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University of Padova 9 – 12 June 1992

edited by

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OPTICAL MATERIALS PRODUCED BY SOL-GEL REACTIONS

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1. Introduction

The sol-gel process represents a chemistry based route to inorganic non-metallic materials and inorganic-organic composites. While pure inorganic materials like glasses and ceramic materials have to be treated at a higher temperature to reach full density, inorganic-organic composite materials can be densified at a lower temperature to achieve almost complete degrees of condensation [1-2] This can be attributed to an enhanced relaxation rate due to the effect of decrease of network connectivity caused by organic substitutants[3]. For the same reasons, it is possible to obtain thick layers in one step coating procedures up to 50 µm, which is hardly possible with pure inorganic sols since cracking occurs very likely with layer thicknesses of more than 1 µm[4-5]. Curing of these films can be carried out either by heat treatment[3] or by photocuring if polymerizable groupings are present[6]. For curing, similar mechanisms can be applied as used for polymerizable organic monomers like methylmethacrylates or epoxides. Based on this, several processing techniques become available. If light is locally applied and the layer shows photoresistant properties, photolithography becomes possible, for example. For optical applications, a sufficient homogeneity of the composite material is required, and therefore, phase separation has to remain on a nano level. This is not critical for optical coatings but may become critical if planar or channel wave guides are envisaged. In this paper, a survey over some film forming systems including synthesis, characterization and processing is given, and properties of systems suitable for optical coatings as well as patterning processes for integrated optics applications will be described. They are based on polymerizable silanes which optionally are crosslinked by modified alkoxides from Zr.

2. Experimental

A general reaction scheme for the preparation of the composite material is given in fig. 1.

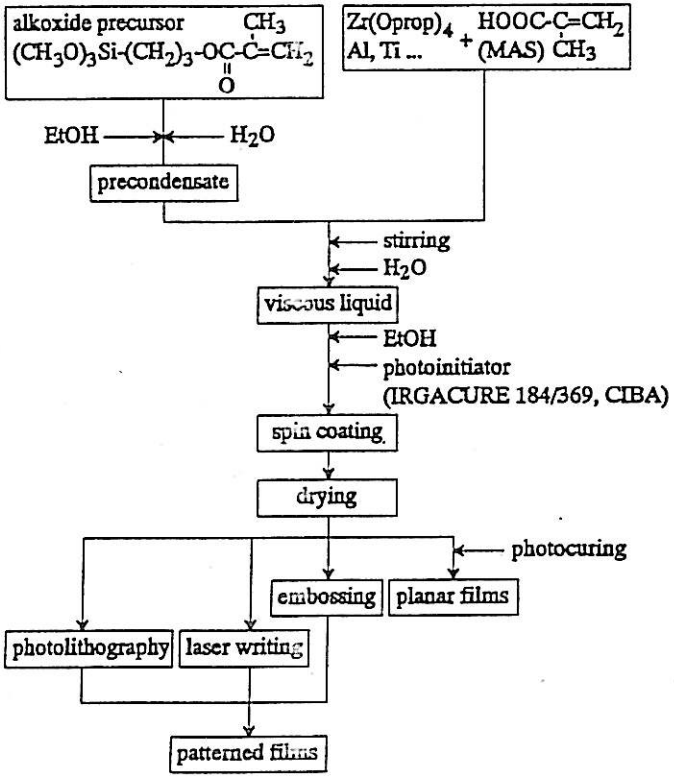


Fig. 1. Flow chart of the preparation scheme of $ZrO_2/MAS/CH_2=C(CH_3)COO-(CH_2)_3SiO_{3/2}$ composites.

Detailed synthesis descriptions are given elsewhere[5-8] Spin coating experiments are carried out on a spin coater at 500 rpm. The viscosity of the spin coating liquid has been adjusted to 6-7 mPa · s by addition of ethanol. Fused silica slides were used as substrates. For photolithography, a maskaligner technique has been used (maskaligner: Electronic Visions, AL4). The irradiation time was 1 min. After irradiation, the films had been developed by treating them with acetone at room temperature for 10 - 30 sec. The patterns were characterized by surface

profiling using a commercial system (SAS Nanosurf 448) and by SEM. For laser writing, the system described in Ref. 6 has been used. Embossing was carried out using commercially available optical gratings and a metal mesh. During embossing the film was irradiated through the substrate.

