SOL-GEL OPTICS
PROCESSING
AND APPLICATIONS

Edited by

Lisa C. Klein
Rutgers, The State University of New Jersey

KLUWER ACADEMIC PUBLISHERS

20

INORGANIC-ORGANIC COMPOSITES FOR OPTOELECTRONICS

Helmut Schmidt
Institut für Neue Materialien
Saarbrucken, Germany

Abstract

The sol-gel process allows the preparation of glasses and composites with homogeneities sufficient for optical applications, since phase dimensions can be kept below the level of undesired Rayleigh scattering. This is of special importance for inorganic-organic composites. By other methods, precipitates of inorganic phase may appear within the organic matrix and cause scattering. By chemical control of the particle surface-free energy, it is possible to tailor particle size and reactivity, and processing and final properties can be adapted over wide ranges. Using these principles, thick SiO_2 layers for waveguides, refractive index tailored planar waveguides patterned by photolithography, and active waveguides containing semiconductor quantum dots or metal clusters can be synthesized.

INTRODUCTION

Inorganic-organic composites have been synthesized now for more than one decade by the sol-gel process [1-10]. A variety of different directions have been developed, such as scratch resistant coatings, low friction coatings, elastomers, abrasives and contact lens bulk materials. Without a doubt, optical materials have become more and more interesting, and the sol-gel process is now able to play an important role in synthesizing future optical materials.

One of the reasons is the possibility of controlling the process in a way to obtain intermediates suitable to prepare films and coatings. This is of high interest for optics, especially for functional coatings as shown by Dislich [11] . However, the films to be obtained by using this process are limited to about one μm in thickness. This is due to some characteristic properties of the processing, where liquid systems have to be used and the solid content of which is comparatively low.
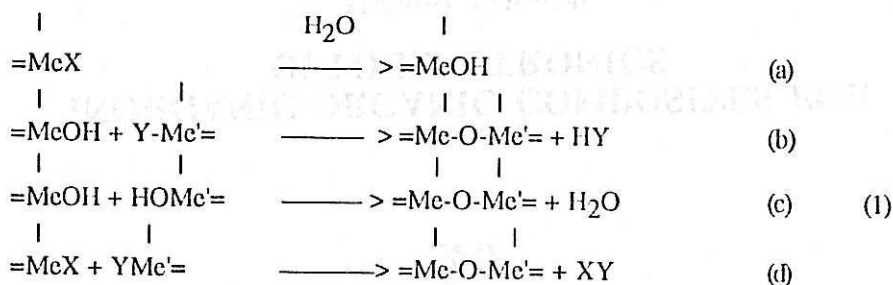
For thick layers, for example, for multimode planar waveguide fabrications, with required thicknesses of 6-10 μm, the process is reaching its limits. In case of the necessity of fabricating active materials from sol-gel oxide glasses, for example lasing materials for amplifier or nonlinear optical materials, active components have to be incorporated. This may be $X^{(3)}$ polymers, as successfully shown by Prasad [12]. In this case, the polymer causes sufficient network relaxation of the composite and film densification does not become a problem at low temperatures. Incorporation of lasing dyes into sol-gel processing does not seem to cause any serious problems [13-15], but densification to full density is no longer possible. This may not be a serious problem, but porous materials, as a rule, are sensitive to H_2O vapour, which is undesired in the majority of cases. For these reasons, impregnation of porous silica by organic monomers was employed in [13], which led to solid dense composites. In this case, however, the process is restricted by the shaping possibilities of porous silica. This is rather difficult as shown by Hench [16, 17], but possible, and large pieces can be fabricated and doped with organic dyes. However, subsequent patterning is difficult and densifying impossible. If sufficient organic components are introduced into gels during the synthesis step, the dried material becomes more flexible with increasing organic concentrations and even can be fabricated as a plastic [18, 19] or thermoplastic material [20].

The question arises to what extent remaining organics in sol-gel matrices can be used to tailor suitable properties for photonic materials. For this reason, a variety of properties have to be taken into consideration. Some of the most important properties are light transmission, meaning homogeneities are required that produce no more than about 0.1 dB/cm. Another important question is patternability. If applications like fabrication of waveguides are considered, it is necessary to produce patterned components such as Y-distributors, in-coupling and out-coupling grids, Mach-Zehnder interferometers or others. A third question is related to refractive index matching, which is necessary to adapt the waveguide to substrates. One of the most important questions, however, is how to obtain active components with lasing (amplifiers), electrooptic ($X^{(2)}$) and $X^{(3)}$ properties. And, last but not least, there is the question of cost. Costs for optical components with photonic materials are strongly dominated by processing costs such as deposition of layers, or micropatterning of waveguides.

There are many materials (glasses, ceramics, polymers) covering several of the discussed topics, but one can hardly find any material covering all requirements in the same way. For this reason, the question has to be discussed how far inorganic-organic sol-gel composites can be used to tackle these problems. In order to approach the described questions, it is necessary to discuss the relations between synthesis, structures of the intermediates, processing properties and final material properties. Of course, it is not possible to provide a comprehensive discussion in this chapter. But some of the questions will be discussed using well investigated examples which will show the basic procedures useful for photonic material tailoring.

SYNTHESIS PRINCIPLE

Sol-Gel Process for Inorganic-Organic Composites - The sol-gel process describes a method for synthesizing organic, mainly oxide networks by a soft chemistry route. It is based on the fact that hydroxides are very reactive components with respect to condensation. The condensation step leads to a metal-oxygen-metal bond, as a rule, which is the first step to forming an inorganic three-dimensional network. Due to the three-dimensional crosslinking, numerous variations of structures are possible, if no crystallization in solution takes place. In the case of SiO_2, amorphous condensates are obtained without exception [21]. In other cases like Al_2O_3 boehmite or bayerite [22], and in case of TiO_2, anatase are obtained. To obtain colloidal sols, a variety of precursors can be used, like salts, soluble oxides or hydroxides, alkoxides, complexed alkoxides or other complexes, especially from transition metals. The network forming steps, in general, are similar (eq. 1).

$$\equiv MeX \quad \xrightarrow{H_2O} \quad \equiv MeOH \qquad (a)$$

$$\equiv MeOH + Y\text{-}Me' \equiv \quad \longrightarrow \quad \equiv Me\text{-}O\text{-}Me' \equiv + HY \qquad (b)$$

$$\equiv MeOH + HOMe' \equiv \quad \longrightarrow \quad \equiv Me\text{-}O\text{-}Me' \equiv + H_2O \qquad (c) \qquad (1)$$

$$\equiv MeX + YMe' \equiv \quad \longrightarrow \quad \equiv Me\text{-}O\text{-}Me' \equiv + XY \qquad (d)$$

X, Y = groupings like Cl^-, NO_3^-, OR^- (R = alkyl), ^-OCOR;

$\equiv Me$, $\equiv Me'$ = metals.

(1b) is the most likely condensation reaction, (1c) takes place at elevated temperatures in gels and (1d) at higher temperatures if no more H_2O is present (> 200°C).

With a few exceptions, e. g. reaction of $Si(OR)_4$ under acid conditions [23, 24], the condensation reaction leads to colloidal systems with very small particle sizes, at least in the early phases of the reaction. If the diameter of these particles is in the lower nanometer range (approximately less than 20 nm, which is less than 1/20 of the wavelength of the visible light), almost no light scattering is observed and high optical quality of these colloidal systems is obtained. Colloidal solutions are only stable if the particle-to-particle interaction is low, which, in general, is brought about by generating electric charges at the particle's surface, e. g. by proper choice of pH. Then, the sol is called "pH-stabilized". But pH is difficult to control throughout further processing and gelation very often occurs when not wanted. Gelation can only be avoided by increasing the particle-to-particle distance by dilution. This is one of the major drawbacks of sol-gel processing. In order to control particle-to-particle interaction, diluted systems have to be used, and, as a consequence, the produced gels possess a very low solid content causing an undesirable high shrinkage during densification. After gelling, the particle-to-particle interaction is extremely strong and, for example, stress relaxation without crack formation is only possible in thin films, as clearly shown by Lange [25]. As a consequence, no thick films have been produced by pure inorganic sol-gel reactions.

An alternate way to solve this problem is the use of organic components. As already shown in [26], by using precursors having organics linked to an inorganic unit, it is possible to obtain crack-free coatings up to several μm in thickness after burning out the organics. As organics, phenyl groups bonded to Si and ethylacetate coordinatively bonded to Al alkoxides have been used in [26]. The results are interpreted as the effect of an increased network flexibility. Moreover, it has been shown by Nass [27] that the use of β-diketones as complex formers during hydrolysis leads to very stable sols with colloidal particles, some up to 10 nm, without gelling. This leads to the interesting question: how far can organics be used for sol-gel processing instead of using pH for stabilization? Similarly, how far can this principle be advantageously used for optical materials?

