Formation of Al-(Ta, Nb, Si, Ti) Composite Oxide Films on Aluminum –Development of Aluminum Electrolytic Capacitors with High Capacitance-

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Introduction

Barrier-type anodic oxide films formed on aluminum play an important role as dielectric films in aluminum electrolytic capacitors, and their physical and chemical properties determine the performance of the electrolytic capacitor. Recent development of mobile electronic devices, such as notebook computers, portable telephones and so on requires strongly smaller electrolytic capacitors with higher electric capacitance. The electric capacitance, C, of the aluminum electrolytic capacitor is expressed by the following equation.

$$C = \varepsilon_0 \varepsilon S / \delta \qquad (1)$$

where, ε_0 is the vacuum permittivity, ε the specific dielectric constant of the anodic oxide film, S the surface area, and δ the film thickness. As the charge accumulated in the capacitor, Q, is expressed by the product of C and the applied voltage, V_{appl}, the following equation can be derived.

$$Q = (\varepsilon_0 \varepsilon S / \delta) V_{appl} \qquad (2)$$

The V_{appl} should be smaller than the film formation potential, E_a, since the application of V_{appl} beyond E_a leads to the film breakdown. Hence, the maximum accumulated charge, Q_{max}, in the aluminum electrolytic capacitors is expressed in the following equation.

$$Q_{max} = (\varepsilon_0 \varepsilon S / \delta) E_a \qquad (3)$$

The film thickness, δ, is proportional to E_a, giving Eq. (4).

$$E_a = \delta / K \qquad (4)$$

where K is the film thickness per unit film formation potential. Substitution of E_a with δ / K into Eq. (3) gives Eq. (5).

$$Q_{max} = \varepsilon \varepsilon S / K \qquad (5)$$

It is obvious from Eq. (5) that larger value of S and smaller values of ε and K gives larger Q_{max}. Increase in S is achieved by electrochemical etching of the aluminum substrate before anodizing in industry.

Another way of the increase in Q_{max} is the increment of ε or decrement of K. These values, however, can not be changed independently, since they are closely related each other. Increase in ε / K-value is, therefore, essential for developing capacitors with high capacitance. The formation of composite oxide films by incorporating valve metal oxides into anodic oxide films on aluminum is considered to be useful for the increase in ε/K because of high ε/K-values of valve metal oxides. In this review paper, the authors introduce several methods for the formation of Al-Me(Me: Ta, Nb, Si, Ti) composite oxide films on aluminum and their application to tunnel-etched specimens with rough surface.

Pore filling method[1)]

In this process, aluminum specimen is anodized in acid solutions to form porous anodic oxide films. Anodized specimen is immersed in solutions containing Me-ions, and then removed from the solution to dry at room temperature. Dried specimens are heated to decompose Me-complexes and to deposit Me-oxide on the pore walls of anodic oxide films. The dipping-heating process is repeated several times before re-anodizing in neutral solutions is carried out in the final step. During re-anodizing, pores are filled with new aluminum oxide, and Me-oxide deposited on the pore-walls is incorporated into the newly formed aluminum oxide.

Combination of MOCVD with anodizing[2)]

In this process, aluminum specimen is covered with Me-oxide by metal organic chemical vapor deposition (MOCVD), where Me-alcoxide vapor is supplied with N_2 gas into the specimen chamber and then heated to decompose the alcoxides. The specimen coated with Me-oxide is anodized in a neutral solution. During galvanostatic anodizing, anodic oxide films grow with time, which consist of two layers: an outer Al-Me composite oxide layer and an inner alumina layer. The formation of the composite oxide layer occurs by the outward transport of Al^{3+} ions across the alumina layer, and the formation of the inner alumina layer is due to the inward transport of O^{2-} ions across the anodic oxide films.

Combination of sol-gel dip coating and anodizing[3, 4)]

This process involves the deposition of Me-oxide by sol-gel-dip coating on aluminum and anodizing in neutral solutions. Aluminum specimen is dipped in Me-sol, and then removed at a steady rate with a linear motor system. Then, the specimen is dried at room temperature and heated at different temperatures in oxygen atmosphere. The specimen deposited with Me-oxide is anodized in neutral solutions to form composite oxide films.

Combination of electrophoretic sol-gel coating and anodizing

Aluminum specimen is anodically polarized in a solution containing small particles of Me-oxide with negative charge to deposit them on the surface. The specimen coated with Me-oxide layer is heated, and anodized in neutral solutions. This process is very useful for the uniform coating of Me-oxide on tunnel-etched specimens.

References

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