Inorganic-Organic Composites by Sol-Gel Techniques

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1 Introduction

The sol-gel process is well known as a chemical synthesis method for the preparation of glasses and ceramics. In general, starting from inorganic precursors like alkoxides, soluble oxides, or hydroxides, a growth process is initiated leading to oligomeric molecules or colloids which then form three-dimensional networks by chemical reaction or aggregation. By control of this reaction, it is possible to stabilize intermediates in solution (sols) which can be used for a variety of interesting shaping techniques such as coating or fiber drawing. The shaping ability of sols depends strongly on the structure and interaction between the oligomeric or colloidal units, and, by controlling this, a variety of properties of the final products can be tailored.

In most cases, however, monolithic processing becomes difficult due to the large shrinkage of the gels. The shrinkage rate is due to the high porosity of the gels. The poor relaxation in the three-dimensionally cross-linked inorganic systems is an obstacle against the processing to monolithic materials or even against thick films. It is difficult, for example, to obtain films thicker than 1 μm by a one-step dip-coating and densification step. The stress formed by uniaxial densification cannot be released by relaxation, and if the stress exceeds the critical stress energy, cracks appear [1]. In order to reduce the interaction, a variety of means seem to be possible. The use of so-called drying-controlling chemical agents [2,3], the mechanism of which is rather complicated (reduction of interfacial tension between solvent and the pore walls, reduction of interaction between colloidal particles), can help to overcome these problems to a certain extent.

Another way to improve relaxation is to introduce high organic contents into the system, a method which was used by Tohge and co-workers for the fabrication of thick coatings to be pre-grooved for CD ROMs on glass [4]. In this case, polyethyleneglycol was used as an organic modifier. After firing out the glycol, however, the porosity remains in the system, which can only be densified to full density on the glass substrate due to the relaxation properties of the SiO_2/TiO_2 films. If low temperatures are used, the organics can remain within the system, and, depending on their volatility or their binding mechanisms, they can remain within the network and modify its properties.

The potential of using organics to modify inorganic backbones has been recognized as an interesting instrument for tailoring new composites a long time ago. As soon as chemistry discovered the ability of the silicon atom to form stable bonds to oxygen and carbon at the same atom, silicone type of materials have already been synthesized. Commercialization of materials based on these properties of silicone started to take place by the time of the discovery of Rochow to synthesize silicone precursors by cheap methods. Silicone chemistry and silicones became an important branch of chemistry [5].

The opposite consideration, to start from inorganic sol-gel networks and to modify the inorganic backbone by introduction of selected organic groupings with a variety of properties, was postulated in the late 70's as a new conception of modifying glasses and ceramics [6,7]. This type of material has been named *Ormosils* (ORganically MOdified SILicates). Another route based on oligomeric polysiloxane precur-
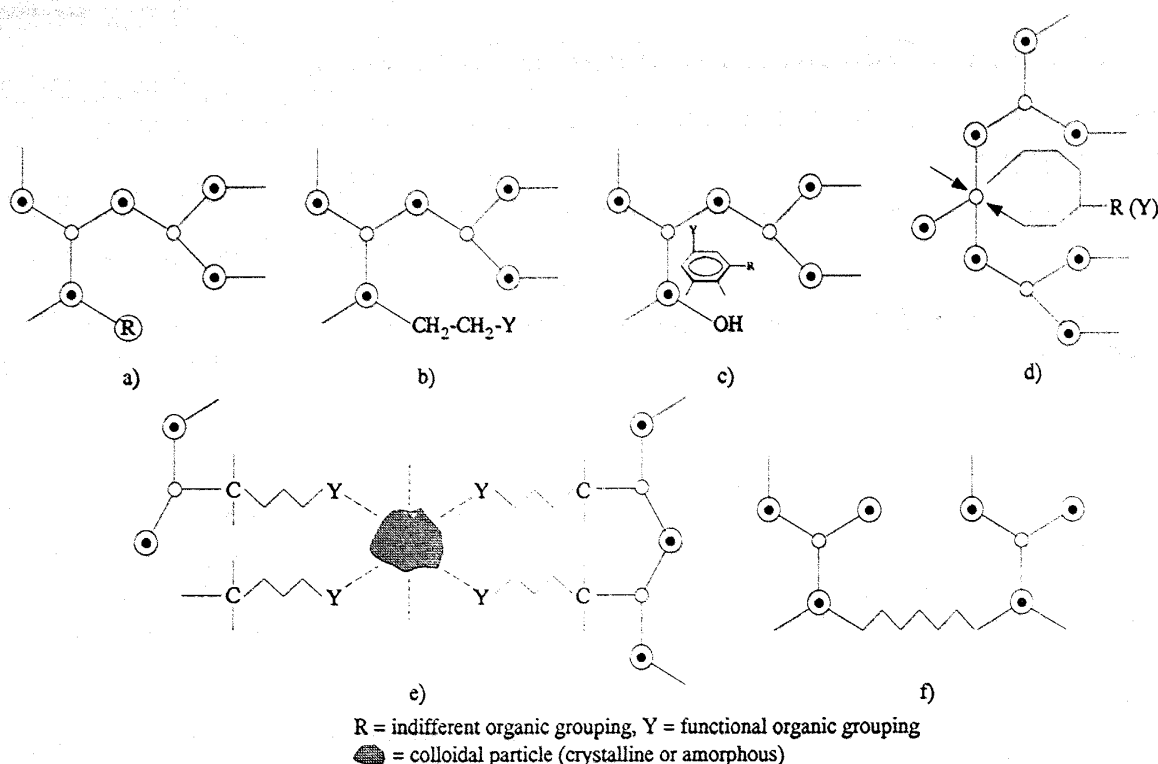
Fig. 1. Some examples for possible structures of inorganic-organic composite materials; inorganic structure modified by a) alkyl groupings; b) organo functional groupings; c) adsorbed dye; e) colloidal particle by surface bounds; f) polymeric chains. o = Si, Al, Ti, Zr; o = oxygen.

sors modified by SiO_2 or TiO_2 from polycondensation processes was synthesized by Wilkes (*Ceramers*, CERAmic PolyMERS) [8]. Uhlmann and coworkers used similar principles (*Polycerams*, POLYmeric CERAMic materials) [9]. In all these materials, two basic principles for the hybridization (linking the organic to inorganic materials) of inorganics and organics have been used. One principle, as already mentioned, is the SiC bond; the second is based on the precipitation of very small inorganic particles like SiO_2 within the polymeric type of networks, for example, silicone type of materials [10,11], χ^3 polymers [12].

Another principle to obtain inorganic-organic composites is the infiltration of porous sol-gel materials by organic monomers and subsequent polymerization, as shown by Mackenzie and Klein [13,14]. This principle can also be used for doping porous materials by organics, as shown by Hench and King [15,16]. Doping with organics is of interest if these organics show special optical properties (nonlinear optical properties or lasing properties). The doping of the organic dyes can be used during the hy-

drolysis and condensation [17,18], and if the dyes remain absorbed to the inorganic units in a molecular dispersion, the dye properties can be transformed from the sol to the gel. Tunable lasers have been postulated by this method [19].

This short survey, which, of course, cannot be a comprehensive one, shows the large variability of inorganic-organic composite material systems. In Fig. 1, a schematic overview of some structural possibilities is shown.

