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Effect of TiO_2 nanostructures on specific capacitance of Al_2O_3–TiO_2 composite film on etched aluminum foil formed by the sol–gel and anodizing

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Abstract

Nano-thin TiO_2 film on etched aluminum foil was prepared by the Sol–gel dip-coating method and annealing post-treatment at different temperatures; then, Al_2O_3–TiO_2 composite oxide film on etched aluminum foil was fabricated by anodization in 13 wt% ammonium adipate solution. Nanostructures of TiO_2 film were characterized by means of X-ray Diffraction (XRD), Raman Spectroscopy (RS), and Atomic Force Microscope (AFM). TiO_2 nanostructured films are composed of anatase nanopartilces in size of 5–12 nm as annealed at 400 °C and 500 °C, and anatase-rutile complex nanopartilces in 5–15 nm at 600 °C. Compared with pure anodic aluminum oxide film, TiO_2 nanostructures effectively improved specific capacitance of the Al_2O_3–TiO_2 composite oxide film on etched aluminum foil, with an increment ratio of about 8.6%, 24.6%, and 33.3%, caused by anatase and rutile content increasing with annealing temperature from 400 °C, 500 °C to 600 °C, respectively. The specific capacitance of dip-coated etched aluminum foil annealed at 500 °C reached to a maximum after two dip-coating times with 28.3% enhancement.

Keywords: Etched aluminum foil; Sol–gel; TiO_2 nanostructures; Al_2O_3–TiO_2 composite film; Specific capacitance

1. Introduction

Aluminum electrolytic capacitors have extensive applications in electric and electronic industries, due to their outstanding characteristics of mini-bulk with large capacitance [1,2]. In the past decades, sustained and rapid developments of electronic technology require continuous miniaturization of aluminum electrolytic capacitors; in another words, miniaturization of the capacitors requires improving the specific capacitance. Recently, a most promising way has been widely accepted to increase specific capacitance by formation of high dielectric composite oxide film.

Different composite oxide films, such as Al_2O_3–SiO_2, $Al_2O_39ZrO_2$, Al_2O_3–Nb_2O_5, and Al_2O_3–TiO_2 etc., were reported to be fabricated by Sol–gel and anodization [1–8]. In our previous investigations [9,10], TiO_2 film was coated on electropolished aluminum foil by the Sol–gel method, and high dielectric Al_2O_3–TiO_2 composite film was confirmed to be formed as an intermediate layer in sandwich oxide film, with TiO_2 film as outer layer and anodic aluminum oxide film as inner layer on aluminum after anodization. The specific capacitance of electropolished aluminum foil coated with anatase TiO_2 film annealed at 500 °C was improved as much as 42% at most.

TiO_2 has superior chemical and physical properties, such as transparency, self-cleaning, non-toxic, long term stability, high mechanical strength, and good insulating properties [11,12]. The physical and chemical properties of TiO_2 depend strongly on the crystallinity of the material [13]. Compared with traditional coarse-grained TiO_2 films, TiO_2 nanostructured films have attracted the attention of researchers owing to their better overall performance [14,15]. TiO_2 thin film has two main crystallographic structures: anatase and rutile [13]. Their relative dielectric constants have significant difference, which are about 48 and 110–117, respectively [16,17]. They are usually obtained at different temperatures. Amorphous TiO_2 film transforms into anatase at 400–700 °C [18,19], and then thermodynamically stable rutile under higher temperature.

In the present work, TiO_2 nanostructured films were coated on low-voltage etched aluminum foil by the Sol–gel dip-coating technique and annealing post-treatment at different temperatures. Al_2O_3–TiO_2 composite film was formed by anodization in 13 wt%

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ammonium adipate solution. The correlation of TiO_2 nanostructures with specific capacitance of the composite film on etched aluminum foil was investigated, and also effect of different dip-coating times on specific capacitance was examined.

