Multifunctional inorganic–organic composite sol–gel coatings for glass surfaces

Helmut Schmidt *

Institut für Neue Materialien, Im Stadtwald, Gebäude 43, D-66123 Saarbrücken, Germany

Abstract

The sol–gel process allows the fabrication of ceramic colloidal particles in the presence of organo alkoxy silanes carrying various functions and the synthesis of multi-functional transparent inorganic–organic composites if the particle size can be kept in the lower nano range. In addition to this, these composites can be used as controlled release systems or designed as gradient systems. Using this approach, a coating with a very low surface free energy (antisoiling properties) and temperature stability up to 350°C, a controlled release system for permanent wettability (anti-fogging) and systems containing metal colloids for optical effects have been developed.

1. Introduction

Glass is a material which plays an important role in architecture and in the automotive and display industries. The unique basic property for this application is its transparency combined with its complete impermeability to gases or liquids. In addition to this, a high stiffness is required for a variety of applications. However, for an increasing number of applications, additional properties are required which, for example, are focussed on the control of light transmission in a passive or even active way or to control surface chemistry in connection with impacts from environment (moisture, dust). For these reasons, coatings have to be developed to adapt or to vary glass properties for the desired purposes. For architectural glazing, reflective coatings reducing the transmission of sunlight have been developed by sputter techniques (magnetron sputtering) or sol–gel techniques [1]. Antireflective coatings have also been developed by sol–gel techniques (Amiran®, Schott Company, Germany).

In the scientific literature sol–gel dip coating techniques on glass have been investigated the most. Dip coating techniques can be carried out by relatively simple technical means. A survey of these investigations can be obtained in a series of conference proceedings [2–6]. Passive coatings (reflective coatings, colored coatings, antireflective coatings) and, more recently, active coatings, also especially for non-linear optics, have become the center of interest. The majority of these coatings are based on pure inorganic systems. In a few cases, inorganic systems modified by organic groupings [7,8], micels or organic molecules [9] play a role. Inorganic–organic composite coatings on substrates like glasses have been mainly investigated for development of active optical systems [10–14]. In this connection, it could be shown

---

* Corresponding author. Tel: +49-681 302 5013. Telefax: +49-681 302 5223.

that, by use of inorganic–organic composite systems, thick layers up to several μm can be obtained without any problems, whereas pure inorganic layers are restricted in most cases to thicknesses up to around 1 μm [15]. Higher thicknesses are of special interest for planar waveguides, especially if multimode light transmission is desired. It is possible to obtain thicker layers with inorganic–organic systems owing to their high relaxation ability compared with pure inorganic structures. Sol–gel processing allows a variety of organic functions to be incorporated. The question arises how far it is possible to produce specific functions, especially multifunctional behaviour on glass surfaces, for example, to control the surface free energy or to obtain photochromic or electrochromic effects. Another interesting part is how far small inorganic particles below their Rayleigh scattering regime can be introduced and lead to specific optical or mechanical surface functions. In this paper, a brief review about the possibilities of synthesis and application of inorganic–organic composite or nanocomposite systems on glass surfaces is given.

2. General considerations

Inorganic–organic composite systems prepared by the sol–gel process have been investigated for several years [16–18]. The sol–gel process is a suitable means to synthesize this type of material since the inorganic backbone can be built up by a low-temperature process, and organics can survive processing. In order to avoid phase separation which is important for transparency and homogeneity, 'links' for attaching the inorganic to organic units are necessary. The basic principles, therefore, have been described elsewhere [19]. The use of organosilanes is one interesting means to combine inorganic with organic structures as well as the formation of chelates, e.g., β-diketones for alumina, zirconia or titania. For the formation of metal complexes, chemicals such as amines, diamines, sulfides and others provide a variety of ligand systems [20–23]. These 'links' can be used to produce relatively homogeneous distributions between inorganics and organics on

an almost molecular range. However, in 'molecular' composites, the inorganic part in most cases loses its identity because, in general, this is related to a crystalline or amorphous solid phase in the range of nm and larger. If this phase size remains in the lower nano range, light scattering can be neglected in most cases and nanocomposites of high transparency can be obtained [24,25]. Nanocomposites with metals, semiconductors or ceramics are of interest since special properties related to solid states of materials (e.g., refractive index of ceramics, quantum confinement of metal and semiconductor colloids) can be used for optical purposes.

Nanoscaled particles can be obtained by sol–gel processing during a growth reaction. In order to stabilize them, the growth reaction has to be stopped at the appropriate size. This can be done by various additives which adsorb to the particle surface and prevent further growth [20,24,26].

3. Passive materials on glass surfaces

3.1. Antifogging systems

Fogging is common on glass surfaces. This is a very undesirable property and is the result of a droplet type of condensation when the temperature goes below the dew point. After intensive cleaning, the glass surface is hydrophilic due to the SiOH groups and an adsorbed water layer [27]. On exposure to the atmosphere, the glass surface changes its behaviour by adsorption of bipolar organic molecules which can be strongly bonded to the surface by the ionic character of the SiOH groups. The contact angle to water, which is below 10° on pristine surfaces, can increase by almost two orders of magnitude to around 75°, and a more or less hydrophobic behaviour is established. In practice, the condensation of moisture leads to the formation of small droplets with a high light scattering effect. This undesired fogging behaviour represents the 'normal state' of a practical glass surface.

For this reason, a permanent wettability is desired for a variety of applications. Many attempts have been made to establish permanent
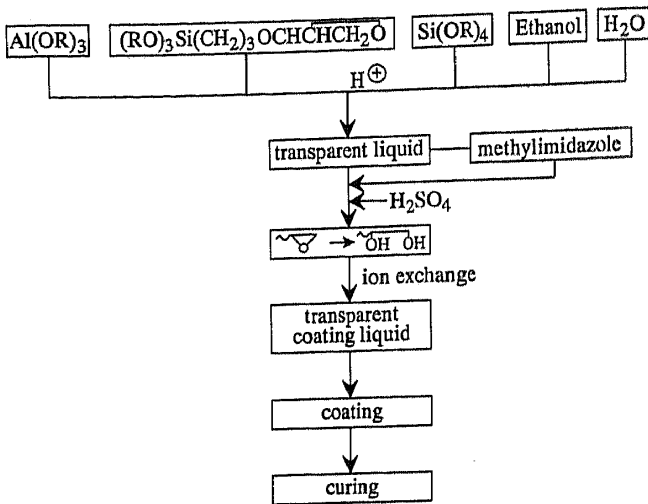
Fig. 1. Schematics of the synthesis of an inorganic–organic matrix system containing a –COH group (after Refs. [30,31]).

