Effect of Annealing on Microstructure and Capacitance Properties of Sol-gel TiO₂ Film on Aluminum

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Sol-gel TiO₂ film prepared by dip-coating on aluminum was annealed under different temperatures, and subsequently anodized in ammonium adipate solution. The microstructure and capacitance properties of TiO₂ film on aluminum was investigated by X-ray diffraction (XRD), Raman spectroscopy (RS), thermogravimetric differential scanning calorimetry (TG-DSC), atomic force microscope (AFM), and capacitance temperature (C-T) test, respectively. The results indicated that TiO₂ film on aluminum annealed at 400 °C and 500 °C showed nanocrystalline anatase in 1-5nm and 5-12nm particles, respectively, while that annealed at 600 °C showed mixed nanocrystalline phase (anatase and rutile) in 5-15nm particles. The anatase quantity developed remarkably with annealing temperature. The controlling factor of phase transformation of Sol-gel TiO₂ film was annealing temperature, and the aluminum foil substrate had little effect. Compared to specimens without TiO₂ film, the specific capacitance of TiO₂ coated specimens after anodizing at 400 °C, 500 °C and 600 °C was increased by 15%, 35% and 74%, respectively.

Keywords: Aluminum electrolytic capacitor; anodizing; annealing; TiO₂ film;

1. INTRODUCTION

Aluminum electrolytic capacitors are extensively used in electric and electronic devices, such as notebook computer, mobile phone, and components in automobile industry, because of its outstanding characteristics of mini-bulk with large capacitance [1-6]. Now its capacitance can be further increased by incorporating high dielectric metal oxide into alumina and forming composite oxide [7,8]. Different composite oxide film prepared by different methods has been studied, such as Al-Si-O, Al-Zr-O, Al-Nb-O, and Al-Ti-O and so on [9-12].

TiO₂ exhibits excellent chemical and physical properties and characteristics, such as non-toxic, long term stability, good mechanical strength, transparency, and good insulating properties [13,14], and has been comprehensively researched and applied by now. TiO₂ has three main kinds of crystallographic
structures, namely brookite, anatase and rutile and their relative dielectric constant are about 30, 48 and 110-117, respectively [15,16]. Phase transformation process of these structures are mainly affected by annealing and preparation technology such as substrate, atmosphere et al [17,18].

Nanocrystalline dielectric thin film is usually observed by many methods, such as TEM, SEM and AFM. TEM has higher revolution, but electron beam would transform the original state of TiO$_2$ film, because high voltage electron beam would lead to re-crystallization. SEM could not distinguish original TiO$_2$ film without aided conductive materials, and the spraying conductive materials would cover the original surface of TiO$_2$. AFM is a method of in-situ and non-destructive investigation, which has high revolution and shows intuitionistic impression.

In some previous studies, an intermediate layer of Al-Ti-O nanocomposite film is confirmed to be formed between outer layer TiO$_2$ film and inner layer Al$_2$O$_3$ film during Sol-gel and anodizing process [19,20]. In this work, the effect of annealing on crystal type of TiO$_2$ film formed on aluminum was characterized by TG-DSC, XRD, Raman spectroscopy and AFM. The associated specific capacitance of the Al-Ti-O nanocomposite film prepared on aluminum was also discussed.

2. EXPERIMENTAL

2.1 Specimens preparation

TiO$_2$ Sol was firstly prepared by mixing tetrabutyl titanate, deionized water, acetyl acetone and dehydrated alcohol according to their molar ratio of 1:3:1:14, subsequently the mixture was stirred by magnetic force with 600 rpm/min for 30min and then aged at room temperature for about 48 h. Then, the electropolished aluminum foil (the aluminum purity is higher than 99.99%) with 50 μm thickness was immersed in TiO$_2$ Sol for 5 min and subsequently taken out with a withdrawing speed of 1 mm/S. The dip-coated aluminum foil was dried at 100 °C in vacuum for 30min. And then the specimens were annealed at 400 °C, 500 °C, and 600 °C for 10min in vacuum. When the annealing performed at different temperatures the heating rate was 50°C/min. And then the dip-coated aluminum foil with TiO$_2$ film after annealing treatment was cut into 1×5 cm$^2$ specimens for the following tests. Finally, the specimens with and without TiO$_2$ film were all anodized at 50 V in ammonium adipate solutions (13wt%, pH≈6.9) at 85 °C for 10 min by oxidation power equipment.

