SOL-GEL SYNTHESIS OF CERAMIC-ORGANIC NANO COMPOSITES

HELMUT K. SCHMIDT
Institut für Neue Materialien, Im Stadtwald, Bldg. 43, D-6600 Saarbrücken 11, Federal Republic of Germany

ABSTRACT

Sol-gel synthesis can be used for generating nano particles from a variety of compositions. In order to avoid aggregation and undesired gelation, it is necessary to react the particle surfaces with ligands reducing their interaction but allowing the incorporation into desired matrices. Three examples (semiconducting and metal quantum dots, ZrO_2 and Al_2O_3 containing composites) are described, their properties and some applications for optics and protective coatings are discussed.

INTRODUCTION

The synthesis of inorganic-organic composites has gained increasing interest for a variety of authors [1 - 11]. Reasons for that are the possibility of developing new and interesting material properties and aspects for application [12]. Various types of structures have been proposed or identified by appropriate analytical tools. Ceramers as developed by J. Mark and G. Wilkes are prepared from elastomers by diffusion of ceramic precursors into the polymeric networks and show phase separation effects resulting in oxide or hydroxide particles of SiO_2 or TiO_2 surrounded by organic polymeric chains. Other techniques lead to interpenetrating network type structures (polyceram) [13], but structural characterization is difficult in these cases. In ORMOCER type of materials, inorganic backbones are modified by organic groupings. Polymerizable groupings can be used for crosslinking with organic monomers [14]. In some cases molecular crosslinking of the different components seem to be the most probable structure [15], especially concerning systems based on SiO_2, phenyl silanes or methyl vinyl silanes. Systems derived from other alkoxides more likely develop phase separated structures containing nano particles, as, for example, described by Naß et al. for the fabrication of monoliths based on ZrO_2 precursors [16]. If materials for optical applications are taken into consideration, phase separation has to be observed very thoroughly in order to obtain sufficient transparency and to keep scattering as low as possible.

In other cases it is of interest to generate particles of special sizes to obtain special properties, e. g. quantum effects of semiconductor dots. In these cases, especially if narrow size distribution is desired, the particle growth in the sol-gel reaction has to be controlled very carefully.

Sol-gel processing can provide the means to control particle size and phase separation and the technique allows organic groupings to be introduced for modification of the sol-gel derived materials. In this case, a variety of synthesis

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routes has been developed, ranging from ≡Si-C≡ modified inorganic networks to organics linked by complex formation to inorganic units, intercalation compounds with clays or elastomers reinforced by nanoscaled sol-gel derived inorganic particles [17 - 21]. In this paper, recent developments based on ORMOCERs [22, 23], leading to novel inorganic-organic nano composites are summarized and special properties are investigated. Three examples of material development will be discussed: semiconductor quantum dot fabrication by sol-gel techniques, ZrO_2 and Al_2O_3 containing coating materials.

MATERIAL DEVELOPMENT STRATEGIES

The synthesis of glasses and ceramics by sol-gel techniques can be started from two basically different types of precursors. There are molecular precursors such as alkoxides, salts, soluble oxides or carboxylates and polymeric or colloidal precursors, which are more or less particulate. Molecular precursors very often, if no special chemistry (like the use of chelate formers blocking reactive sides) is applied, lead to colloids (SiO_2 under acid conditions is an exception) and gel formation takes place by a condensation reaction between the colloidal particles. If the structure of these gels is based on units (particles, pores, liquids in pores) in the nano range, the gels are, as a rule, of high transparency. In most cases, however, this state of homogeneity is lost by ageing, aggregations or other mechanisms leading to structural rearrangements, as schematically shown in fig. 1.

