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Anodic ZrO$_2$-WO$_3$ Nanofilms by Incorporation of Silicon Species

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Anodic ZrO$_2$-WO$_3$ films with the conductivity being sufficient for fuel cell operation even below 200°C have been characterized using transmission electron microscopy (TEM) and Rutherford backscattering spectrometry (RBS). The dry atmosphere was selected because the proton conductivity deteriorates at high annealing temperatures, which is associated with the diffusion-induced formation of a poorly-conducting layer near the alloy/anodic oxide interface.

Experimental

The Zr$_{37}$W$_{47}$Si$_{16}$ films, ~350 nm thick, were prepared by DC magnetron sputtering on to flat glass and aluminum substrates. Prior to sputtering, the latter substrates were electropolished and subsequently anodized to provide a flat and smooth surface. The specimens prepared on aluminum substrates were used mostly for characterization of the anodic films by a transmission electron microscope (TEM) and Rutherford backscattering spectrometry (RBS). The target used for the preparation of the alloy films consisted of two layers, comprising an outer thin ZrO$_2$ layer, free from tungsten and silicon species, and an inner main layer containing all zirconium, tungsten and silicon species. The results in this study suggest that the conductivity deterioration at high annealing temperatures is associated with the diffusion-induced formation of a poorly-conducting layer near the alloy/anodic oxide interface.

Improving the thermal stability of proton-conducting anodic ZrO$_2$-WO$_3$ films is crucial for their application in intermediate-temperature fuel cells (ITFCs), where they are used as solid electrolytes. In this study, silicon incorporation into the anodic oxide layers was investigated using silicon-containing sputtering gas mixtures.

Anodic ZrO$_2$-WO$_3$ films were deposited on Zr$_{37}$W$_{47}$Si$_{16}$ alloy films by incorporating silicon species obtained from the silicon-containing sputtering gas mixture. The anodic films were prepared by anodizing Zr$_{37}$W$_{47}$Si$_{16}$ in a phosphoric acid electrolyte at 20°C. The resultant anodic oxide film showed markedly improved thermal stability. Even after thermal treatment at 300°C in dry Ar atmosphere, the anodic ZrO$_2$-WO$_3$ films revealed stable proton conductivity in the temperature range of 50–225°C, while the anodic ZrO$_2$-WO$_3$ films on the Zr$_{37}$W$_{47}$Si$_{16}$ lose the proton conductivity by annealing at 250°C. The anodic film on the Zr$_{37}$W$_{47}$Si$_{16}$ consisted of two layers, comprising an outer thin ZrO$_2$ layer, free from tungsten and silicon species, and an inner main layer containing all zirconium, tungsten and silicon species. The results in this study suggest that the proton conductivity deterioration at high annealing temperatures is associated with the diffusion-induced formation of a poorly-conducting layer near the alloy/anodic oxide interface.

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Novel proton-conducting amorphous anodic ZrO$_2$-WO$_3$-SiO$_2$ films, 200 nm thick, are prepared by anodizing Zr$_{37}$W$_{47}$Si$_{16}$ at 100 V with current decay for 1.8 ks in 0.1 mol dm$^{-3}$ phosphoric acid electrolyte at 20°C. The resultant anodic films have high proton conductivity and are characterized using transmission electron microscopy, Rau and Rutherford backscattering spectrometry (RBS). The addition of silicon species to the anodic ZrO$_2$-WO$_3$ films significantly enhanced the thermal stability. Even after thermal treatment at 300°C in dry Ar atmosphere, the anodic ZrO$_2$-WO$_3$ films revealed stable proton conductivity in the temperature range of 50–225°C, while the anodic ZrO$_2$-WO$_3$ films on the Zr$_{37}$W$_{47}$Si$_{16}$ lose the proton conductivity by annealing at 250°C. The anodic film on the Zr$_{37}$W$_{47}$Si$_{16}$ consisted of two layers, comprising an outer thin ZrO$_2$ layer, free from tungsten and silicon species, and an inner main layer containing all zirconium, tungsten and silicon species. The results in this study suggest that the conductivity deterioration at high annealing temperatures is associated with the diffusion-induced formation of a poorly-conducting layer near the alloy/anodic oxide interface.

