New materials by the sol-gel-process and their potential for microelectronic application

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Neue Werkstoffe über den Sol-Gel-Prozeß und ihre Anwendungsmöglichkeiten für die Mikroelektronik


1. Introduction

1.1. Definition of the Sol-Gel Process

The sol-gel process describes a chemical route to synthesize 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; 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, efforts 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 MOM groups (M: metal like Al, Ti or elements like Si) react with other condensable groups: MX (with X = OH, OR, halogen, OOCR, NR₂ or others) to form a MOM bond (1):

\[
\text{EMOH + MOM} \rightarrow \text{MOME} + \text{HOR},
\]

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

\[
\text{AlCl}_3 + \text{H}_2\text{O} \rightarrow \text{AlCl}_2\text{OH} + \text{HCl},
\]

in buffered systems, destabilization of colloids like water glass derived silica sols by surface charge control, hydrolysis of metalorganic compounds like acrylates, annies or alkoxides (3)

\[
\text{Ti(OR)₄} + \text{H}_2\text{O} \rightarrow (\text{RO})_3\text{TiOH} + \text{HOR}.
\]

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 polymerization 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, have to be introduced, very good homogeneities not obtainable by other processes, stoichiometries and distributions can be achieved, which is 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 incorpo- rated into inorganic networks, thus leading to hybrid polymers (organically modified ceramics, ORMOCERS) with interesting new properties.

2. Preparation and Processing

A survey of the variety of Material synthesis is given via eq. (4) /4/:

\[
\begin{align*}
\text{NoOR} & \quad \text{Si(OR)}_4 \\
\text{B(OH)}_3 & \quad \text{Ti(OR)}_4 \\
\text{Be(OR)}_2 & \quad \text{R'Si(OR)}_3 \\
\text{R'YSi(OR)}_2 & \quad \text{R'Si(OR)}_2
\end{align*}
\]

\[
\begin{align*}
P & = \text{polymerizable ligand (e.g. methacroyl, epoxy)} \\
R & = \text{CH}_2, \text{C}_2\text{H}_4 \\
R' & = (\text{CH}_2\text{H}_2\text{Si})n \quad \text{C}_6\text{H}_5
\]

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 is demonstrated in the flow chart given below.

In general, ceramic processing temperatures are much lower than in the "use of corresponding oxide mixtures. For example RSi ceramics can be obtained as low as at 900 °C, compared to 1500 °C with oxides as starting materials.

1) lead zirconium titanate piez ceramic
3. Materials

The sol-gel process can be advantageously used for three types of materials:

Ceramic materials

In this case, the preparation of highly reactive powders can help to overcome the usually high sintering temperatures of ceramic bodies. For ceramic substrates, powders with a high sintering activity have to be prepared /5/. In this case, as indicated above, substantial reduction of sintering temperatures can be obtained, as shown in /6/. For coatings, gel powders can be used as a slurry and thick film or tape casting techniques can be applied. Not much work is done in this field so far. For thin film techniques, homogeneous gels can be used. There is a basic difference to physical deposition techniques: sol-gel films are amorphous after deposition and have to be crystallized by heat. The formation of crystalline phases follows the phase diagrams (thermodynamics). The films are very smooth and can equalize surface flaws. Dopants can be incorporated even in small concentrations very homogeneously and reinforcing components such as whiskers can be incorporated, e.g. in order to reinforce substrate materials. The following applications seem to be possible or are already done:

- Substrate materials (mechanical strength, low firing temperature (Al,Si, cordierite, /6/, mullite, coated metal core).

- Coatings (dielectric coatings for multilayers, thick films, thin films, active components, PZT /-9/, titanates /10/, niobates, ionic conductors, micro batteries, photosensitive ceramics, passivation, housing, active components for sensors, e.g. TiO₂, NbO₂, ZnO, ZrO₂).

As indicated above, different types of techniques can be used for coating procedures. For tape coating (e.g. PZT films), common procedures can be applied. For thin films, the desired technological data of gels can be established in a wide range. For dip coating, the film thickness d can be established by the Landau-Levich equation (5):

\[
d = k \cdot \gamma^{1/6} \cdot \frac{\rho \cdot v^{1/2}}{\rho \cdot g^{1/2}}
\]

where:
- \(d\) = thickness of the coating
- \(k\) = gravitational constant
- \(\rho\) = density of coating solution
- \(K\) = constant
- \(N\) = capillary number
- \(V\) = lifting speed.

