Organic-inorganic composite materials: optical properties of laser patterned and protective coated waveguides.

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ABSTRACT

A composite material based on organically modified Si alkoxides and modified alkoxides from Zr were prepared. The index of refraction of the system was tailored by the variation of the modified Zr component. Channel waveguides were prepared by a laserwriting technique based on the ability to photopolymerize this material. To decrease optical loss caused by effects of the waveguide surface and to be independent of the used substrate, a buffer layer and a protective layer of the same material of lower index of refraction was combined with a waveguiding film and optical losses were determined.

1. INTRODUCTION

Composite materials are an interesting material group for the preparation of passive and active optical devices. Low optical loss is one of the major requirements for optical applications. Therefore the dimension of phase separations must be in the lower nm range to avoid Rayleigh scattering. The intrinsic optical absorption of the material at the used wavelength and surface roughness of waveguiding elements also has to be minimized. Sol-gel chemistry offers a very useful tool to control microstructure and particle size of nanocomposites.

Pure inorganic films made by sol-gel techniques combine good mechanical and thermal stability with low optical losses and the index of refraction can be varied over a wide range by multicomponent systems like TiO_2/SiO_2[1]. The preparation of channel waveguides within these films by laser treatment has been difficult since local laser densification led to carbon particles increasing the optical loss to more than 5 dB/cm[2]. Moreover, preparation of crackfree films with thickness of more than one micron is considered to be extremely difficult[3-5]. But Mennig et al.[6] recently described a synthesis procedure to prepare pure inorganic dense SiO_2 films of about 7 μm thickness, which seems to be a promising technique for multimode planar waveguides and chip-to-fiber coupling procedures.

Sol-gel chemistry combined with organic polymer chemistry allows to synthesize organic-inorganic composite materials of the ORMOCER type and tailoring of different properties by structure variation[7]. Thick layers (20 μm and more) have been produced in one processing step by simple coating techniques like spin-on or dip coating. Decreased network connectivity by organic substituents leads to an enhanced relaxation rate and to lower densification temperatures[8-10]. Promising results concerning microoptical applications were obtained for a system based on methacryloxypropyl trimethoxysilane and zirconium n-propoxide complexed with methacrylic acid. Compared to pure organic polymers, these systems can be synthesized with relatively high T_g values, thus being less sensitive against high temperatures than optical polymers. As described elsewhere[7,10-15], thick films with low surface roughness, high breakthrough voltages suitable for poling, low optical losses and resist properties to be used for photo assisted embossing, laser writing and photolithography have been fabricated. In order to use this material on different substrates and to prevent surface scattering by dust contamination, the material was optimized in order to serve as buffer layer, waveguiding material and cladding in the same system. For this, appropriate techniques for refractive index tailoring, coating and cladding techniques and photolithography had to be developed.

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2. EXPERIMENTAL

A general reaction scheme for the preparation of the basic composite material based on methacryloxypropyl trimethoxysilane (I), zirconium n-propoxide (II) complexed with methacrylic acid (III, MAS) and the subsequent processing steps is shown in fig. 1. Irgacure 369 was used as a photosensitive initiator (1 weight-%). Detailed synthesis descriptions are given elsewhere[11,16].