Figure 1. Cole-Cole plots of the impedance spectra of ∼200 nm-thick ZrO$_2$-WO$_3$ and ZrO$_2$-WO$_3$-SiO$_2$ films measured at 175 °C in dry Ar atmosphere. a) The anodic ZrO$_2$-WO$_3$ films on the sputter-deposited Zr$_{43}$W$_{57}$ after post-annealing at 200 and 250 °C in dry Ar atmosphere for 1.5 h and b) the anodic ZrO$_2$-WO$_3$-SiO$_2$ films on the sputter-deposited Zr$_{37}$W$_{47}$Si$_{16}$ specimens after post-annealing at 215, 250, 300, 350 and 400 °C in dry Ar atmosphere for 1.5 h.

Vertical cross-sections of the anodic oxide films were observed using a JEOL JEM-2000FX transmission electron microscope (TEM) operating at 200 kV. The ultrathin cross-sectional specimens were prepared by using a microtome (RMC, MT-7). The compositions of the anodic films and alloy films were determined by RBS, using a 2.0 MeV He$^{+}$ 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

It was reported that the anodic ZrO$_2$-WO$_3$ films formed on Zr$_{50}$W$_{50}$ did not show proton conductivity under as-anodized condition. The proton conductivity was activated by post annealing at 200 °C. Thus, in this study the anodic ZrO$_2$-WO$_3$ films formed on the Zr$_{43}$W$_{57}$ and the ZrO$_2$-WO$_3$-SiO$_2$ films on the Zr$_{37}$W$_{47}$Si$_{16}$ were annealed at several temperatures in dry argon atmosphere for 1.5 h, and then the proton conductivity was measured. The necessity of post-annealing for activation of proton conductivity is the subject of further study. Figure 1 shows the Cole-Cole plots of the impedance spectra of the anodic ZrO$_2$-WO$_3$ (Fig. 1a) and ZrO$_2$-WO$_3$-SiO$_2$ (Fig. 1b) films annealed at 200 °C reveals a semicircle in the high frequency region and a spike in the low frequency region, which are typical of ionic conductors with blocking electrodes. The spectrum of the anodic film on the present Zr$_{43}$W$_{57}$ is similar to that on the Zr$_{50}$W$_{50}$ reported previously. The high frequency semicircle, which is associated with the ionic conduction in the oxide film, disappears after annealing of the silicon-free specimens at 250 °C, indicating that the anodic film loses the proton conductivity.

In contrast to the anodic ZrO$_2$-WO$_3$ film, the anodic ZrO$_2$-WO$_3$-SiO$_2$ film shows a semicircle at annealing temperatures up to 300 °C (Fig. 1b). The high-frequency semicircle becomes smaller at the annealing temperatures of 250 and 300 °C than at 215 °C. Further increase in the annealing temperature to 350 °C enlarges the semicircle and the semicircle disappears completely after annealing at 400 °C. It should be worth mentioning here that the conducting species are proton, as confirmed by the change in conductivity in H$_2$O- and D$_2$O-containing atmospheres due to the isotope effect. The presence of spike in the low frequency region in Fig. 1 suggests the negligible contribution of electronic conduction in the anodic film.

Figure 2 shows the Cole-Cole plots of the anodic ZrO$_2$-WO$_3$-SiO$_2$ film measured at three different temperatures after annealing at 250 °C. The high-frequency semicircle becomes smaller at higher temperatures, indicating the increased proton conductivity at higher temperatures. The temperature dependence of the proton conductivity of the ZrO$_2$-WO$_3$-SiO$_2$ films annealed at different temperatures.
Figure 4. Transmission electron micrographs of ultramicrotomed sections of the ∼200 nm-thick anodic films on the sputter-deposited Zr$_{37}$W$_{47}$Si$_{16}$ after post-annealing at a) 250°C, b) 300°C, c) 350°C and d) 400°C in dry Ar atmosphere for 1.5 h. Selected area diffraction patterns from the outer and inner layers of the anodic film are also shown in a).

(Fig. 3a) follows Arrhenius behavior. The highest proton conductivity is obtained at each temperature for the specimens annealed at 250 or 300°C. The increase in the annealing temperature from 215 to 250°C increases the conductivity by a factor of five at temperatures above 150°C and by a factor of almost ten at temperatures below 100°C. Thus, the annealing temperature of 215°C is not sufficiently high for the activation of proton conductivity of the ZrO$_2$-WO$_3$-SiO$_2$ film. The conductivities of the ZrO$_2$-WO$_3$-SiO$_2$ film annealed at 250 and 300°C are similar and comparable to those of the ZrO$_2$-WO$_3$ film of similar thickness, reported previously.