Fig. 2. Dependence of contact angle to HO on diol silane; ●; after addition of 5% polyoxyethylenoleylcetylether.

wettability, mainly by application of coatings with hydrophilic matrices. This type of 'static' modification, in general, shows a strong decay of wettability due to continuous contamination from the environment. The basic concept is the development of composite systems with a tailored intrinsic hydrophilicity and the incorporation of tensides (e.g., polyoxyethylenoleylcethylether, polyoxyethylen-(20)-sorbitanmonooleat) in a way to obtain a controlled release behaviour for long-term wettability. The released tensides can de-
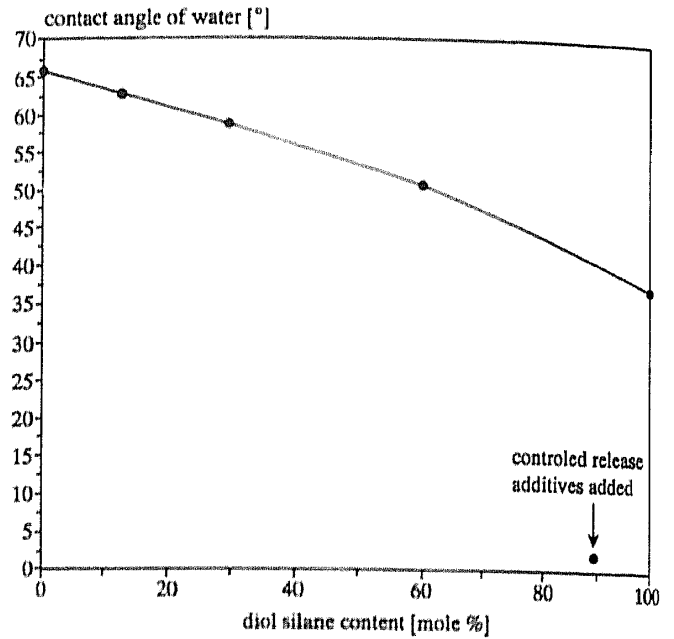
crease the interfacial tension of condensing water droplets to provide further condensation. For inside automotive glazing, an antifogging system has been developed by Vegla company (Securiflex) which is based on polyurethane with incorporated tensides. These tensides slowly diffuse to the surface and lead to a reduction of the interfacial tension against water [28]. These polyurethane
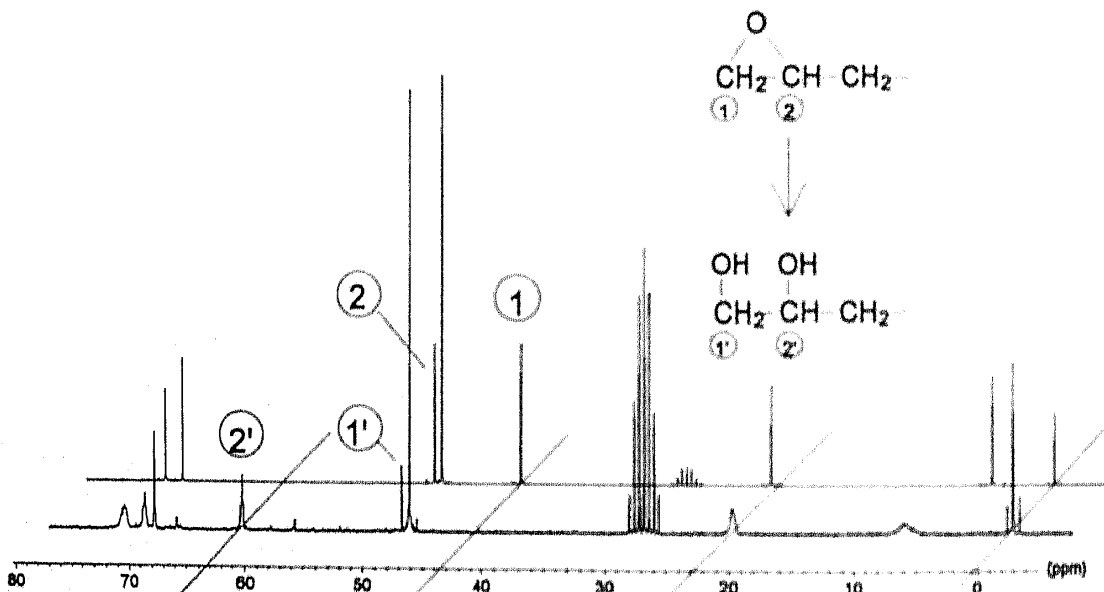

Fig. 3. Hydrolytic ring opening shown by ^{13}C NMR. Peaks at 43.3 ppm and 50.4 ppm (1) and (2) (epoxy group) disappear completely and the signals attributed to the diol (50.7 and 64.8 (1') and (2')) appear.

surfaces are soft but show a self-healing be-haviour if they are not destroyed by indentation impacts or cuts. For heavy duty applications where high scratch resistance is required, however, these coatings cannot be applied (automotive glazing at the outside surface, mirrors, architectural glazing and others).

For this reason, inorganic–organic nanocom-posite coating systems to be prepared by sol–gel techniques seem to be an interesting alternative, since high scratch resistance is achievable.

In order to be able to achieve several require-ments in one system (hardness and wetting behav-ior), a sol–gel system has been developed with abrasive resistant properties as described else-where [29].

As shown elsewhere [30,31], inorganic–organic composite types of materials have been devel-oped with incorporated tensides which lead to a wettable surface. In Fig. 1, the schematics of the synthesis matrix material are shown, and in Fig. 2, the wetting behaviour of the tenside-free sys-tem is shown as a function of COH group con-centration.

In this case, the SiOH groups have been re-placed by COH groups which do not show the ionic behaviour of silanols. The adsorption of particles or bipolar molecules should be reduced. If tensides are added, the contact angle drops towards zero. In Fig. 3, ^{13}C nuclear magnetic resonance (NMR) spectra are shown, demonstrat-ing the glycol formation within the composite material by acid-catalyzed hydrolytic attack.

The system has been used for coating glass surfaces (e.g., mirrors). The mirrors have been tested for about 1 year with only a very slight decay of the contact angle. Condensation of wa-ter takes place in the form of a film condensation and not as droplets. Since these films are not visible, the condensation effect does not lead to fogging. In Fig. 4, the effect of film versus droplet condensation is shown.

