

Peculiarities of amorphous and crystalline dielectric films prepared by sol-gel method

Korobova Natalya*, Deawha Soh**

* Kazakh American University, Kazakhstan; **Myongji University, Korea

ABSTRACT : The important parts of material science in the film preparation fields and sol-gel technology are presented. For the present work, a series of amorphous films was prepared in air by sol-gel method without using some alkoxide stabilizer, which reduces the reactivity of the metal alkoxides. The choice of precursors can affect the chemical-reaction kinetics, microstructures and properties of the product. In this report author compared the crystallization behavior of oxide functional films derived from the same precursors, stressing the influence of experiment conditions and where it was possible to obtain the uniform amorphous or crystalline dielectric films. A short analysis of sol-gel technology and thin film methods about development of dielectric materials has been given.

Introduction

The need for miniaturization of electronic components will certainly continue. Advances in system technology in many respects have become materials limited. This recognized situation has resulted in research and development of imported electronic oxides ceramic materials. In general, sol-gel processing requires a densification step at higher temperature to obtain dense glasses. Organic groupings can act as network modifier, reducing network connectivity and can affect a drastically change of properties compared to inorganic glasses, if organic groupings are cross linked, they can act as network formers.

A variety of unique microstructures (grades, multiphase, partially porous to fully dense, etc.) with unique properties can be investigated when processing is performed by electrophoresis. In addition, the precursor can be used to both increase the relative density and strengthen the films without shrinkage.

Purpose of the current work is to determine the kinetic preparation of electrophoretic films for Seria A sol formed by mixing the aluminum alkoxide and silica sol was gelled at a pH of 3. Glacial acetic acid and 2-methoxy ethanol were used as the solvents. For Seria B formed with organic solvent plus Zr + Y alkoxides that pyrolyzes to a ZrO₂ or Zr(Y)O₂ solid solution.

Experimental part

a) Seria A - (Al₂O₃ + SiO₂) films

Sol was synthesized using aluminum iso-propoxide and stoichiometric amount of silicon tetraethoxide = 15g, and 3,7 g 95% ethanol, which were commercially obtained and used without further purification and 0,5-1 h under vigorous stirring to obtain translucent, homogeneous, stable sol. The stainless steel substrate was cleaned with ethanol-acetone solution in an ultrasonic bath for 20 min, washed with distilled water and then dried before used. Thin films of (Al₂O₃ + SiO₂) were manufactured on a stainless steel substrate by electrophoretic deposition process from prepared alcohol sol. We try to keep attention to the sol aging time - that is the time passed from its preparation to the moment of utilization. In the work [1] we have considered the influence of aging sol on the morphology and structure of sol particles and also the sol-gel chemistry of Al(iso-C₃H₇O)₃ and Si(C₂H₅OH)₄ in various alcohols. The deposition always occurred at the cathode with a constant electric field of 200-300 V/cm for a time period of 0,5-2 min. The thickness of a deposited gel layer was usually in the range of 1-3 μm.

b) Seria B- stabilized ZrO₂ films

For the preparation Zr(Y)O₂ films zirconium and yttrium butoxides were used as the precursor materials and 2-methoxy ethanol as the solvent. With this precursor solution ethylene glycol has been added as an additive in order to avoid the film cracking which degrades the electrical properties of the films. The precursor solution of ZY was then deposited Pt substrates by spin coating at 2300 rpm for 60 sec and by electrophoretic deposition as in Seria A. The substrates were ultrasonically cleaned in acetone, methanol and rinsed in deionized water, followed by a drying process. After coating process, the films were kept in a preheated furnace at 300 °C for 10 minutes to remove the volatile components. The as-deposited amorphous films were subsequently annealed at different temperatures from 400° to 700°C in order to convert them into crystalline films.

The phase identification of the films was done by powder X-ray diffraction analysis using CuK_α radiation (λ=1.5418 Å). Surface morphology and microstructure of the films were observed using Scanning Electron Microscopy (SEM, Stereoscan 440model). X-ray Photoelectron Spectroscopy (XPS) for composition analysis was performed in a VG Microtech MT-500 Spectrometer with MgK_α radiation in the binding energy range of 0 to 1000 eV. In-depth chemical composition of the films was also investigated by field emission type Auger Electron Spectroscopy (AES, PHI 670 nanoprobe). Capacitance-Voltage properties were measured in a metal-insulator-metal configuration using capacitance bridge.

Results

X-ray diffraction studies:

Powder X-ray diffraction pattern of the films heat treated at 300 °C indicated the amorphous nature of the films. This amorphous behavior remains unaltered up to an annealing temperature of 400 °C. While annealing at 500 °C, the Al₂O₃-SiO₂ film was found to be crystalline with (110), (111), (200) peaks arising at 2θ values. With further increase in the annealing temperature, peaks became increasingly sharp. After annealing the Y₂O₃-ZrO₂ film at 700 °C, the intensity of the diffracted peaks increased showing an increase in the crystallinity of the film. The structure was found to be tetragonal with grain size about 10-20 nm for 3,0 mol.% of Y₂O₃.

Micromorphological studies:

Fig. 1a shows the SEM image of the micro cracks observed on the Y_2O_3 - ZrO_2 film annealed at $700^\circ C$, which degrades the electrical properties of the film. The cause of the film cracking was due to the large volume change when the wet solution is fired to inorganic oxides during annealing. This problem was overcome by the addition of ethylene glycol in the precursor solution. The high boiling point and latent heat of vaporization of ethylene glycol retains the atom mobility and significantly reduces the tendency to crack. Fig. 1b shows the dense film with fine grains and without any cracks annealed at $700^\circ C$. It was also observed that with the increase in annealing temperature the grain size also increases.

