

## A New Trend in the Sol-Gel Method and Thin Films from Metal Alkoxides

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### Abstract

The progress in the field of electronic materials has been especially significant for applications involving a range of electrical properties. Its importance is increasing with the increasing demand for integrated circuits.

The sol-gel technique has been used for many years, and the metal alkoxides have featured prominently as source materials. The method consist of making a homogeneous solution of the component metal alkoxides in a suitable solvent, usually the parent alcohol; and then causing the hydrolysis under controlled conditions to produce a gel containing the hydrated metal oxide. The gel is then dried, and fired to produce a ceramic or glassy material at a temperature much lower than that required by the conventional melting process.

This project consists of important theoretical considerations, processing techniques and applications related to electrophoresis derived thin films. In the electrophoretic process a metal alkoxide solution is gelled through hydrolysis-polymerization and converted the gel thin layer to an oxide by heating at relatively low temperatures.

### Introduction

Sol-gel processing is a method for the preparation of materials, which offers the possibility of a good compositional control of multicomponent systems. Sol-gel technology arose as a method of fabrication of high-quality ceramics and glasses. In recent years this technique has been extended to the fabrication of thin films on different substrates. In particular, attention has been given to the production of films of such materials as dielectrics, ferroelectrics, the high-temperature superconductors (HTS), conductive coatings of indium tin oxide, and optical and protective coatings of complex oxides [1-2]. This report will be restricted to the discussion of sol-gel processing of oxide films based on alkoxide precursors.

### Advantages of Sol-Gel

Sol-gel processing offers advantages over other fabrication techniques, such as

- homogeneity,
- stoichiometry control,
- purity,
- ease of processing,
- close control over composition and microstructure,
- lower processing temperatures,
- large-area films of desired composition and thickness can be easily formed on a substrate of complex geometry,
- low cost.

Another advantage of sol-gel processing is that, because of the solution form of the raw materials, trace elements can be easily introduced into the solution by adding the elements in the form of

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organometallic compounds. Such trace elements can be important in adjusting the microstructure or in improving the properties of oxide films. The methods of application of the film can be by: dipping, spinning, spraying, electrophoretic deposition, even painting. This allows for tailoring the process to specific requirements. The factors that determine the quality of a thin film are: 1. Film-substrate interactions, 2. Composition and structure, 3. Thickness variations, 4. Epitaxial or columnar growth, 5. Inhomogeneous nucleation, 6. Residual stress, 7. Cracking, 8. Surface roughness.

Compared to conventional thin-film forming processes such as evaporation, sputtering, or chemical vapor deposition, the cost of sol-gel film processing is low. However, the most important advantages of sol-gel processing over conventional coating methods are easier fabrication of films of complex oxides and easier control of composition and microstructure of the deposited films.

### Sol-Gel Processing

The basic principle of the sol-gel process is:

- to form a solution of the elements of the desired compound in an organic solvent;
- polymerize the solution to form a gel,
- dry this gel,
- fire this gel to displace the organic components,
- to form a final inorganic oxide.

Important and typical precursors for making sol-gel solutions are alkoxides of the general composition  $M(O-R)_n$ , where **R** is an alkyl radical ( $CH_3$ ,  $C_2H_5$ ,  $C_3H_7$  ...).

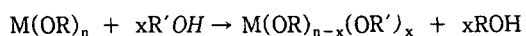
Their properties and reactions affect the preparation process and determine the product features. The precursors are dissolved in a suitable organic solvent to form the solution. In order to get a solution with high concentration of the necessary components and proper viscosity, surface tension, and boiling point, the solvent must be carefully selected. In order to obtain a suitable solution for making thin films, various properties of the solution are adjusted. Different alkoxides of different elements show a wide range of reactivity toward water which makes the

preparation of multicomponent homogeneous systems difficult and also present difficulties with premature gelation during film processing. This can be overcome by adding a chelating organic ligand into the solution to control the hydrolysis rates of the highly reactive alkoxide. Chelated solutions are more stable in air and are easy to handle in processing. In thin-film production the viscosity of the solution becomes a particularly critical parameter. This depends on concentration, the kind of solvent, the possible interactions between components of the solution.

