

## Thin Oxide Functional Films by Metal Alkoxide Method

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### Abstract

A survey over the role of sol-gel processing and metal alkoxides in the thin film preparation is given. The basic chemistry of the sol-gel process is complex due to the different reactivities of the network forming and the wide variety of reaction parameters. Despite the important progress in the investigations of the mechanisms of thin film formation, a direct relation of reaction parameters to functional oxide properties is still very difficult.

### 1. Introduction

From new materials used for electronic applications, oxide materials are particularly noteworthy, because they are superior to single crystals and thin films in physical and chemical stability and they are easily mass-produced. Recently developed oxide materials have insulating, dielectric, piezoelectric, pyroelectric, semiconducting, and superconducting properties. Research on oxide materials for electronics is not only currently active, but will surely actively continue well into the 21-st century [1-2]. Although the oxides themselves are not all of new materials, their applications represent the development of a completely new processing technology. Some of these new processing methods will be discussed as well as some of the characteristics of the ceramic materials themselves.

Functional materials needed by modern industry can be met by ceramic that possess properties useful for electromagnetic, optical, and biochemical applications. This potential usefulness has accelerated the development of excellent materials that meet some of these current needs.

The sol-gel technique has been used for many years, and the metal alkoxides have featured prominently as source materials [3-5]. The distinction between sols and gels can be summarized as follows: a sol represents a suspension or dispersion of discrete colloidal particles; while a gel represents a colloidal or polymeric solid containing a fluid component. The most obvious features of this reaction, the transition from a liquid (solution or colloidal solution) into a solid (di- or multiphase gel) led to the expression sol-gel process. The utility of the sol-gel method for producing glass and ceramic materials in the form of powders, fibers, thin films and bulk shapes with high purity, functional microstructures and potentially high chemical homogeneity at relatively low temperature (compared to conventional processing) is now well established.

The hallmarks of the technique are its simplicity and relative inexpensiveness. The areas of material development where sol-gel processing has made its mark are many. Some broad areas [1-5] are :

**Electronic Materials:** precursor powders (fine powder for device applications), electronic coatings, thin film sensors.

**Engineering Materials:** fibers (as reinforcement materials) and composites, precursor powders (for advanced ceramics, for translucent ceramics), etc.

The method consists 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, compacted, and fired to produce a ceramic or glassy material at a temperature much lower, than that required by the conventional melting process [6]. Sol-gel processing offers advantages over other fabrication techniques, such as

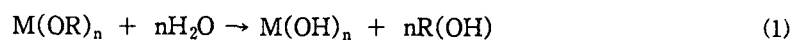
- homogeneity,
- stoichiometry control,
- purity,
- ease of processing,
- close control over composition and microstructure,
- lower processing temperatures,
- large-area films of desired composition and thickness can be easily formed on a substrate of complex geometry,
- low cost.

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 organometallic compounds. Such trace elements can be important in adjusting the microstructure or in improving the properties of oxide films [7,8]. These features are all of paramount importance in fabricating electronic ceramics. A wide range of electronic materials may be deposited by using the sol-gel process and the literature is voluminous. Usually  $\text{Si(OR)}_4$  [9,10] and  $\text{Ti(OR)}_4$  [11,12] alcohol solutions were used to obtain thin amorphous oxide films. On the other hand, more and more attention is being attracted now by complex oxide films, which characteristics being strongly dependent on the peculiarities of their structure. However, the problem of crystallization in the thin films obtained from solutions remained unsolved. It is well known, that in the course of the crystallization of such films their smoothness and continuity is frequently destroyed. Our main idea is to understand the microstructure - processing - property interrelationships with a view towards prediction of oxide systems with good functional properties.

## II. General Considerations

Metal alkoxides, among the metal-organic compounds, are of particular interest to inorganic material scientists. Alkoxides of almost any metal can be synthesized, and those of group III and IV metals - which encompass a large portion of the glass and ceramic compositions - are available commercially at relatively low cost.

