Thin Films, the Chemical Processing up to Gelation

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The sol–gel process is an interesting method of synthesizing coating materials and applying them in the form of thin films. The techniques are similar to those of conventional coating techniques such as dip, spin or spray coatings. These techniques allow one to prepare coatings with smooth surfaces or planarization effects. Based on the chemistry of the synthesis, a large variety of materials can be obtained: glasses, ceramic materials and composites. One of the most interesting features is the possibility of synthesizing multicomponent compositions or composites. For multicomponent materials, the stoichiometry can be controlled very exactly and composites can include glass–ceramic, ceramic–ceramic and ceramic–organic compositions. Especially, the composites open a field of coatings which is difficult to achieve by other than sol–gel techniques. The exploitation of the potential will be an interesting future task.

1 Introduction

The sol–gel process has gained importance in science as well as in industry during the last twenty years. The process describes, in general, the formation of solid materials, mainly inorganic non-metallic materials from solutions. This can be a solution of monomeric, oligomeric, polymeric or colloidal precursors. In nature, for example, minerals like agate or chalcedony have been formed by a polycondensation reaction from aqueous siliceous solutions [1]. Similar reactions are commercially used for the preparation of silica from aqueous solutions of alkali silicates [2]. In these reactions, the "solid" forming step is the condensation reaction of $\equiv$SiOH groups, which forms $\equiv$Si–O–Si$\equiv$ bonds by elimination of H_2O, Eq. (1).

$$\equiv Si\text{--}OH + HO\text{--}Si\equiv \rightarrow \equiv Si\text{--}O\text{--}Si\equiv + H_2O \tag{1}$$

By this reaction an inorganic backbone is built up, leading to a solid material, the so-called gel. The gel state is a not very well defined state but it is widely accepted to consider a gel as a material which, at least, is diphasic (where pores can be considered as one phase). Due to the ability of Si to crosslink three-dimensionally, an almost infinite number of structures becomes possible.

Condensation reactions are very common in organic as well as inorganic chemistry, and the progress of chemistry made new precursors available for many synthetic products, e.g. ceramic precursors like alkoxides. Although they have been known since the second half of the last century [3], they were considered as significant for material synthesis at this time. Other condensation step containing reactions, e.g. the precipitation of hydroxides are widely used in industry for the synthesis of oxidic powders but are not considered as a sol–gel process. The breakthrough of sol–gel technologies occurred from 1970 to 1980 and was based on the pilot work of Geffcken [4], Roy [5] and Dislich [6]. Widespread interest developed in the material science community. The idea of synthesizing real glasses far below melting temperatures and especially the formation of thin films by this method encouraged a great number of material scientists to investigate this route. A similar development took place in the ceramic community and the idea of lowering the sintering temperature or the increase of the sinter activity of new ceramic powders was an important driving force.

However, the limits of the sol–gel processing soon became very clear: The chemistry behind the reactions turned out to be much more complicated than expected and material tailoring and reproducibility of properties required a very thorough knowledge of the parameters influencing reaction mechanisms, structure and properties. Moreover, the processing of monoliths turned out to be extremely difficult due to the unavoidable gel step, characterized by a low density as a result of pores. The pores are formed by a three-dimensional crosslinking of oligomeric units (colloidal particles or macromolecules) leading to a rigid network, the gel. Due to the relative weakness of the gel and the

building up of high stresses as a result of the rigidness, the gel tends to crack due to an anisotropic shrinkage during drying and heating [7]. Thus, the idea of monolithic component processing was abandoned with a few exceptions. For example, as shown by Hench et al. [8] or Yamane [9], the preparation of high quality silica or GRIN materials requires special methods such as drying aids.

The sol–gel process includes several steps as the following schematics indicates:

starting material		sol		gel		final material
A	→	B	→	C	→	D
molecular		colloidal		solid (porous)		solid (dense)

Since the B phase can be stabilized in most cases, it can also be used as starting material. As already mentioned B → C and C → D are critical for technical application, if large three-dimensional parts are considered. This leads to the conclusion, that the fabrication of products with one or two very small dimensions should be the preferable way for sol–gel processes. The step A → B is important as a formation step for intermediates. If viscosity can be controlled, shaping techniques such as fiber, film or foil formation become possible [10]. Therefore, the investigation of sol–gel techniques for the formation of thin films has gained much interest, especially since with the work of Dislich [6] the industrial application of sol–gel films has become popular.

In order to illustrate the important features of sol–gel technology for film formation, one has to realize the specific features of the different processing steps, which include a large variety of parameters.

2 The Basis of Sol–Gel Chemistry

As shown in Ref. [11], the majority of the elements of the periodic table have already been introduced into sol–gel processes. The question whether an element is suitable for sol–gel processes or not cannot be answered very simply. However, there are some rules which can be drawn from the basics of the process. In order to form an inorganic network from a solution (pure or colloidal solution) a network-forming step is required. This step mainly depends on the structure of the sol and can roughly be divided into two alternative mechanisms. The first is a mechanism which is based on the growth of molecules, leading to macromolecules which then grow together to an infinite network. This mechanism leads to the so-called polymerized gels and is very common in the acid-catalysed hydrolysis and condensation of tetraalkyl silicates [2, 12]. The other type is based on the aggregation of colloidal particles from

a so-called colloidal sol and requires a fairly stable sol as intermediate. Otherwise the whole procedure would end up in a precipitation process with no sol phase to be identified. The network-forming step in these sols is the aggregation of particles to an infinite network. In the case of acid-catalyzed silica from alkoxides the polymerization process can be simply controlled by the limitation of water which leads to stable sols if enough unhydrolysed ≡SiOR groups can be maintained to keep the average molecular weight small.

The influence of protons and water on the structure of SiO_2 sols has been intensively studied by Sakka [10, 13] who showed by rheological analysis, that various structures of viscous sols can be obtained just by varying H^+ and H_2O concentration in the starting solution.

The stabilization of the colloidal sol includes the control of surface chemistry and can be successfully performed by charging the surface electrically (control of the ξ potential) or by the adsorption of neutral molecules acting as steric barriers [14]. The stabilization of sols is of high importance in sol–gel processing because it defines very strongly their processing properties which are of special importance for film formation. These are, for instance, the rheology, the maximum solid content and the particle size and distribution. Rheology is a complex parameter and depends on particle shape, temperature, solvent, concentration and particle interaction. The reduced viscosity η/c of non-interacting particles does not depend on concentration [15, 16] (Eq. 2).

$$\frac{\eta}{c} = \frac{k}{\rho} \tag{2}$$

k represents a constant and ρ the density of the particles. For an organic polymer solution, the intrinsic viscosity η_i is related to the average molecular weight M by Eq. (3),

$$\eta_i = k \cdot M^\alpha \tag{3}$$

where k is a constant depending on temperature, solvent and the chemistry of the polymer and α represents a parameter depending mainly on the polymer structure [16, 17]. Thus, a rough distinction can be made between "basic macromolecular forms", for example, $\alpha = 0$ for rigid spherical particles; $\alpha = 0.5$ – 1.0 for flexible chainlike molecules, and for rigid, rod-like molecules α becomes 1.0–2.0. The determination of α allows one to tailor processing properties, if the mechanisms of particle shaping can be controlled. An interesting example was given by Sakka [13, 18, 19] who was able to demonstrate that in the hydrolysis and condensation process of tetraethylorthosilicate, α can be selected for optimal fiber spinning. The process has been industrialized by Asahi Glass Co. for the production of high quality SiO_2 fibers [20]. In this case hydrolysis under acid conditions leads to chainlike flexible polymers suitable for fiber drawing.

In contrast to this, according to Stöber [21], at high pH values, particulate sols are obtained. These sols are not useful for fiber drawing or spinning. The basic ability of film formation, however, does not depend so strongly on the sol

structure parameters, but the film properties can be affected strongly again, as pointed out by Frye and Brinker [22, 23]. They compared acid- and base-catalyzed SiO_2 films after dip coating by N_2 adsorption. Whereas from acid-catalyzed sols pretty dense structures were observed (Type II isotherms, refractive index $n_D \approx 1.43$), in the base catalyzed systems, particulate sols (≈ 20 nm SiO_2 particle diameter) were obtained leading to porous film structures (type IV isotherms, 45% porosity, $n_D \approx 1.24$) (Fig. 1). This demonstrates clearly the influence of the sol structure on the coating properties.

The SiO_2 system has received the highest scientific interest up to now. This may be due to the fact that SiO_2 precursors in the form of alkylortho silicates have been readily available for almost 150 years, and, compared to almost all other common alkoxides they are relatively insensitive to moisture which means in this case, that the hydrolysis and condensation to gels take place pretty slowly (depending on concentration, type of alkoxides, and solvent, between hours and weeks). Therefore, it is possible to study the reaction kinetics and structure forming mechanisms of sols by condensation in details relatively conveniently compared to other systems. In the recently published book by Brinker and Scherer [24], the reaction of tetraethyl orthosilicates as interesting precursors in sol–gel reactions are intensively discussed.

The sol structure also influences the maximum film thickness. As shown in [25], for given systems, the "cracking thickness" of coatings is defined by the system parameters only. It is shown that films can be transformed to dense layers by temperature treatment only if the thickness of them does not exceed certain limits defined by the intrinsic system parameters. In general, the film thicknesses to be obtained in a one-step coating process (spin or dip coating) does not exceed some tenths of a μm. If the viscosity of a system is adjusted to obtain thicker films, cracks occur during drying.

In the work of Dislich [6], who developed an industrial coating technology for plate glass, the question of film thickness does not play an important role since he was able to prove that the dip-coating process employed leads to dense chemically very stable thin films of SiO_2, TiO_2 or combinations. Therefore, two requirements had to be fulfilled: the films had to be very perfect (pinhole-free) and they had to be very dense. Since these films on plate glass as substrate have never been fired to temperatures around Tg, the densification process has to be different from the "normal" viscous flow sintering of glasses.
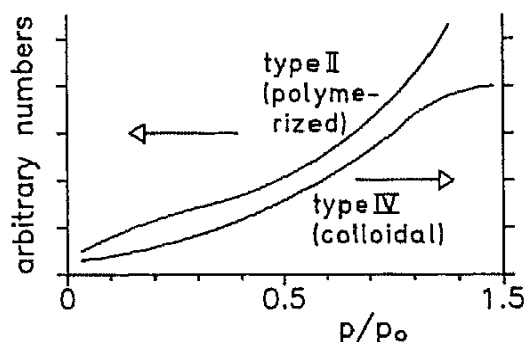

Fig. 1. Influence of the structure of two different sols on the N_2 adsorption of dry films (data after 22 and 23)

The observation of Brinker et al. that weakly branched SiO_2 polymers from hydrolysis of TEOS or highly branched borosilicate polymers lead to very dense films after dip coating by simply drying them [less than 5% porosity, type II isotherms] is explained by a special particle packing process taking place at the drainage and drying front of a dip coating process (Fig. 2).