The gelation of a solution means the formation of a network in the solution. The hydrolysis and polycondensation of organometallic compounds such as alkoxides leads to gelation. During the drying stage the wet coating is converted to a relatively dry, harder coating, and considerable shrinkage of the coating occurs. It is at this stage that problems related to film cracking and surface smoothness in the final film become most acute. The firing step converts the gel coating into a densified complex oxide film. This process includes the removal of residual  $-OH$  or  $-OR$  groups by polycondensation reactions, pyrolysis of the organic compounds or groups left in the film into carbon, oxidation of the carbon, and gradual densification of the film. In some cases a higher-temperature anneal may be required to develop desired structure in the films.

### The Role of Metal Alkoxides

In the choice of an alkoxide and a solvent, which is usually an alcohol, the reactions between the components must be taken into account [3]. Alkoxides tend to react with all hydroxy compounds resulting in the replacement of their alkoxy groups. Since alkoxides with different alkyl groups show different reactivities with water, it is possible to adjust the rate of gelation of a given alkoxide by using a different solvent. This may be due to the presence of electronegative alkoxy groups making the metal atoms highly prone to nucleophilic attack. The reaction with alcohol can be written as

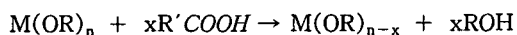


Although, in general, the facility of interchange of alkoxy groups decreases in the order methyl > ethyl > propanol > ....., even for slow reactions the interchange can generally be pushed to completion if the alcohol produced in the reaction is continuously fractionated out.

In sol-gel processing, homogeneity of the gels is very important for the further processing of material properties. However, in multicomponent systems, since different alkoxides of different elements show a wide range of reactivity toward water if the hydrolysis and condensation rates of different components are different, inhomogeneity of the gel may result. This can be solved by using chelating organic ligands to control the hydrolysis rate of the more reactive alkoxides. Chelating organic ligands such as organic acids, glycol, or -diketones are used in sol-gel processing [4]. The mechanism of stabilization is outlined in the next part of the report.

### Organic Acids and Glycols

Metal alkoxides react with organic acids according to the reaction



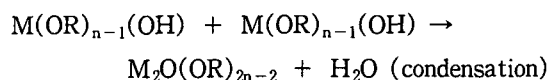
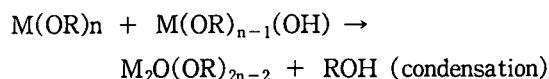
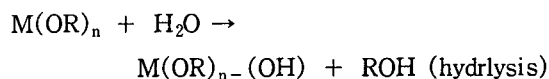
Glycols are dihydroxy alcohols and have been found to be sufficiently reactive with alkoxides to form the corresponding glycolated or mixed alkoxide glycolated derivatives. In some cases, the glycolate derivatives are more resistant to hydrolysis than their counterpart metal alkoxides. It is also very interesting in sol-gel processing that glycolate derivatives of alkoxides have the tendency to form highly polymeric derivatives compared to the analogous alkoxide derivatives.

$\beta$ -Diketones exhibit keto-enolic tautomerism. The enolic form of  $\beta$ -diketone contains a reactive hydroxyl group and these molecules react very readily with alkoxides. The same behavior can be

extended to  $\beta$ -ketoesters. The hydrolysis of the acetylacetonate complex is expected to be difficult since the chelation is stable against nucleophilic substitution. Acetylacetonate is one of the most often used  $\beta$ -diketones in the sol-gel process. It has been used to stabilize alkoxides of aluminum, zirconium, titanium [5].

