Sol-gel processing - an alternative way to glasses for optoelectronics

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ABSTRACT

The sol-gel route to glass offers considerable advantages. Among these the control of composition, low processing temperatures, organical modifications of inorganic polymers leading to a new a class of glass-like materials, the processing of sols to coatings or powders, and the possibilities to structurize glasses are interesting for optoelectronic glasses. Future perspectives of sol-gel processing of optoelectronic glasses as well as some experimental results concerning the state of the art are given.

1. INTRODUCTION

During the last years glasses have found a variety of applications in the field of optoelectronics, e. g. as wave guides or laser hosts [1, 2, 3]. Concurring production techniques for glasses are conventional melting, CVD (chemical vapour deposition) or PVD (physical vapour deposition) processes, and sol-gel processing. Ion exchange at the interphase glass/salt melt is used to introduce gradients of the index of refraction [4]. Each technique has its own advantages. Melting of glasses is usually less expensive than the other techniques, but requires higher temperatures and is most suitable for bulk materials. CVD and PVD processes are applied to produce thin films or preforms for high purity optical wave guides. By sol-gel processing various glass materials have been produced, e. g. bulk glasses, porous glasses, coatings, fibres, and powders. Nevertheless, only few applications in the field of optoelectronics have been published.

2. FEATURES OF GLASSES FOR OPTOELECTRONICS

According to a survey of the literature concerning materials for optoelectronics glasses might be used for example as:

- o optical fibers for UV, VIS (visible range), and IR radiation [1],
- o microstructurized branched wave guides for optical circuits (as composites with semiconductors and metals) [5],
- o gradient index lenses [6],
- o glasses showing the Faraday effect [7],
- o laser glasses [8],
- o glasses with a high nonlinear optical constant [9], and as
- o coatings for optoelectronic devices and displays [10].

From the view point of glass science the following features play an important role: purity (especial for low loss glasses), homogeneity, structurization on a microscopic scale (e. g. for branched optical circuits), strange and new compositions (for glasses with physical effects), and the application as coatings.

The sol-gel process was used only in a few cases to produce materials for optoelectronics. Nasu and Mackenzie [9] stated that gel based composits made from porous glasses might be good candidates for materials with high nonlinear optical properties. Prasad [11] and Knobbe et al. [12] reported sol-gel derived materials as suitable hosts for organic molecules with nonlinear optical properties. Yamane reported the development of gradient index lenses [13]. More literature is available on the application of sol-gel coatings for optoelectronic devices and displays [e. g. 10]. Also electrochromic coatings have been investigated [14]. Ceramic materials like $LiNbO_3$ were processed by sol-gel technology and structurized by photolithographic processes [15, 16].

3. OUTLINE OF SOL-GEL PROCESSING

The chemistry of the process is reported in detail by [17]. Sol-gel processing means basically the synthesis of an (at least in a first stage) amorphous network in solution. The process consists of the following steps (Fig. 1.):

Dissolution of the components

The precursors used should be soluble in the applied reaction media in order to form a homogeneous solution. A large variety of components can be introduced as alkoxides, chelated complexes, hydroxides, salts, or even oxides. Silica for instance can also be introduced as colloid.

Hydrolysis of precursors

Alkoxides are the most common way to introduce networkforming components into gels. The stepwise reaction of these alkoxides with water is the source of reactive monomers or oligomers for the subsequent condensation step. For the different hydrolysis steps different reaction rates are found. Important parameters influencing the rates are solvent, temperature, complex ligands, and pH value. If more than one networkforming element is introduced by alkoxides care has to be taken that the reaction rates allow the formation of a common network. In some cases partially hydrolized precursors have to be used. One of the most important

