

Mechanism of formation and growth of sunflower-shaped imperfections in anodic oxide films on niobium

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Abstract

Anodizing of niobium has been investigated to develop niobium solid electrolytic capacitors. Chemically polished niobium specimens were anodized in a diluted phosphoric acid solution, initially galvanostatically at $i_a = 4 \text{ A m}^{-2}$ up to $E_a = 100 \text{ V}$, and then potentiostatically at $E_a = 100 \text{ V}$ for $t_{pa} = 43.2 \text{ ks}$. During the galvanostatic anodizing, the anode potential increased almost linearly with time, while, during potentiostatic anodizing, the anodic current decreased up to $t_{pa} = 3.6 \text{ ks}$, and then increased slowly before decreasing again after $t_{pa} = 30.0 \text{ ks}$. Images of FE-SEM and in situ AFM showed that nuclei of imperfections were formed at the ridge of cell structures before $t_{pa} = 3.6 \text{ ks}$. After formation, the imperfection nuclei grew, showing cracking and rolling-up of the anodic oxide film, and crystalline oxide was formed at the center of imperfections after $t_{pa} = 3.6 \text{ ks}$. The growth of imperfections caused increases in the anodic current between $t_{pa} = 3.6$ and 30.0 ks . Long-term anodizing caused a coalescence of the imperfections, leading to decreases in the anodic current after $t_{pa} = 30.0 \text{ ks}$. As the imperfections grew, the dielectric dispersion of the anodic oxide films became serious, showing a bias voltage dependence of the parallel equivalent capacitance, C_p , and a dielectric dissipation factor, $\tan \delta$. The mechanism of formation and growth of the imperfections, and the correlation between the structure and dielectric properties of anodic oxide films is discussed.

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1. Introduction

Tantalum solid electrolytic capacitors are used in many electronic applications, like mobile phones, personal computers and so on, since they can be made small and still have large capacitances. Furthermore, good frequency characteristics and temperature characteristics are obtained in tantalum capacitors because highly conductive solid electrolytes, such as manganese dioxide and polypyrrole, are used for electrolytes. However, tantalum is rare and expensive, and anodizing of niobium has been investigated to develop alternatives to tantalum capacitors.

The dielectric constant of anodic oxide films on niobium is 42 [1], which is larger than that of anodic oxide films on tantalum (23–27) [1]. Therefore, if niobium capacitors are used,

the size could be smaller than that of tantalum capacitors for the same performance. However, anodic oxide films on niobium have dielectric properties that are unsuitable for capacitors: (i) there are increases in capacitance and leakage current by heat treatment [2–12], and (ii) there is a bias voltage dependence of the capacitance [11–18]. A previous investigation reported that these properties are caused by imperfections in the anodic oxide films, which are grown by heat treatment [10] or by potentiostatic anodizing [13]. Recently, Habazaki et al. showed that the dielectric properties of anodic oxide films on sputter-deposited Nb–N alloys [11] and Nb–Si alloys [12] are superior to those of anodic oxide films on sputter-deposited pure niobium.

The present investigation details the growth process of imperfections in anodic oxide films on niobium by in situ atomic force microscopy (AFM) as well as field emission scanning electron microscopy (FE-SEM) and scanning confocal laser microscopy (SCLM) to correlate the structure with the dielectric properties. Further, the mechanism of formation and growth of imperfections is discussed.

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2. Experimental

2.1. Preparation

Highly pure niobium foil (99.98%, 100 μm thick) was cut to $1\text{ cm} \times 1\text{ cm}$ with a handle, and then chemically polished for 120 s in a mixed solution of HF, H_2SO_4 , and HNO_3 at 273–275 K. The solution used for the chemical polishing was prepared by mixing HF: H_2SO_4 : HNO_3 : H_2O in a 2:5:2:5 volume ratio. To remove fluoride ions adsorbed on the specimen surfaces, the chemically polished specimens were immersed in boiling doubly distilled water for 600 s. The handle of the specimens was shielded by a Shin-Etsu silicone coating to leave only the square $1\text{ cm} \times 1\text{ cm}$ part exposed.

