Formation of Al₂O₃–BaTiO₃ composite thin film to increase the specific capacitance of aluminum electrolytic capacitor

Xianfeng Du, Youlong Xu⁎

Electronic Material Research Laboratory, Key Laboratory of the Ministry of Education, Xi’an Jiaotong University, Xi’an 710049, PR China

Received 26 June 2007; received in revised form 30 March 2008; accepted 8 April 2008

Available online 18 April 2008

Abstract

To increase the specific capacitance of aluminum anodic foil, barium titanate BaTiO₃ (BT) sol was dip-coated on the etched aluminum foils by a sol–gel process. After annealed at different temperatures, the foils were anodized in ammonium adipate solution. The phase transition of BT powder was investigated. The voltage–time variations during anodizing were monitored, and the electric properties such as specific capacitance, dissipation factor, withstanding voltage, and leakage current of these foils were also examined. It was found that BT started to crystallize at 550°C. The anodizing time of the foils covered with BT films decreased with annealing temperature. The specific capacitance and the product of specific capacitance and withstanding voltage of anodic foils with a BT coating increased with annealing temperature, and the largest increases were about 46% and 39% compared to that without a BT coating, respectively. The obtained anodic foils with the largest specific capacitance were assembled into aluminum electrolytic capacitors, and the load and shelf life tests were measured. There was no significant difference between Al/BT-600 and Al during the load and shelf life tests. The capacitor life time is larger than 2500h. From the results, BaTiO₃ is promising to be used as the partial dielectric of aluminum electrolytic capacitor to increase the specific capacitance.

© 2008 Elsevier B.V. All rights reserved.

Keywords: Aluminum electrolytic capacitor; Sol–gel; Barium titanate; Load and shelf life

1. Introduction

With the characteristics of the large capacitance and low cost, aluminum electrolytic capacitors are widely used in home appliances, computer motherboards, peripherals, power supplies, industrial electronics, communication products and automobiles [1,2]. They can mainly provide filtering, bypassing, rectifying, coupling, blocking, energy storing and transforming functions, which play an important role in the electric and electronic products [2,3].

The aluminum electrolytic capacitor basically consists of two aluminum electrodes separated by thin dielectric layers for accumulating electrical charges. The barrier-type anodic oxide layers on aluminum processed by formation treatment are used as dielectric layers in aluminum electrolytic capacitors, and the capacitance of these dielectric layers mainly determines the capacitance of capacitors. Recently, the requests of the global market that the aluminum electrolytic capacitors should be miniaturization, large capacitance is improving with the increasing development of the large-scale integration of the electron element product and the miniaturization of the mobile products all over the world [3]. In order to meet the requirement, it is an effective way to increase the specific capacitance of dielectric layers. The basic equation relating to the capacitance can be expressed by:

\[ C = \frac{\varepsilon_0 \varepsilon_r S}{d} \]

where \( C \) is the capacitance, \( \varepsilon_0 \) is the dielectric constant of vacuum atmosphere, \( \varepsilon_r \) the relative dielectric constant of the dielectric layers, \( S \) the effective surface area of the dielectric (electrode), and \( d \) the thickness of the dielectric layers. From Eq. (1), we know that there are three ways to increase the \( C \) value: increases in \( S \), decreases in \( d \), and increases in \( \varepsilon_r \) [4,5].
The increases in \( S \) can be generally obtained by electrochemical etching a high purity aluminum foil before anodization, but now it faces with the limit \([6,7]\). It is also very difficult to decrease \( d \) because \( d \) is related to the working voltage of the aluminum electrolytic capacitor. While the working voltage is decided, the \( d \) value is largely decided \([2,6]\). Increases in \( \varepsilon \) may be possible by incorporating relatively large \( \varepsilon \) value compounds into aluminum anodic oxide film to form composite dielectric layers. Many groups have tried to increase the electric capacitance by incorporating value metal oxides such as Ta2O5, Nb2O5, TiO2, ZrO2 and others \([4–9]\).