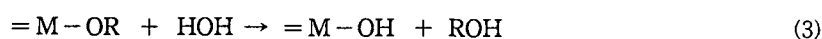
Thermal degradation of metal alkoxides produces highly reactive oxide materials with particle sizes below 100 Å. When brought into contact with water, these materials hydrolyze vigorously, forming metal hydroxide and oxide powders:



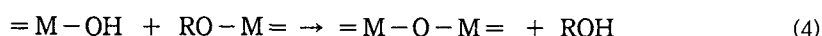
It is latter reaction that makes the alkoxides rather unusual in the pursuit of formation of ceramic materials by chemical polymerization.

The hydrolysis reaction shown in equation 1, although frequently adequate, is oversimplified. Actually, there are two simultaneous reactions involved in the hydrolysis of metal alkoxides:

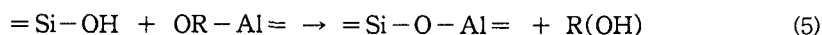
Hydrolysis:



Polymerization:



Where M is a metal with three valence, for example. Both reactions between the OH and R groups occur concurrently. The second reaction, however, by creating an oxygen bridge between two metal ions, leads to the formation of an oxide network. Under normal circumstances, the growth of this network is limited, that is, condensation occurs in particles whose diameter is 20 to 50 Å. The internal oxide network of these particles is framed by hydroxyl, organic groups. However, if the kinetics of the hydrolysis and polymerization reactions can be controlled, it is possible to form an extended oxide network. This yields a *monolithic material in almost all oxide systems*. The extent of polymerization depends on the relative rates of reactions (3) and (4) which, in turn, are determined by the type of alkoxide, availability of water, dilution of the system, reaction temperatures, et. Chemical polymerization in these systems eventually leads to gelation, and the nature of such gels is fundamentally different from that of the gels produced in colloidal systems [3]. One other relevant aspect of chemical polymerization is that, once the soluble intermediate species are formed, polymerization of complex compositions, which are homogeneous at the molecular level could be achieved. For example, partially hydrolyzed ethoxysilanol can be reacted with aluminum alkoxides to give desired compositions:



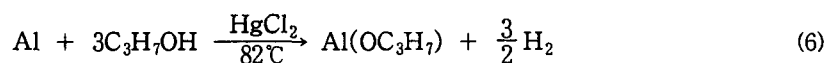
The occurrence of this type of reaction at room temperature allows the thermal stabilization of ceramic materials, which cannot be stabilized by conventional ceramic forming processes. In the metal alkoxide process, a metal alkoxide solution is gelled through hydrolysis-polymerization and converted to an oxide glass by heating at relatively low temperatures.

Coating film can be prepared by this method. The most noticeable advantage of the metal alkoxide process is the low temperature of heating; heating up to several hundred degrees is often sufficient to obtain product. This paper discusses the preparation of thin sheets of several tens of microns in thickness and very thin coating films of less than one micron in thickness from metal alkoxide sols.

Electrophoretic deposition of the complex alkoxide sol on a metal plate is the new method. The requirements to be satisfied by the metal alkoxide solution for the formation of sheets in this technique were examined. The films were then heated to convert the gel film to glass or ceramics. The requirements to be satisfied by the solution for preparing uniform, strong coating films by factors affecting thickness and other properties of the films were examined.

#### a) Synthesis of Metal Alkoxides

Aluminum tris isopropoxide was prepared by a reaction reported by Bradley [13]. Metal foil of 99.999 + % purity was reacted with excess isopropyl alcohol using a small amount of  $HgCl_2$  ( $10^{-4}$  mol/mol of metal) as a catalyst:



A starting solution (Solution A) consisting of aluminum tris isopropoxide and  $\text{C}_3\text{H}_7\text{OH}$  were employed to make thin sheets by the electrophoretic method.

#### b) Electrophoresis

Electrodeposition of organic coatings has found wide spread industrial application during the past ten years. The rapid worldwide acceptance of electrodeposition - usually called "electrocoating" - is due to many advantages. They are: obtaining an uniform and dense coating, controlling easily the coating thickness by the deposition voltage and deposition time, obtaining various shapes and sizes of coating on various substrates.

