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# $Al_2O_3$–$(Ba_{0.5}Sr_{0.5})TiO_3$ composite oxide films on etched aluminum foil by sol–gel coating and anodizing

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**Abstract**

$(Ba_{0.5}Sr_{0.5})TiO_3$ (BST) coating was applied to the etched aluminum foils by sol–gel dip-coating with $(Ba_{0.5}Sr_{0.5})TiO_3$ sol prepared by mixing tetrabutyl titanate, barium acetate, strontium acetate, diethylene glycol, acetic acid and distilled water. After annealing under 500–600 °C in air, $Al_2O_3$–BST composite oxide film was formed on the surface of the etched aluminum foil by anodizing galvanostatically in a neutral adipite and borate solution. The BST powders annealed under different temperatures were characterized by TG–DTA and X-ray diffraction (XRD), and the specific capacitance of the coated samples annealed under different temperatures and times was measured. It was experimentally shown that the specific capacitance of the samples with BST coating is greater than without BST coating. The composite films are promising to be used as the dielectric of electrolytic capacitor.


*Keywords:* A. Sol–gel processes; A. Films; B. Composites; Aluminum electrolytic capacitor; BST; Anodizing

## 1. Introduction

Aluminum electrolytic capacitors have the characteristics of high capacitance, the ability to sustain high voltages, low cost, convenient production and are used widely in electric circuits with rectifiers, switching regulators, ac–dc inverters, storing energy and others [1]. Barrier-type anodic oxide films formed on aluminum play an importance role as dielectric films in aluminum electrolytic capacitors, and their physical and chemical behaviors determine the performance of the electrolytic capacitors. Recent developments in mobile electronic devices, such as notebook computers, mobile telephones, digital video cameras, digital still cameras, etc. and electric vehicles strongly require small electrolytic capacitors with high capacitance [1].

The electric capacitance, $C$, of an aluminum electrolytic capacitor is expressed by

$$C = \frac{\varepsilon_0 \varepsilon_r S}{d} \quad (1)$$

where $\varepsilon_0$ is the dielectric constant of vacuum atmosphere, $\varepsilon_r$ relative dielectric constant of the anodic oxide film, $S$ the effective surface area, and $d$ the film thickness. While the working voltages are decided, the $d$ value is largely decided. Even if electrochemical etching can enlarge $S$, now it is difficult to increase further. Watanabe et al. have tried to increase the electric capacitance by formation of composite oxide films with sol–gel coating and anodizing [2,3].

Normally, the ferroelectric materials have the relative dielectric constant more than hundreds, even thousands, and can be prepared easily by sol–gel method. $(Ba_{0.5}Sr_{0.5})TiO_3$ (BST) is one of usually studied ferroelectric materials. BST with ferroelectric structure can be obtained by annealing below 600 °C [4–6].

In the present paper, BST coating was applied to the etched aluminum foils by sol–gel dip-coating with $(Ba_{0.5}Sr_{0.5})TiO_3$ sol prepared by mixing tetrabutyl titanate, barium acetate, strontium acetate, diethylene glycol, acetic acid and distilled water. After annealing, the $Al_2O_3$–BST composite films were formed by anodizing in a neutral adipite and borate solution. The structure and properties of the composite films are discussed.

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## 2. Experimental

### 2.1. Specimen treatment

The four nines purity commercially etched aluminum foils with tunnel pores were cut to square of 2 cm side length, then boiled in distilled water for 5 min.

### 2.2. BST film preparation

The specimens were coated with BST film by sol–gel dip-coating. The BST sol was prepared by using tetrabutyl titanate, barium acetate, strontium acetate as the starting materials, diethylene glycol as the complex agent, acetic acid and distilled water as the solvent. The specimens were dipped in the sol for 5 min, followed by drying in air at room temperature. After drying, the specimens were annealed at 400–600 °C.

### 2.3. $Al_2O_3$–BST composite film preparation

The BST coated specimens were anodized in 5 wt.% ammonium adipite and 1 wt.% ammonium pentaborate solution with a constant current of 50 mA/cm$^2$. The specimens with and without BST coating were held under 200 V for 30 min. The electric capacitance of all specimens were measured in 10 wt.% ammonium adipite solution.

### 2.4. Characterization of BST sol and powders

The BST crystallization temperature was determined by TG–DTA. The BST powders were obtained by annealing in air under 400–650 °C. All powders were characterized by X-ray diffraction (XRD).

## 3. Results and discussion

### 3.1. The BST crystallization temperature determination

The TG–DTA curves of the BST sol are shown in Fig. 1. There is a endothermal peak near 117 °C, corresponding to the volatilization of water and acetic acid. There are two small endothermal and exothermal peaks near 283 and 390 °C, corresponding to the removal of complex, respectively. The sharp and tall exothermal peak near 552 °C relates to the formation of perovskite BST phase, which is verified by XRD (see Fig. 2).