2. Experimental

2.1. Specimens preparation

TiO_2 Sol was prepared as mixture of tetrabutyl titanate, deionized water, acetyl acetone and dehydrated ethanol, with their molar ratio of 1:3:1:14, and stirred by magnetic force for 30 min and subsequently aged for 36 h in air. Electropolished and etched aluminum foils (99.99%) were immersed in TiO_2 Sol for 1 min, with a withdrawing speed of 1 mm/s. The dip-coated aluminum foils were dried at 100 °C for 30 min in an oven. Then the specimens were annealed at 400 °C, 500 °C, and 600 °C for 10 min in ambient atmosphere, respectively. A series of dip-coated specimens were cut into $1\times5\ cm^2$ from one piece of dip-coated aluminum foil. The thickness of TiO_2 film on aluminum by once dip-coating was about 50 nm.

Etched aluminum foil with TiO_2 film were anodized under constant current density 50 mA cm^{-2} until reaching to 25 V, and then potentiostatic anodized for 10 min in ammonium adipate aqueous solutions (13 wt%, pH $\approx$ 6.9) at 85 °C. Stainless steel was used as solution container and counter electrode. Etched aluminum foil without TiO_2 film was anodized under the same condition as reference.

2.2. Characterization

TiO_2 film was exfoliated from coated aluminum foil annealed at different temperatures in 10 wt% Bromine Methanol solutions, and ground into fine powders. TiO_2 powders were compressed into a $\Phi6\ mm\times1.5\ mm$ pallet, and quantitatively characterized by X-ray Diffraction (XRD, Rigakn D/max-2200, Japan) using Cu target. Raman spectroscopy (Lab RAM HR800, JY Horiba, France) was used to identify crystalline phase of TiO_2 film on aluminum foil annealed under different temperatures. The surface morphology of TiO_2 film coated on electropolished aluminum foil was carried out by Atomic Force Microscope (AFM, MutiMode Nanoscope III a, Veeco, USA) using tapping mode. Field Emission Scanning Electron Electrode (FE-SEM, S-4800, Hitachi, Japan) was used to observe surface morphology of etched aluminum foil after different dip-coating times of TiO_2 film. The specific capacitances of etched aluminum foil with and without TiO_2 film after anodization were measured by multi-frequency LCR meter (TH2615C, Changzhou Tonghui Electronic Ltd., China) with a setting frequency of 120 Hz in 13 wt% ammonium adipate solution at 30 ± 2 °C.

3. Results and discussions

3.1. Microstructure

Fig. 1 shows XRD patterns of TiO_2 film annealed at different temperatures. According to JCPDS card No.21-1272, it shows that TiO_2 is composed of only anatase at annealing temperatures of 400 °C and 500 °C. The peak intensity of anatase at 500 °C is twice as high as that at 400 °C. Abundant anatase and a certain amount of rutile are both observed in the XRD patterns at 600 °C. The intensity of anatase at 600 °C increases 80% more than that at 500 °C. According to Formula (1), the content of rutile and anatase in TiO_2 film annealed at 600 °C accounts for about 14.3% and 85.7%, respectively.

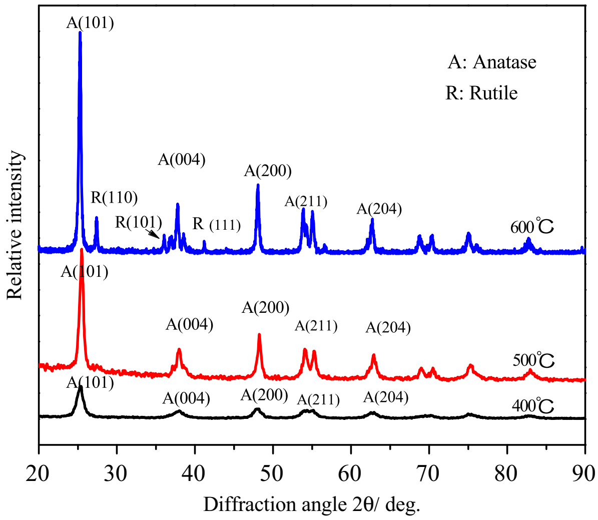

Fig. 1. XRD patterns of TiO_2 film annealed at different temperatures.