In order to improve the scratch resistance, suspensions of boehmite ($\leqslant 50$ nm) can be incor-porated in such systems by dispersing boehmite powder during synthesis. This leads to a very high scratch resistance compared with conventional hard coatings such as Ormocer coatings [32]. The
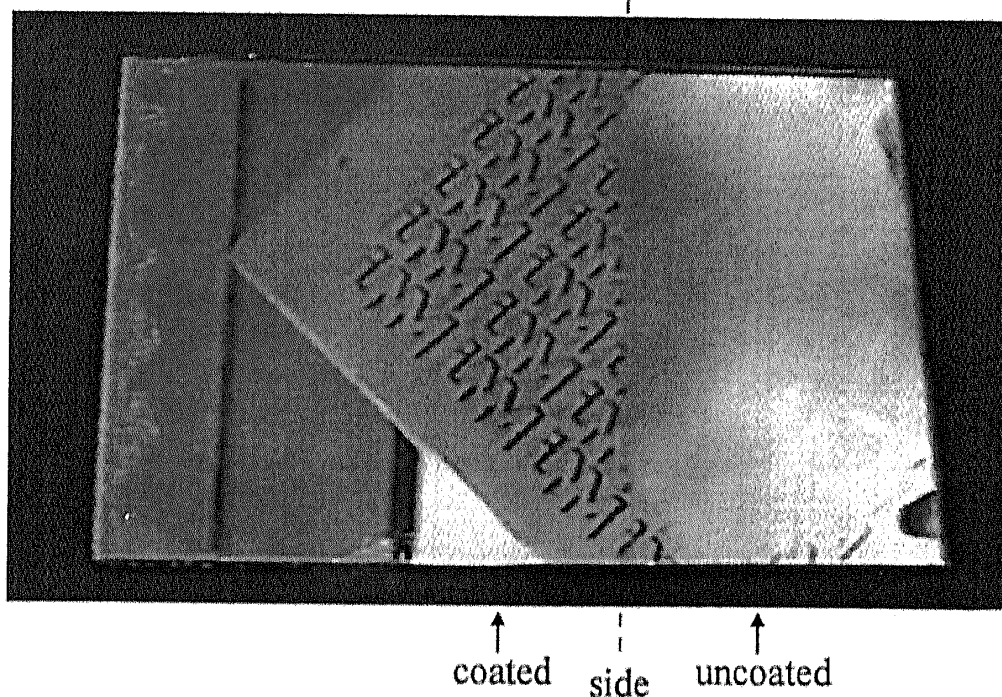

coated   side   uncoated

Fig. 4. Fogging experiment of a coated mirror; the right-hand side has been fogged by the water vapour, whereas the left-hand (coated) side remains completely transparent.
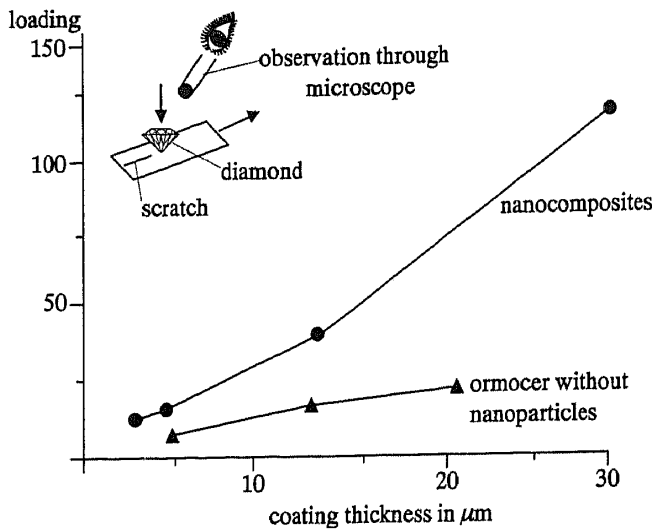
Fig. 5. Comparison of an Ormocer coating and an inorganic-organic nanocomposite.

scratch resistance, especially if a scratch test is simulating scratching of hard particles under load, is used. In this test, a Vickers diamond is scratched over the surface, and the load causing the first visible scratch is registered. The 'load number' in grams is dependent on the coating thickness. Fig. 5 shows the dependence of the load on thickness for the Ormocer coating according to Ref. [32] and the nanocomposite.

Whereas conventional hard coatings (systems based on polysiloxanes or Ormocers) show scratch resistance in the range of 5–20 g, this type of coating shows a scratch resistance up to 120 g.
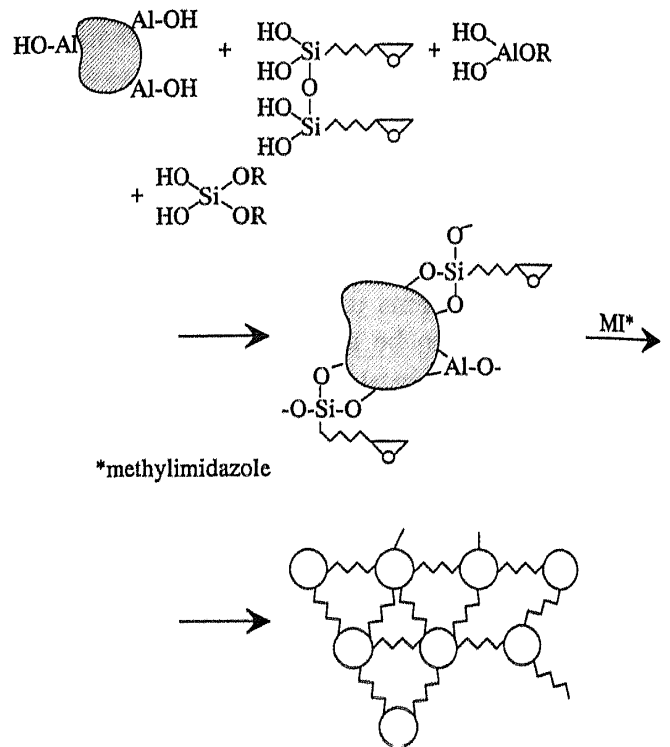

Fig. 6. Model of an inorganic-organic nanocomposite.

