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ELECTRICAL and ELECTROCHEMICAL APPLICATIONS OF ORMOCERS

M. Popall and H. Schmidt
Fraunhofer-Institut für Silicatforschung
Würzburg (F.R. of Germany)

1. Introduction

ORMOCERs (ORganically MOdified CERamics) will be synthesized within the well established sol-gel process. Definition, mechanisme and advantages of this powerfull tool will be described first.

1.1. Definition of the Sol-Gel Process

The sol-gel process describes a chemical route to sythesize inorganic polymers like glass or ceramics via a colloidal phase in solution. The basic chemistry is known since a period of more than 140 years /1/, the systematic investigation for material development has taken place since about 25 years, starting with the preparation of ceramic powders /2/. Since about 15 years, effords to evaluate basic mechanisms are made especially using the alkoxide route and silica-containing systems /3/. The basic material forming step can be considered as a polycondensation step, where for example reactive MOH groups (M: metals like Al, Ti or elements like Si) react with other condensable groups: MX (with X = OH, OR, halogen, OCOR, NR_2 or others) to form a MOM bond, eq. (1):

$$\equiv MOH + ROM\equiv \longrightarrow \equiv MOM\equiv + HOR. \quad (1)$$

The generation of reactive "inorganic" monomers can be carried out by different ways: Hydrolysis of metal salts in aqueous solutions, eq. (2):

$$AlCl_3 + H_2O \longrightarrow Cl_2AlOH + HCl, \quad (2)$$

in buffered systems, destabilization of colloids like water glass derived silica sols by surface charge control, hydrolysis of metalorganic compounds like alkylates, acetates or alkoxides, eg. (3):

$$Si(OR)_4 + H_2O \longrightarrow (RO)_3SiOH + HOR. \qquad (3)$$

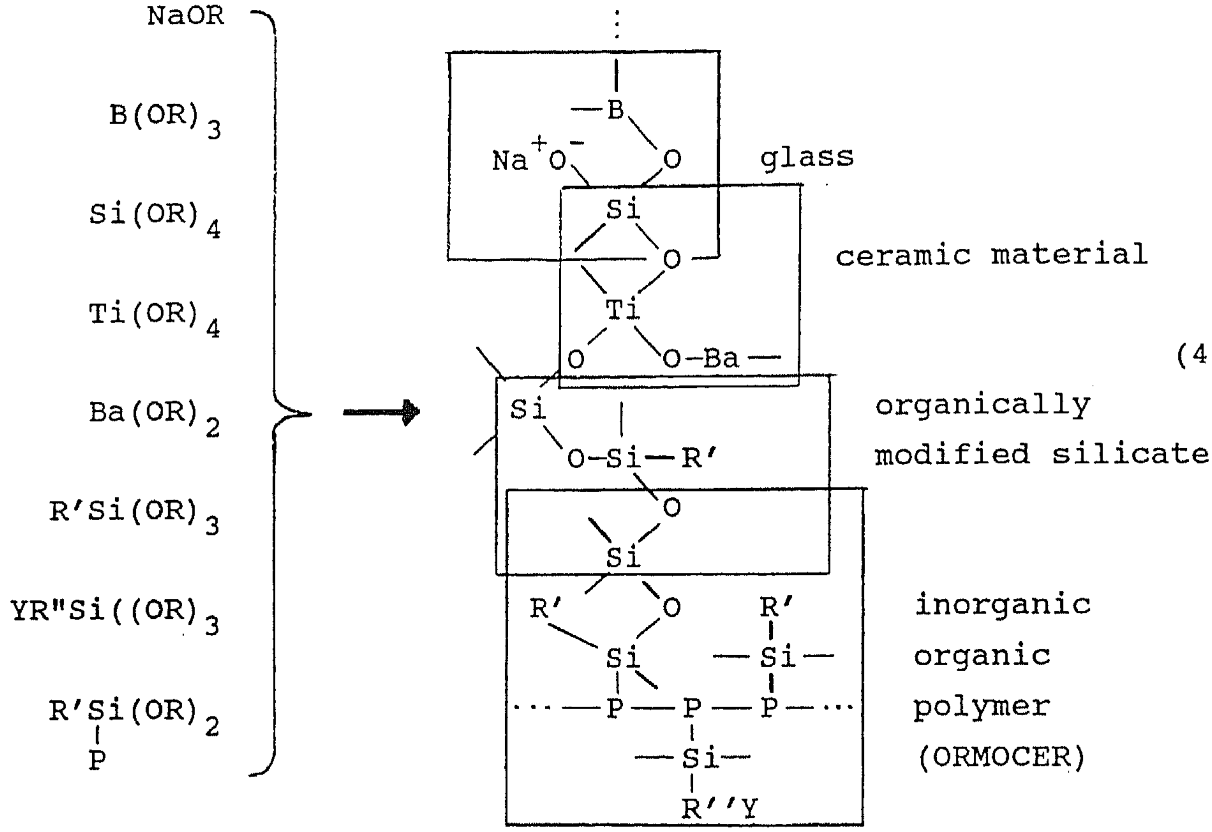
During the growth reaction, a colloid phase with particles or macromolecules in the nm range appears (sol), finally leading to a solid with a second phase within its pores (gel). During the growth step, different states of polycondensation are undergone, thus leading to liquids with viscosities to be adjusted in a wide range.

