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Phase Transformation and Capacitance Enhancement of Anodic $\text{ZrO}_2\text{-SiO}_2$

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Capacitance enhancement of anodic oxide films on zirconium by adding silicon is reported here with correlation to the phase transformation of the oxide. The anodic oxide film formed on zirconium consists mainly of monoclinic ZrO_2 , which changes to tetragonal ZrO_2 phase on the Zr–5.5 atom % Si. Further increase in the silicon contents to 10 and 16 atom % results in the formation of amorphous oxide up to 30 V, above which two-layered films, comprising an outer crystalline tetragonal-phase oxide layer and an inner amorphous layer, are developed. The relative thickness of the outer crystalline layer to the total film thickness increases with formation voltage. The highest capacitance of the anodic oxide films is obtained on the Zr–10 atom % Si. The changes in capacitance, permittivity and formation ratio of anodic oxide films with alloy composition are discussed with phase transformation and growth process of anodic oxides.

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ZrO_2 is an important inorganic material for high-temperature applications, due to many useful properties such as high strength and stability at high temperatures, oxide ion conductivity at elevated temperatures and radiation-resistant properties. These features make ZrO_2 attractive for oxygen sensors, solid oxide fuel cells, and nuclear materials. Moreover, in recent years, zirconia-based materials, including $\text{ZrO}_2\text{-SiO}_2$, have been proposed as a promising high- κ gate dielectric material for metal-oxide-semiconductor (MOS) transistors.^{1–3}

Thin films of ZrO_2 can be prepared by a range of methods, including physical vapor deposition,⁴ chemical vapor deposition,⁵ atomic layer deposition,⁶ chemical solution deposition,^{3,7} and anodizing.^{8,9} Anodizing is the most simple and easiest method to form dielectric oxides, and this has been extensively used to form dielectric oxide films on aluminum and tantalum for electrolytic capacitor applications. Tantalum electrolytic capacitors are widely used in electronics industry, but due to limitation of natural resources of tantalum and for high demand of increasing capacitance, alternative abundant materials that form oxides with higher permittivity, such as niobium and titanium, have been studied.^{10–16}

Zirconium forms usually crystalline anodic oxide films, in contrast to the formation of amorphous anodic oxides on a range of valve metals, including aluminum, bismuth, niobium, tantalum and tungsten.¹⁷ The crystalline structure of anodic zirconium oxide films is influenced by surface treatments prior to anodizing and electrolyte for anodizing. When magnetron-sputtered zirconium is anodized in ammonium pentaborate electrolyte without pretreatment of the deposited surface, crystalline oxide films, consisting mainly of monoclinic ZrO_2 , are developed.⁹ The monoclinic phase of ZrO_2 is thermodynamically the most stable at ambient temperature, but amorphous and high-temperature stable phases of cubic or tetragonal ZrO_2 are also often found in the anodic oxide films formed on chemically polished zirconium, particularly at low formation voltages.^{18,19} It is also reported that the film structure is dependent on the electrolyte for anodizing.^{20,21} Such dependence should be associated with the incorporation of foreign species from pretreatment bath or electrolyte for anodizing.

Foreign species can be incorporated also from substrate by alloying of zirconium. Film growth and properties of anodic oxide films are examined for the Zr–Ti alloys with a wide composition range.^{9,15} In these studies, large enhancement of the capacitance and permittivity of the anodic oxide films by incorporation of titanium species has been found. The formation of a high-temperature stable phase of

cubic or tetragonal ZrO_2 , which possesses higher permittivity compared with monoclinic ZrO_2 ,^{22–24} attributed to the capacitance enhancement.

Recently, the authors have examined the growth, structure and dielectric properties of anodic oxide films on Zr–16 atom % Si alloy.²⁵ The alloy forms the anodic oxide films with enhanced capacitance, compared with those on zirconium. The outer part of the anodic film consists of the crystalline tetragonal phase, with the remaining inner layer being still amorphous. Further capacitance enhancement is likely to occur due to optimization of alloy composition and controlled film crystallization. The largely enhanced capacitance by alloying of zirconium with silicon makes the Zr–Si alloys attractive as alternative of tantalum capacitor. In the present study, a systematic study of the structure, composition and capacitance of the anodic films on the Zr–Si alloys with several silicon contents has been carried out.

Experimental

Zirconium and Zr–Si alloy films, ~200 nm thick, with various silicon contents were prepared by DC magnetron sputtering on to flat glass substrates and aluminum substrates. Prior to the sputtering, the latter substrates were electropolished and subsequently anodized to provide flat surfaces. The specimens prepared on aluminum substrates were used mostly for characterization of the anodic oxide films by transmission electron microscope (TEM) and Rutherford backscattering spectroscopy (RBS). The target used for the preparation of the alloy films was 99.9% zirconium disk of 100 mm in diameter with selected numbers of 99.999 % silicon plates (7.5 × 7.5 mm) located symmetrically on the erosion region. The zirconium disk without silicon plates was used for the preparation of the zirconium films. The silicon contents in the alloy films were determined using TEM-EDX analysis.

The specimens were anodized at several formation voltages up to 100 V for 900 s in stirred 0.1 mol dm^{−3} ammonium pentaborate electrolyte at 298 K, using a two-electrode cell with a platinum counter electrode. Initially, a constant current density of 50 A m^{−2} was applied to reach the selected formation voltage. Electrochemical impedance measurements were carried out in the same electrolyte by applying 50 mV (rms) of sinusoidal alternating voltage in the 10⁰ to 10⁴ Hz range, and the capacitances of the anodic oxide films were determined by analyzing the Bode diagrams.

Vertical cross sections of the anodic oxide films were observed using a TEM (JEOL JEM-2000FX) operating at a voltage of 200 kV. High-resolution transmission electron microscopy (HR-TEM) of the films was carried out using a FEG-TEM (JEOL JEM-2010F) operating at a voltage of 200 kV. Electron transparent sections, about 30 nm thick, were generated using an ultramicrotome

