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$(Ba_{0.5}Sr_{0.5})TiO_3$ modification on etched aluminum foil for electrolytic capacitor

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Abstract

A new method was proposed to form $(Ba_{0.5}Sr_{0.5})TiO_3$–Al_2O_3 composite oxide film on etched aluminum foils. The specimens were covered with $(Ba_{0.5}Sr_{0.5})TiO_3$ (BST) layer by dip-coating in citrate solution and subsequent heat-treatment under 400–650 °C, finally by anodizing in a hot boracic acid and borate solution. The BST powders heated under different temperatures were characterized by X-ray diffraction (XRD) and the specific capacitance of the coated specimens heat-treated under different temperatures and times was measured. It is found that the specific capacitance increases initially with enhancing the temperature and reaches to maximum at 550 °C, but slightly decreases with the heat-treatment time. The capacitance was increased by about 35% after BST coating.

Keywords: Electrolytic capacitor; Aluminum foil; $(Ba_{0.5}Sr_{0.5})TiO_3$; Capacitance

1. Introduction

Aluminum electrolytic capacitors are used widely in electronic devices and their production scale and market demands have been increasing continually with rapid development of electric industry. Recent development of small electronic devices requires small electrolytic capacitors with high capacitance. The static electric capacitance C of electrolytic capacitors is expressed by

$$C = \frac{\varepsilon_0 \varepsilon S}{\delta} \quad (1)$$

where ε_0 is the vacuum permittivity, ε the relative dielectric constant of the anodic oxide film, S the effective surface area of the film, and δ is the film thickness [1]. It can be seen that C value of electrolytic capacitors can be increased by increasing ε and S, and decreasing δ. However, the δ value is largely determined by working voltage, and now it is difficult to increase C value by enlarging S further [2]. Therefore, it is essential to increase ε in order to increase C value. Barrier type anodic oxide films formed on aluminum have value of 8–10, while the other valve metal oxides or ferroelectric materials have more than hundreds, even thousands ε values. The ε value of $BaTiO_3$ and $SrTiO_3$ ceramic materials is, respectively, 500–6000 and more than 200,000 [3]. Increase in ε is possible by incorporating these oxides into the aluminum anodic oxide films [3–6]. BST is one of the usually studied ferroelectric materials and has large ε value [2].

In the present investigation, BST layer was formed on the etched aluminum foils by dip-coating in citrate solution unlike the common sol–gel method and subsequent anodizing. The structure and properties of the BST powders heated under different temperatures are shown. The influences of the heating temperature and time on the specific capacitance of the coated specimens were examined.

2. Experimental

2.1. Specimen

Highly pure (99.99%) etched aluminum foils with tunnel pores were cut into specimens in a size of 1 cm × 5 cm.

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2.2. The solution preparation

The reagents used for preparing the solution were barium nitrate ($Ba(NO_3)_2$), strontium nitrate ($Sr(NO_3)_2$), tetra-*n*-butyl titanate ($Ti(OC_4H_9)_4$), citric acid ($C_6H_8O_7 \cdot H_2O$) and deionized water [7]. The appropriate amount of citrate acid was dissolved in deionized water, then barium nitrate and strontium nitrate powders were added into the above citrate acid solution stirred at 50 °C until the powders were dissolved and then cooled it down to room temperature. The tetra-*n*-butyl titanate was added in an appropriate amount of citric acid solution by stirring at room temperature whose pH value had been adjusted to 6 with ammonia solution. After the above solution turned clear, the BST solution was prepared by mixing the barium and strontium solution and titanium solution stoichiometrically.

2.3. BST film preparation

The BST coating was applied to the specimens by immersion and heating. Firstly, the specimens were dipped in the BST solution for 10 min, followed by drying in air at room temperature. Secondly, the dried specimens were heated at 400–650 °C in air. Finally, the BST coated specimens were anodized in hot boracic acid and ammonium pentaborate solution ($H_3BO_3 + (NH_4)_2O \cdot 5B_2O_3$) with a constant current of 50 mA/cm^2. Specimens with and without BST coatings were held under 200 V for 30 min. The capacitances of all specimens were measured in ammonium pentaborate solution at room temperature. The testing frequency was set to 100 Hz.

2.4. Characterization of BST powders

The BST powders were obtained by drying the solution and then heating in air under 400–650 °C. All powders were characterized by X-ray diffraction (XRD).

3. Results and discussion

3.1. The influence of heating temperature on XRD patterns of BST powders

The XRD patterns of BST powders heated in a temperature range from 400 to 600 °C are shown in Fig. 1. It can be seen that powders are amorphous oxides when heated at about 400 °C and the peaks of pervoskite structure appeared when heated above 500 °C. The higher the temperature is, the stronger the diffraction peaks are.

3.2. Influences of heating temperature and time on the specific capacitance

The heat-treatment is very important to form the BST-Al_2O_3 composite oxide film. Firstly, it can make the citrates transfer to metal oxides; Secondly, it helps to form thin Al_2O_3 film and make the BST combine with Al_2O_3 partially, which is favorable for the final growing of BST-Al_2O_3 composite oxide film.