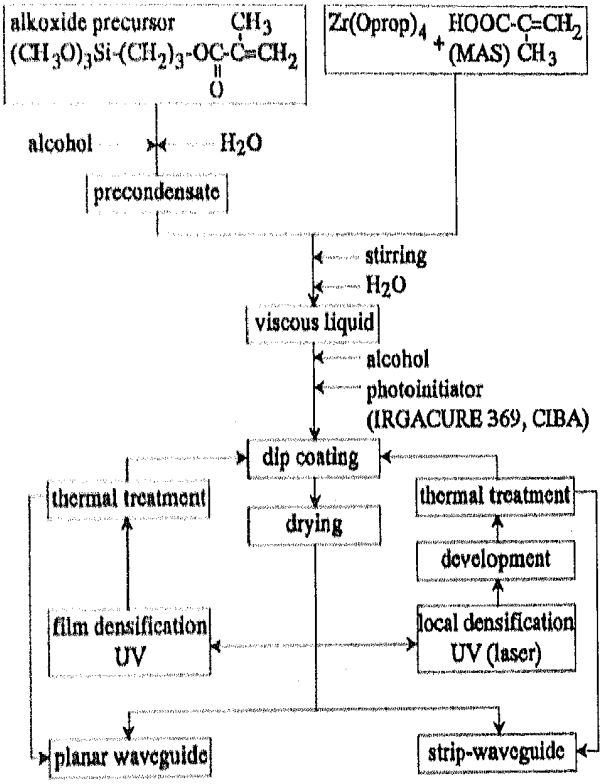

Fig. 1. Flow chart of the preparation scheme for a system based on alkoxysilane/Zr-alkoxide/ methacrylic acid.

In order to tailor the refractive index, the composition of the system was varied between 10:1:1 and 10:10:10 (I:II:III). The particle size in the sol was determined by photon correlation spectroscopy (PCS). The microstructure of the cured material was investigated by X-ray scattering. Thermal properties of the system were investigated by differential scanning calorimetry (DSC).

For the preparation of the pure methacryloxy silane condensate, the synthesis was carried out following the preparation scheme of fig. 1 without addition of the Zr/MAS component. For the preparation of the composition 0:10:10, the following variation was used: to avoid uncontrolled precipitation, the water for the hydrolysation and condensation was mixed with propanol in the ratio 1:10 weight-%. The zirconium n-propoxide was complexed with the methacrylic acid and the water/propanol solution was added very slowly to the Zr/MAS system. After a reaction time of 12 h under stirring, the alcohol was evaporated and the photoinitiator was added.

Thin films were prepared by dip coating and film thickness was investigated as a function of the drawing velocity. The film thickness was determined by surface profiling using a commercial system (SAS Nanosurfe 448). The viscosity of the dip coating liquid was adjusted to 17.1 mPas · s by addition of butanol. The films were dried at room temperature, photocured and thermally postbaked at 130 °C for one hour. Polycarbonate substrates (n_d=1.58) were used for the measurement of index of refraction (Abbé refractometer). Microscopic slides were used as substrates for measurements of optical losses and for laser patterning experiments. The fabrication of planar waveguides was carried out by UV exposure in a Beltron UV curing apparatus with 1200 W UV power and a coveyor speed of 1 m/min. Optical

losses were measured by prism coupling in combination with a digital image processing system[11]. Strip waveguides were patterned by local laser densification with an Ar^+ laser at 351 nm. The laser writing equipment is described in detail elsewhere[11] with the difference that no frequency doubling was necessary by the photoinitiator used in this process. The quality of the written waveguide was controlled by scanning electron microscopy. For the determination of the optical loss, a laser beam of a 10 mW HeNe laser was coupled in the waveguide by a focusing microscope objective lens. A sandwich structure of the composite material was built up in the form of a buffer/waveguide/protective layer by subsequently coating the substrate, photocuring, preparation of the channel waveguide by coating and patterning and final cladding of the patterned system.

3. RESULTS AND DISCUSSION

The complex formation of carboxylic acids with alkoxides is a well-known reaction[17]. The hydrolysis and condensation of the Zr alkoxide complexed with methacrylic acid was carried out in the presence of precondensated alkoxy silanes. Thus, precipitation can be avoided completely and nanosized ZrO_2-particles are obtained. PCS measurements of the liquid composite showed particle diameters (hydrodynamic diameter) of 2-4 nm. By application of the photocuring step described in the experimental part, a nanocomposite is obtained. In the cured material, particle diameters of 1.6 nm were calculated by wide angle X-ray measurements (WAXS) which is in good agreement with the PCS measurements. Results of WAXS measurements for the pure condensated alkoxy silane (10:0:0), the pure Zr/methacrylic acid system (0:10:10) and different compositions are shown in fig. 2. The materials are x-ray amorphous and the broad peak at $2\Theta=6°$ can be attributed to ZrO_2 particles chemically bonded to the organic part of the alkoxy silane over polymerized methacrylate groups. These peaks are not visible in the pure condensed alkoxy silane (10:0:0). The particle diameter is constant for all compositions which can be explained by the constant ratios Zr:MAS presuming that the Zr alkoxide to MAS ratio is the govering parameter for the particle size. Preliminary small angle X-ray experiments (SAXS) lead to the same results. Particle diameter in dependence of complexation ratios is discussed in detail in[7]. Based on the evaluated particle diameter, a model was developed using the different bond length of Zr-O, C-O and C-C, which is schematically shown in fig 3.

