Dielectric Properties of Amorphous and Composite Alkoxi-derived Alumina Thin Films

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Abstract

The development of new improved type of dielectric materials on the conception of multiphase structure has been carried out in this paper. Metal alkoxides solutions were used for application of thin film by electrophoretic deposition technique. We succeeded in preparation of amorphous and composite dielectric films from Al alkoxides. Specific features of the preparation technique were considered. Microstructure of the films was examined as well as their dielectric properties. TEM analyses reveals that films deposited from aging sols and heat-treated at temperatures as low as 400℃ contain small whiskers of δ-Al_2O_3.

Key Words : dielectric material, alkoxide, electrophoretic deposition, microstructure, aging sol

1. Introduction

The alkoxide-based sol-gel process is one of the most promising methods for synthesizing ceramic powders and, especially, films at relatively low-temperatures. Over the last decades, sol-gel thin films have found wide applications in optical, microelectronics, photo-electronic industries [1-2]. The study of alumina/semiconductor or alumina/metal systems are very important for the realization of MOS (metaloxide semiconductor) or MOM(metal-oxide-metal) structures for sensor system, because their quality depends strongly on the quality of the insulating layers and the interface insulator/semiconductor or metal. Al_2O_3 is a technologically important material due to its excellent dielectric properties, good adhesion to many surfaces, and thermal and chemical stability. These properties make Al_2O_3 attractive in microelectronics and thin film device industry as an insulator, ion barrier, and protective coating. Usually, the metal alkoxides used in synthesizing dielectrics are very unstable, because of the high electropositive nature of the metal atoms. Methoxyethanol has been widely used as a solvent and stabilizer for preparing precursors, because of its chelating properties and low viscosity, but it is very toxic and hazardous solvent. For the present work, a series of Al_2O_3 films was prepared in air by sol-gel method without using some alkoxide stabilizer, which reduces the reactivity of the metal alkoxides. Because the choice of precursors can affect the chemical-reaction kinetics, microstructures and properties of the product, this paper compares the crystallization behavior of Al_2O_3 films derived from the same precursors, stressing the influence of experiment conditions. Dense oxide films were prepared by electrophoretic deposition method, and the electrical properties of the sintered dielectric films were measured and reported. This work will discuss the changes during the aging sol period and also upon heating in the procedure of preparation the uniform amorphous or composite dielectric films.

2. Experimental Procedure

Al_2O_3 powder in the suspension was synthesized using aluminum iso-propoxide (99.99%, Tri-chemical, Yamanashi, Japan) and ethanol, which were commercially obtained and used without further purification and 0,5-1 h under stirring at room temperature to obtain translucent, homogeneous, and 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 in an atmospheric oven before used. Thin films of Al_2O_3 were prepared on a stainless steel substrate by electrophoretic deposition (EPD) process from specially prepared alcohol sols. We try to keep attention to the aging time that is the time passed from its preparation to the moment of utilization and hydrolysis from moisture air.

3. Results and Discussion

3.1 Film structure after heat-treatment

It was found, that after evaporation of the remainder of the solvent, hydrolyzed aluminium isopropoxide was decomposed. The absence of O_2 leads to a change in the decomposition pattern of the gel and dielectric properties. In the low temperature region, the decomposition runs parallel to the one in dry air, but starting from approximately 400℃ the decomposition pathway diverge.

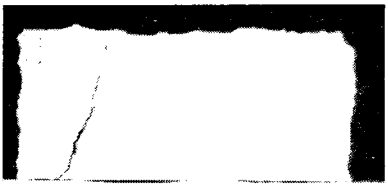

Fig. 1. SEM Micrographs of transparent amorphous film after 350℃, prepared from 0.5 h aging sol.

The final temperature of electrophoresis deposits was 350℃ in the air and it was connected only with the tens-resistive properties of stainless steel substrates and good dielectric properties of prepared films. Later we investigated the influence of heat-treatment conditions on the dielectric properties (Table 1). XRD and TEM patterns show that ~350 nm thick Al_2O_3 film is amorphous deposited at 350℃ from fresh sols and no crystalline peak is observed after 650℃ post-annealing for 30 min. However, the TEM analysis gives evidence for the formation of δ-Al_2O_3 whiskers embedded in an amorphous matrix of the films deposited at temperatures as low as 400℃ from old sols (Fig. 2). This apparent inconsistency can be resolved by taking into account the limitations of the X-ray method, which can be used successfully only for the size determination of small crystallites (~0.01 ㎛). This is why the results of X-ray analysis should always be checked by electron microscopy. In the case of the Al_2O_3 crystallization they give correct information concerning the crystallite size distribution only in the first stage of crystallization when the crystallites are small (0.01 to 0.02 ㎛).

Fig. 2. The appearance of composite coincides with the formation of Al_2O_3 whiskers.

The hydrolysis product is a complex alkoxide-hydroxide containing a certain amount of alkoxy groups, its dehydration leading directly to Al_2O_3.