This role of ceramics is manifold. As shown in Fig. 1a-e, organics can act as network modifiers (1b), as additional network formers (1c), as included dopants (1d), or as a link for a second inorganic phase (e. g. colloids or clusters). These examples for the "structural" role of organics raise the question about the nature of bonds between organic and inorganic units. Two examples have already been mentioned: the =Si-C= bond and the complex formation to alkoxide. While the =Si-C= bond provides a covalent link stable under "sol-gel" conditions, the formation of β-diketones raises doubts about its stability against hydrolytic attacks. Sanchez has investigated the complex formation with Zr alkoxides [28], but no data about long term hydrolytic stability are given. In Fig. 2, some examples for "links" between inorganic and organic units are shown [29].
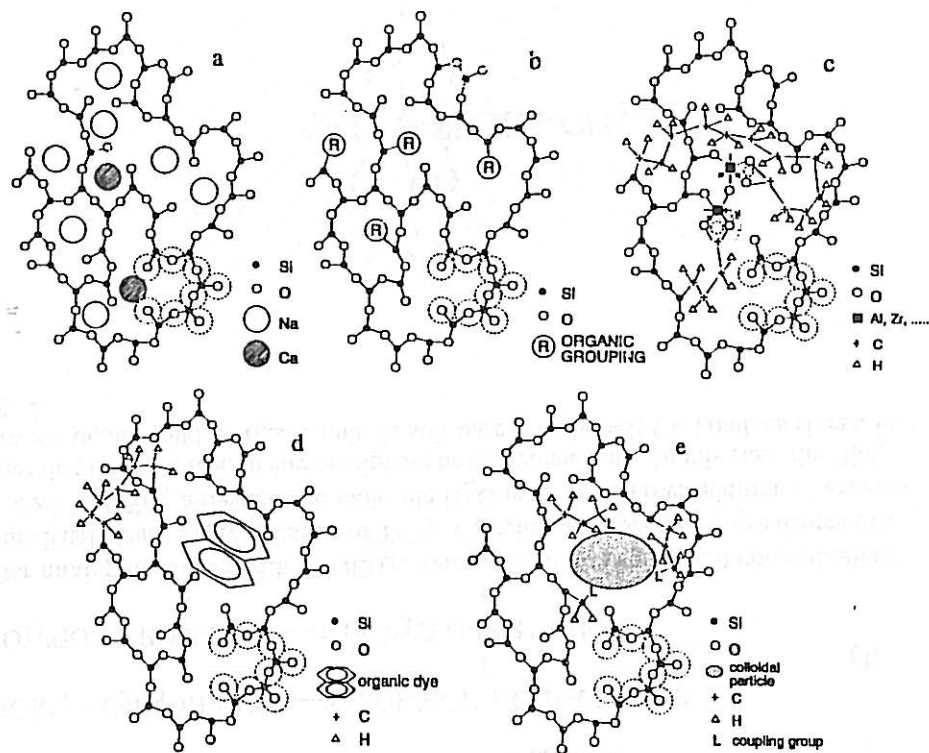
Fig. 1: Some possibilities of structures from organic groupings in glassy sol-gel matrices. 1a: glass network after Zachariasen; 1b: organic group acting as a network modifier within the glass structure; 1c: crosslinked organic groupings acting as additional network formers; 1d: organic molecules adsorbed to inorganic units or "stored" in pores; 1e: organic groupings used for fixation of clusters.
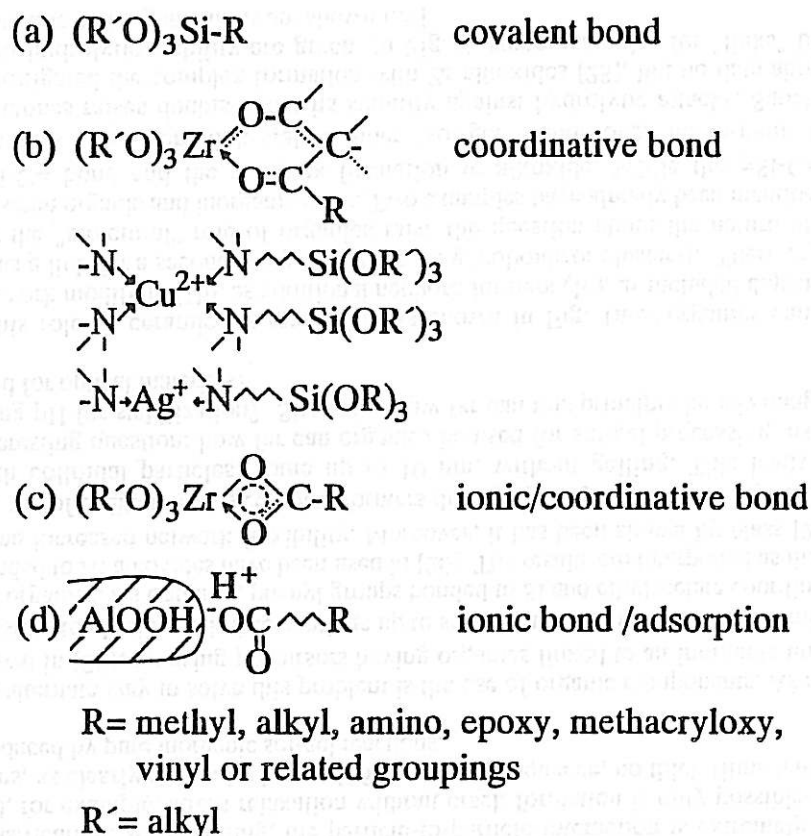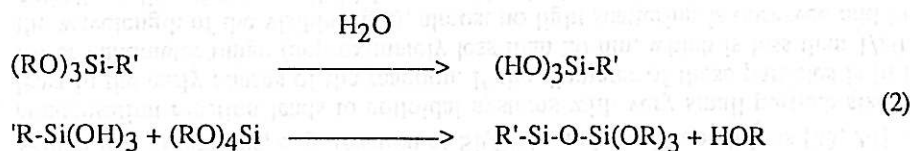
(a) $(R'O)_3Si-R$ covalent bond

(b) $(R'O)_3Zr$ coordinative bond

-N N$\sim\sim$Si(OR')$_3$
  Cu^{2+}
-N N$\sim\sim$Si(OR')$_3$

-N$\rightarrow$Ag$^+$$\cdot$N$\sim\sim$Si(OR)$_3$

(c) $(R'O)_3Zr$ C-R   ionic/coordinative bond

(d) AlOOH OC$\sim\sim$R   ionic bond /adsorption

R= methyl, alkyl, amino, epoxy, methacryloxy,
vinyl or related groupings

R'= alkyl

Fig. 2: Various types of chemical bonds used as links between inorganic and organic units.

The "simplest" link is represented by the =Si-C= bond in organo alkoxysilanes. Since the silanes contain RO-Si= bonds, they can be used like common alkoxy precursors in the sol-gel process. If the synthesis reaction is well controlled, cocondensation can be performed with tetraalkyl orthosilicates, and composites with high optical quality can be prepared [30, 10] (eq. 2).

$$(RO)_3Si-R' \xrightarrow{\quad H_2O \quad} (HO)_3Si-R'$$

$$'R-Si(OH)_3 + (RO)_4Si \longrightarrow R'-Si-O-Si(OR)_3 + HOR$$

(2)

R' = alkyl, methacryloxy, vinyl, glycidyloxy, propylamino, ...

Other precursors like Ti, Al or Zr alkoxides can be used, but the question whether Si-O-Me bonds are formed cannot be answered in most cases. As shown with γ-glycidyloxypropyl triethoxysilane (R") and tetraethylorthotitanate [10], the reaction can be carried out in a way that particle sizes of TiO_2 can be in a range not to be detected by TEM (< 1 nm). In this case, $Ti(OR)_4$ was reacted by water generated slowly and *in situ* by a second reaction (eq. 3), and from the results of the reaction analysis, the formation of a Si-O-Ti bond can be suggested.

$$Ti(OR)_4 + C_2H_5OH + Cl \longrightarrow (RO)_3TiOH + C_2H_5Cl + HOR$$

$$(RO)_3TiOH + ROSi-R" \longrightarrow (RO)_3Ti-O-Si-R" + HOR \tag{3}$$

After mixing the silane with $Ti(OEt)_4$, water addition (even a small concentration) immediately leads to precipitation of TiO_2. Carrying out reaction (3) to a degree that for each $Ti(OEt)_4$ molecule one molecule H_2O is formed allows addition of excess water that does not lead to any precipitate or particulate sols. In this case, the "link" between organic and inorganic units is still based on the =Si-C= bond, as shown in Fig. 3.

Fig. 3: Schematics of the inorganic-organic interface in $TiO_2/R"SiO_{3/2}$ composites after [3].

458

However, the amount of TiO_2 using this chemically controlled condensation principle (CCC principle) is limited to about 20 mole %. Higher concentrations led to increased light scattering and to extremely brittle properties of the hard materials, probably due to an interpenetrating inorganic backbone. With decreasing amounts of organics, the systems become more and more glass-like and brittle, due to the increase of three-dimensional crosslinking and with very high inorganic contents; porous materials can be obtained [31].

Regarding optical properties like the refractive index n in these composites, one can find that, due to the low densities, despite high concentrations, n remains comparatively low. This means, the "inorganic" properties are not sufficiently effective, probably due to the more "molecular" structure of the inorganic units within a polymer-like network, as schematically shown in Fig. 4. For these reasons, it seems to be more suitable to generate something like a 0-3 composite with particles small enough not to contribute to light scattering but large enough that they already show sufficient "bulk" properties. In this case, however, it is of great importance to control the size of the "0" phase and to keep it in the lower nanometer range (Fig. 5).

organic polymeric chaine   inorganic units

Fig. 4: Model of a "molecular" type of inorganic-organic composite.

