Research Paper

Effects of Electrolyte Temperature during Anodization on Properties of ZrO_2 -coated Al Foils

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ABSTRACT

The effects of electrolyte temperature during anodization on the microstructure and electrical properties of the ZrO_2 coated Al foils were investigated. The specimens were prepared by coating ZrO_2 sol on etched Al foils and anodization in MPD-boric acid electrolytes at 30, 60, and 90 °C, respectively. Anodization potential was 700 V. The thickness of oxide layer anodized increased with increasing the electrolyte temperature. In contrast, the crystallization of ZrO_2 and Al_2O_3 decreased at higher anodizing temperature. Compared with the specific capacitance of the sample anodized at 90 °C, the specific capacitances of which anodized at 30 and 60 °C are enhanced about 12.8 % and 8.8 %, respectively. Therefore, the anodization at 30 °C can effectively improve the specific capacitance of the samples, and save the thermal energy during anodization.

Keywords: 2-methyl-1, 3-propanediol, Anodization, ZrO_2 , Al_2O_3 , Specific capacitance

1. Introduction

With the advance of exploitation on new energy resources, energy-storage technology correspondingly acts a significant role in our life. Capacitors as well as batteries known as two kinds of essential energy-storage devices are now researched by numerous experts. In comparison with batteries, capacitors possess an even higher power, and the basic construction of capacitors is a sandwich structure of anode/dielectrics/cathode. The capacitances of the capacitors can be characterized by $C = \epsilon_0 \epsilon_r S/d$, where C is the capacitance, ϵ_0 is the dielectric constant in vacuum, ϵ_r is the dielectric constant of the dielectrics in capacitor, d is the thickness of the dielectrics, and S is the effective surface area of the electrode. Al electrolytic capacitor as one kind of economic and environment-friendly energy-storage device has been widely applied in electronics used in defense, aerospace, and transportation fields, etc. The key part of Al electrolytic capacitor is the Al_2O_3 dielectrics formed by anodization in various electrolytes such as phosphoric acid solution [1], boric acid solution [2], malonic acid solution [3], ammonium penta-borate solution [4], and citric acid solution [5], etc. Anodization is an economic and convenient approach for the formation of Al_2O_3 layer, in which the Al_2O_3 is formed by the combination of O^{2-} ions and Al^{3+} ions, starting at the both Al/native Al_2O_3 and native Al_2O_3 /electrolyte interfaces. The properties of formed Al_2O_3 can be determined by the anodization modes consisting of galvanostatic and constant potential. In addition, the electrolyte parameters also act as a significant role in anodization process. The parameters of electrolyte during anodization such as temperature, pH, conductivity, and viscosity, etc. can largely affect the performances of

Al_2O_3 on microstructure and electrical properties, and a lot of outstanding researches have handled these topics [6–8]. However, an eager requirement for the study of the electrolyte used for anodization of Al foils worked in high-voltage field is salient.

The composition and type of the electrolyte used for anodization significantly affects the anodizing efficiency and electrical properties of the Al foils. Although many electrolytes have been extensively researched [5,9–12], the withstanding voltages of anode foils formed by these electrolytes are still relatively low. So, organic electrolyte has received attention to further increase the withstanding voltage. Kinard *et al.* showed that when Al foils were anodized in borate polyester, which is a compound of boric acid and 2-methyl-1, 3-propanediol (MPD), a significantly high withstanding voltage, even higher than 3000 V, could be obtained [13]. Based on our previous work, MPD-boric acid electrolyte used for high-voltage anodization can effectively inhibit the micro-arcs caused by oxygen evolution when anodization is conducted at high voltage (over 700 V) [14].

ZrO_2 shows a much higher permittivity of 22 – 25 than 9.8 of Al_2O_3 [15], which could effectively enhance the specific capacitance (C_p) by enlarging the ϵ_r of the dielectrics in conventional Al electrolytic capacitor. Simple and convenient sol-gel process was selected to prepare the ZrO_2 -coated Al foils. ZrO_2 -coated Al foils were anodized to secure appropriate withstanding voltage and ZrO_2 - Al_2O_3 (ZAO) composite oxide. It was generally accepted that the temperature of an electrolyte used for anodizing aluminum is one of important factors which determines the type of oxide grown on the surface. In this work, the effects of anodization temperature of MPD-boric acid electrolyte on the microstructure and electrical properties of the ZrO_2 - Al_2O_3

dielectrics formed on the etched Al foils were studied.

