Dielectric Al$_2$O$_3$-SiO$_2$ Films from Metal Alkoxides

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Abstract

The preparation of Al$_2$O$_3$-SiO$_2$ thin films from less than one micron to several tens of microns in thickness had been prepared from metal alkoxide sols. Two methods, dip-withdrawal and electrophoretic deposition, were employed for thin films and sheets formation. The requirements to be satisfied by the solution for preparing uniform and strong films and by the factors affecting thickness and other properties of the films were examined. For the preparation of thin, continuous Al$_2$O$_3$-SiO$_2$ films, therefore, metal-organic-derived precursor solutions contained Si and Al in a chemically polymerized form has been developed and produced in a clear liquid state. In the process of applying to substrates, this liquid left a transparent, continuous film that could be converted to crystalline Al$_2$O$_3$-SiO$_2$ upon heating to 1000℃. And, a significant change of the film density took place in the crystallization process, thus leading to the strict requirements as to the film thickness, which could survive crystallization.

Keyword

Al$_2$O$_3$-SiO$_2$, Alkoxide, dip-withdrawal, electrophoretic deposition, thin films

1. Introduction

The progress in the field of electronic materials has been especially significant for applications involving a range of electrical properties, such as insulating and dielectric properties. Its importance is increasing with the increasing demand for integrated circuits (IC). Ceramics used as insulators in electronic circuits must possess the following properties: (1) mechanical strength for chip construction, (2) good insulation without bulk, (3) inertness to other electronic elements, (4) compatibility with metal conductive materials, (5) stability in a chemical atmosphere, and (6) high thermal conductivity for heat removal. Al$_2$O$_3$-SiO$_2$ almost satisfies these properties.

The sol-gel technique has been used for many years and the metal alkoxides and alkoxysilanes have featured prominently as source materials. 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. The advantages of the sol-gel process reside in the high purity of the metal alkoxide precursors, the homogeneity of the components at the molecular level, and the low processing temperature. These features are all of paramount importance in fabricating electronic ceramics.

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 temperature [1]. The most noticeable advantage of the metal alkoxide process is the low temperature of heat treatment. Heating up to several hundred degrees is often sufficient to obtain product. This paper discusses the preparation of dielectric Al2O3-SiO2 films of several tens of microns in thickness and very thin coating films (less than one micron) from metal alkoxide sols.

Two methods were employed for thin sheet formation. In the first method the sheet was formed in a thin metal foil by putting the foil into the solution and pulling it up. Electrophoretic deposition of the complex alkoxide sol on a metal plate is the second method [2]. The films were then heated to convert the gel film on substrate to glass or ceramics. The requirements to be satisfied the solution for

preparing uniform, strong coating films by factors affecting thickness and other properties of the films were examined.

2. Experimental Procedure
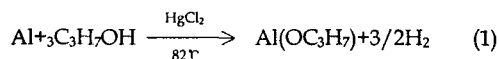
2.1 Powder preparation
: Stoichiometric Aluminum Silicate

Since the studies of phase relation in the Al_2O_3-SiO_2 system by Bowen and Greig [3], considerable effort has been directed toward the synthesis of polycrystalline stoichiometric mullite with the composition $3Al_2O_3 \cdot SiO_2$. In the usual method of preparing mullite, kaolinite and related materials are thermally decomposed to mixed oxides [4]. The major problem is that, regardless of the starting Al_2O_3-SiO_2 ratio (in the range from 3:2 to 2:1), sintering the powder in the absence of a liquid phase produces mullite of 3:2 composition with a chunky granular habit, whereas rapid cooling from the liquid phase forms a 2:1 composition with a needlelike habit. Many authors concluded that the compositions attempted so far produce nonstoichiometric mullite. Invariably the product contains excess SiO_2 or Al_2O_3 as a second phase.

This method was applied to the preparation of mullite powder with a composition of $3Al_2O_3 \cdot 2SiO_2$ from metal alkoxides.