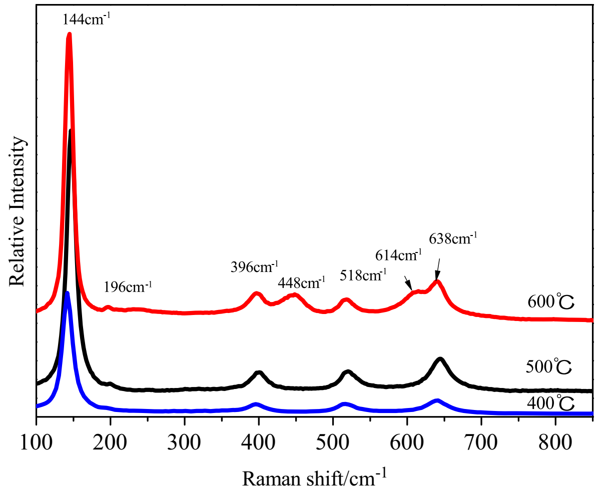

Fig. 2. Raman spectra of TiO_2 film annealed at different temperatures.

$$X_A(\%)=\frac{100}{1+1.265(I_R/I_A)}\ \text{and}\ X_R(\%)=1-X_A \qquad (1)$$

In which X_A and X_R are the content proportion of anatase and rutile in crystalline TiO_2 film, respectively. I_R and I_A denote the intensity of rutile and anatase phase in XRD patterns, respectively.

Raman spectra of TiO_2 film annealed at 400 °C, 500 °C and 600 °C is shown in Fig. 2. Five well-defined peaks at 146 cm^{-1}, 141 cm^{-1}, 396 cm^{-1}, 518 cm^{-1} and 638 cm^{-1} are supposed to be characteristic peaks of anatase [20,21]. Peaks at 144 cm^{-1}, 448 cm^{-1} and 614 cm^{-1} are characteristically defined as rutile