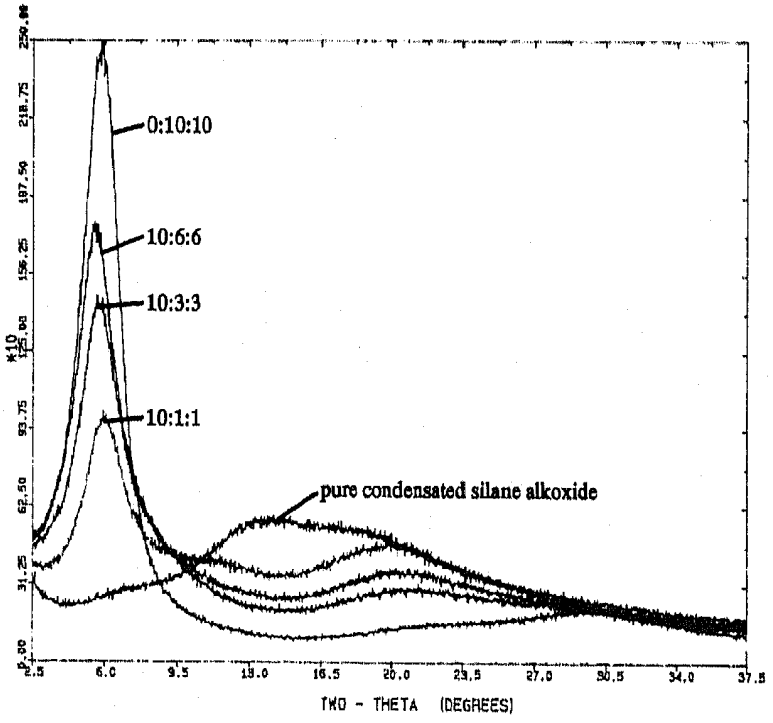

Fig.2. WAXS measurements of different composites (I/II/III) of the system: alkoxy silane (I), Zr alkoxide (II) complexed with methacrylic acid (III)

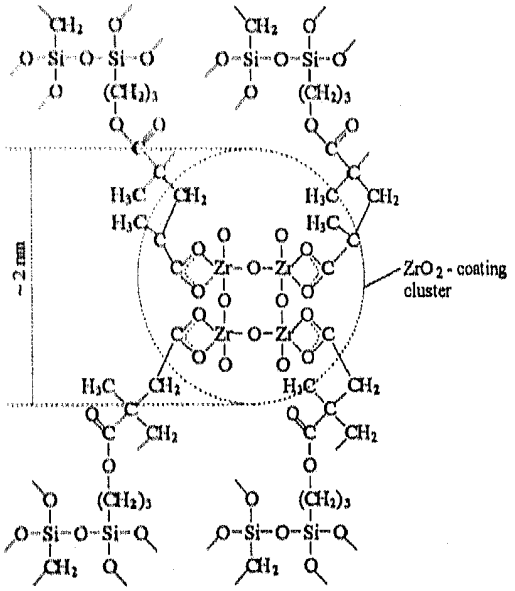

Fig. 3. Model for the ZrO_2-cluster formation

A direct formation of Zr-O-Si bonds seems to be unlikely from the chemistry of these elements. On the other side, ZrO_2 containing clusters are formed under these reaction conditions, still containing the complex bonds of methacrylic acid to Zr. The complex bond is stable under hydrolytic conditions[1] and thus providing an interesting tool to incorporate the clusters into the matrix of silane polycondensates by photopolymerisation of the methacryloxy groups to the methacrylic ligands. DSC-measurements show no glass transition and decomposition starts at temperatures > 200 °C (fig. 4). The lack of a glass transition temperature is a very promising property with respect to the incorporation of organic chromophores in order to avoid relaxation of poled chromophores. The lack of a glass transition also indicates a high crosslinking rate between organic and inorganic units.