II. Experimental procedure

1) Preparation

Etched Al foils (99.99 %, thickness: $\sim 125 \mu\text{m}$, hole density: $\sim 2.0 \times 10^7 \text{ cm}^{-2}$, hole diameter: $1 - 2 \mu\text{m}$, and hole length: $20 - 50 \mu\text{m}$) were placed into alcohol (purity: 99.5 %) and ultrasonically cleaned for 20 min to remove surface contaminants. ZrO_2 sol of 0.8 M were prepared by mixing zirconium butoxide ($\text{Zr}(\text{OC}_4\text{H}_9)_4$, 80 wt% in 1-butanol, Sigma-Aldrich, USA), 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$, anhydrous, 99.8 %, Sigma-Aldrich, USA), acetic acid (CH_3COOH , 99.7 %, Daejung Chemicals & Metals, Korea), and nitric acid (HNO_3 , 60–62 %, Daejung Chemicals & Metals, Korea). Finally, the transparent precursors were aged for 3 days. The ZrO_2 sol was coated on the surface of the etched Al foils by vacuum infiltration, which can be described in detail as a bath with Al foils was placed into a chamber, thereafter, evacuation was carried out. Subsequently, ZrO_2 sol was injected into the bath, followed by ventilated and the etched Al foils were lifted from the ZrO_2 sol bath. The ZrO_2 film on the etched Al foils was dried at 100°C for 1 h and annealed at 500°C for 10 min in ambient environment. The same coating process was repeated four times to achieve the optimal thickness. Subsequently, the ZrO_2 -coated Al foils were firstly anodized at a mode of constant current (0.1 A/cm^2) until the settled voltage (700 V), subsequently, the anodization at a fashion of constant voltage was carried out, lasting until the current flowing through the sample is 0.01 A in MPD-boric acid electrolyte of 30, 60, and 90°C , respectively. The anodization electrolytes were MPD:boric acid electrolyte (100 g of H_3BO_3 /1 L of H_2O) with volume % ratios of 3:10. The MPD-boric acid electrolyte must be kept at greater than or equal to 30°C to avoid the precipitation of boric acid [Fig. 1(a)]. Lastly, the anodized samples were annealed in a furnace of 500°C for 2 min for characterization.

2) Characterization

Crystalline structure of the oxide layer formed on the Al foils was analyzed using X-ray diffraction (XRD, X'pert Pro MRD, PANalytical). The cross-sectional structures of the coated layer and anodized oxide layer were characterized using field emission-scanning electron microscopy (FE-SEM, JSM-6700E, Jeol) and field emission-transmission electron microscopy (FE-TEM, titan G2 ChemiSTEM Cs probe) performed at 200 kV . The SEM samples were prepared by polishing the anodized Al foils and eroding them for 3 min in KOH solution. The TEM samples were thinned with a focused ion beam (FIB, versa 3D LoVac) to a thickness of about 100 nm . The elemental distributions of the samples were examined by TEM coupled to energy-dispersive X-ray spectroscopy (EDS). The cyclic voltammetry (C_V) were conducted from -2 to $+2 \text{ V}$ at sweep rate of 1 V/s using a three-electrode system (Ag/AgCl reference electrode, working electrode connected with samples, and Pt counter electrode) connected with a digital analyzer (VersaSTAT 3, Princeton Applied Research) and signals were monitored by a computer. The withstanding voltage and leakage current of the samples were measured using a source meter (2410, Keithley) and the capacitance were determined utilizing an impedance/gain phase analyzer (4194A, Hewlett-Packard) in $(\text{NH}_4)_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$ aqueous solution of 80 g/L at 30°C .

III. Results and discussion

Figure 1(b) shows the conductivities of MPD-boric acid electrolytes at a series of temperatures. The conductivity of electrolyte rises with increasing the temperature. So, a higher ionic transport rate at higher temperature may be acquired, promoting the efficiency of anodization. Meanwhile, the ionic resistivities of the MPD-boric acid electrolytes correspondingly decrease as the temperature of electrolyte increase. The conductivity of the mixed electrolyte decreases as the ratio of MPD increase, because MPD exhibits high resistivity as shown in previous work [14]. The ionic migration are weakened and a relatively high voltage can be sustained as the conductivity of the solution decrease [16]. Therefore, it is expected that an electrolyte with a lower conductivity can facilitate anodization at a higher voltage but leads to a decrease in the anodization rate.

Figures 2(a)–(c) shows the SEM cross-sectional images of the dielectric oxides formed inside etch pits at different temperature. A compact combination between the coated ZAO layer (inner) and deposited Al_2O_3 layer (outer) is shown in each sample. The Al_2O_3 grows at both Al/ ZrO_2 interface and ZrO_2 /electrolyte interface by the transport of Al^{3+} coming from etched Al foils and O^{2-} coming from electrolyte under electric field. The outer Al_2O_3 layers demonstrates that the formation of Al_2O_3 is principally depending on the transport of O^{2-} ions under the driving force given by the electric field, further implying that the O^{2-} penetration in ZrO_2 -coated layer is much easier than Al^{3+} . The total thicknesses of the dielectric oxides are approxi-

Figure 1. (Color online) (a) MPD-boric acid electrolyte at 25°C . (b) Conductivity of the MPD-boric acid electrolyte at a series of temperatures.