Usually, electrically charged, colloidal dispersed particles are attracted by the electrode of the opposite polarity in an electric circuit. Electrocoating materials will also require other special properties, which are enumerated below. First, the film former must be compounded to form dispersions of macro-ions from which films can be electrodeposited. Second, these films must volatile at temperatures below the softening point of the ceramics. Third, the metal alkoxide must cause high electrical resistance during the deposition process. Fourth, the metal alkoxide must be compounded to give a coating bath, which remains stable over long periods of agitation, etc. The solution was hydrolyzed at 40 or 80 °C by air humidity. The possibilities of formation the thin sheet was checked by scooping the solution. No sheet was formed when the viscosity of the solution was low. When the hydrolysis-polymerization does not proceed sufficiently, the thin sheet can be formed, but is broken immediately after its formation, probably due to abrupt shrinkage of the sheet caused by a marked, rapid vaporization of water and alcohol. Thin sheet formation becomes possible when the solution reaches viscosity ranging from 10 to 15 cP. The thin sheet displays an elastic character at the early stage of gelation, then becomes gradually rigid. At the same time, the thin sheet shrinks in area. On further increase in viscosity, the solution scooped by the foil forms a bulky mass, which makes thin sheet formation impossible. The gel sheet thus prepared becomes a transparent  $\text{Al}_2\text{O}_3$  glass sheet, 0.10 - 0.40 m thick, on heating to 300-400 °C. No crystalline peak was detected in the X-ray diffraction pattern of the products.

#### c) Gel formation

The major distinction of the present work lies in the method of accomplishing the hydrolysis reaction. In our case, water is not added to the system. Instead of the metal alkoxide complex/alcohol solution is exploited by the electrophoretic deposition in order to prepare thin solid films. Gels prepared by hydrolysis of metal alkoxides during electrophoretic deposition at room temperature and standard atmospheric pressure are generally porous and contain water and alcohol (Fig.1). When the gels are heated, they liberate the (water+alcohol) and convert into the nonporous impervious glasses. The preparation of the transparent  $\text{Al}_2\text{O}_3$  coating films by the sol-gel method was reported in [14].



Fig.1. (a, b) Formation of gel net during electrophoretic deposition on charged electrode.

d) Hydrolysis, condensation and homogeneity

Many variables, such as composition of starting materials and low or big water content affect the gels produced during the sol-gel transition. The rheological property of a sol may provide information on sol and gel structures. During electrophoretic deposition, viscosity changes near the electrode position. In the case of electrode gel the results exhibits Newtonian flow behavior and spinnability at viscosity higher than 18 Poise, while the "open system" exhibits no spinnability. It has been found that the viscosity of electrode gel and as-prepared "open system" was changed against "aging time" of alkoxide complex at 25 °C. The viscosity of "aged" alkoxide electrode gel increased rapidly within a short time showing a rapid gelation whereas the "open system" of alkoxides shows much slower gelation. It seems that long-shaped structures or linear polymers are developed in the pH electrode gradient with a low water content (from air moisture) during electrophoresis of mixed alkoxides. On the other hand the "open system" with the same mole % of alkoxide and water does not contain chain-like or one dimensional structured polymers near gelling point.

e) Aging, drying, processing

The surface microstructure of the film, particularly surface roughness, is shown in Fig.2. The surface of the film using as-prepared sol (Fig. 2 a) is of finer texture compared to the surface obtained using the 24-h solution (Fig. 2 b). The reason for this difference in microstructure is likely caused by the difference in the extent of hydrolysis of  $Al(OR)_3$  alkoxide solutions.

