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Anodizing Properties of High Dielectric Oxide Films Coated on Aluminum by Sol-Gel Method

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Abstract. In order to obtain the high capacitance in aluminum electrolytic capacitor, ZrO_2 and Nb_2O_5 films were coated on aluminum foils by sol-gel method, and then the properties of anodized films were examined. The triple layer of ZrO_2/Al-Zr(Nb)O_x/Al_2O_3 was formed on aluminum substrates after anodizing of ZrO_2(Nb_2O_5)/Al film. The thickness of Al_2O_3 layer decreased with increasing the annealing temperature due to the densification of ZrO_2 film and the capacitance of ZrO_2 coated aluminum foil annealed at low temperature was higher than that at high temperature. The increase of capacitance was due to the high capacitance of ZrO_2 film annealed at low temperature. The capacitance of ZrO_2 and Nb_2O_5 coated aluminum increased about 3 and 1.7 times compared to that of Al_2O_3 layer anodized with 400 V, respectively. From these results, the aluminum foils with composite oxide layers are found to be applicable to the aluminum electrolytic capacitor.

Keywords: Al electrolytic capacitor, sol-gel, anodizing, ZrO_2, Nb_2O_5

1. Introduction

Aluminum electrolytic capacitors, which are passive electronic parts, have been widely used in electric and electronic devices. Anodized aluminum oxide, Al_2O_3 has been used as dielectric material of aluminum electrolytic capacitor and the capacitance of the electrolytic capacitor is expressed by the following equation.

$$C = (\varepsilon_0 \cdot \varepsilon_r \cdot A)/d$$

where, C is capacitance, ε_0 permittivity in vacuum, ε_r dielectric constant of oxide film, A the surface area of electrode, and d thickness of dielectrics. Increase of capacitance in the capacitor of same volume can be obtained by increase of ε_r and A and decrease of d, whereas in order to increase the withstanding voltage, the thickness of dielectrics must be increased. Recent trends for small electronic devices require high capacitance of electrolytic capacitors, and so extensive studies have been performed to increase the capacitance. Many researches were focused on an enlargement of surface area and improvement of oxide properties [1–3]. Though the surface area was enlarged greatly by electrochemical etching method, the development of smaller capacitor was very difficult because an enlargement of the surface area by etching process was faced with the limit. Increase in dielectric constant of oxide films is very important in addition to increase of surface area and decrease in film thickness, therefore the application of high dielectric material is necessary for the increase of capacitance. Increase in dielectric constant may be possible by incorporating valve metal oxides as such Ta_2O_5, Nb_2O_5, TiO_2, ZrO_2 and others. In this study, aluminum foils were coated with ZrO_2 and Nb_2O_5 films by sol-gel method. Up to now, the properties of ZrO_2 and Nb_2O_5 films for various applications were shown by PVD (physical vapor deposition) and chemical method, but many problems were involved in capacitor application. Takahashi et al. demonstrated the properties of aluminum composite oxide films prepared by pore-filling method [4], MOCVD (Metal-organic Chemical Vapor Deposition) [5] and sol-gel method

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[6] for aluminum electrolytic capacitor. In this work, ZrO_2 and Nb_2O_5 films were coated by sol-gel method and films were annealed at various temperature. The crystal structure, interface and dielectric properties of films were studied with annealing temperature after anodizing.

2. Experimental

The ZrO_2 films were obtained from the solution containing zirconium *n*-butoxide [$Zr[O(CH_2)_3CH_3]_4$ (Aldrich), 0.05 mol/l], 2 methoxy ethanol[$CH_3OCH_2CH_2OH$], Diethanolamine [$(HOCH_2CH_2)_2NH$] and de-ionized water (100:10:1.5) and Nb_2O_5 films from niobium butoxide [$Nb(OC_2H_5)_5$(Aldrich), 0.05 mol/l], 2 methoxy ethanol, acetic acid and de-ionized water (100:0.02:1.0). High purity Al foil (99.99%, 100 μm) was used as substrate after electro-polishing in a perchloric acid and acetic acid mixture. The electro-polished substrates were coated by sol-gel dip method with the procedure indicated in Fig. 1. The coated films showed the thickness of 15–20 nm per cycle for ZrO_2 films and 30–35 nm per cycle for Nb_2O_5 films. The foils coated with ZrO_2 and Nb_2O_5 films were dried at 150°C and annealed at vacuum furnace for 60 min. The annealed specimens were anodized by capacitor charging power supply (Fug, HCK 750M-1250) with a constant current of 10 A/m^2 in water (1000 ml) and boric acid (H_3BO_3, 70 g) mixture of pH 3.2. The change in the anode potential with time during anodizing was monitored by a PC system. The microstructure and thickness of specimens were determined using field emission scanning electron microscopy (FE-SEM (TOPCON DS-130C)) and transmission electron microscopy (TEM (JEM 2010)). The composition of films was identified by Rutherford backscattering spectroscopy (RBS (NEC 3SDH)) using 2.236 MeV $4He^{2+}$ ion and energy dispersive X-ray spectroscopy (EDS). The capacitance and dissipation factor as a function of frequency were measured with impedance-gain phase analyzer (HP 4194A) after anodized two specimens were immersed in parallel at water (1000 ml) and ammonium adipate (150 g) mixture.