2.2 Synthesis of Metal Alkoxides

Aluminum tris isopropoxide was prepared by a reaction reported by [5]. Metal Al foil of $99.999 + \%$ purity was reacted with excess isoproply alcohol using a small amount of $HgCl_2$ (10^{-4} mol/mol of metal) as a catalyst:

$$Al + 3C_3H_7OH \xrightarrow[82\,\text{℃}]{HgCl_2} Al(OC_3H_7) + 3/2H_2 \qquad (1)$$

Silicon tetrakis isopropoxide was formed by the methods of Bradley et al. [5]:

$$SiCl_4 + 4C_3H_7OH \xrightarrow{82\,\text{℃}} Si(OC_3H_7)_4 + 4HCl \qquad (2)$$
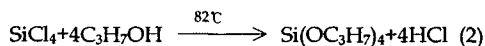
The 99.95 % SiCl4 was used as-received. Analytical grade isopropyl alcohol was dried over CaH_2 and fractionally distilled at its boiling point.

2.3 Powder Preparation and Analysis

The mixed oxide containing 71.8 wt% Al_2O_3 and 28.2 wt% SiO_2 was prepared by the hydrolytic decomposition of a solution of the corresponding metal alkoxide. Aluminum tris isopropoxide was added to a stoichiometric amount of silicon tetrakis isopropoxide. The mixed alkoxide were refluxed in excess isopropyl alcohol for 16h before hydrolysis to ensure thorough mixing. The hydroxyaluminosilicate was prepared by slowly adding the alkoxide solution to ammoniated triply distilled deionized water according to the reaction:

$$6Al(OC_3H_7) + 2Si(OC_3H_7 + xH_2O \xrightarrow{H2O+NH_3} 2Al_3Si(OH)_{13} \cdot H_2O + 26C.H_7OH \qquad (3)$$
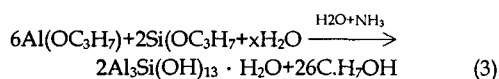
The resulting hydroxyaluminosilicate was repeatedly washed with dry isopropyl alcohol and dried in vacuum at 60℃ for 16h:

$$2Al_3Si(OH)_{13} \xrightarrow{vacuum} 3Al_2O_3 \cdot 2SiO_2 + 13H_2O \qquad (4)$$
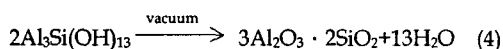
At this stage in the preparation, the mixed was amorphous to X-ray diffraction. Quantitative analysis for the Al_2O_3-SiO_2 ratio and emission spectrographic impurity analysis was performed.

2.4 Crystallite Growth and Morphology

The powders as-prepared and calcined at 600℃ statically for 1h and 24h and dynamically for 24h were examined by electron microscopy. The powders were dispersed ultrasonically in a solution of absolute ethyl alcohol; a small amount of the dispersion was then placed in a Freon nebulizer and sprayed into a carbon substrate on a Cu mesh screen.

In the alkoxy-derived mullite at near-room temp-erature condition and calcined to higher temperatures, the needlelike morphology of the crystallites is retained in the absence of a liquid phase, contrary to the findings of previous investigators. The intimate mixing of highly active fine particulates in the alkoxide decomposition process described is apparently responsible for form-ation of the acicular morphology which is characteristic of crystalline mullite.

2.5 Lattice Parameters

Minor compositional changes and different thermal histories of mullite samples result in a significant variation in the observed cell dimensions of the orthorhombic crystal structure. These variation result mainly from the many possibilities for Al-Si order-disorder [6].

Debye-Scherrer X-ray diffraction data were obtained for alkoxy-derived aluminum silicate with a nominal composition of 3Al$_2$O$_3$·2SiO$_2$ heat-treated at 600℃ for 15 and 30 min. These data were used to compute the lattice parameters and theoretical density of mullite as listed in Table 1. The unit-cell volume of the specimen fired at 600℃ for 30 min is larger than that of the specimens with the same composition fired at 650℃ for 15 and 30 min. This behavior may result from an amorphous phase and disorder still present in the microstructure at the lower firing temperature. This point is discussed further.