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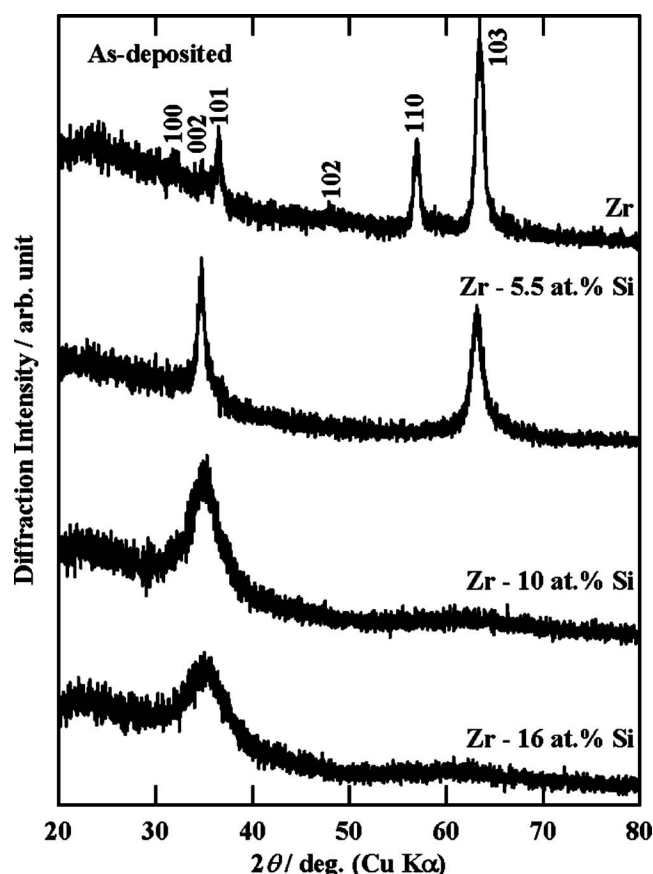


Figure 1. Grazing incidence X-ray diffraction patterns of the sputter-deposited Zr and Zr-Si alloys containing 5.5, 10, and 16 atom % silicon.

(Reichert-Nissei Ultracut S) with a diamond knife. The structures of the deposited zirconium and Zr-Si alloys, as well as the anodic oxide films, were identified by grazing incidence X-ray diffraction (GIXRD) using Cu K α radiation with the incident angle of 2° (Rigaku, RINT-2000 system). Raman measurements of anodic oxide films were performed using a 531.9 nm laser with Synapse CCD detector. Laser power at the sample was kept to 6 mW. Compositions of anodic oxide films and alloy films were determined by RBS, using a 2.0 MeV He²⁺ ion beam supplied by a tandem-type accelerator at Tohoku University. The scattered particles were detected at 170° to the incident beam direction, which was normal to the specimen surface. The data were analyzed using the RUMP program.

Results

Phases of deposited alloy films.— Figure 1 shows GIXRD patterns of the sputter-deposited zirconium and Zr-Si alloys. The pattern of the zirconium reveals an hcp structure. The pattern of the Zr-5.5 atom % Si also shows an hcp structure, but only two diffraction lines of 002 and 103 appear, indicating different grain orientations between zirconium and Zr-5.5 atom % Si films. The diffraction lines shift slightly to lower angles by silicon addition, suggesting dissolution of silicon in zirconium. The Zr-10 and 16 atom % Si alloy films show only a halo at about 35°, typical of an amorphous structure. Since the equilibrium solubility of silicon in hcp zirconium is less than 1 atom %, ²⁶ the deposited alloys are non-equilibrium single-phase solid solutions supersaturated with silicon. This is in agreement with the fact that sputter-deposited binary alloys often form non-equilibrium single-phase alloys in a wide composition range for a range of binary alloy systems. ²⁷

Voltage-time and current-time curves.— Figure 2 shows the voltage-time curves of the zirconium and Zr-Si alloys during initial

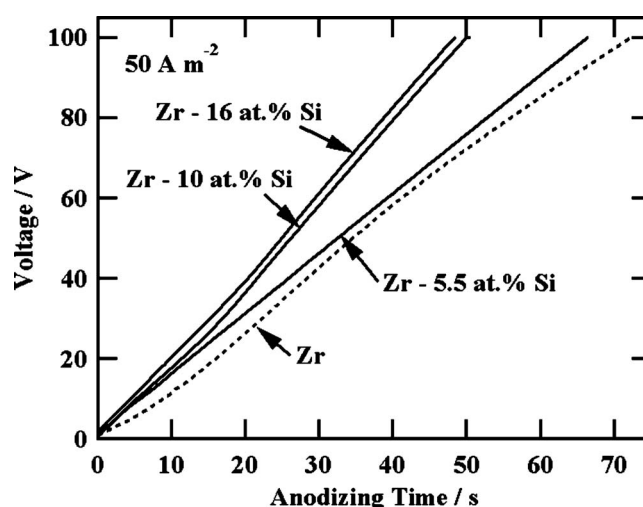


Figure 2. Voltage-time responses of the sputter-deposited Zr and Zr-Si alloys during initial anodizing at a constant current density of 50 A m⁻² in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 298 K.

anodizing at a constant current density of 50 A m⁻² in 0.1 mol dm⁻³ ammonium pentaborate electrolyte. All specimens show an initial voltage surge of about 2 V, reflecting the presence of a thin air-formed film. After the surge, the voltages increase approximately linearly with anodizing time. The slope changes at 60 V for zirconium, probably due to reduced ratio of a high-temperature stable phase (cubic or tetragonal) ZrO₂ in the anodic oxide films, consisting of a mixture of monoclinic and a high-temperature stable phase ZrO₂. ⁹ For Zr-5.5 atom % Si, the voltage increases completely linearly with anodizing time, suggesting no structural change of the anodic oxide films during anodizing. The slope change again occurs for the Zr-10 atom % Si at ~30 V from 1.7 V s⁻¹ to 2.2 V s⁻¹, and for Zr-16 atom % Si at ~40 V from 1.9 V s⁻¹ to 2.3 V s⁻¹, being probably associated with an amorphous-to-crystalline transition of the anodic oxide films, as described later.

After reaching the selected voltages, the voltage was kept for 900 s for further film growth. Figure 3 shows examples of the current transients at 100 V. During anodizing at a constant voltage, all the specimens show linear current decrease with anodizing time in a double logarithmic plot, following a high field mechanism. The current transient discloses the film growth at high current efficiency under the high field growth mechanism. ²⁸

Transmission electron micrographs.— Figure 4 shows transmission electron micrographs of ultramicrotomed sections of the Zr-Si alloy specimens anodized at several formation voltages. Obviously, the anodic oxide films with flat and parallel alloy/film and film/electrolyte interfaces develop on the alloy films, which appear at the bottom of each micrograph. Anodic films are crystalline on the Zr-5.5 atom % Si alloy at all formation voltages examined (Fig. 4a). The film thickens in proportion to the formation voltage with a formation ratio of about 2.2 nm V⁻¹.