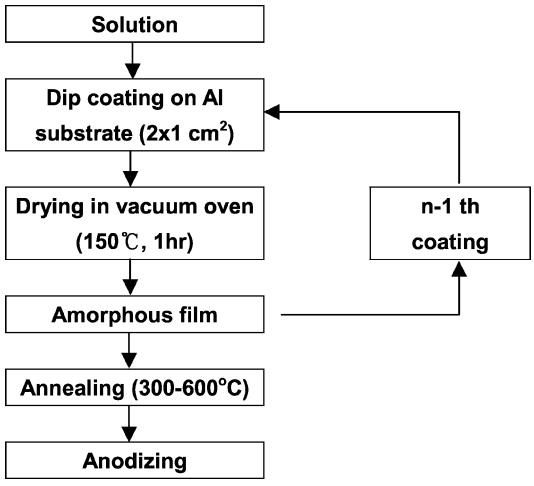

Fig. 1. Procedures for preparation of ZrO_2 and Nb_2O_5 films.

3. Results and Discussion

Figure 2 shows the TEM images of ZrO_2 films anodized up to 200 V and Nb_2O_5 films anodized up to 400 V after 6th coating. The ZrO_2 layer annealed at 300°C of Fig. 2(a) shows a uniform thickness, and the anodized specimen shows two layers below ZrO_2 layer. The two layers were identified as Al-Zr composite oxide and Al_2O_3 layer by EDS and RBS analyses. It may be considered that the growth of aluminum oxide layer during anodizing is due to that O^{2-} ions dissociated from water or electrolyte at the bottom of the ZrO_2 layer transport inwards across the anodic oxide film to form pure aluminum oxide at the interface between the Zr-oxide layer and Al substrate. The diffraction pattern of right upper end obtained from ZrO_2 layer suggested that ZrO_2 layer annealed at 300°C had crystalline structure. Figure 2(b) shows the HRTEM surface image of ZrO_2 layer annealed at 300°C. As can be expected from diffraction pattern of Fig. 2(a), the lattice image of surface shows that ZrO_2 layer is composed of polycrystal of nano-size. Figure 2(c) shows the cross-section image of ZrO_2 layer annealed at 600°C. The specimen shows only a part of ZrO_2 layer at surface due to exfoliation during the preparation of TEM sample, and this suggests that the ZrO_2 layer annealed at 600°C shows poorer adhesion than that at 300°C. Judging from that many samples show the same results, it may be assumed that the bonding force of ZrO_2 layer with substrate decrease by the stress of film due to the annealing at high temperature. Figure 2(d) shows TEM image of Nb_2O_5 films anodized up to 400 V after 6th coating and annealing at 600°C. Nb_2O_5 coated aluminum foil also showed two layers below crystalline Nb_2O_5 layer and the layers consisted of Al-Nb composite oxide and