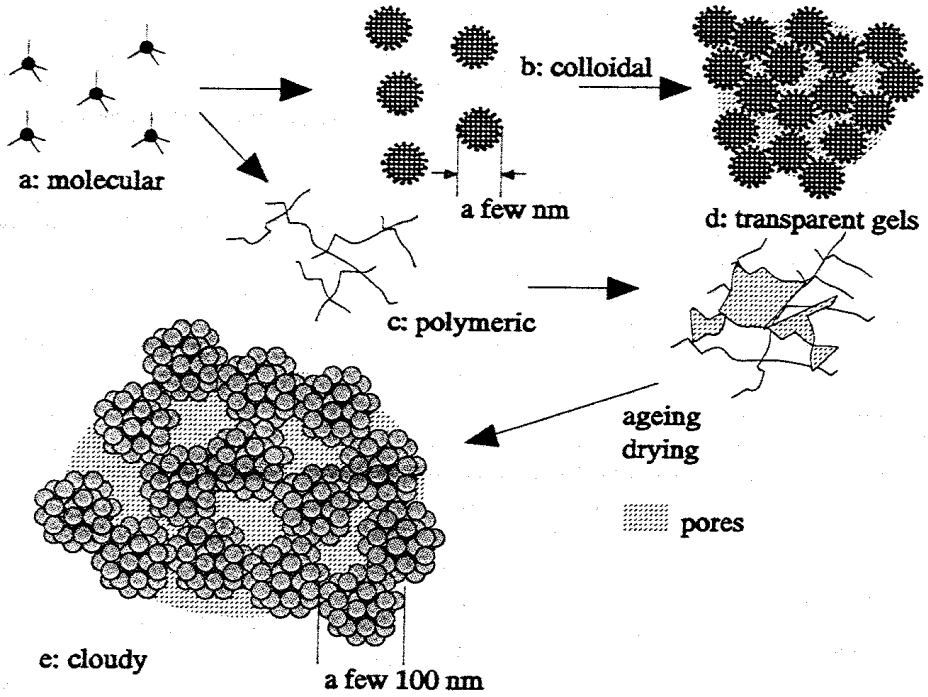

Fig. 1: Formation and coarsening of gels leading to larger structural units accompanied by loss of transparency.

As already mentioned, it is necessary to maintain the structural dimensions on a level indicated in fig. 1c, espe-

cially when optical applications are envisaged or special properties related to the nano scale shall be generated. Stabilization of this state of dispersion can be carried out easily in the liquid sol state by electrostatic stabilization by generating a charged double layer around the particles, which is well-known, for example, for ceramic slips or boehmite sols stabilized with HNO_3. But if compact materials shall be prepared from these sols, a destabilization step (e. g. pH change) has to be carried out leading to the problems indicated in fig. 1.

In order to maintain the colloidal particle properties within compact materials and to avoid structural units leading to disturbing optical properties, a new conception using colloid stabilization by well defined ligands has been developed. It is well-known that ceramic slips or suspensions can be stabilized not only by charging them electrically (ξ potential) but also by the adsorption of polymeric organic compounds to the surface. This route can be applied successfully with particles in the μm range since the volume of an adsorbed layer still remains relatively small compared to particle volume. The advantage of the adsorption of polymers is the fact that one molecule can react with more than one active site, leading to high overall adsorption coefficients. This concept cannot be used with nano scale particles if nigh package densities are required since the volume fraction of the particle decreases drastically (fig. 2).

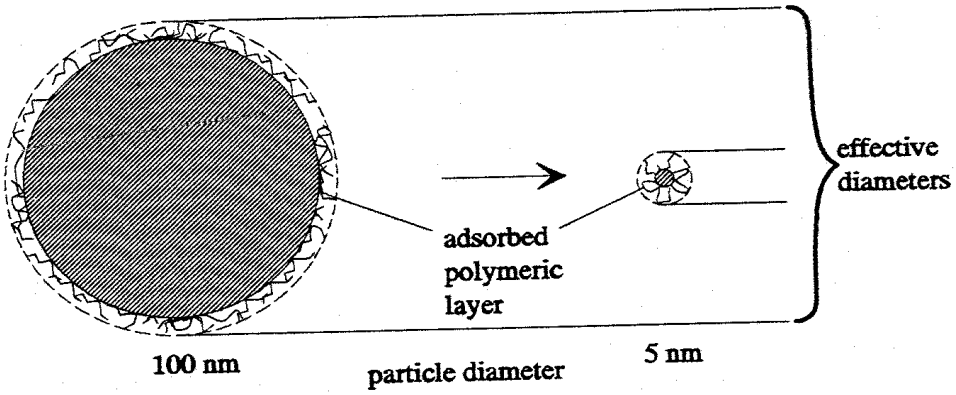

Fig. 2: Comparison of the effective diameters of polymer stabilized particles with two different particle diameters.