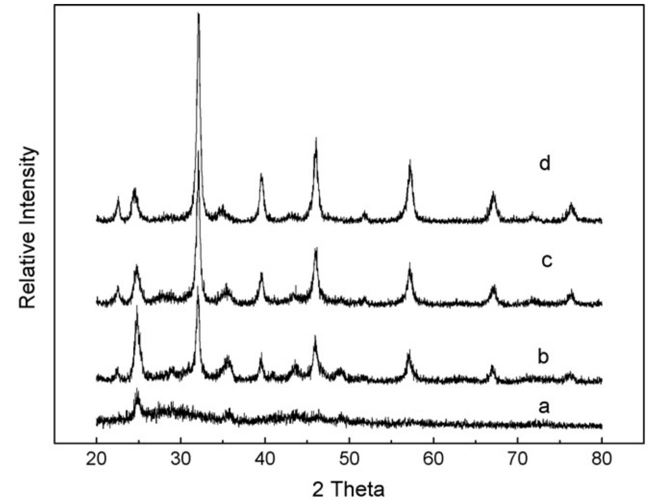

Fig. 1. XRD patterns of BST powders heated for 1 h under (a) 400 °C; (b) 500 °C; (c) 550 °C; (d) 600 °C.

Fig. 2 shows the influence of heating temperature on the specific capacitance. It is clear that the specific capacitance increases from 2.2 to 2.6 μF/cm^2 when the temperature enhances to 550 °C, and declines above 550 °C. In fact, when the heating temperature exceeds 580 °C, highly pure aluminum would melt down and recrystallization occurs around the tunnel structure layer [8]. This would result in decrease in the effective surface area and the specific capacitance would become smaller.

Fig. 3 shows the influence of heating time on the specific capacitance. The capacitance decreases slightly at 550 °C, when heating time increases from 30 to 90 min. Our investigation indicates that the heat-treatment time for 30 min is enough to complete BST crystallization to a perovskite structure at 550 °C. So far it remains unclear why the capacitance is likely to decrease when the heat-treatment time increases. One possibility is that sintering for a longer time reduces the surface area.

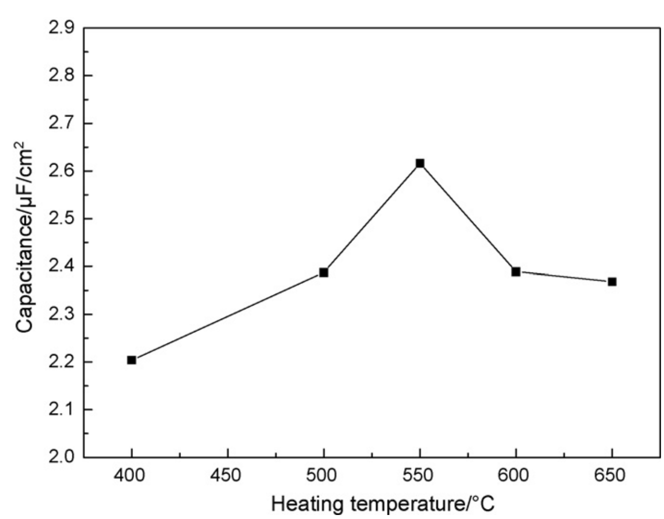

Fig. 2. Influence of heating temperature on the specific capacitance.

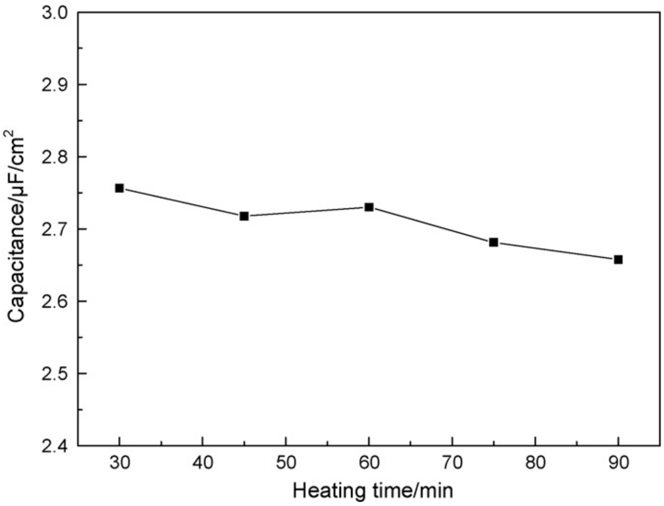

Fig. 3. Influence of heating time on the specific capacitance.