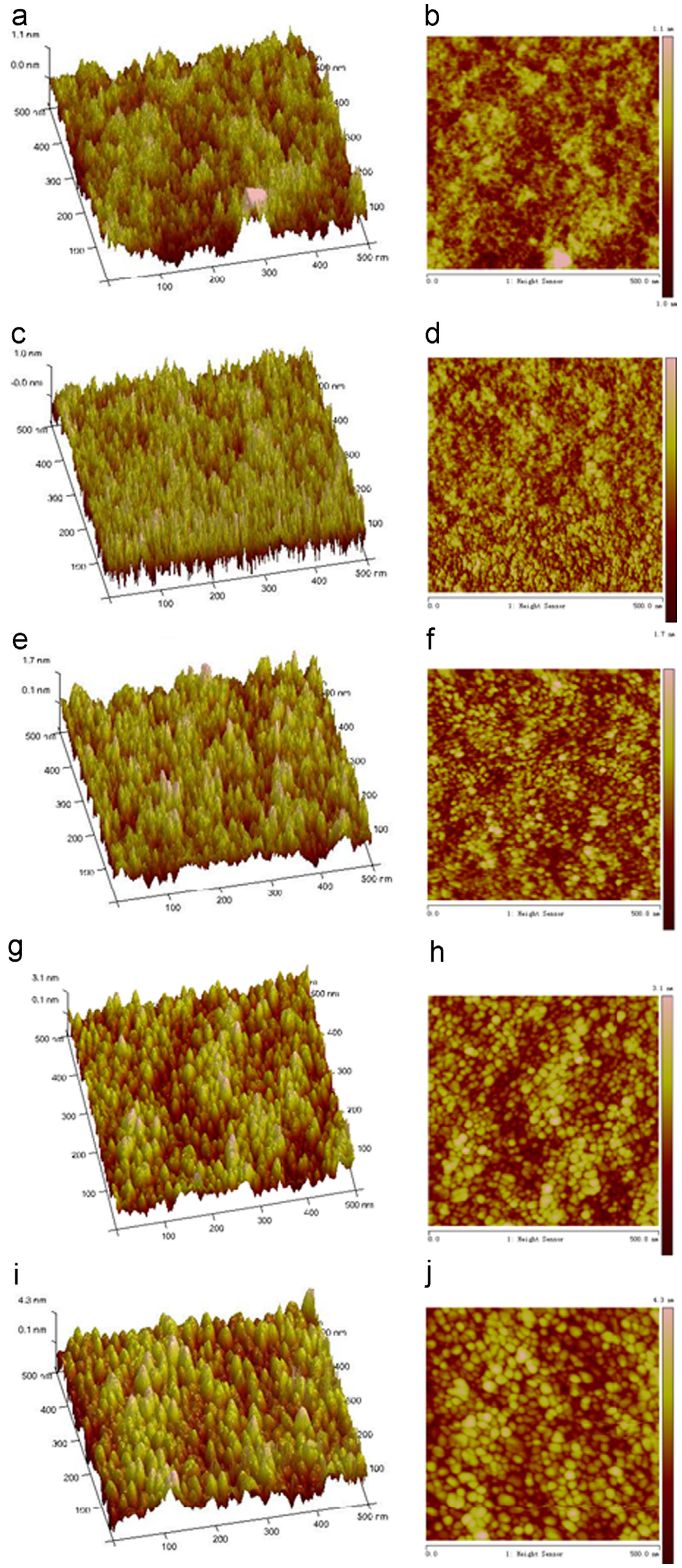

Fig. 3. AFM surface morphologies in 3D and 2D of electropolished aluminum (a and b) and TiO_2 film before (c and d) and after annealing at 400 °C (e and f), 500 °C (g and h), and 600 °C (I and j).

[20,21]. It indicates that there are only anatase in TiO_2 film annealed at 400 °C and 500 °C, and duplex phase of anatase and rutile at 600 °C. The intensity of characteristic peak at 144 cm^{-1} increases remarkably with annealing temperature increasing from 400 °C to 600 °C, which indicates that anatase increases greatly with annealing temperature.

The results of Raman spectra are in agreement with XRD. It can be confirmed that there is only anatase phase in TiO_2 film annealed at 400 °C and 500 °C, and anatase-rutile duplex phase at 600 °C; content of anatase in TiO_2 film increases greatly with an annealing temperature range from 400 °C to 600 °C. Anatase at 500 °C is much more than that at 400 °C; anatase at 600 °C is about 80% more than that at 500 °C. Rutile occupies about 14.3% in crystalline TiO_2 film at 600 °C.

Fig. 3 shows AFM microstructural morphologies in 3D and 2D of TiO_2 nanostructured film before and after annealing at different temperatures. Fig. 3(a and b) shows that electropolished aluminum has minimal surface roughness, which indicates that eletropolished aluminum has extremely smooth surface. Gel TiO_2 film is very dense, and is composed of fine nanoparticles about 2–4 nm (Fig. 3c and d). As the annealing temperature increases from 400 °C to 600 °C, the size of TiO_2 nanoparticles in the film increases. As shown in AFM 3D and 2D images of Fig. 3(e–j), diameter of TiO_2 nanoparticles are about 5–7 nm at 400 °C, 5–12 nm at 500 °C, and 5–15 nm at 600 °C. The average size of TiO_2 nanoparticles and RMS of TiO_2 film annealed at 400 °C, 500 °C and 600 °C is shown in Table 1. It shows that with temperature increasing, TiO_2 film becomes denser and more compact.

3.2. Surface morphology

The surface morphology of etched aluminum foil after different dip-coating times is shown in Fig. 4. Pure etched aluminum foil shows etched holes with diameters of 100–300 nm and smooth surface on the wall surface of holes, as shown in Fig. 4(a). The wall surface of etched holes was coated with thin TiO_2 film after 1 dip-coating (Fig. 4b). With 2 dip-coatings, etched holes were coated with thicker TiO_2 film (Fig. 4c). Much thicker TiO_2 film was coated on etched aluminum foil after 4th dipping, and even some etched holes were covered (Fig. 4d).

3.3. Specific capacitance

3.3.1. Effect of TiO_2 microstructure

The increment ratio of specific capacitance of etched aluminum foil coated once with TiO_2 film annealed at different temperatures is shown in Fig. 5(a). With annealing temperature, the specific capacitance of coated etched aluminum foil increases obviously; the specific capacitance of coated etched aluminum foil increases about 8.6% at 400 °C, 24.6% at 500 °C, and 33.3% at 600 °C, compared with pure etched aluminum foil.

