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 $^\circ$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$_2$O$_3$ decreased at higher anodizing temperature. Compared with the specific capacitance of the sample anodized at 90 $^\circ$C, the specific capacitances of which anodized at 30 and 60 $^\circ$C are enhanced about 12.8 % and 8.8 %, respectively. Therefore, the anodization at 30 $^\circ$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$_2$O$_3$, Specific capacitance

I. 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 $C = \varepsilon_0 \varepsilon_r S / d$, where $C$ is the capacitance, $\varepsilon_0$ is the dielectric constant in vacuum, $\varepsilon_r$ is the dielectric constant of the dielectrics, $d$ 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$_2$O$_3$ 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$_2$O$_3$ layer, in which the Al$_2$O$_3$ is formed by the combination of $O^2-$ ions and $Al^{3+}$ ions, starting at the both Al/native Al$_2$O$_3$ and native Al$_2$O$_3$/electrolyte interfaces. The properties of formed Al$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ [15], which could effectively enhance the specific capacitance ($C_p$) by enlarging the $\varepsilon_r$ 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$_2$O$_3$ (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$_2$O$_3$...
dielectrics formed on the etched Al foils were studied.

II. Experimental procedure

1) Preparation

Etched Al foils (99.99%, thickness: ~125 μm, hole density: ~2.0 × 10^7 cm^-2, hole diameter: ~2 μm, and hole length: 20 – 50 μm) 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 (Zr(OCH_2CH_3)_4, 80 wt% in 1-butanol, Sigma-Aldrich, USA), 2-methoxyethanol (CH_3OCH_2CH_2OH, 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, there after, 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 etching 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 elements were examined by TEM coupled to energy-dispersive X-ray spectroscopy (EDS). The cyclic voltammetry (C, V) were conducted from -2 to +2 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 determined using an impedance/gain phase analyzer (4194A, Hewlett-Packard) in (NH_4)_2B_10O_16·8H_2O 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-
Al2O3 layer were approximately 440, 590, and 625 nm, respectively. From etch pit to Al substrate is viewed, which is Al2O3 layer of about 30 nm, ZrO composite layer of about 100 nm, Al2O3 layer of about 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 °C can inhibit the ionic transport even more largely than the electrolyte with ionic resistivity of 1.2 Ω-cm at 90 °C. After anodization at 30, 60, and 90 °C, the thicknesses of the Al2O3 layer were approximately 440, 590, and 625 nm, respectively. The ratio between the thickness of anodized Al2O3 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 °C, respectively. Lower K value in ZrO2-coated Al compared with Al specimens results from a hindrance in the movement of Al3+ and O2- ions through ZrO2 layer.

Figure 2(d) shows the XRD diffraction patterns of the samples anodized at 30, 60, and 90 °C, respectively. The intensities of Al2O3 peaks are increased gradually, suggesting that the crystallization of Al2O3 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 ZrO2-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 ZrO2-coated Al foils, and the high electric field can effectively increase the nucleation rate, thereby promoting the crystallization of Al2O3. Also an increase in intensity of ZrO2 peaks after anodization suggests that coating layer is more crystallized during anodization. Since the same ZrO2 coating and annealing processes are applied, this phenomena proves that the anodization process can modify the crystallized ZrO2 by the way of re-crystallization. More detailed information about the re-crystallization of crystallize ZrO2 under the high electric field was presented in our previous work [17]. Herein, the difference of the crystallization of Al2O3 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 samples anodized in MPD-boric acid electrolyte of 30 °C, 60 °C, and 90 °C, respectively. The crystallinity of the Al2O3 anodized in the electrolyte of 30 °C is evidently higher than that formed in the electrolyte of 90 °C as corroborated by the diffraction patterns and visible Al2O3 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 Al2O3. A well crystallized samples could possibly raise the εr of the dielectrics. The micro-cracks marked with arrows in Al2O3 formed in the electrolyte of 30 °C [Fig. 3(a)] are not shown in sample anodized in the electrolyte of 90 °C [Fig. 3(b)], strongly proving that these micro-cracks are caused in the anodization process rather than in annealing at 500 °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 °C. A profile of multi-layer structure from etch pit to Al substrate is viewed, which is Al2O3 layer of about 30 nm, ZAO composite layer of about 100 nm, Al2O3 layer of about 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 O2- ions ionized from the electrolyte transport through the ZrO2 coated layer to bond with Al3+ ions dissolved from the etched Al foils. Simultaneously, slight Al3+ ions dissolved from Al foils diffuse to the electrolyte through the ZrO2 coated layer to form Al2O3. The Al2O3 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) Al2O3 layer and (b) ZrO2 in ZAO composite oxide layer formed at 30 °C.
The effects of electrolyte temperature on the microstructure and electrical properties of the dielectrics on etched Al foils are explored.