Fig. 5: Model of a 0-3 nanocomposite
with particles ≤ 20 mm as "O" phase.

During sol-gel synthesis, the condensation reaction in most cases provides nano-phased states as a result of growth reactions. The process offers an interesting opportunity for the formation of these types of nanocomposites.

In this case, the formation of the nanoparticles should be prepared by a strictly controlled sol-gel reaction, including stabilization mechanisms of the particles allowing easy further processing. That means, alternatives for pH stabilizations have to be developed. The benefits of this type of processing then will be new routes for fabricating novel optical composites from a variety of compositions.

Nanocomposites by Use of Stabilized Colloids - As already pointed out above, it is possible to obtain sols derived from alkoxides by the use of complex formers. In the case of Al alkoxides, β-diketones seem to be adequate (Fig. 6), and transparent films can be obtained with 1 μm thickness [26].

For Zr alkoxides, β-diketones can be used, as shown by Sanchez [28] and Rinn [32]. The results of these authors show that ZrO_2 particles can be stabilized by β-diketones starting from a few nm up to some μm. While with Al alkoxy β-diketones [27] and with Zr alkoxy β-diketones [28] particle sizes between several nm and 50 nm were obtained, Rinn was able to stabilize particles up to 3 μm. Due to the fact that these particles are "coated" with relatively "inert" organic groupings, they do not agglomerate and even can be calcined without agglomeration [32]. This leads to the interesting question: how far can this principle be used to prepare nanocomposites while maintaining the small particle sizes?

a) $Al(OR)_3$:

b)

Fig. 6: a) Complex formation of Al alkoxides with acetylacetone.
b) Formation of linear structures after hydrolysis [27].

If the particles can be kept below 20 nm, Rayleigh scattering does not play an important role, and these composites should be useful for optical purposes. Furthermore, it may be possible to use stabilizing ligands with bifunctional properties with sol-gel active groups like silanes or polymerizable groups like epoxides or methacrylates. Then, a new class of precursors can be synthesized, having functions now based on the solid state properties of the small particles. Solid state properties of small particles have gained great interest, since in the case of semiconductors, they show quantum effects that are highly interesting for nonlinear optics. In Fig. 7, the concept is shown in a schematic view of the colloid stabilization principles.

Fig. 7: Schematic of the concept of functionally stabilized sol-gel precursors for optics.

Growth Control by Use of Growth-Controlling Agents - If particles grow from solution, a nucleation process has to take place. After exceeding the critical size, the nuclei can grow. The growth rate can be controlled by several mechanisms. These questions have been investigated in detail for crystal growth reactions [33]. The formation of a solid phase, that means precipitation, only takes place in supersaturated systems. It is a question of consideration whether colloidal particles of some nanometers in diameter, not interacting with each other, may be considered as a suspension (that means, a solid phase dispersed in a solution) or as a solution (with relatively large units "dissolved" in a liquid). Macromolecules dissolved in an organic solvent are considered as solutions, and the molecular weight of macromolecules and nanoparticles can be on the same order of magnitude.

Aggregation of nanoscaled primary particles to larger units, e. g. like SiO_2 particles of several 100 μm in diameter as shown in the Stober process, requires overcoming the repulsive forces between two particles. The question about the mechanisms seems to be difficult. Smochulowski's model may be used as an interpretation [34], but is not very satisfying. Strehlow developed a hypothesis using the free surface energy as the driving force, which is governed by state of the interface between the liquid and the particle. In his calculations [35], he used the "covering" of the particle surface with electric charges as stabilizers and calculated free energy minima as a function of various thermodynamic parameters of the system (e. g. interfacial tension as a function of the solvent). The simple transformation of Strehlow's hypothesis to Rinn's results can explain his data easily. He was able to prepare monosized ZrO_2 particles between 100 nm and some μm by only varying the β-diketone concentration in a sol-gel system while keeping all other parameters (H_2O content, H^+ concentration, solvent, precursor concentration) constant. With increasing complex former concentration, he obtained decreasing particle sizes. Thus, the surface covering unit of the stabilizing agents must be the governing parameter for controlling growth, size and aggregation of the small particles.

If this concept can be generally applied, it can be used as a tool for tailoring sol-gel systems to maintain their highly dispersed state during processing to inorganic-organic composites and to obtain sufficient optical quality. Furthermore, the growth controlling agents (GCA) can be used to provide further reactivities, if they contain additional functions such as reactive silanes or double bonds. This basic principle can be demonstrated with Zr alkoxides. As shown in [36], Zr alkoxides can be reacted with methacrylic acid (MA) to form a variety of complexes. The reaction of alkoxides with carboxylic acids is well known [37] and leads to relatively stable complexes. The complex formation of Zr alkoxides can be followed by IR spectroscopy, as shown in Fig. 8. As one can see from the IR spectra, no free acid can be observed up to a ratio of Zr:MA$\leq$ 1 = 1.8.
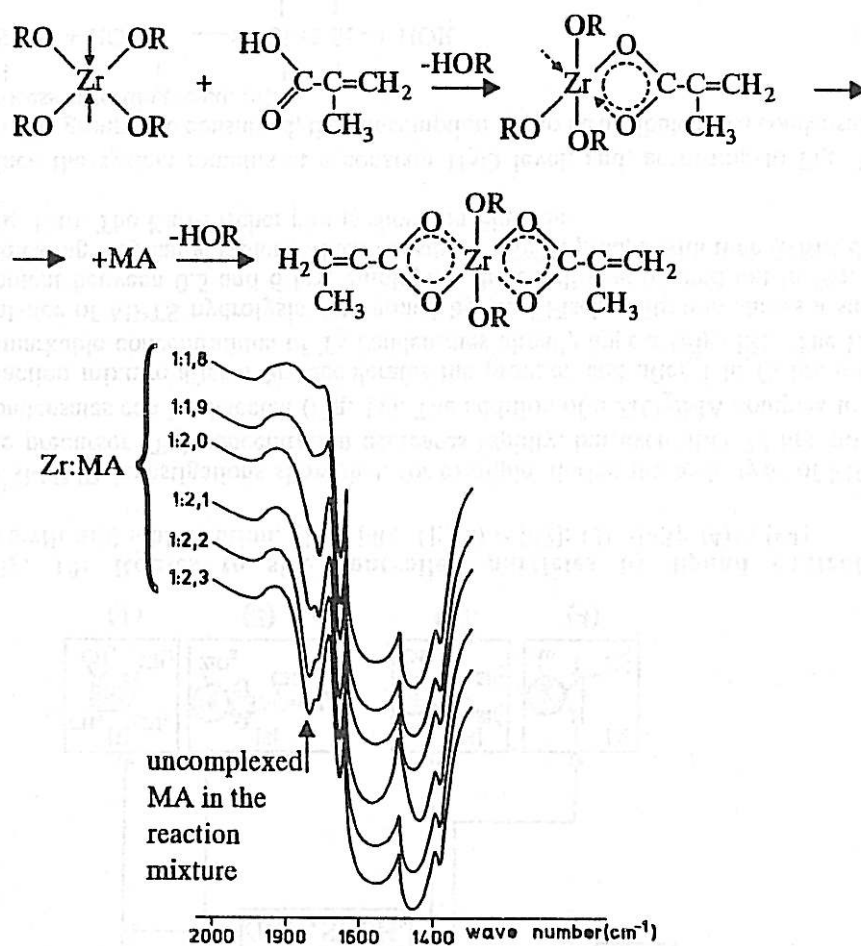
462

Fig. 8: Complex formation of Zr alkoxides with methacrylic acid (MA).

The hydrolytic stability of the complex is shown in Fig. 9 by ^{13}C NMR. It compares the chemical shift of the carboxylic group C atom of free MA, MA complexed to $Zr(OR)_4$ and the $Zr(OR)_3/MA$ or $Zr(OR)_2(MA)_2$ complexes after hydrolysis. No traces of free acid can be detected in the liquid system. Similar results can be obtained with either alkoxides like Al, Ti or lanthanides. The carboxylic acid controlled hydrolysis and condensation offers an easy route to obtain functional small particles to be used for further processing.

Fig. 9: ^{13}C NMR spectrum of MA and Zr alkoxide/MA complexes in solutions; molar ratio Zr:MA = 1:1, I: free methacrylic acid; II: Zr/MA complex; III: b after hydrolysis [after 38, 39].

A variety of systems can be tailored using this method. A survey is given in Fig. 10 and below. These examples will be discussed in detail. By control of hydrolysis and condensation, as shown with ZrO_2, the particle size can be established on a level between 2 and 10 nm. The ratio MA:Zr can be varied in the range of 1:0.8 and 1:1.3 without precipitation with excess of water. Lower concentrations of MA lead to precipitates, but the complex bond is not affected.