The maximum obtainable thickness of the films does not seem to depend strongly on the sol structure. Films up to 0.2 and 0.3 μm can be obtained from most sols. With increasing thickness, the "bulk" behavior gains more and more importance, as shown in the model according to Fig. 3.
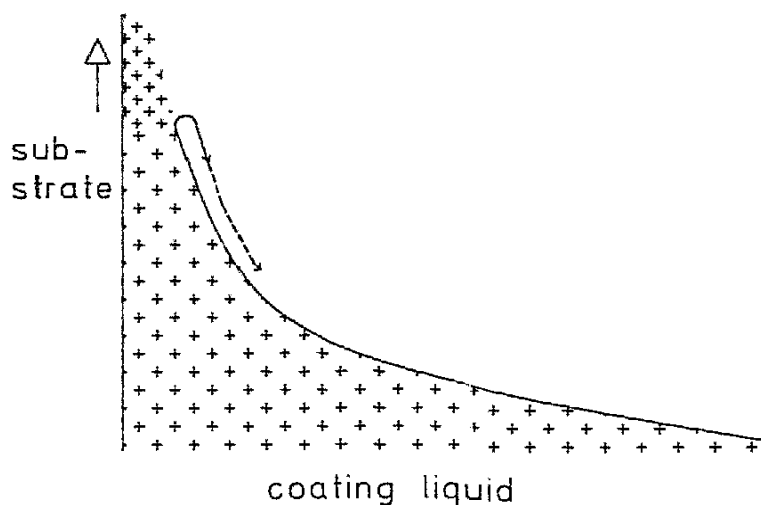
Fig. 2. Model of the densification process during the dip coating step from a sol
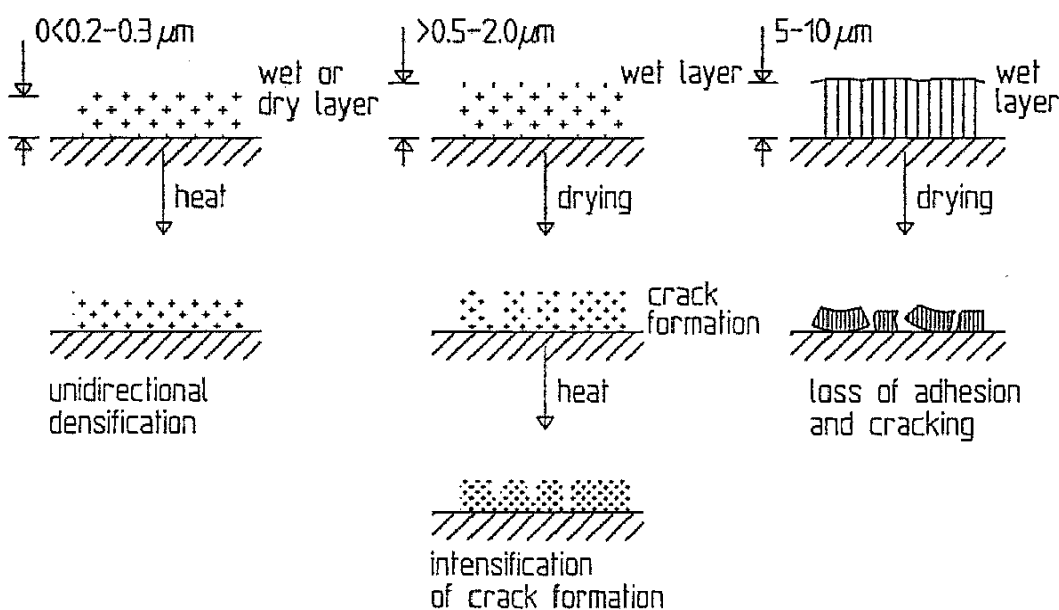
Fig. 3. Model of the effect of thickness on the drying/densification behavior of sol–gel coatings

There exist some qualitative rules, which can act as guidelines to influence film thickness:

● If the interaction of the sol particles is high, the densification process will be stopped at a very porous gel structure with a low-density brittle system leading to crack formation during drying and sintering.

● Densely packing particles and easily relaxing networks can help to obtain dense films even at increased thicknesses.

Unfortunately, there have been no systematic investigations on the influence of solvents other than alcohols and other systems than SiO_2 on film thickness depending on processing parameters. The most important progress in understanding the film formation from sols is shown in [24] and it is amazing, that these investigations were carried out about 20 years later than the first successful industrial application of sol–gel coatings had been performed by Schott Glaswerke, Mainz. The findings of Dislich and coworkers that they could succeed in coating large dimensioned plate glass and densify the films at T ≪ Tg had found a late explanation.

3 Chemistry as a Tool For Sol Tailoring

As mentioned in Sect. 2, it is highly important to control particle size and properties of sols in order to obtain optimum coatings. In the case of SiO_2, the reaction control is rather easy since the reactivity of SiO_2 precursors can be adjusted by the pH and the H_2O addition over a wide range. These methods cannot be employed in highly reactive systems such as Ti, Zr, Al alkoxides or glass forming systems containing alkaline and earth alkaline components since the addition of water leads to insoluble precipitates in the majority of cases and no homogeneous sols suitable for coating processes are obtained. In these cases, it is necessary to control the reaction by other means, e.g. by complex formation, as demonstrated by Livage et al. in the system TiO_2/acetic acid [26]. In this case, the hydrolysis is not completed with acetic acid present due to the formation of an intermediate complex (Fig. 4). The first reaction step is the substitution of an OR group by an acetic acid molecule. By water addition, a complex where two OR groups are substituted by OH groups is obtained, which is stable against further hydrolysis and which does not form insoluble precipitates. As shown by LaCourse, the viscosity of TiO_2 sols can be controlled by
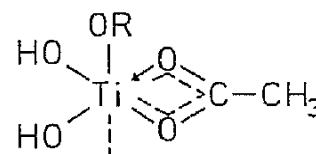

Fig. 4. Acetic acid complex with titania

complexing Ti(O'prop)$_4$ by addition of β-diketones, e.g. bis acetyl acetonate [27, 28].

This type of precursor is suitable for fiber drawing but no data on the film-formation properties of these sols are available. But there seems to be a good chance of adjusting the viscosity for optimum film forming conditions.

In the case of alumina, investigations into the film forming properties of β-diketone-modified sols have been carried out by Naß et al. [29, 30]. In these investigations, two types of Al containing sols (with and without a complex former) have been compared with respect to their film forming properties. It could be shown that Al propoxides complexed with acetyl acetonate (acac) or acetoacetates form clear sols with nanosized particles (2–5 μm depending on the complex former concentration). The solid content of these sols can be increased up to 25 wt % without gelation (≈ 5 wt % in the uncomplexed case).

The film formation ability of the complexed sol is substantially better than that of the non-complexed one. In Fig. 5a and 5b two SEM micrographs with
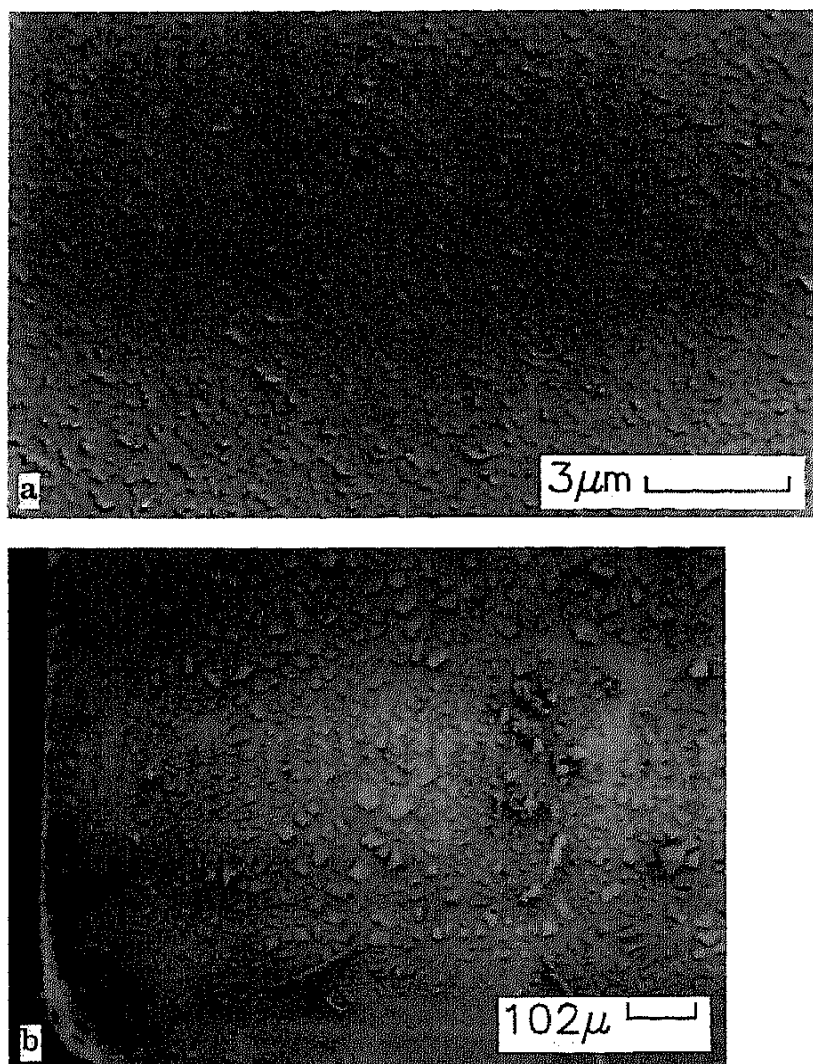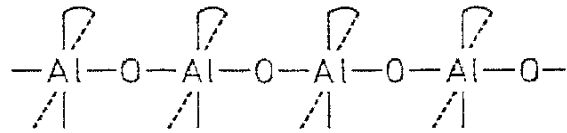

Fig. 5a, b. SEM micrograph of a film obtained from a non-complexed sol with intensive crack formation. SEM micrograph of a film obtained from a complex sol. Coating thickness 1 μm

Fig. 6. Structural model of complexed Al sols obtained by NMR data according to [29]

$$-\overset{\displaystyle \square}{\underset{/|}{Al}}-O-\overset{\displaystyle \square}{\underset{/|}{Al}}-O-\overset{\displaystyle \square}{\underset{/|}{Al}}-O-\overset{\displaystyle \square}{\underset{/|}{Al}}-O-$$

films of the two sols are shown. NMR and IR analysis show that chainlike molecules are obtained (Fig. 6). The coatings obtained from complexed precursors can be densified at 600 °C to clear transparent layers. These sols can be used for fiber-drawing processes, too. Bulk gels are amorphous up to 800 °C and then turn directly into α-Al_2O_3 [31].