The use of ligands interacting specificly with the colloid surface enables the use of low molecular weight compounds thus reducing the "ligand volume". In addition to this, very specific properties can be obtained by proper choice of the ligands, too. This is of special interest if ligands with reactive properties are chosen to be used for anchoring the particles within a matrix. In our case, ORMOCER matrices have been investigated, since the ORMOCER system offers a high flexibility with respect to matrix composition and processing techniques. The strategy of the composite development is given in fig. 3. It includes the synthesis of small particles, the stabilization of the particles by ligand/particle interaction and the incorporation into ORMOCER matrices.

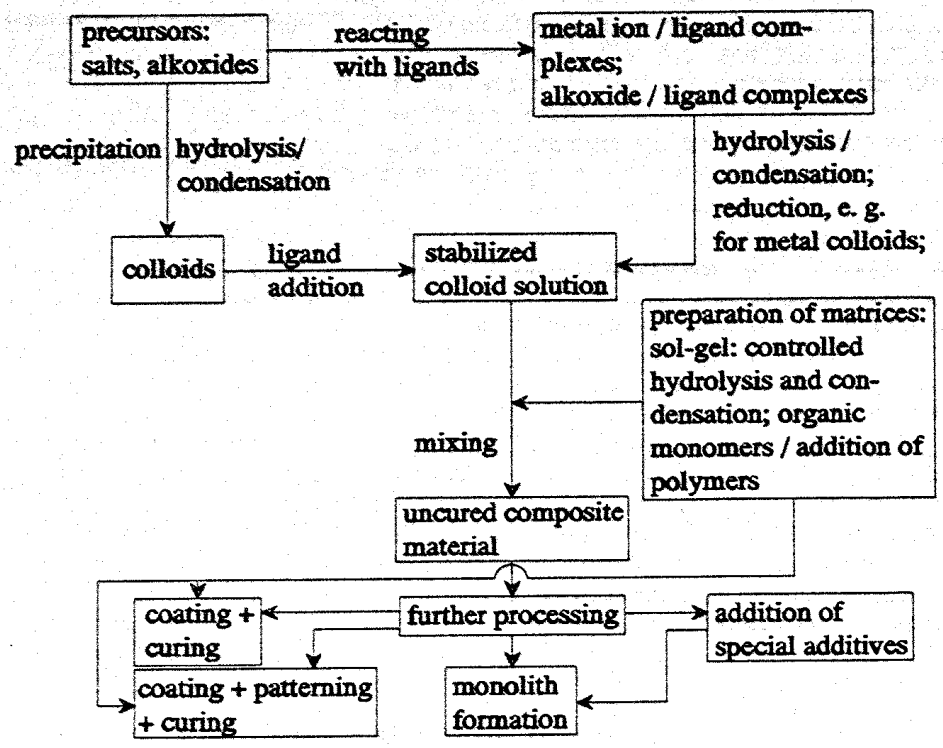

Fig. 3: Draft of sol-gel preparation of nano composites using ligand interaction stabilization.

QUANTUM DOT CONTAINING COMPOSITES

Semiconductor and metal quantum dots have become of high interest due to their potential for χ^3 applications. As shown by Henglein et al. [24], CdS and other II/VI semiconductor colloids can easily be prepared by precipitation from aqueous solution using Cd salts and sulfides. However, it is difficult to produce compact materials due to the problems mentioned above. Other work has been reported on generation of sol-gel derived CdS/glass composite by impregnation of gels by Cd salts or simultaneous precipitation [25, 26] or by phase separation from melted glasses. But it is difficult to obtain narrow size distributions of the colloids by these methods. The application of methods indicated in fig. 3 led to stable sols with narrow size distributions (indicated by the optical spectra) for a variety of systems. Details of the synthesis procedures have already been described by Spanhel and coworkers for CdS. For quantum dot systems and the incorporation of the dots into ORMOCER matrices the following processes have been developed [27] (fig. 4 and fig. 5):