In Fig. 6, the synthesis and a structural model of this type of coating are shown. The model represents a 'flexible suspension' of small particles (e.g. γ-Al_2O_3, 'Degussa Aluminiumoxid C', average diameter $\leqslant 20$ nm) with a tailored interface. The composites are highly transparent with no light scattering to be detected in films. The
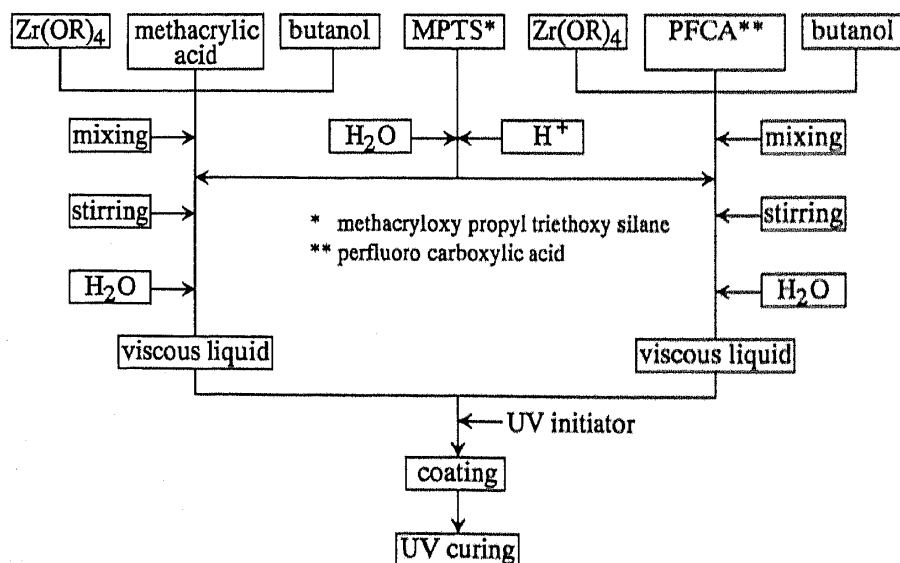

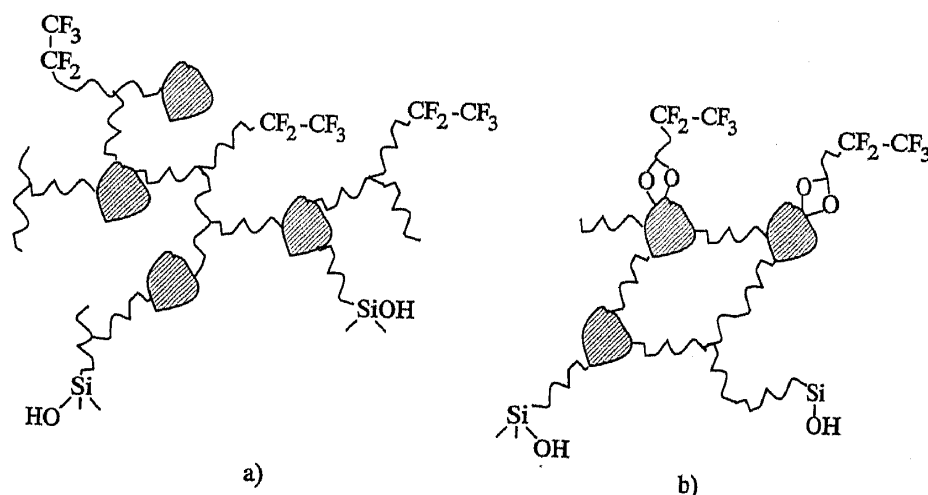Fig. 7. Schematic diagram of the synthesis of fluorinated Ormocers.

Fig. 8. (a) Model of nanocomposite structure with perfluoro alkyl groups covalently bond to the inorganic structure (I). (b) Model of a nanocomposite with perfluoro alkyl groups coordinatively bonded to ZrO_2 clusters (II).

mechanical behaviour is attributed to a structure comprising hard particles flexibly suspended in an elastic network (Fig. 6).

This type of coating can be applied at low temperatures but cured either by photo-polymerization or thermal curing. In the case of photopolymerization, methacryloxy-containing groups can be incorporated.
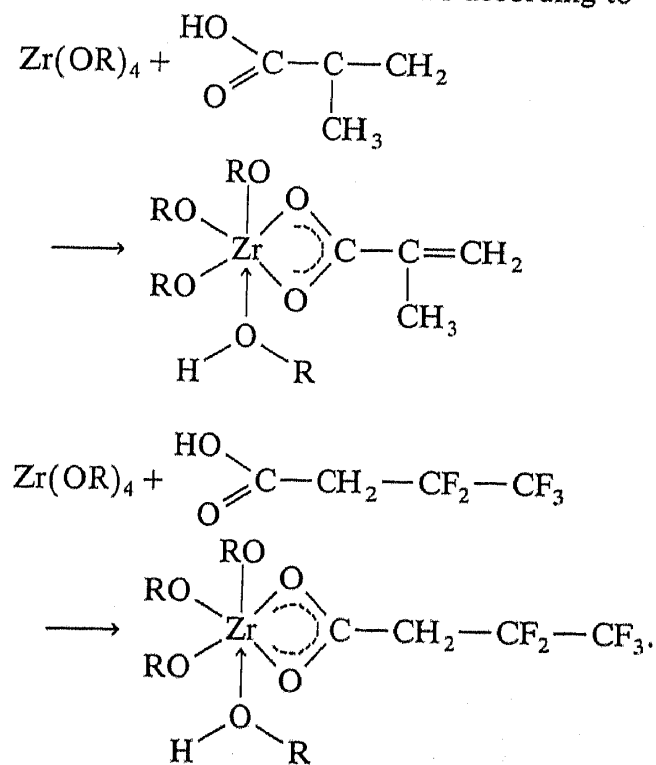
It is assumed that a surface bond between silanols and surface OH groups of the γ-alumina will be formed. Agglomeration of nanoparticles of alumina is avoided by reacting the silanes to produce an optimum amount of silanols as characterized by ^{29}Si-NMR. As shown elsewhere [33], SiOH groups under slightly acid conditions are formed which then slowly react with SiOR groups to form siloxane bonds. Depending on the reaction conditions (concentration, pH and temperature), the optimum content of OH groups can be determined by Karl–Fischer titration combined with ^{29}Si-NMR spectroscopy. Using this concept, nano-scale particles can be incorporated into Ormocer systems, and agglomeration can be avoided during further processing leading to highly transparent nanocomposites.

3.2. Dust-repellent coatings

Whereas permanent wettability reduces the adsorption between all types of contaminate on the glass surface, another concept to avoid soiling is to prepare surfaces with low surface free ener-

gies. The basic concept and the experimental procedures for this type of coating have been shown elsewhere [30,34]. As sources for the fluorinated compounds, side chain fluorinated silanes [35] and perfluorinated organic acids [36] have been used. A schematic diagram of the preparation process is shown in Fig. 7.