1.2. Characteristics of the Sol-Gel Process

Based on this basic chemistry, there are a series of different very typical features, which are important for the application of this technique.
In multicomponent systems, especially if low concentration components, e.g. dopants for conductivity, have to be introduced, very good homogeneities not obtainable by other procedures, stoichiometries and distributions can be achieved, which are not possible with other processes. Due to the high reactivity of the gels, ceramics and glasses can be obtained at temperatures, substantially lower than those to be used with conventional techniques. Precursors can be purified to obtain ultrapure final materials. Glasses with unusual compositions can be synthesized since the low temperature processing avoids rapid crystallization ranges. This is of special interest for alkaline-free glasses. Most compositions (glasses and ceramics) can be applied as thin (some to 100 nm) and medium thick (0.1 to several µm) films. Due to the low temperature processing, organics can be incorporated into inorganic networks, thus leading to hybrid polymers (ORMOCERs) with very interesting new properties.

2. Preparation and Processing

A survey of the variety of material synthesis within sol-gel processing is given in eq. (4) /4/:



(4)

P = polymerizable ligand (e.g. methacryl, epoxy, vinyl)
R = CH_3, C_2H_5
R'= $(CH_2)_3NH_2$, C_6H_5
R"= ion mobilisating and immobilisating ligand
Y = ions (e.g. H^+, alkalines, Ag^+ and Cu^+)

Actually, this is only a small view of the full scope. The preferred route at present is the alkoxide path, since the reaction control is more easy than in aqueous or colloidal systems.
A typical general scheme for the sol-gel process and parallel as an example the processing of an scratch resistant ORMOCER are demonstrated in the flow chart given below.

