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Ceramics International 38 (2012) 2501–2505
www.elsevier.com/locate/ceramint

Formation of Al_2O_3–TiO_2 composite oxide films on aluminum foil by cathodic electrodeposition and anodizing

Zhe-Sheng Feng [*], Jin-Ju Chen, Chuan Zhang, Ning Zhao, Zi Liang

State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China

Received 9 August 2011; received in revised form 4 November 2011; accepted 5 November 2011
Available online 25 November 2011

Abstract

Titanium dioxide (TiO_2) thin films were deposited on aluminum foils by cathodic electrodeposition, and then Al_2O_3–TiO_2 (Al–Ti) composite oxide films were formed on aluminum foils by anodizing in 15 wt% ammonium adipate solution. The composition and structure of TiO_2 coating layer were investigated by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). The morphologies of specimens at different stages in the preparation process were characterized by atomic force microscope (AFM). The growth mechanism of the Al–Ti composite oxide film was discussed. It was found that TiO_2 coating layer with anatase structure was obtained on aluminum foil after heat treatment. The TiO_2 film showed an island growth pattern, which favored the growth of Al_2O_3 from uneven channel in the coating layer, thus promoting the formation of the Al–Ti composite oxide film. The anodic oxidation efficiency of specimens increased with the current density of cathodic electrodeposition increasing. The specimen with the Al–Ti composite oxide film exhibited about 26.3% higher product of specific capacitance and withstanding voltage than that with pure aluminum oxide film.

Keywords: Aluminum foil; Al–Ti composite oxide films; Cathodic electrodeposition; Anodizing

1. Introduction

With the particular performance of large capacitance, low cost, and high voltage resistance, aluminum electrolytic capacitors are widely used in the field of electric and electronic circuits systems. Barrier-type anodic oxide films formed on etched aluminum foils play an important role as dielectric layers in aluminum electrolytic capacitors, and their physical and chemical behaviors have a great effect on the performance of the capacitors. Recently, the rapid development of mobile electronic devices requires large amount of small-size electrolytic capacitors with high capacitance. Increasing the specific capacitance of aluminum anode foils is an effective way to realize the miniaturization of aluminum electrolytic capacitors.

The electric capacitance (C) of aluminum electrolytic capacitor is defined by the following equation:

$$C = \frac{\varepsilon_0 \varepsilon_r S}{d} \tag{1}$$

where ε_0 represents the dielectric constant of vacuum atmosphere, ε_r is the relative dielectric constant of the anodic oxide film, S is the effective surface area of dielectric layer, and d is the film thickness. It is obvious from Eq. (1) that the capacitance of electrolytic capacitors can be improved by increasing S and ε_r or decreasing d. Although S can be enlarged by changing electrochemical etching conditions, it is difficult to increase further; the d value depends largely on the working voltage, so it is difficult to decrease it when the working voltage is fixed. Current studies show that the most effective and facile solution to improve specific capacitance of aluminum foils is to form composite oxide films by incorporating aluminum anodic oxide films with relatively high dielectric constant compounds, such as TiO_2, ZrO_2, Ta_2O_5, Nb_2O_5, $BaTiO_3$ and so on [1–11].

Various techniques have been used to form composite oxide films on aluminum foils, including pore filling technique [1], sol–gel method [2–8], hydrolysis deposition method [10,11]

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[*] Corresponding author.
E-mail address: fzs@uestc.edu.cn (Z.-S. Feng).

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doi:10.1016/j.ceramint.2011.11.019

and others. However, these methods have disadvantage of time consuming or difficulty in controlling the amount of incorporating materials. Generally, cathodic electrodeposition method is used in photocatalysis or nano-materials preparation. Compared with other methods, cathodic electrodeposition method has following advantages: the deposition particle size and film thickness can be controlled by adjusting electrochemical parameters, and particles can be easily deposited on complex surfaces of etched aluminum foils. Besides, this method is a low energy process carried out under environment-friendly conditions. As a consequence, the electrodeposition method could become a promising and facile approach for the formation of high dielectric constant materials on etched aluminum foils. In this paper, we reported a cathodic electrodeposition and subsequent anodizing method for the preparation of Al–Ti composite oxide films with high dielectric constant. The components and crystal structures of deposition layers were characterized, and the properties of the composite oxide films were investigated.

2. Experimental procedures

Titanium tetrachloride ($TiCl_4$) was selected as titanium resource. Under the conditions of magnetic stirring at 1 °C, 0.5 mL $TiCl_4$ was dissolved in 300 mL methyl alcohol–water solvent (3:1 volume ratio). With instillation of 1.25 mL H_2O_2 solution, the solution turned orange and formed the stable titanium peroxide complex.