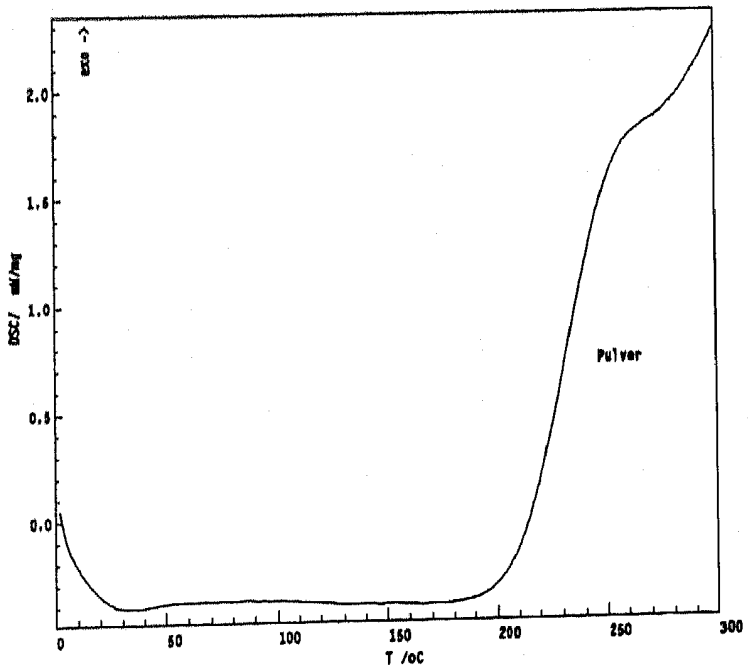

Fig. 4. DSC measurement of a composite (10:3:3) of the system: alkoxy silane (I), Zr alkoxide (II) complexed with methacrylic acid (III)

In order to be able to tailor film thicknesses, the dependency of the drawing velocity on film thickness was investigated (fig. 5). For the adjusted viscosity of 17.1 mPas · s, film thicknesses between 4 and 20 μm could be obtained by a single drawing step. Films of very high surface homogeneity could be attained by this method. For the pure Zr/methacrylic acid system, it was not possible to get crackfree films and therefore, this system was not used for further investigations.

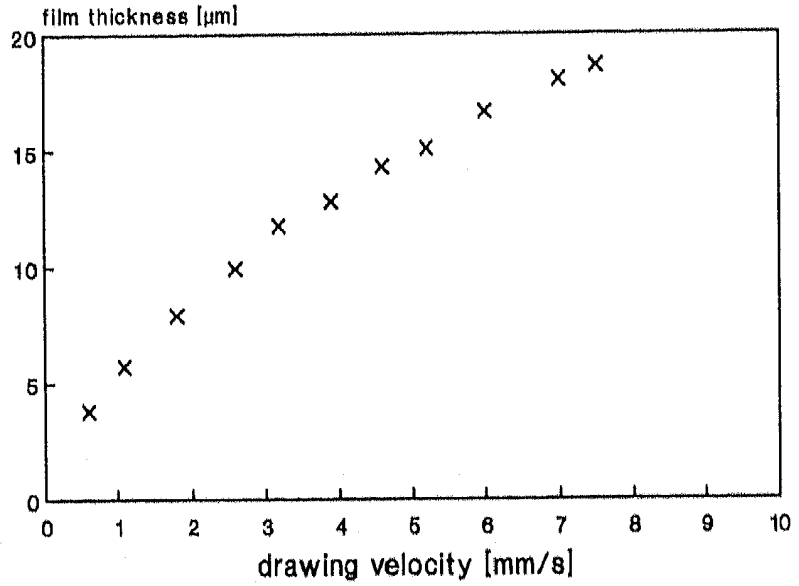

Fig. 5. Film thickness in dependence of drawing velocity for a composite (10:1:1) of the system: alkoxy silane (I), Zr alkoxide (II) complexed with methacrylic acid (III)

The experiments show that only by varying the withdrawing speed suitable film thicknesses can be chosen for buffer, waveguide and cladding layers. The optical loss for all compositions could be determined to be < 0.5 dB/cm which is a reasonable value for microoptical applications and indicates low scattering effects by the Zr clusters and small surface scattering. In order to use the same basic system for buffer, waveguide and cladding, the influence of the ZrO_2 content on n_D was investigated. Results of change of index of refraction by different ZrO_2 content is shown in fig. 6.