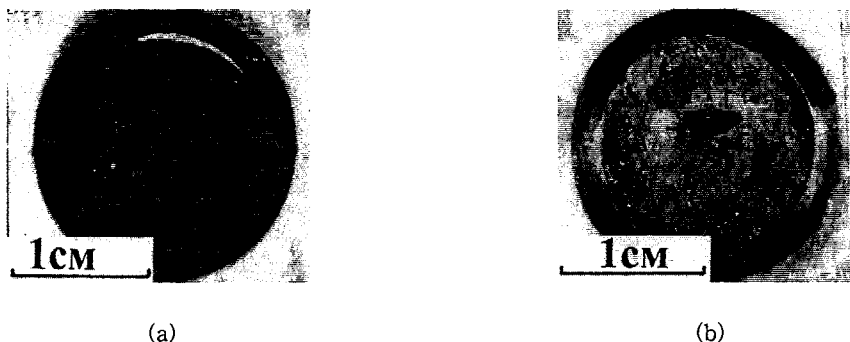


Fig.2. Microstructures of film surfaces from (a) as-prepared sol and (b) 24-h sol (bar =1 cm)

The influence of the following conditions on the quality of the films was studied: (a)concentration of the solution, (b)successive operations of electrophoretic deposition and thermal treatment, (c)the presence of moisture traces in the solution and the "age" of the solution, that is the time passed from its preparation to the moment of utilization. The quality of the films was controlled by scanning electron microscopy (Jeol - 2). The details of the procedure are summarized in Table.

We investigated the application of these films to other substrates. Brilliant transparent and colorless and strongly adherent films were obtained on Pt, Al and stainless steel foils. In the case of Al and stainless steel foils, particularly, it is observed that the color is like gold, because of the addition of reflective light from the substrates. All films obtained from solutions with concentration more than 10 wt.% crack during crystallization (d). The same phenomenon is observed when a few amorphous layers, applied without thermal treatment after each layer, undergo crystallization. High-quality crystalline films can only be obtained from diluted solutions (1 to 5 wt.%). Such solutions lead to the formation of films with a thickness 200 to 300 nm which survive crystallization without cracking.

Table. Conditions of Al<sub>2</sub>O<sub>3</sub> film preparation on Pt foils and room temperature properties

Al <sub>2</sub> O <sub>3</sub>	(a)	(b)	(c)	(d)
"Age" of sol	1h	8h	24h	1 week
Particle size, nm	3-5	10-15	30-50	> 100
Heat-treatment °C,30min	400	450	450	450
Present phases	amorphous	amorphous + $\delta$ -Al <sub>2</sub> O <sub>3</sub>	Amorphous + Crystalline	Crystalline + amorphous
Thickness, nm	1300	1500	1500	1500
Resistivity, Ohm · cm	$7 \cdot 10^{10}$	$9 \cdot 10^8$	$10^7$	$10^6$
Electric strength. $10^7$ V/m	4.5	3.9	3.0	2.1

In order to obtain thicker layers, application should be repeated with obligatory heat treatment at 400 °C for 15 min the crystallization conditions for a thin film.

Utterly different types of defect in the crystalline films are caused by the existence of hydrolysis products in the precursor alcohol solutions. Insufficient drying of the solvent or prolonged storage of the diluted solutions before their utilization lead to the formation of "bubbles" (50 nm in depth) in the layer (b).

The addition of a very small amount of water containing alcohol leads to a significant increase in the quantity of "bubbles", and application of the same solution a week after the addition of water spoils the surface completely (c). At the same time, application of a freshly prepared solution in ethyl alcohol subsequently leads to the formation of films without any "bubbles".

The amount of air moisture, as well as the "age" and types of alkoxides and solvents and also the electrophoresis conditions should be considered to investigate the structure development during the sol-gel transition. Different age sols may be, as precursors, for composite Al<sub>2</sub>O<sub>3</sub> films with different crystalline structure of  $\delta$ -Al<sub>2</sub>O<sub>3</sub> whiskers as reinforcement materials (Fig.3).