2.2 Characterization

Calorimetry measurement of dried Gel-Sol TiO$_2$ powder were performed by thermogravimetric differential scanning calorimetry (TG-DSC, Netzsh STA449C, Germany) at temperature range of 50 to 800 °C with a heating rate of 20 °C/min in the protective atmosphere of argon gas. The X-ray diffraction analysis (XRD, Rigakn D/max-2200, Japan) was also employed to characterized the crystal type of TiO$_2$ film which was stripped from coated specimens and of the dried Gel-Sol TiO$_2$ powder in a 2θ range of 20° to 90° at a step size of 0.02° using Cu K$_\alpha$ radiation. The Raman spectroscopy (Lab RAM HR800, JY Horiba, France) was also used to identify crystal phase of TiO$_2$ film annealed under different temperatures in an incident laser light at 633 nm wavelength and 4 × 4 μm$^2$ spot size. The surface
morphology of electropolished aluminum and TiO$_2$ film on aluminum annealed at different temperatures was observed by atomic force microscope (AFM, MutiMode Nanoscope, Veeco, USA) in tapping mode.

The values of specific capacitance for specimens were measured by multifrequency LCR meter (UC2852, Jiangsu Youce Electronic Ltd., China). The testing specimens were anodized aluminum foil with and without TiO$_2$ coating film and annealed at different temperatures. The specific capacitance was performed at volt potential of 3 V under constant current of 1mA and with a setting frequency of 120 Hz in 13 wt% ammonium adipate solution at room temperature. The LCR meter could directly figure out the specific capacitance values of different specimens during measurement.

3. RESULTS

3.1 Gel Powers structural properties

3.1.1 TG-DSC

Fig. 1 shows TG-DSC results of dried Gel TiO$_2$ powders in the temperature range from 50 °C to 750 °C. Residual water and some adsorbed alcohol molecular are gradually volatilized from 50 °C to 250 °C. An exothermic peak around 300 °C indicates that the TiO$_2$ transforms from amorphous to brookite. And an exothermic peak between 400 °C and 500°C implies a process of amorphous transforming to anatase. A lot of mass loss occurs in a temperature range from 50 °C to 500 °C. While, there is little of mass loss beyond 500 °C, which indicates that all of Gel TiO$_2$ powder totally transforms into anatase. The nearly flat curve after 500 °C shows a slow process of anatase transforming to rutile. A tiny peak between 600 °C and 700 °C indicates that anatase begins to transform into rutile [19,20].

![Figure 1. TG-DSC results of Gel TiO$_2$ powder](image)

3.1.2 XRD

XRD results of dried Gel TiO$_2$ powder annealed at different temperatures are illustrated in Fig.2. There is only anatase phase in TiO$_2$ powder after annealing at 400 °C and 500 °C, and the TiO$_2$ powder annealed at 500 °C has higher anatase intensity than that annealed at 400 °C. The rutile characteristic...
peak at about $2\theta=27^\circ$ is detected with weak intensity in 600 °C annealed TiO$_2$ powder, which implies that a little content of rutile is formed. The rutile content in TiO$_2$ powder increases remarkably when annealing temperature increasing to 650 °C. While, the TiO$_2$ powder annealed at 700 °C completely transforms into rutile phase.