One of the basic problems of synthesizing this type of materials is homogeneity. The formation of organic-rich and inorganic-rich phases, especially if unpolar organics are not covalently bound to the inorganic backbonds, are introduced. Heterogeneity can be based on different effects. The organics can form a separate phase within the liquid system (liquid-liquid phase separation) or can form separate phases by migration mechanisms during drying and heat treatment. Formation of organic phases automatically results in the formation of inorganic phases at the same time. If the inorganic phase size can be controlled, homogeneity can be controlled, too. In order to control inorganic phase sizes,

the interaction between the colloidal particles or macromolecules has to be controlled. For these reasons, conceptions have to be developed to establish interface controlling agents. A second interesting perspective related to the interface control is the possibility to improve package densities allowing thick film or monolithic part processing techniques. For these reasons, in this paper the possibilities of chemistry to control interaction particle size and processing are discussed and some examples of material development based on these considerations are given.

2 General Considerations

Organic groupings can be linked to the inorganic backbone by a variety of "chemical links." In the case of additional organic monomers to be crosslinked to polymerizable groups—for example, of the silanes with methacryloxy groups—phase separation on a nonometer or sub-micron range could be observed [20]. Furthermore, the question arises how far the properties attributed to inorganic units and properties attributed to organic units can determine the overall properties of the resulting composites. For example, in the case of zirconia-containing composites incorporated into the networks by an access of methacrylic acid [21], no phase separation can be determined by electron microscopy down to a level of 10–20 nm. But that does not mean that phase separation has occurred on smaller ranges. Dislich and co-workers investigated how far incorporation of zirconia can lead to an increased refractive index and concluded that distribution of inorganic components on a molecular level in organically modified ceramics (ormocers) does not lead to optical properties similar to those of crystalline or amorphous pure inorganics. The molar refraction data of the crystalline phase could not be used to predict the composite properties in the Lorentz-Lorenz equation [22].

Phase-separated materials with controlled phase dimensions may be of interest for reasons of obtaining solid state properties of the dispersed phase in the composite. If the phase separation can be kept in a nanometer range, materials with high transparency or optical qualities

should be accessable.

The interface between the inorganic and the organic phases plays an important role, e.g., for anchoring the particles to the polymer matrix. Interfacial structures of the surrounding matrix do not play an important role in μm-sized "fillers" because they contribute only negligibly to the composite volume. If particle sizes become smaller, the interfacial volume increases, and if the particle size reaches the nanometer range, depending on the total volume of the inorganic phase, interfacial structures can dominate properties. In the molecular range, the inorganic "ceramic" part loses its "identity," whereas organic groupings or organic polymeric chains still maintain their identity or functionality. With increasing particle size, the identity of ceramic or glass or amorphous properties becomes important and the typical composite type of behavior becomes more and more apparent. The interesting range is the nanometer range (some up to 10 or 20 nm), because in this dimension, light scattering in many cases can be neglected, the interfacial phase can be dominant and result in interesting properties, inorganic bulk properties should also be remarkable, and, if semiconductors or metals are used, quantum size effects should also be observable.

In all cases, the question of the connection between the inorganic particle and the organic unit is of high importance. Whereas in the case of the molecular type of composites, the identification of the chemical link from the inorganic to the organic part follows conventional rules of chemistry, and the classification into covalent, coordinative or ionic bonds can be carried out in most cases, (as shown in a few examples, the connection of small clusters or nanoscaled particles to the organic environment seems to be more difficult. The formation of tailored surface bonds, e.g. silanization, can help to overcome these problems, but silanization is restricted to a few systems only (e.g., SiO_2 or other silicates). Some "linking models" are shown in Fig. 2. Depending on particle-to-particle interaction, textures are possible, too.

For these described reasons, inorganic-organic composite materials gained high interest in optics, especially nonlinear optics, as substrate ma-
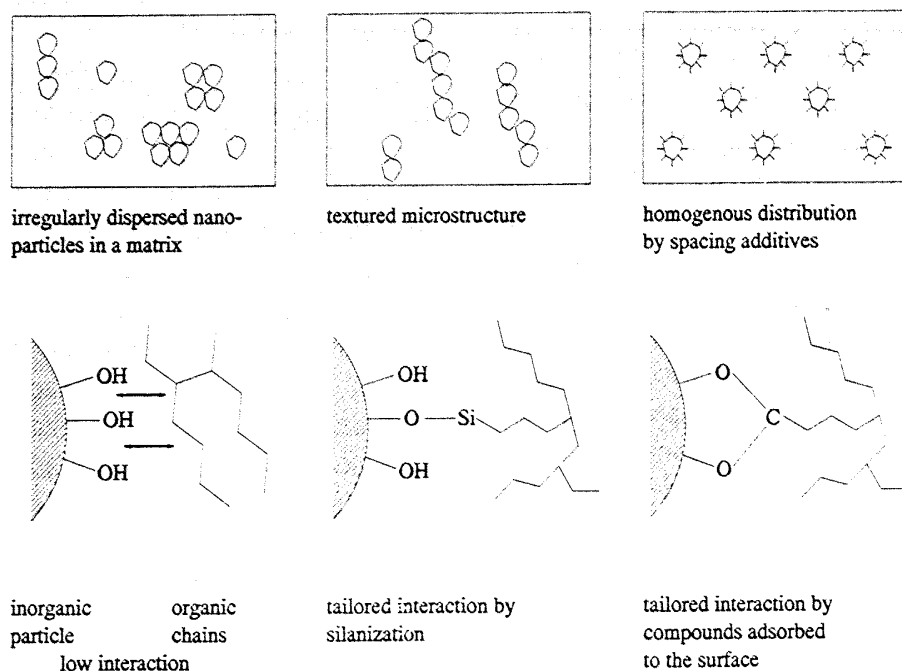
irregularly dispersed nano-   textured microstructure   homogenous distribution
particles in a matrix   by spacing additives

inorganic   organic   tailored interaction by   tailored interaction by
particle   chains   silanization   compounds adsorbed
        low interaction   to the surface

Fig. 2. Models for linking particles to the surrounding matrix.

terial (which allows tailoring of a variety of properties like refractive index) for incorporation of dopants, for the ability of forming thick films, combined with micropatterning methods for optical components, and for microlens arrays, waveguides and others.

Another interesting field is related to a variety of types of coatings like protective coatings on plastics. These types of composites have been more or less defined as so-called molecular composites [23–25]. They can be synthesized by mainly using modified silanes in connection with a variety of inorganic sol-gel precursors like titania, silica, alumina, and others. The chemical principle is to co-hydrolyze and co-condensate the alkoxide precursors together with functionalized silanes and to control the reaction in order to avoid phase separation or precipitation.

Some important basic properties of these materials are their hardness and abrasion resistance compared to organic polymers, which is attributed to the inorganic backbone. This question is critical since the density of these materials is more like that of polymers, and the free volume of these composites is much closer to that of polymers than to that of inorganic materials like glasses or ceramics. Another interesting property is the matrix rigidity which seems to be an advantageous property with respect

to the storage or the doping of organic dyes leading to interesting photostabilities [19]. The third point, of course, is the processing property which is close to soluble organic polymers. The enhanced relaxation behavior to obtain full density is by orders of magnitudes higher than that of inorganic sol-gel materials, and monolith and thick film processing becomes very easy.

3   Materials Based on Molecular Type of Composites

As already described, the molecular type of composites is still of interest, mainly based on the fact that functions to be attributed to organic groupings can be introduced in inorganic structures. Typical functions of organic polymers or organic molecules are solubility in organic solvents, low modulus of elasticity, high fracture toughness, low temperature curing, low density, adsorption in the visible and UV (based on the molecular electronic structure), nonlinear optical properties, and the possibility of carrying out curing techniques such as thermal or photoinitiated polymerization or addition reactions. For example, for scratch resistant coatings on soft substrates, the combination of hardness and flexibility is used to establish a proper mod-

ulus of elasticity and a thermal coefficient of expansion to obtain hard coatings on plastic substrates [25].