The anodic films on the Zr-10 and 16 atom % Si alloys are relatively featureless and no diffraction contrast is visible at 20 V, indicating that the anodic oxide films are amorphous. Crystalline oxide is developed in the outer part of the anodic films formed at 50 and 100 V, with the remaining inner layer being amorphous. The ratio of thickness of the outer crystalline oxide layer to the total film thickness increases from 0.47 at 50 V to 0.76 at 100 V, and from 0.36 at 50 V to 0.39 at 100 V for the Zr-10 atom % Si and Zr-16 atom % Si alloys, respectively. Associated with the formation of the outer crystalline layer, the formation ratios of anodic oxide films on both alloys decrease from 2.2 nm V⁻¹ at 20 V to 1.6 nm V⁻¹ at 100 V. High resolution TEM image of the crystalline

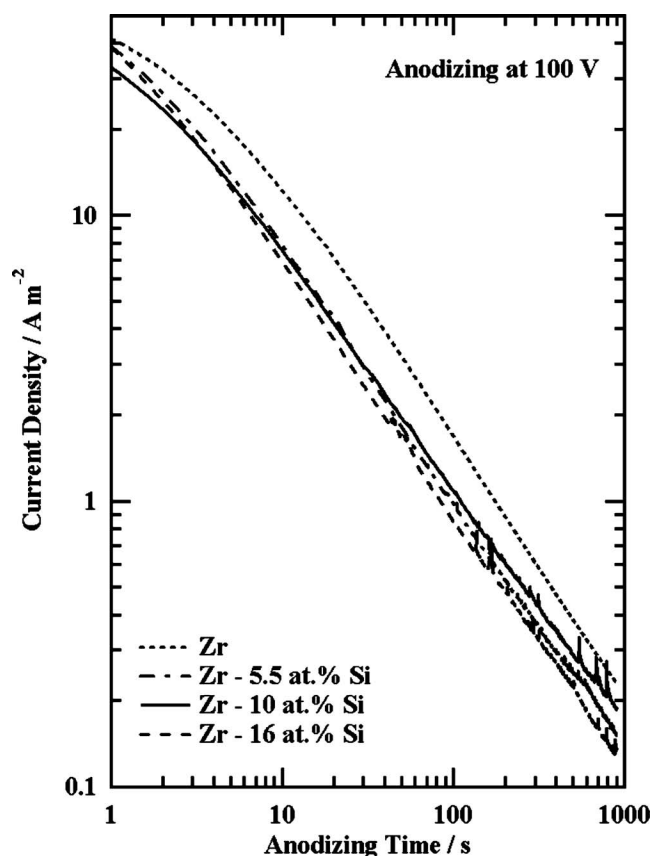


Figure 3. Current-time curves of the sputter-deposited Zr and Zr-Si alloys during anodizing at 100 V in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 298 K. Initially, a constant current density of 50 A m⁻² was applied to reach the selected formation voltage of 100 V. In this plot, the anodizing time of 0 s was set at the time when the cell voltage reached the selected formation voltage.

outer layer in the anodic film formed at 100 V on the Zr-16 atom % Si (Fig. 5) reveals that the size of crystalline grains is 20–30 nm and the crystalline grains appear to be surrounded by thin amorphous layers.

Phases in anodic oxide films.—The anodic oxide film formed on zirconium at 100 V consists of a mixture of monoclinic ZrO₂ and a high-temperature stable phase ZrO₂, with the former being a major phase (Fig. 6). In contrast, only a high-temperature stable phase with no monoclinic phase is detected in the GIXRD patterns of the Zr-Si alloys anodized at 100 V. However, due to similarity of diffraction patterns for tetragonal and cubic phases, it is difficult to identify whether the high-temperature phase is cubic or tetragonal from XRD patterns.

Raman spectroscopy has been often used to identify the structure of ZrO₂,^{29,30} such that we measured Raman spectra of the specimens anodized at 100 V (Fig. 7). All the specimens show characteristic peaks for tetragonal phase ZrO₂. For Zr-5.5 atom % Si specimen, there are also the peaks that can be assigned to the monoclinic phase, although the amount of this phase is assumed to be small from the relative intensities of individual phases. Thus, it can be concluded that the main crystalline phase in the anodic films formed on the Zr-Si alloys examined is tetragonal ZrO₂. The stabilization of tetragonal zirconia by SiO₂ doping has also been reported in sol-gel derived ZrO₂-SiO₂ ceramics.^{31,32}

RBS analysis.—The compositions of the anodic oxide films are analyzed quantitatively using RBS analysis. Figure 8 shows the experimental and simulated spectra for the Zr-Si alloys anodized at

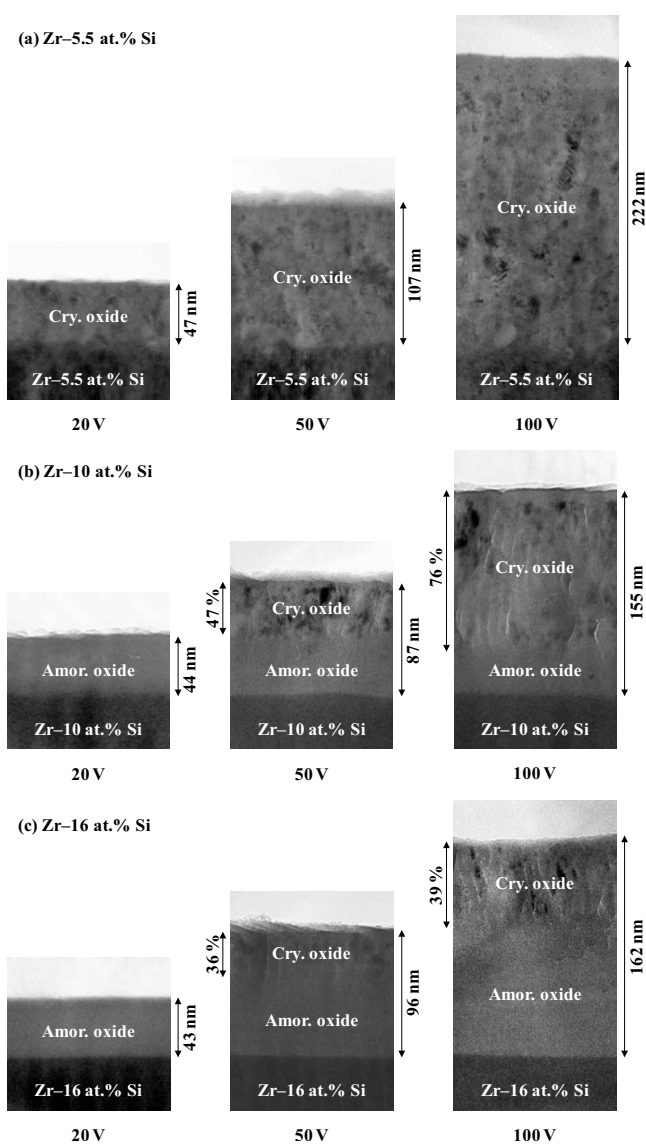


Figure 4. Transmission electron micrographs of ultramicrotomed vertical cross sections of the sputter-deposited Zr- (a) 5.5, (b) 10, and (c) 16 atom % Si alloys, after anodizing at 20, 50, and 100 V in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 298 K for 900 s, following constant current anodizing at 50 A m⁻² to the respective formation voltages.