The problem of the homogeneity of multicomponent systems in sol–gel processing becomes obvious if one considers the large hydrolysis and condensation rate differences and solubilities of the various precursors. We can distinguish between several types of basic properties important for sol–gel processing:

● slow reacting components like ethylortho silicates
● fast reacting components like $Ti(OR)_4$, $Zr(OR)_4$, $Al(OR)_3$, $P(OR)_{3/5}$, halides, alkaline or earth alkaline alkoxides (alcoholates), $B(OR)_3$
● soluble species (especially in alcohols) like $B(OH)_3$, alkaline and earth alkaline hydroxides, P_2O_5.

In order to obtain homogenous sols and gels one has to obey some rules: It is necessary to introduce at least one good gel former into the system in order to obtain homogenous sols and gels [32]. The additional components can be either linked to the gel network or gel particles or entrapped in pores (Fig. 7).

In the case of the PZT gel, for example, it depends strongly on the processing conditions whether the homogeneity can be maintained during the drying and heating step.

If the network formers are very different in hydrolysis or condensation rates one has to take care that no phase separation occurs as a consequence of these reaction rate differences. To overcome these difficulties in the case of $Ti(OR)_4/Si(OR)_4$ mixtures, Yoldas suggested that prehydrolyzed $Si(OR)_4$ with
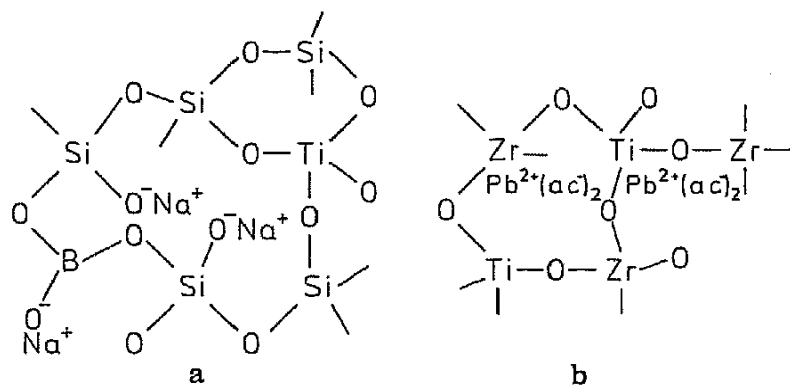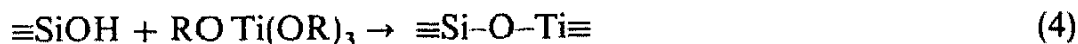

Fig. 7. Sodium ions linked to a glass network by ionic bonds (a) and lead acetate entrapped within a PZT gel (b)

high $\equiv$SiOH concentrations should lead to the formation of $\equiv$Si–O–Ti$\equiv$ bonds by (Eq. (4)) [33]

$$\equiv SiOH + RO\,Ti(OR)_3 \rightarrow\ \equiv Si\text{–}O\text{–}Ti\equiv \tag{4}$$

Closer investigations of this hypothesis by Basil and Lin [34–36] showed that the number of $\equiv$SiOH groups is drastically reduced by the addition of Ti(OR)$_4$ to a prehydrolysed Si(OR)$_4$ but no $\equiv$Si–O–Ti$\equiv$ bonds could be detected by NMR. The authors conclude that Ti(OR)$_4$ acts as a condensation catalyst leading to an increase of the condensation rate including ring structures but with no incorporation of the Ti(OR)$_4$ into the silica network taking place. The authors, however, did not test their hypothesis by adding water to the system but by just looking to see whether the precipitation behavior of the Ti(OR)$_4$ had changed or not.

This test was made by Schmidt et al. [37] with another, more complicated system in connection with the development of a sol–gel coating system for plastic eye glasses. It was found out, that TiO$_2$ in combination with SiO$_2$ and an organically modified silicic acid ester leads to very hard coatings being densified at surprisingly low temperatures (90–110 °C) suitable to be employed on plastics. This system was prepared from Si(OMe)$_4$ (I), Ti(OEt)$_4$ (II) and (MeO)$_3$Si(CH$_2$)$_3$–O–CH$_2$–CH–CH$_2$–O (III) as precursor. The epoxide polymerizes partially to polyethylene oxide chains. The hydrolysis reaction rate at neutral pH decreases in the order $k_I < k_{III} \ll k_{II}$. Direct addition of water to the precursor mixture (I : II : III = 5 : 25 : 70, molar ratio) leads to the precipitation of
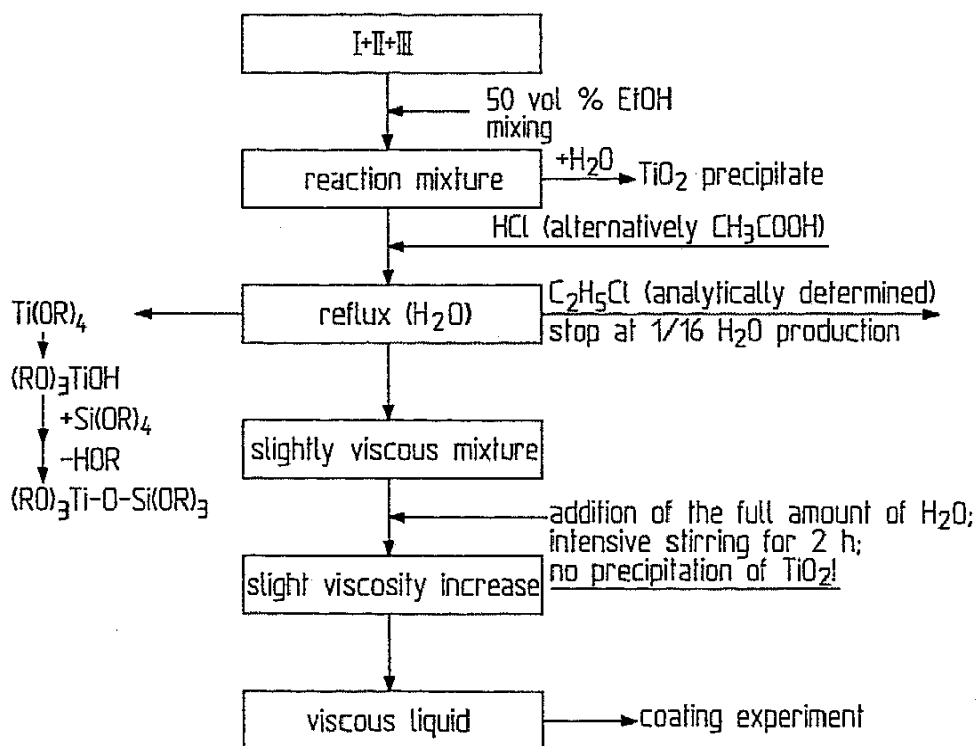

Fig. 8. Schematics of the process of preparing Ti containing hard coatings

TiO_2. H_2O, however, can be generated homogeneously within the reaction mixture (ethanolic solution), e.g. by adding HCl and refluxing the system (Eq. 5).

$$C_2H_5OH + HCl \rightarrow C_2H_5Cl + H_2O \tag{5}$$

In the system I + II + III, it is sufficient to generate about 1/16 of the amount of water necessary to hydrolyze the OR-groups of the system completely to prevent any precipitate after adding the full amount of H_2O. In the precondensation step, $Ti(OR)_4$ was linked to the silicate precursors, thus being prevented from precipitating.

Figure 8 shows the process schematically for easier understanding. The findings can only be interpreted by the formation of a $\equiv$Si–O–Ti$\equiv$ bond. In this case, the reaction runs the opposite way to that in Yoldas' experiment. Due to the higher reactivity, $(RO)_3TiOH$ is formed. Of course, the statistic consideration leads to the fact that an already hydrolysed $(RO)_3TiOH$ will be hydrolysed a second time at the expense of an unhydrolysed one, but the probability is low compared to the probability of the consumption of the $\equiv$TiOH groups by ROSi$\equiv$. The resulting prepolymers can be used for coating experiments as shown later.

The establishment of a suitable viscosity is an important means for coating experiments. It is important to know whether it is possible to predict film thicknesses by physical data of the coating solution. As shown in [38] and [39] independently, the relationship derived by Landau and Levich [40] (Eq. 6), which describes the coating thickness h as a function of various parameters, fits fairly well for sol–gel derived coatings (Figs. 9a and 9b).

$$h = 0.94(\eta \cdot U/\gamma)^{1/6} \, (\eta \cdot U/\rho \cdot g)^{1/2} \tag{6}$$

(γ = surface tension, η = dynamic viscosity, ρ = density, g = gravity constant, U = withdrawal speed)

Both findings represent slow withdrawal rates (up to some cm/min) where the dependence of the viscosity on shear rates can be neglected.

A general schema for the different steps includes precursor chemistry, reaction to coating liquids (e.g. by viscosity and molecular weight control), the coating step, post treatment of the coating (e.g. curing, densification, patterning) is given in the following.

The schema of course, can only represent a selection of important or interesting techniques. In special cases, others are used. But it shows the large variety of possibilities.

4   Precursor Chemistry

There is no general difference in the precursor chemistry between the preparation of intermediates for coatings or for gels. The problem with precursor

chemistry is its complexity once the first hydrolyzed species are formed which are able to react along a large variety of reaction paths.