Another interesting point of view is the tailoring of viscoelastic properties in order to generate a stress dissipation behavior. This is an important property for sealing materials. For example, glass seals based as sealing material (glass solder) can only be applied under very special conditions since glass is not able to dissipate stresses once cracks are formed. The advantage of glass seals, of course, is their high temperature stability compared to that of organic seals. Organic polymers used for sealings, in general, are one- or two-component materials specially optimized for adhesion on a special type of substrates. It is difficult to optimize them for two sealing substrates with very different surface properties and to obtain temperature stabilities above 150°C.

Based on this consideration, investigations have been carried out in order to synthesize an inorganic-organic molecular composite system for sealing copper to polyimide (which is an important problem in microelectronics). The objectives were to combine high temperature stability (250°C) with high sealing strength to both polyimide and copper surfaces and to establish a viscoelastic behavior with a sufficient stress dissipation mechanism, an indispensable requirement for high sealing strength. In addition to this, a thermosetting behavior (hot melt type of sealant) was required.

It could be shown that just by tailoring the inorganic crosslinking, length and type of organic crosslinking, and reaction conditions, structures could be developed which show surprising results (the experimental techniques and detailed results are described elsewhere). The basic structure of this inorganic-organic composite is represented by chain-like polycondensates of diphenyl silanes with relatively short chain lengths and methylvinyl bifunctional silanes incorporated into these systems. However, without modification, these systems show a glass-like behavior under stress conditions, cracks formed in the seal cannot be dissipated [26], and low sealing strengths are observed. The modification of these systems by the formation of epoxy-
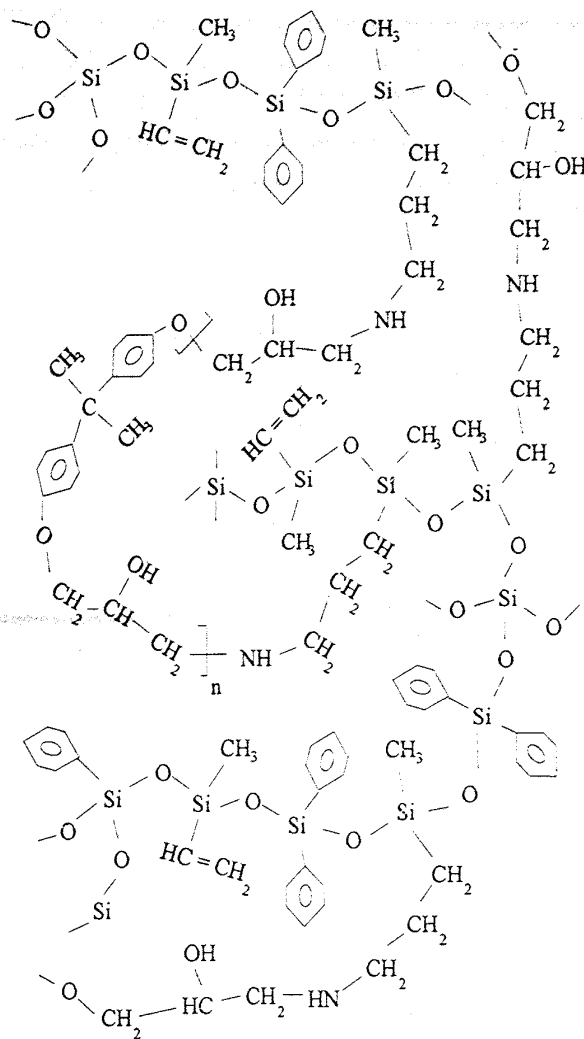

Fig. 3a. Structural model of the sol-gel derived inorganic-organic sealant.

crosslinked amines introduced as aminosilanes allowed tailoring of the mechanical properties such that stress dissipation by plastic deformation could be adjusted. In this way, high sealing strengths of 10 N/cm² could be obtained, and the sealing strength does not change up to temperature of 180°C. Using this optimization route, a sealing system for copper and polyimide had been developed which is remarkably higher in sealing strength and temperature stability as the commercially available silicon-based sealants. In addition, using the aminosilanes and epoxides, a good wettability of both types of surfaces (polyimide and copper) could be established, another requirement for high adhesive strength [27]. In Figs. 3a–c, a structural model of the composite is shown, and in Fig. 4, the adhesive strength as a function of composition is shown. It is
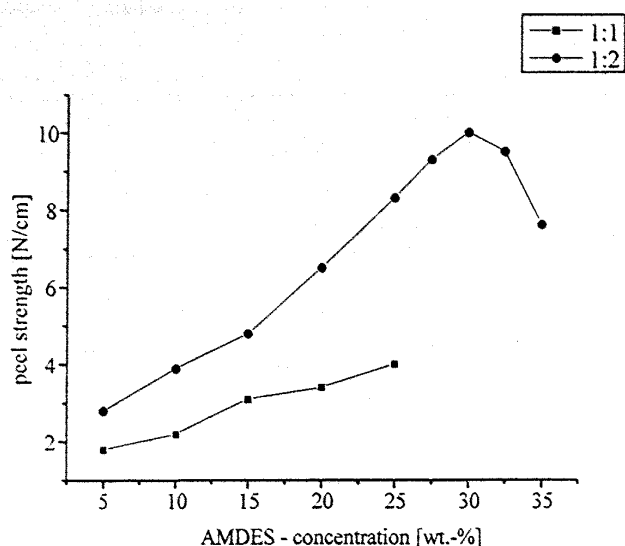
Fig. 3b. Composition dependence of the sealing strength: AMDES: $((RO)_3Si(CH_3)CH_2CH_2NH_2)$ ratio amino: diole = 1:1, 1:2, after [27].
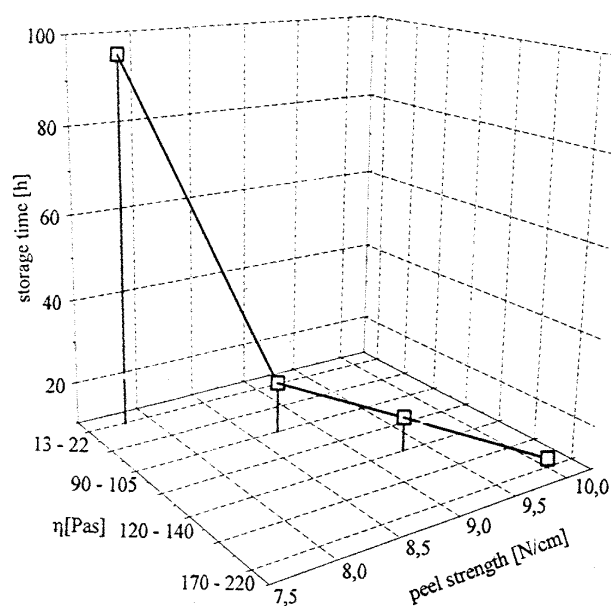

Fig. 3c. Sealing strength as a function of viscosity (established by preheating treatment) and storage time.

Fig. 4. Peel strength as a function of the OH content (type 1:2 sealant, see Fig. 3).

Table 1. Intensity ratio of OH:CH

A	0.358 ± 0.03
B	0.3 ± 0.02
C	0.3 ± 0.02
D	0.3 ± 0.02

ing to Table 1. This allows the tailoring of the wetting behavior by IR monitoring.

