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Dielectric properties of anodic films on sputter-deposited Ti–Si porous columnar films

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For electrolytic capacitor application of the single-phase Ti alloys containing supersaturated silicon, which form anodic oxide films with superior dielectric properties, porous Ti–7 at% Si columnar films, as well as Ti columnar films, have been prepared by oblique angle magnetron sputtering on to aluminum substrate with a concave cell structure to enhance the surface area and hence capacitance. The deposited films of both Ti and Ti–7 at% Si have isolated columnar morphology with each column revealing nanogranular texture. The distances between columns are ~500 nm, corresponding to the cell size of the textured substrate and the gaps between columns are 100–200 nm. When the porous Ti–7 at% Si film is anodized at a constant current density in ammonium pentaborate electrolyte, the growth of a uniform amorphous oxide film continues to ~35 V, while it is limited to less than 6 V on the porous Ti film. The maximum voltage of the growth of uniform amorphous oxide films on the Ti–7 at% Si films is similar for both the flat and porous columnar films, suggesting little influence of surface roughness on the amorphous-to-crystalline transition of growing anodic oxide under the high electric field. Due to the suppression of crystallization to sufficiently high voltages, the anodic oxide films formed on the porous Ti–7 at% Si film shows markedly improved dielectric properties, in comparison with those on the porous Ti film.

1. Introduction

Titanium and its alloys are an important member of engineering materials with light weight, high weight-to-strength ratio, biocompatibility and high corrosion resistance even in very aggressive environments. The oxide formed on titanium is an n-type semiconductor with many attractive properties. The thickness of a native oxide film on titanium at ambient temperature is only a few nm, but can be increased greatly by anodizing in suitable electrolytes.

The anodic oxide films on valve metals are important dielectric materials. In fact, those on aluminum and tantalum have been used widely in electrolytic capacitors. Tantalum capacitors play a major role in passive components industry, due to their high reliability, excellent volumetric efficiency and low equivalent series resistance [1]. However, due to limitation of natural resources of tantalum and a strong demand of further increase in capacitance, the industry is seeking new materials with higher permittivity, which are composed of abundant elements.

Titanium dioxide has high permittivity ($\varepsilon_{ox} = 40–120$) and is a promising dielectric oxide for electrolytic capacitors [2]. However, anodizing of titanium results readily in an amorphous-to-crystalline transition at low formation voltages [2–7]. After crystallization of the anodic oxide, film growth accompanies oxygen gas generation, introducing a high density of flaws in the developed anodic oxide films [3,7]. Thus, an amorphous-to-crystalline transition must be avoided for the formation of dielectric oxide suitable for capacitor application.

Recently, effective suppression of crystallization of anodic TiO_2 has been demonstrated by incorporation of silicon species from metal substrate, i.e., a Ti–6 at% Si alloy [7–9]. Alloying of titanium with other metals, such as aluminum [7], molybdenum [10,11], niobium [12], tungsten [13] and zirconium [14,15], is also effective, although higher concentrations of alloying elements, compared with silicon addition, are required to form amorphous oxide without crystallization to voltages higher than 100 V.

For capacitor application of the Ti alloys that form flaw-free anodic oxide films, porous alloy films with high surface areas must be tailored to enhance the capacitance, since the capacitance, *C*, is proportional to surface area, *S*, as follows

$$C = \varepsilon_0 \varepsilon_{ox} \frac{S}{d} \quad (1)$$

in which, ε_0 is the permittivity of vacuum, ε_{ox} is the relative permittivity of oxide and *d* is the thickness of oxide film. In tantalum electrolytic capacitors, a high-temperature sintering process has

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been utilized to produce porous tantalum anode with high surface area. However, such high-temperature process is not applicable for the Ti–Si alloy system, since the solubility of silicon to titanium is limited to less than 1 at% at equilibrium [16].

In the present study, oblique angle magnetron sputtering has been used as an alternative approach for fabrication of single-phase porous alloy films supersaturated with alloying element. Oblique angle deposition (OAD) is one of the useful and attractive physical vapor deposition techniques to tailor porous films with tilted isolated columnar structure [17]. The porosity is generated due to a self-shadowing effect and limited surface diffusion of adatoms. Recently, it has been reported that controlled rotation of substrate during OAD enables to create sculptured micro- and nano-structured thin films, such as nanopillars [18–23], zigzag [24–27], nanospirals [28,29] and Y-shape [30] columns. This advanced technique, often referred to as glancing angle deposition, allows us to develop a range of engineered micro- and nano-structures [17,31]. However, complex substrate rotation during deposition is not suitable for the production of capacitor anode because it limits the production rate of the anode. The authors have recently reported that the utilization of a substrate with regular concave cell structure is effective in enhancing the shadow effect in OAD and thus in fabrication of isolated columnar films [32–34].

In this work, we have deposited Ti and Ti–7 at% Si isolated columnar films by oblique angle magnetron sputtering on to the substrate with a concave cell structure. The anodic oxide films are grown on the porous metallic films in ammonium pentaborate electrolyte, and their dielectric properties are examined. The composition of Ti–7 at% Si has been selected since further increase in silicon content decreases the capacitance as a consequence of incorporation of an increased amount of silicon species that reduces the permittivity of oxide [35].