Alkoxides are used as precursors in most cases. The well-established field of alkoxide chemistry considered hydrolysis as an undesired side reaction for a long time [41, 42]. It is only recently that Mehrotra emphasized the significance of alkoxide chemistry for sol-gel processing [43-44]. The effect of the structure of alkoxide solutions on hydrolysis and condensation reaction is not very well investigated in most cases, but there are some examples that clearly demonstrate processing advantages if the chemistry is controlled. Hirano [45] showed that LiNbO₃ films could be prepared much more homogeneously and crystallized at lower temperatures if the alkoxide precursors were reacted to a double alkoxide
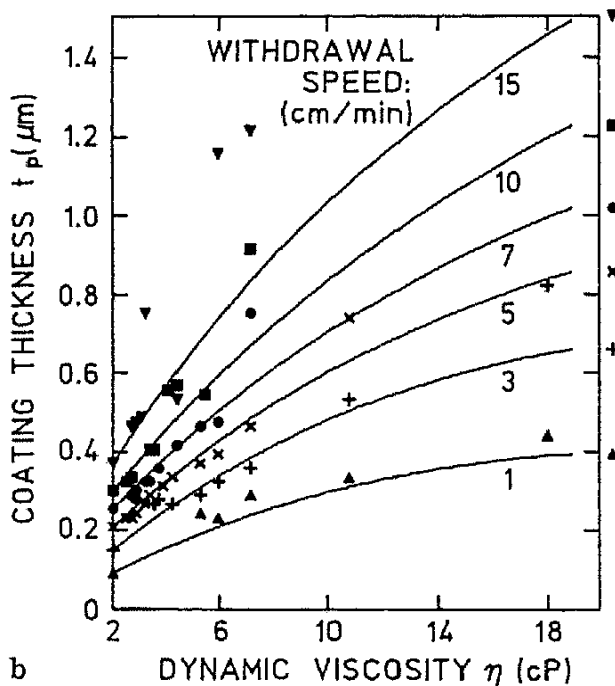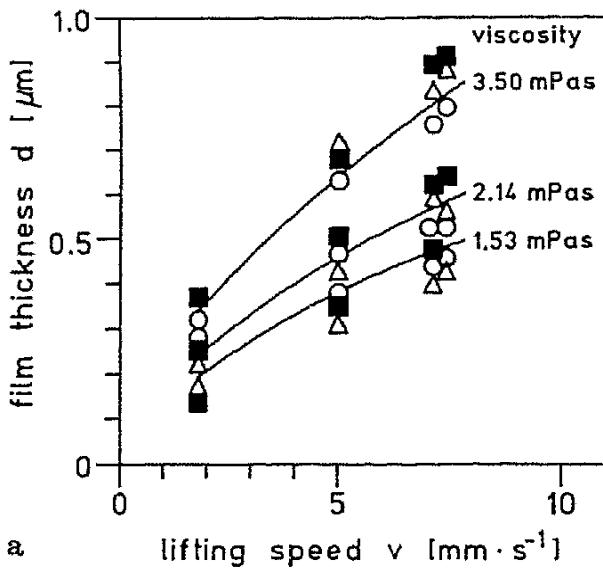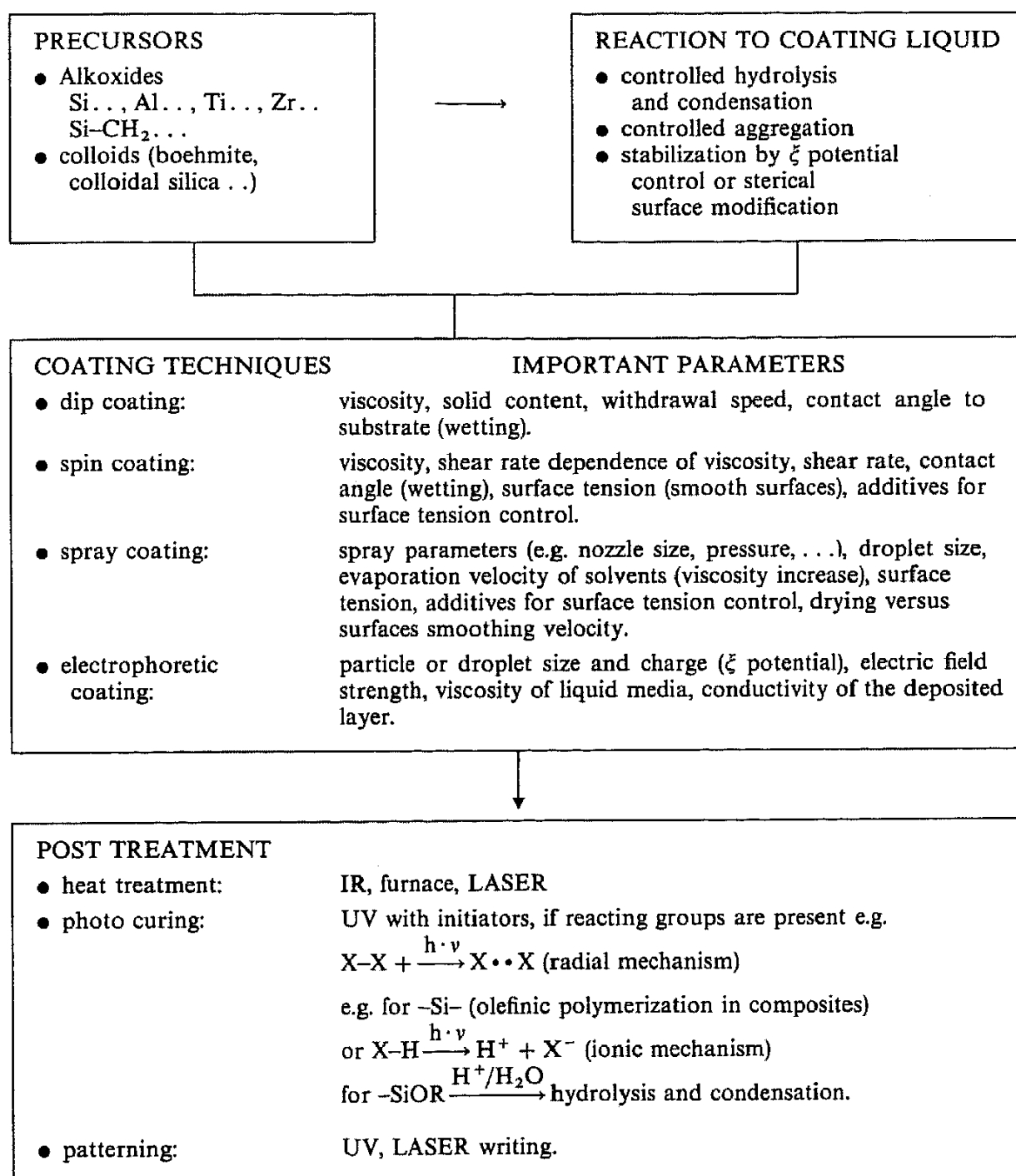

Fig. 9a, b. Dependence of dynamic viscosity η on coating thickness of acid catalyzed solutions of TEOS according to [37]. Dependence of coating thickness on withdrawal speed at various viscosities of a solution representing a sodium borosilicate glass system according to [39]

complex before hydrolysis. Results indicating the important role of double alkoxides were reported by Pouxviel [46] by NMR analysis of the $Si(OR)_4/Al(OR)_3$ two component system. The problem of all these investigations seems to be the fact, that structural analysis, especially on the short range level can only be carried out in homogeneous media and only give clear results up to complexes or aggregates of only a few monomeric units. There is a gap between the "oligomeric" or even macromolecular state on the one side and the gelified (infinite molecular size) state on the other side which is very difficult to characterize by structural analysis. More recently, efforts have been made to

PRECURSORS	REACTION TO COATING LIQUID

• Alkoxides
   Si.., Al.., Ti.., Zr..
   Si–CH₂...
• colloids (boehmite,
   colloidal silica . .)
	• controlled hydrolysis
	   and condensation
	• controlled aggregation
	• stabilization by ξ potential
	   control or sterical
	   surface modification

COATING TECHNIQUES	IMPORTANT PARAMETERS
• dip coating:	viscosity, solid content, withdrawal speed, contact angle to substrate (wetting).
• spin coating:	viscosity, shear rate dependence of viscosity, shear rate, contact angle (wetting), surface tension (smooth surfaces), additives for surface tension control.
• spray coating:	spray parameters (e.g. nozzle size, pressure, . . .), droplet size, evaporation velocity of solvents (viscosity increase), surface tension, additives for surface tension control, drying versus surfaces smoothing velocity.
• electrophoretic coating:	particle or droplet size and charge (ξ potential), electric field strength, viscosity of liquid media, conductivity of the deposited layer.

POST TREATMENT

• heat treatment:	IR, furnace, LASER
• photo curing:	UV with initiators, if reacting groups are present e.g.

$$X\text{--}X + \xrightarrow{h\cdot v} X\bullet\bullet X \text{ (radial mechanism)}$$

e.g. for –Si– (olefinic polymerization in composites)

$$\text{or } X\text{--}H \xrightarrow{h\cdot v} H^+ + X^- \text{ (ionic mechanism)}$$

$$\text{for --SiOR} \xrightarrow{H^+/H_2O} \text{hydrolysis and condensation.}$$

• patterning:	UV, LASER writing.

"construct" complex oligomers with well-defined crystal structures acting as "molecular building block precursors". The significance of this concept was shown by Payne [47] on $BaTiO_3$ clusters prepared by understoichiometric addition of water to Ba and Ti alkoxides.

As a general rule, it seems to be suitable to tailor the oligomeric state very carefully for coating. This is valid, too, for fiber drawing, as shown in [19] for SiO_2. Similar behavior was found by LaCourse for "linearized" TiO_2 precursors [26]. Naß [48] found that Al-alkoxides complexed with β-diketones lead to precursors from which excellent coatings can be obtained compared to uncomplexed prehydrolyzed precursors. These few examples demonstrate the importance of sufficient knowledge of the precursor chemistry for sol tailoring. This is valid for precursors leading to inorganic compositions (glasses, ceramics) as well as for precursors containing chemically bonded organics.

There are various means of controlling precursor chemistry with respect to tailor sol structures. The majority of investigations concerns SiO_2 as a one-component system [49–50]. In this system, the pH dependence of the sol structure is obvious. At pH values from about 1 to 5 the macromolecular types of sols with more or less linear molecules are obtained whereas at higher pH values sols containing spherical particles are obtained. From the work of Thomas [51] it is known that the particulate type of sols can be obtained in the system Al_2O_3/SiO_2 which was advantageously used for preparing laser damage protective coatings with excellent optical properties. If the optical properties of the coatings are satisfactory they do not necessarily have to be fully densified if the requirements for chemical stability are not critical [51]. The sols used in this case are colloidal sols with nanometer-sized particles.

For sol property tailoring, precursor chemistry is the key issue. In contrast to its tremendous importance, the state of the art is rather low. It is possible, however, to formulate some general rules helpful for sol development.

4.1 Homogeneity

Homogeneity or controlled heterogeneity affects the properties of films in various ways. The "molecular" homogeneity of precursor solutions can be changed by different processes as shown in [52], e.g. different rates of hydrolysis and condensation, phase separation during ageing or transport phenomena in wet gels. Therefore, the control of reaction rates or avoiding the effect of different reaction rates becomes an important objective. Two different routes are of interest: First one can try to slow down the rate of faster reacting species by chemical modification of precursors, by increasing the chain length of alkoxides, e.g. $\equiv MeO(CH_2)_nCH_3$ with n increasing. In this case, the hydrolysis rate decreases with increasing n and the overall condensation rate decreases by keeping the concentration of condensable species low. The effectiveness of this method is very limited and can only effectively be applied to silicon alkoxides.

To overcome reaction rate differences of very different metal alkoxides as Si and Ti seems rather unlikely.

Another means is to block reactive sites by complex formation which can be used for adapting rates as well as for molecular design of sols. As shown by Yamane [53], the formation of $acac_2$-Ti-alkoxides leads to a sol without precipitation through water addition (Fig. 10). b is stable against hydrolysis but can be used for further synthesis with reactive alkoxides. In the case of SiO_2–TiO_2 systems [53] the most homogeneous glasses have been obtained with precursors with similar reaction rates. As shown in [29] in the case of ß-diketone complexed Al alkoxides there is no significant difference in the H_2O consumption rate to the uncomplexed alkoxide, but the complexed form leads to a clear solution with polymeric unit sizes in the range of 2–5 nm, indicating that by complexation the condensation process is slowed down drastically. Keeping particle sizes in the nano range in sols restricts the maximum heterogeneity dimension in multicomponent sols, even if complete phase separation of the different components occurs during the growth process. It depends on further processing whether this inhomogeneity dimension is disturbing or not. In case of consecutive high temperature processes e.g. for glass or ceramic phase formation nano-range inhomogeneities as a rule, are not serious. If the particle size can be controlled by chemical means, e.g. by desactivating the surface by reaction with organics as complex formation, polymeric coating or adsorption of the tenside type of molecules onto the surface, the independent preparation of sols with different composition and mixing after preparation seems to be a comfortable way for the preparation of multicomponent sols as shown in [54] for the preparation of semiconductor cluster containing glasses by the sol–gel process.