The increase of specific capacitance of coated aluminum foil after anodizing is due to the Al_2O_3–TiO_2 composite film [9,10]. Incorporation of TiO_2 nanoparticles in the Al_2O_3–TiO_2 composite film is responsible for the increase of specific capacitance. On one side, TiO_2 film on aluminum contained more anatase and rutile with annealing temperature increasing. The dielectric constant of

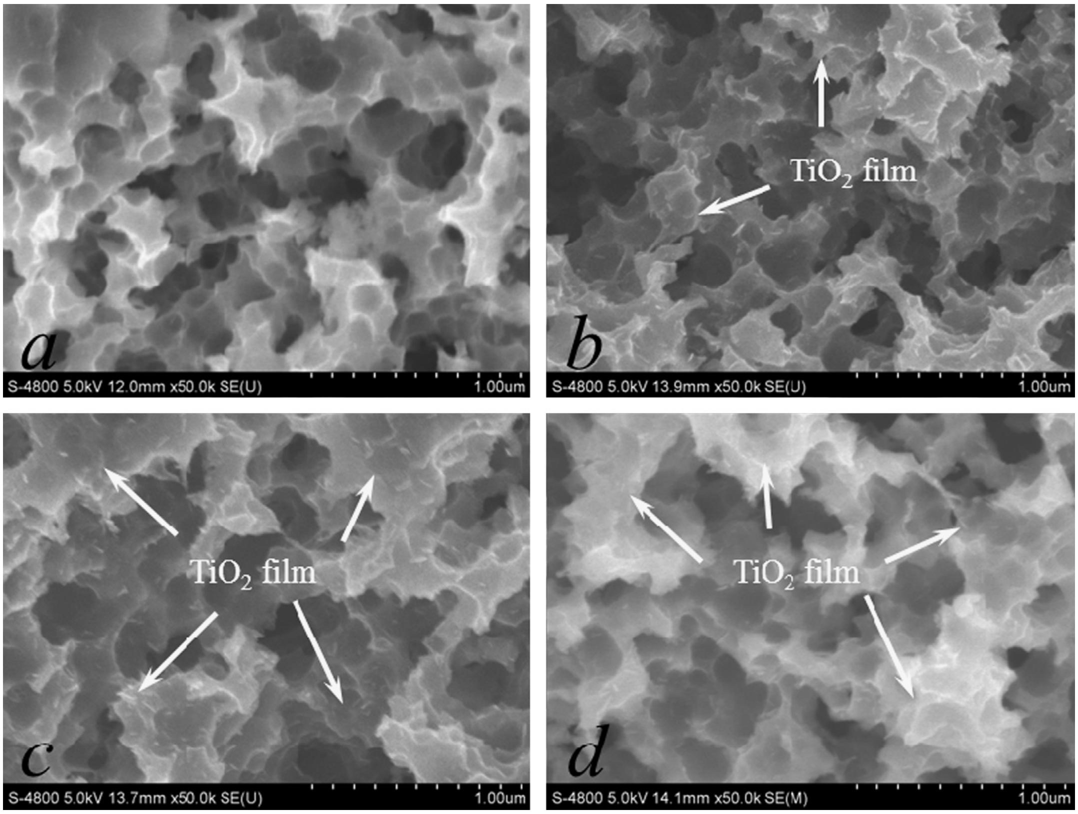

Fig. 4. Etched aluminum foil with Sol–gel TiO_2 film by different dip-coating times (a, blank; b, 1 times; c, 2 times; 4 times).

Table 1
Average grain size and roughness of TiO_2 film annealed at different temperatures.