The progress of the hydrolysis and condensation was investigated by following the H_2O content by Karl-Fischer titration and by ^{29}Si NMR. Polymerization yield was determined by IR spectroscopy following the decay of the C=C double bond.

3. Results and Discussion

3.1 Reactions of the System $Zr(OR)_4$/MAS

The complex formation of carboxylic acids with alkoxides is a well-known reaction[9,10]. Methacrylic acid (MAS) forms complexes with Zr alkoxides up to a ratio of Zr:MAS ≤ 1:1.8. Higher ratios yield in non-complexed acid, as shown in Ref. 11. Between 1:1.8 and 1:0.8, no precipitates or gels can be obtained from alcoholic solutions, even if excess water is added. IR and NMR spectra do not show any traces of the free acid. Gelation can be obtained with excess water if the ratio Zr:MAS becomes < 0.8. But in this case, too, no free acid formation could be observed, indicating the high stability of the carboxyl complex. Zr alkoxide with aliphatic acids, for example acetic or propionic acid do show different behavior under equal reaction conditions. Between r=1:0.8 and 1.8, the system shows the formation of nanoscaled clusters (determined by photon correlation spectroscopy, PCS) with increasing Zr:MAS ratio (fig. 2). The PCS measurements also mainly indicate spherical particle shapes.

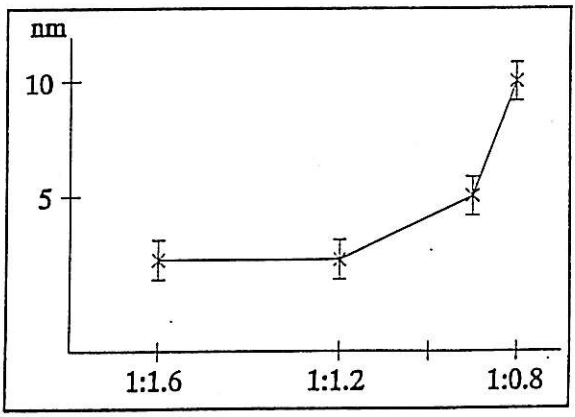


Fig. 2. Particle diameter of Zr alkoxide (MAS complexes after excess water addition).

This means, the ratio Zr:MAS can be used

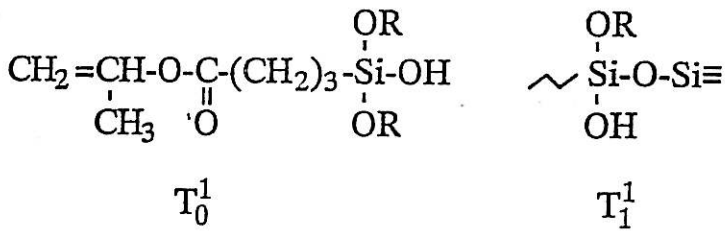


Fig. 3. Classification of threefold binding silanes by T symbols.