3.2 Dielectric properties of amorphous and composite films

The quality of the samples prepared by electrophoretic deposition technique has been closely studied. The density of the coatings as well as the resultant microstructure can be changed because of aging sol and condition preparation. Ellipsometer was used to determine the film thickness. The electrical properties of the Al_2O_3 films were dependent on sample preparation conditions(Tables 1, 2). The dielectric constant of the films was calculated from the accumulation capacitance. For the amorphous ~ 350 nm thick films, the dielectric constant was about 7.2 at 1 kHz and for composite Al_2O_3 films with reinforced whiskers was about 7.6. Dielectric constants for the Al_2O_3 films grown from 4-8 h sols were slightly lower than the dielectric constants for the films grown from >12 h sols. At large positive potentials where the metal surface is in accumulation and there is no space charge region, the capacitance measured is the capacitance of the Al_2O_3 film. It is worth noting that the oxygen annealing leads to significant reduction of carbon concentration, which can increase during electrophoresis in the open cell. This is attributed to the reaction of carbon residue with injected O_2 and desorption as CO or CO_2 from films during post-annealing.

Table 1. Influence of heat-treatment conditions on the dielectric properties of amorphous Al_2O_3 films prepared from the same aging sols and electrophoresis conditions.

Surrounded medium	Temperature ℃	Thickness nm	Capacity pF	Dielectric breakdown strength MV/cm	% of yield
H_2O vapor	300	350	740	2.50	82
Air	300	320	760	2.72	66
Argon	300	375	690	2.53	53
H_2O vapor	350	375	720	4.6	82
Air	350	410	747	5.7	70
Argon	350	400	775	3.5	63
H_2O vapor	400	390	685	5.8	68
Air	400	350	714	7.5	63
Argon	400	360	725	5.3	55

From the data (Table 1) it was found, that heat-treatment in the air atmosphere is a key and essential step in the Al_2O_3 film preparation processing. The curve of Capacitance-Temperature calculated from the measurement made at two different frequencies (1 kHz and 0.5 MHz) are also shown in Fig.6. The capacitance appears to increase slightly with growth temperature. Comparing of dielectric properties of Al_2O_3 films prepared on stainless steel substrate by electrophoresis and by the dip coating process at RT was shown in Table 2.

Table 2. Comparing of dielectric properties of Al_2O_3 films prepared on stainless steel substrate by electrophoresis and by the dip coating process at RT.

Series of exp.	Loss factor, tanδ (frequency= 0.1 MHz)	Resistance Ohm (U=30B)	Dielectric breakdown strength, MV/cm	Adhesion 10^{-6}N/m²	View on the film surface
A Dip coating (fresh sol)	- - 0.02 (separate-pieces)	- - 1.5×10^9	- - 4.0	- - 2.10	Porous, rough Surface
B Dip coating (9h sol)	0.02 0.02	- - -	- - -	1.90 2.10	Porous, broken pieces of film
C Electro-phoresis (fresh sol)	0.005 0.010 0.006 0.008 0.010 0.009	2×10^{11} 2.5×10^{11} 6×10^{11} 3×10^{11} 1.2×10^{12} 1.3×10^{12}	3.1 3.2 5.6 5.4 5.1 5.8	2.50 2.49 2.62 2.60 2.56 2.55	Uniform, smoothest non-porous
D Electro-phoresis (9h sol)	0.01 0.009 0.01 0.015 0.008 0.01 0.01 0.005	1.7×10^{10} 1.37×10^9 6.02×10^9 1.5×10^{10} 2.3×10^{10} 5.30×10^9 2.10×10^{10} 1.52×10^{10}	3.0 2.9 3.1 2.8 3.8 3.1 3.5 4.0	2.40 2.45 2.50 2.55 2.60 2.59 2.48 2.58	Uniform smothest, non-porous

The process of film formation by the hydrolysis of metal alkoxide alcohol solutions consists of three main stages shown below: (1) Application of the solution on the substrate; (2) Dehydration of the thin film; (3) Crystallization of the amorphous film. 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. The same phenomenon was observed in this work when a few amorphous layers, applied without thermal treatment after each layer, undergo crystallization(Fig.3, Table 2).

Fig. 3. Micrograph of crystalline Al_2O_3 film on stainless steel substrate by dip coating

Micrographs of breakdown voltage of amorphous (a), and composite Al_2O_3 films (b) was shown in Fig. 4.

(a) (b)

Fig. 4. Micrographs of breakdown voltage of amorphous (a), composite Al_2O_3 films (b).

The breakdown voltage of room temperature film is >5 MV/cm and this value decreases with the increasing temperature for amorphous films. It is about 2.1 MV/cm at 400 and 500℃.

4. Conclusions

Our study reveals that, through electrophoretic process using the metalorganic precursor Al(iso-OPr)$_3$, it is possible to obtain coatings containing amorphous or crystalline alumina at temperatures as low as ~400℃. Amorphous Al_2O_3 films were fabricated on stainless steel substrates by electrophoresis as a candidate for the dielectric layer in sensor devices. The best dielectric breakdown strength of 4.0 MV/cm has been obtained from the 0.5-1.0 h prepared sols. The smoothest surface is also observed from the oxide layer deposited on metal substrate by using fresh sols. It is concluded that the electrophoresis deposited Al_2O_3 films are promising to be the good dielectric of thin film sensors. Electrophoretic deposition offers a new approach for coating oxides on the conducting substrates. Coatings in the range of 250-400 nm thick are readily produced on a variety of shapes including wires and coils as well as plates.

It is clearly established that the aging effect plays a vital role in crystallization and leads to the composite films with whickers.

Acknowledgements

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