2. Experimental

Thin porous films of Ti–7 at.% Si were prepared by magnetron sputtering at an oblique angle of 85°, with respect to the substrate normal, on to textured aluminum substrate for 3.6 ks, using a target consisting of 99.9% titanium disk of 100 mm in diameter and silicon pieces of 20 mm^2, with the latter placed symmetrically on the erosion region of the former disk. The substrate holders were rotated along the chamber axis and its own axis to get alloy films of uniform thickness and composition. The porous Ti films were also prepared under the same condition using Si-free target. The Ti and Ti–7 at% Si films with flat surfaces were also deposited on flat glass substrate at an angle of 0° (the substrate surface is parallel to the target surface). The structures of the deposits were identified by grazing incidence X-ray diffraction (incident angle of X-ray = 2°) using Cu $\mathrm{K}\alpha$ radiation. Surface and cross-sections of deposits were observed by a JEOL JSM-6500F field emission scanning electron microscope (SEM) operated at 5 kV.

The textured aluminum substrate was prepared as in our previous reports [33,34]. Briefly, high purity aluminum sheet was anodized at 195 V in 0.3 mol dm^{-3} phosphoric acid electrolyte at 278 K for 1.8 ks, followed by chemical dissolution of the resultant porous anodic film in a mixed solution of chromic acid–phosphoric acid at 333 K.

The deposited films were anodized at a constant current density of 10 A m^{-2}, relative to the apparent geometrical surface area, up to 50 V in stirred 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 293 K. Two-electrode cell with a platinum counter electrode was used for the galvanostatic anodizing. In addition, potentiostatic anodizing of the deposited films were carried out in the same electrolyte for 1.8 ks between 2 V and 10 V. In this case a three-electrode cell with Ag/AgCl reference electrode was used. In this paper all potentials for potentiostatic anodizing were referred to this electrode. The electrochemical impedance spectroscopy (EIS) was used to evaluate the dielectric properties of the anodic films formed as well as the surface roughness. The EIS data were obtained by applying 20 mV ac signal amplitude in the frequency range of 0.01–10 kHz using Solartron SI 1287 potentiostat/galvanostat and Solartron 1255B frequency response analyzer. The leakage current density, defined as the current density recorded after application of 70% of the formation voltage for 120 s, was also measured in 0.1 mol dm^{-3} ammonium pentaborate electrolyte.

3. Results and discussion

3.1. Morphology and phases of deposits

SEM images of the Ti and Ti–7 at% Si films deposited on textured substrate (Fig. 1) reveal porous nature with the size of pores between neighboring columns being 100–200 nm. The films have isolated columnar morphology with the column diameter of 300–400 nm and the column-to-column distance is ~500 nm, which is in agreement with the cell size of substrate. The thickness of the columnar films is ~600 nm. Due to an incidence of deposited atoms from the right-hand side of the micrographs, the columns obtained are tilted at an angle of 28°–30° from substrate normal to the right-hand side. The smaller tilted angle of deposits, compared with the incident angle, is usual in the oblique angle deposition [31,36]. The deposition occurs mainly on substrate cell walls faced on the incident direction, while the deposition is limited in the opposite faces due to a shadowing effect, such that isolated columns are developed on the cellular substrate. However, a thin deposit layer, 50–100 nm thick, is present between columns, covering the entire substrate surface with either Ti or Ti–7 at% Si layer. The surface appearance of the Ti and Ti–7 at% Si deposits is similar, and both columns reveal granular morphology. This is contrast to the different morphologies found between the Nb columns that show subcolumnar morphology and the amorphous Nb–Si columns with smooth columns surface [34]. Similar column morphology for both Ti and Ti–7 at% Si deposits arises from the fact that both deposits consist of an hcp phase (Fig. 2). Although the diffraction intensities for the Ti–7 at% Si are weak, 002 and 103 lines are clearly detected. The absence of other diffraction lines suggests possible preferred orientation of deposits, as is often found in PVD films.

3.2. Growth of anodic titanium oxide

Fig. 3 shows the voltage–time responses during anodizing the flat and porous films of Ti and Ti–7 at% Si alloy. The deposited films were anodized galvanostatically at a constant current density of 10 A m^{-2} in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 293 K. The formation voltage increases linearly only up to ~5 V for flat and porous Ti films. The reduced slope for the porous Ti film is associated with the increased surface area. Then, both the Ti films show the same constant voltage of 8 V, during which gas, probably oxygen, was evolved on the specimen surface. It is known that the gas evolution occurs after crystallization of anodic titanium oxide [7], because of introduction of an electron-conducting path in the anodic oxide film [3]. Thus, the crystallization on the Ti films should occur at ~5 V in the present anodizing condition. Such a low crystallization voltage is in agreement with previous reports [4,6].

In contrast to the Ti films, the flat Ti–7 at% Si film reveals a linear voltage rise up to ~35 V, indicating growth of amorphous oxide to the high voltage by suppressing nucleation of crystalline oxide. Following the linear voltage rise, the slope increases gradually to 72 V, at which a sudden drop of voltage is observed. The gradual slope rise is an evidence of nucleation of crystalline oxide and sub-