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Field crystallization of anodic niobia

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Abstract

Influences of electrolyte, pre-thermal treatment and substrate composition have been examined to elucidate the mechanism of field crystallization of anodic niobia formed on magnetron-sputtered niobium. The field crystallization occurs during anodizing at 100 V in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 333 K, with the crystalline oxide growing more rapidly than the amorphous oxide, resulting in petal-like defects. The nucleation of crystalline oxide is accelerated by pre-thermal treatment of the niobium at 523 K in air, while vacuum treatment hinders nucleation. Notably field-crystallization is also absent in 0.1 mol dm^{-3} phosphoric acid electrolyte or when anodizing Nb–10at.%N and Nb–29at.%W alloys in the ammonium pentaborate electrolyte. The behaviour is explained by the role of the air-formed oxide in providing nucleation sites for field crystallization at about 25% of the thickness of the subsequently formed anodic film, the location being due to the growth mechanism of the anodic oxide and the nature of crystal nuclei. Incorporation of tungsten, nitrogen and phosphorus species to this depth suppresses the field crystallization. However, boron species occupy a relatively shallow layer and are unable to affect the nucleation sites.

Keywords: A. Sputtered films; B. SEM, GDOES, RBS; C. Anodic films

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1. Introduction

Niobium and tantalum form generally amorphous anodic oxides, with the growth proceeding simultaneously at the metal/film interface by anion ingress and at the film/electrolyte interface by cation egress with a cooperative mechanism of ionic transport [1,2]. Such anodic films are of practical importance as dielectrics of solid electrolytic capacitors. However, when a high electric field is applied to the films in electrolyte at increased temperatures, field crystallization occurs. Crystalline oxide is nucleated in the amorphous oxide, followed by its radial growth, leading to the progressive deterioration of the dielectric properties [3–9]. Field crystallization was first described by Vermilyea for anodic films on tantalum [3]. The logarithm of incubation time for crystalline oxide formation increased linearly with decrease of the field strength, while formation voltage, electrolyte temperature and impurity at the metal surface strongly influenced the nucleation of the crystalline oxide. Jackson examined the influence of electrolyte parameters, concluding that increase in pH and electrolyte concentration retarded the nucleation of the crystalline oxide in anodic films on tantalum [6]. The influence of thermal oxide on the field crystallization has also been reported [10].

Field crystallization occurs more readily in anodic films on niobium compared with those on tantalum [11]. Similar to anodic tantala, cracks are developed at the nucleation sites, with the pre-formed, outer, amorphous oxide layer being rolled up, forming petal-like defects, during subsequent growth of the crystalline oxide. The crystalline oxide is nucleated preferentially at the convex surfaces of chemically polished niobium leading Nagahara et al. to suggest an association with strong tensile stress [8]. Impurity at such regions, from preferred cathodic activity, may have played a role in the crystallization. Indeed, for anodic tantalum, it has been reported that inclusions provide nucleation sites [4]. A strong influence of electrolyte has been reported, with phosphoric acid suppressing markedly the field crystallization [6,11], although the reason is not yet clarified. Thus, additional studies are needed to gain further insight into the mechanism of field crystallization of niobia and tantala and dielectric degradation.

In contrast to bulk metallic materials, often containing inclusions, precipitates and second phases, it is well known that sputtering deposition results in the formation of single phase materials with impurity and alloying elements dissolving homogeneously into the primary phase [12–14]. The single phases are formed exceeding the solubility limit of the impurity and alloying elements at equilibrium. In the present study, field crystallization of anodic niobia has been investigated using magnetron sputtered niobium and niobium alloys. By using magnetron sputtered materials, the influence of chemical heterogeneity of metal substrate on field crystallization of anodic niobia can be eliminated. Thus, the influences of the type of electrolyte, pre-thermal treatment and substrate composition have been examined with particular attention paid to the beneficial influence of foreign species incorporated into the oxide.

2. Experimental

Niobium and niobium alloy films containing nitrogen and tungsten were prepared by magnetron sputtering on to glass, silicon and aluminium substrates. Aluminium substrates were electropolished and subsequently anodized in 0.1 mol dm^{-3} ammonium pentaborate electrolyte to 200 V to provide highly flat surfaces. A 99.9% pure niobium disk of 100 mm