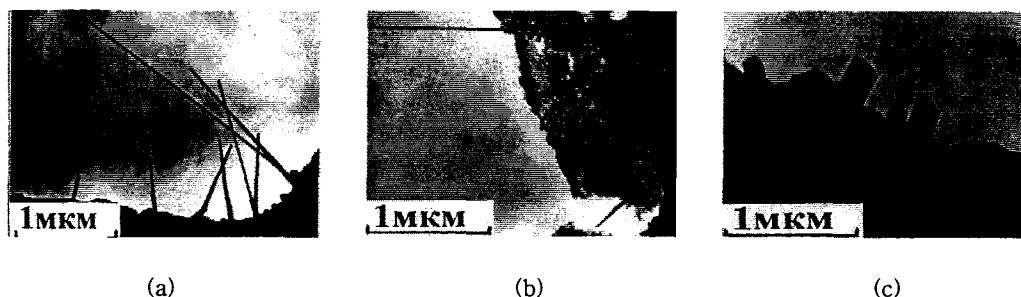


Fig.3.  $\delta$ -Al<sub>2</sub>O<sub>3</sub> whiskers as reinforcement materials in the composite films using by electrophoresis different age sols: (a) from 2 to 4 h, (b) from 4 to 8 h, (c) more than 24 h (bar=1 $\mu$ m).

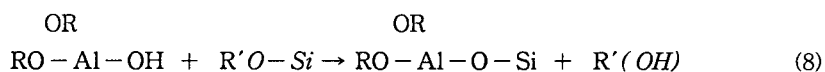
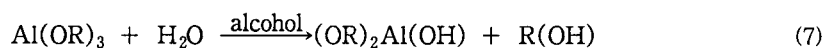
Here we may draw the following conclusions to the electrophoretic deposition and preparation of thin alumina films:

- Using a sol-gel process, transparent films of Al<sub>2</sub>O<sub>3</sub> were prepared by electrophoretic deposition 1300-1500 nm in thickness.

- The coating films using the as-prepared (fresh) sol appeared more transparent and had stronger dielectric properties compared with the coating obtained from the 24-h sol.
- The electron diffraction analysis showed that the alumina film from "fresh" sol was amorphous, and the heat-treated gels from 24-h sol were crystallizing.

### III. Role of Organic and Material Science

Organic in sol-gel processes may play different roles. Concerning precursors, the organic groupings of alkoxides lead to solubility in organic solvents. In all methods of producing monolithic films, the chemical polymerization of metal oxide is accomplished by use of metal - organic compounds. One alkyl in the alkoxide molecule is converted to a hydroxyl group by partial hydrolysis and reacts with the alkyl groups of the other alkoxide, as shown in Eqs. (7), (8):



The resultant material contains Si and Al bound via oxygen. Excess water in alcohol must be accompanied by the addition of acid to act as a peptizing agent, preventing the agglomeration of large particles. The organic groups in general are removed during hydrolysis, but very often not completely, and this can cause problems (e.g. carbon formation by pyrolysis). Once the clear liquid precursor is obtained, it can be applied to a substrate by any liquid application method, e.g., dipping, spraying, electrophoretic deposition, etc. Almost any substrate can be used, so long as the thickness of the coating is kept below a critical value, e.g., less than 1  $\mu\text{m}$ , which varies slightly from one substrate to another. Heat treatment at the temperature more than 400  $^{\circ}\text{C}$  converts the film to an essentially organic-free amorphous oxide; upon further heating above 600  $^{\circ}\text{C}$  crystal phase takes place (Fig. 4). A significant change of the film density takes place in the crystallization process, thus leading to strict requirements as to the thickness of the film, which can survive crystallization.

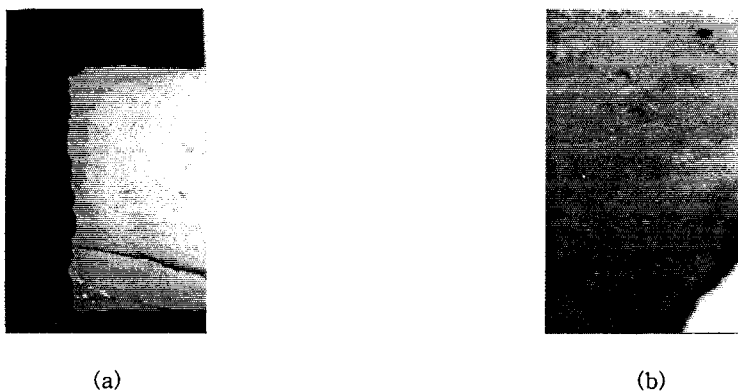


Fig.4. Transparent, amorphous film (a), containing  $\text{Al}_2\text{O}_3$ , is prepared by heating the electrophoretic gel to 400  $^{\circ}\text{C}$ . When further heated to 600  $^{\circ}\text{C}$  for 1 hr, film transforms to polycrystalline (b). These flakes of material have been separated from their platinum substrates