From the material tailoring point of view, it is desirable to increase the ZrO_2 content in such complexes. For these reasons, a "water-free" condensation process was developed involving additional precursors necessary for special material properties. It could be shown that organofunctional silanes as γ-glycidyloxypropyl trimethoxysilane (GPTS) or γ-methacryloxypropyl trimethoxysilane (MPTS) can be hydrolyzed with substoichiometric amounts of water to precondensates (viscous liquids) with very low free H_2O contents. This can be controlled by Karl-Fischer titration [45, 46]. Water then is present in the form of "latent" -SiOH groups.
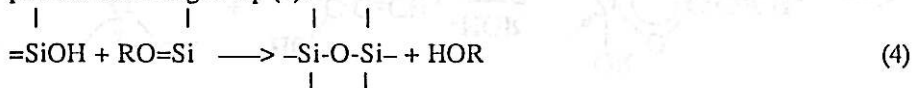
Fig. 10: Routes to size controlled particles by ligand controlled growth and stabilization. (1) = [40,41]; (2) = [42]; (3) =[43]; (4) = [44].

^{29}Si-NMR investigations show that, for example, during the hydrolysis of MPTS the precursor (T_0) concentration decreases rapidly, but even after 27 hrs, no T_3 condensates can be detected (Fig. 11). The addition of a ZrO_2/MA complex to the reaction mixture after 4 hrs accelerates the process, and after 1 hr (5 hrs total), remarkable concentrations of T_3 condensates already appear (Fig. 12). The H_2O balance of MPTS hydrolysis determined by Karl-Fischer titration shows a stable content between 0.5 and 6 hrs, employing the conditions pointed out in Fig. 13, indicating a dynamic system which consumes =SiOH groups with time (NMR data, Fig. 13b). The Karl-Fischer plot is shown in Fig. 13a.

Since the system remains at a constant H_2O level, and, according to Fig. 13a, =SiOH groups are consumed, the consumption has to be attributed to a condensation process according to eq. (4).

$$\overset{|}{=}SiOH + RO \overset{|}{=} Si \longrightarrow -\overset{|}{Si}-O-\overset{|}{Si}- + HOR \qquad (4)$$

This means, that the optimum time scale for the addition of fast reacting alkoxides to avoid precipitation under the described reaction conditions is 0.5 to 1.0 hrs after the beginning of MPTS hydrolysis.
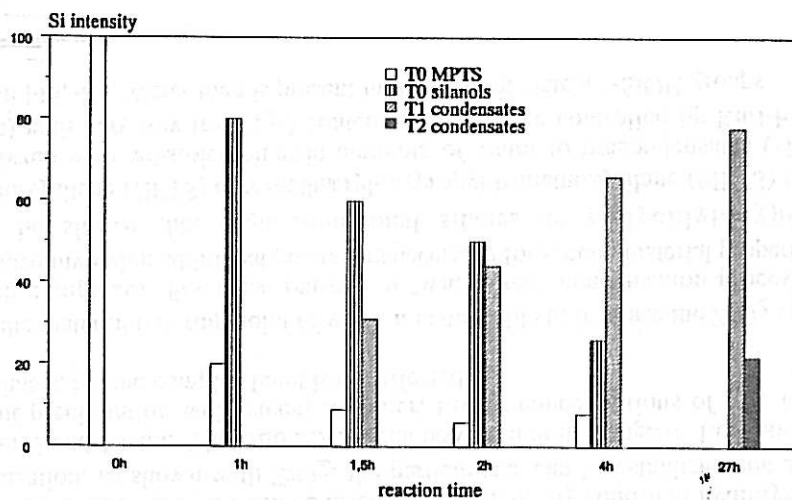
Fig. 11: ^{29}Si-NMR investigation of hydrolysis and condensation of MPTS; T = 50°C with methanol as solvent; 1.5 mole H_2O/1.0 mole MPTS [after 46].

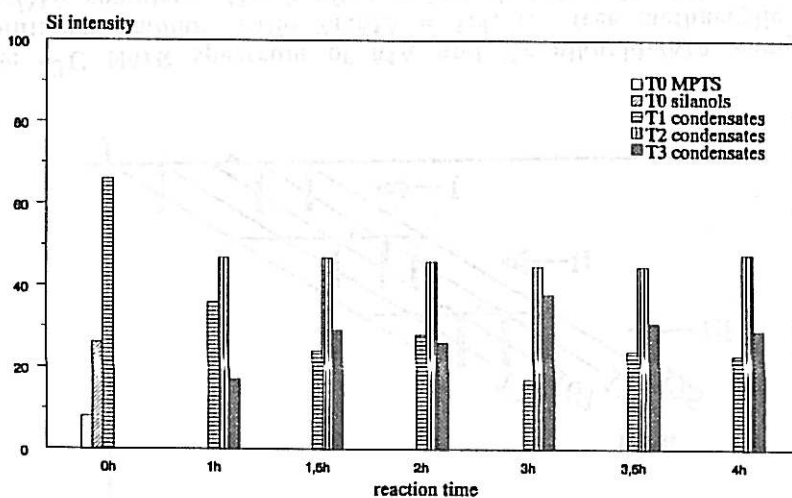**Fig. 12:** ^{29}Si-NMR investigation of prehydrolysed MPTS (50°C/3 hrs); addition of 0.1 mole ZrO_2/MA = 1:1 [after 44]; 0 h = 4 h after hydrolysis and condensation start of MPTS.
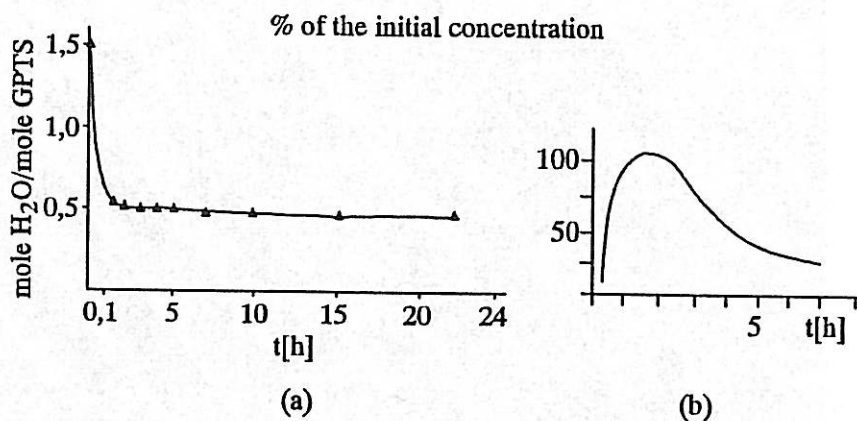
466

Fig. 13: a: Karl-Fischer plot of the hydrolysis of MPTS T = 80 °C with 1.5 mole H_2O/1.0 mole MPTS; solvent: methanol [after 46]; b: ^{29}Si NMR of MPTS (T_0 silanols).

Experiments have been carried out in order to investigate how far Zr alkoxides or ZrO_2/MA complexes can be added to the system without ending up with precipitates. It could be shown that independent of Zr:MA stoichiometry, concentrations up to 50 mol% of $Zr(OR)_4$ or ZrO_2/MA complexes can be added and, after refluxing, excess water can be added to the system without precipitation [47]. The incorporation of the ZrO_2/MA clusters into the backbone provided by MPTS are not quite clear so far. But it could be shown, that by employing constant reaction conditions, particulate systems with different compositions and particle sizes of about 2 nm can be obtained, as determined by wide angle X-ray scattering (Fig. 14) [41].

Other particle diameters can be obtained by varying reaction conditions, as systematic investigations show [47]. Using the GCA concept together with the "latent water" hydrolysis, which is a variation of the CCC (chemically controlled condensation) reaction scheme shown elsewhere [10] a variety of materials have been synthesized.
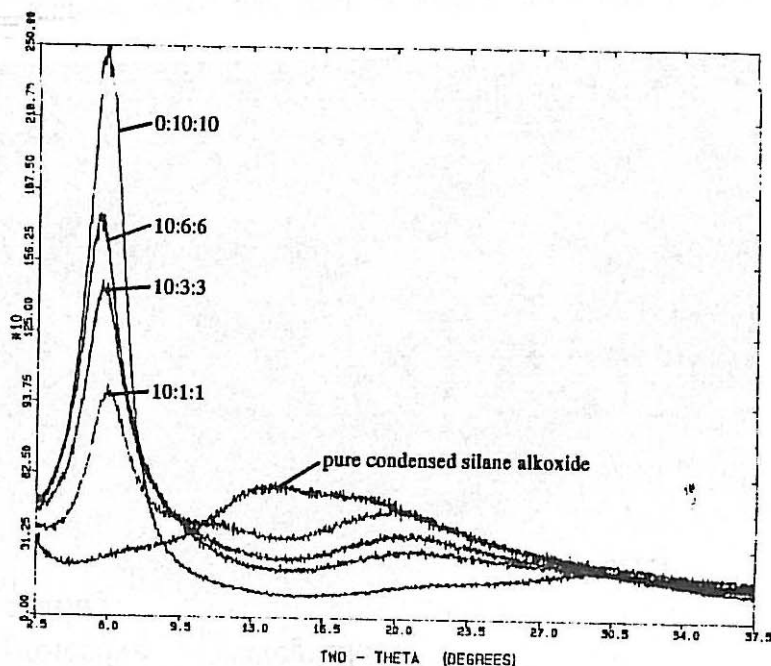
Fig. 14: WAXS plots of various compositions of MPTS:ZrO$_2$:MA. The peak maxima represent particles with 2 nm in diameter; 0:10:10 means MPTS-free system with low water contents.