For the preparation of particle size controlled sols, which can be used for coatings, the control of surface chemistry of colloids by surface active additives is the most important point. In this case, the maximum heterogeneity is defined by the particle size distribution of the colloidal phase. Examples for sol processing by proper colloid chemistry are given by Messing [55] and Aksay [14]. Aksay processed 20 nm SiO_2 sols by surface treatments controlling the hydrodynamic radius (Fig. 11), thus being able to end up with densely packed (close to theoretical hexagonal or cubic packing) nano sols. These findings are
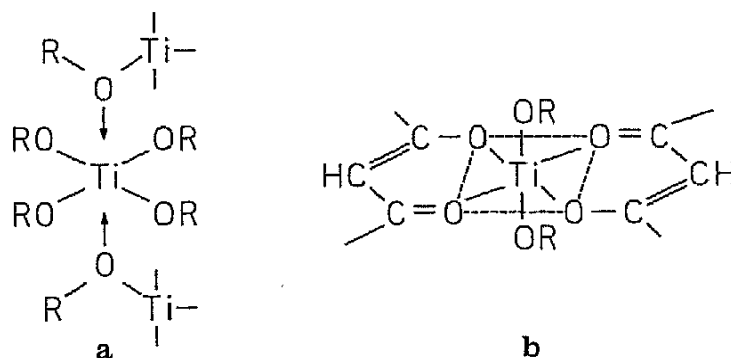

Fig. 10a, b.
Structures of Ti alkoxides

surface active
additive
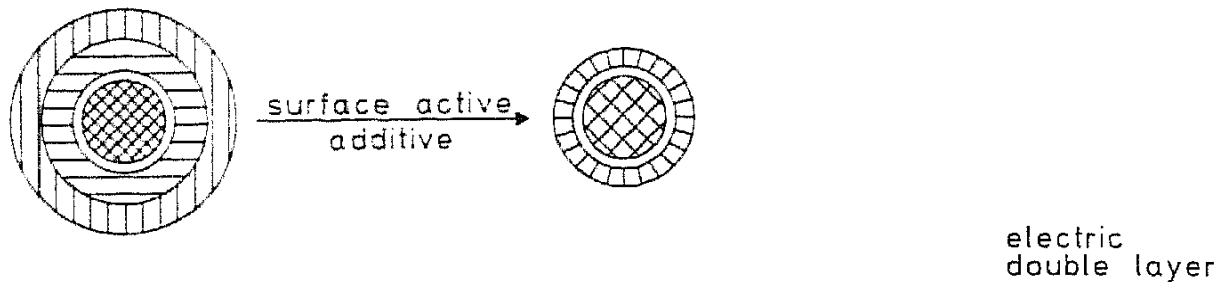
electric
double layer

Fig. 11. Reduction of the hydrodynamic radius by surface treatment

highly important, if the preparation of coatings is considered, but details regarding this step and sol structure to coating performance relationships have been published. Compared to conventional ceramic processing, the homogeneity gain using nanosized sols is up to three orders of magnitude. The benefits of colloidal sol processing for ceramic coating has been shown by a variety of authors [56–60] who could show a substantial reduction of sintering temperatures compared to conventional processing. The standard coating process for sols is the dip coating process. The main interest is focussed on the film

Material	Characterisation		next reaction step	properties to be affected
precursor	IR, UV//VIS, GC, GC/MS, phys. data (m.p.; b.p.), NMR	ÅÅÅ	I purification	purity level, all properties depending on purity
mixed precursor	IR, UV/VIS, NMR reaction kinetics	ÅÅ	II hydrolysis/ condensation	solution or sol structure, rheology, particle size, ξ-potential
colloidal macromolecular type sol	light scattering, SAXS, ξ-potential, viscosity (NMR), SAX, LAXS	Å	III gelation	gel structure, porosity, pore size distribution, homogeneity (phase distribution)
wet gel	porosity, density, mechanical properties, thermal analysis, thermoporometry, NMR, IR, SAXS	Å*	IV drying ageing	homogeneity, pore distribution, gel structure, further processing properties
dry gel	porosity (adsorption, isotherms), densification mechanisms, thermal analysis, crystallization, mechanical properties, X-ray	* * *	V processing to materials	crystallization, phase formation, density, mechanical, optical, electrical, chemical or other properties

*   bulk   Å   thin films

ÅÅÅ well investigated for silica and a few other systems [24 and literature cited herein]

ÅÅ only a few systematic data available, mainly on silica

Å no systematic data and only a few others available

properties, but not to the influence of sol structure or coating parameters on film properties. Meanwhile, coatings are prepared from almost all compositions to be obtained by sol–gel processing, reviewed in [61–79], but the deficiency in the wet-step mechanisms is growing rather than decreasing. Two main reasons can be identified. First, it is very difficult to characterize sol structures and second, the structural characterization of thin films is also very difficult. Examples of investigations to correlate film properties to sol properties are given in [12, 18, 24, 80–82].

The complex processing and the interdependencies are schematically overviewed in the schema on page 00. Step II is extremely important since it represents the homogeneity determining step for sol preparation and thus will affect strongly the coating properties. This is essential since especially for thin films characterized by one very small dimension homogeneity is very difficult to achieve by thermal diffusion after coating.

4.2 Molecular Design

Therefore, it seems to be necessary to take care of sufficient homogeneity during step II. As already mentioned, if the sol particle size can be controlled on a nanometer-sized level, homogeneity can be sufficient for a variety of applications, even for optical purposes as shown by Zarzycki [83] and Nogami [84] with sol–gel glasses containing semiconductor crystallites such as CdS or CdSe. To obtain dense glasses from particulate sols as well as from polymerized sols the densification temperature has to be high enough, probably around Tg. There are no exact data available, since it is extremely difficult to measure the low porosities of thin films. In the case of crystalline coatings, the development of crystalline micro-structures is a complicated process, where nucleation and crystal growth play an important role [85]. But it can be generalized that only in sols with nanometer-phased micro-structures resulting in optically transparent coatings. According to suggestions from Payne [86] the microstructure of crystalline films can be tailored by molecular design of the precursors where the different components already have positions in a crystal close to their final structure. As shown in $BaTiO_3$, thin films, this can lead to nanocrystalline films with domains in the nanometer range but already showing good electrical properties otherwise observed only on much larger domain dimensions.

Other interesting examples has been given by Hirano [45] who was able to demonstrate the effect of the formation of a double alkoxide on the sintering temperature of $LiNbO_3$ and its optical performance. By use of the double alkoxide (Fig. 12), the crystallization temperature of thin films could be reduced to less than 300 °C. The results can be interpreted with the reduced diffusion paths within a super amorphous solid and the high level of free energy. In the early papers of Dislich [6] it was demonstrated that the addition of a β-diketone and subsequent refluxing leads to much better coatings. This can be attributed to the formation of precursor complexes in which the several compounds are
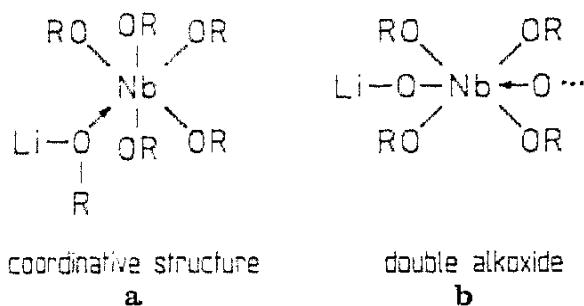
coordinative structure   double alkoxide   **Fig. 12a, b.** Mixture of lithium-niobium alkox-
a   b   ide and double alkoxide

already immobilized on a molecular level. Livage and coworkers pointed out in an extensive review [25] the possibilities of molecular tailoring of precursors. His considerations are based on an electrostatic reaction control model and on the role of complex formation with complexing acids or β-diketones. In [87] they try to give some first interpretations of correlations between precursor and the structure of the resulting product.

The control of colloidal particle size and agglomeration cannot of course, be considered as "molecular design". Molecular design has to take into consideration the formation of precursors representing desired structural elements, the formation or maintainance of such an element by reaction control and the structural control during the various processing steps.

4.3 Reaction Control

The possibilities of controlling reaction rates with respects to oligomer, macromolecule or colloid tailoring are limited as already pointed out. An interesting alternative is to avoid the undesired effects of rate differences. This was first suggested by Yoldas [32] in the system SiO_2/TiO_2, as already mentioned. The general idea is to prehydrolyse the slower reacting precursor in order to supply it with an "advantage on the time scale" (Fig. 13).
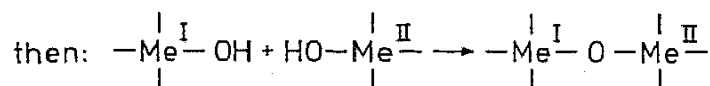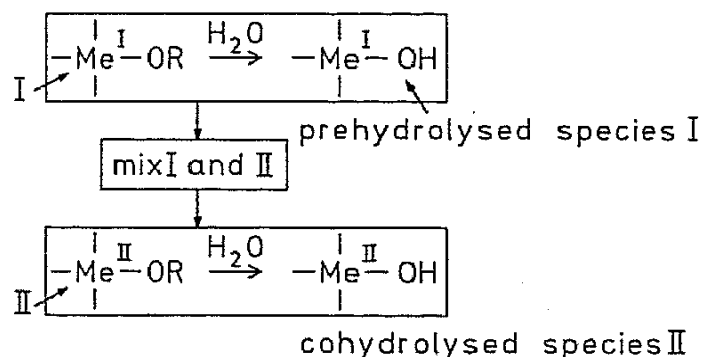

Fig. 13. Prehydrolysation of slower reacting precursors for improvement of homogeneity

But this model can be only employed if the $\equiv Me^I OH + HOMe^{II} \equiv$ condensation step is fast. This is, as pointed out by Livage [26], not the case in the presence of an $\equiv MeOR$ bond at the same time. Another route was suggested by Schmidt [88] who proposed to prehydrolyse the fast reacting species by controlled generation of water in a reaction mixture (Fig. 14). In this case, the $\equiv MeOH_{fast}$ can react with all types of $\equiv MeOR$ and would lead to a homogeneous immobilization of the fast reacting species to other precursor molecules in accordance with Livage's theory. The effectiveness of this method was demonstrated on the eye glass lens coatings and contact lens materials. The use of this route allows the synthesis of optical materials from multi-component systems with very different reaction rates [88, 89, 90].