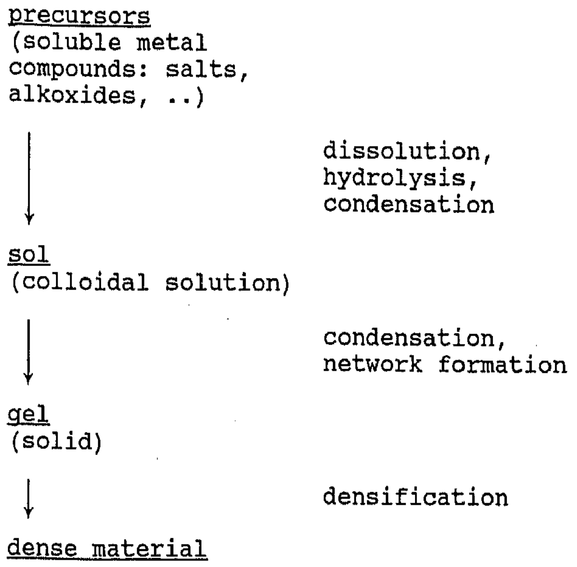

Fig. 1. Reaction scheme of the sol-gel process

parameter for the application of the sol-gel process is the viscosity of the sol, which is increasing during the network formation until the gel state is reached. Sols can be processed to coatings or fibers (depending on their viscosity) as well as spray dried to powders.

Condensation of the network (gelling)
The characteristic step of the sol-gel process is the transition of the liquid (solution or colloidal solution) into a solid (di- or multiphasic gel). This step is caused by the condensation of hydrolyzed networkforming monomers or by the coagulation of colloids (e. g. initiated by changing pH).

Densification of the gel
To obtain applicable materials the gels have to be densified in most cases. By thermal treatment (up to 150 °C) the solution is evaporated. The drying step is generally connected with shrinking. It has to be taken care to minimize strains and to avoid cracks due to nonuniform drying. Shrinkage usually constrains the size of the materials which can be obtained. Further heat treatment can be applied to drive out the residual organic components (up to 400 °C) and to fully densify the gel (temperature depends on composition). An option of the process is to leave the organic components partly in the gel. This option leads to materials with functional organic groups (e. g. hydrophilic) or to inorganic-organic polymers, which can also be regarded as glass-like materials.

4. Advantages of sol-gel processing

The sol-gel process offers some advantages:

Homogeneous mixing.
The process starts with a solution. Therefore, homogeneous mixing of precursors which are dissolvable in the same reaction medium is no problem (some restriction arise when colloidal precursors are used).

Multicomponent materials.
Most metallic elements can be introduced in varying concentrations into gels. By varying the concentrations and by introducing new components into amorphous materials various properties can be adapted like index of refraction, Abbe number and thermal expansion.

Control of impurities.
As the precursors can be purified in solution (e. g. by destillation or reprecipitation) materials with a low level of impurities can be achieved. This is especially important to avoid light absorption effects.

Distribution of dopants.
Again homogeneous mixing and the possibility to control the addition and distribution of minute amounts of dissolvable precursors allows the easy production of doped materials.

Low processing temperatures.
Conventional melting processes are limited with respect to crystallization or phase separation in the melt or with respect to the evaporation of highly volatile components (e. g. PbO, B_2O_3, alkalis). Crystallization and phase separation might be overcome by high cooling rates, but not in all cases glasses which are suitable for optical purposes are obtained. At low processing temperatures these effects can be avoided. The sol-gel process is also favourable for glasses with high melting temperatures (e. g. glasses in the system SiO_2-TiO_2).

Low processing temperatures allow also the incorporation of highly volatile components into glasses and (which is even more important) the exact control of their concentrations. On the other hand problems arise, when volatile precursors are used in the sol-gel process.

Another advantage of low processing temperatures is the possibility to use temperature sensitive substrate materials. This is especially valid for organically modified materials, which can be processed below 200 °C.