Both systems contain nanoparticles of ZrO_2 of about 2–4 nm in diameter. In both cases, complexes are formed with the acids according to

$$Zr(OR)_4 + \ \overset{HO}{\underset{O}{\diagdown}}C\!\!=\!\!C\!-\!CH_2$$
$$\overset{|}{CH_3}$$

$$\longrightarrow \ \begin{array}{c} RO \\ RO\diagdown \ | \ \diagup O \\ Zr \diagdown \diagup C\!-\!C\!\!=\!\!CH_2 \\ RO \diagup \ \uparrow \ \diagdown O \\ \overset{O}{\underset{H \diagup \ \diagdown R}{}} \ \overset{|}{CH_3} \end{array}$$

$$Zr(OR)_4 + \ \overset{HO}{\underset{O}{\diagdown}}C\!-\!CH_2\!-\!CF_2\!-\!CF_3$$

$$\longrightarrow \ \begin{array}{c} RO \\ RO\diagdown \ | \ \diagup O \\ Zr \diagdown \diagup C\!-\!CH_2\!-\!CF_2\!-\!CF_3. \\ RO \diagup \ \uparrow \ \diagdown O \\ \overset{O}{\underset{H \diagup \ \diagdown R}{}} \end{array}$$
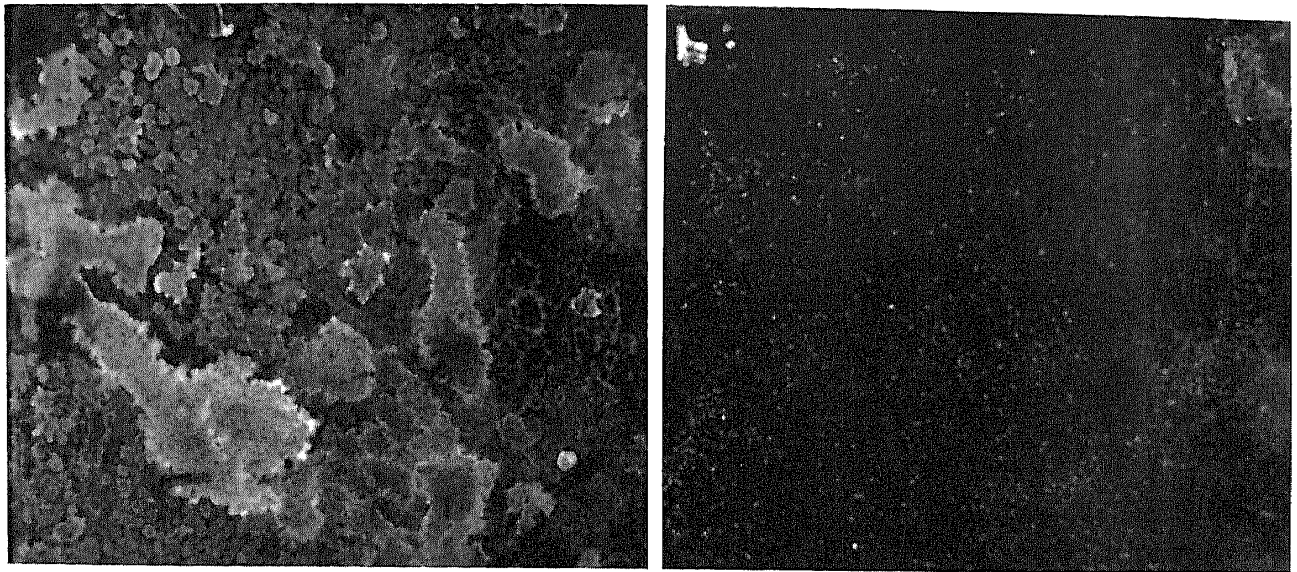
$$(1)$$

Fig. 9. Coated (right) and uncoated (left) glass surface after the soiling test (suspension of fumed silica doped with 2% motor oil).

The formation of the complexes has been proven by infrared and ^{13}C NMR spectroscopy.

An enrichment of the perfluorinated groups takes place in the surface exposed to the air. On the other hand, if polar substrate surfaces are used like activated polymers or glasses, a good adhesion of the coating systems on surfaces can be obtained leading to the assumption that the polar groups (silanols) of the systems turn to the substrate/coating interface. The 'formation' of these interfaces can be explained by thermodynamics which tend to decrease the interfacial energies by specific interactions. If these systems incorporate nano-scale particles, as it is shown in Ref. [30], where zirconia nanoparticles have been

used, these systems obtain a high scratch resistance. After hydrolysis, in the particulate system the IR spectrum does not show any vibrations attributable to the free acids indicating the cleavage of the Zr/carboxy bond. Fabrication of methacryloxy by methyl and subsequent firing up to 350°C leads to hard, glassy surfaces without destroying the perfluorated surface. It is of interest that only very low concentrations of perfluorinated silanes have to be used to show surface free energies the polar and dispersive parts of which are close to polytetrafluoroethylene. Due to the CF_2CF_3 groupings, the dispersive part of the surface free energy [17–19 J/m^2] is even lower than that of polytetrafluoroethylene. In Fig.
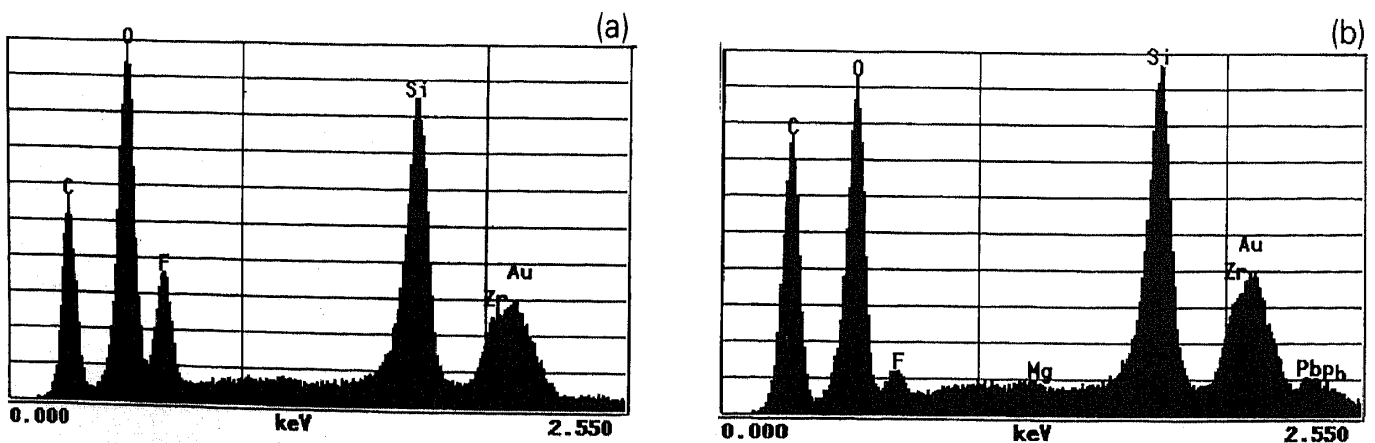

Fig. 10. Surface EDX from a carboxylic acid modified coating: (a) before and (b) after weathering.