The usefulness of prehydrolysed precursors for homogeneous distribution can be demonstrated very clearly with "stable hydroxides" such as $(C_6H_5)_2Si(OH)_2$. Transparent coatings can be prepared by reacting $(C_6H_5)_2Si(OH)_2$, which is a solid non-sensitive to moisture solvent, e.g. toluene with $Ti(OR)_4$. The reaction can be followed by monitoring the OH vibration by IR [91] (Fig. 15).

The condensation reaction takes place at room temperature and the $\equiv SiOH$ groups are consumed almost completely by condensation with $\equiv TiOR$ groups. A viscous liquid results from this process and it can be used for coatings. The refractive index of this coating is between 1.65 and 1.7. The reaction can be interpreted by the formation of polymers with alternating $-O-Si(C_6H_5)_2O-$ and $-O-Ti-O-$ units, as shown in Fig. 16.

These sols (Ti can also be substituted by Si) can be densified at low temperatures (150 °C) and fired to organic-free materials at surprisingly low temperatures, as shown in [92].

These examples show that control of precursor chemistry is an adequate means for property tailoring by design of the sol especially if homogeneity plays an important role.
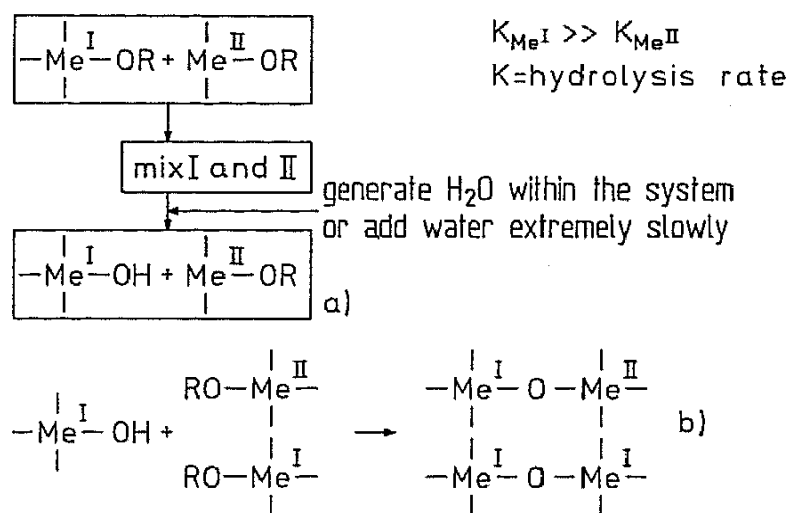

Fig. 14. Prehydrolysation of faster reacting precursors for optimum homogeneity

$(C_6H_5)_2Si(OH)_2$ $(C_6H_5)_2Si(OH)_2 \cdot Ti(OEt)_4$ $(C_6H_5)_2Si(OH)_2 \cdot Ti(OEt)_4$
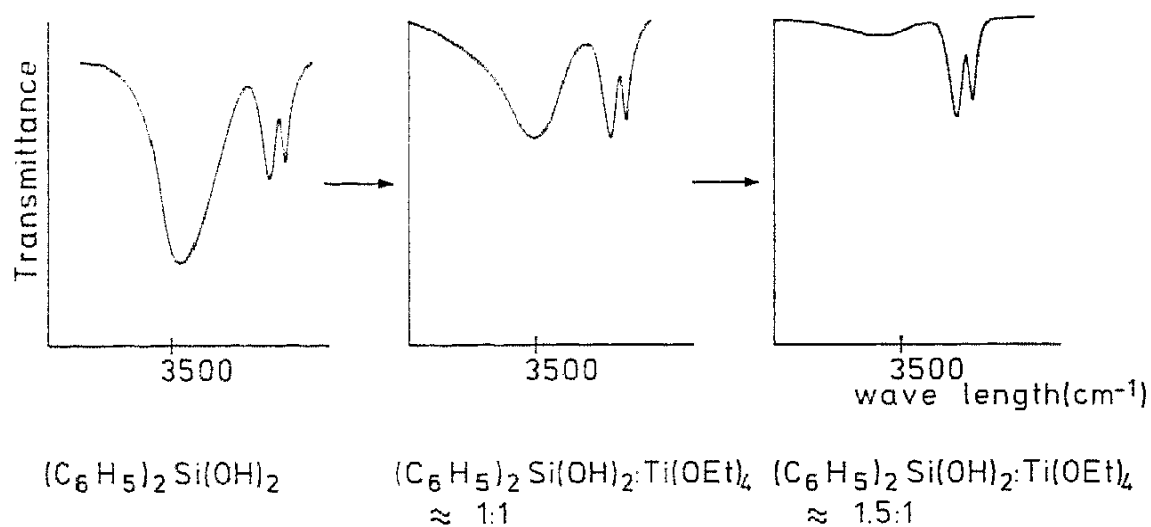 $\approx$ 1:1 $\approx$ 1.5:1

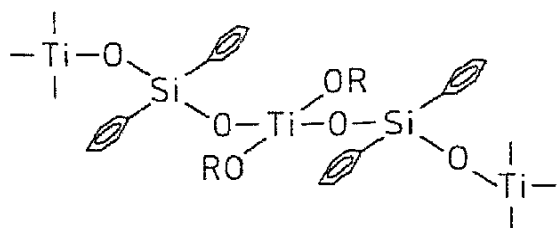Fig. 15. IR controlled reaction of $(C_6H_5)_2Si(OH)_2$ in toluene with $Ti(OEt)_3$ in toluene as solvent

Fig. 16. Suggested structures of $(C_6H_5)_2$-Si–O–Ti-sols

The results from Sanchez and Livage [26] and also from Naß [28] point out that the control of precursor chemistry by the proper design of intermediates or oligomers can be used for increasing homogeneity, but since organic groups chemically bound to inorganic precursors are used this means at the same time that a homogeneous distribution of organic components within an inorganic network occurs. For example, it is possible to disperse more than 50 mole % of ZrO_2 within a polymeric system using complex formers [93]. In this case, the methacrylic acid (MMA) was used as "link" as shown in Fig. 17 [94, 95].

The possibility of molecular design of sols can be extended to almost innumerable variations, but, therefore, possibilities of organic chemistry, organometallic chemistry and coordination chemistry are exploited for these objectives. Especially the latter one is only at its infancy and a few examples can show the importance of these routes. As shown by Schubert and coworkers [96], a homogeneous distribution of metal ions is possible by the formation of complexes with sol–gel precursors (Fig. 18a). Cu can be incorporation by complexation with $NH_2(CH_2)_3Si(OR)_3$. The viscosity can be adjusted by hydrolysis and condensation control, films and foils can be received and the colour intensity can be varied by the Cu content [97] (Fig. 18b). Another type of complex formation was suggested by Charbouillot [98] and Ravaine [99]
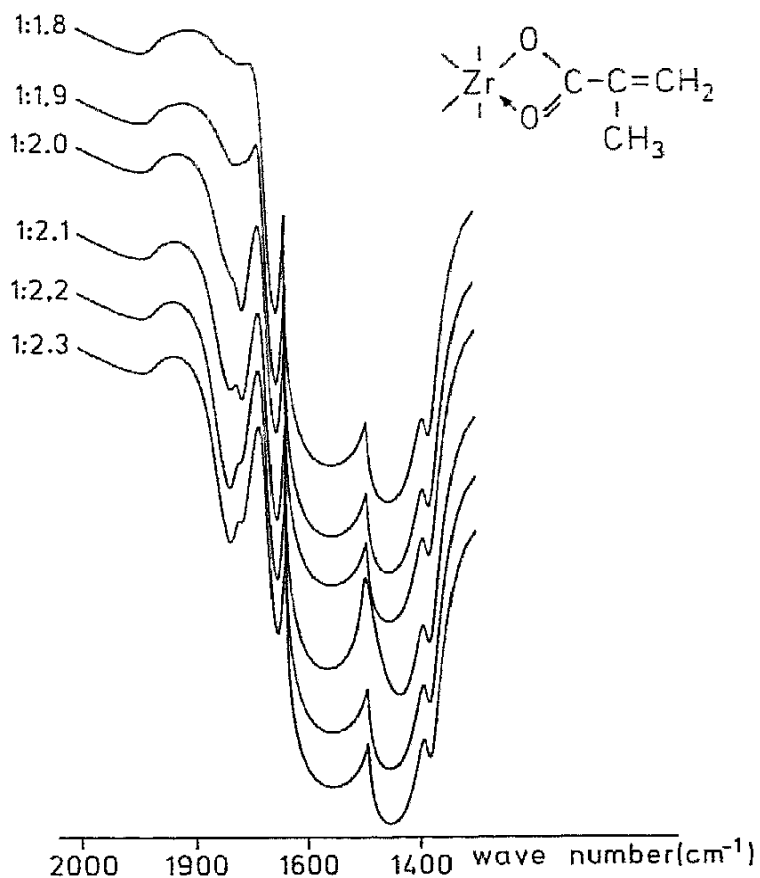
Fig. 17. Complex formation of Zr alkoxides with MMA and IR analysis of increasing MMA to Zr ratio
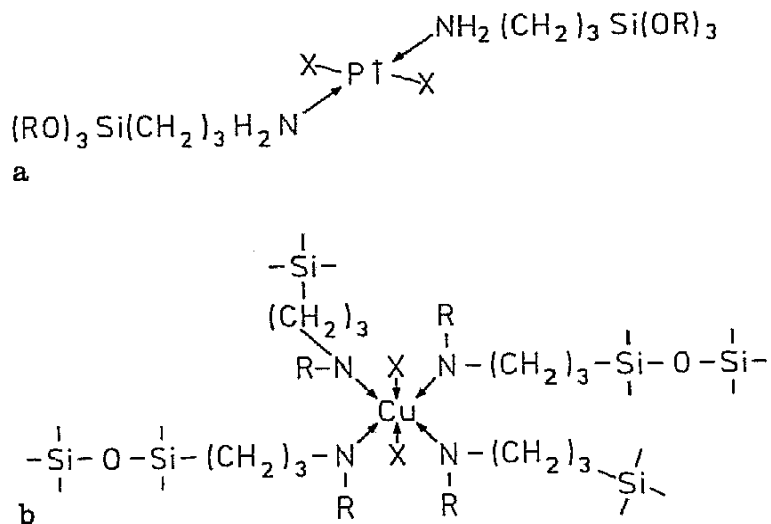

Fig. 18a, b. Structure of a soluble Pt complex and of a film containing a copper tetrammine complex [96]

who prepared proton conducting films by doping condensates from $H_2O(CH_2)_3Si(OMe)_3$ with acids such as $HClO_4$ or CF_3SO_3H postulating a structure stabilized by an anionic complex within the gel network (Fig. 19) and protonic transport mechanism by a chain movement step.
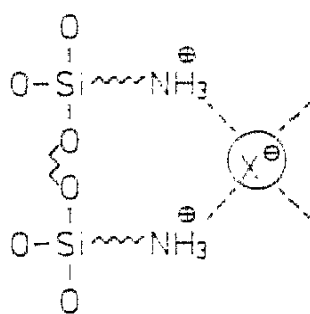
O
|
O—Si ⌇⌇ NH₃ ⊕
|
O
O
|
O—Si ⌇⌇ NH₃ ⊖

X ⊖

Fig. 19. Structure of a proton conducting anionic complex

5 Material Developments For Coating Application

The key issue for tailored material development is structure tailoring in connection with correct structure analysis, the knowledge of the mechanisms of the reactions and the correlation of these data to material properties. One has to distinguish between two basic features when considering property tailoring: the tailoring of processing properties and/or the tailoring of final product properties. It depends mainly on the product type and application to which of them has to be given priority. A very important point of view is the question of to what extent is it possible to maintain properties, designed by sophisticated precursor chemistry through all the processing steps up to the final product. To illustrate this, Hirano's and Payne's results [45, 87, 100] can be taken as an example. To obtain high quality $LiNbO_3$ films, various sol–gel routes can be employed, e.g. mixing the precursors or synthesize double alkoxides. The main benefit of the double alkoxide route in this case is to reduce processing temperature which opens the application to a variety of substrates and devices as well as the film properties. Another benefit, which is based on low temperature processing, is the slow crystal growth which can lead to extremely small crystal sizes down to nanosized microstructures. But despite this, to maintain the precursor structure is not the objective. If we think of doping silica or oxide glasses with lanthanides, the precursor structure may play an important role if a special coordination structure can be maintained as demonstrated by the preparation of complexed Eu containing films [101, 102] or SiO_2 sol–gel glass films which are heat densified at low temperatures.