100 V. The simulated spectra obtained using the thickness, composition and density for each layer, shown in Table I, fitted well with the experimental spectra. Simulation for the Zr-5.5 atom % Si specimen reveals that the composition of anodic oxide film is uniform throughout its thickness. Cationic ratio of zirconium and silicon in the anodic film is in agreement with the alloy composition. In addition, the charges calculated from the amounts of Zr⁴⁺ and Si⁴⁺ ions in the anodic films are close to those passed during anodizing for all three specimens, indicating film growth at high current efficiency. Slightly lower density (5.3 Mg m⁻³), compared with bulk crystalline ZrO₂ (5.8 Mg m⁻³), may be associated with incorporation of silicon species.

For the Zr-10 and 16 atom % Si specimens, three-layered oxide films are formed. The thin outermost layer is free from silicon species (Table I). The silicon-free layer should be developed before the amorphous-to-crystalline transition, as described later. The intermediate layer that is crystalline has lower silicon content in comparison with the innermost amorphous oxide layer. The cationic percentage of silicon in the innermost layer is higher than the atomic percentage

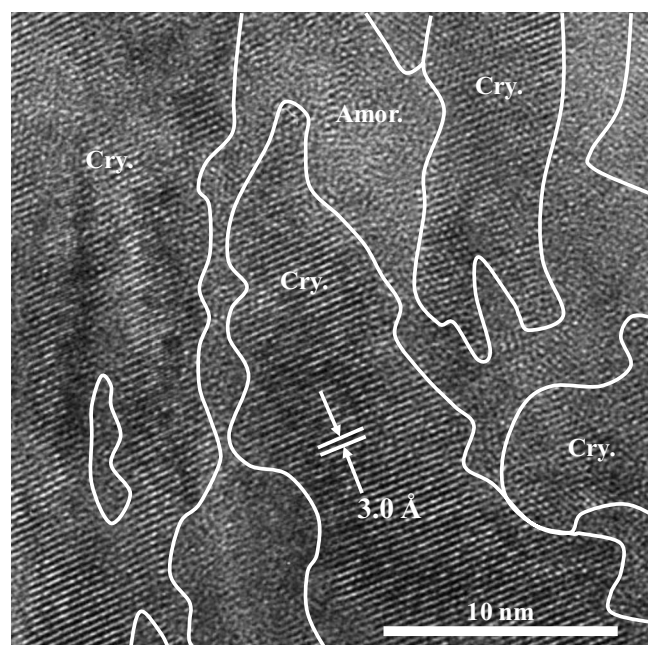


Figure 5. High-resolution TEM image of the crystalline layer in the anodic oxide film formed on the sputter-deposited Zr-16 atom % Si alloy at 100 V.

of silicon in the respective alloy, as in the case of amorphous anodic oxide films formed on silicon-containing alloys.^{16,33-35}

Impedance measurements and dielectric properties.—Capacitances of the anodic oxide films formed on the zirconium and Zr-Si alloy films at various formation voltages are determined from electrochemical impedance measurements. Figure 9 shows the Bode diagrams of the specimens anodized at 50 V. All the specimens show the similar behavior of linear change in impedance with a slope close to -1 , and phase shift to -90° in a wide frequency region. This behavior is typical of dielectric materials. Similar curves were also obtained for specimens anodized at other formation voltages. The impedance data were curve fitted using the equivalent electric circuit inserted in Fig. 9.

Figure 10 shows the relationship between the film formation voltage and the reciprocal capacitance of anodic oxide films on the zirconium and Zr-Si alloy films. The reciprocal capacitances of anodic oxide films on zirconium and Zr-5.5 atom % Si alloy increase linearly with formation voltage, since the capacitance is inversely proportional to the film thickness. However, in the case of the anodic oxide films formed on the Zr-10 and 16 atom % Si alloy films, the slope reduction occurs at 30–40 V, being associated with the structural change in the anodic films (Fig. 4). Obviously, the capacitance of the anodic film on the Zr-5.5 atom % Si film is higher than that on the zirconium film at each formation voltage. The capacitance is further enhanced by increasing the silicon content to 10 atom % at the formation voltages higher than 40 V, where the outer part of the anodic films are crystallized. However, further increase in the silicon content to 16 atom % reduces the capacitance at all formation voltages, although the values are still higher than those on the zirconium film. Thus, the highest capacitance is obtained for the Zr-10 atom % Si film, which is 1.9 times that on the zirconium film at 100 V.

Leakage current densities of the anodized specimens were also measured in 0.1 mol dm^{-3} ammonium pentaborate electrolyte by applying a constant voltage that was 70% of the formation voltages. Figure 11 shows the change in the leakage current density with alloy composition for the specimens anodized at 20 and 50 V. The lowest leakage current is obtained for the Zr-10 atom % Si film, which possesses the highest capacitance. We also measured the leakage

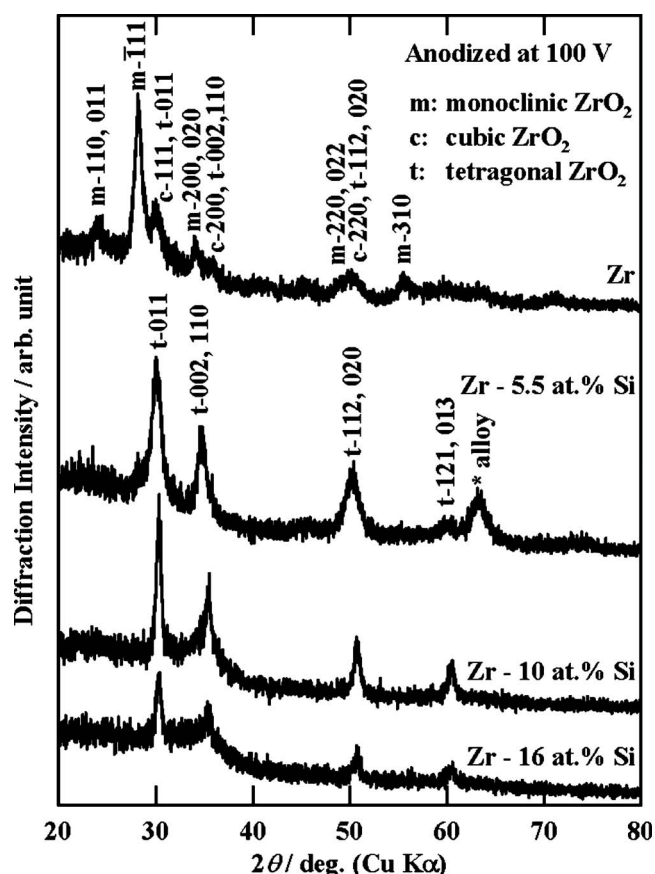


Figure 6. Grazing incidence X-ray diffraction patterns of the sputter-deposited Zr and Zr-Si alloy specimens anodized at 100 V in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 298 K for 900 s, following constant current anodizing at 50 A m^{-2} to the selected formation voltage.

current of the sputter-deposited tantalum film anodized under the same conditions, since tantalum is currently used as capacitors in industry. It may be worth mentioning here that the leakage current of the Zr-10 atom % Si film was comparable or even lower than that of sputter-deposited tantalum film.