Normally, the ferroelectric materials have the relative dielectric constant more than hundreds, even thousands, and can be easily prepared by sol–gel method. BaTiO3 (BT) is a typical ferroelectric material, which was widely studied \([10–12]\). In the present investigation, BT was attempted to introduce into dielectric layers of aluminum electrolytic capacitor to enlarge its capacitance. The electric properties of anodic foil incorporated with BT were examined as functions of the annealing temperature of the BT coating, and the capacitor life manufactured with this foil was measured. The phase transition of BT was also discussed.

2. Experimental details

2.1. BT sol preparation

The required amount of barium acetate was dissolved in 36% acetic acid by stirring at room temperature up to achieving complete dissolution. Meanwhile, stoichiometric tetra-n-butyl titanate was dissolved in lactic acid. Then the two solutions were mixed under stirring. The resultant solution was stirred at room temperature for 2h and filtered. Thereafter, adding deionized water and 36% acetic acid, the solution was diluted to 0.3mol/L and pH was controlled between 1 and 2.

2.2. Coating and anodizing

The 99.99% purity commercially low-voltage etched aluminum foils with sponge pores were used as specimens. They were first dipped in the BT sol for 5min, followed by drying in air at room temperature. Afterwards, the foils were annealed at 500°C, 550°C, or 600°C for 30min. Then the foils with or without BT coating were anodized (respectively marked as Al/BT-500, Al/BT-550, Al/BT-600, and Al) in 15wt.% ammonium adipate solution using an Al foil as the counter electrode. The constant current is 25mA/cm². The voltage–time variations were monitored by a PC system. They were held under 21V until the residual current density is less than 1.25mA/cm². Then the specimens were annealed at 500°C for 2min, followed by re-anodization. At last, the specimens were dried at 300°C for measurement. The flow chart is illustrated in Fig. 1.

2.3. XRD characterization

BT gels were prepared by evaporating water from the BT sol at 70°C under vacuum. Then they were calcined at 500°C, 550°C and 600°C for 1.5h in air. The phase transition of the obtained powders was investigated by X-ray diffraction (XRD), CuKα, 40kV, 40mA (X’Pert PRO, PANalytical Ltd., Holland). The scan rate was 10°/min and step size was 0.02° for the phase identification in the \( 2\theta \) range 20–80.

2.4. Electric properties test of anodic foil

The specific capacitance (\( C \)) and dissipation factor (\( \tan \delta \)) of all anodic foils at 120Hz were checked by Multi-Frequency LCR Meter (4272A, HP Co., USA) in 15wt.% ammonium adipate solution at 30°C. The withstanding voltage (\( V \)) of specimens was tested by the TV Meter (YTV-11, Yangzhou Shuanghong Ltd., China). The leakage current (\( I \)) was investigated by the Leakage Current Meter (TH2685, Tonghui Electronic Ltd., China). Above electrical parameters were measured according to the standard of the Japan Capacitor Industrial Co., Ltd. (JCC).

2.5. Load and shelf life tests of capacitor

A pilot-testing was carried out to manufacture the capacitors with Al/BT-600 in Shenzhen City DongYangGuang Industrial Development Co., Ltd., China. Capacitors with 16 WV, 18.4 AV, 1000µF, 10mm × 16mm were used as the examples in this study. The capacitor elements except anodic foil included: (1) the cathode aluminum foil, model 50KX, specific capacitance of 400µF/cm², thickness of 50µm; (2) the separator, model MEX2-40, thickness of 40µm; (3) electrolyte, model D2; (4) lead type 15115.

Load/shelf life test of capacitor were performed at 85 °C, with/without applying a working voltage 16V. The electric
properties including capacitance reduction (CR), dissipation factor, and leakage current were measured at 25 ± 3 °C every specific time period according to the standard of the Japanese industrial standard (JIS) [13].

