

Inorganic-organic Polymers for Micro-Optic Applications

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1 Introduction

The realisation of microoptical devices is strictly correlated to the development of new materials and technologies. Simple processing techniques and multifunctionality of the materials is mostly not available by a single but only by the combination of several materials. Materials which are used nowadays for optical applications are inorganic glasses, silicon, lithium niobate, semiconductor materials and organic polymers. For integration, these different materials have to be combined on a single substrate, which leads to very complex and cost intensive processing techniques. The industrial development of high performance materials with high development costs is strongly limited by small market volumes, if the added value of down stream systems based on these materials cannot be included.

Chemical synthesis by sol-gel techniques allows to fabricate materials with a lot of very interesting optical properties [UHL 90]. Multicomponent systems with wide variations can be synthesized and thick layers can be produced by simple techniques like spin-on and dip-coating. To achieve inorganic materials like glasses, temperatures of about the glass transition have to be employed in order to get fully dense final materials.

But the sol-gel process also allows the incorporation of organic compounds or groupings [SCH 88, SCH 89, Bri 90]. The integration of such organic groupings can reduce the densification temperature drastically [DUN 90, MAC 91, SCH 91a], and thick and dense layers can be produced at moderate temperature. Sol-gel chemistry combined with organic polymer chemistry makes it possible to synthesize materials with different compositions of organic and inorganic components. The structure of this materials can be controlled by the bonds between the organic and inorganic units, as well as phase separation phenomena to provide high optical quality. The materials can be used as matrix-materials for various types of optical active depends. These manyfold variation possibilities in combination with their good optical properties provide an interesting application potential for this type of inorganic-organic composites (ORMOCER \equiv ORganically MODified CERamics) in integrated optics. Due to their sol-gel based synthesis they can be produced in small quantities, too, and a system and problem oriented material development are possible.

2 Structure elements

For the synthesis of inorganic materials by the sol-gel process, reactive monomers, oligomers or colloids can be used as starting materials. By polycondensation step, a polymeric network can be formed especially if silanes are used. A common route is the use of alkoxides as precursors which hydrolyse in the presence of water, condensing spontaneously to polymeric species. An other route is the hydrolysatation and condensation of inorganic salts by pH-change. Precipitation can also be started by the destabilization of colloidal sols by pH-change either in organic solvents or in water. These condensation reactions lead to gels, in which solvent or air are contained after first drying. Depending from processing steps, they contain water, organic or unhydrolysed

alkoxy groups. Drying and densification of the gels is made by heat treatment to convert them into glasses or ceramics.

Introducing organic groupings decrease the network connectivity of the gel and leads to dense materials at temperatures between 50 °C and 150 °C. Several chemical links and bonds between organic units and the inorganic backbone can be considered and the type of connection between organic and inorganic units is the main structure determining factor.

Covalent bonds can be used to form links to organic groups as well as to inorganic backbones (Fig. 1). Silicon for example is able to form stable bonds to oxygen as well as to carbon, but some other bonds like $=P-C\equiv$ or $\equiv Sn-C\equiv$ are possible whereas transition metal Me-C bonds, as a rule, are not stable against hydrolysis. This covalent bond can be used as a general link between organic and inorganic components. In case of non-reactive organic groups, organic network modification leads to so called spin-on glasses [BAG 90] which can be densified at low temperatures of 200 - 300 °C, and which can be applied in thickness of more than 20 μm .

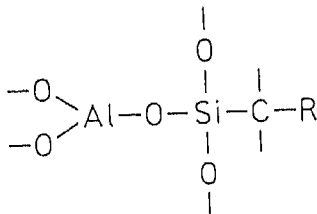


Fig. 1: Structure model for a covalent link between oxide network and organics

For incorporation of a wider range of oxides, complexing agents like β -diketons, conjugated organic acids or amines can be used, forming coordinative bonds and allowing organic modification with polymerizable chelating ligands. Examples of alkoxy dicarbonates (a) or methacrylates (b) are shown in Fig. 2 a, b. These complexing ligands are acting as termination sites for condensation and, therefore are responsible for spatial extensions of the transition metal-oxo core [SAN 91]. Furthermore, inorganic ions can be incorporated by using amine complexes as chelating ligands (Fig. 2 c, d).

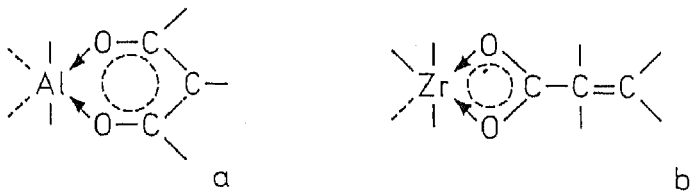


Fig. 2 a, b: Structure model of β -diketone and methacrylate complexes connecting transition metal oxide and organics

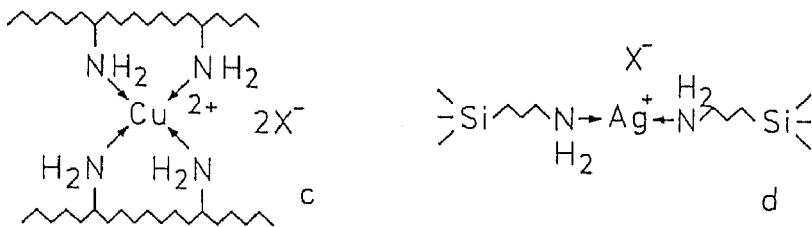


Fig. 2 c, d: Structure model of amine complexes to incorporate metal ions

The combination of the described principle with functional groups, which are able to be polymerized, polyadded or polycondensed leads to inorganic-organic polymers (hybrid polymers). These reactive groupings can be directly crosslinked, or organic chains can be built up by incorporation of organic monomers or oligomers (Fig. 3 a, b). Reactive crosslinking can be achieved by thermally or photochemically initiated polymerization and polycondensation reactions. E.g. oligomeric acrylates in combination with a photoinitiator can be used to build up crosslinked organic-inorganic polymers.