The specimen (2 cm × 5 cm with handle), cutting from commercial aluminum foil with 99.99% purity, was used as the substrate of cathode. An inert platinum foil was used as the counter electrode. These electrodes were ultrasonically washed for 5 min in the acetone, then washed in deionized water and dried under room temperature. Electrodeposition was carried out by applying constant current density for 10 min. Then the specimen was dried in air at 80 °C for 5 min, followed by a heat-treat process at 500 °C for 10 min to obtain the TiO_2 coating layer. Afterwards, the specimen was anodized by conventional anodizing. The aluminum foil without TiO_2 coating was anodized under the same condition for comparison.

The components of deposition layers were identified by XPS (XSAM800, Kratos Ltd., UK). The crystal structures of TiO_2 coating layers were measured by XRD (D/maxIIIA, Rigaku Industrial Corporation, Japan) using Cu Kα radiation. The surface morphologies of specimens were observed by atomic force microscopy (AFM, SPA-300). The variations of anodizing voltage with anodizing time were monitored by multi-meter data acquisition system (2700, Keithley Instruments, Inc., USA). When anodizing voltage reached the selected 20 V, the voltage was held constant for 10 min and the current was allowed to decay, and the final current was recorded as the leakage current of the anodic oxide film. The specific capacitances of specimens were measured by multi-frequency LCR meter (Wayne Kerr 4225, Tonghui Electronic Ltd., China) in 15 wt% ammonium adipate solution. The withstanding voltages of anodic oxide films were tested by T-V meter (XY2690, Wuxi Xinyuan Electronic equipment, China) in 15 wt% ammonium adipate solution at 85 °C.

3. Results and discussion

$TiCl_4$ is very susceptible to hydrolysis, so it has to be dissolved in methyl alcohol. Reaction mechanism is as follows:

$$TiCl_4 \rightarrow Ti^{4+} + 4Cl^- \quad (2)$$

Then the solution was mixed with H_2O_2, and finally a stable peroxo complex of titanium was obtained:

$$Ti^{4+} + H_2O_2 + (n-2)H_2O \rightarrow [Ti(O_2)(OH)_{n-2}]^{(4-n)+} + nH^+ \quad (3)$$

When the current went through, reduction reaction occurred on surface of the cathode. The peroxo complex of titanium reacted with OH^-, and eventually the peroxotitanium hydrate was formed:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (4)$$

$$[Ti(O_2)(OH)_{n-2}]^{(4-n)+} + (4-n)OH^- + (x-1)H_2O \rightarrow TiO_3(H_2O)_x \quad (5)$$

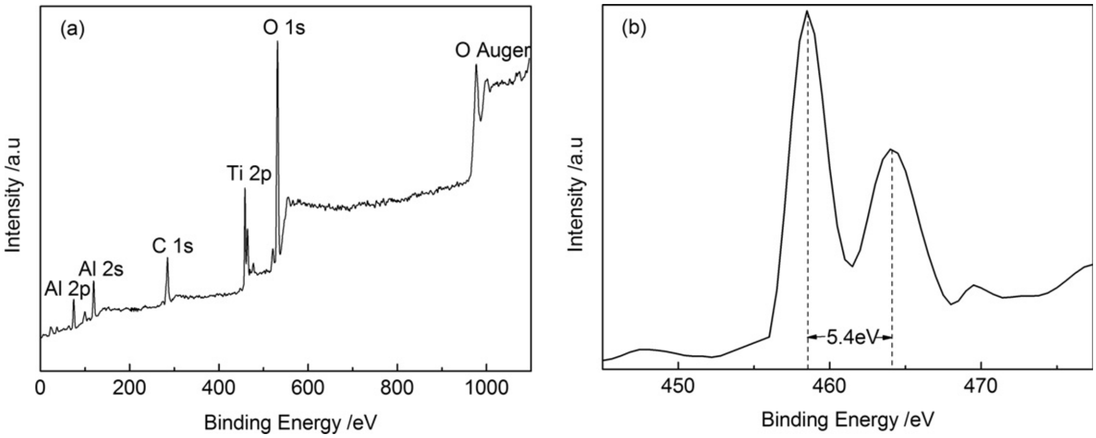

Fig. 1. (a) XPS profile of aluminum foil coated with titanium deposition after heat treatment over a wide binding energy region and (b) the binding energy region around Ti 2p.