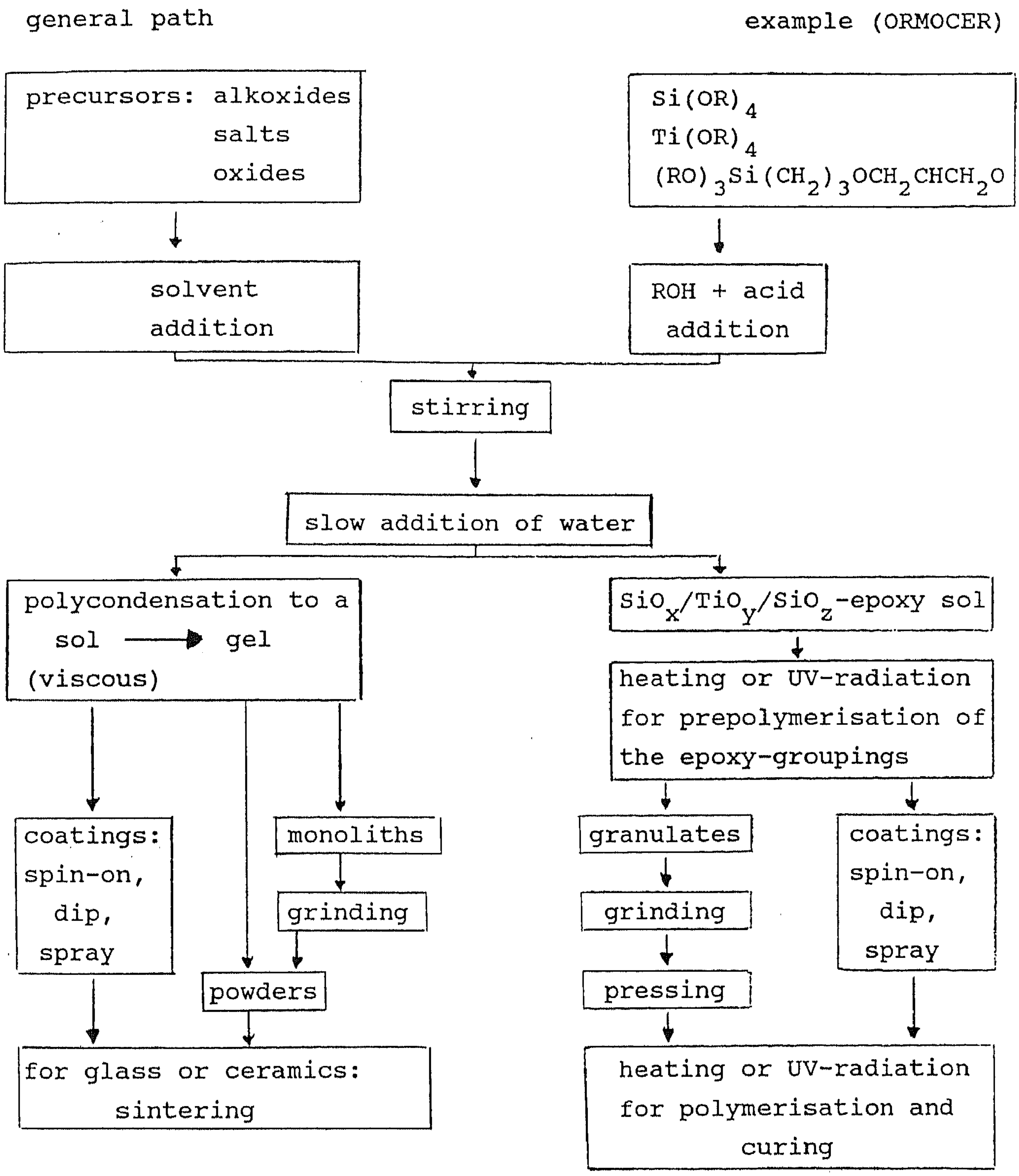


fig. 1: flow chart of sol-gel processing generally and ORMOCER - preparation as an example

3. ORMOCERs (ORganically MOdified CERamics)

ORMOCERs are inorganic-organic composites hybrids on an atomic scale and can be prepared by the sol-gel process. Organics, like polyolefines, polyethylenoxides, polymethylmethacrylates /5/ and others, can be included either by copolymerisation of the organic monomers, incorporation of soluble organic polymers, cocondensation of organic group containing inorganic units (e.g. $R'Si(OR)_3$, R'= organofunctional grouping) or combinations of these paths (see eq.4).
The materials can be prepared in different shapes: as coatings, foils, fibers, dens materials, compactable powders with porosity. Prepolymers with adjusted viscosities for different coating and fiber drawing techniques can be prepared also. The material property is variable in a wide range and depends as well on the functional groups of the silans as on the cocondensation with network formers like $Al(OR)_3$, $Zr(OR)_4$, $Ti(OR)_4$, $Sn(OR)_4$ or others /6, 7, 8/.

4. ORMOCERs and their potential for microelectronic application

These new inorganic-organic polymers allowes to establish by appropriate choice of parameters material properties like thermal resistance, chemical durability, permittivity constant (ϵ), electrical resistance, conductivity, adhesion, mechanical properties, chemical reactivity, rheology of intermediates (e.g. for coatings), curing behavior (e.g. thermal or photocuring) and photo resist properties. Since the materials contain a ceramic backbone, they can be fired to ceramics or glasses. For SiO_2, this was pointed out by Baglin /9/. Based on these properties, a promising potential arises for microelectronic applications.

4.1 ORMOCERs as coating material

First results for dielectric application show that, in combination with low ε values, high bulk resistances (up to $10^{16} \Omega *cm$), high dielectric strength (more than $10^6 Vcm^{-1}$) and temperature stabilities can be achieved. Coatings can be obtained by spin coating, dip coating and kataphoretic deposition coating procedures. The thermal resistance in the system $(C_6H_5)_2SiO(O)-Si(O_2)-(CH_2=CH)CH_3Si(O_2)$ (vinyl groups polymerized) is up to 280°C. Chemical durability and moisture resistance are exellent. The system shows a perfect adhesion to different surfaces (metals, ceramics) and can be cured by UV or heat, as desired.

Moisture protective coatings /10/ containing an inorganic diffusion barrier in form of mica or glass flakes or having special hydrophobic organic substituents have been developed which may be a good potential for microelectronics, too.

As indicated above, different types of techniques can be used for coating procedures. For thin films, the desired rheological data of sols can be established in a wide range. For dip coating, the film thickness d can be established by the Landau-Levich equation (5)

$$d = K*N_c^{1/6}*\left(\frac{n*v}{\rho*g}\right)^{1/2} \qquad (5)$$

d = thickness of the coating; g = gravitational constant; ρ = density of coating solution; K = constant; N_c = capillary number; n = viscosity; v = lifting speed.

Thus, film thicknesses ranging from 0.5 to several micrometers can be obtained in a one-step-procedure.

Based on first results, ORMOCERs containing reactive groupings like methylmethacrylates and ethylenoxides are photostructurable in a direct manner and passivation and isolation layers on selected areas seem to be available.