Heat treatment temperature was raised stepwise at intervals of $100^\circ C$ for 10 min. The thickness of the coating films, as measured by surface profilometer, was in a range of 1300 to 1500 nm, depending on the mole ratio $Zr(OR)_4 / Y(OR)_3$ and on the degree of dilution of the coating solution by organic solution in $Al(OR)_3 / Si(OR)_4$. 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.

In-depth chemical composition of the film was analysed by Auger Electron Spectroscopy with Ar^+ ion beam of 2kV as the sputtering beam. From the depth profile, the film is believed to be divided into three regions: the surface, the bulk film and the interface. Although a carbon peak was detected on the surface of the films, as soon as the first monolayers are removed by the Ar ion bombardment, the carbon peak intensity decreases to the level which cannot be distinguished from noise. The peak is assumed to be from contamination during the sample handling and preparation.

Electrical characterization:

The dielectric and leakage current density measurements were made on the films fabricated on platinum or steel foils. A metal-insulator-metal (M-I-M) structure was fabricated by evaporating circular platinum dot electrodes of 0.5mm diameter on to Al_2O_3 - SiO_2 film by shadow masking. Platinum has been widely used as the electrode because of its excellent oxidation resistance. Also the use of platinum for top and bottom electrode resulted in good electrical properties.

A ramp bias voltage with a superimposed a.c signal of amplitude 100 mV and frequency (100 kHz) was applied to the Al_2O_3 - SiO_2 capacitor, and the applied bias voltage was swept at a ramp rate of 0.5 V/s for both polarities. Dissipation factor was 0.0236. This value is comparable with other sol-gel deposited films, but lower than that of epitaxial films. This may be due to the variation in the microstructure. But in the present case the films were polycrystalline with random orientation.

Table 1. Properties of Al_2O_3 - SiO_2 films

Substrate material	No. of layers	$\rho_s \times 10^{-11}$, $\Omega\cdot m$	ϵ	$tg \delta$, % at 1kHz	$U_{strength}$, 10^8 V/m	TCC 10^{-5} , $^\circ C^{-1}$
Platinum foil	3	4,8	7,3	0,007	4,5	5,4
	2	3,9	6,9	0,012	4,2	5,6
	2	3,8	7,2	0,011	4,1	5,8
	1	3,8	7,1	0,008	3,9	5,9
Stainless steel	3	4,2	7,1	0,020	4,4	5,0
	2	3,8	7,2	0,006	4,1	5,5
	2	3,4	6,9	0,011	4,2	5,7
	1	3,0	6,8	0,015	4,0	5,1

Pyrolysis data associated with the ZrO_2 or $Zr(Y)O_2$ precursor showed, that the weight loss during heating of the Zr-methylcellozolvat precursor occurred in two major steps: a 5 % weight loss between $200^\circ C$ and $275^\circ C$ and a 30 % weight loss between $400^\circ C$ and $550^\circ C$. The first loss is expected to be due to volatile, low molecular weight oligomers. The ceramic yield of the precursor was ≈ 60 wt %. After pyrolysis large cracks and frozen bubbles are observed in specimens of the pyrolyzed precursor.

Table 2. Properties of stabilized ZrO_2 films before and after heat treatment

T, $^\circ C$	τ , h	$\rho_s \times 10^{-14}$, Ohm cm	ϵ	$tg \delta \times 10^4$	σ_{shrink} , MPa	σ_{bend} , MPa
Starting films		2,8	22,3	4,2	535 \pm 10	170
800	0,5	3,1	21,8	4,4	530	170
900	0,5	3,0	22,4	4,8	532	170
1000	0,5	4,3	22,7	7,3	435	162
1100	0,5	3,6	22,8	13,6	380	143
1200	0,5	3,8	22,9	26,5	309	106
1300	0,5	3,4	22,9	27,3	233	94
1400	0,5	3,0	22,8	18,4	257	90
1400	1,0	2,7	22,9	30,2	218	84
1400	2,0	2,6	23,2	35,1	197	79
1400	3,0	2,7	23,5	48,7	180	76
1500	0,5	2,2	23,4	53,9	168	72

Conclusions

A method of forming thin, continuous Al_2O_3 - SiO_2 and ZrO_2 - Y_2O_3 films from metal-organic-precursor solutions has been developed. The precursor is produced in a clear liquid state that contains Si and Al and Zr-Y in a chemically polymerized form. When applied to substrates, this liquid leaves a transparent, continuous film that converts to crystalline Al_2O_3 - SiO_2 and ZrO_2 - Y_2O_3 upon heating to $400^\circ C$. 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.

References

1. Korobova N. The metal alkoxides as source materials in the sol-gel technique. Book 1. Aluminum silicate sol-gel materials: ceramics and thin films. Almaty, 1997. 110p.
2. Korobova N., Soh Deawha, Sung-Jai Choi, "Properties of Al_2O_3 - SiO_2 films prepared with metal alkoxides", International Journal of KIMICS. Vol.1, No3 pp.133-137.
3. Korobova N. "Thin Oxide Amorphous Functional Films from Metal Alkoxides", Proceeding of IX Intern. Conf. on the Structure of Non-crystalline Materials, July 11-15 2004, NY USA.
4. Korobova N. "Amorphous and composite alumina thin films by sol-gel technology", X Internat. Conf. on "Physics of Non-Crystalline Solids", Italy, Parma 13-17 July, p.O-30