Al_2O_3-TiO_2 composite oxide films on etched aluminum foil by hydrolysis precipitation and anodizing

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Barrier-type anodic oxide dielectric films which are formed on aluminum play an important role in aluminum electrolytic capacitors, and the performance of the electrolytic capacitors is determined by the physical and chemical behaviors of these films [1]. Recent developments in mobile electronic devices, such as notebook computers, mobile telephones, etc., and electric vehicles strongly require small electrolytic capacitors with high electric capacitance [2]. The electric capacitance, C, of electrolytic capacitors can be calculated by the formula (1),

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

where ε_0 is the dielectric constant of vacuum atmosphere, ε_r represents relative dielectric constant of the anodic oxide film, S is on behalf of the effective surface area, and d is the film thickness. In formula (1), d value can be largely decided by working voltage. Even if electrochemical etching can enlarge S, now it is difficult to increase further [3]. Increases in ε_r may be possible when Al-valve metal composite oxide films are being formed by integrating valve metal oxides such as TiO_2, ZrO_2, Nb_2O_5, and others with relatively large, ε_r values. Watanabe *et al.*, tried to increase the electric capacitance by producing composite oxide films with sol-gel coating and anodizing [4, 5], and Shikanai *et al.*, also tried to reach the aim with pore filling technique [6]. However, these methods have disadvantages for long time use, and are also difficult for industrial application [7].

In the present research, Ti-oxide coating was applied to produce composite oxide films on the etched aluminum foils by hydrolysis precipitation of Ti-bearing cation in inorganic solution. Once being annealed, the Al_2O_3-TiO_2 composite oxide films were formed by galvanostatically anodizing in ammonium adipate solution, and the structure and properties of the composite films were determined by Auger electron spectroscope (AES) and X-ray diffraction (XRD).

Specimens of 2 cm^2 with a handle were cut from highly pure etched aluminum foil (100 μm thick), and subsequently immersed in the solution containing Ti^{4+} compound with parameters of the hydrolysis precipitation process shown in Table I. Consumption of H^+ ions reacted with Al increased the pH value in micropores of the etched aluminum foil during the immersion, which can accelerate the hydrolysis precipitation of Ti-bearing cation. Further details of the hydrolysis precipitation process have been described in Chen *et al.* [8]. Afterwards, the treated specimens were thoroughly rinsed in double-distilled water, air-dried at 80 °C, and eventually annealed at 550 °C for 10 min to obtain TiO_2 coating layer.

The TiO_2 powders were obtained by annealing in air at 450–600 °C for 10 min after hydrolysis of Ti-bearing cation. The XRD patterns of the TiO_2 powders annealed under different temperatures are shown in Fig. 1. All powders annealed above 500 °C have an anatase structure (Fig. 1). Among the temperature range that we used, higher annealing temperature induced higher and sharper diffraction peaks in the powders.

The specimens coated with TiO_2 were anodized in ammonium adipate solution (150 g/1000 g H_2O) at 85 °C, and a 304 stainless steel plate was used as the counterelectrode. A constant current density of 50 mA/cm^2 was run through the cell between the specimens and the counterelectrode until the potential difference reached the selected anodization voltage. The voltage was then held constant for 10 min and the current was allowed to decay. Specimens without TiO_2-coating were also anodized under the same conditions to determine the effect of TiO_2-coating on anodizing. The change in the anode potential with time (E_a vs. t_a curve) was followed on an Agilent 34401A digital multimeter which was connected to a PC system.

The E_a versus t_a curves for the specimens with and without TiO_2-coating were shown in Fig. 2. The coated specimens displayed a voltage surge of ~2.5 V at the beginning of anodizing, while the specimens without

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0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-005-2507-5

TABLE I Parameters of hydrolysis precipitation process

Ti^{4+} (mol/L)	pH	Temperature (°)	Time (min)
0.002	1.5–2.0	65–70	8

TiO_2-coating exhibited a voltage surge of ~1.3 V followed by an increase in E_a with t_a (Fig. 2). The slopes of the E_a versus t_a curves for TiO_2-coated specimens were much steeper than those without TiO_2-coating, and thus can save charge that was consumed in the anodizing process. In TiO_2-coated specimens, as a thin thermal aluminum oxide film may be formed at the interface between the Ti-oxide layer and the metal substrate during annealing treatment [9], the E_a jump at the very early stage of anodizing may be induced by the aluminum thermal oxide layer rather than the Ti-oxide layer. A similar E_a jump has been observed in the anodizing of aluminum after being annealed in air at 550 °C for 10 min. However, in specimens without TiO_2-coating, the early E_a jump was due to the presence of a thin natural oxide layer. It has been thought that the Ti-oxide layer has a network structure of micropores and cracks, and it is unable to sustain an electric field. When the TiO_2-coated specimens were immersed in anodizing solution, water and electrolyte could penetrate into the micropore network.

During the anodizing after TiO_2-coating, O^{2-} ions were dissociated from water at the bottom of the Ti-oxide layer, and transported across the anodic oxide film to form pure aluminum oxide at the interface between the inner Ti-oxide layer and the metal substrate. The outward transport of Al^{3+} ions formed the composite oxide by filling micropores at the interface between the outer layer and the Ti-oxide layer with aluminum oxide. The AES depth profiles of component elements in Al_2O_3-TiO_2 composite oxide film were shown in Fig. 3. The composite oxide film is obviously composed of two layers: the outer layer thought to be a Ti-containing layer, and the inner layer consisting of pure aluminum oxide (Fig. 3).

