

EFFECT of PREPARATION METHODS and CONDITIONS of PRECURSORS on the PROPERTIES of $BaTiO_3$ ALKOXIDE FILMS

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Abstract

Usually for the commercial preparation of barium titanate films or ceramics the reaction atmosphere must be preferably in air. However, normally air is not used because it contains carbon dioxide, which can easily react with barium to form the undesired product barium carbonate, leading to unwanted second-phase formation in the final stages of the process. In the present work a series of perovskite barium titanate films was prepared by the sol-gel method, using a metal alkoxide solutions in the electrophoretic deposition (EPD). The influence of several process parameters, like sintering temperature of sol preparation before EPD and heat-treatment temperature and non-oxidized atmosphere, on the film properties is described.

Key Words : barium titanate, carbon dioxide, perovskite, sol-gel method, electrophoretic deposition

1. Introduction

Many studies have been reported on $BaTiO_3$ [1] as a well-known material for multilayer ceramic and thick-film capacitors because of its high dielectric constant. Lowering the sintering temperature of $BaTiO_3$ is required in multilayer bulk stack devices or integrated memory thin film capacitors; the different layers and the substrate are co-fired in one single step. Therefore, To know firing temperatures are desirable, to avoid interdiffusion between layers and also to allow the use of inexpensive non-noble-metal-containing electrodes. In contrast to the traditional mixed-oxide solid-state reaction methods, sol-gel preparation allows mixing of the components at a molecular level, resulting in materials with high compositional homogeneity, low sintering temperatures and ability to produce uniform film over large area. Chemical processes are also involved in the gelation, growth, and microstructure of films deposited by a sol-gel process. In our laboratory, several oxide films

have been synthesized successfully via sol-gel routes. Here an alcoholic sol-gel route is presented for the preparation of $BaTiO_3$, which was chosen because of its excellent electric properties. A major processing stage involves solution chemistry, whereby a sol is produced from suitable alkoxides to yield necessary composition (Ba:Ti) upon heating. The chemical phase purity of the coating is thus determined early in the process and is dictated by the purity of the precursor materials and the aging time of the solution. In this paper the preparation of $BaTiO_3$ films a nitrogen atmosphere is used. In the present work a series of perovskite barium titanate films was prepared by the sol-gel method, using a stoichiometric starting compositions in the electrophoresis and final heat-treatment in vacuum. It was undertaken to clarify the oxygen dependence of the electrical conductivity. The influence of several process parameters, like sintering temperature of sol preparation before EPD and heat-treatment temperature, on the film properties is described.

2. Experimental Procedure

Electrophoresis describes the migration of the charged microscopic particles through a stationary liquid under the influence of an electrostatic field [2]. A surface charge of an originally neutral colloidal particle may be produced by the adhesion of ions, which are dissolved in the liquid. When the charged particles reach their corresponding electrode they discharge, and adhesion forces lead to a deposition of most of the particles at the surface of the electrode and may in the end result in a complete and homogeneous coating [3-5]. After a number of experiments we found the following procedure. As a first step a fine particles of sol was prepared by dissolving barium metal (Furu-uchi Chemical, Tokyo, Japan) in $\text{Ti}(\text{OBU})_4$ (Tri-chemical, Yamanashi, Japan) with mixing of absolute butanol until the barium metal was completely dissolved. The handling of chemicals and procedures was conducted in a dry argon chamber. The mixed solution was reacted at a reflux temperature for 1-2 h at room temperature (Series A) and at 50°C (Series B). Then the solution was diluted in the butanol solvent up to 0.1-0.4 % of metal phase. Al foil, Pt substrates were cleaned with absolute ethanol using ultrasonication and carbon grids were soaked in absolute ethanol to clean the surface. The hydrolysed metal alkoxide complex particles charge positively in the sol and the sample therefore has to be the cathode. The distance between the electrodes was 2 cm and the applied voltage 150-200 V. After 30-60 seconds a layer of typically $>1 \mu\text{m}$ has formed, the electrophoresis is interrupted and the sample is removed from the suspension. The atmosphere moisture hydrolyzed the sol particles. Then deposited films were dried in the flowing dry nitrogen gas. After the film was calcined for 1/2 h at 400-600 °C and higher in vacuum or in the atmosphere of argon. The thermolysis of film gels was studied using thermo-gravimetric analysis (TGA: Rigaku Denki model TG-8110) at a heating rate of 5°C/min and differential

thermal analysis (DTA: TAS-100). SEM (Hitachi S700) was used to examine the grain structure at the surface of the fired films. The dielectric constants were obtained by measuring the capacitor dimensions (inner and outer diameters on the order of 100 μm) and the dielectric thickness ($\sim 400 \text{ nm}$). To verify the capacitance values, additional measurements were conducted after depositing conductive dots with smaller contact areas between 3.6×10^{-3} and 0.15 mm^2 on the BaTiO_3 films. Dielectric properties of sintered films were measured using an impedance analyzer (Model 4192 A LF, Hewlett-Packard, Japan). All of the electrical properties were measured 7 days after firing to avoid variations due to ferroelectric aging effects.