![XRD patterns of TiO$_2$ powder annealed at different temperatures](image)

**Figure 2.** XRD patterns of TiO$_2$ powder annealed at different temperatures

The content of anatase and rutile phase in TiO$_2$ powder could be calculated by the following Formula (1) and (2), respectively [21]. Where, the $X_A$, $X_B$ are the content proportion of anatase and rutile phase in crystalline TiO$_2$ powder, respectively. $I_R$ and $I_A$ denote the intensity of rutile phase and anatase phase in XRD pattern, respectively.

$$X_A(\%) = \frac{100}{1 + 1.265 \frac{I_R}{I_A}} \quad (1)$$

$$X_B(\%) = 1 - X_A \quad (2)$$

The crystallization proportion in TiO$_2$ powder annealed at different temperatures is shown in Table 1. TiO$_2$ powder annealed at 600 °C contains 91.7% anatase and 8.3% rutile; TiO$_2$ powder annealed at 600 °C includes 63.5% anatase phase and 36.5% rutile phase.

<table>
<thead>
<tr>
<th>Annealing temperature/°C</th>
<th>Anatase /%</th>
<th>Rutile /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 °C</td>
<td>100%</td>
<td>0%</td>
</tr>
<tr>
<td>500 °C</td>
<td>100%</td>
<td>0%</td>
</tr>
<tr>
<td>600 °C</td>
<td>91.7%</td>
<td>8.3%</td>
</tr>
<tr>
<td>650 °C</td>
<td>36.5%</td>
<td>63.5%</td>
</tr>
<tr>
<td>700 °C</td>
<td>0%</td>
<td>100%</td>
</tr>
</tbody>
</table>
3.2 Structural properties of TiO$_2$ film on aluminum

3.2.1 XRD

TiO$_2$ film stripped from coated specimens was analyzed by XRD, which is displayed in Fig. 3. It shows that there is only anatase in TiO$_2$ film after 400 °C annealing. And at 500 °C, the intensity of anatase in TiO$_2$ increases remarkably compared to that annealed at 400 °C. At 600 °C, more anatase and a quantity of rutile are formed. The anatase phase intensity in XRD pattern increases remarkably with increasing annealing temperature. The other peaks are suggested to be Al(OH)$_3$ X-ray diffraction pattern, which are supposed to be coated on TiO$_2$ particles when metal aluminum was dissolved in NaOH aquatic solution. Al(OH)$_3$ reflections in XRD could be worked as an internal standard for intensity comparison between anatase and rutile annealed at different temperatures. According to Formula (2), the content of rutile phase in TiO$_2$ film annealed at 600 °C is about 30%. The peak at 2θ=25° for TiO$_2$ film annealed at 600 °C is much sharper than that annealed at 500 °C. According to Scherrer equation, it could be confirmed that the crystalline size of anatase grain in TiO$_2$ film becomes much bigger as temperature increased from 500 °C to 600 °C.

![Figure 3](image)

**Figure 3.** XRD patterns of TiO$_2$ film on aluminum foil annealed at different temperatures

3.2.2 Raman spectroscopy

Raman spectroscopy of TiO$_2$ film annealed at different temperatures is shown in Fig.4. Five well-defined peaks at 146cm$^{-1}$, 141cm$^{-1}$, 396cm$^{-1}$, 518cm$^{-1}$ and 638cm$^{-1}$ are supposed to be characteristic peaks of anatase. Peaks at 144cm$^{-1}$, 448cm$^{-1}$ and 614cm$^{-1}$ are defined as characteristic ones of rutile in Fig.4 [22,23]. It indicates that there is only anatase in TiO$_2$ film on aluminum when the annealing temperature being 400 °C and 500 °C. By contrast, both the anatase and a spot of rutile exists in TiO$_2$ film on aluminum when the annealing temperature being 600 °C. The intensity of characteristic peak around 144cm$^{-1}$ of TiO$_2$ film annealed at 500 °C is two as big as the 400 °C annealed one. Anatase phase intensity of TiO$_2$ film annealed at 600 °C keeps increasing compared to the 500 °C annealed film. It
indicates that the anatase content increases greatly with increasing annealing temperature. At 600 °C, the intensity of rutile phase is remarkable, about 30% of anatase.