8, schematics of the preparation and the structure of this type of coating are shown.

Applied on glass surfaces, this coating produces an antisoiling glass surface, and in Fig. 9, the difference of the transparency is shown after soiling with a mixture of fumed silica and motor oil.

After weathering, the two types of system show different behaviour: system (I) (Fig. 8(a)) does not show a decay of the wetting angle to H_2O (> 100°); system (II) (Fig. 8(b)) shows a decay to about 70°. Whereas in system (I) a decrease of the surface content of F is observed system (II) shows a strong decrease under weathering conditions (see Fig. 10). This shows that the fluorosilanes are bonded more strongly to the network than the carboxylic acids. However, the latter system is suitable for applications under dry conditions. All coatings are transparent, scratch-resistant (20 g according to Fig. 5) and show a very good adhesion to glass, ceramic and polymer surfaces (as proven in tape and cross cut tests, DIN 53151/ASTM 03359).

3.3. Coloured coating systems

As shown above, surface chemical and physical functions can be introduced into the nanocomposite systems. Another type of function, the incorporation of organic dyes into inorganic–organic sol–gel systems, basically has been demonstrated in a variety of examples [37–39]. If pure inorganic systems are used, full density cannot be achieved since the temperature stability of organic dyes, in general, is too low for the densification temperature necessary for full densification (≥ 500°C). On the other hand, if inorganic–organic matrix systems are used, the surface properties and thermostability is in the range of about 150°C. The high content of organics in some cases may be a problem if heavy mechanical impact takes place.

Investigations have been carried out [40] in order to develop systems as a compromise between the pure inorganic and the inorganic–organic Ormocer system. For this reason, compositions based on tetraethylorthosilicate and glycidyloxypropyltriethoxy silanes and/or methyltriethoxy silane have been synthesized in various ratios. These systems show a continuous transition between the inorganic–organic and the pure inorganic system by heating without the formation of cracks and without losing adhesion in the temperature range between room temperature and 500°C. In Fig. 11, a schematic diagram of the preparation of these systems is shown.
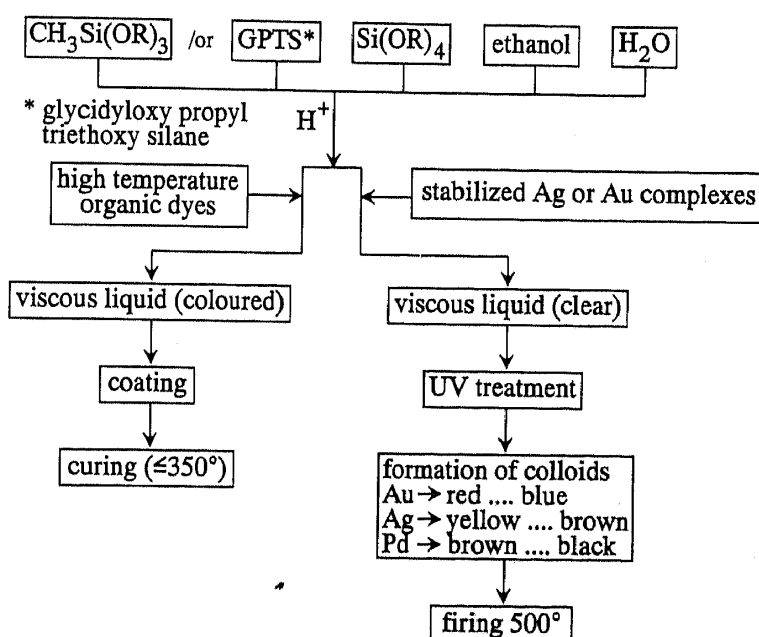

Fig. 11. Synthesis principles for dye coloured (left-hand side) and metal colloid coloured composite systems.

High-temperature-stability organic dyes such as triphenylmethane dyes, phthalocyanines or perylenes can be incorporated into these systems and fired up to 350°C. By doing this, very hard surfaces similar to those of glass and very intensive dye colours can be obtained. Since the basic system is extremely UV stable, this coating system can be used for glass coating even under outdoor conditions if the dye by itself is stable to UV [40].

Another type of colouring can be obtained by incorporation of metal colloids. Metal colloids show, due to the plasmon vibrations, extremely intensive colouration with coefficients of extinction up to 10^5. As shown elsewhere [22,41], using the method of linking metal colloids via complex formation to the backbone, colloids can be incorporated into a variety of sol-gel systems. In Eq. (2), a schematic of this type of process is given:
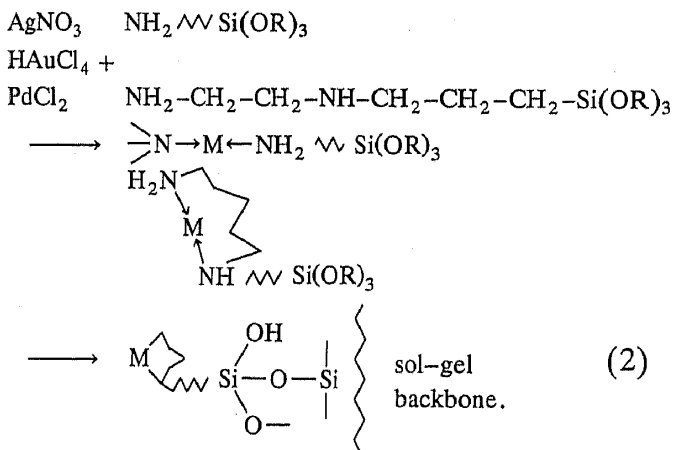
After hydrolysis and condensation, colloid growth can be initiated by UV and thermal treatment.