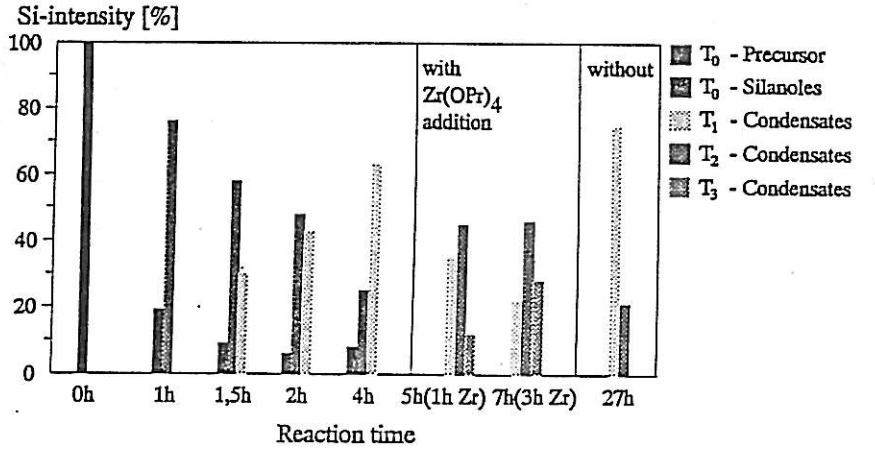


Fig. 4. Influence of $Zr(OR)_4$ on hydrolysis and condensation of methacryloxypropyl trimethoxy silane by ^{29}Si NMR spectroscopy.

for variation of the cluster size in a derived range. In order to avoid precipitation during further hydrolysis and cocondensation process an alternative for the process of reacting the Zr/MAS complex was investigated with the methacryloxysilane as polymerizable unit. Therefore, the hydrolysis and condensation of the silanes was followed by ^{29}Si NMR spectroscopy. In fig. 4, the formation of a sequence of the T species is shown. $T0^0$ is the unhydrolysed precursor, $T0^1$ indicates one silanole group, $T1^1$ one silanole group and one siloxane bond (fig. 3).

Fig. 4 shows the time dependance of the hydrolytic reaction without and with the addition of Zr propylate.

As one can see from the data, there is a remarkable acceleration on the formation of higher T species. But it is no discussion possible whether ≡Si-O-Zr≡ bonds are formed or not. The reaction of the

prehydrolysed methacryloxysilane with the Zr/MAS complex is shown in fig. 5. A comparison of the kinetics in fig. 4 and fig. 5 shows, that the complexed alkoxide (1:1) acts basically the same way as the uncomplexed form.

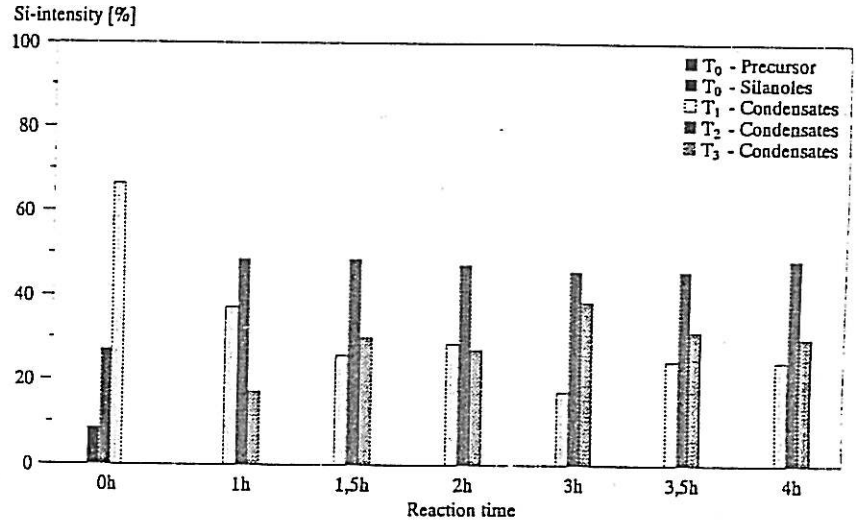


Fig. 5. Reaction of the complexed alkoxide with prehydrolysed methacryloxysilane by ^{29}Si NMR spectroscopy.

PCS measurements of the system of prehydrolysed methacryloxy silane with the Zr:MAS complex with the ratio 1:1 show that over a period of more than two weeks the particle size does not exceed 5 nm. So it can be concluded that this type of nanocomposite should show sufficient homogeneity for optical waveguide application.

3.2 Film Formation and Patterning Processes

The liquid system was diluted with ethanol to obtain a viscosity of about 6 - 7 mPa·s suitable for a spin coating process. The films are dried at room temperature and then photocured by UV irradiation. The process resulted in films of about 10 µm in thickness with smooth surfaces. In fig. 6, a three dimensional surface roughness plot of the film is shown.