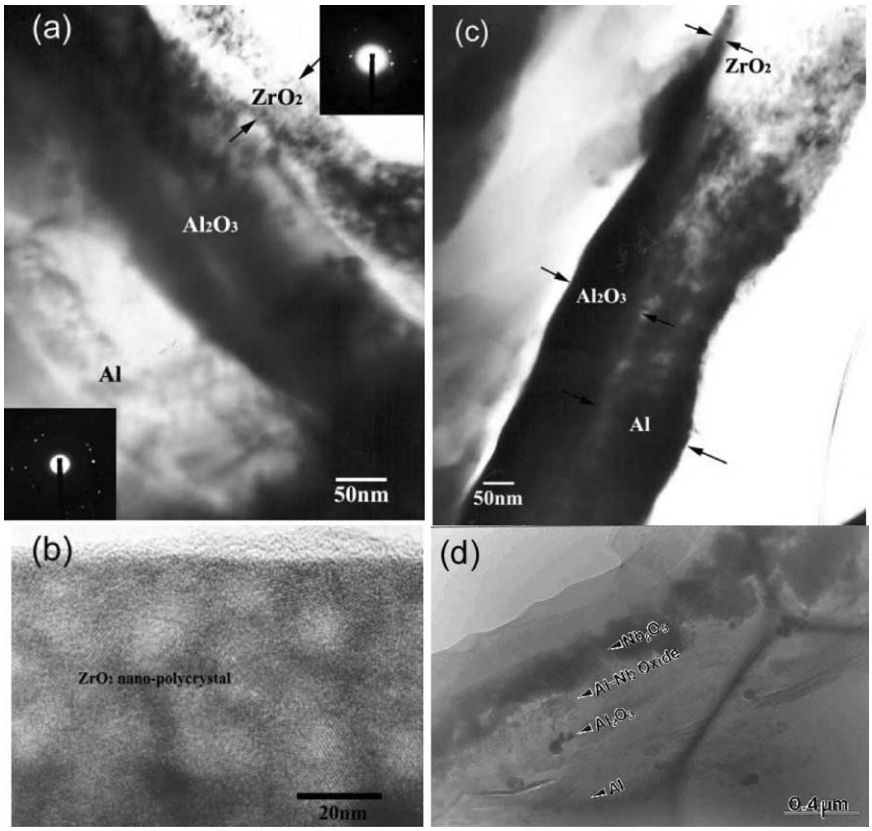

Fig. 2. TEM images of ZrO_2 and Nb_2O_5 films anodized with 200 and 400 V, respectively. Annealing temperature was 300°C in (a) and (b) and 600°C in (c) and (d).

Al_2O_3 layer. These results suggest that the composite oxide layers are formed irrelevant to coating materials after anodizing. When the ZrO_2 coated and non-coated Al specimens were anodized up to 400 V with constant current of 10 A/m^2, Al_2O_3 layer showed the thickness of 440 and 510 nm, respectively. The anodic oxide films composed of an amorphous oxide have the growth rate of 1.3–1.7 nm/V [7–9] and crystalline anodic oxide films after thermal treatment have 0.8–1.3 nm/V [10–12]. The Al_2O_3 layer of ZrO_2 coated specimens show thinner and denser structure compared to that of non-coated specimens. Considering these results, it may be assumed that dense crystalline ZrO_2 layer in surface inhibited the inward diffusion of O^{2-} ions in electrolyte.

Figure 3 shows the RBS spectra and concentration depth profile obtained from ZrO_2 and Nb_2O_5 coated specimens. Figure 3(b) shows that oxide layer consists of ZrO_2/Al-ZrO_x/Al_2O_3 on aluminum substrate and the thickness of ZrO_2 and Al-ZrO_x layer is about 95 and 55 nm, respectively. Watanabe et al. reported [13] that Al-Zr composite oxide was not formed in films annealed at 600°C after repeat of coating and heat treatment at 300°C, however, in this study, Al-Zr composite oxide was formed after annealing at 600°C. This may be explained from that Al^{3+}, Zr^{4+} and O^{2-} ions are diffused easily due to increase of micro-crack and pore because films are heat-treated at 600°C finally after repeat of coating and drying at 150°C. Figure 3(d) shows the concentration profiles of Nb, Al and O in depth, which is obtained by an analysis of Fig. 3(c). The triple layer of Nb_2O_5/Al-NbO_x/Al_2O_3 was formed on aluminum substrate, which was similar to ZrO_2 coating and the thickness of Nb_2O_5 and Al-NbO_x layer was about 180 and 98 nm, respectively.

Figure 4(a) shows the change of the anode potential with anodizing time after ZrO_2 coating of 6 times. The anode potential of specimen without annealing did not rise due to evaporation of organic compound. The