The lower the processing temperatures are, the more likely structures generated by chemistry in the sol can be maintained in the final product or in other words, if one wants to maintain structures, one has to use low processing temperatures adapted to the temperature sensitivity of these structures.

5.1 Glass Coatings

The development of glass coating materials during the last decade was devoted to fundamental questions, mainly related to hydrolysis condensation and

rheology. Models for sol–gel film formation have been developed by Bornside and Macosko [103, 104]. Basic methods to determine rheological parameters are summarized and related to structural models.

Glass coatings were developed for coating plate glasses very early [6]. Since this time only a few large scale applications have been developed, for example for head-up dislays in cars. The only well understood system up to now is the SiO_2 system but this system has only a limited application potential. The SiO_2 films have become interesting for integrated optic systems. Since high grade SiO_2 exhibits extremely low losses, it is a potential material for planar wave guides in the form of passive waveguides or doped with lanthanides for active wave guides. Due to the high densification temperature of SiO_2 gels, direct laser densification including laser patterning was investigated [105]. The same process was used for Ta_2O_5 and SiO_2/TiO_2 films. The problem of this technique is the heat transfer by a laser beam to the surface and the heat dissipation into the non-irradiated gel or sol. It seems to be difficult to obtain smooth surfaces of the patterned channels, which are necessary for low losses for integrated optics. The structure of the sol, the resulting gel and the sol–gel transition by prebaking should be of high relevance for this interesting process. This is true for another interesting technique developed to pattern gel glass films: the embossing step. The prerequirement therefore is, that the gel transition is not completed. The viscosity has to be low enough to allow the embossing of patterns in the range of some μ or less (Fig. 20). This can be obtained by condensation control of the sol
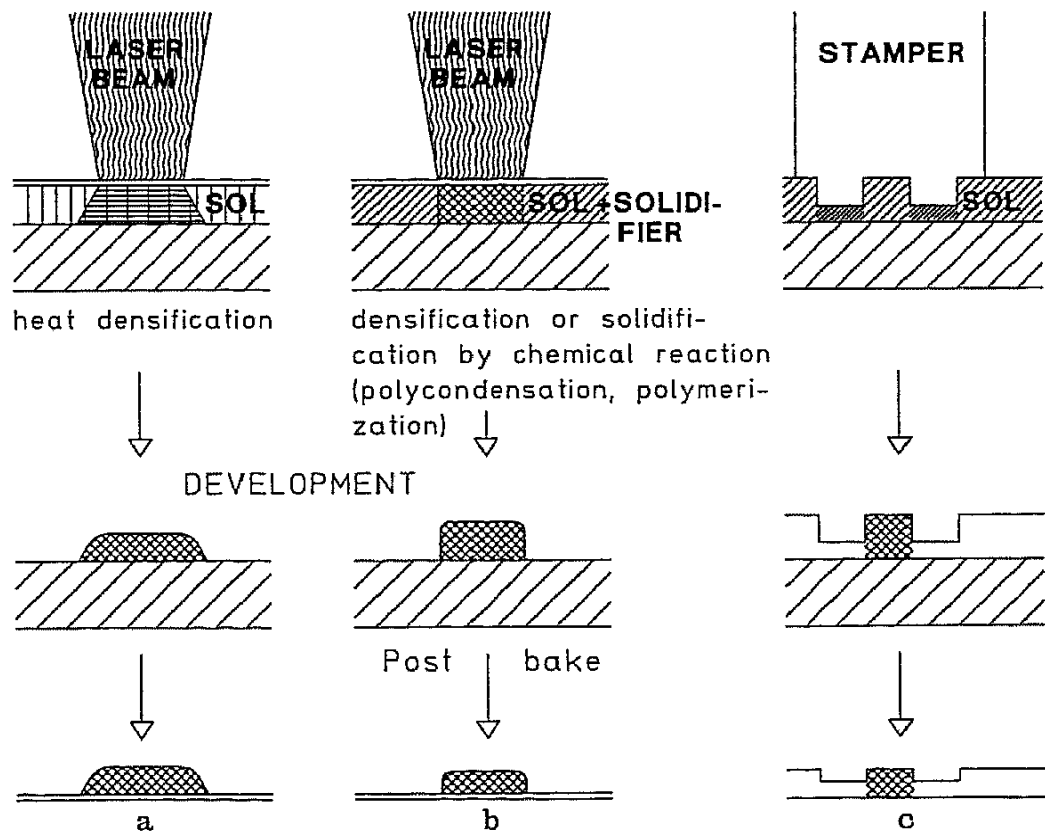

Fig. 20a–c. Patterning processes to produce waveguide channels; a) direct laser densification; b) chemically processed material e.g. photoinitiator assisted crosslinking; c) embossing

or, as shown by Matsuda and coworkers [106, 107] by addition of an organic additive, in this case polyethylene glycol (PEG), acting as a softener. With PEG it was possible to emboss a gel layer on a glass disc for a CD–ROM.

The development of direct densification of sol layers is at its beginning and it is not yet possible to estimate the potential of this method. The chemical-reaction-assisted densification route which is very well developed for organic polymer patterning in microelectronic processes, is an interesting way for patterning ceramics, too. It can be advantageously used in the form of a composite (Fig. 21a) or in the form of an inorganic–organic hybrid material (ceramer, polyceram or ORMOCER) (Fig. 21b) [108–109]. This route which includes, in general, a development step (e.g. dissolving the non-irradiated areas) has an interesting potential for the development of patterned ceramics as well as for composites to be used in optical as well as in electronic application. Therefore, it is necessary to investigate the reaction mechanisms and structure formation in detail. For the exploitation of this potential it is necessary to close this gap in our knowledge. The embossing process seems to be rather simple compared to the described processes. If the sol preparation can be controlled in a way that the viscosity allows the embossing step, the method is very promising for optics. Whereas laser writing is limited by the laser focus, heat dissipation, and reaction control (some μm resolution up to now) by embossing, patterns in the sub-μm range could be obtained, as shown in [110]. Titania–silica was used preferably since it allows one to adjust the refractive index between 1.46 and 2.60. In [111–112] the embossing of thin films of TiO_2–SiO_2 to produce complex gratings with 1200 lines/mm is shown. These gratings were used for sensors [113–114] and thermo-optical switches [115]. With ORMOCERs containing polymerizable organic ligands, the embossing step can be combined with a polymerizing step leading to high quality patterns in a quick process [116].

Another interesting field of applications is antireflection (AR) and reflective coatings. Of course, it is possible to produce antireflection coatings by sol–gel techniques. There are two approaches for AR coatings: Coatings which fulfill the quarter wave length conditions and coatings with or based on the index discontinuity of the interface. Interesting recent developments are AR coatings for solar cells [117–119] for TV screens or computer terminals [120–121] for the near infrared region [122] or for increasing the damage threshold for glass lasers

organic phase
inorganic phase
a
ceramic particles
or colloids with
organic monomers

F =polymerizable ligands
inorganic backbone with organic
monomers or organic groups linked
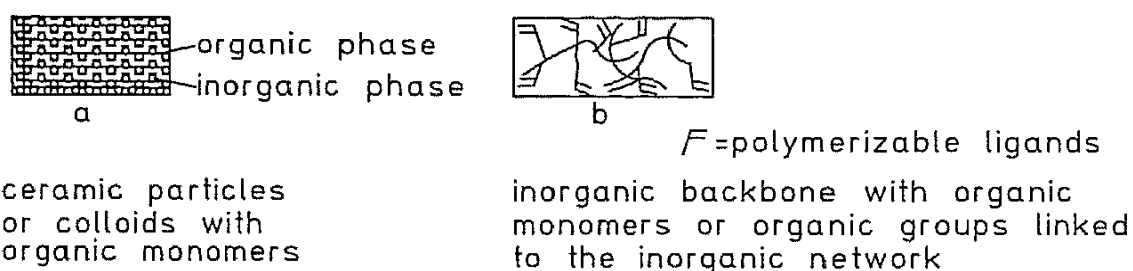to the inorganic network

Fig. 21a, b. Various types of composites for patterning

[123]. Two routes have been used for these approaches. The one is to evaluate sol properties and coating conditions to obtain the desired film thickness after densification, the second to obtain desired n variations by adjusting the film density (or porosity). For both approaches it is desirable to tailor the sol properties and to work out the correlation of sol structure and film properties, which is only at its beginning.

The sol–gel method which can be very promising even with respect to costs will be successful in future if these basic questions can be answered. Therefore, more investigations are to be carried out in this respect.

Another interesting question is how far sol–gel coatings are able to improve mechanical strength or chemical stability of glass surfaces. As shown in [39] sol–gel coatings can act in various ways for improving strength either by flaw healing or by building up compressive strain or by combination of both (Fig. 22).

Compressive stress can be built up by use of a coating with a TEC α smaller than that of the substrate glass. In [39] rheological analysis led to the conclusion that particulate sols which follow the Landau–Levich expression exactly can be used to calculate the coating thickness in dip coating experiments. Whereas with flaw healing a bending strength increase up to 70% was observed [124], with sol–gel coatings including the formation or surface compressive stress an increase by a factor of four was achieved [39].

Another interesting development is electrochromic films based on WO_3, MoO_3 and V_2O_5 or combinations of them [125–133]. Although a variety of systems with electrochromic properties have been prepared, the structure to property relationships are poorly understood and the influence of the chemistry on the electrochromic performance is not known.