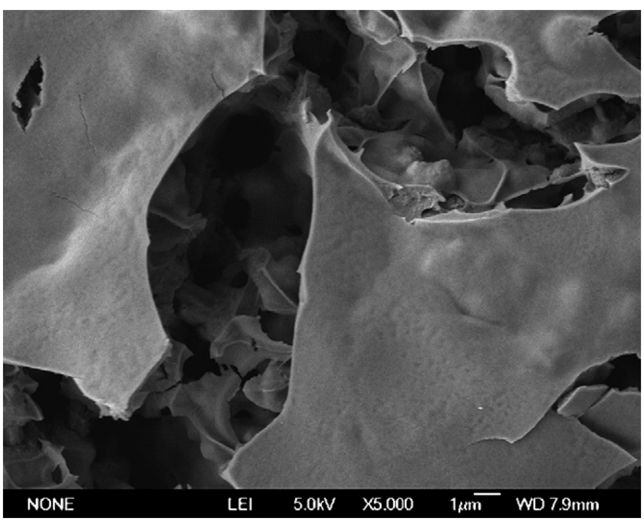

Fig. 4. SEM picture of heated sample with a thick BST film.

3.3. *Influences of thickness of BST films on the specific capacitance*

In order to get high capacitance, BST films cannot be too thick. In Fig. 4, the etched aluminum foil is coated by a layer of BST film, which is so thick that it covers the surface of the etched aluminum foil. This leads to decrease of effective surface area and smaller capacitance. Whereas in Fig. 5, the surface structure of the etched aluminum foil is clearly shown after dipping and heating treatment. In this case, the capacitance is significantly increased. Therefore, it is essential to consider the thickness of BST films, which could affect the effective surface area of etch aluminum foil and finally affect the capacitance. Moreover, it is easy to understand that composite oxide films can increase the capacitance by increase relative dielectric constant ε as long as the effective surface area would not be reduced too much.

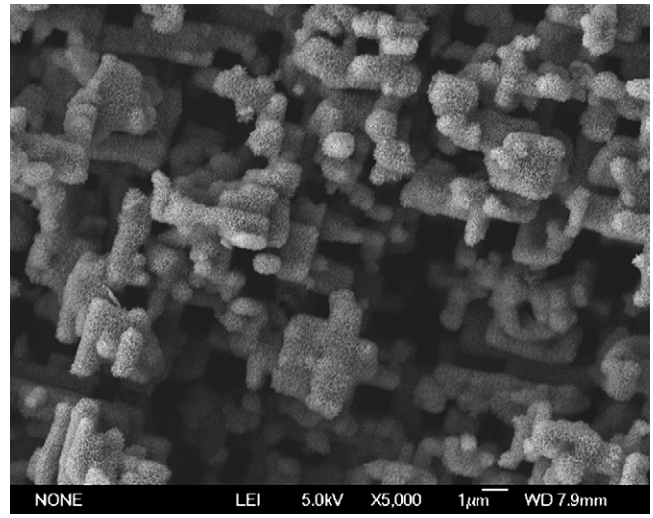

Fig. 5. SEM picture of heated sample with a thin BST film.

4. Conclusion

The proposed method is effective to form the BST-Al_2O_3 composite oxide film on etched aluminum foils. The specific capacitance of the specimens without coating and heat-treatment is about 2.0 $\mu F/cm^2$ under the anodizing voltage of 200 V, whereas the specific capacitance of BST coated specimens can reach to 2.7 $\mu F/cm^2$. This result indicates that BST coating can remarkably enhance specific capacitance of the specimens. In addition, the specific capacitance of BST coated specimens using the proposed method is larger than that using sol–gel method reported [2].

References

[1] K. Watanabe, M. Sakairi, H. Takahashi, S. Hirai, S. Yamaguchi, Formation of Al–Zr composite oxide films on aluminum by sol–gel coating and anodizing, J. Electroanal. Chem. 473 (1999) 250–255.
[2] Y. Xu, Al_2O_3–$(Ba_{0.5}Sr_{0.5})TiO_3$ composite oxide films on etched aluminum foil by sol–gel coating and anodizing, Ceram. Int. 30 (2004) 1741–1743.
[3] K. Yang, X. Shen, A new method to increase specific capacitance of formed aluminum foil—to introduce metal or ceramic oxides with high permittivity into it, Electron. Compon. Mater. 16 (1997) 14.
[4] M. Shikanai, M. Sakairi, H. Takahashi, M. Seo, Formation of Al/(Ti, Nb, Ta)-composite oxide films on aluminum by pore filling, J. Electrochem. Soc. 144 (1997) 2756–2766.
[5] K. Watanabe, M. Sakairi, H. Takahashi, K. Takahiro, S. Nagata, S. Hirai, Anodizing of aluminum coated with silicon oxide by a sol–gel method, J. Electrochem. Soc. 148 (2001) B473–B481.
[6] S.S. Park, B.T. Lee, Anodizing properties of high dielectric oxide films coated on aluminum by sol–gel method, J. Electroceram. 13 (2004) 111–116.
[7] J. Wang, X. Yao, L. Zhang, Preparation and dielectric properties of barium strontium titanate glass-ceramics sintered from sol–gel-derived powders, Ceram. Int. 30 (2004) 1749–1752.
[8] J.J. Chen, M.L. Jiang, Z.S. Feng, B.C. Yang, Effect of technological parameters on specific capacitance of Al–Ti composite oxide films, Electron. Compon. Mater. 24 (2005) 10.