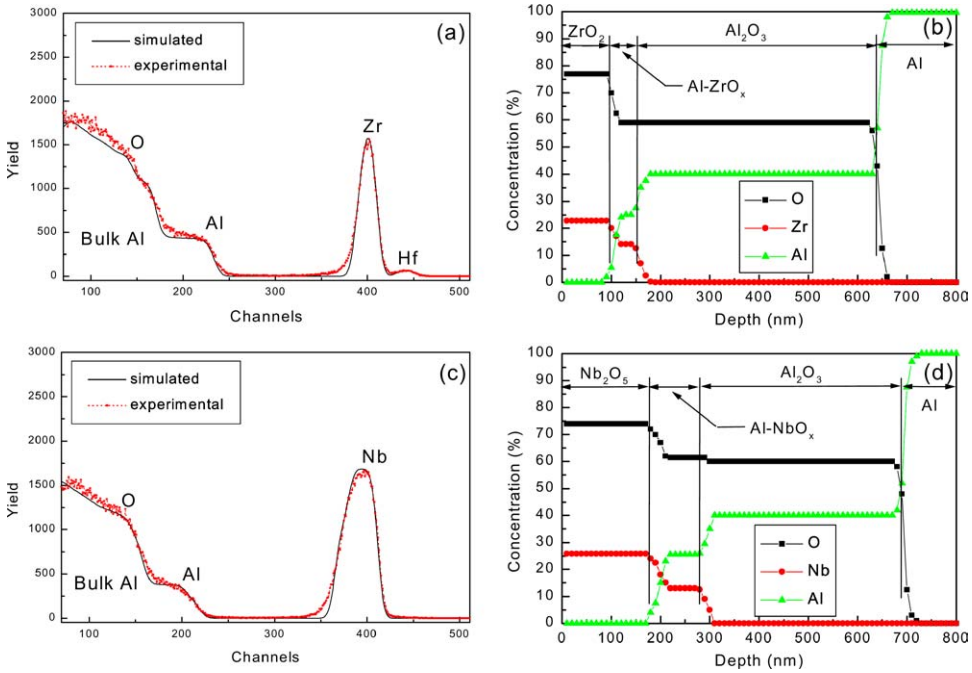

Fig. 3. RBS spectra and concentration depth profiles of ZrO_2 and Nb_2O_5 films anodized with 400 V. ZrO_2 (a, b) and Nb_2O_5 (c, d) films were coated 6 times and annealed at 600°C.

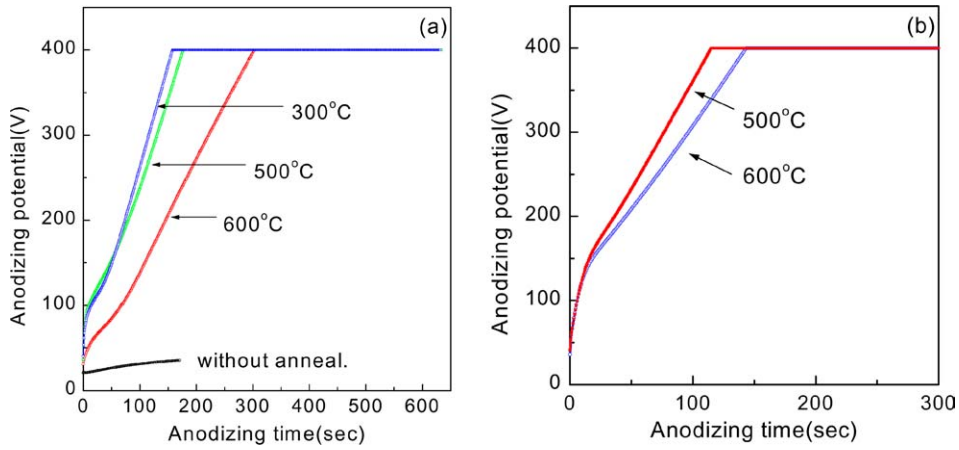

Fig. 4. Variations of anode potential with applying time for (a) ZrO_2 and (b) Nb_2O_5 films annealed at various temperature.

annealed specimens show a linear increase in anode potential and the slope of potential curve become flatter with increasing annealing temperature. The result of Fig. 2, that the thickness of Al_2O_3 in film annealed at 600°C is thinner than that at 300°C, can be explained by slow anodizing of films anodized at high temperature. This result suggests that the crystallinity and density of ZrO_2 increase due to heating at 500 and 600°C, and then, inward diffusion of O^{2-} ions from electrolyte is more difficult. Also, Nb_2O_5 film of Fig. 4(b) shows the similar behavior to ZrO_2 film.

Aluminum foils without oxide coating were anodized for comparison to oxide coated aluminum foil. Figure 5 shows the capacitance and dissipation factor of