MATERIAL DEVELOPMENTS

Photocurable, Patternable Films - If MPTS is used as a precursor in combination with ZrO$_2$/MA, photocurable systems with low optical loss (< 0.1 dB/cm at 780 nm) can be prepared. Films up to 10 µm thickness can be obtained by dip or spin coating. The photocuring process can be optimized up to 95 % conversion (= 5 % remaining C=C double bonds only). Patterning can be preformed by embossing during curing, by photolithography, laser writing or light intensity fluctuations generated by two wave mixing interferences. Thus, holograms, in- and out-coupling gratings or channel waveguides can be prepared. In Fig. 15, the principle of the fabrication of a diffraction grating to be used as an in and out coupling grating on a planar waveguide is shown. The line width can be adjusted by the optical system. The intensity fluctuation generates a replica of the degree of polymerization, and after development (by acetone or NaOH) the grating becomes visible. Fig. 16 shows a diffraction grating made by two wave mixing. Photopolymerization also can be carried out by direct laser irradiation, schematically shown in Fig. 17.
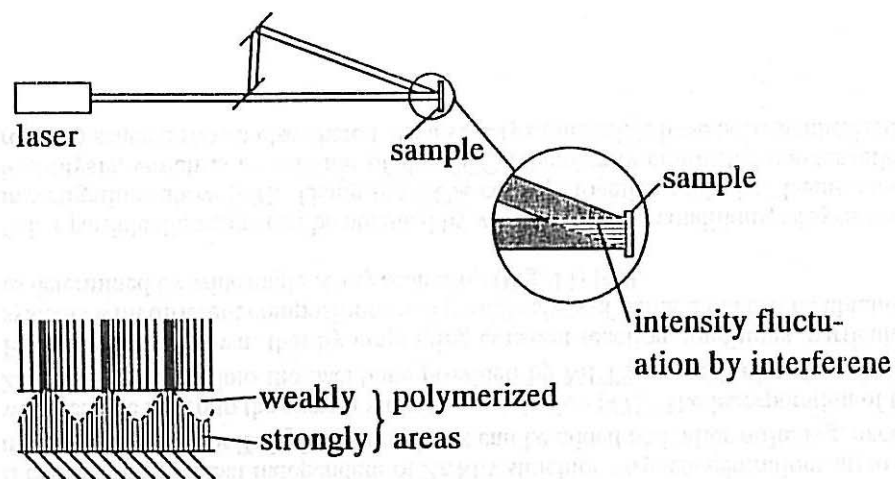
468

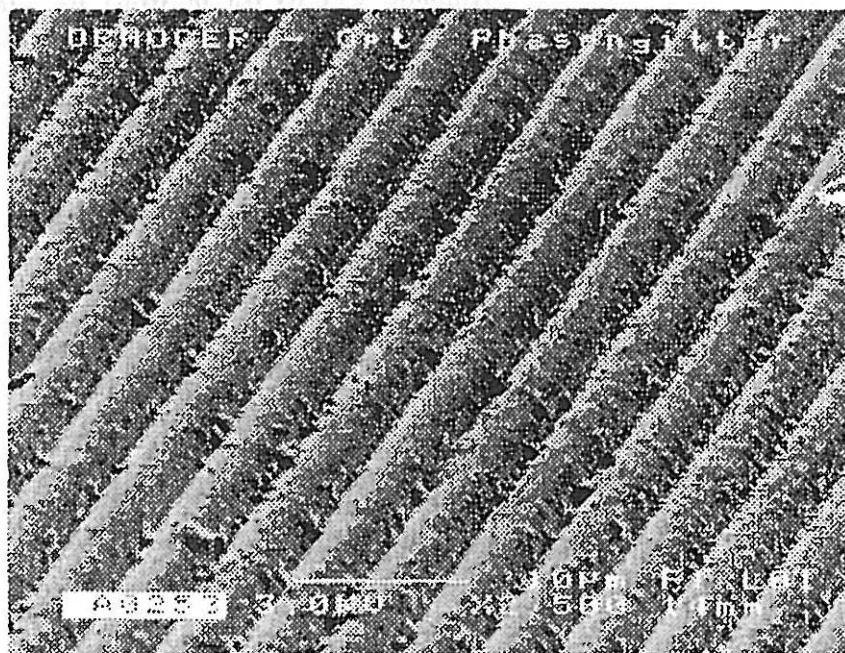Fig. 15: Draft of the two-wave mixing system for grating fabrication.

Fig. 16: Diffraction grating by two wave mixing. Development after irradiation in diluted NaOH. ZrO_2:MA:MPTS = 1:1:1 (molar ratio).
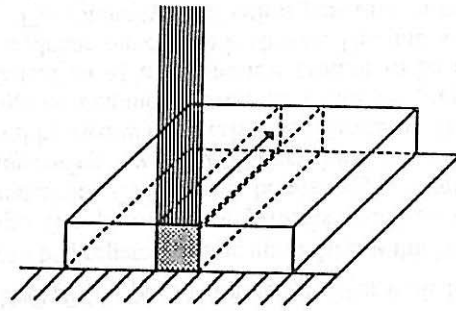
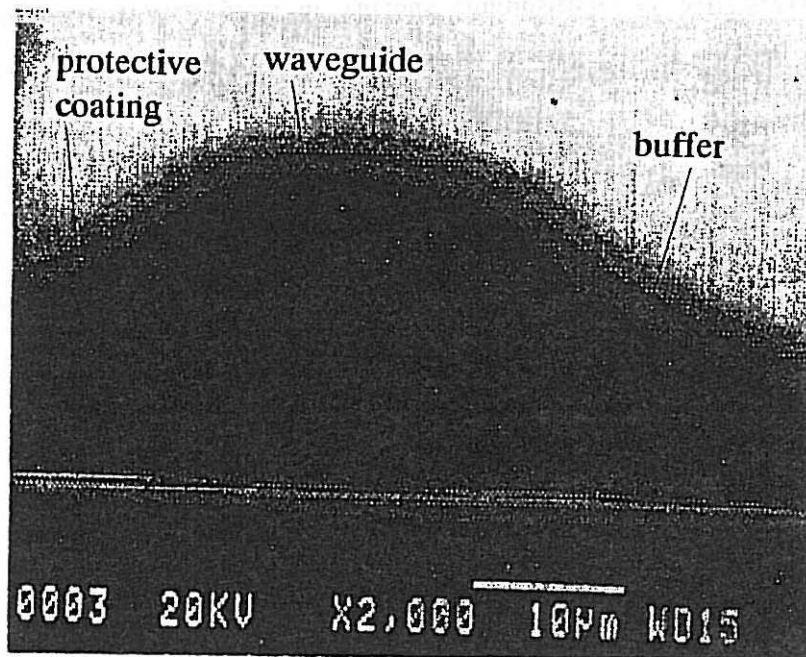Fig. 17: Schematic of the direct laser writing principle.

Fig. 18: Channel waveguide from a system according to Fig. 16; buffer and cladding with slightly lower ZrO_2 contents [after 41] .

470

In order to guide the light beam within the channels, buffer and cladding layers have been prepared by using one and the same system only with slightly reduced Zr contents for lower refractive indices. Fig. 18 shows a channel waveguide comprising a buffer layer (low index) obtained by laser writing and spin coating from the system MPTS/ZrO_2/MA [41, 39].

Alternative types of processing are fine patterning by embossing and photolithography (mask aligner techniques). After spin or dip coating, the soft films can be embossed with stampers, e. g. optical grids. If UV initiators are added, as described in [38] and UV irradiation is carried out. The films are cured during embossing. Due to the low shrinkage of the precondensed films, which is in the range of 5-6 vol%, a near net shaping embossing process can be carried out. Fig. 19 shows the patterning on an optical grid with a line width of ~300 nm. Fig. 20 shows the surface roughness of the embossed surfaces, which are in the range of 2-3 nm.
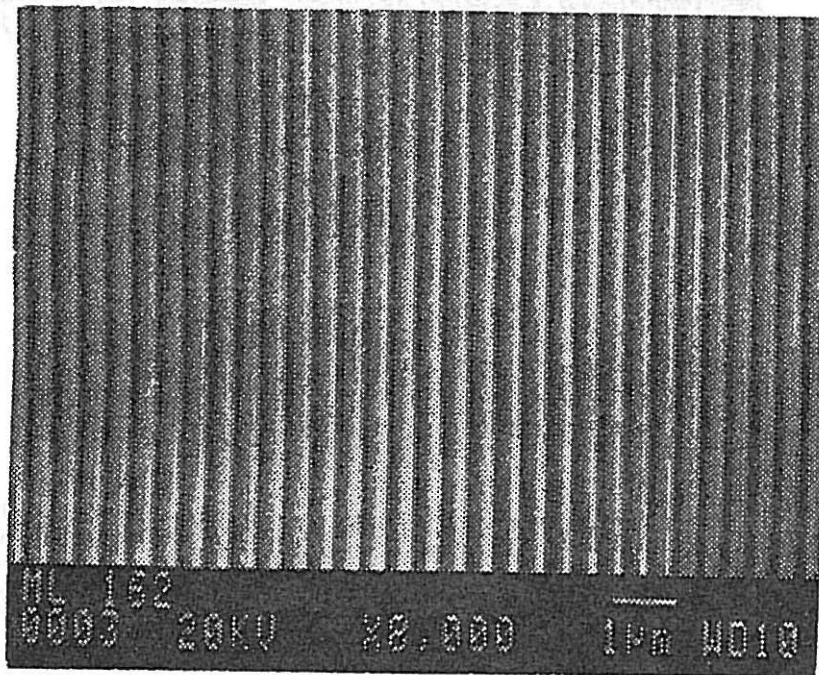