Discussion

Dielectric properties.—As shown in Fig. 10, the capacitances of anodic oxide films are enhanced by the addition of silicon, with the maximum value obtained at the silicon content of 10 atom % in the alloy. Figure 12a shows the CV values, i.e., the product of the capacitance and formation voltage, of the anodic oxide films formed at 20 and 100 V, as a function of the silicon content in the alloy. The CV values are plotted instead of capacitance, since the values are independent of the formation voltage when the structure and composition of the anodic oxide films do not change with the formation voltage. Thus, the CV values are useful to compare the dielectric properties of the anodic oxide films formed at different formation voltages. The maximum CV value is obtained at the silicon content of 5.5 atom % at 20 V, but shifting to 10 atom % Si at 100 V with the value increasing further to $\sim 160 \text{ mF V m}^{-2}$. The CV value can be expressed by the following equation

$$CV = \epsilon_0 \epsilon_{ox} / k$$

where, ϵ_0 is the permittivity of vacuum, ϵ_{ox} is relative permittivity, and k is formation ratio of anodic oxide film. The k value was derived by dividing the film thickness, d , by the film formation voltage, V . It is obvious from this equation that the CV value can be enhanced by enlarging ϵ_{ox} and/or reducing k value.

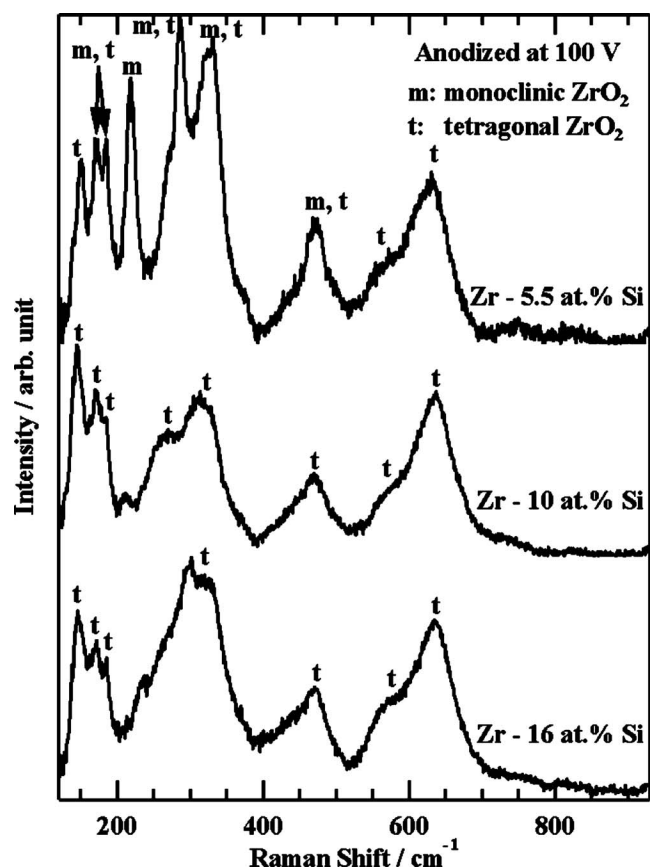


Figure 7. Raman spectra of the sputter-deposited Zr-Si alloy specimens anodized at 100 V in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 298 K for 900 s, following constant current anodizing at 50 A m⁻² to the selected formation voltage.

Figure 12b shows the relative permittivity of the anodic oxide films, ϵ_{ox} , as a function of silicon content. The ϵ_{ox} value of anodic oxide films on pure zirconium is $\epsilon_{ox} = 23.0$ at both 20 and 100 V, and this value is comparable to those reported previously ($\epsilon_{ox} = 22-28$).³⁶ The ϵ_{ox} value increases to 31.6 when 5.5 atom % of silicon is added. The increased ϵ_{ox} should be associated with the phase transformation from monoclinic to tetragonal, since it is known that the latter phase has larger permittivity than that of the former phase in bulk form.²²⁻²⁴ Further increase in the silicon content results in the reduction of ϵ_{ox} value. At the silicon content of 16 atom %, the average ϵ_{ox} value is 21.7, being slightly smaller than that of pure zirconium.²⁵ Larger ϵ_{ox} value of the anodic film formed at 100 V on the Zr-10 atom % Si film in comparison with that at 20 V may be associated with an amorphous-to-crystalline transition of the anodic film. The formation voltage dependence of ϵ_{ox} becomes less significant for the anodic films on the Zr-16 at % Si film, probably because the relative thickness of the outer crystalline layer is reduced largely by the increase in silicon content to 16 atom %. The general trend of the reduction of ϵ_{ox} values by increasing silicon content from 5.5 to 16 atom % may be due to the incorporation of SiO₂ unit in the anodic films, because amorphous SiO₂ has relatively low ϵ_{ox} of 3.5. As reported previously, amorphous anodic TiO₂-SiO₂¹⁶ and Nb₂O₅-SiO₂³⁴ films also show the reduction of ϵ_{ox} with increasing silicon content.

In contrast to the relative permittivity, the formation ratio of the anodic films is voltage-dependent (Fig. 12c). The formation ratio for anodic oxide film formed at 20 V decreases moderately with increasing silicon content in the alloy, due to increase in electric field. Marked reduction of k occurs due to an increase in the formation voltage from 20 to 100 V for the alloys containing 10 and

