

Characterization of Anodic Oxide Film Formed on Niobium in Alkaline Solution

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Anodic oxide film formed on niobium has attracted a considerable interest as an alternative material to tantalum electrolytic capacitor because niobium is more abundant in deposit. We reported the fundamental aspects of anodic oxide films formed on niobium with focusing on the effects of anodizing conditions including electrolyte type, concentration, temperature, heat treatment on the dielectric properties of oxide films [1]. In the present study, the effect of electrolyte pH on the dielectric properties of oxide films and detailed structure were investigated.

High purity (99.93%) niobium foil was anodized in phosphate solution at constant current density until voltage went up to 60V. The subsequent voltage holding was carried out for 30 min. The pH of phosphate solutions was adjusted by the addition of NH₄OH. The film properties were evaluated by means of voltage–time curves on re-anodizing, measurement of capacitance, and TEM observation, as described previously [2].

Figure 1 shows the dependence of capacitance and voltage jump (*V_j*) on electrolyte pH [2]. The values of *V_j*, that is, withstand voltages were almost same regardless of electrolyte pH. *V_j* is generally assumed to be proportional to the film thickness. This result indicates that the film thickness evaluated electrochemically was independent of electrolyte pH. On the other hand, the capacitance of the oxide film formed in alkaline region increased with increasing pH.

For the direct evaluation of film thickness, cross sectional investigation was carried out using TEM combined with focused ion beam micro-processing. TEM images of the anodic films formed in phosphoric acid with different electrolyte pH showed that the films were composed of two layers: outer layer having light contrast and inner layer having dark contrast. The film composition has a connection with transport numbers of Nb⁵⁺ and O²⁻ and anion incorporation behavior: the outer layer is thought to be an anion-containing layer, while inner layer consists of pure niobium oxide. In addition, the thickness of the film formed at pH 10 was slightly thicker than that of the film formed at pH 1.6. Table 1 shows the changes in capacitance and relative permittivity of those in Fig.2. The relative permittivity was calculated from the measured capacitance and film thickness. In the case of pH 10, the relative permittivity was remarkably high such as 80.5, in comparison with a general value of 43.7 at pH1.6.

Figure 3 shows the variation of the *V_j* with dissolution time. This result implies that the dissolution behavior of anodic film was strongly affected by the electrolyte pH. The solubility of the film was suppressed with increasing pH of electrolyte. These characteristic properties are caused by anion incorporation behavior, and reflected in specific dielectric properties.

[1] S Ono, M Baba, M Shimoyama and H Asoh, 204th Meeting of the Electrochemical Society, Abstr. 1308 (2003)

[2] K Kuramochi Asoh, T Mochizuki and S Ono, 71st annual Meeting of the Electrochemical Society of Japan, Abstract p.276 (2004)

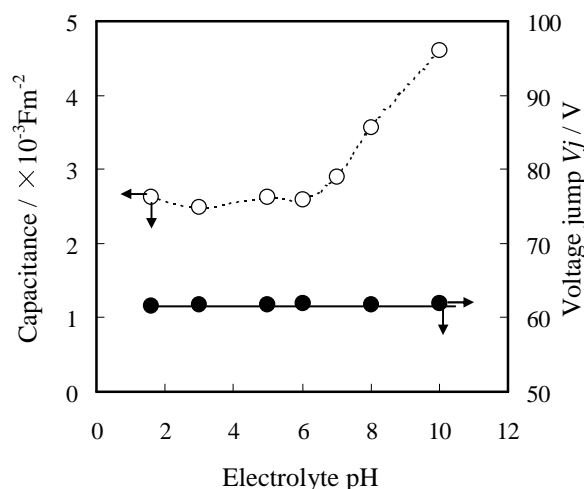


Fig.1 Changes in capacitance and voltage jump with electrolyte pH. Anodizing was carried out at constant current up to 60V. The subsequent voltage was kept at 60V for 30 min. (after ref.2)

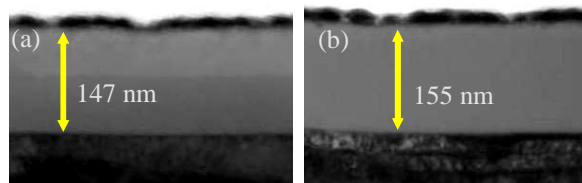


Fig 2 TEM cross sections of anodic films formed in electrolytes of (a) pH1.6 and (b) pH10 at 1mAcm⁻² followed by voltage hold at 60V for 30min.

Table.1 Changes in capacitance and permittivity.

pH	Capacitance(× 10 ³ Fm ⁻²)	Relative permittivity
1.6	2.6	43.7
10	4.6	80.5

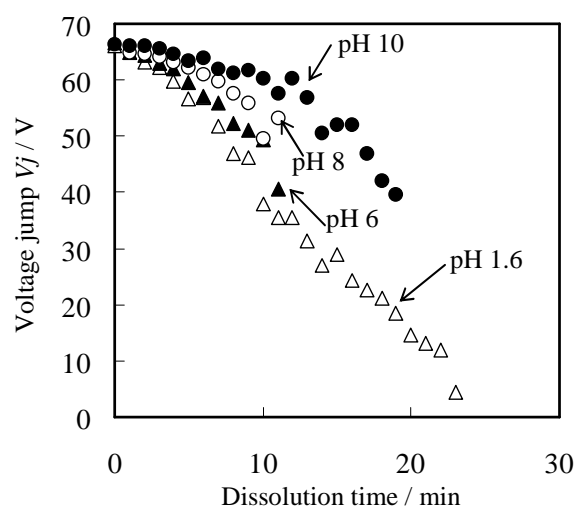


Fig 3 Changes in voltage jump (film thickness) with dissolution time. Anodic films were formed at 1mAcm⁻² up to 60V. The subsequent voltage holding was carried out for 20 min.