Fig. 19: Optical grid fabricated by embossing of a ZrO_2/MA/methacryloxypropyl-silane system.
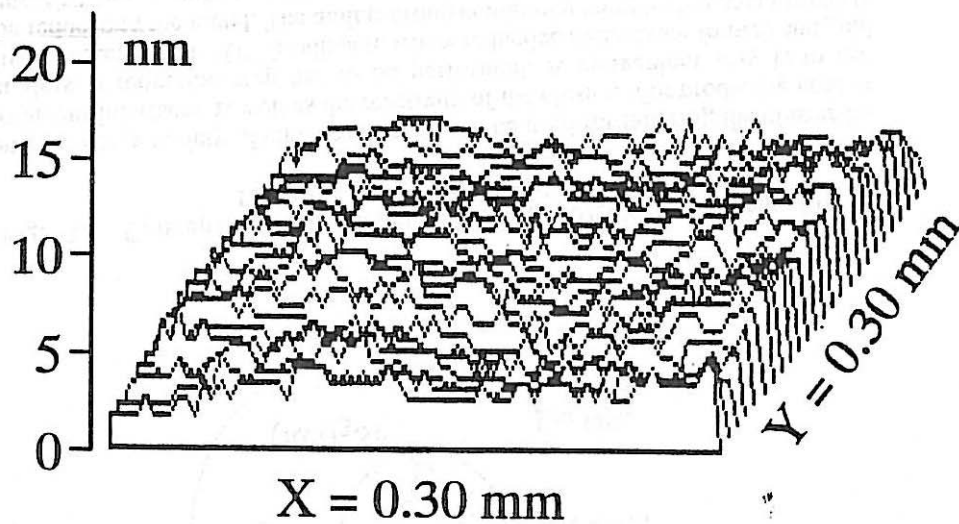
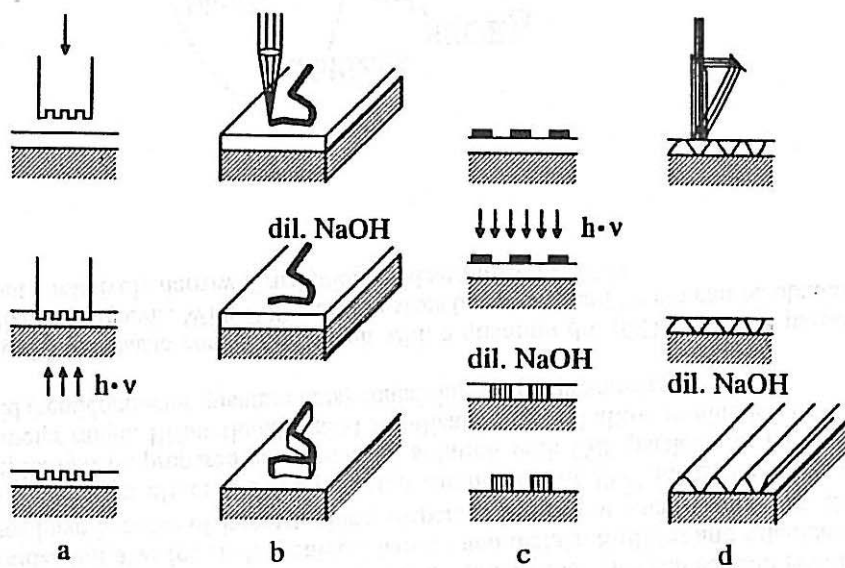**Fig. 20: Profilometer plot of an embossed surface after photocuring.**

Fig. 21: Patterning processes used for patterning of inorganic-organic nanocomposites by various techniques; (a): embossing, (b): laser writing; (c): mask aligner technique; (d): two-wave mixing.

472

Another patterning process is photolithography by use of mask aligner techniques. The basic mechanisms of the process are identical to the other processes described in this chapter. For UV curing a UV lamp can be used. For development of the patterns, diluted aqueous NaOH is sufficient, since the non-polymerized regions contain a siliceous network soluble in bases.

In Fig. 21 a survey of the methods to be used for patterning the nanocomposites is given. Fig. 22 shows a profile produced by mask aligner techniques. The profilometer plot shows how very deep profiles with high aspect ratios can be obtained.
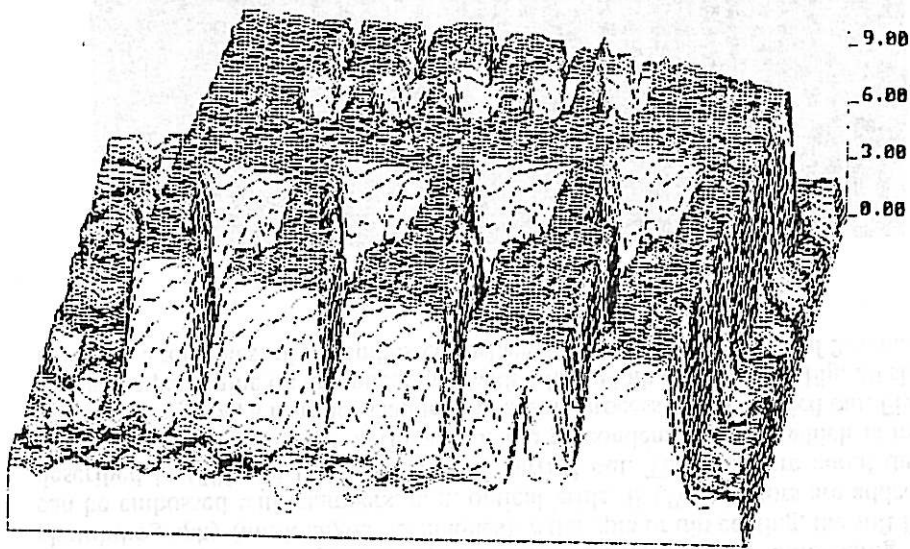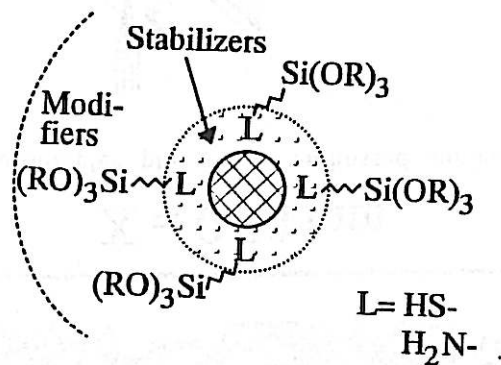

Fig. 22: Pattern and plot derived from mask aligner patterning process. The optical losses obtained from waveguides are less than 1 dB/cm and can be improved by clean-room techniques.

Optically Active Materials - As shown in the previous sections, the ligand stabilization concept can be used with bifunctional ligands, providing colloid stabilization and special reactivities for sol-gel processing. This can be used not only for oxides but also for chalcogenides, halides and metals. Sulfides and selenides in glasses have become of interest, since, dispersed in form of small crystallites, they show a quantum effect and are potential candidates for $\chi^{(3)}$ materials. CdS, for example, can be prepared as a colloidal solution with CdS particles in the lower nanometer range. Bifunctional ligand stabilization should allow production of CdS colloid (semiconductor quantum dots) containing sol-gel precursors.

In Fig. 23, the basic concept is shown with a quantum dot (QD) colloidal particle stabilized by ligands. With CdS, particle sizes between 2 and 20 nm can be obtained without a relatively narrow distribution, as determined by TEM .

Fig. 23: Concept of the bifunctional ligand/colloid system for further sol-gel processing.

As one can see, a variety of chemical means can be used for tailoring the cluster-to-environment-interfaces as well as the reactivity of the cluster. For producing gold or silver dots, a reduction step has to be performed. A convenient way is to use aldehydes or ketones and UV-irradiation, where reductive radicals are formed and gold can be reduced to the metal. The amino-group containing complexing agent protects the metal from forming large aggregates and establishes desired sizes and distributions. This can be performed in various ways.

Silver nitrate has been reacted in alcoholic solutions and then reduced by UV irradiation. Ag colloids are formed which are stable and do not aggregate, which is attributed to the amino group containing ligands. Soluble gold compounds can also be reacted with amino group containing ligands such as $(RO)_3Si(CH_2)_3NH_2$ or $(RO)_3Si(CH_2)_3NH(CH_2)_2NH_2$.