![Raman spectroscopy of TiO₂ film formed on aluminum annealed at different temperatures](image)

**Figure 4.** Raman spectroscopy of TiO₂ film formed on aluminum annealed at different temperatures

### 3.2.3 AFM morphologies

The surface morphologies of specimens before and after annealing at different temperatures were observed by AFM, as shown in Fig. 5. According to Fig. 5 (a, b), the electropolished aluminum has the lowest roughness, which means that aluminum has extremely smooth surface. Gel TiO₂ film is very dense, and composed of fine particles about 2-4 nm (Figs. 5c, d). The size of TiO₂ particles on the annealed film increases with increasing annealing temperature. The TiO₂ particle size on film annealed at 400 °C is about 5-7 nm; its value is about 5-12 nm at 500 °C annealing, and increases to about 5-15 nm as annealing temperature increased to 600 °C. As shown in AFM 3D and 2D images of Fig. 5 (e-j), the average particles size and roughness of TiO₂ film annealed at different temperatures are listed in Table 2.

**Table 2.** Average grain size and roughness of TiO₂ film annealed at different temperatures

<table>
<thead>
<tr>
<th>Annealing temperature/°C</th>
<th>Average grain size/nm</th>
<th>Roughness/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 °C</td>
<td>7.086</td>
<td>0.398</td>
</tr>
<tr>
<td>500 °C</td>
<td>13.036</td>
<td>0.768</td>
</tr>
<tr>
<td>600 °C</td>
<td>15.102</td>
<td>1.163</td>
</tr>
</tbody>
</table>

The TiO₂ film becomes denser and more compact with temperature increasing. AFM morphology of TiO₂ film annealed at 400 °C is similar with that of Gel film. It indicates that crystal quantity in film
annealed at 400 °C is smaller than that annealed at 500 °C and 600 °C. The AFM result is in close agreement with the measurements of Raman spectroscopy and XRD test.

**Figure 5.** AFM surface morphology in 2D and 3D of electropolished aluminum (a, b), and TiO₂ on aluminum before (c, d), and after annealing at 400°C (e, f), 500°C (g, h), and 600°C (i, j)
3.3 Capacitance-Temperature tests

The specific capacitance of coated specimens annealed at different temperatures is shown in Fig. 6. Compared to the specimens without TiO$_2$ film, the specific capacitance of coated specimens is improved about 15.6%, 38.3% and 74% after 400 °C, 500 °C and 600 °C annealing, respectively. It indicates that the specific capacitance of coated specimens increases remarkably with increasing annealing temperature. It shows that the dielectric constant of Al-Ti-O composite film prepared by sol-gel and anodizing increases with more crystal phase content in TiO$_2$ film.

![Figure 6. Specific capacitance of specimens with and without TiO$_2$ film annealed at different temperatures](image)

4. DISCUSSION

4.1 Structural properties

As mentioned above, the TiO$_2$ powder and TiO$_2$ film had similar phase transformation during annealing in the temperature range from 400 °C to 600 °C. Crystal state in TiO$_2$ powder was nearly consistent with the TiO$_2$ film at different annealing temperature. But at 600 °C, the content of rutile in TiO$_2$ film was 20% higher than that in TiO$_2$ powder. It indicated that aluminum substrate had little effect on phase transformation of TiO$_2$ film, and the annealing temperature was a main effect on transformation of crystal phase for TiO$_2$ film.

Amorphous TiO$_2$ began to transform into anatase with minor amount at temperature range of 400 to 500 °C. TiO$_2$ film on aluminum consisted of massive anatase and a small number of rutile in about 30% when annealing temperature being 600 °C. The quantity of anatase increased remarkably with increasing annealing temperature. Anatase would entirely transform into rutile at 700 °C. TiO$_2$ film on aluminum annealed at different temperatures was composed of nano-particles. Higher temperatures promoted the nucleation and growth of crystals, and thus the size of TiO$_2$ particles increased with
4.2 Dielectric properties