Figure 2. (Color online) SEM cross-sectional images of the oxide anodized at (a) 30°C , (b) 60°C , and (c) 90°C . (d) XRD diffraction patterns of the samples anodized at different temperatures.

mately 625, 680, and 750 nm, increasing with enlargement of the conductivity at higher temperature. The electrolyte with a higher ionic resistivity of 1.8 Ω/cm at 30 $^{\circ}\text{C}$ can inhibit the ionic transport even more largely than the electrolyte with ionic resistivity of 1.2 Ω/cm at 90 $^{\circ}\text{C}$. After anodization at 30, 60, and 90 $^{\circ}\text{C}$, the thicknesses of the Al_2O_3 layer were approximately 440, 590, and 625 nm, respectively. The ratio between the thickness of anodized Al_2O_3 layer and the anodizing voltage, K , has been reported to be approximately 1 nm/V in pure Al [5]. In this work, these ratios were approximately 0.62, 0.84 and 0.89 nm/V after anodizing at 30, 60, and 90 $^{\circ}\text{C}$, respectively. Lower K value in ZrO_2 -coated Al compared with Al specimens results from a hindrance in the movement of Al^{3+} and O^{2-} ions through ZrO_2 layer.

Figure 2(d) shows the XRD diffraction patterns of the samples anodized at 30, 60, and 90 $^{\circ}\text{C}$, respectively. The intensities of Al_2O_3 peaks are increased gradually, suggesting that the crystallization of Al_2O_3 is increased by making use of an electrolyte at lower temperature. This result may be explained that an electrolyte with a lower ionic conductivity require a higher applied potential on the ZrO_2 -coated samples to reach at the constant current density of 0.1 A/cm² during anodization. That is, a higher electric field is needed on the ZrO_2 -coated Al foils, and the high electric field can effectively increase the nucleation rate, thereby promoting the crystallization of Al_2O_3 . Also an increase in intensity of ZrO_2 peaks after anodization suggests that coating layer is more crystallized during anodization. Since the same ZrO_2 coating and annealing processes are applied, this phenomena proves that the anodization process can modify the crystallized ZrO_2 by the way of re-crystallization. More detailed information about the re-crystallization of crystallize ZrO_2 under the high electric field was presented in our previous work [17]. Herein, the difference of the crystallization of Al_2O_3 may also be due to the permeation of electrolyte species. Koyama *et al.* pointed out that the electrolyte component would intrude into the formed dielectrics and decrease with going deep into the dielectrics [18]. The transport rate of the electrolyte species increases at higher anodizing temperature. Therefore, high electrolyte temperature may enlarge the permeation rate of the electrolyte species thereby decreasing the crystallization.

Figures 3(a) and 3(b) show the TEM cross-sectional images and diffraction patterns of the Al_2O_3 formed in MPD-boric acid electrolyte at 30 and 90 $^{\circ}\text{C}$, respectively. The crystallinity of the Al_2O_3 anodized in the electrolyte of 30 $^{\circ}\text{C}$ is evidently higher than that formed in the electrolyte of 90 $^{\circ}\text{C}$ as corroborated by the diffraction patterns and visible Al_2O_3 grains in Fig. 3(a). This result also well agrees with the trend in the XRD diffraction patterns [Fig. 2(d)] that the anodization in the electrolyte of low temperature can effectively optimize the crystallization of Al_2O_3 . A well crystallized samples could possibly raise the ϵ_r of the dielectrics. The micro-cracks marked with arrows in Al_2O_3 formed in the electrolyte of 30 $^{\circ}\text{C}$ [Fig. 3(a)] are not shown in sample anodized in the electrolyte of 90 $^{\circ}\text{C}$ [Fig. 3(b)], strongly proving that these micro-cracks are caused in the anodization process rather than in annealing process at 500 $^{\circ}\text{C}$ conducted after anodization. These micro-cracks may be associated with the tension generated by volume expansion in crystallization process. Indeed, the volume expansion accompanied by mechanical stresses is generated in anodization process [19]. Figure 3(c) shows the TEM-EDS depth profiles of the O, Al, and Zr species in the sample anodized in the MPD-boric acid electrolyte of 90 $^{\circ}\text{C}$. A profile of multi-layer structure from etch pit to Al substrate is viewed, which is Al_2O_3 layer of about 30 nm, ZAO composite layer of about 100 nm, Al_2O_3 layer of about

Figure 3. (Color online) TEM cross-sectional images and diffraction patterns of the Al_2O_3 anodized at (a) 30 and (b) 90 $^{\circ}\text{C}$. (c) EDS depth profiles of the sample formed at 90 $^{\circ}\text{C}$.