### The Gelation Process

Gel or gelation (the transition from a solution into a solid) involves the hydrolysis and condensation of alkoxides. These reactions are usually written as follows:



By hydrolysis and condensation of alkoxides a polymeric product is formed, leading to the gelation of the solution. To some extent it may be possible to control the degree of gelation by using the proper amount of water. Other parameters which have been found empirically to affect the gelation process are solvent, temperature, complex ligands, and pH value, although the method and rate of water addition are also very important. There are many examples of the application of controlled hydrolysis to obtain a preferential molecular structure and a suitable viscosity of the solution in order to improve coatibility.

The homogeneity of the gels is very important since the major advantage of sol-gel processing for the preparation of oxide material is the fact that in a dried homogeneous gel, the atoms are arranged in a manner closer to that in the desired final crystalline phase than would be the case in a mixture of crystallites of the same composition. The sintering behavior is therefore improved. The

homogeneity of a gel is related to the quantity and distribution of voids within the gel and the distribution of different elements. In order to achieve maximum homogeneity, phase separation should be avoided and control of the hydrolysis rates of the alkoxides by the methods discussed previously is necessary. Prehydrolysis of slower-reacting components can also be used to obtain homogeneous multicomponent gels.

### Gel Drying Procedure

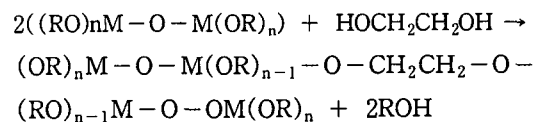
The gel consists of two phases, the network solid phase and connected pores filled with liquid phase. Initially the surface of the gel is covered with liquid phase. The liquid phase evaporates so that the solid phase is exposed. Since the solid network is wetted by the liquid phase, the liquid phase tends to cover all the solid surface and a capillary force will be imposed on the solid network. Since the gel network is compliant, the gel shrinks under capillary force as the liquid evaporates.

As the gel shrinks, its stiffness increases because the solid network is becoming more tightly bound. When the gel is too stiff to contact under the capillary force, shrinkage stops and the meniscus of the liquid phase in the pores at surface begins to recede into the interior of the gel. The menisci in the bigger pores have a greater radius of curvature so that the liquid phases in the bigger pores have higher vapor pressure and therefore evaporate faster. If the bigger pore is connected with some smaller pores, the liquid in the bigger pore will flow to the smaller pores to compensate for liquid evaporated from there, since the liquid phase in the smaller pores is subject to greater capillary force. Therefore, the menisci in the bigger pores recedes farther into the body so that bigger pores dry much faster. When the bigger pores are dry, the interior wall of the bigger pores is not subject to the surface tension of the liquid while the smaller pores around the bigger pores are still filled with liquid phase. The region with smaller pores shrinks under the surface tension and usually

causes a stress concentration at the bottom of bigger pores. The bigger pore acts as a microscopic flaw and, when the stress concentration of the pore is great enough, a macroscopic crack will develop. That is why the gels with different pore sizes are easily cracked during drying. According to the literature [6] only gel films with a thickness less than 1 m can be dried on a substrate without cracking.

Since the aforementioned stress concentration is caused by the capillary force and the variation of pores sizes, the stress concentration should be reduced by limiting the interaction between the liquid and the pore walls, and by methods which reduce the variation of the pore sizes. Several methods have been proposed for this purpose including the use of surfactants [7], drying control chemical additives (DCCA) [8], and hypercritical drying [9].

We try to solve the problem of the cracking of gel films during drying, cross-linking agents such as ethylene glycol are added to the precursor solution to introduce organic chains in the inorganic network of the gel.



The hybrid polymer obtained can then dissolve in organic solvents to form polymer solutions. The viscosity of the polymer solution can be adjusted by controlling the degree of cross-linking and by proper chelating of the alkoxides. When the solvent evaporates, a polymer film containing the desired elements forms on the substrate. Since the polymer film is a plastic or viscoelastic solid, its tendency to crack during drying and firing is substantially reduced. By this method, thick transparent oxide films of a range of oxides up to 2 m thick have been made.