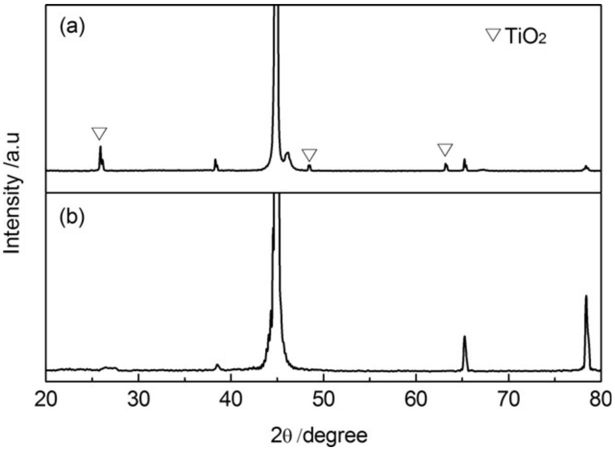

Fig. 2. XRD patterns of (a) aluminum foil with TiO_2-coating and (b) normal aluminum foil.

Afterwards, titanium complex on aluminum foil was heat-treated at 500 °C for 10 min, and then the TiO_2 thin film was obtained. Reaction mechanism is as follows:

$$2TiO_3(H_2O)_x \rightarrow 2TiO_2 + O_2 + 2xH_2O \quad (6)$$

The specimen with TiO_2 coating layer was characterized by XPS. Fig. 1(a) shows the wide-scan XPS spectrum for the specimen. It can be seen that there are Al, Ti, and O elements on the surface of aluminum foil, as well as C from surface contamination. Fig. 1(b) shows the XPS spectrum around the Ti 2p region. Two peaks at 458.5 and 463.9 eV, which are corrected to 459.5 and 464.9 eV on the basis of the C 1s peak, are found in the profile, and they correspond to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks for TiO_2, respectively. It demonstrates that TiO_2 is successfully deposited on the aluminum foil.

Fig. 2 shows XRD patterns of TiO_2-coating aluminum foil (a) and normal aluminum foil (b), respectively. It is obvious that the aluminum foil coated with TiO_2 layer has characteristic diffraction peaks in Fig. 2(a) compared with Fig. 2(b). They are in perfect match with those reported for anatase type TiO_2 (JCPDS card No. 21-1272). This result clearly shows that the TiO_2 deposition transforms into anatase TiO_2 after the high-temperature heat treatment.

The surface structures and morphologies of specimens in different stages during the process of forming the Al–Ti composite oxide films were observed by AFM, as shown in Fig. 3. There are four kinds of specimens, including (a) the aluminum foil without being treated; (b) the aluminum foil after cathodic electrodeposition and heat treatment; (c) the aluminum foil coated with TiO_2 layer in the process of anodizing; and (d) the aluminum foil with Al–Ti composite oxide film. The RMS roughnesses of the specimens in Fig. 3(a), (b), (c) and (d) were evaluated to be 3.7 nm, 27.2 nm, 25.1 nm and 6.3 nm, respectively. Comparing Fig. 3(a) with (b), we notice that the growth mode of TiO_2 layer on aluminum foil is island growth and the surface of aluminum foil becomes rather rough with the growth of TiO_2 film. In the anodic oxidation process, the island growth pattern is conducive to the full contact of electrolyte and aluminum matrix. We can see a lower surface roughness in Fig. 3(c) comparing with Fig. 3(b), which