In the case of the monoamine, photo reduction has to be carried out. Organic components (e.g. ketones) will be oxidized. In the case of the diamine, a spontaneous reduction of the gold takes place which is not easily understood. In this case, the formation of the gold colloids is the driving force, which only can be explained thermodynamically by decreasing the surface free energy by strong ligand-to-particle surface interaction by the bidentate chelating ligand (eq. 5).

$$\text{x HAuCl}_4 + \text{yH}_2\text{N} \sim\!\!\text{NH} \sim\!\!\text{Si(OR)}_3 + \text{2x RCHO} \longrightarrow$$

(5)

$$+\ \text{2x RCOOH}$$
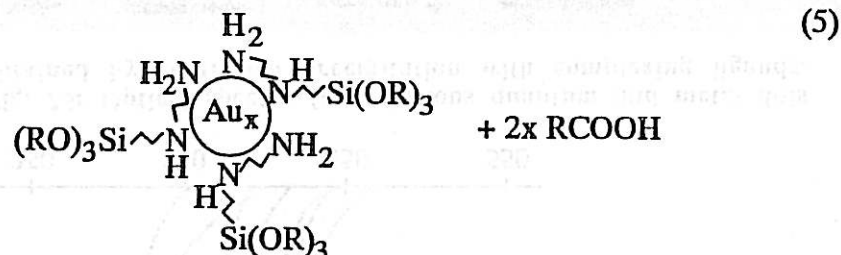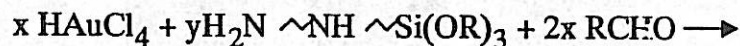
If MPTS is added, hydrolysed and polymerized, films containing the colloids can be prepared. If monoamino ligands are used, MPTS can be photocured during the photoreduction step, and colloid and film formation can be carried out in a one-step reaction.

In Fig. 24, a survey of several reaction paths leading to semiconductor quantum dots and gold dots is given. After photopolymerization, films and monoliths can be obtained showing typical spectra of QD or metal colloids. The spectra depend strongly on ligands and particle sizes. Some spectra are shown in Fig. 25. CdS spectra, for example, (1 and 4) are showing exitonic bands, the position of which depends on the type of the ligand, pointing out a decrease of the band gap energy by changing from sulfide to amino ligands. $X^{(3)}$ values have been determined on CdS/PbS systems showing susceptibilities of about 10^{-9} esu.

The concentration of the gold colloids can be varied over a wide range by irradiation time as shown in Fig. 26. Numbers indicate irradiation time in minutes. The films have been investigated by self-diffraction experiments as shown in Fig. 27. $\chi^{(3)}$ values obtained from different species range from 10^{-9} to 10^{-5} esu.

Pre-complexing step

Ethanol
Cd^{2+}, Pb^{2+}, Zn^{2+}
Ag^+, Au^{3+}, Pd^{2+}
$(OR)_3 Si(CH_2)_3 - L$
L: SH, NH$_2$, COOH
$NH(CH_2)_2 NH_2$

Cluster growth

Chalcogenide source:
$(CH_3)_3 Si-S-Si(CH_3)_3$
or
photoreduction via
alcohol radical attack

Matrix precursor

pre-hydrolysed
pH - controlled
$(OH)_3 Si(CH_2)_3 - L$
L: Methacryloxy
or
Glycidyloxy

Coating sols

Stabilized
chalcogenide Q-dots:
CdS, PbS, Ag S
or
quasi-metallic Q-dots
Au, Ag, Pd

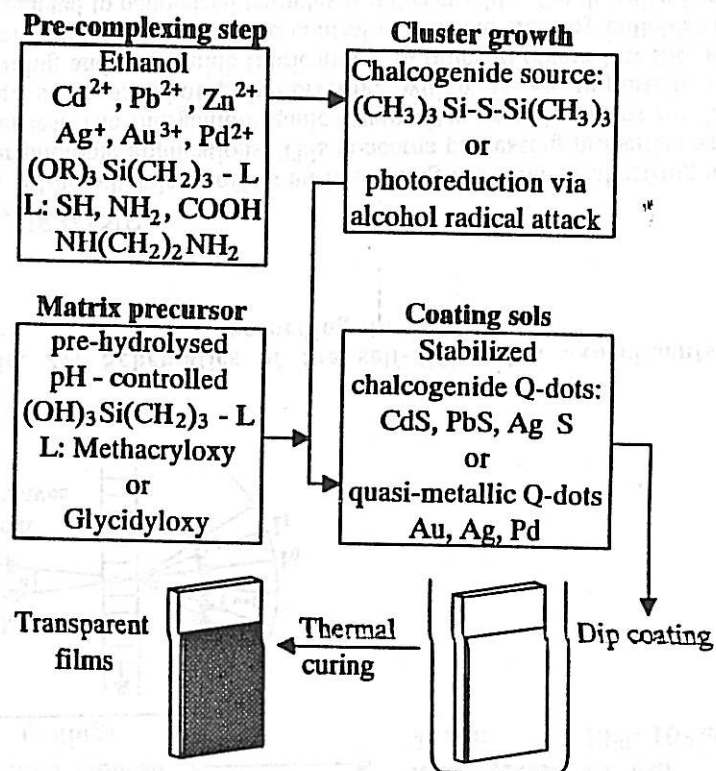Transparent films ← Thermal curing ← Dip coating

Fig. 24: Survey of chemical routes to semiconductor quantum dots and metal dots [after 42, 43, 48].
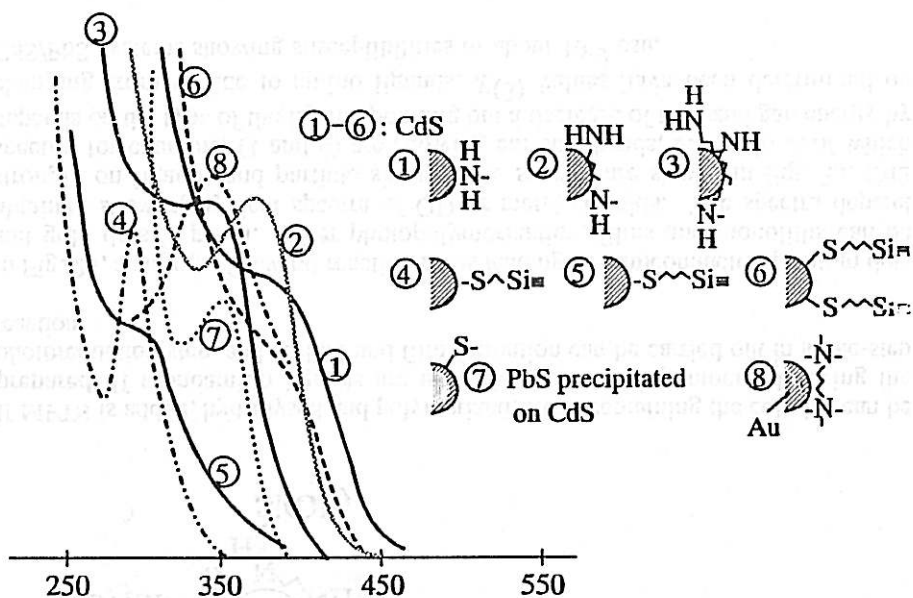
476

Fig. 25: Optical spectra from various quantum and metal dots obtained by controlled precipitation with complexing ligands.
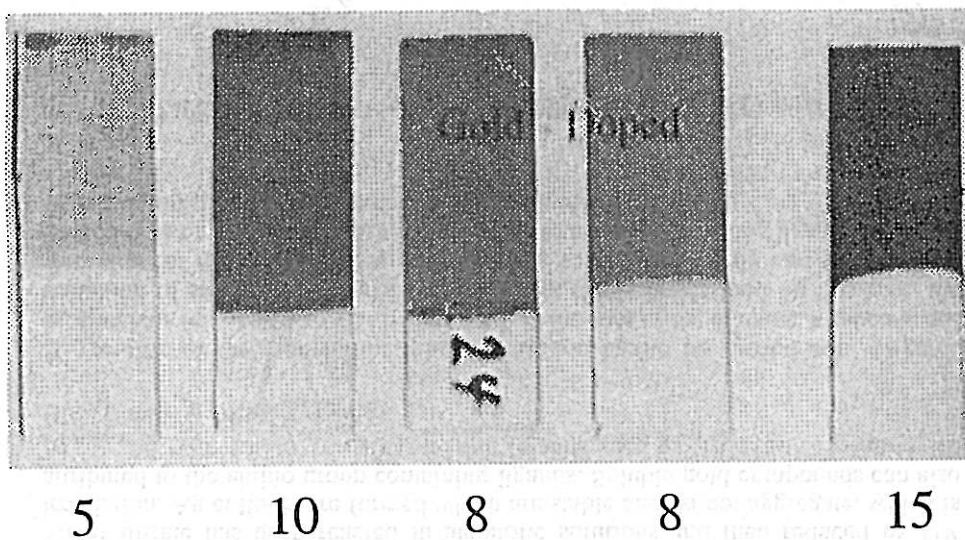

Fig. 26: Increasing Au-colloid concentration with increasing irradiation times.

NLO-Measurements

```
┌─────────────────┐
│ Self-diffraction │
│ on laser-induced │ ─────────────▶
│    gratings      │
└─────────────────┘
```

χ^3 CdS/PbS : 10^{-9} esu

χ^3 Au: 10^{-8} - 10^{-5} esu

I_p

θ

v-θ

I_0

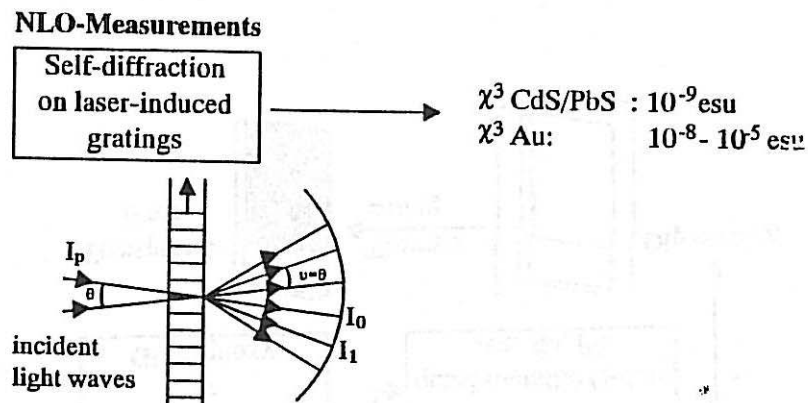I_1

incident
light waves

Fig. 27: Schematics of the self-diffraction experiments
according to [48].