Organical modification of inorganic materials.
By introducing functional or polymerizable organic groupings one can modify the structure and properties of gels or gel-derived materials [18]. Even χ^2 (second order susceptibility) and χ^3 (third order susceptibility) materials can be processed. These

organically modified materials, often labeled ORMOCERs (organically modified ceramics), are from the structural point of view at least glass-like materials. The organic modification allows the introduction of a polymeric organic network besides the inorganic network (inorganic-organic polymers). One of the challenging features of these materials, which might be important for optoelectronics, is the initiation of the organic polymerizations by UV-sensitive starters. A second positive feature of the inorganic-organic materials is their higher resistance to crack formation during densification, which makes the formation of thicker coatings possible.

Processing in the liqid phase.

In the course of hydrolysis and condensation the viscosity of the liquid phase increases. The viscosity-time relation depends on the reaction parameters. This allows to control the viscosity by means of temperature and dilution for instance. Thin films can be produced by dip-coating or spin-on coating. The thickness of the films can be controlled by viscosity and substrate speed. Glasses, crystalline ceramics, metals, or polymers [19] were used as substrates. In each case the coating material as well as the preparation of the surface has to be optimized. Fibers can be drawn from liquids having a higher viscosity and powders can be prepared by spray drying. The solvent content of gels allows the application of diffusion processes at room temperature to obtain concentration gradients [13].

Structurization on a microscopic scale.

To structurize materials, processes have to be developed, which are able to deposit or to remove material in a spatial selective way with high resolution. In sol-gel processing the difference in leachability between densified and nondensified gels might be used. To achieve spatial selective densification or polymerization laserwriting (densification by heat) and photochemical processes (UV-starters for the polymerization of inorganic-organic polymers) are possible.

5. PERSPECTIVES FOR SOL-GEL PROCESSING IN THE FIELD OF OPTOELECTRONICS

Comparing the advantages of sol-gel processing with the demands in the field of optoelectronics some future perspectives can be identified. Sol-gel derived materials might be applied for:

- thin films or thick coatings with optical, dielectric or protective functions for displays, optoelectronic devices or optical wave guides;
- branched wave guides derived from microstructurized coatings as well as the introduction of glasses or dielectrica into structurized composites with metals or semiconductors;
- host materials for laseractive components (e. g. transition metals or organic dyes) or for nonlinear optical components.

Thin films

Various glass coatings have already been developed [20]: silica, titania, silica-titania (e. g. with 10 wt.-% TiO_2), sodium silicate (up to 25 wt.-% Na_2O), sodium borosilicate, and sodium alumoborosilicate. Additionally, refractory coatings with alumina or mullite were also realized. The coating were 0.1 to 1.0 μm thick; multiple coating was possible to reach thicker layers. The densification temperature was between 1100 (silica) and 600 °C (sodium borosilicate).

Thick coatings

With respect to optical considerations thicker coatings are necessary for wave guide applications of structurized coatings. As stated before the thickness of the purely inorganic coatings is limited by crack formation during densification. Silica bulk glasses were obtained by influencing the drying process by chemical additives [21], which is perhaps a way to achieve thicker coatings. The above cited thin films were realized with sols having an oxide content of 5 - 10 g/100 ml. The thickness of these coatings shrinks by a factor > 20 during densification. Hence, another option to achieve thicker crackfree coatings is to use sols with higher oxide contents. The disadvantage of higher oxide contents (if they are dissolvable to get a sol) is usually a higher viscosity and a shorter gelling time, i. e. the time for processing in the liquid state is rather short. Nevertheless, higher oxide contents of coating sols were realized by introducing silica in a colloidal form (Aerosil from Degussa/Hanau). Fig. 2 shows a coating obtained with such a sol. The thickness of the (not yet fully densified) coating is 1.9 μm.

With inorganic-organic polymers coating thicknesses between 2 - 20 μm were realized. The coating systems were synthesized for instance from 3-Glycidyoxipropyltrimethoxisilane, 3-aminopropylsilane, aluminium-sec-butylate, and another monosubstituted silane (e. g. propylsilane) and were developed as hard-coating for the protection of surfaces. The coatings have optical quality [19].