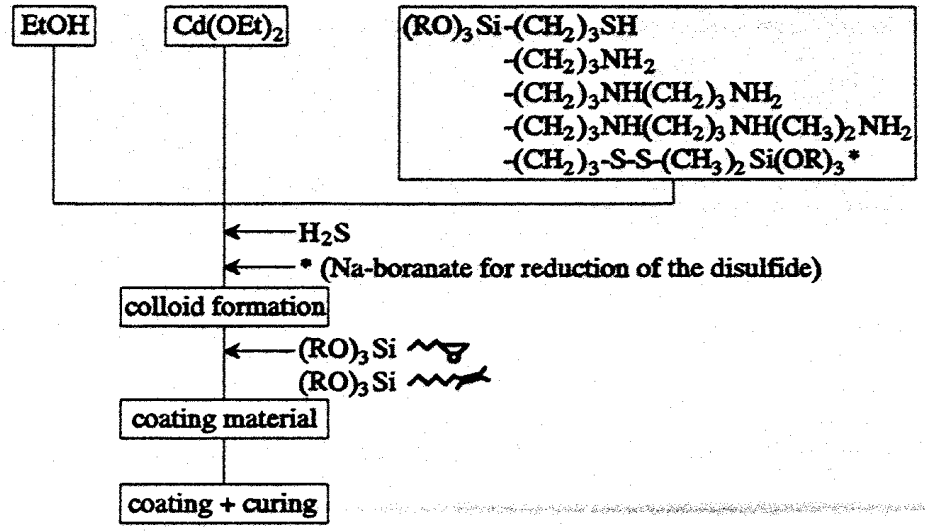

Fig. 4: Flow diagram of the preparation of ligand stabilized CdS quantum dots.

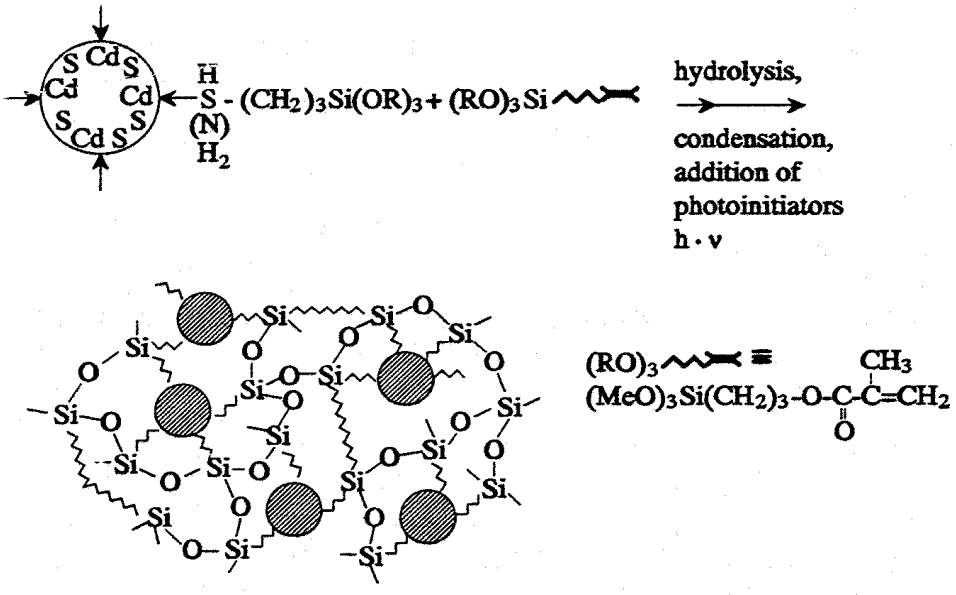

Fig. 5: Reaction and structure model of the incorporation of ligand stabilized CdS quantum dots into ORMOCER matrices.