The TiO$_2$ film was homogeneously coated on the wall surface of the etched aluminum foils, and thus the holes were covered by TiO$_2$ film, which decreased the real area of etched aluminum foils. Besides, the coated TiO$_2$ film increased the total thickness of specimens. Therefore, the specific capacitance of aluminum foil should decrease theoretically after TiO$_2$ film coating according to the equation (3), where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the relative permittivity of the anodic oxide film, $S$ is effective surface area of the dielectric oxide film, and $d$ denotes the thickness of the oxide film.

$$C = \frac{\varepsilon_0 \varepsilon_r S}{d} \quad (3)$$

However, the real area and real thickness of specimens were mainly determined by the anodic oxide layer formed after anodizing. The anodic oxide layer is highly multihole and far thicker than the pure aluminum foil and TiO$_2$ film, and its specific surface area is also far bigger than the original surface area of etched aluminum foil. Therefore, the original thickness of aluminum foil and TiO$_2$ film as well as the surface area of etched foil had relatively light effect on the specific capacitance of specimens. The specific capacitance of specimens was mainly determined by the crystal texture of the composite film.

For the porous structure of TiO$_2$ film, the improvement of specific capacitance of specimens was owed to the Al-Ti-O nanocomposite film. The Al-Ti-O composite film is suggested to be a compact composite structure which is composed of TiO$_2$ particles and anodic alumina [20]. With annealing temperature increasing from 400 $^\circ$C to 600 $^\circ$C, TiO$_2$ film on aluminum becomes denser and more compact, as well as with more anatase and rutile. As a result, Al-Ti-O composite film contains more anatase or rutile phase after a higher temperature annealing. Therefore, dielectric constant of the composite Al-Ti-O film increases greatly with increasing annealing temperature. In consequence, specific capacitance of specimens coated with TiO$_2$ film is improved remarkably.

Mitra [24] used mechanical milling to introduce different strain-leaves to the multiphase TiO$_2$ powder. A longer time mechanical milling resulted in a more significant strain induced partial phase transformation to the rutile phase and more oxygen vacancies. These phases changes could increase about 30% to about 60% capacitive performance compared to the commercial TiO$_2$ powder. Besides, Mitra found that the powder size had little effect on the capacitive properties. While, Ashery [25] believed that the effect of TiO$_2$ phase changes on capacitive properties was still limited. He designed a composite GO/TiO$_2$/n-Si MOS device, and obtained a specific capacitance up to about 5.0×10$^{-7}$ F/cm$^2$, which was 60% to 100% higher than our work, however with a more complicated preparation process. Raj [26] pointed out that the increased specific surface area could remarkably increase the areal capacitance of the TiO$_2$ electrode. He prepared a TiO$_2$ nanotube arrays electrode with a very high carrier density and a huge specific area, which resulted in a highest areal capacitance of 20.09 mF/cm$^2$ to this TiO$_2$ electrode. Zhang [27] developed a manufacturing process to produce a TiO$_2$ nanotube arrays/C/MnO$_2$ composite electrode and obtained an amazing specific areal capacitance of 492 mF/cm$^2$, which was the highest value can be found in literatures in present. Compared to these above studies, it
can be found that the improvement of specific capacitance caused by TiO$_2$ phase transformation is limited but with the most simplified preparation process. The composite TiO$_2$ nanotube arrays electrode embellished by metallic oxides always showed a far better specific areal capacitance but with a very complex manufacturing process, which would obviously increase the cost. Which preparation route being the best depends on the cost performance.

5. CONCLUSIONS

(1) In summary, annealing temperature is a controlling factor on phase transformation of TiO$_2$ film formed on aluminum, and the substrate has little effect on phase transformation. In TiO$_2$ film on aluminum, there were only anatase phase after 400 °C and 500 °C annealing. Both rutile and anatase phases formed in TiO$_2$ film during 600 °C annealing, and the rutile phase accounted for 30% in hybrid crystal phases. Anatase phase in TiO$_2$ film increased remarkably with temperature increasing.

(2) The specific capacitance of coated specimens after anodizing increased with annealing temperature. Compared to the pure aluminum foil, the specific capacitance of specimens with TiO$_2$ film annealed at 400 °C, 500 °C and 600 °C increased by 15%, 35% and 74%, respectively.

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