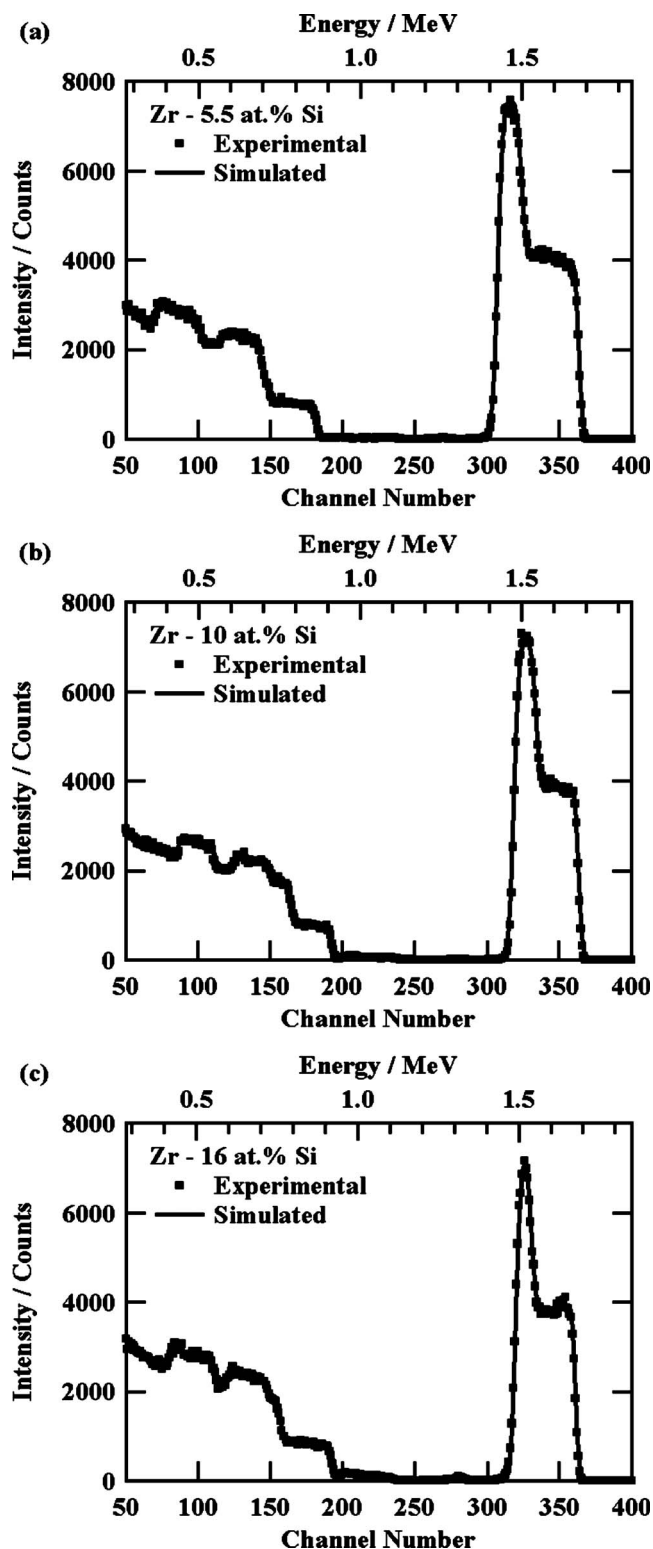


Figure 8. Experimental and simulated RBS spectra of the sputter-deposited Zr- (a) 5.5, (b) 10, and (c) 16 atom % Si alloys anodized at 100 V in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 298 K for 900 s, following constant current anodizing at 50 A m⁻² to the selected formation voltage.

16 atom % Si, as a consequence of crystallization of an outer part of the anodic films. Since the structure of the anodic films formed on the zirconium and Zr-5.5 atom % Si is similar at both formation voltages, the k values are little voltage-dependent.

Table I. Results of RBS analysis of the Zr–Si alloys anodized at 100 V in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 298 K for 900 s, following constant current anodizing at 50 A m⁻² to the selected formation voltage.

Specimen	Thickness (nm)	Composition ^a	Density (Mg m ⁻³)
Zr–5.5 atom % Si	222	c-(Zr _{0.945} Si _{0.055})O ₂	5.3
Zr–10 atom % Si	15	c-ZrO ₂	5.8
	103	c-(Zr _{0.90} Si _{0.10})O ₂	5.6
	37	a-(Zr _{0.86} Si _{0.14})O ₂	5.4
Zr–16 atom % Si	15	c-ZrO ₂	5.8
	48	c-(Zr _{0.88} Si _{0.12})O ₂	5.5
	100	a-(Zr _{0.82} Si _{0.18})O ₂	5.3

^a a, amorphous; c, crystalline.

A question arises why the k value is markedly reduced by crystallization on the Zr–10 and 16 atom % Si films, although the k value of the fully crystalline anodic film on the Zr–5.5 at% Si film is comparable to those of amorphous anodic films on the alloy films with higher silicon contents. Thus, the simple crystallization to the tetragonal phase may not reduce the k value. High resolution TEM image of the crystalline layer of the anodic film on the Zr–16 atom % Si film (Fig. 5) discloses the presence of amorphous thin layers surrounding nano-grained crystalline oxide. The crystallization-induced phase segregation may occur to form such two-phase outer layer. The amorphous layer may be rich in silicon species, thus being able to sustain higher electric field. Due to the

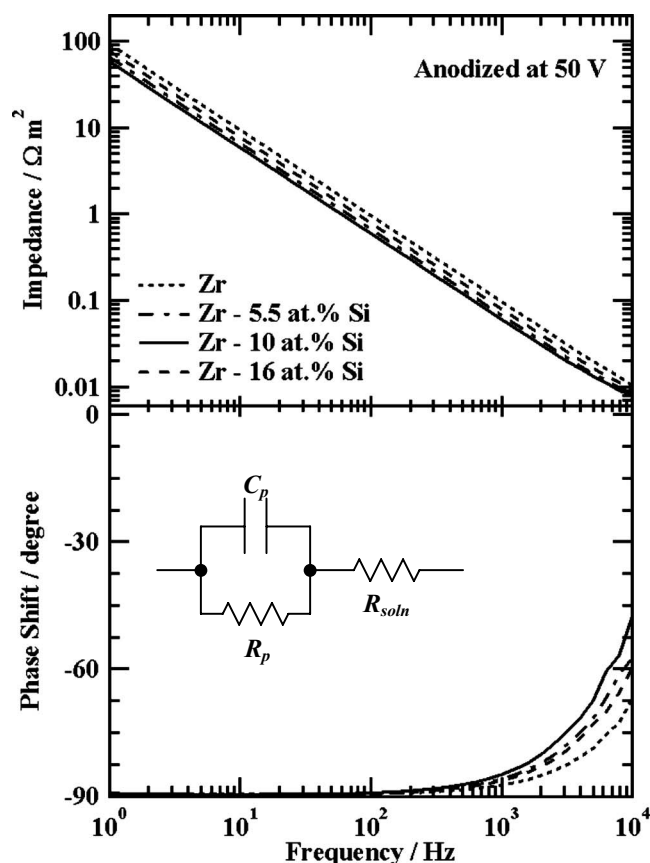


Figure 9. Impedance Bode diagrams of the sputter-deposited Zr and Zr–Si alloy specimens anodized at 50 V in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 298 K for 900 s, following constant current anodizing at 50 A m⁻² to the selected formation voltage.