4.2. ORMOCERs as gassensitive layers

Selective adsorbing layers play an important role in the development of sensing devices based on microelectronic structures. The sensitive material should be able to be adapted to various problems (e.g. different gases, sensitivities or selectivities)

without varying basic compositions or procedures.
The new inorganic-organic polymers (ORMOCERs) proved to be an ideal multicomponent layer in which sensitive groupings can be easily incorporated by sol-gel processing. For the detection of SO_2 we have developed an ORMOCER-layer containing functional groups like $-(CH_2)_3-N(C_2H_5)_2$ on an interdigitated capacitance structure or a field effect transistor /11,12/. The selective formation of reversible adducts between SO_2 and the tertiary amine may cause an increase of the dielectric constant and with it a change of capacity and conductivity as shown in figure 2.

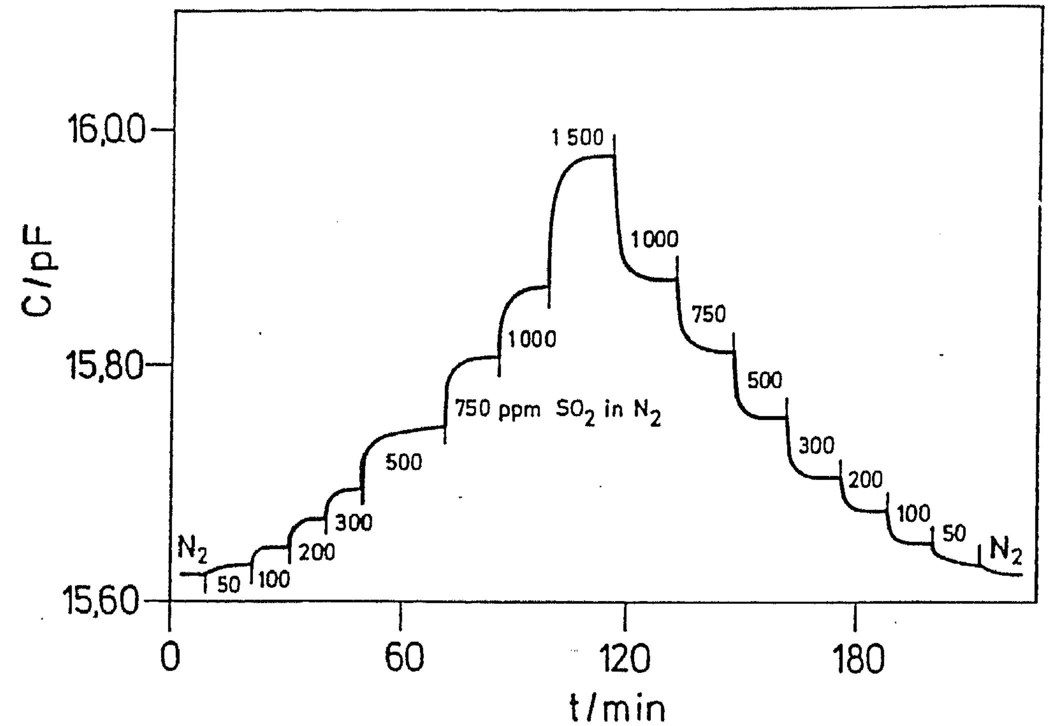


fig.2: Change of capacitance with the amount of SO_2 and time of an interdigitated planar capacitor coated with an ORMOCER

This simple and very cheap sensor configuration, yet, allowes a SO_2 detection of amounts, less than 10 ppm. Similar sensors for NO_x and NH_3 are on work.

4.3. ORMOCERs as solid ionic conductors

ORMOLYTEs (ORganically MOdified ceramic electroLYTEs) have been developed recently. First results have been published on proton

conducting "aminosils" /13/. An important advantage of these materials for electrolytes is their amorphous character up to high temperatures due to the threedimensional inorganic backbone. Mechanical (e.g. flexibility) and chemical (e.g. solubility of salts and acids) properties can be varied by the organic groupings (e.g. acids, bases, hydrophilic or complex forming groupings). Within a cooperation between the LABORATOIRE D'IONIQUE ET D'ELECTROCHIMIE DU SOLIDE (LIES) at Grenoble and the FRAUNFOFER INSTITUT FÜR SILICATFORSCHUNG (ISC) at Würzburg we are working on these new applications of ORMOCERs, the potential of this new material is not yet exploited. Conductivities within the range of $10^{-3}\Omega^{-1}cm^{-1}$ up to $10^{-2}\Omega^{-1}cm^{-1}$ for proton conductors at ambient temperatures within a first check up are a good perspective.
Applications like mini and micro batteries on microelectronic devices by standart structurising and printing techniques seem to be possible and will be only one aspect of future application.

5. Conclusion

The new inorganic-organic polymers on an atomic scale (ORMOCERs) prepared by the powerful methode of sol-gel processing can be used advantageously in microelectronics for packaging, housing, passivation, new substrates, sensors, and ion conducting systems.

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