The plot shows the high quality of the film with a measured peak-to-trough value of 4.7 nm and a root mean square of 0.7 nm. For

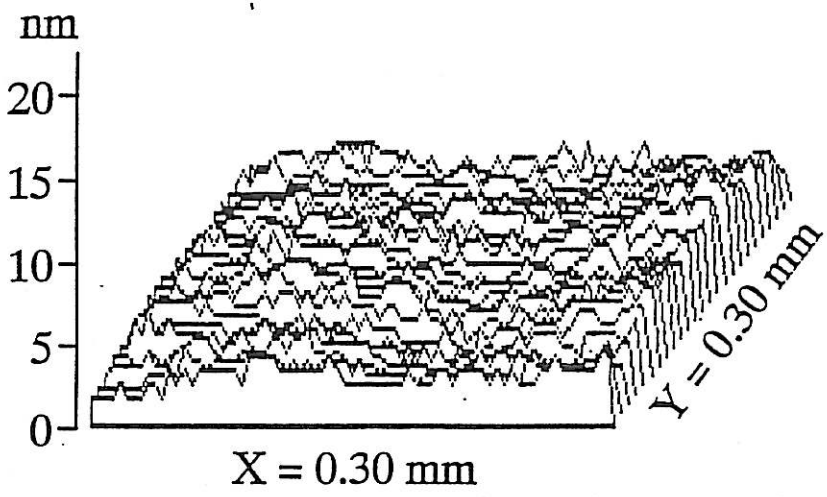


Fig. 6. Surface roughness of a cured film on glass.

measuring the optical loss, the incoupling system shown in fig. 7 was used.

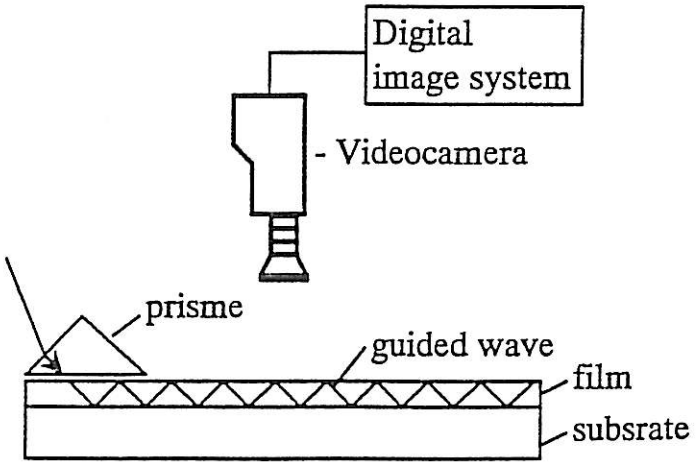
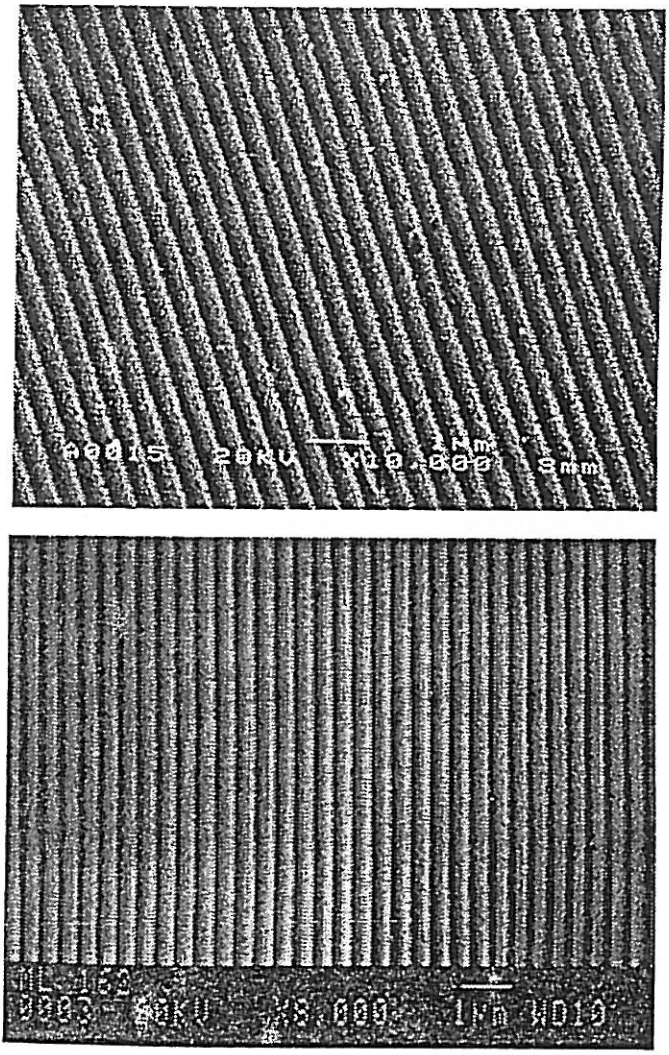