3. Results and Discussion

3.1 Electrophoretic transition sol-gel

The basis of the technique is to coat a substrate with a polymeric precursor solution containing the requisite metal components in the required proportions, which then, because of solvent evaporation and/or continuing chemical reactions, transforms to a gel layer. The organic components of the gel are then eliminated by various heat treatments to form the desired crystalline oxide film.

In contrast to order sol-gel routes, electrophoretic deposition relies on the hydrolysis-condensation reactions within the initial sol to form the polymeric species by electric field and colloidal effects that lead to gelation (Fig.1). The rate of gelation of an alkoxide-derived sol depends on a number of parameters like temperature, concentration, and medium of gelation.

The hydrolysis and polycondensation processes produce polymers in solution leading to rigid gels containing cations interconnected with anion intermediates (-OH, -O-, etc). The increase in the limiting thickness of crack-free layers could therefore be attributable to this type of linear structure, which may allow the chains to rearrange during drying and shrinkage of the

gel layer, making for a more compliant gel system. However, further studies, including an assessment of pore-size distributions in the gels during drying and thermolysis, would be required to explain fully the factors governing the limiting thickness of barium titanate films prepared by the different sol-gel routes.

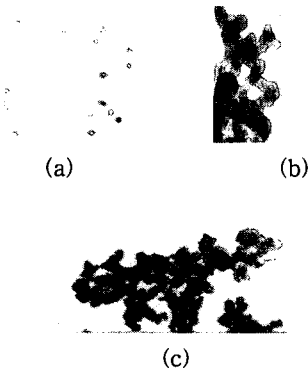


Fig. 1. Schematic representation of gel formation during electrophoretic deposition: (a) separate particles; (b) formation of gel clusters under the electric field; (c) gel cluster chains moving to electrode.

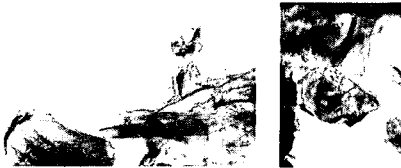


Fig. 2. Photograph of a typical single crystals of barium titanium alkoxide complex (sol B).

The use of different prepared sols and post-EPD conditions probably led to a different mechanism of gel-film formation. In all our studies the major phase is $\text{BaTi}(\text{OC}_3\text{H}_7)_6$ but each preparation technique probably left a small quantity of a different second phase that could have been undecomposed impurities that changed the sintering drastically. The sols (B) contained transparent crystals, square and platelike in shape, and a few nm in size. A typical photograph of such crystals is shown in Fig.2. Drying of electrode gel was carried out in

the nitrogen atmosphere at 100°C (Fig. 3a) and by frizzling 3b.

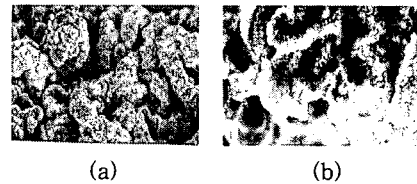


Fig. 3. Micrographs of (a) gel drying in nitrogen atmosphere at 100°C (a) and by frizzling (b).

The sol-gel method of film formation is limited to the production of only small bodies because of the cracking and fragmentation, which occurs during the processing. This is especially evident in the case of organometallic sol-gel materials, that are barium titanate gels prepared by the hydrolysis of complex alkoxide in nonaqueous solvents. It is well recognized that the mechanical stresses generated during drying and firing are responsible for the fracture, but there have been only a few attempts to model them in terms of the capillary forces, density gradients, and their dependence upon the rate of drying or firing. The development of such models requires information concerning the elastic modulus of the gels as a function of the textural parameters (i.e., the matrix structure and pore-size distribution) and the relative humidity (i.e., the effects of adsorbed / condensed water). And independent of their role in determining the mechanical integrity of these materials during drying and firing, the structure and mechanical properties of the gel matrix are of fundamental interest.

3.2 Thermal evolution of electrode gel

TG and DTA analysis of the gel dried at 100°C revealed the occurrence of exothermic reactions accompanied by weight loss near 200°C and 420°C probably due to the decomposition of organic residues. Since no appreciable weight loss and exothermic peaks were found at higher temperatures, calcination at 500°C may be assumed to form an essentially oxide coating

film. It was found that the thickness of the film is reduced by calcination at 500°C to 50–60 % of that of the film dried at 100°C. The thickness of the calcined film formed by one EPD deposition was about 1–2 μm. It is noted that cracks occur in the calcined film formed by one application if the film thickness of electrode gel coating exceeds about 2 μm. The crystallization behavior of the electrode gel was followed by thermal analysis. The DTA and TGA results for the dried gels indicated the critical temperature ranges for the removal of organic species and for crystallization of pyrochlore and perovskite phases.

