Effect of Formation Voltage on Structure of Anodic Barrier Films Formed on Aluminum

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Anodic barrier film formed on aluminum is industrially used as a dielectric film of electrolytic capacitor. The thickness and anion incorporation behavior of anodic films are important factors because they affect to the capacitance. Since the film thickness is proportional to the formation voltage, the thin film formed at the low voltage region under 10V is especially important as a high capacitance film. In the previous work[1], we reported that the anion incorporation behavior was strongly affected by current density, i.e., electric field strength. Further, it was shown that the structure of the films formed at low voltage region was different from those of the films formed at high voltage region[2]. In this study, the effect of formation voltage on the structure and property of anodic barrier film formed in various electrolytes were investigated.

High purity (99.99%) aluminum sheets were electropolished in a 4:1 mixture of ethanol-perchloric acid solution. Anodic films were formed in 0.1mol dm^{-3} ammonium adipate solution or 0.5mol dm^{-3} boric acid - 0.05mol dm^{-3} borate solution at 20℃ at constant current density of $5mAcm^{-2}$ up to the voltage range from 5V to 80V. The film thickness and anodizing ratio were measured by using a transmission electron microscope (TEM). Depth profiles of constituent elements in the films were measured by glow discharge optical emission spectroscopy (GD-OES) to evaluate transport number of Al^{3+}.

Figure 1 indicates the effects of formation voltage on film thickness and anodizing ratio. The anodizing ratio of the film formed at 5V was 1.8nm/V, while it was 1.5nm/V for the film formed at 80V. Generally, it is believed that the film thickness is proportional to the formation voltage. However, the anodizing ratio increased with decreasing formation voltage. Therefore, it is clear that the electric field strength decreases with decreasing formation voltage.

GD-OES depth profiles of constituent elements in the films formed at 5 $mAcm^{-2}$ is shown in Fig.2. Since boron is suggested to be immobile under the electric field, transport number of Al^{3+} can be estimated by boron containing depth. Transport number of Al^{3+} of the film formed at 80V was 0.44, while it was 0.34 for the film formed at 5V. As summarized in Fig.3, the transport number of Al^{3+} decreased with decreasing voltage although the films were formed at the same current density. Furthermore, when the anion concentration in the films was evaluated by the spectral intensity ratio of boron to oxygen, it also decreased with decreasing formation voltage. Therefore, it is concluded that the structure and property of the films formed at the low voltage region are different from those of the films formed at the high voltage region because of the change in electric field strength.

1) S. Ono, F. Mizutani, M. Ue and N. Masuko, ECS Proc. Vol 2001-22, p.1129 (2001)
2) S.Ono, C.Wada, H.Asoh, 13th Meeting of Asian-Pacific Corrosion Control Conference, Abstracts No.P038 (2003)

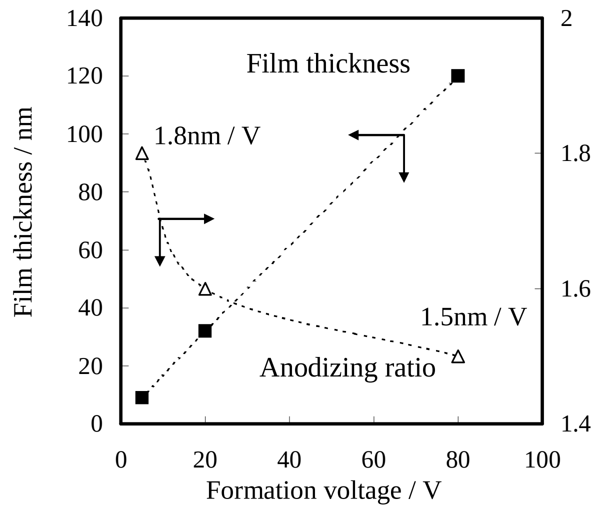

Fig.1 Changes in film thickness (left) and anodizing ratio (right) with formation voltage. Anodic films were formed in ammonium adipate solution at $5mAcm^{-2}$.

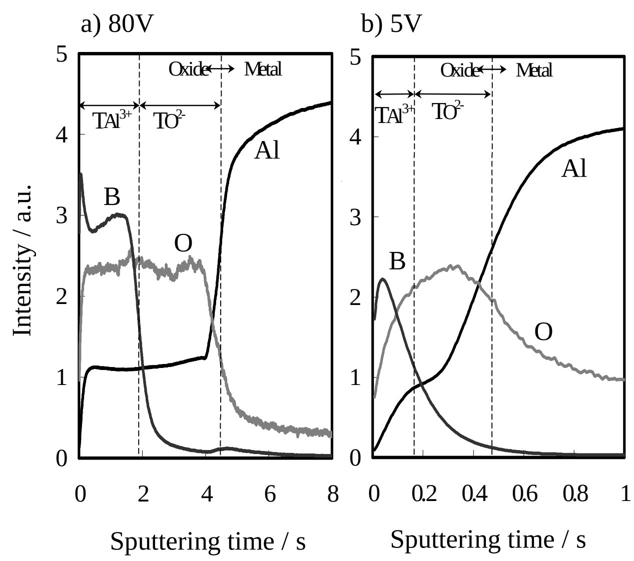

Fig.2 GD-OES depth profiles of constituent elements in the anodic films formed at 5 $mAcm^{-2}$ in 0.5mol dm^{-3} boric acid-0.05mol dm^{-3} borate solution. a) 80V b) 5V

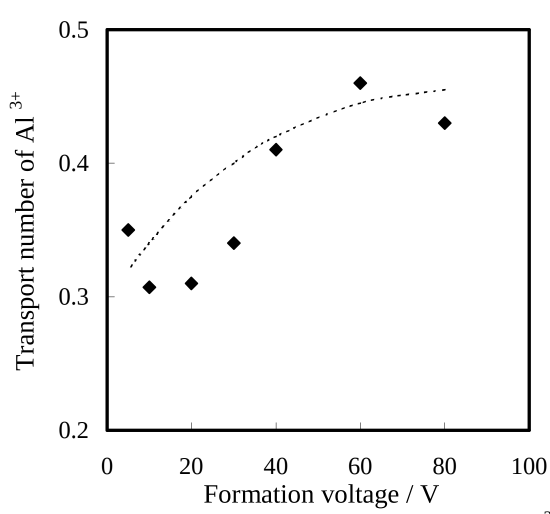

Fig.3 Relation between transport number of Al^{3+} and formation voltage. Anodic films were formed in 0.5mol dm^{-3} boric acid-0.05mol dm^{-3} borate solution at $5mAcm^{-2}$.