5.2 Ceramic Coatings

These coatings have become very interesting for optical application in the last decade and a special emphasis can be observed on the synthesis of electrooptic materials such as PZT, PLZT, SBN, PMN, $LiNbO_3$, $Li_2B_4O_7$ TiO_2/B_2O_3 TiO_2/CeO_2 and others [134–136]. The objectives of these investigations are, in general, to obtain thin films with high electrooptic coefficients [137–144]. Surveys on electrooptic sol–gel films are given in [145, 146]. The comparison of
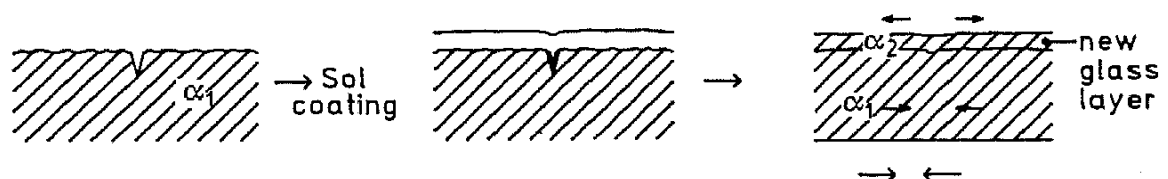
Fig. 22. Sol–gel layers effective in flaw healing and compressive strain formation α_1, α_2 = TCE; $\alpha_1 > \alpha_2$

these films with bulk materials generally show lower linear and quadratic electrooptic coefficients. The mechanisms of the influence of sol structure to crystallization behavior is not well investigated and poorly understood and it is not clear whether it caused the crystallization effects (e.g. pyrochlore formation), interface phases or defects in the films (pores, microcracks). The film thicknesses which can be realized in a one-step process are in the range of 0.1 to 0.5 μm. In [147, 148] it is reported that planar wave guides have been prepared with a 1 μm thickness by using as many as 15 dip coating steps.

Hutter et al. [149] synthesized 50 nm particulate sols from WCl_6, Ti- and V-alkoxides which were used for the coating of cordierite honey comb structures to form a catalytically active coating for NO_X conversion in waste gases of power plants. These coatings were built up within the pores and on the surface of the cordierite ceramic body [150].

5.3 Composite Films with Organics

The sol process as a low temperature synthesis process for inorganic networks has the unique potential to incorporate organic components into the inorganic structure. There are a variety of possibilities of linking organic with inorganic components. A survey of some important mechanisms is shown in Fig. 23a–e.

The chemistry of the synthesis of these structures is very complicated and only a few structures have been proposed [151–154]. The basic advantage of the sol–gel process is its ability to form inorganic structures at low temperatures which allow organics to survive the processing. Organics can be organic groupings chemically linked to the inorganic backbone, organic polymers or entrapped organic molecules such as molecules with special electrical or optical properties (e.g. NLO, lasing dyes).

For the incorporation of dyes two routes have been investigated, the adsorption of dyes in pores or the condensation of dye-containing sols. In the first case the sol–gel process is not influenced by the dye molecule, in the second case, the dye molecule can either interfere with the reacting species, e.g. as catalysts or can "form" its own tailormade environment during the gelation step. This interesting reaction which allows one to control interaction and the properties of the dye molecule has not been investigated in these preparations.

The films prepared by these novel methods have been developed for solid-state dye lasers, solar light collectors and optical memory devices [155–158] where SiO_2 has been used as the matrix. In Al_2O_3 or Al_2O_3/SiO_2 films, rhodamine 6G shows lower degrees of aggregation and a remarkable increase in stability [159, 160]. New χ^3 materials have been prepared by Prasad using an inorganic backbone stabilizing a χ^3 organic polymer [161]. In [160] the use of an ORMOCER type as described in [88] was used as a matrix for incorporating lasing dyes showing a remarkable stabilization of rhodamine 6G against laser shots.

Covolent link
by ≡Si-C≡ bond

a

"complex bond" link by various complex
formers like amines, β-diketones or other
chelate ligands

Me=Al,Zr,Ti....

b

ionic bond by organic acids

c

adsorption of organic molecules
in pores

Me=Cu,Ag,Ni....

d

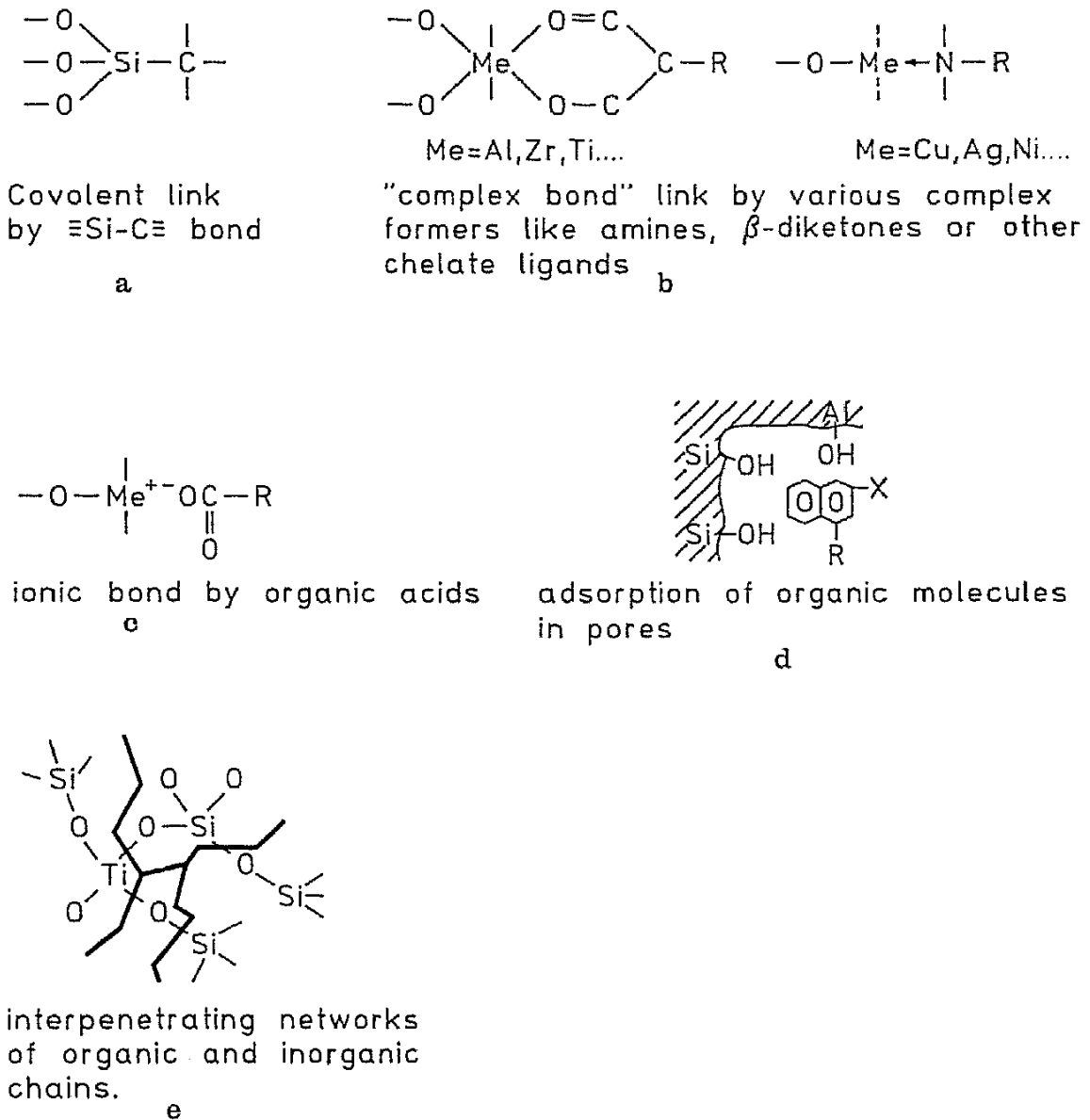interpenetrating networks
of organic and inorganic
chains.

e

Fig. 23a–e. Suggested connections of inorganic with organic units

Further developments of inorganic–organic composites have been carried
out by Teowee and coworkers [162], using butadienes, polyurethanes and
polyethyleneimines as matrices and modifying them with SiO_2 for low DK
coatings.

Another development of inorganic–organic hybrid films has been carried out
by Schmidt [163–166] who was able to show that some of these films exhibit an
abrasion resistance close to inorganic coatings [153]. The interesting feature of
these coatings is, first, the fact that due to the organic groups they can be
densified at remarkably low temperatures (70–150 °C) and thus, can be applied
to plastic surfaces, and second, that the Young's modulus can be varied over
a wide range without affecting the abrasion resistance too much. The modulus
adaption becomes important for plastic surface protection.

The moduli difference has to be low enough to overcome the TCE mismatch between the coating and the substrate and to keep the internal stresses low. The high homogeneity of this type of material was achieved by exact reaction control during the synthesis as demonstrated in Sect. 4.3, and structural models were developed in [152]. These coatings are used for mechanical protection on CR 39 polymers for eye-glass lenses and additionally act as a "hard" interface for sputtered inorganic antireflection coatings, which are otherwise difficult to apply to polymeric surfaces for reasons shown in Fig. 23. By careful adjustment of the chemistry, especially the formation of the organic chain in epoxy polymerization, it is possible to create surprising elasticity within such coatings. These types of hard coatings can not only be used on optical polymers but also on metals where in addition to their scratch protection they can also provide corrosion protection [167]. Another type of inorganic–organic film forming material has been developed for electronic purposes. It is based on the $-(C_6H_5)_2SiO-$ chain forming unit which allows one to control the structure in combination with three-dimensional crosslinking units [e.g. SiO_4^{4-}, TiO_4^{4-}, ZrO_4^{4-}] and organic chain forming units [e.g. $-CH_3Si(CH=CH_2)-$ or $-Si-methacryl$]. Thus, coatings on Al for adhesion purposes [168–169], for corrosion protection on glass surfaces [170], for electronic application as low dielectric constant material with high thermal and chemical resistance [163, 171, 172] have been developed. Variations of this type have been tailored for direct laser writing to generate patterns for microelectronic application [108].

There are almost unlimited material variations to be synthesized just by varying the organic component, the inorganic backbone and the sequence of crosslinking. This opens the interesting potential of multifunctional coatings, where basic function, such as mechanical strength are used as a starting point and additional functions are added by structure tailoring. First results have already been obtained e.g. with respect to low permeation for small molecules [167], special chemical properties to link biological compounds· [173], to incorporate functional transition metal ions [174] or to incorporate dyes [97].

6 Conclusions

Sol–gel processing covers a wide range of compositions to produce thin films on a variety of substrates. The basic advantages of sol–gel processing are low costs, obtaining precisely the desired stoichiometries in multicomponent systems, the homogeneous incorporation of low concentrations of dopants, the use of conventional wet coating techniques and the synthesis of inorganic organic composites on a molecular level. In order to make a breakthrough with this technology, a better understanding of the structure to property correlation has to be worked out with special focus on the structures of the coating materials, which, in general, are oligomeric or colloidal solutions.

7 References

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