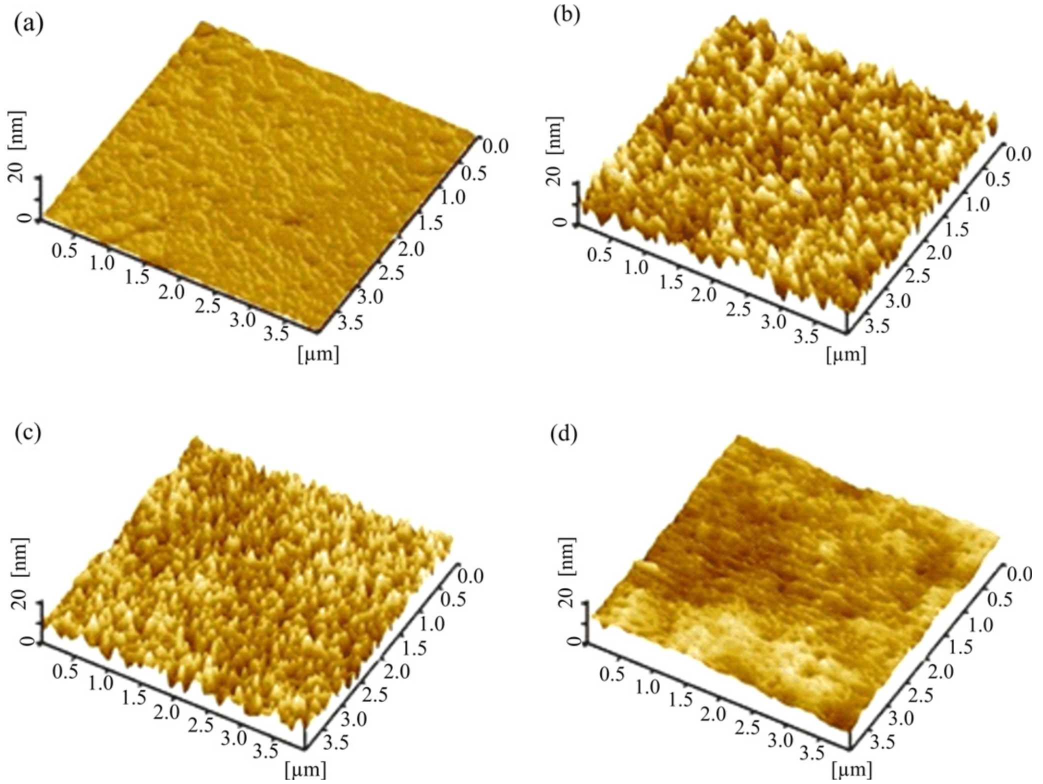

Fig. 3. AFM images for each step during forming the Al–Ti composite oxide film, (a) aluminum foil without being treated, (b) aluminum foil coated with TiO_2 layer before anodizing, (c) aluminum foil coated with TiO_2 layer in the process of anodizing, and (d) aluminum foil coated with Al–Ti composite oxide film after anodizing.

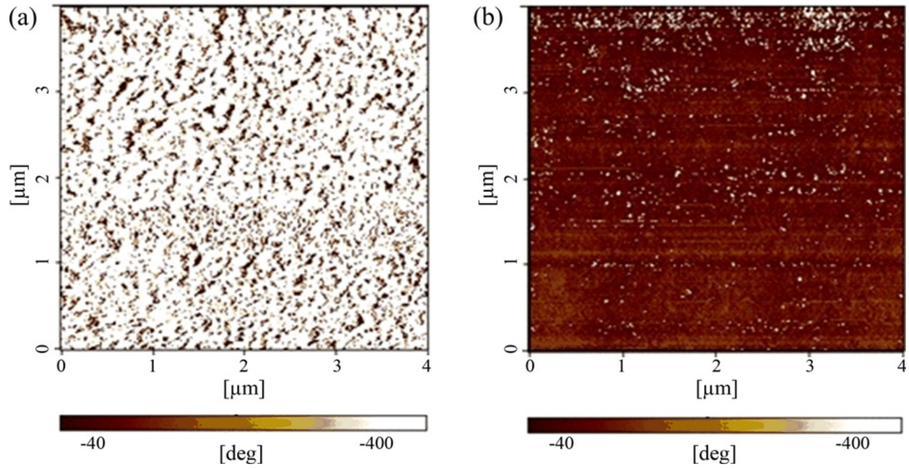

Fig. 4. Phase imaging in tapping-mode AFM for different specimens, (a) aluminum foil with TiO_2 coating, and (b) aluminum foil with Al–Ti composite oxide film after anodizing.

indicates that alumina grows preferentially from uneven channel of the island structure at the early stage of anodization through the inward transport of O^{2-} ions and the outward transport of Al^{3+} ions. Meanwhile, micro-pores and cracks in TiO_2 coating layer may be formed during the high-heat treatment, which can consume some electric charges to form Al_2O_3 for repairing [1]. Thus the growth of alumina fills the depressions and micro-pores during anodic oxidation process and finally forms the Al–Ti composite oxide films. It is obvious that the surface roughness drops dramatically and the surface tends to smooth from Fig. 3(c)–(d). This fully illustrates that continuous aluminum oxide films are formed on the aluminum foil after filling the islands channel with anodizing process.