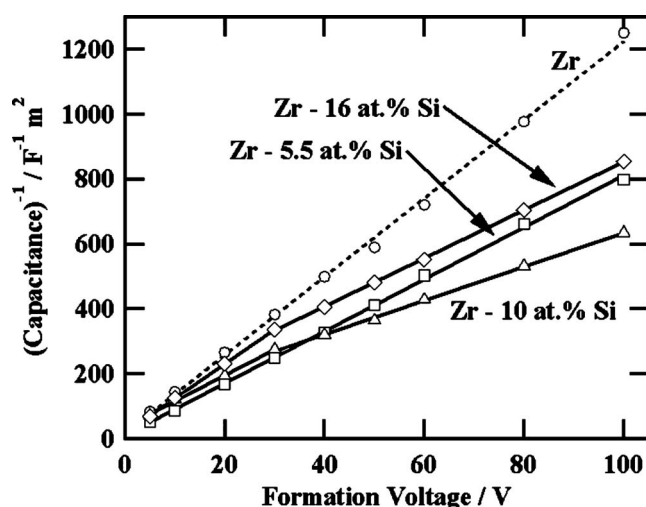


Figure 10. The formation voltage dependence of the reciprocal of capacitance of the anodic oxide films, formed on the sputter-deposited Zr and Zr–Si alloys in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 298 K.

presence of silicon-rich amorphous phase in the crystalline layer, the k value becomes significantly low, i.e., relatively thin anodic films are developed.

As seen in Fig. 12a, the maximum CV value is obtained on the Zr–10 atom % Si film at 100 V. This CV value is 1.9 times that of anodic oxide film formed on the zirconium film at the same formation voltage. From the compositional dependence of the ϵ_{ox} and k^{-1} values (Fig. 12b and c), it is obvious that both the increase of ϵ_{ox} and the reduction of k contribute to the high CV value of the anodic film on the Zr–10 atom % Si film.

Film structure depending on alloy composition and formation voltage.— The anodic oxide films formed on the Zr–5.5 atom % Si alloy are crystalline throughout their thickness. During growth of crystalline oxide, new film materials are formed at the metal/oxide interface by inward migration of O²⁻ ions (Fig. 13a). The uniform distribution of silicon species, which are generally immobile during film growth, throughout the film thickness supports the predominant anion migration with little contribution of cation migration during growth of crystalline oxide.

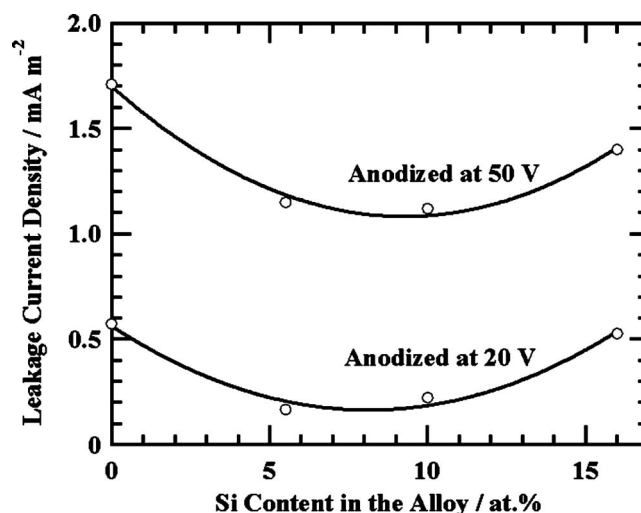


Figure 11. Changes in the leakage current density with alloy composition for anodic oxide films formed at 20 and 50 V.

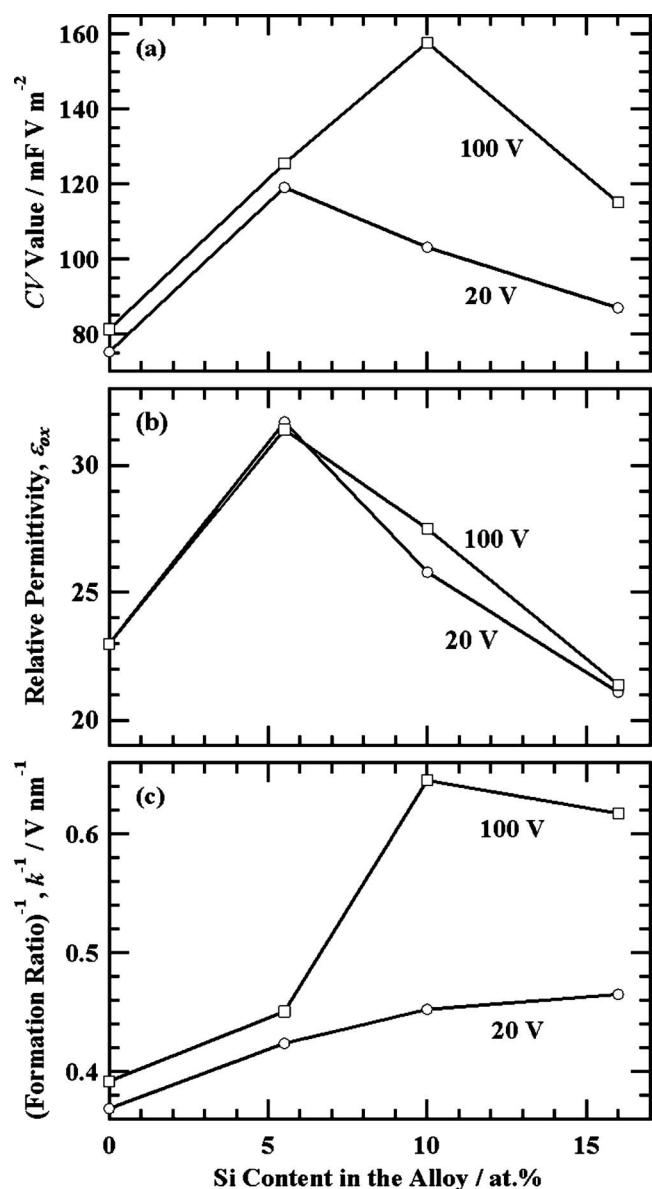


Figure 12. (a) CV value, (b) permittivity, and (c) reciprocal of formation ratio of the anodic oxide films formed on zirconium and Zr–Si alloys, as a function of silicon content in alloy.

Furthermore, the anodic oxide films formed on the Zr–5.5 atom % Si film consist of tetragonal phase of ZrO_2 , in contrast to the formation of mainly monoclinic ZrO_2 on the sputter-deposited zirconium. The tetragonal phase is a high-temperature stable phase and usually transforms to the monoclinic phase reversibly below ~ 1200 K. It is well known that the high-temperature phase can be stabilized to ambient temperature by incorporation of lower valent foreign species, such as Mg^{2+} , Ca^{2+} and Y^{3+} , or by reducing the grain size to less than 30 nm.³⁷ From TEM images shown in Fig. 4, the grain size of the crystalline anodic oxide film is apparently less than 30 nm, and such small grain size may be one of the reasons for the formation of the high-temperature stable phase.