Another system has been developed for the incorporation of organic dyes with push-pull properties (for non-linear optical second-order effects, χ^2) [28]. In this type of composite, organic dyes could be stabilized in a $Zr(OR)_4$ methacrylic acid/methacryloxysilane system during poling [29]; however, the obtained χ^2-effects still are low due to the low poling efficiency. Kim et al. show that using different systems, fairly high second-order effects could be observed [30].

Summarizing, one can say that the molecular type of composite (ormocer type) still is of high interest, especially if low processing temperatures are required.

remarkable that these systems in a liquid state show a strong aging effect, as shown in Fig. 3c, which affects sealing strength considerably.

The wetting behavior (and through this, the adhesion strength) strongly depends on the SiOH concentration of the seal. A simple method is to observe the IR absorbance at 3620 cm^{-1} (OH) in relation to 3070 cm^{-1} (aromatic CH). Fig. 4 shows the peel strength as a function of different ratios of OH:CH accord-
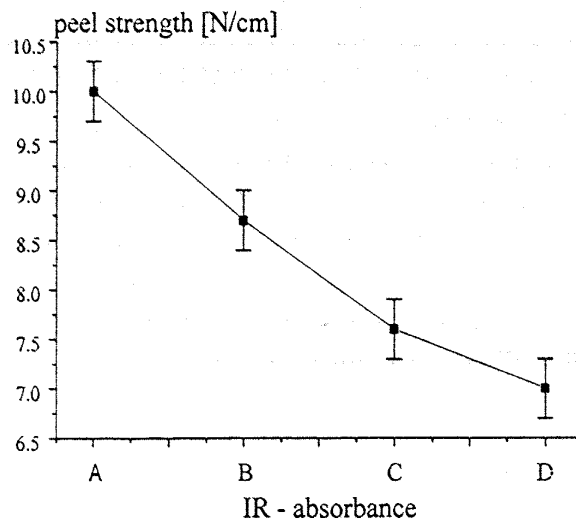
4 Inorganic-Organic Nanoscaled Composites

Meanwhile, the molecular type of composite has gained much interest in the scientific community [31–34]. The nanoscaled type only recently became interesting [11,35–38]. Sol-gel reactions, with a few exceptions, are growth reactions

starting from molecular precursors and ending up in colloidal systems with particle diameters up to hundreds of nanometers. In general, the colloids have to be stabilized in order to avoid precipitation or agglomeration leading to larger units (or gels if a three-dimensional "agglomeration" takes place). Colloidal systems can be used for further processing steps like coating or casting techniques. The stabilization, in general, is carried out by generation of surface charges leading to a repulsion force between the particles. The growth reaction is initiated by a nucleation process generating nuclei around which the growth reaction takes place. For the growth reaction, two models can be considerated. Using La Mer's model, which deals with saturated and supersaturated phases, Maiijevic could show that it is possible to obtain a variety of monosized deagglomerated particles in spherical or other shapes [39]. Electron microscopic investigation of larger units, however, generally shows substructures of primary particles in the lower nanometer range, supporting Smoluchowski's model based on a diffusion controlled nanoscaled particle aggregation [40]. Colloids with substructures are formed mainly from network-forming elements.

As shown by [35,41,42], other structures can be obtained by using chelating agents during hydrolysis and condensation. In this case, active sides are blocked, preventing the formation of aggregates and leading to chain-like or spherical structures. From this point of view, it is interesting to know how far organics can be used to tailor shape and size of colloids during sol-gel processing. A prevention of phase separation seems to be much more difficult than in the molecular type of systems. The question arises, of course, whether chelating agents, electron donating, or accepting ligands can be used as links between colloidal inorganic particles and an organic matrix. In this case, the ligands have to be anchored to the surface.

So far, a series of interesting questions arises with respect to particle tailoring, particle stabilization, and particle reactivity. Ligand-stabilized systems with controlled reactivity should be obtainable if bi- or multifunctional ligands were used with one "stabilizing function"

directed to the particle surface and one "reactive function" representing the interface of the particle to the environment, and if the proper reactivity can be established within these interfaces, e.g. polymerizing groupings. Then, the interface reactivity can be used for further processing or for incorporating the particles into the desired matrix systems.

Since colloidal systems represent very large surface areas, the free surface energy (ΔG_s) per volume should be very high. A decrease of ΔG_s should be achieved by use of ligands with a selected interaction to the particle surface and the desired stabilization effect should be observed. Moreover, as a hypothesis, when using well-defined surface agents, a minimum of ΔG_s should be attributed to a specific surface coverage (number of ligands per surface area unit). If the colloids are in dynamic equilibrium with the solution phase, each ligand concentration can be attributed to a well-defined total coverage, which consequently controls the particle size.

In order to get experimental data to support this hypothesis, reactions were carried out with different colloidal systems. As shown by [43], it is possible to stabilize gold colloids by amino ligands formed in solution from $HAuCl_4$. The colloid-forming reaction was carried out by using different ligand concentrations. As shown in Fig. 5a, the equilibrium particle size is a function of the stabilizing ligand concentration, and the particle size decreases with increasing concentration of amine (NH_2-CH_2-CH_2NH-$CH_2CH_2/Si(OR)_3$) in the solution.

Similar results have been obtained with $AgNO_3$/amine complexes (Fig. 5b).

Figs. 5a–b show that there is no linear dependence on particle size, indicating something similar to the quadratic dependence of surface to volume. Both systems show plasmon vibration in the visible region, indicating that real metal colloids are formed and not metal ion ligand clusters. In this case, no plasmon frequencies should be observed. The experiments indicate that stable colloid/ligand systems can be obtained and that the particle size can be influenced or tailored by ligand to colloid concentration ratio. With the metal amino ligand systems no data about chemical stability have
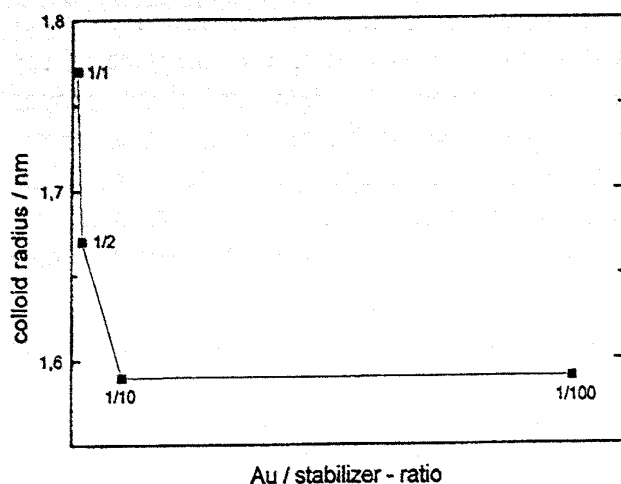
Fig. 5a. Dependence of Au colloid size on ligand concentration after UV irradiation (irradiation time close to saturation), after [43].
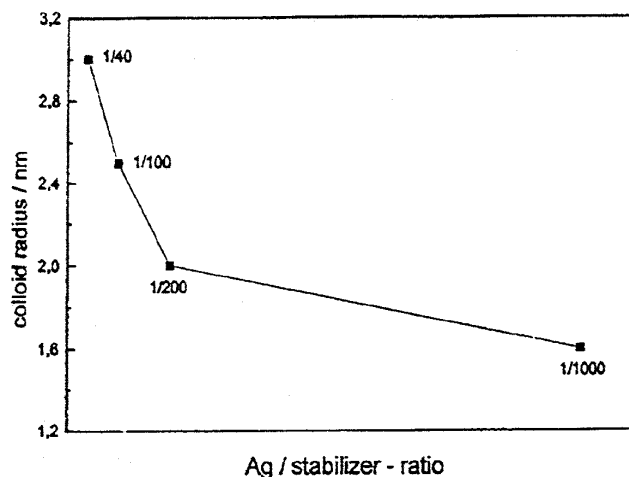

Fig. 5b. Dependence of Ag colloid size on ligand concentration, after [44].

been obtained so far.