Fig. 7. Optical loss measurement device for an ORMOCER composite planar waveguide.

The optical loss could be determined to be < 0.5 dB/cm, which is a reasonable value and indicates the good quality of the composite. The films were patterned with three different procedures. The development of the methods is described in detail elsewhere[6-8].

For embossing, a mesh with a width of 10 µm and an optical grating were used. The embossed patterns show steep flanks for the mesh and a very close reproduction of the master mould (fig. 8 and fig. 9).



a

b

Fig. 8. SEM micrograph of the master mould (a) and the embossed ORMOCER replica (b) of an optical grating with 2400 lines/cm.

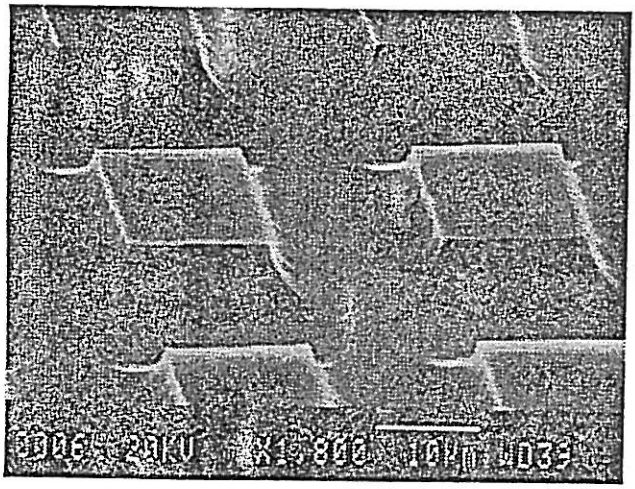


Fig. 9. SEM micrograph of the embossed replica of a mesh with 10 μm width.

The laser writing was carried out by using a laser beam focus to 30 μm in diameter. The writing step was performed by moving the substrate with a computer controlled support. The laser light initiates the polymerization process and the non-irradiated section remains soluble. The irradiated films were kept in acetone for 30 sec. Fig. 10

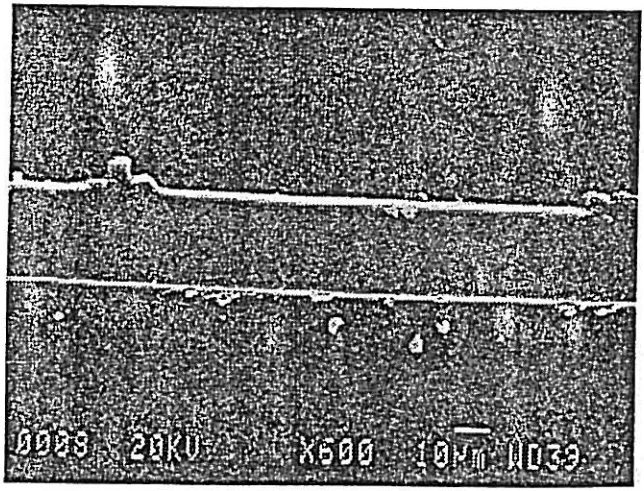


Fig. 10. SEM micrograph of a laser patterned strip-waveguide.

shows the SEM micrograph of a developed strip-waveguide. The strip-waveguide has smooth surface and optical loss measurements show alternations of about 3 dB/cm, which is mainly due to defects and dust particles on the surface.