#### IV. Conclusions

The role of chemistry for the steps after gelation may not look very important but there are some interesting aspects especially with respect to homogeneity and purity. Other chemical reactions may occur during drying, like the transport of alkalines; this can lead to carbonate formation, it transported to the surface and affects homogeneity strongly.

One can conclude from this that for material synthesis in most cases only a limited number of variation parameters can be investigated and it is necessary to find out the important parameters with respect to the desired material properties (e.g. thin film parameters). In order to attain these objectives experience with sol-gel chemistry is still indispensable. But this field of material development not be restricted to chemistry. The research is interdisciplinary. It involves, in many cases, besides chemistry: chemical engineering, material science, physics or even computer science.

#### References

1. C.J.Brinker, D.E.Clark, D.R. Ulrich (eds.), Materials Research Society Symposia Proceedings, Vol.32, *Better Ceramics through Chemistry*, North-Holland Publishing Co., Amsterdam, The Netherlands, 1984.
2. H. Matijevich, in: *Science of ceramic chemical processing*, eds. H.L. Hench and D.R. Ulrich . Wiley, New York, 1986, pp. 463-470.
3. H. Schmidt, Chemistry of material preparation by the sol-gel process, *J. Non-Cryst. Solids*, vol. 100, 1988, pp. 51-64.
4. J.D. Mackenzie, Application of the sol-gel process, *J. Non-Cryst. Solids*, vol.100,1988,pp.162-68.
5. R.Roy, Ceramics by the solution-sol-gel route, *Science*, vol. 238, 1987, pp. 1664-69.
6. J.D. Mackenzie, Nonlinear optical materials by sol-gel method, *J. Sol-Gel Sci. Tech.*, vol. 1, 1993, pp.7-19.
7. 4. L.M. Sheppard, Advances in processing of ferroelectric thin films, *Am. Ceram. Soc. Bull.*, vol. 71, N.1, 1992, pp. 85-95.
8. S. Hirano, T. Yogo, K. Kikuta, W. Sakamoto, Processing and Characterization of thin films from metal alkoxide derived gels, *J. Sol-Gel Sci. Tech.*, vol. 2, N.1-3, 1994, pp.329-34.
9. Y. Chujo, H. Matsuki, S. Kure, T. Saegusa, T. Yazawa, Control of pore size of porous silica by means of pyrolysis of an organic-inorganic polymer hybrid, *J. Chem. Soc., Chem. Commun.*, 1994, pp. 635-36.
10. N. Korobova, The metal alkoxides as source materials in the sol-gel technique. Book 1.*Aluminum silicate sol-gel materials: ceramics and thin films*, Almaty, 1997, pp. 110.
11. T. Hashimoto, T. Yoko, S. Sakka, Sol-gel preparation and third-order nonlinear optical properties of TiO<sub>2</sub> thin films, *Bull. Chem. Soc. Jpn.*, vol. 67, 1994,pp. 653-60.
12. J.L. Keddie, P.V. Braun, E.P. Giannelis, Interrelationship between densification, crystallization and chemical evolution in sol-gel titania thin films, *J.Am.Ceram.Soc.*,vol 77, N.6, 1994, pp.1592-96.
13. D.C.Bradley, R.C. Mehrotra, D.P. Gaur, *Metal Alkoxides*. Academic Press, London, U.K., 1978, pp. 50-51.
14. N. Korobova, Deawha Soh, Aluminum oxide film using electrophoresis, *J. RIIT*, vol.16, 1997,pp. 380-82.