Annealing temperature/ °C	Average grain size/nm	RMS/nm
400	7.015	0.488
500	12.085	0.888
600	14.505	1.28

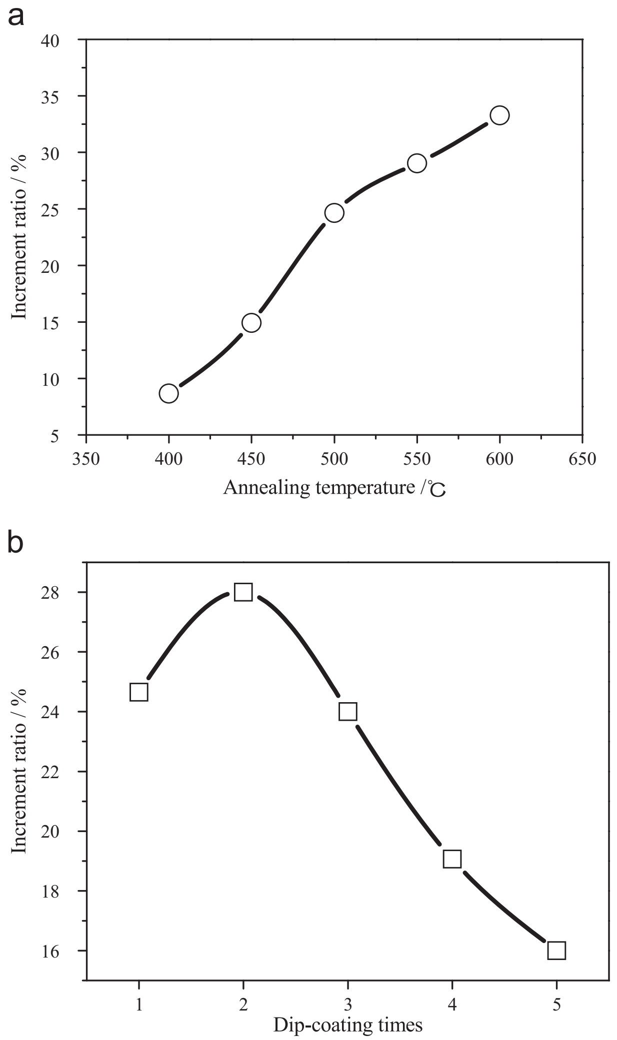

Fig. 5. Specific capacitance of etched aluminum foil coated once with TiO_2 film annealed at different temperatures (a) and different dip-coating times annealed at 500 °C (b).

rutile is much greater than anatase. On the other side, TiO_2 film became denser and more compact with increasing annealing temperature. As a result, TiO_2 nanoparticles accounted a higher proportion in the Al_2O_3–TiO_2 composite film.

3.3.2. Effect of dip-coatings times

The effect of dip-coating times of TiO_2 film on increment ratio of specific capacitance of etched aluminum foil annealed at 500 °C is shown in Fig. 5(b). The specific capacitance of coated etched aluminum foil reaches to maximum at 2 dip-coatings, which increases about 28.3%. However, with more dip-coatings, the specific capacitance gradually decreases.

Thin TiO_2 film was homogenously coated on the wall surface of etched holes after 1 dipping. With more dipping times, the thickness of TiO_2 film increased, and TiO_2 film was coated on the external surface of etched aluminum foil, which decreased real area of etched aluminum foil. Therefore, according to Formula (2), the specific capacitance of coated etched aluminum foil showed an increase firstly and then a decrease with more dip-coatings.

$$C = \frac{\varepsilon_0 \varepsilon_r S}{d} \qquad (2)$$

where ε_0 represents the vacuum permittivity, ε_r denotes the relative permittivity of anodic oxide film, S is effective surface area of the dielectric oxide film; d represents thickness of the oxide film.

4. Conclusions

(1) Anatase nanostructured TiO_2 films with nanoparticle size of 5–7 nm and 5–12 nm were obtained at annealing temperatures of 400 °C and 500 °C, respectively. TiO_2 film annealed at 600 °C was consisted of rutile-anatase complex nanoparticles with size of 5–15 nm, in which rutile occupied for 14.3%. With annealing temperature increasing, anatase increases remarkably.

(2) The specific capacitance of low voltage etched aluminum foil with TiO_2 film after 1 dip-coating increased with annealing temperature, about 8.6%, 24.6% and 33.3% more than that of pure etched aluminum foil annealed at 400 °C, 500 °C and 600 °C, respectively. The specific capacitance of low voltage etched aluminum foil reached to maximum with two dip-coating times, which had improvement about 28.3%.

Acknowledgments

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