Table 1. Lattice parameters of aluminum silicate (mullite)

a$_0$ (Å)	b$_0$ (Å)	c$_0$ (Å)	V(Å^3)	Density (g/cm^3)
7.528±0.0042	7.685±0.0043	2.879±0.0016	166.56	3.18
7.525±0.0021	7.680±0.0022	2.878±0.0008	166.32	3.19
7.530±0.0016	7.681±0.0016	2.876±0.0006	166.34	3.19

2.6 Starting solution preparation

The starting solution (Solution A) consisting of aluminum tris isopropoxide and a stoichiometric amount of silicon tetraethoxide = 15 g, and 0.75 g 35 % HCl, and 3.7 g 95 % C2H5OH was employed to make thin sheets by the first and second methods. The solution was hydrolyzed at 40℃ or 80℃. The possibility of thin sheet formation was checked from 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 20 to 100 cP in the first method and from 10 to 15 cP in the second electrophoresis. 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 Al$_2$O$_3$-SiO$_2$ glass sheet, 10-40 μm thick, on heating to 500-700℃. No crystalline peak was detected in the X-ray diffraction pattern of the products.

Table 2 shows the compositions of the

solutions used. When the viscosity reacted about 3 or 5 cP, 1 cm^3 of the viscous solution was poured onto a thin metal foil of 3×3 cm with frames and was spread to cover the whole foil plate as a sheet. The sheet was about 200 μm thick initially and about 100 μm thick on solidification, although the thickness depended upon the composition of the solution. It was found that some solutions formed sheets without severe cracks but others were not. The ease of sheet formation was evaluated by the number of fragments which was produced as a result of fracture of the sheet during formation. Table 2 shows the number of fragments found in a square of 1.5×1.5 cm as a measure of ease of sheet formation.

Table 2. Tests on thin sheet formation

solution	Mole ratio				Number of fragments in sheet
	Al(OR)$_3$/Si(OR')$_4$	H$_2$O	C$_2$H$_5$OH	HCl	
A1	1	0.5	1	0.1	35
A2	1	1	1	0.1	2
A3	1	2	1	0.1	4
A4	1	3	1	0.1	3
A5	1	5	1	0.1	20
A6	1	10	1	0.1	100
A7	1	1	1	0.01	1
A8	1	2	1	0.01	2
A9	1	3	1	0.01	5
A10	1	1	1	0.3	8
A11	1	5	1	0.3	30
A12	1	0.5	0,5	0.1	45
A13	1	3	3	0.1	10
A14	1	10	10	0.1	130

Electrodeposition of organic coatings has found widespread industrial application during the past ten years. Alkali-free Al$_2$O$_3$-SiO$_2$ films have potential for applications in the field of electronics, e.g., as passivation layers. Hydrolysis of metal alkoxides is usually accomplished by contact with liquid water [1-3]. 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 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.

When the gels are heated, they liberate the water+alcohol and convert into the nonporous impervious glasses. The present communication reports the preparation of the transparent

Al₂O₃-SiO₂ (1/4; 1/2; 1/1 in mole %) coating films by the sol-gel method.

Tetraethoxysilane $Si(OEt)_4$ was mixed with ethanol EtOH, the mole ratio $EtOH/Si(OEt)_4=$ 5/1. An appropriate amount of aluminum triisopropoxide $Al(O-iPr)_3$ was then poured into the solution and the reflux was continued at 70 ℃ for 1h. The clear solution obtained was diluted with EtOH and served as a coating solution. The coating was carried out in an electrophoresis manner in a humidity-controlled glove-box. Two platinum electrodes that were connected to the two poles of a conventional electrophoresis power supply produce the lateral electric field. Gel on the electrode of 1.3 ㎜ thickness electrophoresed for about 3-5 min at 200 V. The pH gradient from 7 to 6 near the electrode position was observed. The quality of the films was very sensitive to the humidity of the atmosphere, as mentioned above. Transparent films were obtained below 20 % relative humidity at 20℃. The substrates coated gel were kept for a while in the glovebox to let the solvents evaporate and then heat-treated in air. The temperature of heat treatment was raised stepwise at intervals of 100℃ for 10 min. The thickness of the coating films, as measured by surface profilometer, was in a range of 1300 to 1500 ㎚, depending on the mole ratio $Al(OR)_3/Si(OR)_4$ and on the degree of dilution of the coating solution by EtOH. The load at scratch was measured on films 60 ㎚ thick; though the IR spectra were measured on films 1300 ㎚ thick. Other films having Al₂O₃ : SiO₂ ratios of 1/2 and 1/1 were prepared by the same procedure. The surfaces of the coating films were observed by scanning electron microscopy (SEM). The shrinkage of the gels on heating was measured by a heating rate of 5 ℃/min. The water concentration in the non-porous films prepared by heating the gels was determined by measuring the infrared absorption at 3670 ㎝⁻¹.