The results of the maskaligner patterning are shown in fig. 11 and fig. 12. They show that both sharp and smooth edges can be obtained

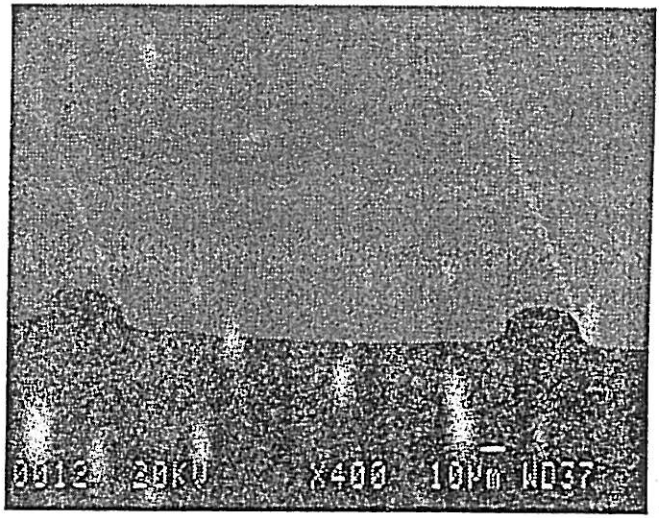


Fig. 11. SEM micrograph of strip-waveguides patterned by maskaligner technique (cross section).

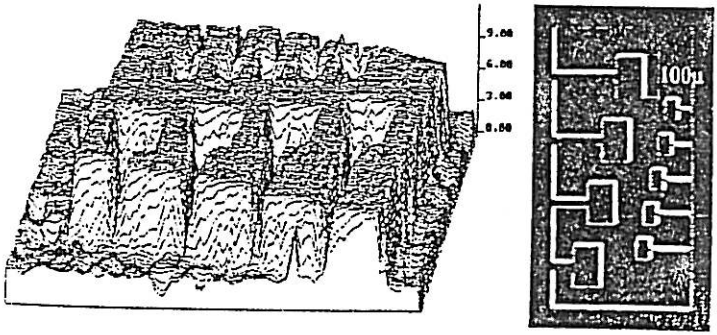


Fig. 12. Complex structure patterned by maskaligner technique; left side: surface profile; right side: micrograph.

by changing process parameters. The patterned strip-waveguides (fig. 11) have a diameter of 10 µm, so that monomode strip-waveguides of the same diameter could be connected with minimization of coupling losses. The complex geometry of fig. 12 has sharp edges with a peak-to-trough value of 10 µm. These two examples show, that the edge sharpness can be manipulated by irradiation time and mask distance, which is one point of further investigations.

4. Preliminary Further Experiments

It was shown that the developed ORMOCER system can be considered as an interesting base for novel optical passive waveguides. In preliminary experiments, the incorporation of active components was tested. It could be shown that it is possible to incorporate organic dyes such as Rhodamine 6 G, DANS, Theorescin, FG sin and photochromic dyes. First poling experiments with DANS have already been successful and showed interesting χ^2 effects. The incorporation of Nd complexed with MAS resulted in photoluminescent composites. Novel CdS and ZnO quantum dots[12] could be incorporated, too. These experiments show the potential of the system for being used as an active material for non-linear optical and laser applications. Laser writing also can be used for writing of surface holograms.

5. Conclusions

The developed ORMOCER system shows that films for optical applications can be prepared. These films can be doped as active components. In combination with various patterning techniques these systems have an interesting potential for a variety of optical applications.

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