IV. Conclusions

The total thicknesses of the dielectric oxide layers increase with increasing the electrolyte temperatures. Additionally, the crystallizations of ZrO$_2$ and Al$_2$O$_3$ were improved when samples were anodized at lower electrolyte temperature, meanwhile, more micro-cracks were observed in the Al$_2$O$_3$ layer formed at lower temperature. Moreover, the withstandin voltage values are independent of the electrolyte temperature and leakage currents slightly enlarge with the decrease in electrolyte temperature. In comparison with the $C_p$ values of the sample formed at 90 $^\circ$C, the $C_p$ improvements of 8.8 % at 60 $^\circ$C and of 12.8 % at 30 $^\circ$C are achieved. The samples anodized at 30 $^\circ$C in MPD-boric acid electrolyte with volume % ratios of 3:10 show best properties.

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References

[1] J. K. Chang, C. M. Liao, C. H. Chen, and W. T. Tsai, J. Power Sources 138, 301 (2004).
[2] K. Watanabe, M. Sakairi, H. Takahashi, S. Hirai, and S. Yamaguchi, J. Electroanal. Chem. 473, 250 (1999).
[3] J. Ren and Y. Zuo, Appl. Surf. Sci. 261, 193 (2012).
[4] H. Habazaki, S. Koyama, Y. Aoki, N. Sakaguchi, and S. Nagata, ACS Appl. Mater. Interfaces 3, 2665 (2011).
[5] C. L. Ban, Y. D. He, and S. Xin, Trans. Nonferrous Met. Soc. China 21, 133 (2011).
[6] S. Ono, K. Kuramochi, and H. Asoh, Corros. Sci. 51, 1513 (2009).
[7] H. Takahashi, K. Fujimoto, and M. Nagayama, J. Electrochem. Soc. 135, 1349 (1988).
[8] C. Ban, Y. He, X. Shao, and Z. Wang, Corros. Sci. 78, 7 (2014).
[9] R. W. Santway and R. S. Alwitt, J. Electrochem. Soc. 117, 1282 (1970).
[10] M. Ue, H. Ashihina, and S. Mori, J. Electrochem. Soc. 142, 2266 (1995).
[11] Y. Li, H. Shimada, M. Sakairi, K. Shigyo, H. Takahashi, and M. Seo, J. Electrochem. Soc. 144, 866 (1997).
[12] S. Stojadinovic, I. Belca, B. Kasalica, L. Zekovic, and M. Tadic, Electrochem. Commun. 8, 1621 (2006).
[13] J. T. Kinard, B. J. Melody, D. A. Wheeler, and P. M. Lessner, U.S. Patent 6,346,185 (2002).
[14] K. Zhang and S. S. Park, Surf. Coat. Technol. 310, 143 (2017).
[15] K. Watanabe, M. Sakairi, H. Takahashi, K. Takahiro, S. Nagata, and S. Hirai, J. Electrochem. Soc. 148, B473 (2001).
[16] X. L. Jin, X. Y. Wang, H. M. Zhang, Q. Xing, D. B. Wei, and J. J. Yue, Plasma Chem. Plasma Process. 30, 429 (2010).
[17] K. Zhang and S. S. Park, Thin Solid Films 636, 688 (2017).
[18] S. Koyama, Y. Aoki, S. Nagata, and H. Habazaki, J. Solid State Electrochem. 15, 2221 (2011).
[19] W. Lee and S. J. Park, Chem. Rev. 114, 7487 (2014).
[20] K. Zhang and S. S. Park, Appl. Surf. Sci. 477, 44 (2019).