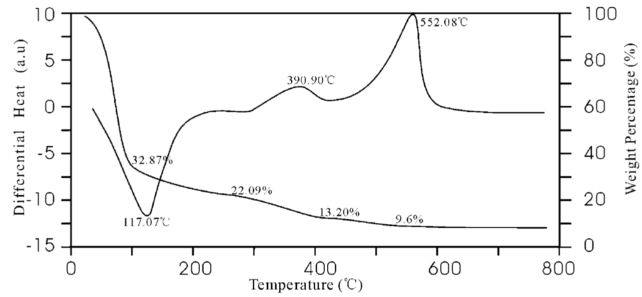


Fig. 1. TG–DTA curves of BST specimen.

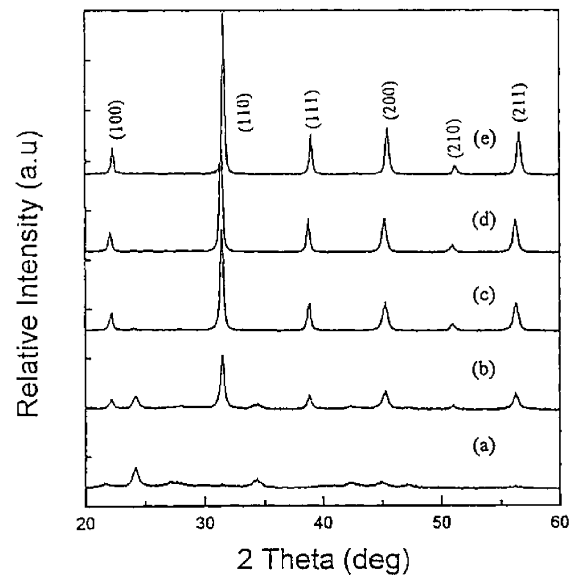


Fig. 2. XRD patterns of different annealing temperature: (a) 400 °C, 2 h; (b) 500 °C, 2 h; (c) 550 °C, 2 h; (d) 600 °C, 2 h; (e) 650 °C, 2 h.

### 3.2. The effect of annealing temperature on XRD patterns

The XRD patterns of the BST powders are shown in Fig. 2, annealed under different temperatures. They show that all powders annealed above 500 °C have a perovskite structure. The higher the annealing temperature is, the higher and sharper the diffraction peaks of the powders are.

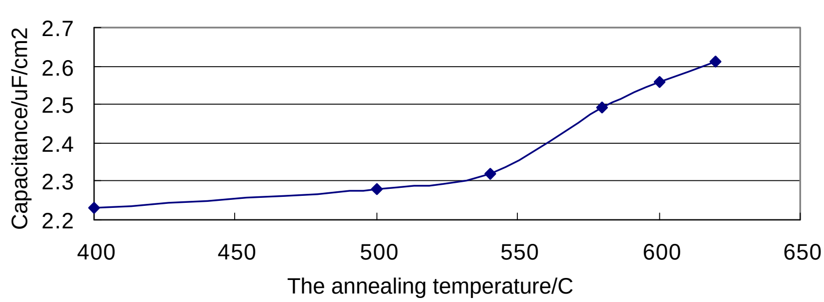


Fig. 3. The annealing temperature dependence of capacitance.

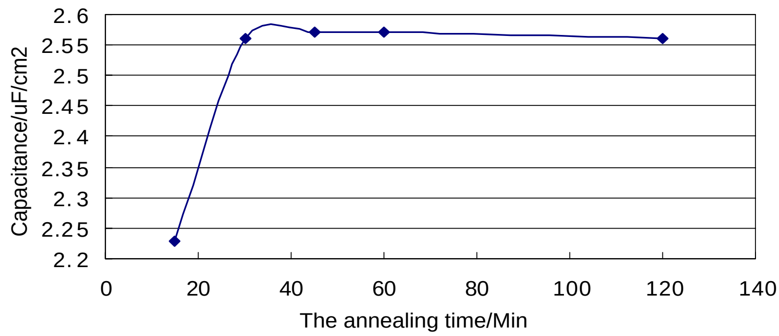


Fig. 4. The annealing time dependence of capacitance.

### 3.3. *The effect of annealing temperature and time on the specific capacitance*

Figs. 3 and 4 show the effect of annealing temperature and time on the specific capacitance. The specific capacitance of specimens increases obviously, when the annealing temperature exceeds 540 °C. While the annealing time is 30 min under 550 °C, the specific capacitance increases rapidly, then nearly remains constant. This is because BST begins to crystallize to a perovskite structure at the annealing temperature of 550 °C. This point agrees with the XRD analysis. This result also shows that the composite film of $Al_2O_3$–BST has a relatively high dielectric constant.

## 4. Conclusion

The $Al_2O_3$–BST composite film can be prepared by sol–gel coating and anodizing. XRD patterns show that BST powders can change to a perovskite structure at the annealing temperature above 550 °C. The composite film reveals to a higher dielectric constant compared to without coating under the anodizing voltage of 200 V. The composite films are promising to be used as the dielectric of electrolytic capacitor.

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