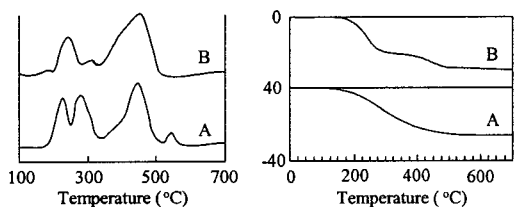


Fig. 4. DTA (a) and TGA (b) spectra of dried gel for B-sols (A) and for room temperature sols (B); heating rate of 10 °C/min.

In the temperature range 200–400°C, (A) and (B) sol electrophoresis gel showed several exothermic peaks in the DTA curves (Fig.4). The TGA curves present marked weight losses in this temperature region. In the temperature range 400–600°C two exothermic peaks are observed in the DTA curves of all of the samples. In this region the samples present a more gradual weight loss.

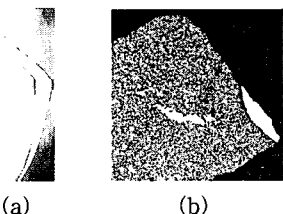


Fig. 8. SEM micrographs of BaTiO₃ films (a) separated from Al foil substrate after 450°C; (b) BaTiO₃ films on the carbon grid after 600°C in vacuum.

The exothermic peak at 400–450°C may be caused by crystallization of the pyrochlore phase, and the last exothermic peak at 515°C may result from perovskite phase crystallization, both probably accompanied by the decomposition of organic residuals. At temperatures > 600°C according to DTA and TGA results, the chemical reactions are complete. The dielectric constant and loss tangent for BaTiO₃ on Pt substrate at room temperature for films prepared from sol(A) and sol(B) are summarized in Table 1. Average grain size after sintering was 0.60–70 and 0.45–50 μm for sol A and B respectively. The value of permittivity in these films was much lower than that for bulk barium titanate.

Table 1. Differences in the properties between BaTiO₃ films prepared from (A) and (B) sols

Sol	Film thickness, nm	Dielectric constant			Loss tangent		
		10kHz	100kHz	1MHz	10kHz	100kHz	1MHz
A	300	543	560	552	0.04	0.04	0.05
A	350	565	571	576	0.05	0.04	0.05
B	400	760	757	755	0.03	0.03	0.04
B	550	820	812	824	0.03	0.05	0.07

The presence of the amorphous phase after 600°C is one of the reasons for the low permittivity in the BaTiO₃ films. Factors such as small grain size and mechanical stress imposed on the films by the substrates may be responsible for the lower dielectric constant. Also, the grain size of BaTiO₃ films was confirmed to be ~50–70 nm for films from (B) sols and 20–30 nm from (A) sols, using TEM micrographs. The effect of grain size on the dielectric constant has been intensively studied, however, it is more important to know the other microstructural parameter, i.e., pore morphology, which have a great influence on the dielectric properties. Based on this point, film processing has to be improved in order to control a better microstructure. Annealing conditions of the BaTiO₃ films were optimized on Pt substrate. XRD data showed that the films annealed ~600

°C from sols (A and B) were all single-phase BaTiO₃. However, based on the crystallinity, dielectric properties, and surface smoothness, the optimum annealing conditions were determined to be at 600°C for 4 h or 700°C for 2 h. Under these conditions, BaTiO₃ films with a dielectric constant of 820-850 and dissipation factor of (0.02-0.03) were obtained.

4. Conclusions

In order to assure highly reproducible and optimized preparation procedures, the individual steps of the sol-gel- film transformation of barium titanium alkoxides were studied. BaTiO₃ films from different kind of sols were electrophoretically deposited on various substrates. The microstructure and properties of the films were characterized using XRD, SEM and TEM, and dielectric constant, dissipation factor and conductivity were determined. Heat-treatment electrode gels in vacuum studied the effect of defect structure on electrical conductivity experimentally. The conductivity in the type region is clear proportional to $PO_2^{1/4}$ in the lower PO_2 region for films prepared from (B) sols and conductivity in the p-type region is proportional to $PO_2^{+1/4}$. However, the electric properties of the sol-gel barium titanate films fired at low temperature are not good enough; improvements must be made in order to reach the levels of the films prepared by other fabrication techniques. The reduced form is associated with a shallow donor level in the band gap of barium titanate, and the sample is semiconducting. The oxidation reactions make the material insulating. So in air, i.e., in the usual conditions of preparation of PTC thermistors, semiconducting samples can be obtained only if the doping level is small.

Acknowledgements

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