In fig. 6 UV/VIS spectra of CdS containing materials are shown.

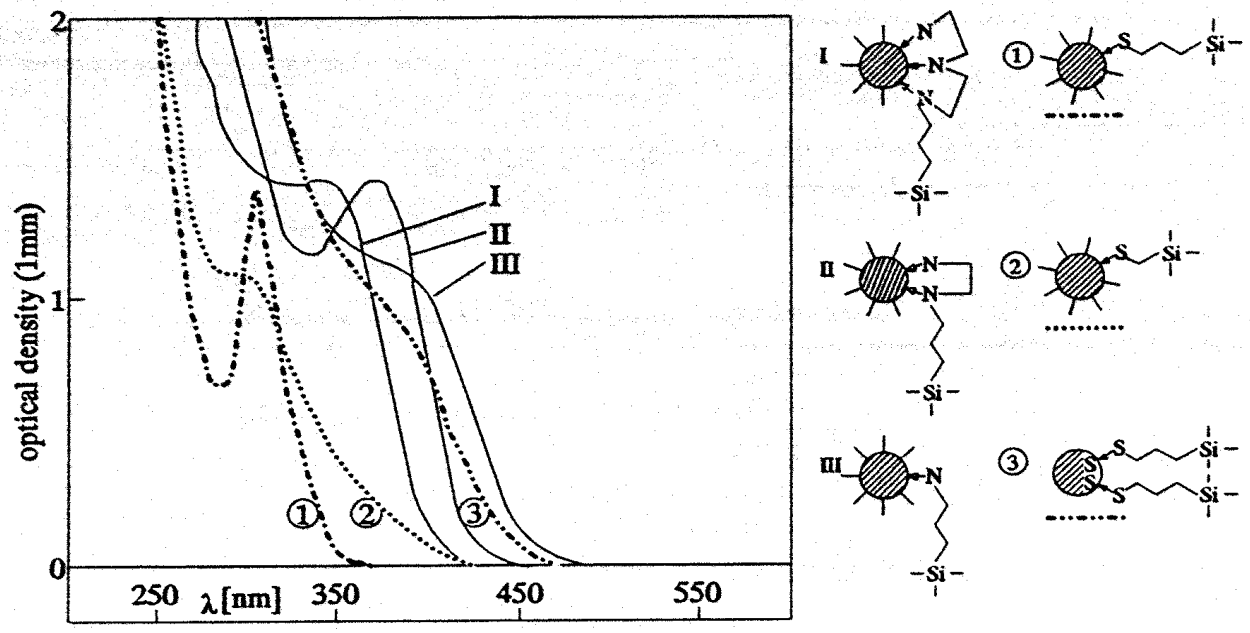

Fig. 6: Absorption spectra of sulfide and ammine stabilized CdS quantum dots.

The optical spectra show that there is a relatively sharp cut off due to the band gap energy of the quantum dots. At smaller particle diameters, sharp exitonic peaks can be detected in the sulfide stabilized systems. TEM investigations confirm particle diameters ≤ 2 nm, but no quantitative analysis is possible.

The spectra of the colloids do not change after incorporating them into ORMOCER matrices. This proves the shielding effect of the ligands, defining the local electronic environment at the particles' surface. This means that it is possible to vary the optical properties of the dots by varying the ligand chemistry, which can also be seen from fig. 6. In a similar way, PbS coated CdS dots can be prepared [28]. χ^3 values of this system are in the range of 10^{-9} esu at present.

Gold containing ORMOCER systems have been synthesized according to the draft in fig. 4, too. The optical spectra of these systems are similar to those known from gold colloids. The incorporation into ORMOCERs is possible by the bifunctional ligand concept [29]. The colloid formation process in films was optimized in a way that gold complexes were introduced into a viscous, partially condensed ORMOCER system containing polymerizable ligands. After the preparation of films on glass substrates, the colloid formation process can be initiated by UV light. The colloid growth process takes place at T ≈ 100 °C during the irradiation used for photopolymerization curing. The fabrication is schematically shown in fig. 7.