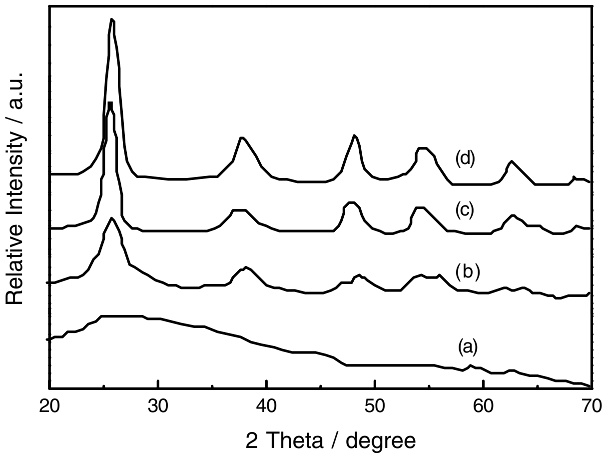

Figure 1 XRD patterns of the TiO_2 powders under different annealing temperatures: (a) 450 °C; (b) 500 °C; (c) 550 °C; and (d) 600 °C.

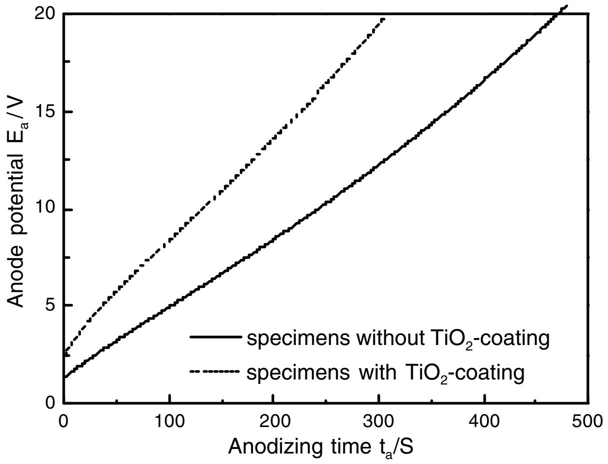

Figure 2 Change in anode potential, E_a, with time, t_a, during anodizing.

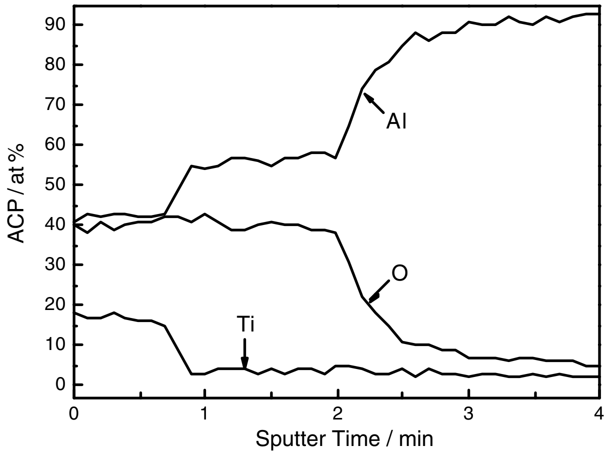

Figure 3 AES depth profiles of Al_2O_3-TiO_2 composite oxide film.

The capacitance of the anodized oxide films in 25 °C-aqueous ammonium adipate solution (150 g/1000 g H_2O) was measured using a general LCR meter at 100 Hz. A pure aluminum sheet with a very large area was used as the counterelectrode. As shown in (Fig. 4, the specific capacitance of the specimens was significantly increased when the annealing temperature was above 500 °C, and then the increase became slow when above 550 °C. This phenomenon is likely due to the fact that TiO_2 begins to crystallize to the anatase structure at the annealing temperature of 500 °C, which is consistent with the XRD analysis. This result also showed that the composite film of Al_2O_3-TiO_2 has a relatively high dielectric constant.

The specimens with Al_2O_3-TiO_2 composite oxide films annealed under 550 °C exhibited ~30% higher specific capacitance than those with pure Al_2O_3 films. There seems to be no effects of the technique used in the present work on the effective surface area, but the film thickness could be increased by TiO_2 incorporation into anodic oxide films [10]. Thus, the fact that the specimens with Al_2O_3-TiO_2 composite films have higher specific capacitance than those with pure Al_2O_3 films should be due to higher dielectric constant. The dielectric constant

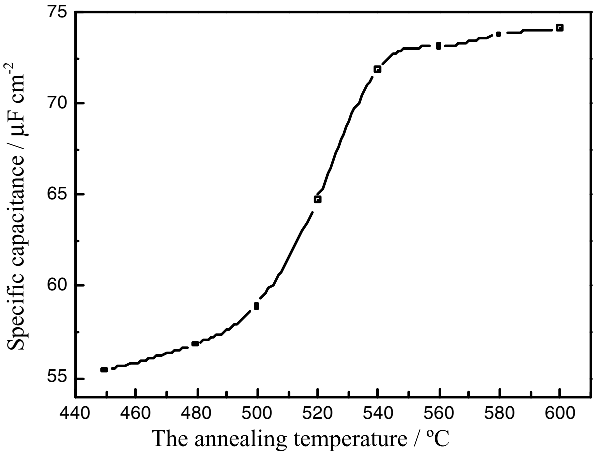

Figure 4 The annealing temperature dependence of specific capacitance.

of Al_2O_3-TiO_2 composite oxide film can be calculated according to the amount of Ti^{4+} ions incorporated into the film [8]. Conclusively, the composite oxide films are the promising materials, which can be used as the dielectric of the aluminum electrolytic capacitors.

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Received 20 January
and accepted 26 May 2005