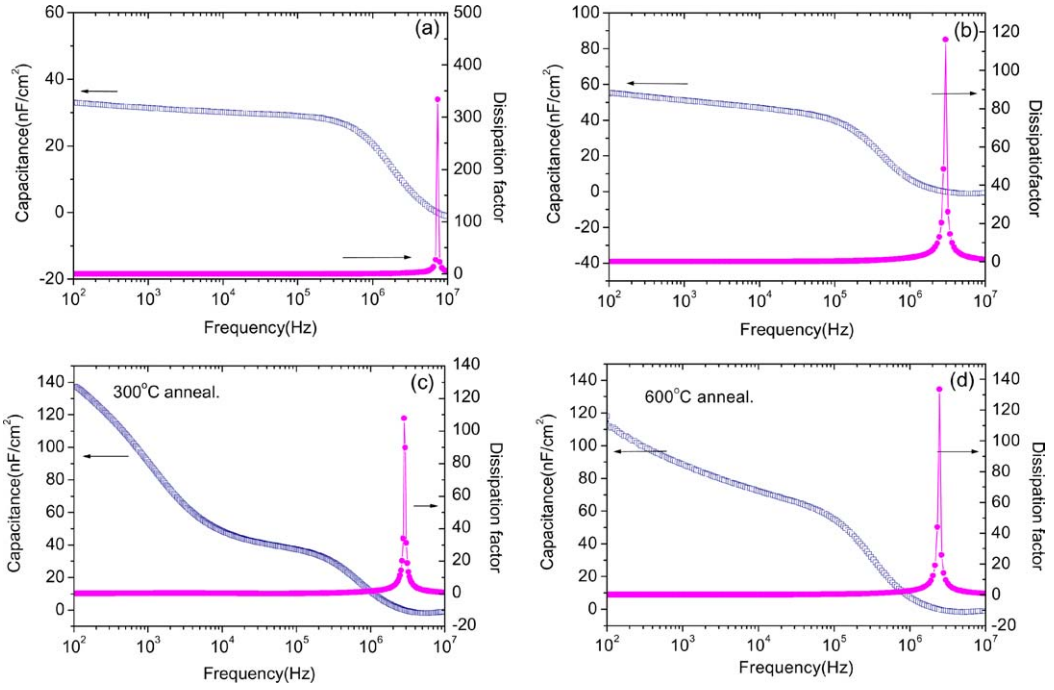

Fig. 5. Capacitance and dissipation factor of (a) Al_2O_3, (b) Nb_2O_5 and ZrO_2 annealed at (c) 300°C and (d) 400°C. The films were anodized up to 400 V.

various oxide films formed by anodizing up to 400 V. The capacitance and dissipation factor at 120 Hz of Al_2O_3 layer (a) and Nb_2O_5/Al-NbO_x/Al_2O_3 layer (b) are 32.9 nF/cm^2, 0.048 and 55.1 nF/cm^2, 0.073 respectively. The capacitance of Nb_2O_5/Al-NbO_x/Al_2O_3 layer is higher 1.7 times compared to capacitance of Al_2O_3 film. Figure 5(c) and (d) shows the dielectric properties of ZrO_2/Al-ZrO_x/Al_2O_3 composite oxide anodized up to 400 V after annealing at 300 and 600°C, respectively. The capacitance and dissipation factor at 120 Hz are 136 nF/cm^2, 0.259 and 111 nF/cm^2, 0.196, respectively. Although the thickness of Al_2O_3 in films annealed at 300°C was thicker than that at 600°C, the capacitance of film at 300°C was higher. The dielectric properties of ZrO_2 films without anodizing were surveyed in order to investigate this discrepancy. The capacitance and dissipation factor of only ZrO_2 films annealed at 300 and 600°C show 810 nF/cm^2, 0.139 and 609 nF/cm^2, 0.031, respectively. Therefore, the capacitance difference of composite oxide layer is due to the properties of ZrO_2 film rather than that of Al_2O_3. The capacitance of ZrO_2/Al-ZrO_x/Al_2O_3 anodized up to 400 V is 3 times larger than that of Al_2O_3 film.

4. Conclusion

ZrO_2 and Nb_2O_5 films were coated on high purity aluminum foils by sol-gel method for application as dielectrics in aluminum electrolytic capacitor. Uniform Nb_2O_5 and ZrO_2 films were coated successfully on aluminum substrates. The ZrO_2 films were crystallized even at 300°C and composed of nano-polycrystal. After the coated aluminum foils were anodized, the triple layer of ZrO_2(Nb_2O_5)/Al-Zr(Nb)O_x/Al_2O_3 was formed onto aluminum substrates. The Al_2O_3 layer in ZrO_2 film annealed at 600°C was thinner and denser than that without ZrO_2 coating because a dense crystalline ZrO_2 layer in surface inhibited the inward diffusion of O^{2-} ions from electrolyte. The Al-Zr(Nb)O_x composite oxide layer was formed at interface between ZrO_2(Nb_2O_5) and Al substrate irrelevant to annealing temperature. The slopes of potential curve become flatter with increasing annealing temperature. The capacitance difference of composite oxide layer is due to the properties of ZrO_2 film rather than that of Al_2O_3. The dielectric constant of ZrO_2 and Nb_2O_5 showed about 3 and 1.7 times compared to that of Al_2O_3, respectively.

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