3. Results and discussion

3.1. XRD patterns

In order to understand the crystallization process of BT, BT powder calcined at 500 °C, 550 °C, or 600 °C for 1.5h was investigated by XRD. The results were shown in Fig. 2. It is clear that the BT powder transformed into barium carbonate, Ti-complex and Ba–Ti intermediate phase (Ba$_2$Ti$_2$O$_5$CO$_3$) at 500 °C. There isn’t any BT phase. As the calcined temperature increases up to 550 °C, BT phase is observed. What’s more, the peaks of BaCO$_3$ become weak which indicates that a part of BaCO$_3$ reacted with TiO$_2$ leading to the formation of BT, and carbon dioxide was released [14,15]. In addition, the peaks of Ba$_2$Ti$_2$O$_5$CO$_3$ become sharp which shows that the grain develops. When the sample was calcined at a higher temperature of 600 °C for 1.5h, all impurity phases disappeared and the pattern showed a fully crystallized cubic pervoskite structure (JCPDS 01-089-2475) [16]. In this temperature interval, Ba$_2$Ti$_2$O$_5$CO$_3$ decomposed and converted into BT while carbon dioxide was released [17–19]. Therefore, the following steps for BT formation were considered:

$$\text{BaCO}_3 + \text{TiO}_2 \xrightarrow{500 \text{ °C} \sim 600 \text{ °C}} \text{BaTiO}_3 + \text{CO}_2 \uparrow$$  \hspace{2cm} (2)

$$\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3 \xrightarrow{550 \text{ °C} \sim 600 \text{ °C}} 2\text{BaTiO}_3 + \text{CO}_2 \uparrow$$  \hspace{2cm} (3)

From the above discussed results, we can see that the crystallization temperature of BT is much lower than the melting point of aluminum (660 °C), which indicates that BT can be applied to the aluminum substrate.

3.2. Anodization behavior

Fig. 3 shows the changes of the anode voltage and current with anodizing time. At the initial moment, there are jumps of anode voltage and they are 1.6, 3.7, 9.1, and 12.6V for Al, Al/BT-500, Al/BT-550, and Al/BT-600, respectively. This is caused by the aluminum oxide film [20,21]. The jump value increases with the annealing temperature because of increase in the thermal aluminum oxide film. Then, the anode voltage of all specimens almost linearly increases with anodizing time. The slopes of voltage–time curves become steeper with the annealing temperature. Therefore, the following steps for BT formation were considered:

$$\text{BaCO}_3 + \text{TiO}_2 \xrightarrow{500 \text{ °C} \sim 600 \text{ °C}} \text{BaTiO}_3 + \text{CO}_2 \uparrow$$  \hspace{2cm} (2)

$$\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3 \xrightarrow{550 \text{ °C} \sim 600 \text{ °C}} 2\text{BaTiO}_3 + \text{CO}_2 \uparrow$$  \hspace{2cm} (3)

From the above discussed results, we can see that the crystallization temperature of BT is much lower than the melting point of aluminum (660 °C), which indicates that BT can be applied to the aluminum substrate.
Table 1
Capacitor characteristic parameters of different anodic oxide films

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$C$ ($\mu$F/cm$^2$)</th>
<th>$\tan \delta$ (%)</th>
<th>$V$ (V)</th>
<th>$I$ (mA)</th>
<th>$CV$ ($\mu$FV/cm$^2$)</th>
<th>$\Delta C$ (%)</th>
<th>$\Delta CV$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>65.36$^{\pm 0.43}$</td>
<td>21.08$^{\pm 0.48}$</td>
<td>23.56$^{\pm 0.39}$</td>
<td>1.5$^{\pm 0.1}$</td>
<td>1540$^{\pm 3}$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Al/BT-500</td>
<td>70.61$^{\pm 1.03}$</td>
<td>24.56$^{\pm 0.78}$</td>
<td>22.93$^{\pm 0.08}$</td>
<td>2.6$^{\pm 0.2}$</td>
<td>1619$^{\pm 31}$</td>
<td>8.03$^{\pm 1.58}$</td>
<td>5.13$^{\pm 2.01}$</td>
</tr>
<tr>
<td>Al/BT-550</td>
<td>81.18$^{\pm 0.76}$</td>
<td>25.34$^{\pm 0.16}$</td>
<td>22.64$^{\pm 0.22}$</td>
<td>3.8$^{\pm 0.4}$</td>
<td>1838$^{\pm 27}$</td>
<td>24.20$^{\pm 1.17}$</td>
<td>19.35$^{\pm 1.75}$</td>
</tr>
<tr>
<td>Al/BT-600</td>
<td>95.66$^{\pm 1.21}$</td>
<td>32.98$^{\pm 0.74}$</td>
<td>22.36$^{\pm 0.34}$</td>
<td>4.0$^{\pm 0.5}$</td>
<td>2139$^{\pm 31}$</td>
<td>46.36$^{\pm 1.85}$</td>
<td>38.9$^{\pm 2.73}$</td>
</tr>
</tbody>
</table>