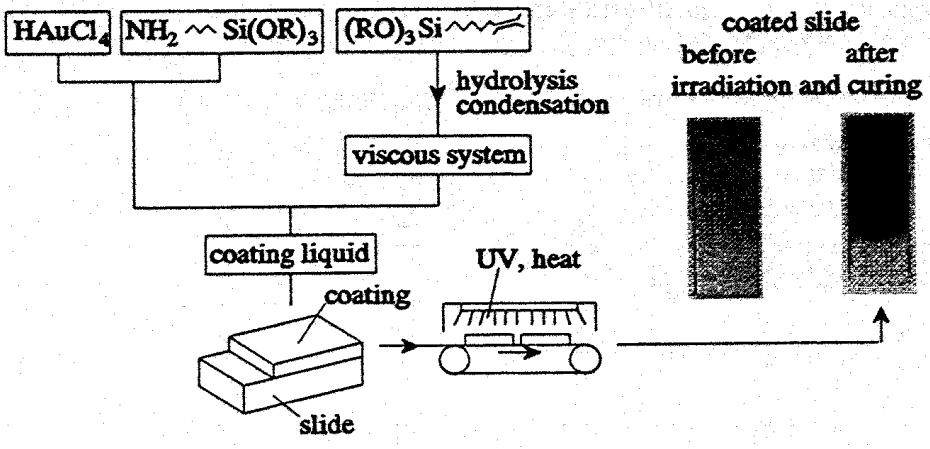

Fig. 7: Draft of the one step preparation of gold colloids in ORMOCERs. T ≈ 100 °C, $t_{irr.}$ = 15 min.

Experimental details about the complex and ORMOCER synthesis are given in [29]. The films can be prepared with high gold contents up to several volume percents and optical densities up to 5. In the four wave mixing experiment the films show a self-diffraction effect attributed to χ^3 NLO properties, but no quantitative evaluation has been carried out so far. The results demonstrate the potential of the sol-gel technique for the fabrication of optical nano composites with interesting properties.

SYNTHESIS AND UTILIZATION OF ZrO_2 PARTICLE CONTAINING COMPOSITES

ZrO_2 in ORMOCERs has been investigated by Dislich [30] for increasing the refractive index of these materials. Naß has shown that high ZrO_2 contents can be obtained by using ß-diketones as complex formers for Zr alkoxides and ORMOCERs as matrix [16]. He found particle sizes of about 10 nm. Sanchez [31] showed that the cluster size of Zr-alkoxides complexed by ß-diketones can be varied between 5 and 50 nm, and Rinn showed that this can be done up to 3 μm [32]. In our investigation we focused on the complexation with methacrylic acid (MAS) due to their ability for undergoing a polymerization reaction. As already shown in [33], complexation of MAS leads to the formation of nano particle containing sols the size of which depends on the ratio r = Zr:MAS. While between r = 1:1.6 and 1:1.2 the particle diameter d remains at about 3 nm, lower r lead to a strong increase of d and above r = 1:0.8, precipitation takes place. But as shown by Wilhelm and coworkers [34], nano scaled clusters can be obtained with r ≈ ≤ 4, if "water" is introduced into the system by ≡SiOH groups, e. g. using prehydrolysed $(RO)_3Si(CH_2)_3OCOC(CH_3)=CH_2$. The particle size in this case mainly depends on the concentration of the "latent" water introduced into the system through the silanes. In fig. 8, the particle size development is shown as a function of composition and time. For the synthesis the process described in [35] was used. As one can see from fig. 8, at first a bimodal distribu-

tion occurs, equilibrizing into a monomodal distribution after several days. The reasons for that probably are structural rearrangements the mechanisms of which are not quite clear so far.