Figure 4. (Color online) HRTEM images and diffraction patterns of (a) Al_2O_3 and (b) ZrO_2 in ZAO composite oxide layer formed at 30 $^{\circ}\text{C}$.

700 nm, and Al substrate. The thickness of the dielectrics is slightly thicker than the thickness obtained from SEM images [Fig. 2] due to the corrosion in the KOH solution during the preparation process of the samples for SEM measurement. The EDS result further corroborates the anodization process mentioned above that O^{2-} ions ionized from the electrolyte transport through the ZrO_2 coated layer to bond with Al^{3+} ions dissolved from the etched Al foils. Simultaneously, slight Al^{3+} ions dissolved from Al foils diffuse to the electrolyte through the ZrO_2 coated layer to form Al_2O_3 . The Al_2O_3 layer mostly is formed at the interface of ZAO composite layer/Al substrate, well agrees with the microstructure in the SEM images [Fig. 2].

Figure 4 shows the HRTEM images of (a) Al_2O_3 layer and (b) ZrO_2 in ZAO composite layer anodized at 30 $^{\circ}\text{C}$. The resolution of the HRTEM used in this study is 0.08 nm. The measured interplanar spacing of the Al_2O_3 and separated crystalline ZrO_2 is 0.45 and 0.295 nm, respectively. These values are matched with the interplanar spacing of cubic Al_2O_3 (111) and tetragonal ZrO_2 (101). Al_2O_3 layer is crystallized with clear lattice, but ZAO composite layer is composed of crystalline ZrO_2 and amorphous Al_2O_3 as shown in our previous

Figure 5. (Color online) (a) Withstanding voltage curves, (b) leakage current curves, (c) cyclic voltammetry curves of the samples anodized at variant temperatures. (d) Specific capacitances of the samples anodized at 30, 60, and 90 °C.

report [20].

Figure 5(a) shows the withstanding voltage of the samples anodized in the electrolyte of 30, 60, and 90 °C, respectively. The withstanding voltages are about 760 V and are almost regardless of the electrolyte temperature. Thus, the voltage sustain-abilities of the samples formed at 30, 60, and 90 °C are about 1.21, 1.11, and 1.01 V/nm, respectively. This demonstrates that the oxide with a higher crystallization has a greater voltage-sustainability than that with a lower crystallization. However, a longer time is needed in the potential evolution process for the samples anodized in the electrolyte of lower temperature. Moreover, correspondingly, the leakage currents in Fig. 5(b) also slightly increase in electrolyte of lower temperature. This appearance can be due to the consumption of stored charges, resulted from the micro-cracks generated in anodization process. However, the leakage currents of the samples are less than 0.01 A at applied voltage of 700 V. Furthermore, in consideration of the self-repairing of the Al foil in charging process, over time, the leakage currents of the samples are supposed to diminish. Thus, the samples anodized at 30 °C show better properties in terms of withstanding voltage and leakage current. To further evaluate the electrochemical properties of the samples, we carried out the cyclic voltammetry measurement [Fig. 5(c)]. A better capability is observed in the ZrO_2 -coated Al foils anodized in the electrolyte of lower temperature. Additionally, there are no evident redox peaks in the C_V curves, suggesting that, independent of electrolyte temperature, a stable dielectric oxide layers is prepared after anodization in MPD-boric acid. Figure 5(d) shows the C_p of the samples anodized at 30, 60, and 90 °C, respectively. The C_p of the samples decrease as the temperature of electrolytes become higher. A sensible enhancement in C_p is shown, which are the enlargements of 8.8 % for anodization at 60 °C and 12.8 % for anodization at 30 °C in comparison with the C_p values of the sample formed at 90 °C. The increase in C_p of samples anodized at lower temperature may be owing to the decline in dielectric thickness, d and the improvement in ϵ_r caused by the higher crystallinity of Al_2O_3 and ZrO_2 .

IV. Conclusions

The effects of electrolyte temperature on the microstructure and electrical properties of the dielectrics on etched Al foils are explored.

The total thicknesses of the dielectric oxide layers increase with increasing the electrolyte temperatures. Additionally, the crystallizations of ZrO_2 and Al_2O_3 were improved when samples were anodized at lower electrolyte temperature, meanwhile, more micro-cracks were observed in the Al_2O_3 layer formed at lower temperature. Moreover, the withstanding voltages are independent of the electrolyte temperature and leakage currents slightly enlarge with the decrease in electrolyte temperature. In comparison with the C_p value of the sample formed at 90 °C, the C_p improvements of 8.8 % at 60 °C and of 12.8 % at 30 °C are achieved. The samples anodized at 30 °C in MPD: boric acid electrolyte with volume % ratios of 3:10 show best properties.

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