The numbers are average values obtained from 8 specimens. The superscript/subscript represent positive/negative deviations.

From Table 1, we can find that the $C$ and $CV$ of anode foils with BT coating increase considerably, depending on the annealing temperature. The $C$ and $CV$ of Al/BT-500 are slightly higher than that of Al. This may be attributed to BT phase doesn’t form at this temperature (see Fig. 2). Above 550°C, the $C$ and $CV$ of BT-coated foils are much greater than that without BT coating. It is due to the formation of BT, which converts into Al$_2$O$_3$–BaTiO$_3$ composite oxide layer with a high dielectric constant during the following anodizing. The higher the annealing temperature is, the more BT is, and the higher the dielectric constant still meet the requirement. During the shelf life test, changes of Al/BT-600 are similar to that of Al except leakage current increases less than 0.01 $\mu$A after 2500 h, which indicates that the method reported in this paper can be applied to the industrial production.

3.4. Load and shelf life tests

The load and shelf life tests of capacitors were measured. The results measured from 12 specimens average are illustrated in Figs. 4 and 5. According to the standard of JIS [13], the judging criteria of failure are defined as follows: (1) leakage current increases more than 0.01 $\mu$A ($P$, the product of initial capacitance and working voltage); (2) capacitance changes greater than ±20% of initial value; (3) $\tan \delta$ goes beyond 30%. In this paper, if one of these three criteria happened, the capacitor was treated as failure.

From Fig. 4, it is found that there is little difference between Al and Al/BT-600 during the load life test. After application of the rated voltage for 2500 h, three parameters of electric properties still meet the requirement. During the shelf life test, changes of Al/BT-600 are similar to that of Al except leakage current (see Fig. 5). The leakage current of Al/BT-600 is always greater than ±20% of initial value; (3) $\tan \delta$ goes beyond 30%. In this paper, if one of these three criteria happened, the capacitor was treated as failure.

4. Conclusion

BT thin film was coated on high purity low-voltage etched aluminum foil by sol–gel method for application as partial dielectric in aluminum electrolytic capacitor. XRD patterns show that BT starts to crystallize at 550°C. The aluminum foils coated with BT, which are annealed at a higher temperature, have a higher V-jump, a steeper slope, and a shorter anodizing time during the anodization. The specific capacitance and the
product of specific capacitance and withstanding voltage of anodic foils with a BT coating increase with the annealing temperature, and they are about 46% and 39% larger than that without a BT coating at 600 °C, respectively. The behavior of capacitor for Al/BT-600 is similar to that for Al during the load and shelf life tests. The capacitor life time is larger than 2500 h. BaTiO₃ is promising to be used as the dielectric of aluminum electrolytic capacitor to increase the specific capacitance.

Acknowledgements

The authors wish to thank Shenzhen City DongYangGuang Industrial Development Co., Ltd. for experimental assistance. The authors are grateful to Dr. Jingping Wang for his help with the drawing of Fig. 1. This work was supported financially by the National “863” Plan Foundation of China (Granted No. 2003AA325030) and the Specialized Research Fund for the Doctoral Program of Higher Education of China (Granted No. 20040698016).

References