The solution with a cross-linking agent loses weight gradually and a crack-free film can be easily obtained. A potential disadvantage of the added cross-linking agents is that some organics

will be strongly bound in the film after drying. However, with appropriate procedures these organics can be removed.

### Adhesion and Firing Parameters

It is important that the film adheres to the substrate during all processing steps. The main adhesion mechanism can be explained by the reactions of M-OH groups on the substrate surface with the M-OH or M-OR groups of the gel films. In order to enhance the adhesion of the film to the substrate, proper cleaning is necessary. Oxidation or the introduction of OH groups onto the substrate surface can also be used to enhance the adhesion of the film. A very thin intermediate oxide layer coated on substrates can also be used to enhance the adhesion. The firing process is strongly dependent on the gel microstructure which is determined by the conditions of gelating, aging, and drying. During firing, the dried gel film shrinks and converts to a densified oxide film.

The firing process can be identified as having several ranges. From room temperature to about 150°C, the gel film shrinks and loses weight through the evaporation of physically absorbed water and solvent and the shrinkage of the film resulting from capillary contraction. From 150°C to about 400°C, the organic residues in the film are pyrolyzed and oxidized and tiny pores are left in the film. From 400°C to about 600°C, the tiny pores in the film collapse and the film is densified. In this temperature range the film is also densified by the mechanisms of poly-condensation reactions with formation of =M-O-M= linkages and structural relaxation caused by diffusion in the polymer network. From 500°C to about 700°C, the film is densified by a viscous flow sintering mechanism. In this temperature range the larger pores in the film collapse and dense films are obtained. Since cross-linking agents are used to form a hybrid polymer solution, when the solvent evaporates the relaxation behavior of the hybrid polymer film can lead to a very dense network. Homogeneously distributed organics can be baked out under controlled conditions and the remaining

pores are very small and can easily be densified at lower temperature.

Another physical factor that has to be taken into account during firing is the mismatch of the thermal expansion coefficients of the film and the substrate. This is of particular importance during cooling after the inorganic film has been developed. A combination of film and substrate, such that the film is in compression during cooling after firing, is preferable. In present study focuses on the fabrication of preferentially oriented HTS-based thin films by controlling the structure of precursor chains in the corresponding sols prior to

Table. Applications of Sol-Gel Films

Field	Property	Examples
Electronics	Ferroelectric	BaTiO <sub>3</sub> , PZT
	Piezoelectric	PZT
	High temperature supercon-ductive films	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7-x</sub> , Bi <sub>2</sub> Sr <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>10-y</sub>
	Magnetic films	Doped iron oxide
	Transparent, conductive films	Indium tin oxide
Optics	Antireflective	TiO <sub>2</sub> /SiO <sub>2</sub> for solar cell
	Solar reflecting	TiO <sub>2</sub> /Pd
	Electrooptic	PLZT
Protective	Corrosion resistant	SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub>
	Abrasion resistant	Organic modified silicates
	Barrier films	YSZ, ZrO <sub>2</sub> for YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7-x</sub>
Biomaterials	Bone cell	Calcium apatites

the thin film deposition. Finally, film properties were characterized with respect to processing and measurement parameters such as annealing temperature/ atmosphere/rate of heating and cooling.

### Sol-Gel Thin Films Applications

A wide range of applications for sol-gel films can be perceived. Table gives examples of the various applications of sol-gel thin films.

The applications of such oxide films formed by sol-gel processing will continue to expand as better understanding of sol-gel processing, structure development and control, and structure-properties relationships is achieved and films of

higher quality are fabricated [10-12]. In principle, sol-gel processing for thin films can apply to most oxide systems. The applications of most interest are for multicomponent ceramics or where the processing technology needs to be rapid and inexpensive. In recent years, a clearer understanding of the mechanisms and chemistry involved has emerged. The great demands for high-quality oxide films in areas such as microelectronics, integrated optics, and biomaterials will promote the development of sol-gel science and technology for a wide range of oxide films.

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