Stability investigations have been carried out with other systems using organic small molecules as surface modifiers on nanometer-sized particles. Proper modification of particle surfaces is of importance if high solid contents processing with colloid particles should be obtained. It is well known that one of the problems of monolithic processing using sols is the fact that high solid contents without gelation are very difficult to obtain, and they are restricted to values of about 10–20 wt%.

For surface modification, boehmite with a particle size of 15–20 nm was used as a model system and reacted with different organic acids. Af-
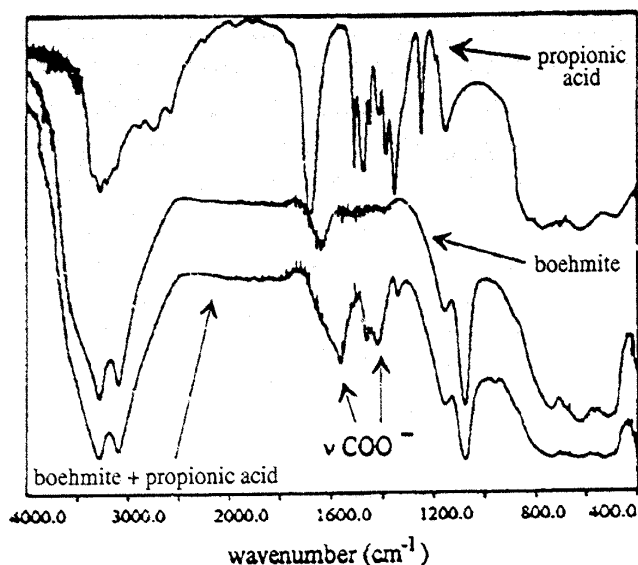

Fig. 6. DRIFT (Diffuse Reflection Infrared Fourier Transform) spectra of free and adsorbed organic acids.

ter washing and drying, infrared spectra (DRIFT spectroscopy) show that the organic residues could be detected, but no free acids can be seen. This means that a salt-like surface compound is present (Fig. 6).

From this modified boehmite, sols with slowly increasing viscosity by solid content, but without gelation up to volume contents of 45%, could be obtained (representing 70–80 wt%), which is quite surprising for solid sols. No agglomeration can be observed by photon correlation spectroscopy, and these sols can be used for ceramic processing like extrusion.

In the case of zirconia, the methacrylic groups have been used as modifying agents. They can be used to polymerize nanoscaled zirconia particles [45] and to incorporate these particles agglomerate-free into various matrices.

These few experiments show that the model of surface-tailored colloids can be generalized and used for the processing of nanoscaled particles for ceramics as well as for inorganic-organic composites. A variety of systems has been investigated up to now. In Fig. 7 a survey over several routes to surface-modified nanoscaled sols are shown. All these systems have been either incorporated into ormocer matrices by dispersing them into the prereacted viscous systems or generated within the reaction mixtures. Films as well as monoliths have been prepared.
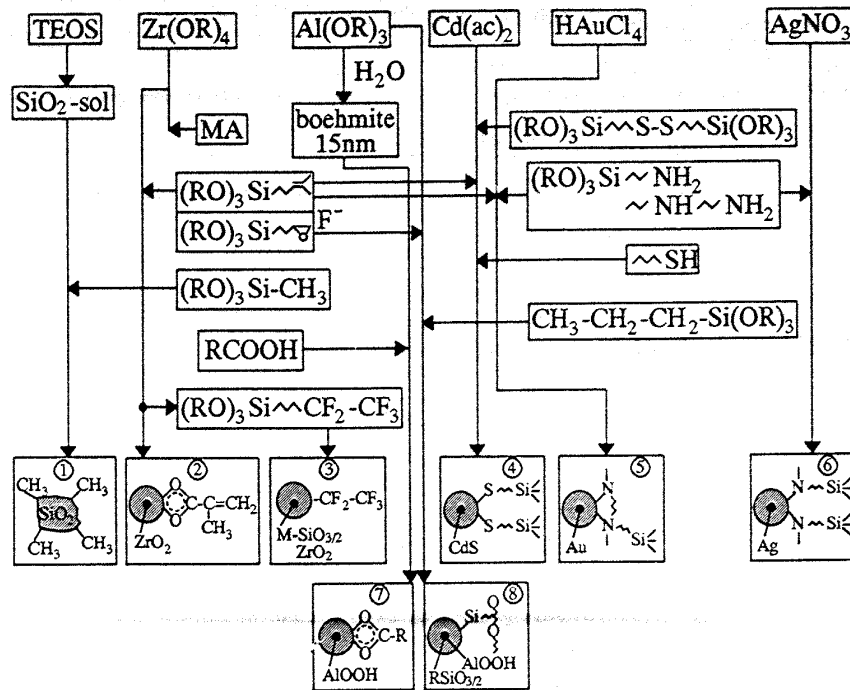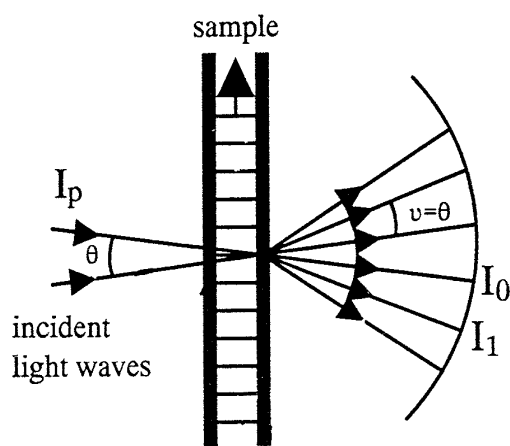
Fig. 7. (1) SiO_2 sol modified by CH_3 through reaction with $(RO)_3Si-CH_3$ [46]; (2) ZrO_2 modified by methacrylic acid [45]; (3) ZrO_2/MA, additionally modified by fluorosilanes [47]; (4) CdS silanes, stabilized by sulfides [48,49]; (5) Gold colloids stabilized by amines [43]; (6) Silver colloids stabilized by amines [44]; (7) Boehmite modified by propionic acid [50]; (8) γ-alumina modified by silanes [47].

$$\chi_{eff}^{(3)} = \frac{4\varepsilon_0 cn^2 \lambda \alpha \eta^{0.5}}{3\pi\, I_p\, (1-T)T^{0.5}}$$

Fig. 8. Schematics of the self-diffraction experiment.