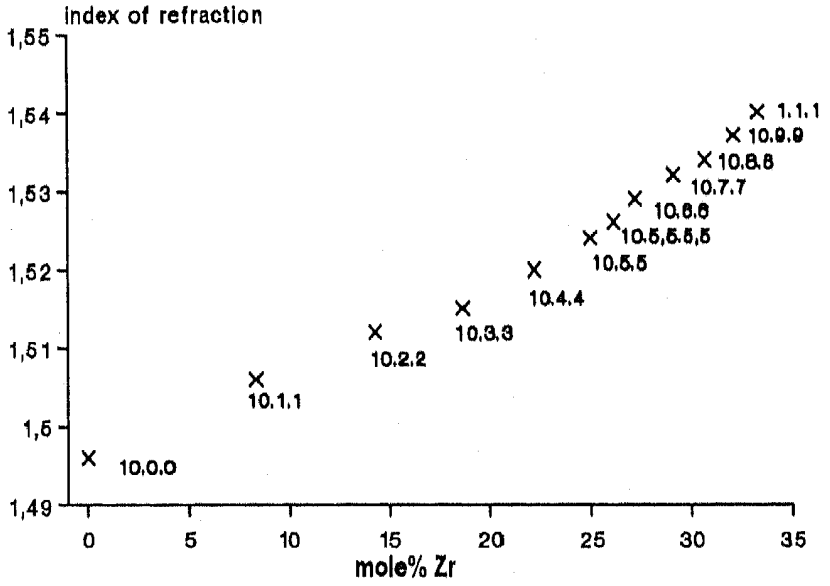

Fig. 6. Index of refraction as a function of ZrO_2 in the (I/II/III) system: alkoxy silane (I), Zr alkoxide (II) complexed with methacrylic acid (III); numbers in the diagram refer to compositions I:II:III

The results show, that the variation of n_D allows the use of the system for all three layers. The use of a buffer layer with smaller index of refraction leads to an independence of the substrate and the protective layer reduces any environmental influences on the guided wave. Moreover, the numerical aperture can be freely adjusted by adequate adaption of the refractive index of the different layers. A SEM micrograph of a sandwich comprising a three layer system is shown in fig. 7.