In contrast to the formation of crystalline anodic oxide films on the zirconium and Zr–5.5 atom % Si films, the anodic oxide films formed on the Zr–10 and 16 atom % Si alloys are amorphous below about 40 V (Fig. 13b). The sufficient incorporation of silicon species, which are well-known glass-former, into the anodic oxide films from alloy substrate stabilizes amorphous structure. In growing amorphous anodic oxides, cooperative transports of cations and an-

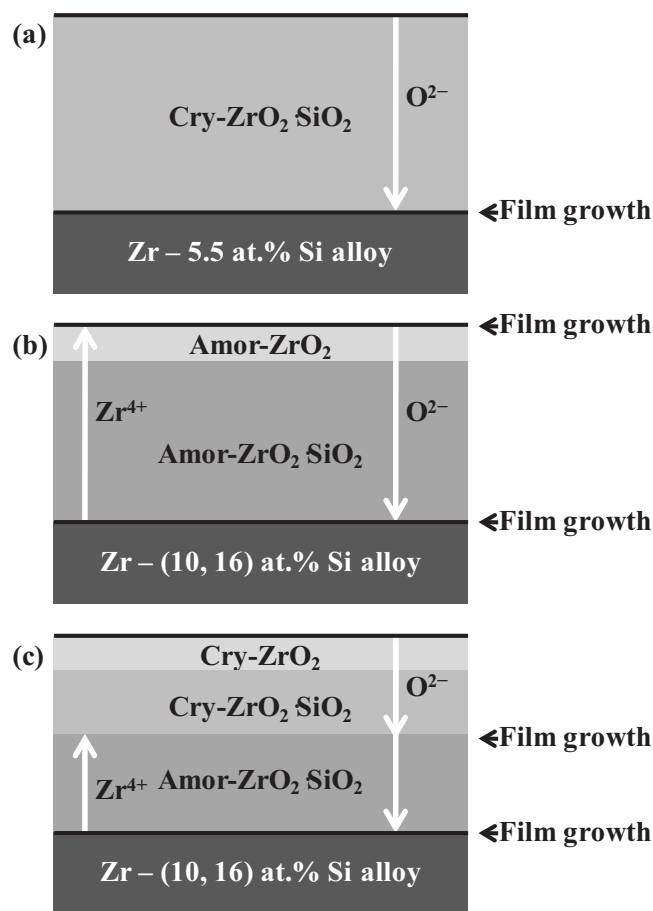


Figure 13. Schematic illustrations showing the growth of anodic oxide films on the Zr–Si alloys. (a) Crystalline oxide on Zr–5.5 atom % Si alloy, (b) amorphous oxide on Zr–(10, 16) atom % Si alloys before crystallization, and (c) after amorphous-to-crystalline transition on Zr–(10, 16) atom % Si alloys.

ions occur, forming new film materials both at the film/electrolyte and alloy/film interfaces.^{38,39} Silicon species are, however, immobile in a range of growing amorphous anodic oxides.^{33,34,40–43} Thus, in the present anodic films formed on the Zr–10 and 16 atom % Si films, a thin silicon-free outer layer, developed at the film/electrolyte interface, is present (Table I). The silicon-free outer layer is relatively thin, for both the Zr–10 and 16 atom % Si films, due to the low transport number of cations in amorphous anodic zirconia.^{15,25}

Since crystalline anodic oxide films are usually developed on zirconium metal, the outer silicon-free amorphous layer should be more readily crystallized during anodizing, compared with the inner silicon-containing layer. In addition, it has been reported that an amorphous-to-crystalline transition of anodic oxides during anodizing of niobium and Ti–Si alloys is initiated at the location that an air-formed oxide film is present before anodizing.^{44,45} The location corresponds to the boundary between the outer silicon-free and inner silicon-containing layers in the present anodic oxide films.

A characteristic feature of the anodic oxide films after crystallization is the presence of an intermediate layer with lower silicon content in comparison with that in the innermost layer (Table I, Fig. 13c). The formation of the intermediate layer should be associated with the formation of new ZrO_2 unit at the boundary of an outer crystalline and an inner amorphous layers as a consequence of the different transport numbers of cations in the outer crystalline layer and in the inner amorphous layer, as explained in our previous report.²⁵ The crystallization extends to the outer 76% of film thickness at 100 V on the Zr–10 at % Si film, while it was limited to 39% on the Zr–16 atom % Si film. The thickness of the inner amor-

phous layer decreases with formation voltage for the Zr–10 atom % Si film (Fig. 4b), while it increases with formation voltage for the Zr–16 atom % Si. The increased silicon content appears to delay the rate of amorphous-to-crystalline at the boundary of the amorphous and crystalline layers. However, if we could crystallize the anodic film throughout the film thickness, the capacitance should be further enhanced, as expected from Fig. 12a, which shows increased CV values of the 100 V film compared with the 20 V film for the Zr–10 and 16 atom % Si. Even if we increased the formation voltages further, the thickness of the outer crystalline layer relative to the total film thickness was not largely increased. Further understandings the mechanism of the crystallization of amorphous oxide during film growth of Zr–Si alloys and the factors controlling the crystallization are crucial for designing anodic oxides with superior dielectric properties.

Conclusions

Through the examination of structure and dielectric properties of anodic oxide films formed on the sputter-deposited Zr–Si alloys with several compositions, following conclusions are drawn.

1. The anodic oxide films formed on the Zr–5.5 atom % Si alloy are crystalline throughout the thickness even at low formation voltages. This oxide film consists mainly of tetragonal phase of ZrO_2 , in contrast to the formation of anodic oxide film consisting mainly of monoclinic ZrO_2 on zirconium.

2. The anodic oxide films formed on the Zr–10 and 16 atom % Si films are amorphous up to 30 V. At higher formation voltages, the outer part of the anodic oxide films crystallizes to tetragonal phase of ZrO_2 , with the relative thickness of the crystalline layer to the total film thickness increasing with formation voltage. The relative thicknesses of the outer layer also decrease with an increase in the silicon content.

3. Capacitances of the anodic ZrO_2 films are enhanced by the addition of silicon at selected formation voltages, with the maximum obtained at 10 atom % of silicon in the alloy. The capacitance of the anodic oxide film formed on Zr–10 atom % Si alloy is 1.9 times than on zirconium at 100 V.

4. The enhancement of CV value of anodic oxide films formed on the Zr–Si alloys has been explained by changes in relative permittivity and formation ratio. The relative permittivity is largely enhanced to be $\epsilon_{ox} = 31.6$ at 5.5 atom % of silicon content, due to the formation of tetragonal phase ZrO_2 , which has larger permittivity than that of monoclinic ZrO_2 . At 10 and 16 atom % of silicon content, formation ratios largely increase with formation voltage, from 2.2 nm V^{-1} at 20 V to 1.6 nm V^{-1} at 100 V, due to the crystallization of outer part of anodic oxide films.

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