CONCLUSIONS

As shown, sol-gel chemistry offers an interesting route for synthesizing materials suitable for photonic applications. This concerns processing properties as well as final properties. The inorganic-organic composites provide means for "organic" processing, such as photopolymerizing, which is an important tool for micropatterning and waveguide fabrication. In order to obtain low-loss materials with tailored refractive indices, the control of particle sizes by colloidal methods especially adapted to nano-sized particles is indispensable. On the other hand, these methods can be used for incorporating non-oxide components into sol-gel matrices, thus ending up with composites with non-linear optical properties. The influence of the stabilizing ligands on band gap energies and on particle sizes has not been studied in detail so far and has to be an objective for further investigations. The combination of the active particle containing films with micropatterning processes will be another interesting issue.

478

REFERENCES

[1]   C. S. Parkhurst, W. F. Boyle, L. A. Silverman, S. Singh, M. P. Andersen, D. McClurg, G. E. Wnek and D. R. Uhlmann, in: Better Ceramics Through Chemistry II, eds.: C. J. Brinker, D. E. Clark and D. R. Ulrich, Materials Research Society, Pittsburgh/PA, USA (1989), p. 769.

[2]   H. Schmidt, *J. Non-Cryst. Solids* 100 (1988), 51.

[3]   G. L. Wilkes, B. Wang, A. Brennan, D. Rodrigues, H. Huang, Mat. Res. Soc. Symp. Proc. 171 (1990), 15.

[4]   L. Garrido, 1. C. Aehermann, J. E. Mark, Mat. Res. Soc. Symp. Proc. 171 (1990), 65.

[5]   G. Teowee, J. M. Boulton, H. H. Fox, A. Koussa, T. Gudgel and D. R. Uhlmann, in: Better Ceramics Through Chemistry IV, eds.: B. J. J. Zelinski, C. J. Brinker, D. E. Clark, and D. R. Ulrich; Materials Research Society, Pittsburgh/PA, USA (1990) p. 407.

[6]   E. Wu, K. C. Cheu and J. D. Mackenzie, Mat. Res. Soc. Symp. Proc. 32 (1984),169.

[7]   P. N. Prasad, in: Ultrastructure Processing of Advanced Materials, eds.: D. R. Uhlmann and D. R. Ulrich, John Wiley & Sons, New York (1992), p.461.

[8]   H. Schmidt, A. Kaiser, H. Patzelt and H. Scholze, *J. Phys.* 43 (1982), Coll.C9, Suppl.12, 275-278.

[9]   H. Schmidt, H. Scholze and G. Tunker, *J. Non-Cryst. Solids* 80 (1986), 557-563.

[10]   G. Philipp and H. Schmidt, *J. Non-Cryst. Solids* 63 (1984), 283 - 292.

[11]   H. Dislich, *Angewandte Chemie* 83 (1971), 428.

[12]   P. N. Prasad, *SPIE* (Sol-Gel Optics) 1328 (1990),168.

[13]   R. Reisfeld, in: Sol-Gel Science and Technology, eds. M. A. Aegerter, M. Jafelicci Jr., D. F. Souza, E. D. Zanotto, World Scientific Publishing Co. PTE Ltd., Singapore (1989), p. 322.

[14]   R. Reisfeld, *J. Non-Cryst. Solids* 121 (1990), 254 - 266.

[15]   E. T. Knobbe, B. Dunn, P. D. Fuqua, F. Nishida and J. I. Zink, in: Ultrastructure Processing of Advanced Materials, eds.: D. R. Uhlmann and D. R. Ulrich, John Wiley & Sons, New York (1992), p. 519.

[16]   L. L. Hench, Mat. Res. Soc. Symp. Proc. 32 (1984), 101.

[17]   L. L. Hench, in: Chemical Processing of Advanced Materials, eds.: L.L. Hench, J. K. West; John Wiley & Sons, New York (1992), p. 875.

[18]   A. Matsuda, Y. Matsuno, S. Kataoka, S. Katayama, T. Tsuno, N. Tohge, T. Minami, *SPIE* (Sol-Gel Optics) 1328 (1990), 62.

[19]   A. Matsuda, Y. Matsuno, S. Kataoka, S. Katayama, T. Tsuno, N. Tohge, T. Minami, *SPIE* (Sol-Gel Optics) 1328 (1990), 71.

[20]   H. Schmidt, G. Philipp, H. Patzelt, H. Scholze, in: Collected Papers XIV Intl. Congress on Glass, Vol. II, (1986) p. 429.

[21]   R. K. Iler, The Chemistry of Silica. J. Wiley & Sons, New York, 1979.

[22]   B. E. Yoldas, *J. Mater. Sci.* 12 (1977),1203.

[23]   S. Sakka, K. Kamiya, *J. Non-Cryst. Solids* 48 (1982), 31.

[24]   G. W. Scherer and C. J. Brinker, Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing. Academic Press, New York/Boston, 1990.

[25]   F. Lange, in: Proceedings of the International Symposium on Molecular Level Designing of Ceramics; eds.: Team of the NEDO International Joint Research Program, Nagoya, 1991, p. 14.

[26]   H. Schmidt, G. Rinn, R. Nass and D. Sporn, Mat. Res. Soc. Symp. Proc. 121 (1988), 743 - 754 .

[27]   R. Nass and H. Schmidt, in: Ceramic Powder Processing Science, eds.: H. Hausner, G. L. Messing, S. Hirano. DKG, Koln, 1989, pp.69 - 76

[28]   C. Sanchez, in: Progress in Research and Development of Processes and Propducts from Sols and Gels; eds.: S. Vilminot, R. Nass and H. Schmidt, North Holland, Amsterdam (1992), pp. 131-140.

480

[29]   H. Schmidt, in: Chemical Processing of Advanced Materials; eds.: L. L. Hench and J. K. West. John Wiley & Sons, New York, 1992, pp.727-735.

[30]   H. Schmidt, B. Seiferling, G. Philipp and K. Deichmann, in: Ultrastructure Processing of Advanced Ceramics, eds. J. D. Mackenzie, D. R. Ulrich, John Wiley & Sons, New York, 1988, p. 651.

[31]   H. Schmidt and H. Bottner, in: Advances in Chemistry Series, Proceedings Iler-Symposium, August 30-31, 1981, Washington; ed.: American Chemical Society (in press).

[32]   G. Rinn and H. Schmidt, in: Cer. Trans. I, Part A, Ceramic Powder Science, ed.: American Ceramic Society, Westerville/USA, 1988, pp.23-30.

[33]   Nucleation and Crystallization in Glasses, eds.: J. H. Simmons, D. R. Uhlmann and G. H. Beall, The American Ceramic Society, Inc., Columbus/Ohio, USA, 1982.

[34]   M. Smoluchowski, *Phys. Z.* 17 (1916), 557.

[35]   P. Strehlow, *J. Non-Cryst. Solids* 107 (1988), 55.

[36]   M. Popall, H. Meyer, H. Schmidt and J. Schulz, Mat. Res. Soc. Symp. Proc. 180 (1990), 995 -1001.

[37]   R. C. Mehrotra, in: Sol-Gel Science and Technology, eds. M. A. Aegerter, M. Jafelicci, Jr., D. F. Souza, E.D. Zanotto, World Scientific Publishing Co. PTE Ltd., Singapore, 1989, p. 17.

[38]   H. Schmidt, H. Krug, R. Kasemann and F. Tiefensee, *SPIE* 1590 (1991), 36-49.

[39]   H. Schmidt, H. Krug, R. Kasemann, N. Merl, V. Gerhard, F. Tiefensee and S. Bruck, in: Homage to Galileo, ed.: P. Mazzoldi, University of Padova/Italy, 1992, 303 - 313.

[40]   M. Mennig, C. Fink and H. Schmidt, *Glastechnische Berichte*, DGG (in press).

[41]   M. Mennig, H. Schmidt and C. Fink, *SPIE* 1590 (1991), 152-159.

[42]   H. Krug, F. Tiefensee, P. W. Oliveira and H. Schmidt, *SPIE* (Sol-Gel Optics II) 1758 (1992), 448 - 455.

[43] L. Spanhel, *J. Non-Cryst. Solids* 147/148 (1992), 657 - 662.

[44] L. Spanhel, M. Mennig and H. Schmidt, *Bol. Soc. Esp. Ceram. Vid.* 31-C, Vol.7 (1992), 9-14.

[45] G. Wagner, Master's Thesis, Saarbrucken 1992

[46] S. Bruck, Master's Thesis, Saarbrucken 1992

[47] R. Wilhelm and H. Schmidt, private communication, to be published.

[48] L. Spanhel, Mat. Res. Soc. Symp. Proc. 272 (1992).