5 Material Development by Nanoscaled Particle Systems

5.1 Metal and Semiconductor Quantum Dot-Containing Systems

Metal colloids or semiconductor colloids in matrices are of interest for various reasons, especially for their optical properties. If the particle size can be kept below 20 or 15 nm, Rayleigh scattering which depends on particle size by the power of 6 becomes negligible for most purposes. Gold colloids in glasses have been known for a long time in gold ruby glasses at $T \approx 500°C$. They are obtained by a phase separation process based on a nucleation and growth step from gold ion-containing glasses. Similar results are obtained from silver in glass. The objective of the present work was the development of methods for synthesizing gold-, silver-, and palladium-containing systems by low-temperature processes, and for this reason, the conception of producing the colloids in a separated reaction and incorporating them into an inorganic-organic matrix after stabilization is introduced. The basic experimental procedure is described elsewhere [43,41]. In the case of gold, the χ^3 values are measured by a self-diffraction experiment [43] in monoliths of several millimeters in thickness. The colloids have been embedded in an ormocer matrix. The χ^3 values (resonant case) of the composite (less than 1 vol.-% of gold) is $\approx 10^{-7}$ esu. In Fig. 8, the χ^3 values of the resulting composites are shown.
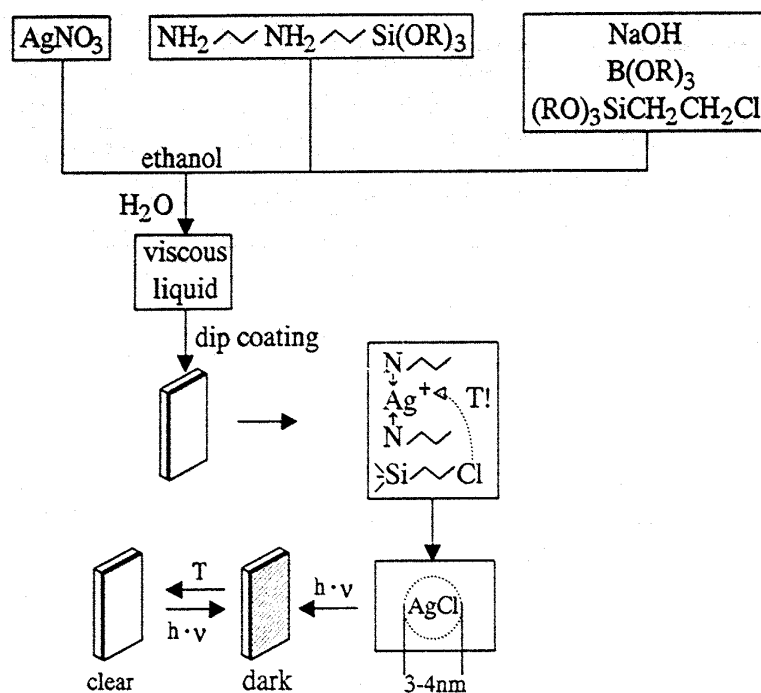
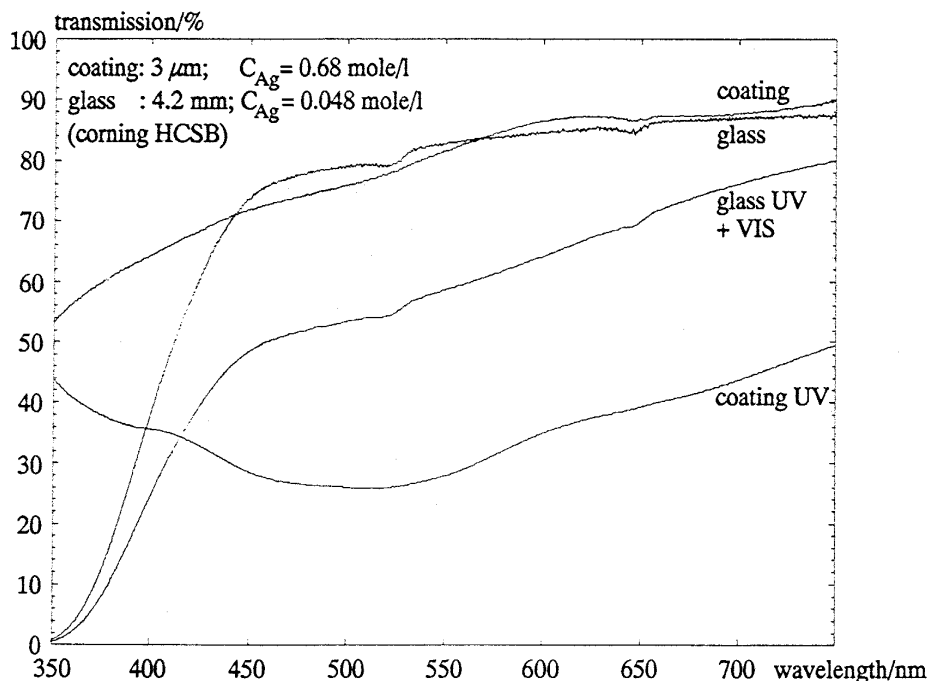*Fig. 9.* Draft of the preparation of photochromic ormocers, after [51].

Fig. 10. Darkening/bleaching of photochromic ormocers.

They are obtained by determining the diffractive efficiency in a self-diffracting process by a two-wave-mixing experiment.

In similar ways, silver colloids can be incorporated in inorganic-organic matrices. If chlorinated compounds are added, the silver colloids can be transformed into silver halides, and they

show photochromic behavior [46]. In Figs. 9 and 10, the schematics of preparation and the bleaching and coloring behavior of this type of silver halide, the inorganic-organic composite, are shown [51].

It is remarkable that even after 30 cycles no decay is observed. For bleaching, elevated tem-
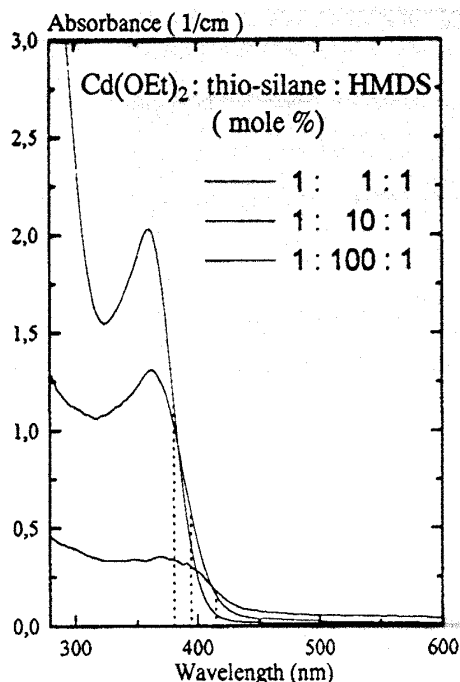
Fig. 11. UV/VIS spectra of thiosilane stabilized CdS colloids.

peratures have to be used at present, but these systems are not yet optimized with respect to synthesizers or bromide-to-chloride ratio.

With similar reactions, cadmium sulfides can be stabilized. If thiosilane ligands are used, for example [52], it could be shown that the excitonic band as well as the UV cut-off are functions of the ligand concentration, too (Fig. 11).

5.2 Passive Materials

This type of material is interesting for a variety of coating applications where high transparency and suitable mechanical properties are requested. In addition to this, for microsystems, micropatternability is important. In this connection, the tailoring of the refractive index is an important feature for waveguides, especially if similar systems can be used with different waveguides, such as buffer layers, waveguiding layers, and cladding layers.

For this reason, zirconia colloids surface-modified with methacrylic acid in combination with methacryloxy silanes as crosslinking agent with the ability of photopolymerization have been investigated.

As already mentioned, one of the most important questions had been whether this type of surface-modified systems is stable to hydrolysis or not. As shown in [45], it could be proven that even under moisture conditions, no traces of hydrolytic reaction at the zirconia particle surface can be detected by IR and NMR spectroscopy, indicating that the surface complexed form of the methacrylate is surprisingly stable.

By proper choice of reaction conditions, it is possible to keep the particle size of the zirconia in the range below five nanometers with negligible Rayleigh scattering. For this reason, the system seems to be suitable for planar waveguides. If films are not polymerized and photoinitiators are added, the systems can be used for photopatterning processes (embossing during polymerization, mask-aligner, laser writing, or holographic techniques). The reflective index can easily be varied between 1.52 and 1.57, and waveguiding systems can be produced without using special substrates. In Figs. 12 and 13, waveguides and gradings produced by various processes are shown. These systems also can be used as carriers for metal colloids or χ^2 dyes.