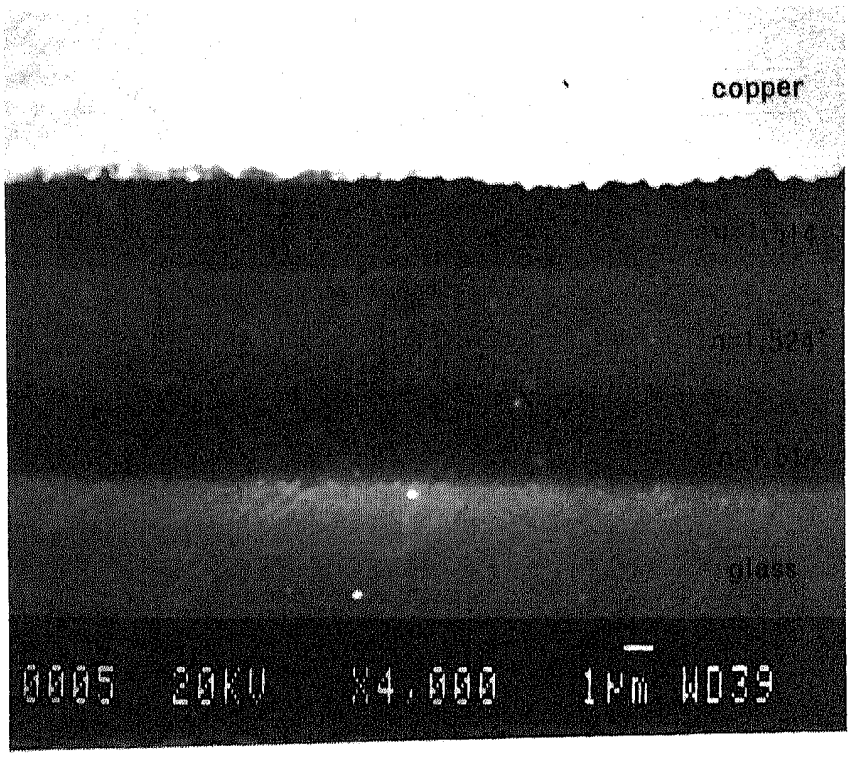

Fig. 7. SEM-micrograph of a sandwich of the composites (10:3:3), (10:8:8), (10:3:3) of the system: alkoxy silane (I), Zr alkoxide (II) complexed with methacrylic acid (III)

To fabricate a strip waveguide, the following procedure was developed: a buffer layer (n_{633} = 1.506) was dip coated, photopolymerised and thermally cured. A second layer with higher index of refraction (n_{633} = 1.514) was dip coated and locally polymerized by a focused laser beam. The non-polymerized regions were removed by butanol as a developing agent and the written strip waveguide was thermally post-baked. A third layer with lower index of refraction (n_{633} = 1.506) was dip coated, photopolymerized and thermally heat-treated. A SEM micrograph of cross section of the final sandwich system buffer/strip waveguide/protective coating is shown in fig. 8. The written structure has good flank steepness and almost a square shape. Optical loss measurements show values < 1 dB/cm, which is low considering the fact that no special clean-room conditions have been employed.

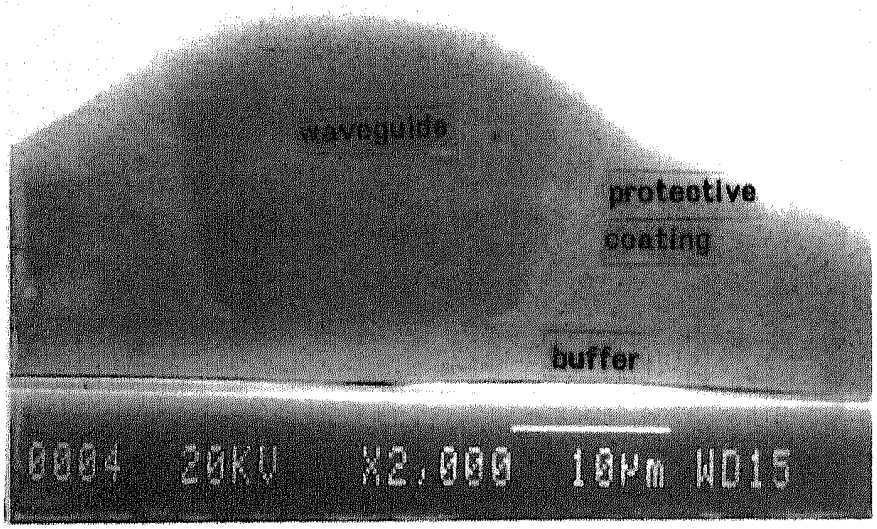

Fig. 8. SEM micrograph of a sandwich buffer/strip waveguide/protective coating of the composites (10:1:1), (10:3:3), (10:1:1) of the system: alkoxy silane (I), Zr alkoxide (II) complexed with methacrylic acid (III)

4. Conclusion

The development of nanocomposites of the ORMOCER type with phase separations in the lower nanometer range allows the preparation of films for optical applications. Low optical losses and the variation of the index of refraction by composition changes facilitate the fabrication of a sandwich system of a buffer/waveguide/protective layer. In combination with photolithographic techniques and nonlinear optical dopends, these organic-inorganic nanocomposites have high application potential for integrated optics.

5. Acknowledgement

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