

Structure and property of anodic barrier films formed on aluminum in low voltage range

Sachiko Ono*, Chieko Wada, Hidetaka Asoh

Department of Applied Chemistry, Faculty of Engineering, Kogakuin University, 1-24-2 Nishi-shinjuku, Shinjuku-ku, Tokyo 163-8677, Japan

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Abstract

The structure and properties of anodic films formed in a relatively low voltage range in ammonium adipate solution have been investigated focusing on the effect of formation voltage. When anodization voltage was identical, the linear relationship of film thickness with the log of the final current density during film growth could be ascertained for all the films formed even at low voltages such as 5 V. The anodization ratio determined from the transmission electron microscopy (TEM) cross section of the film formed at 5 mA cm⁻² until voltage increased to 5 V was 1.8 nm/V suggesting a lower electric field strength during anodization than that for the film formed at the voltage higher than 20 V. Furthermore, the transport number of Al³⁺ ions and amount of incorporated anions decreased with decreasing formation voltage, particularly at the voltage lower than 10 V. Changes in chemical dissolution rate in the depth of the films in an acid solution indicated that the films formed in the voltage range from 20 to 80 V were composed of one layer and the films formed at voltages lower than 10 V were composed of two layers with different dissolution rates. However, when applied voltage was kept constant following current decay, the film formed one layer, implying the inward migration of the incorporated anions to the film/metal interface. It was suggested that the outer layer with the higher dissolution rate contains electrolyte anions and the inner layer with the lower dissolution rate consists of pure alumina. Thus, it is clarified that the structure and properties of anodic film change with increasing anodization voltage because of the change in electric field strength, even if anodization is conducted at a constant current density.

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1. Introduction

The growth of anodic oxide films in neutral electrolytes proceeds at both film/electrolyte and film/substrate interfaces giving a duplex structure [1,2]. The oxide layer formed at the former interface includes electrolyte anions, while a pure-alumina layer is formed at the latter interface. The thickness ratios of each layer, respectively, represent the transport numbers of Al³⁺ and O²⁻ if the incorporated anions are immobile in the film. It is suggested [3] that borate is immobile in the film but phosphate migrates inward after incorporation. Species such as chromate, tungstate and molybdate migrate outward. The depth and content of incorporated anions must affect the dielectric properties of anodic

oxide films as a capacitor material as well as film thickness [4].

Concerning the thickness of anodic films, it is generally taken to be proportional to applying voltage. However, the classical theory of ionic conduction at high field strengths for various metals [1,5–7] indicates that film thickness must be inversely proportional to the logarithm of ionic current, when a film is formed at an identical voltage. The precise clarification of the factors determining film thickness is essential in the capacitor industry because film thickness directly affects capacitance.

Recently, one of the present authors [4,8–10] reported that the changes in current density and electrolyte temperature induce notable changes in film structure as well as in composition, which were evaluated by the transmission electron microscopy (TEM), secondary ion mass spectroscopy

* Corresponding author.

(SIMS) and glow discharge optical emission spectroscopy (GD-OES). Namely, the thickness of the film formed in a borate solution at a constant current density up to an identical voltage decreases with increasing current density and markedly increases with temperature. The thickness ratio of the boron incorporated in the outer layer is 0.4 at a current density of 2 mA cm^{-2} and increases to 0.45 at 20 mA cm^{-2} at an anodization voltage of 80 V. A porous cell structure is developed when the film is formed at a current density higher than 10 mA cm^{-2} . Boron content in the outer layer increases 1.5 times when current density increases 10 times [4].

The main purpose of this work is to evaluate the effect of anodization voltage, particularly at the voltages lower than 80 V as well as current density on film thickness and microstructure. Since capacitance is inversely proportional to film thickness, precise information on the nature of the films formed in the low voltage range must be beneficial to obtain high-capacitance and high-quality dielectric films.