Another interesting feature is the potential of abrasion resistant surfaces using nanoscaled particles in combination with other functions. As shown in [47], in a three-component system using zirconia nanoscaled particles stabilized by methacrylic acid, silanes with polymerizable methacryloxy groupings and silanes with perfluorinated grouping films can be obtained with a thermodynamically controlled formation of composition gradient, showing good adhesion to glass and polymer surfaces, high scratch resistance, and extremely low surface-free energy, the dispersive part of which is even lower than that of polytetrafluoroethylene. In Fig. 14, a structural model of this coating is shown.

The system after coating in the wet state minimizes its interfacial free energies. The polar groups of the silanols are turned to the polar surfaces of the surfaces (glasses, ceramics, or activated polymer substrate), and the perfluorinated groups are turned to the outside surface. The gradients have been proven by ESCA measurements as shown elsewhere [47]. These systems can be used as highly transparent scratch resistant coatings to a variety of substrates if modified in composition. Heated up to 350°C,
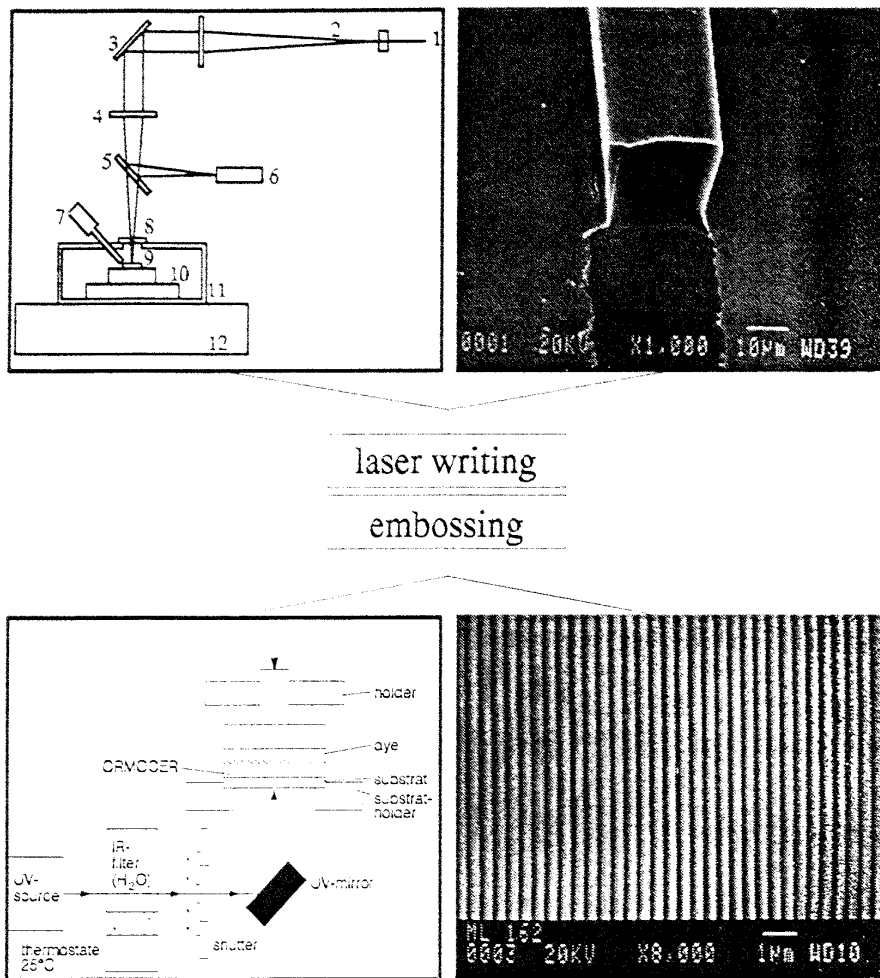
Fig. 12. Left side: Laser writing and embossing techniques. 1–4: laser optics; 5–7: observation optics; 8: window; 9: waveguide film; 10: x-y table; 11-12: vibration-free suspension; right side: developed waveguide and grating.

the low surface energy effect can be maintained, but now the system is more or less glass-like with an abrasion resistance similar to glass.

Interface tailoring is an interesting tool for tailoring coating properties. For example, for aluminum surfaces it could be shown that the interface to the metal surface can be stabilized against corrosion by use of a three-component system from epoxy group containing silanes, alumina alkoxides, and diols [43]. If F⁻ is used as catalyst, nanoscaled alumina particles are formed, increasing scratch resistance. These coatings show an excellent corrosion protection on untreated aluminum even under heavy-duty conditions, such as over concentrated HCl. Fig. 15 represents the draft of the synthesis of the coating material.

Fig 16 shows the corrosion behavior after salt-spray and HCl treatment from an unprotected and protected aluminum surface.

Only by use of the short chain organic crosslinking by diols has it been possible to obtain scratch resistance and corrosion inhibition, as well as sufficient flexibility (bending after coating does not affect the protection). It is assumed that the interface is formed by heterocondensation of silanoles with surface = AlOH. This interface is then stabilized by the ormocer matrix, and the corrosion process cannot proceed. This hypothesis is supported by the fact that no corrosion takes place along the interface on crossants made through the coating.

6 Conclusion

As already shown by various synthesis experiments, the sol-gel process is a very interesting
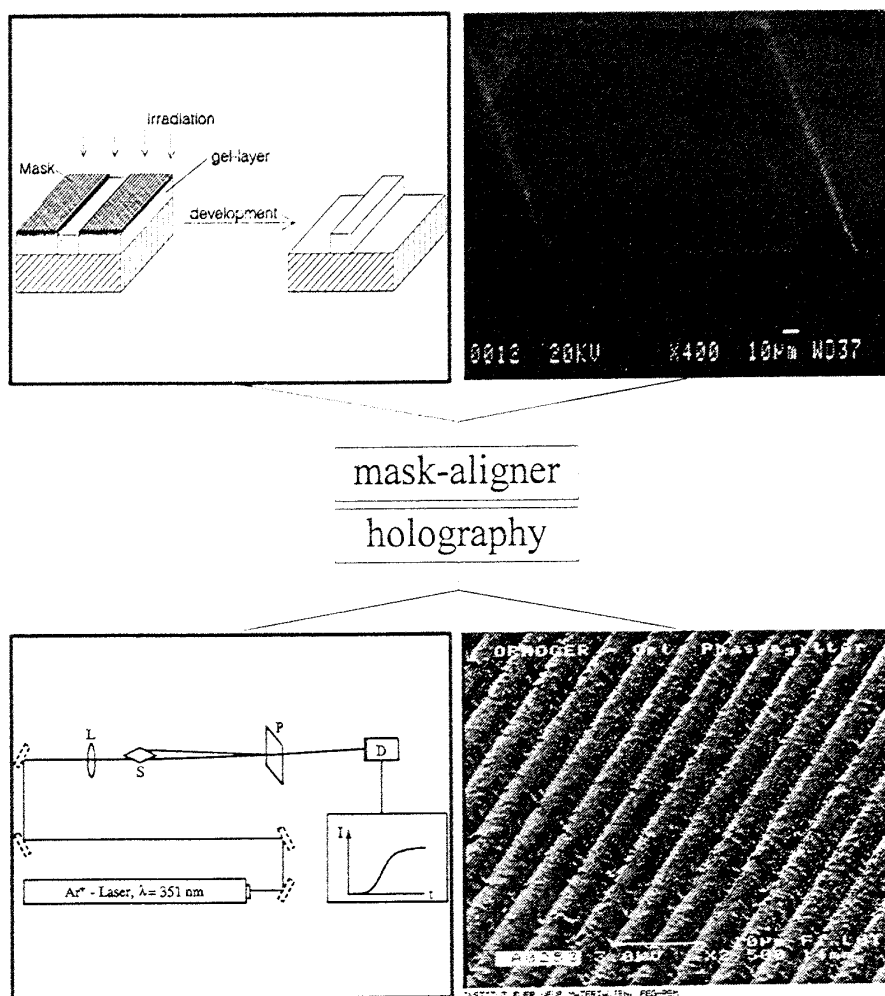
Fig. 13. Left side: mask-aligner and holographic techniques; I: collimator lens; S: beam splitter for two wave mixing; P: filter; D: detector; right side: developed channel waveguide and diffractive gratings.