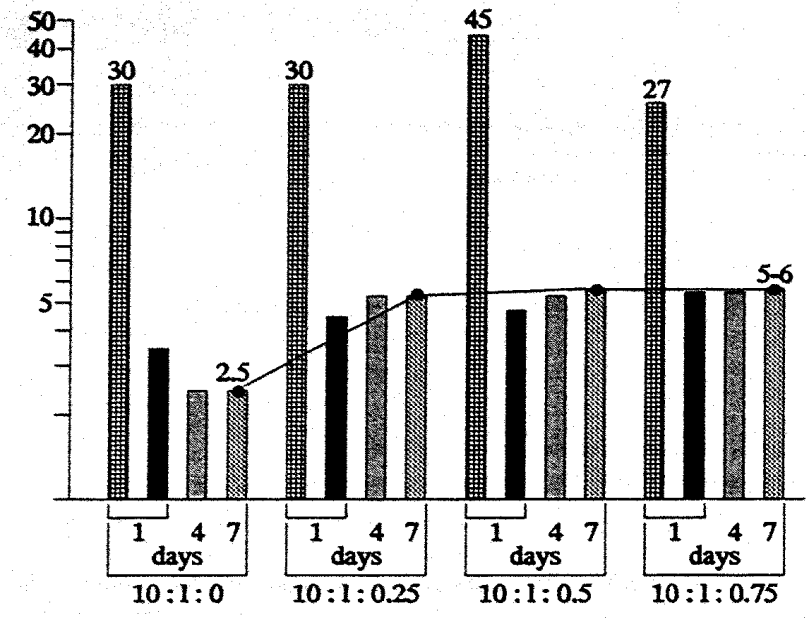

Fig. 8: Particle size distribution in liquid uncured composite materials after [29]. a:b:c = methacryloxy silane: Zr propylate:MAS; days: reaction time at room temperature after mixing the (complexed) alkoxide with the silane prereacted after [30].

The tendency of increased particle sizes by increasing the ratio x = (b+c)/a was supported by an experiment using the ratio a:b:c = 10:3:2.25, ending up with a particle size of about 15 nm. The particle analysis was carried out by photon correlation spectroscopy. The analysis of the data shows almost monodispersed systems and spherical particles.

Mechanical tests carried out on cured coatings show a good scratch resistance of these systems (1 - 2 % haze after the standard test with a taber abrader). The refractive index can be varied between 1.52 and 1.58. The most interesting properties of the system, however, are their photoresist behavior and their ability to adjust the viscosity as a function of the processing condition. It can range from some mPa·s to almost solid systems in the uncured form, being able to be embossed during the final curing step. The resist behavior was used for patterning of planar waveguides, as described in [33 and 35]. Embossing can be carried out using a UV source and a transparent substrate. The photopolymerization occurs during the embossing step. Photolithographic method (laser writing, mask-aligner techniques, beam energy fluctuation by two wave mixing interferences) have been developed for patterning, too. The irradiated areas get polymerized and the non-irradiated areas can be redissolved by diluted NaOH or organic solvents. The two wave mixing experiment is of interest due to the possibility of continuing with one wave and thus "writing" incoupler gratings and channel waveguides in one step. In fig. 9 the schematics of

the two wave mixing writing and a grating produced by this technique is shown [36].