These systems can be densified now at temperatures up to 500°C which leads to an almost complete transformation of the matrix into SiO_2. Similar systems can be obtained using methyl group modified SiO_2 sols. In this case, thick SiO_2 layers can be fabricated [42] up to 10 μm, prepared at 500°C in a one-step coating. The methyl group reduces the particle-to-particle interaction in the sols (5-7 nm particle diameter) leading to an improved relaxation behaviour for the formation of thick films.

Using the described approach of short-chain organically modified nanoparticles (ZrO_2/SiO_2) sols, a variety of composite type systems can be obtained which can be used on glass surfaces.

3.4. Photochromic glass surfaces

In Ref. [41] it has been shown that silver colloids can be formed within inorganic-organic coating systems. These silver colloids can be transformed into silver halides by a variety of means (HCl, vapour treatment or thermal decomposition of chlorosilanes). From the point of view of the coating, it is very simple to coat glass surfaces by an Ormocer system in a dip coating process. Dip coating has been extensively described by Brinker and Scherer [43], but the ap-
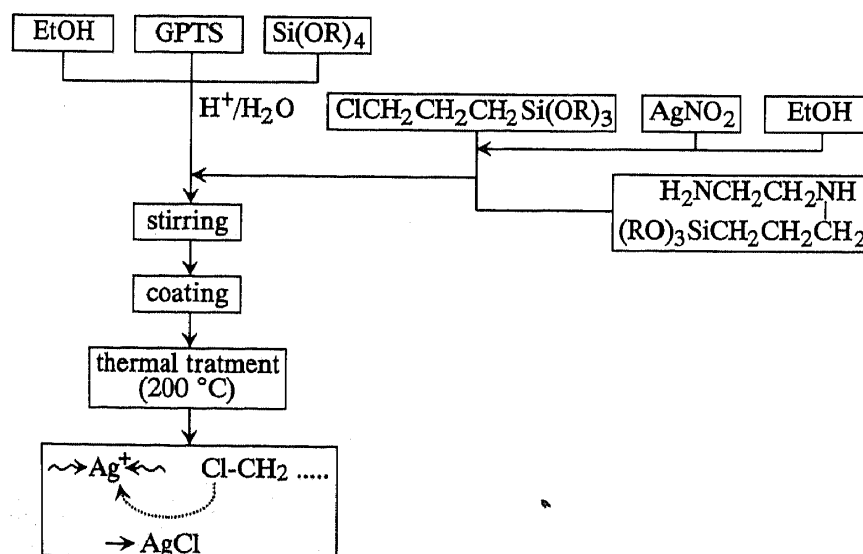

Fig. 12. Schematic diagram of the synthesis of photochromic Ormocers.

proaches there cannot be completely transformed onto Ormocer systems, because these systems more or less show polymerized structures close to polymers and the interaction between the polymeric chains and particles is different. However, as shown in Ref. [44], Levich's equation can be used for estimating coating thickness as well.

The question has been discussed whether it is possible to obtain photochromic glasses based on Ag halides using the sol–gel route. As shown in Ref. [42], this can be achieved by transforming Ag colloids into Ag halides by treatment of Ag containing porous sol–gel glasses (powders or coatings). As shown above, the stabilization of Ag^+ ions through complex formation with alkoxy silanes can be used for homogeneous distribution of the Ag^+ within sol–gel networks. Another approach is to incorporate Ag halides into Ormocer coatings, which would allow low-temperature processing. In order to avoid the halogen treatment, an intrinsic source of Cl^- has been incorporated. Fig. 12 shows a schematic diagram of the synthesis of AgCl-containing Ormocer films [45].

In Fig. 13, the bleaching/colouring behaviour is shown.

Within the tested cycles, no decay can be observed. For bleaching, 200°C has to be applied at present. So far, no sensitizers or Cl^-/Br^- mixtures have been used. After coating, the system is insensitive to UV if no temperature treatment is used to form AgCl, as shown in Fig. 12. This
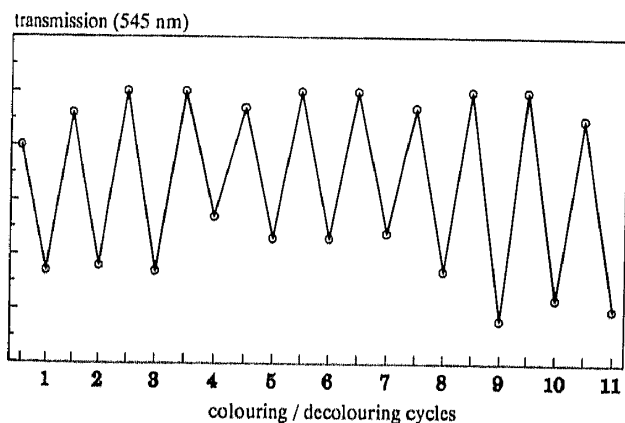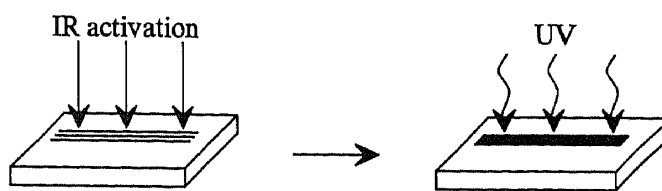

Fig. 14. Generation of photochromic patterns by IR activation.

allows the generation of dark, light-absorbing patterns by UV irradiation (Fig. 14) after heat treatment.

The particle size of the Ag colloids can be established by the amino ligand concentration, as shown elsewhere [26], leading to the model of a surface interaction controlled particle size tailoring.

4. Conclusion

It is possible to tailor surface chemistry as well as optical functions of Ormocer coatings for glass surface application. Using the concept of inorganic–organic nanocomposites, surface functional properties in combination with special mechanical properties can be obtained for a variety of applications of glass for automotive as well as for architectural glazing. The incorporation of nanocomposites can lead not only to interesting mechanical properties, but also to functional properties, if the nanoparticles are stabilized in the nano range (e.g., metal colloids). The stabilizing function of ligands can be used to obtain suitable processing properties to incorporate the colloids into transparent films. The inorganic–organic coating system, moreover, opens the possibility of obtaining thick layers which are very important for a variety of applications, especially if long-term mechanical stability or long-term effects, e.g., controlled released behaviour, are desired. The latter is based on the incorporation of releasable components such as tensides, creating a long-term wettability which cannot be obtained by surface modification with appropriate functional groupings only.

Fig. 13. Colouring/decolouring cycles of an AgCl composite coating.

References

[1] H. Dislich, Angew. Chem 83 (1971) 428.

[2] M. Aegerter, ed., J. Non-Cryst. Solids 121 (1990).