2.2. Anodizing

Chemically polished niobium specimens were anodized in 0.015 kmol m^{-3} H_3PO_4 solution at $T_a = 333\text{ K}$. Anodizing was carried out galvanostatically at $i_a = 4\text{ A m}^{-2}$ up to $E_a = 100\text{ V}$, and then potentiostatically at $E_a = 100\text{ V}$ (CCP 500-005 MR, Takasago). Anodizing conditions described above have been widely used in electrolytic capacitor industry. The starting time of the anodizing was defined as $t_a = 0$, and the starting time of the potentiostatic anodizing as $t_{pa} = 0$. Changes in anode potential, E_a , and anodic current, i_a , with t_a (or t_{pa}) during anodizing were monitored with a digital multi meter (R6452A, ADVANTEST) connected to a personal computer system (PC9821 Xa10, NEC) at a sampling rate of 1 point/s. A platinum plate was used as the counter electrode, and a saturated KCl–Ag/AgCl electrode as the reference electrode. The amount of niobium ions dissolved during anodizing was measured by inductively coupled plasma optical emission spectrometry (ICP-OES).

2.3. Electrochemical impedance spectroscopy (EIS)

After anodizing for different t_{pa} , specimens were immersed in 0.5 kmol m^{-3} $\text{H}_3\text{BO}_3/0.05\text{ kmol m}^{-3}$ $\text{Na}_2\text{B}_4\text{O}_7$ solution (pH

7.4) at 293 K, and the impedance, $|Z|$, and phase shift, θ , were measured by applying $V_b = 0, 1, 2,$ and 3 V of bias voltage and 100 mV of sinusoidal alternating voltage in the $f = 10\text{ mHz} - 10\text{ kHz}$ range with a frequency response analyzer (FRA 5095, NF). A platinum net with a large surface area was used as the counter electrode. Parallel equivalent capacitance, C_p , and the dielectric dissipation factor, $\tan \delta$, were estimated by analyzing Bode diagrams.

2.4. Characterization of anodic oxide films

Contrast images of the surface of anodic oxide films were observed by SCLM (1SA21DM, Lasertec). More details of the morphology of the surface of the anodic oxide films was obtained by FE-SEM (JSM-6500F, JEOL). Before the observation of the surface by FE-SEM, thin platinum layers were sputter-deposited on the specimens for 120 s (0.6 nm thick) to avoid charging of the specimens by electron beam irradiation (JVC-5000, JEOL).

2.5. In situ AFM

Chemically polished niobium specimen was set in an electrochemical cell on an AFM stage, and then anodized in 0.015 kmol m^{-3} H_3PO_4 solution at 293 K. Anodizing was carried out galvanostatically at $i_a = 0.5\text{ A m}^{-2}$ up to $E_a = 100\text{ V}$, and then potentiostatically at $E_a = 100\text{ V}$ for up to $t_{pa} = 10.8\text{ ks}$. It was found by preliminary experiments that high temperature and low galvanostatic current density enhance the formation of imperfections. The lower current density (0.5 A m^{-2}) was employed to enhance the imperfection formation at room temperature (293 K) on AFM stage. The growth process of the imperfections during anodizing was observed by in situ AFM (SPA400, Seiko Instrument) with an Si probe. The probe had a triangular cantilever with sharpened pyramidal tip with a 50 N m^{-1} spring constant, and the AFM observations were carried out with a contact mode at 40 nN of contact force on open circuit.

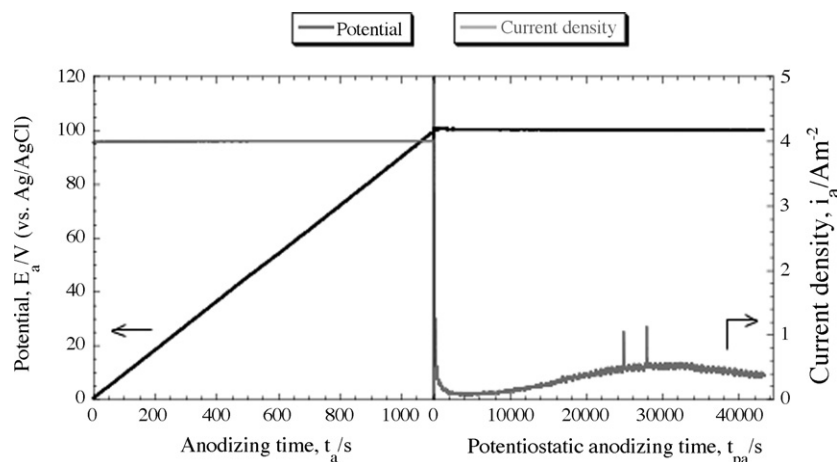


Fig. 1. Changes in anode potential, E_a , and anodic current, i_a , with anodizing time, t_a , obtained for chemically polished niobium specimens. Anodizing was carried out by a constant current of 4 A m^{-2} up to $E_a = 100\text{ V}$ (vs. Ag/AgCl) and then by keeping the potential at $E_a = 100\text{ V}$ in 0.015 kmol m^{-3} H_3PO_4 solution at 333 K.

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