3. Results

The coating of metal or glass substrates with using metal alkoxide solution is attracting a great deal of attention as a technique enabling new functions for the substrate or to improve its surface characteristics. Dip coating makes it possible to coat the substrate at relatively low temperatures. Also it is easily applied to very large surfaces compared with sputtering and vapor deposition. The formation of a coating film is different from that of a thin sheet in the following respects:

1) Very small film thickness. Very thin films 0.05-0.2 ㎛ in thickness are produced by one coating run, that is through a dip-withdrawal-heating process. Thicker films can be prepared by repetition of the whole coating process.
2) Use of diluted solutions. Use of diluted solutions is important for obtaining uniform coating films, which firmly adhere to the substrate.
3) Application of solutions at low viscosities. The successful coating can be made with the solution 1-6 cP in viscosity. This viscosity is very low compared with about 5 cP when thin sheets are prepared.
4) Importance of adhesion of the coating film to the substrate. Most of the coating defects can be caused by poor adhesion between coating film and substrate.
5) Change of oxidation-reduction equilibrium. The oxidation-reduction equilibrium of a transition metal tends towards the oxidation side because of the low temperatures of preparation.

Coating was performed in ambient atmosphere. After dipping into the alkoxide solution, the glass or stainless steel substrate was withdrawn upwards at a rate of 0.150-0.60 ㎜/s, and heated for 10 min at 500℃. This was repeated many times to increase the film thickness. Uniform and transparent films were obtained.

Figure 2 shows the change of thickness with the number of applications or the soda-lime-ilica glass substrate. A linear relationship is found. Further, the thickness is larger for larger Al₂O₃-SiO₂ concentrations of the solution.
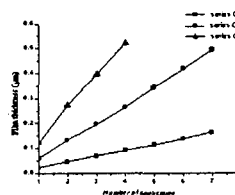

Fig. 1. Film thickness (㎛) versus number of application for Al₂O₃-SiO₂ films by the dip-coating technique. Solutions C1, C2 and C3 contain 1.7 wt%, 4.3 wt%, and 6.4 wt% Al₂O₃-SiO₂, respectively.
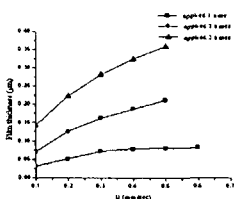
Fig. 2. Change of film thickness (μm) with the rate of withdrawal U for Al_2O_3-SiO_2 coating films.

Electric streng. 10^7 V/m	4.5	3.9	3	2.1
Tangent (at f=1kHz)	0.007	0.011	0.012	0.024
Dielectric constant	7.2	7.2	7.1	6.9
Capacity, 10^{-2} F/m' at U=30V	0.06	0.05	0.04	0.02
Fracture toughness, MN/m$^{3/2}$, K_{1c}	2.73	2.95	2.85	2.13
Young's modulus, GPa, E	246	254	241	219
Sintered density, d, g/cm'	3.160	3.653	3.435	3.369

All films obtained from solutions with concentration more than 10 wt% crack during crystallization (Table 3d). 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. In order to obtain thicker layers, application should be repeated with obligatory heat treatment at 400℃ 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 and prolonged storage of the diluted solutions before their utilization lead to the formation of "bubbles" (50 nm in depth) in the layer (Table 3b).

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 (Table 3c). At the same time, application of a freshly prepared solution in ethyl alcohol subsequently leads to the formation of films without any "bubbles".

Table 3. Conditions of Al_2O_3-SiO_2 film preparation on Pt foils and room temperature properties.