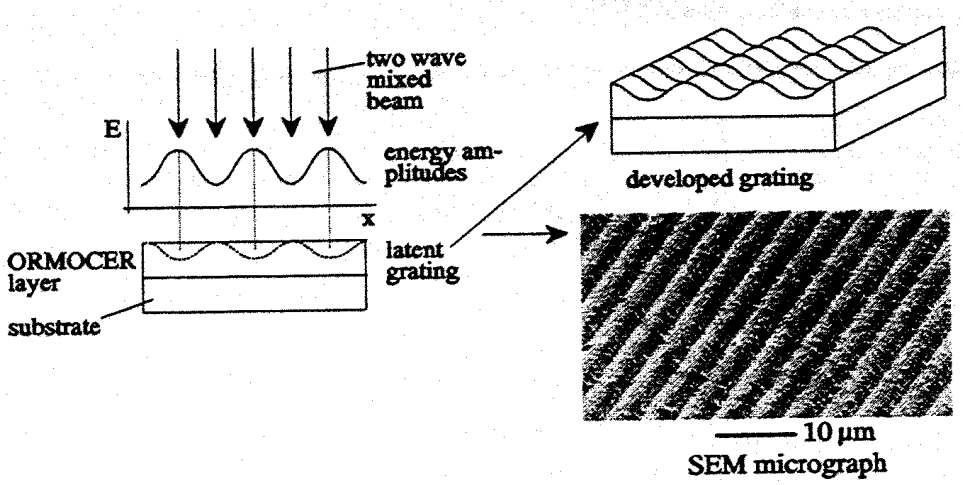

Fig. 9: Fabrication of a diffraction grating by a two wave mixing photolithography process [after 36].

Optical losses of the system are in the range of ≈ 1 dB/cm without using clean room conditions at present. The nano composite seems to be a suitable matrix for processing of optical waveguides. They can be doped either with push-pull molecules (dyes), lanthanides or quantum dots, which already has been proved experimentally.

Al_2O_3 CONTAINING COMPOSITES FOR COATINGS

As described elsewhere, transparent hard coatings have been developed for plastics [12] and brass protection [37], but no structural analysis was carried out. Since Al containing composites have shown a good corrosion protection for brass, the question arose how far corrosion protection for other metal surfaces can be obtained and how far structures can influence the properties. In [38] a system synthesized from $(RO)_3Si(CH_2)_3OCH_2\text{-}\overline{CH\text{-}CH_2O}$, $(RO)_3Si(CH_2)_2CH_3$ and $Al(oBut)_3$ is described and experimental details are given. The epoxide is polymerized with methyl imidazole as catalyst. In order to avoid precipitation, the Al butylate was reacted with ethoxy-butanol to form a complex according to [39]. Details of the reaction are given in [36]. The complexed system was reacted with the silanes according to fig. 8. Different types of catalysts were used. Only F^- catalysis leads to the formation of non-spherical particles which cannot easily be explained. Further investigations by photon correlation spectroscopy show that particles can be obtained from the silane precursors without Al, too, but they are nearly spherical. In fig. 10 the particle size development in the three component system is shown as a function of time.

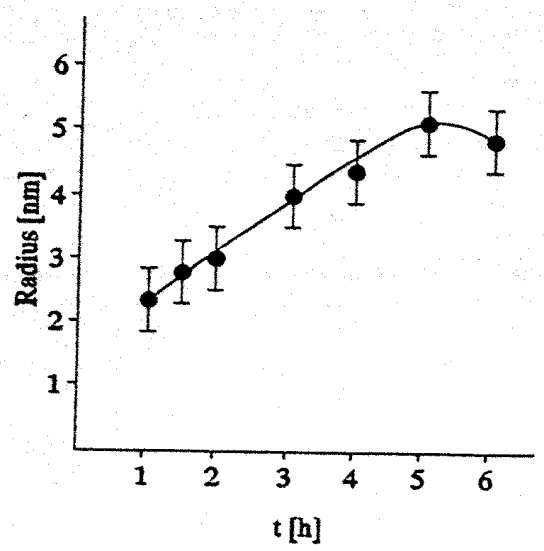

Fig. 10: Development of nano particles in the three component system according to fig. 8 after [36], method: photon correlation spectroscopy.

So far, the mechanisms for these complex reactions are not clear, but the effect on the nano particle containing systems as coatings on Al sheets is surprising: Only the particle containing system shows the highest corrosion protection effect on the Al surface combined with a very good scratch resistance. No traces of corrosion can be detected after two weeks of salt spray test at 35 °C and 100 % r.h. While the high scratch resistance can be attributed to the nano particles, for the increased corrosion resistance no simple explanation exists so far. But the results show that by development of nano scaled particles within ORMOCERs interesting properties can be generated.

CONCLUSION

The investigations show that by specific chemical means nano sized particle containing composites can be generated. The chemistry is mainly based on sol-gel or related techniques. It seems to be of high importance to tailor the interface between the particles and the matrix. This influences the optical properties and probably the particle distribution, too. But in any case it is necessary to avoid undesired reactions between the particles leading to aggregation.

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