Phase-imaging tapping-mode AFM can be used to reveal the microstructural changes of specimens during the process. The phase images of specimens in Fig. 3(b) and (d) are shown in Fig. 4(a) and (b), respectively. It clearly shows that there are different elemental distributions on the surfaces of different specimens. Specimen surface exhibits apparent dispersive stress sections after cathodic electrodeposition without anodizing. Compared with other formation of Al–Ti composite oxide film [1,10], the island structure of TiO_2 formed by the cathodic electrodeposition will not hamper the transports of O^{2-} ions and Al^{3+} ions to form aluminum oxide, and TiO_2 layer will gradually be covered with Al_2O_3 layer. After TiO_2 is covered with Al_2O_3, the dispersive stress sections in film still exist. However, these areas are significantly reduced.

Fig. 5 shows the variation of anodizing voltage with anodizing time for different specimens. Current density of cathodic electrodeposition is 2 mA/cm^2, 3 mA/cm^2, 4 mA/cm^2 and 5 mA/cm^2 for different specimens, respectively. The rise of the curves is in accordance with the stage in which the anodization is conducted in the constant current mode. The growth rate of composite oxide film is accelerated and the stage of constant current mode is shortened when the current density of cathodic electrodeposition is increased from 2 mA/cm^2 to 5 mA/cm^2. The use of higher current density has the advantage of higher deposition rate of titanium complex, and more deposition amount of titanium complex is obtained. Anatase TiO_2 and γ-Al_2O_3 can be generated on the surface of aluminum foil in the subsequent heat treatment process. The existence of these crystalline oxides improves the oxidation efficiency. These can be used to interpret the phenomenon that the specimens with higher deposition current density have higher rate of anodic oxidation in Fig. 5.

The dielectric property parameters of composite oxide films under different deposition current densities (J), such as specific capacitance (C), withstanding voltage (V), and leakage current (I) were measured and listed in Table 1. Table 1 demonstrates that the composite oxide film has higher specific capacitance than the normal oxide film. As the deposition current density increases, the withstanding voltage of oxide film drops, and the

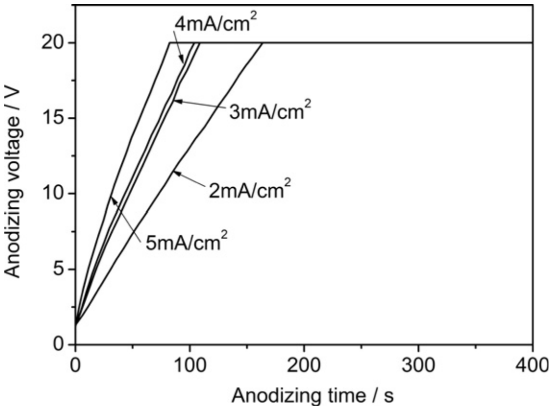

Fig. 5. Anodizing curves of specimens with deposition current density of (a) 2 mA/cm^2, (b) 3 mA/cm^2, (c) 4 mA/cm^2, and (d) 5 mA/cm^2.

Table 1
The dielectric property parameters of anodic oxide film.

J (mA/cm^2)	C (μF/cm^2)	V (V)	I (mA)	CV (μF V/cm^2)
0	66.1	25.5	1.9	1685.55
2	73.9	24.9	2.5	1840.11
3	84.6	24.4	3.0	2064.24
4	88.3	24.1	3.2	2128.03
5	91.2	23.2	3.8	2115.84

leakage current increases. These facts indicate that the incorporation of TiO_2 can improve the dielectric constant of oxide film, as well as causes degradation of other dielectric properties. The specimen with deposition current density of 4 mA/cm^2 shows the highest product of specific capacitance and withstanding voltage, which is about 26.3% above that of the normal oxide film.

4. Conclusion

Al_2O_3–TiO_2 composite oxide film was prepared by cathodic electrodeposition and anodizing process. Anatase TiO_2 with high dielectric constant was obtained after electrodeposition followed by high-temperature heat treatment. TiO_2 deposited on the surface of aluminum foil distributed as island structure, which was helpful for forming the Al–Ti composite oxide films. Anodic oxidation efficiency of specimens increased with the deposition current density increasing. The product of specific capacitance and withstanding voltage of specimen with Al–Ti composite oxide film was about 26.3% higher than that of specimen with only aluminum oxide film, which was due to the higher ε_r value of the composite oxide film. It suggests that the method of cathodic electrodeposition and anodizing is an effective way of increasing the specific capacitance of anodized aluminum foils, which promises to be used in aluminum electrolytic capacitors with large capacitance and small volume.

Acknowledgements

This work was supported by the National Nature Science Foundation of China (Grant No. 60601006) and the National Defense Pre-Research Foundation of China (Grant No. 9140A12070210DZ02).

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