Properties of sol-film	(a)	(b)	(c)	(d)
Al_2O_3:SiO_2 in sol/film	1/1.03	1/1.2	1/1.4	1/1.7
"Age" of sol	1h	24h	1 week	2 week
Heat-treatment ℃, 30 min	400	450	450	500
Phases present	amorph	amorph.+ -Al_2O_3	amorph. + cryst.	cryst. + amorp.
Thickness, nm	1300	1500	1500	1500
Electric resistivity, Ohm cm	7×10^{10}	9×10^{8}	10^{7}	10^{6}

The process of making monolithic thin coating film involves four basic steps: 1) Hydrolysis of alkoxides, 2) Peptization of the hydroxides to a clear sol, 3) Gel formation, 4) Pyrolysis to Al_2O_3-SiO_2.

(1) Hydrolysis was performed by introducing the alkoxides into 95 % C_2H_5OH under vigorous stirring for 15 to 20 min on the hot plate before acid addition.

(2) Peptization requires that a critical amount of certain acids be introduced into the slurry, and that the slurry be kept above 80℃ for a sufficient time. Acid additions are generally specified in terms of pH. However, in this case it was observed that the type of acid played a much more important role than the pH of the system. For instance, additions of H_2SO_4 or HF did not produce the desired effect, regardless of the range of pH. It became apparent that the reproducibility of resultant sols required a more sensitive designation of acid additions than pH. The specification of acid: alkoxide ratio was adequately sensitive to assure excellent reproducibility. To define the type of acid suitable for the peptization of the hydroxides, a number of samples were prepared by hydrolyzing a mixture of 1 mole of $Al(OC_3H_7$-iso$)_3$, $Si(OC_2H_5)_4$ and C_2H_5OH of 95 %; then 0.01 mole of representative organic and inorganic acids were added. The sample were covered and placed in ovens at 95℃. Effects of these acids on the slurry were checked at various intervals.
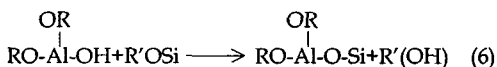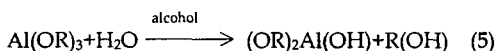
(3) Heat-treatment temperature: to check the effect of temperature on the rate of peptization, ten samples were prepared and were held at temperatures from 25℃ to 95℃.

(4) Pyrolysis: DTA curve characterizied by the presence of a broad exothermic peak between 300-350℃, and a small endothermic peak at 120℃. The first peak result from the loss of physically adsorbed water, the last exothermic peak is attributed to the oxidation of chemically adsorbed alcohol. With increasing

temperature you change the film structure from amorphous to crystalline.

4. Discussion

In all methods of producing monolithic films, the chemical polymerization of Si and Al 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. (5) and (6):

$$Al(OR)_3 + H_2O \xrightarrow{\text{alcohol}} (OR)_2Al(OH) + R(OH) \quad (5)$$

$$RO-\underset{|}{\overset{OR}{Al}}-OH + R'OSi \longrightarrow RO-\underset{|}{\overset{OR}{Al}}-O-Si + R'(OH) \quad (6)$$

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. 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., 1 μm, which varies slightly from one substrate to another. Porous a -Al_2O_3 tubes that are available commercially were coated with continuous films successfully. Detailed discussion of suitable substrates is not presented herein, since this paper is intended to report primarily on the newly developed Al_2O_3-SiO_2 formation technique.

5. Conclusions

A method of forming thin, continuous Al_2O_3-SiO_2 films and coating sheets from metal-organic-derived precursor solutions had been developed. The precursor was produced in a clear liquid state containing Si and Al in chemically polymerized form. By this liquid, the transparent, continuous film was prepared, which was converted to crystalline Al_2O_3-SiO_2 upon heating from 600 to 1000℃.

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 that can survive crystallization.

Electric properties of thin film with thickness of 1300 nm prepared in 1hr sol solution were 7 ×10^{10} Ω cm of resistivity, 4.5×10^7 V/m of electric field strength, tanδ ~0.007 (1㎑) and dielectric constantε ~7.2, respectively.

Acknowledgements

6. References

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