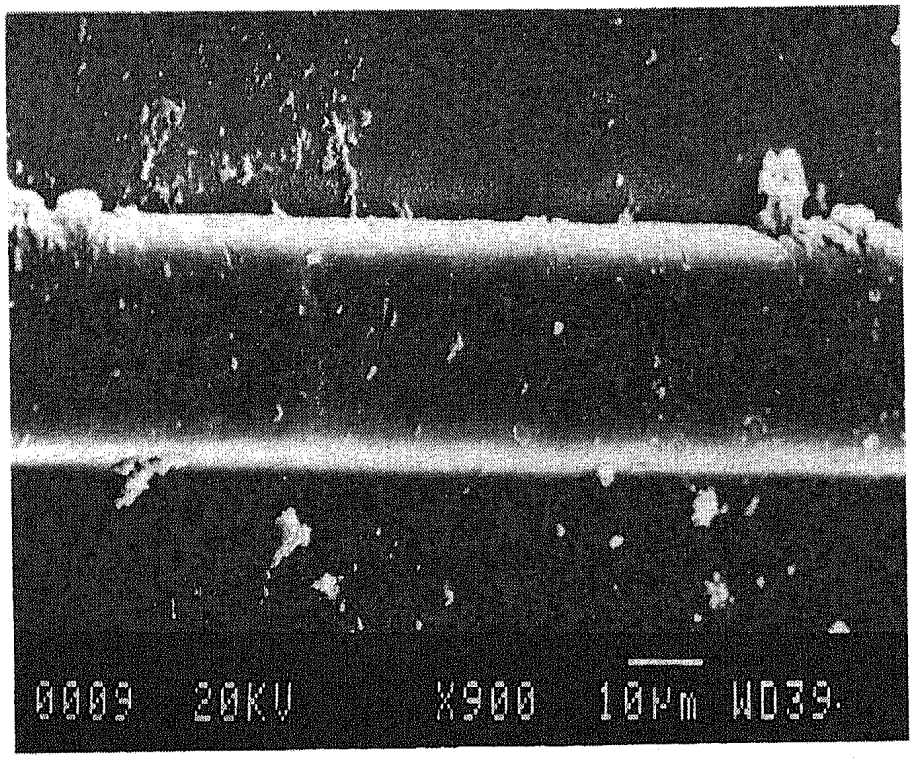

Fig. 5. SEM micrograph of the patterned ORMOCER-system at 14 W/mm² laser intensity, 30 µm laser focus, 0.5 mm/s writing speed, 1 % initiator concentration and developed in propanol.

Although again a lot of dust is visible, the strip-waveguide shows smooth surfaces and therefore, low surface scattering and consequently low optical loss should be obtained. In fig. 6, the three-dimensional profile of this laser-written strip-waveguide is shown.

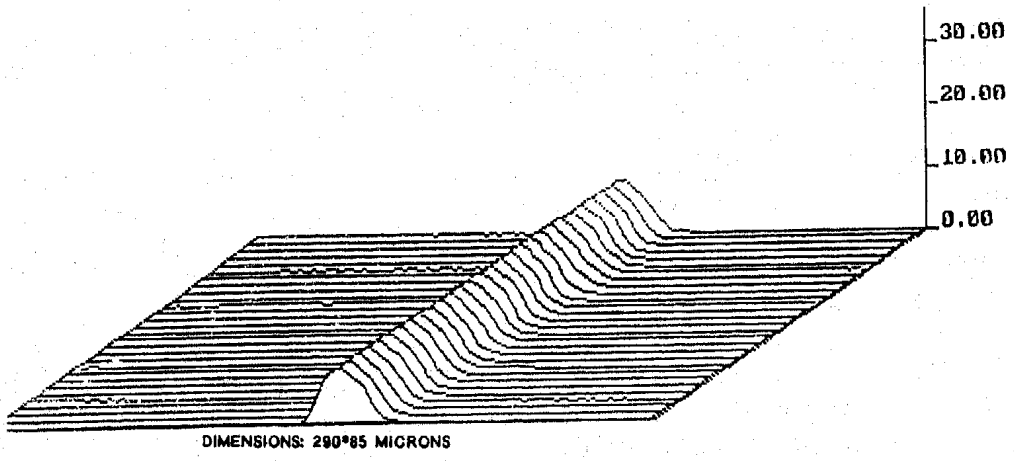

Fig. 6. 3D-profile of the strip-waveguide shown in fig. 5.

5.ELECTRICAL PROPERTIES

For the preparation of active waveguides, the incorporation of organic molecules with non-linear optical properties (v^2, push-pull systems) is necessary. Poling experiments require high breakthrough voltages, which can become a serious question in sol-gel systems (H_2O content, acid or base catalysts). For the synthesized ORMOCER system with lowest solution content, a breakdown voltage of $> 1.5 \cdot 10^5$ V/cm was determined. A value which is sufficient for poling experiments. The real breakdown voltage of a dried film can be assumed to be higher than $1.5 \cdot 10^5$ V/cm, as such a film has less solution contents than the film prepared for dielectric strength measurements. This result shows that ORMOCERs are potential matrix materials for poling organic molecules with NLO-properties.

5.CONCLUSION

The experiments show that it is possible to synthesize ORMOCER materials with a high potential for waveguide application. These materials have low optical loss and can be patterned by a laser writing technique. Due to a high breakdown voltage, they are potential matrix materials for NLO-molecules.

6.ACKNOWLEDGEMENTS

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