Microstructurization

The possibility to produce glass coatings by the sol-gel process has already been demonstrated (see above). The microstructurization of these coatings might be achieved by partial densification of the coating by means of a laser (laser writing), IR radiation, or micro waves. Those parts of the coating which are not densified will be dissolved (e. g. in water).

Inorganic-organic polymer (or ORMOCER) coatings are also canditates for microstructurization. Alternative ways to achieve microstructurized ORMOCER coatings are partial densification by heat (laser, IR, micro waves) or photostructurization. At the Fraunhofer-Institut für Silicatforschung

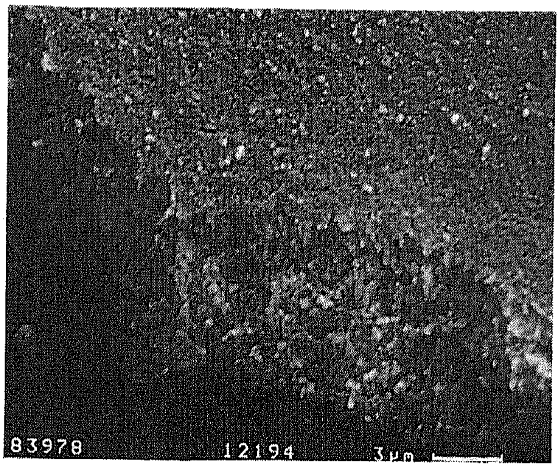

Fig. 2. SEM micrograph of a coating obtained with a sol having a high oxide content (not fully densified)

inorganic-organic polymers have been developed, which use commercial UV-sensitive photo initiators to start polymerization. Thus, photostructurization of inorganic-organic polymers seems to be possible. Fig. 3 shows a structurized coating as a first result. Due to a rough structurization technique (metal mask and UV-lamp) only a spatial resolution of about 100 µm was achieved. As the test was designed to demonstrate the possibilities of the technique further improvements are expected.

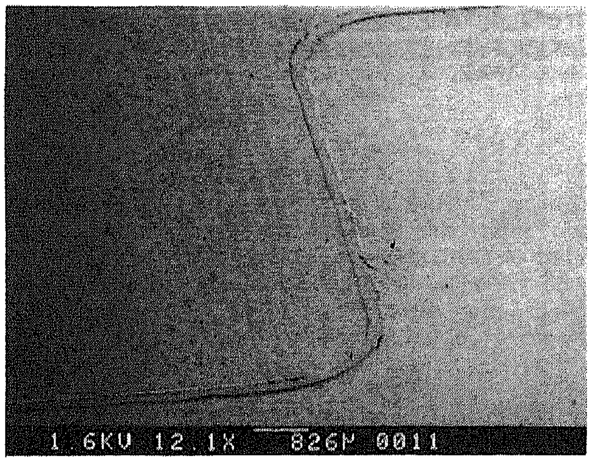

Fig. 3. SEM micrograph of a structurized ORMOCER coating

Host materials

As stated above, various inorganic or organic components can be introduced into gels, distributed uniformly, and processed to applicable materials. This should allow to produce glasses containing for instance Nd^{3+} as a laseractive ion.

The incorporation of dyes into sol-gel matrices opens a variety of opportunities, reaching from simple color filters [22] to dye molecules for photochemical hole burning processes [23].

In the case of inorganic-organic polymers it is possible to stabilize nonlinear optical molecules in the matrix, which is of special interest for χ^3 type components. The advantage of this type of matrix is the easy way to process thick films, bulk materials, or even fibers and (in contrast to most organic polymer matrices) their structural stability, which is due to the inorganic network [24].

6. CONCLUSION

The sol-gel process offers considerable advantages for the developement of glasses for optoelectronics. Until now only few results are available concerning applications of sol-gel derived glasses in this field. The exploitation of the potential of sol-gel processing especially by developing specialized coating materials and of structurization methods based on sol-gel technology should change this situation.

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