[3] L. Esquivias, ed., J. Non-Cryst. Solids 147&148 (1992).

[4] B.J.J. Zelinski, C.J. Brinker, D.E. Clark and D.R. Ulrich, eds., Mater. Res. Soc. Symp. Proc. 180 (1990).

[5] M.J. Hampden-Smith, W.G. Klemperer, C.J. Brinker, D.E. Clark and D.R. Ulrich, eds., Mater. Res. Soc. Symp. Proc. 271 (1992).

[6] J.D. Mackenzie, ed., SPIE Proc. Sol–Gel Optics II, Vol. 1758 (1992).

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

[8] B. Dunn, E. Knobbe, J.M. McKiernan, J.C. Pouxviel and J.I. Zink, Mater. Res. Soc. Symp. Proc. 121 (1988) 331.

[9] D. Levy, J. Non-Cryst. Solids 147&148 (1992) 508.

[10] L. Spanhel, E. Arpac and H. Schmidt, J. Non-Cryst. Solids 147&148 (1992) 657.

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

[12] C.-Y. Li, J.Y. Tseng, K. Morita, C.L. Lechner, Y. Hu and J.D. Mackenzie, SPIE Proc. Sol–Gel Optics II, Vol. 1758 (1992) 410.

[13] S. Motakef, J.M. Boulton, G.T. Teowee, D.R. Uhlmann and B.J.J. Zelinski, SPIE Proc. Sol–Gel Optics II, Vol. 1758 (1992) 432.

[14] P.N. Prasad, in: Ultrastructure Processing of Advanced Materials, ed. D.R. Uhlmann and D.R. Ulrich (Wiley, New York, 1992) p. 461.

[15] F. Lange, in: Proc. Int. Symp. on Molecular Level Designing of Ceramics, ed. Team of the NEDO International Joint Research Program, Nagoya, Japan, 1991, p. 14.

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

[17] G. Teowee, J.M. Boulton, H.H. Fox, A. Koussa, T. Gudgel and D.R. Uhlmann, in: Better Ceramics Through Chemistry IV, Mater. Res. Soc. Symp. Proc. 180, ed. B.J.J. Zelinski, C.J. Brinker. D.E. Clark and D.R. Ulrich (Materials Research Society, Pittsburgh, 1990) p. 407.

[18] H. Schmidt and O. v. Stetten, German patent no. 27 58 507 (28. Dec. 1977).

[19] H. Schmidt, in: Chemical Processing of Advanced Materials, ed. L.L. Hench and J.K. West (Wiley, New York, 1992) p. 727.

[20] C. Sanchez, in: Progress in Research and Development of Processes and Products from Sols and Gels, ed. S. Vilminot, R. Nass and H. Schmidt (North-Holland, Amsterdam, 1992) p. 131.

[21] M. Iwasaki, T. Burkhart, M. Mennig and H. Schmidt, in: Proc. 1st. Int. Conf. on Application and Commercialization of Sol–Gel Processing, Saarbrücken, Oct. 1993 (TransTech, Aedermannsdorf) in press.

[22] L. Spanhel, H. Schmidt, A. Uhrig and C. Klingshirn, Mater. Res. Soc. Symp. Proc. 272 (1992) 53.

[23] J. Livage, M. Henry and C. Sanchez, Prog. Solid State Chem. 18 (1988) 259.

[24] H. Schmidt, H. Krug, R. Kasemann and F. Tiefensee, SPIE Proc. 1590 (1991) 36.

[25] H. Schmidt, H. Krug, R. Kasemann, N. Merl, V. Gerhard, F. Tiefensee and S. Brück, in: Homage to Galileo, ed. P. Mazzoldi (University of Padua, Padua, 1992) p. 303.

[26] H. Schmidt, J. Sol–Gel Sci. Techn. 1 (1994) 217.

[27] H. Dunken, Physikalische Chemie der Glasoberfläche (VEB Verlag der Deutschen Grundstoffindustrie, Leipzig, 1981).

[28] H. Raedisch and W. Scholz, VEGLA, Aachen, European patent no. 0 113 111 A1.

[29] H. Schmidt and B. Seiferling, Mater. Res. Soc. Symp. Proc 73 (1986) 739.

[30] R. Kasemann, H. Schmidt and S. Brück, Bol. Soc. Esp. Ceram. Vid. 31-C, Vol. 7 (1992) 75.

[31] R. Müller, in: Proc. 1st. Int. Conf. on Application and Commercialization of Sol–Gel Processing, Saarbrücken, Oct. 1993 (TransTech, Aedermannsdorf) in press.

[32] H. Schmidt, B. Seiferling, G. Philipp and K. Deichmann, in: Ultrastructure Processing of Advanced Ceramics, ed. J.D. Mackenzie and D.R. Ulrich (Wiley, New York, 1988) p. 651.

[33] H. Schmidt, Proc. 2nd Izumi Forum – Workshop on Sol–Gel Technology in Materials Science, Osaka, Nov. 1992 (Izumi Science and Technology Foundation) in press.

[34] R. Kasemann, T. Benthien, C. Bersin and H. Schmidt, in: Proc. 1st. Int. Conf. on Application and Commercialization of Sol–Gel Processing, Saarbrücken, Oct. 1993, (TransTech, Aedermannsdorf) in press.

[35] S. Brück, master thesis, University of Saarbücken (1992).

[36] C. Bersin, master thesis, University of Saarbrücken (1993).

[37] J. McKiernan, J.I. Zink and B.S. Dunn, SPIE Proc. Sol–Gel Optics II, Vol. 1758 (1992) 381.

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

[39] L. Kador, R. Fischer, D. Haarer, R. Kasemann, S. Brück, H. Schmidt and H. Dürr, Adv. Mater. 5 (1993) 270.

[40] M. Mennig, private communication.

[41] C. Fink-Straube, PhD thesis, University of Saarbrücken (1993).

[42] M. Mennig, H. Krug, C. Fink-Straube, P.W. Oliveira and H. Schmidt, SPIE Proc. Sol–Gel Optics, Vol. 1758 (1992) 387.

[43] C.J. Brinker and G.W. Scherer, Sol–Gel Science (Academic Press, London, 1990).

[44] P. Strehlow and H. Schmidt, oral presentation at S.G.T. Symp. on Glass Strength, Harrogate, UK, May 1988.

[45] M. Mennig, H. Schmidt and C. Fink-Straube, SPIE Proc. Submolecular Glass Chemistry and Physics, Vol. 1590 (1991) 152.