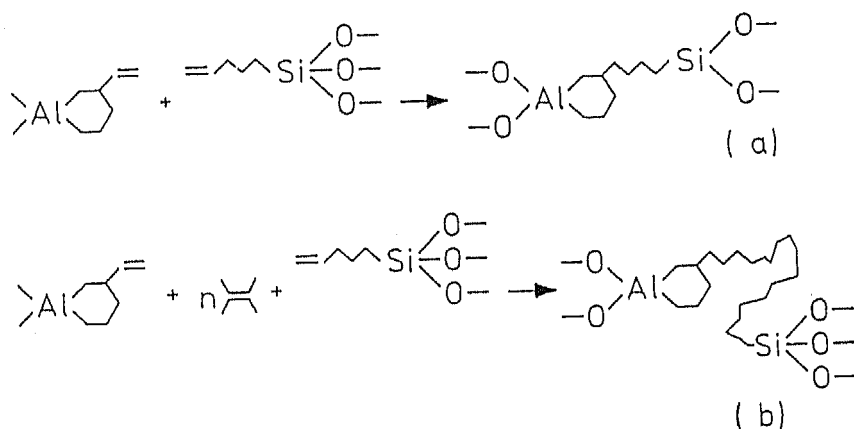


Fig. 3 a, b: Reaction scheme to build up organic-inorganic polymers

These few examples of structure elements, which can be used to build up the bulk material should demonstrate the numerous possibilities to tailor structure and thereby properties of the final product. Only small changes in synthesis conditions can result in large changes of the gel structure and organic-inorganic composites with completely different properties can be obtained. Some variations of optical properties by variation of synthesis conditions will be presented in the following examples.

3 Optical properties

As indicated above, the introduction of organic groupings into inorganic networks leads to a broad variation of structure and properties. For example, the reduced network connectivity decreases T_g and increases the thermal expansion coefficient α [SCH 90a]. T_g and α can be tailored over a wide range by synthesis parameters. Applications of such composite materials for microelectronics are for example described in [POP 90]. The low temperature at which the chemical synthesis of gels is performed allows to incorporate organic chromophores as the side chain or based on the host/guest idea [HAA 89, REI 90]. In contrast to organic materials, ORMOCERs have an excellent network stability [SCH 90b] and poling and polymerization can be done at room temperature. Relaxation phenomena of the chromophores could be avoided resulting in a long term stable SHG-signal. CdS or ZnO clusters can be precipitated in methacryloxy silane containing solutions [SPA 91a]. The size of these clusters in the nm range is controlled by stabilizing agents like amines and mercaptanes. These semiconductor quantum dots can be directly combined with the organic-inorganic network and stabilized by interconnectable ligands over polymerization and polycondensation. The sharp absorption band of these materials can be shifted by size-variation [SPA 91b] (cut-off effect), and interesting materials for optoelectronic and opto-optic applications can be obtained.

An ORMOCER system based on ZrO_2 methacrylate complexes, polymerized with methacrylate derivatives shows optical losses < 1 dB/cm for planar waveguides [KRU 91]. Films of $10 \mu\text{m}$ thickness prepared by spin-on have a surface roughness of less than 5 nm which is responsible for low surface scattering. The complexed ZrO_2 -sols contain ZrO_2 particles of about 10 nm [NAS 89] which contribute to small Rayleigh-scattering. By variation of ZrO_2 -content, the index of refraction can be change in the range $1.52 < n < 1.54$ at 633 nm.

Diffraction gratings with up to 2400 lines/mm and peak-to-peak values of 100 nm could be obtained by embossing techniques [SCH 91b]. These high amplitudes of the grating are available by the small shrinkage rate < 5 Vol-% of the liquid (non cured) material to the finally cured system. Multimode strip-waveguides were prepared by direct laser writing, which possess optical loss < 3 dB/cm [SCH 91c], and complex microstructures were obtained by maskaligner techniques. The higher optical loss compared to planar waveguides can be attributed to surface roughness of the written structure which is due to not yet optimized processing.

Fluorine modified ORMOCER's allow to change index of refraction to lower values $1.38 < n_D < 1.52$. Lowering the index of refraction also diminishes optical losses, as in case of density fluctuations, the loss is proportional to the eight power of the refractive index. The same is true for anisotropy fluctuations (proportional to the fourth power) which are pronounced in polymers with aromatic groups. An other interesting point of fluorine modification is the minimization of optical losses in the near infrared by suppressing C-H overtone absorption. Minimization of attenuation by fluorination of PMMA is already described in literature [GRO 89]. Fluorine modified ORMOCER's are also already described as hydrophobic dust repellent coatings [KAS 91]: by using only 2 mole-% of fluorinated precursors, surface energies comparable with PTFE could be obtained. Optical losses of such fluorinated ORMOCER's in the near infrared are to be measured.

4 Conclusions

Sol-gel chemistry in combination with organic polymer chemistry is a promising synthesis route to get tailor-made composite materials for microoptic applications. Structure, and thereby properties of these composite materials can be varied over a wide range by synthesis

parameters. These materials have high application potential for passive/active lightguidance and system and problem oriented tailoring is possible.

5 Acknowledgement

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