Thus, film thicknesses ranging from 0.05 to several micrometers can be obtained in a one-step procedure.

Glasses

The preparation of glasses by the sol-gel process follows the same basic rules as described for ceramic materials. It is important that glasses can be prepared which never exceed temperatures higher than Tg. For micro electronics, especially the preparation of alkaline-free glasses is of high interest. Since these glasses tend to crystallize during cooling, glass frits can be preferably prepared by sol-gel techniques avoiding melting and high crystallization rate temperature ranges during cooling down. Thus, glasses, extremely difficult to be melted, (e.g. BaO/B₂O₃/SiO₂/Al₂O₃) /11/ can be prepared by sol-gel with desired variations of composition.

Inorganic-organic polymers

The introduction of organic groupings, e.g. by use of organosilanes (see eq. (4)) leads to mixed inorganic-organic polymers. The properties of these types of materials can be varied between almost pure inorganic materials and organic polymers. Organic groupings, linked to an inorganic backbone can act as network modifiers. If polymerizable groupings are used, they can act as network formers, too.

Thermal resistance, chemical durability, permittivity constant (ε), electrical resistance, conductiviety, adhesion, mechanical properties, chemical reactivity, rheology of intermediates (e.g. for coatings), curing behavior (e.g. thermal or photocuring), and photo resist properties can be established by appropriate choice of parameters. Since the materials contain a ceramic backbone, they can be fired to ceramics or glasses. For SiO₂, this was pointed out by Baglin /12/. Based on these properties, a promising potential arises for microelectronic applications. First results for dielectric application show that, in combination with low ε values, high surface resistances (up to 10¹²Ω·cm⁻¹) and temperature stability can be achieved. Coating can be improved obtained by spin coating, dip coating and kataphoretic deposition coating procedures. Thermal resistance in the system (C₆H₅N₃)_xSiO₁₀SiO₁₀-(CH₂=CH)-SiO₂ (vinyl groups polymerized) is up to 260 °C. Chemical durability and moisture resistance are excellent. The system shows a perfect adhesion to different surfaces (metals, ceramics) and can be cured by UV or heat, as desired.

Other systems have been developed as gas sensitive layers and can be used for gas sensors (interdigitated capacitor structures or on field effect transistors /13,14/). The sensitive groupings can be easily incorporated into the sol-gel derived multi-component layer. Materials having been developed for protective coatings on glass show a very low diffusivity for H₂O due to an inorganic diffusion barrier in form of glass or glass flakes /15/. These types of coatings seem to have a good potential for moisture protective coatings for microelectronics, too. Recently, first results have been published on proton conducting inorganic-organic polymers (amino- silsesquioxide /16/), exhibiting good conductivities (up to 10⁻¹²Ω⁻¹·cm⁻¹), good mechanical and coating properties. The potential of this group of materials is not yet exploited.
4. Conclusion

The sol-gel process is a suitable synthesis principle for the preparation of novel material and thus can be used advantageously in microelectronics for packaging, housing, passivation, new substrates, sensors, and to achieve compounds. Since the field is just at its beginning, numerous new developments can be expected.

References


/11/ Private communication.


High speed, high density packaging

F. Aldinger and S. Günther, Frankfurt/Main

Aufbautechnik mit hoher Schaltgeschwindigkeit und hoher Packungsdichte


1. Introduction

It is known that electronic systems meanwhile reached levels of capability that were never believed to be possible in the past. Yet projections for the future go even further.

As far as the technological progress of the hardware is concerned the key role is played by the semiconductor chip and its development towards higher and higher integration density. Nonetheless it is often overlooked that the hardware performance is not only governed by the capability of the semiconductor chip but also about equally by the applied packaging and interconnection technology. Actually the packaging technology is already lagging behind the rapid advancements of semiconductor technology and is now increasingly becoming a limiting factor.

For further progress in microelectronics it is therefore crucial to develop new advanced packaging concepts including new interconnection technologies and new substrates for chips and interconnections. This applies especially for the requirements of the current VLSI technology and even more for those of the upcoming ULSI and GSI technology.

Not mentioning the permanent need for the reduction of costs per unit, these emerging new integrated circuit technologies follow mainly three driving forces:

- Increase in signal processing capacity
- Increase in signal processing speed
- Space reduction

All three are logically connected among each other. They implement on hardware