2. Experimental

High-purity (99.99%) aluminum sheets were electropolished in a 4:1 mixture of ethanol–perchloric acid solution before anodization. Anodic films were formed in 0.1 mol dm^{-3} ammonium adipate, which is generally used in the capacitor industry in a low voltage range, at 20°C at various constant current densities up to 80 V. The iR -drop at various anodization current densities induced by electrolyte resistance, which was 3.7 V in maximum at 10 mA cm^{-2} at 20°C , was compensated by applying voltage [11]. Galvanostatic polarization was conducted to prevent the iR -drop induced by solution resistance when the anodization voltage was lower than 10 V. An electrochemical measurement called the “pore-filling (PF)” technique [12–14], i.e. re-anodization of an anodized specimen, was adopted in evaluating the thickness and imperfections of anodic oxide films. For this evaluation, voltage–time (V – t) curves were measured during re-anodization at 0.1 mA cm^{-2} in 0.1 mol dm^{-3} ammonium adipate at 20°C , where voltage jump (V_j) is suggested to be proportional to film thickness. Details were described in our previous paper [4]. Anodic film structures were observed by TEM (Hitachi H-9000) operated at 300 kV. The cross sections of films with a thickness of 30–50 nm were prepared using an ultramicrotome with a diamond knife attached. Glow discharge optical emission spectroscopy (Jobin-Yvon JY5000RF) was used for measuring the depth profiles of constituent elements in the films accompanied by argon ion sputtering at 40 W.

3. Results and discussion

3.1. Relation between current density and film thickness

Anodic films were formed in 0.1 mol dm^{-3} ammonium adipate solution at 20°C at various constant current densities

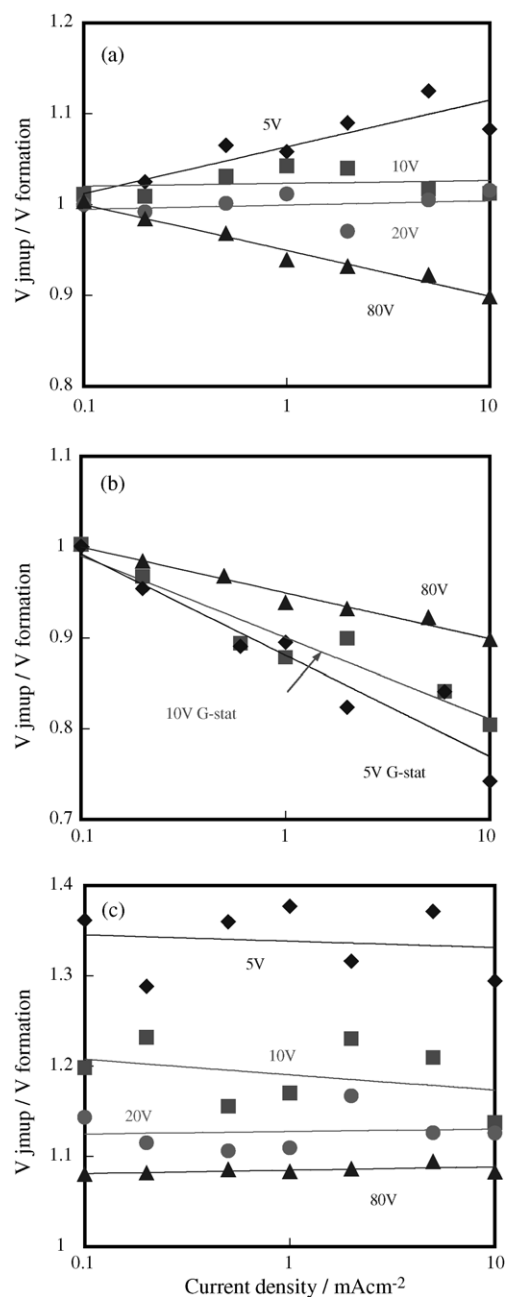


Fig. 1. Relationship between ratio of voltage jump V_j to formation voltage V_f and log of current density: (a) constant current; (b) constant current and re-anodization was conducted by Galvanostatic polarization at the voltage lower than 10 V; (c) constant voltage followed by current decay for 20 min.

of 0.1 – 10 mA cm^{-2} up to an identical voltage ranging from 5 to 80 V. Galvanostatic polarization was used for anodization at a voltage lower than 10 V. The thickness of the films was evaluated from the voltage jump V_j in re-anodization in a mixed borate solution as described above. As shown in Fig. 1a, the voltage jump V_j , namely, the thickness of the films had a linear relationship with the log of current density and decreased with increasing current density if the formation voltage was higher than 40 V, as we previously reported

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