synthesis route for the preparation of inorganic-organic composites. Two main types of composites can be distinguished, the more or less molecular type and the nanoscaled type. No clear line can be drawn between these types of composites, but if properties are to be attributed clearly to the inorganic phase, the nanocomposite seems to be the more suitable type of composite since it allows introduction of the solid state properties of the ceramic or metal phase. In addition to this, quantum size effects can be introduced into these composites, if the particle size can be kept in the lower nanometer range. Up to now, the hypothesis of a thermodynamically controlled model for particle size tailoring seems to be realistic since first results show that size and stability can be tailored by interfacial control. For these reasons, ligands with special interaction to the colloid surface

can be used. In addition to this, if these ligands are multifunctional, they can be used for further processing of nanoscaled particles in the desired way. Due to the fact that incorporated particles represent large interior interfacial areas, especially if higher volume fractions are used, the question arises how far the structure of the interface (which should be different from the rest of the matrix) can attribute to the overall material properties. It seems to be likely that in the case of nanoparticle volume fractions above 50%, the interfacial structure should determine the material properties, and a new type of material, a so-called interfacial area determined type of material, could be synthesized. These questions, however, have not yet been investigated. Summarizing, it is to say that the chemistry for synthesizing inorganic-organic nanocomposites is at its infancy.
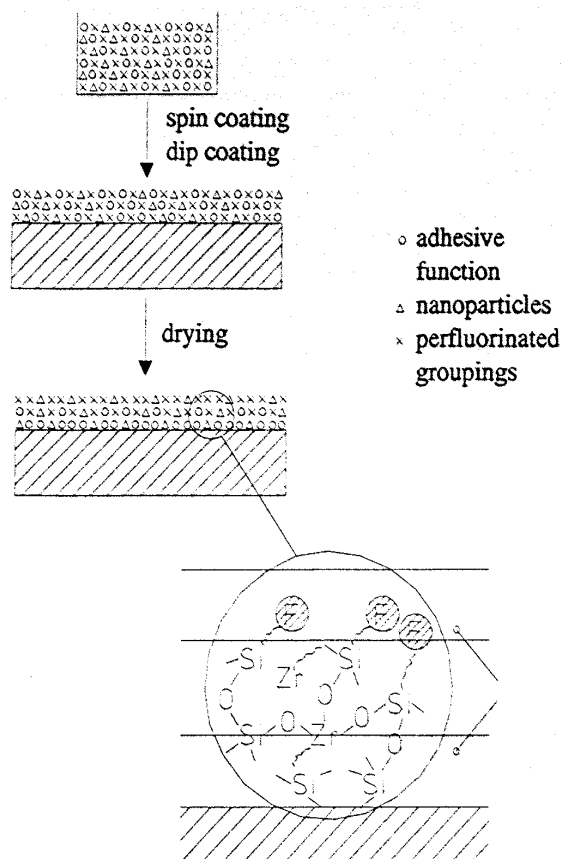
o adhesive
function

△ nanoparticles

× perfluorinated
groupings

Fig. 14. Schematics of the preparation of gradient coatings using nanocomposite sol-gel systems.

Fig. 15. Schematics of the preparation of Al corrosion protection systems.

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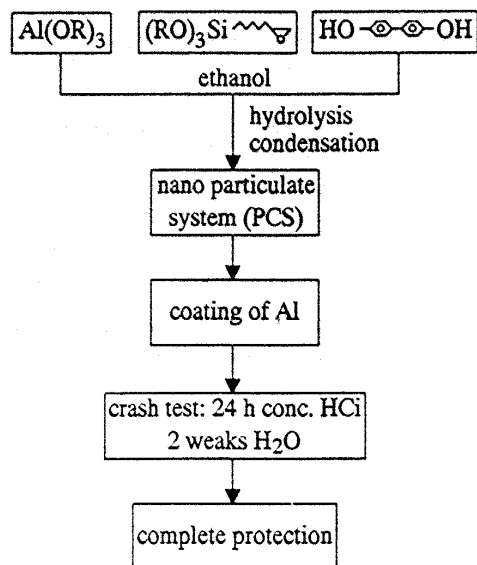12. P.N. Prasad, in *Ultrastructure Processing of Advanced Materials*, edited by D.R. Uhlmann and D.R. Ulrich (John Wiley & Sons, New York, 1992), p. 461.
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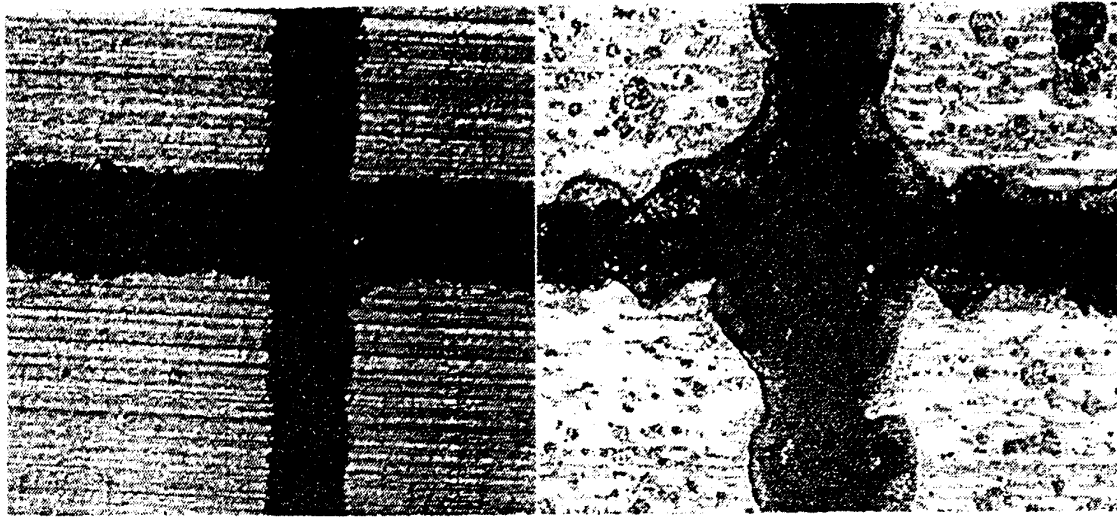27. T. Burkhart, PhD Thesis, Saarbrücken, October 1993.

Fig. 16. Comparison of a cross cut of an ormocer-coated and of a conventionally coated Al plate (1 hr. conc. HCl, 2 weeks saturated water vapor atmosphere at 40°C). Left side: ormocer coating; right side: conventional coating.

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