The activation energy is dependent upon the annealing temperature, decreasing with an increase in the annealing temperature (Fig. 3b).

In order to clarify the role of silicon species in improving the thermal stability of the anodic ZrO$_2$-WO$_3$ film, the anodized specimens were characterized after annealing at several temperatures. Figure 4 shows TEM images of ultramicrotomed sections of the ZrO$_2$-WO$_3$-SiO$_2$ films after annealing up to 400°C. The ZrO$_2$-WO$_3$-SiO$_2$ film of 200 nm thickness is two layers after annealing at 250°C. The outer layer, 18 nm thick, shows diffraction contrast, suggesting the presence of crystalline oxide. The outer layer is composed of ZrO$_2$ free from tungsten and silicon species as shown in later GDOES and RBS analyses. The remaining inner layer, 182 nm thick, is apparently featureless, typical of amorphous structure. The amorphous structure is also confirmed from the selected area diffraction pattern shown in Fig. 4a, while the outer layer contains a spot of crystalline oxide.

The film structure and the thickness of each layer after annealing at 300°C (Fig. 4b) is the same as that annealed at 250°C. However, the thickness of the outer layer increases to 23 nm, while the remaining inner layer becomes thinner after annealing at 350°C (Fig. 4c). The alloy/anodic oxide interface is also not as sharp as those annealed at and below 300°C. Further increase in the annealing temperature to 400°C reduces markedly the thickness of the anodic film to 166 nm, suggesting the diffusion of oxygen species in the anodic oxide to the alloy film. For the anodic ZrO$_2$-WO$_3$ films formed on the silicon-free Zr$_{43}$W$_{57}$, the film thickness changes from 203 nm to 197 nm by increasing the annealing temperature from 200°C to 250°C (Fig. 5). The
revealed similar purple color up to 300 °C from the change in the interference color of the specimens. Figure 6 shows optical images of the sputter-deposited Zr$_{37}$W$_{27}$Si$_{16}$ and Zr$_{43}$W$_{57}$ specimens anodized at 100 V for 1.8 ks in 0.1 mol dm$^{-3}$ phosphoric acid electrolyte at 20°C to form ~200 nm-thick anodic films and then post-annealed at different temperatures.

TEM observations revealed the change in the thickness of anodic film with annealing temperature. This was also obvious from the change in the interference color of the specimens. Figure 6 shows the digital camera images of the anodized Zr$_{37}$W$_{27}$Si$_{16}$ and Zr$_{43}$W$_{57}$ specimens after annealing at several temperatures. In agreement with TEM observations, the Zr$_{37}$W$_{27}$Si$_{16}$ specimens anodized to 100 V reveal similar purple color up to 300 °C and the color change occurs only at and above 350 °C. The navy-blue color of the Zr$_{43}$W$_{57}$ specimen anodized to 100 V becomes darker even at 250 °C as a consequence of the change in the film thickness.

Figure 7. GDOES elemental depth profiles of the ~200 nm-thick anodic films formed on the sputter-deposited Zr$_{43}$W$_{57}$ at 100 V for 1.8 ks in 0.1 mol dm$^{-3}$ phosphoric acid electrolyte at 20 °C and then post-annealed at a) 200 °C and b) 250 °C in dry Ar atmosphere for 1.5 h.

The elemental depth distributions in the anodic ZrO$_2$-WO$_3$-SiO$_2$ films were examined by GDOES (Fig. 7). The presence of an outer layer practically free from tungsten and silicon species is obvious in the anodic film annealed at 250 °C (Fig. 7a). Both tungsten and silicon species are present in the remaining inner layer. Peaks of zirconium and tungsten intensities at the boundary between the inner and outer layers may be artifact, because the enrichment of these species at this boundary region was not detected by RBS analysis as shown later. The ratio of the sputtering time for the outer layer to that for the inner layer is not consistent with their thickness ratio (Fig. 4a), indicating slower sputtering in the outer layer in comparison with the inner layer during depth profile analysis. The phosphorus species are incorporated in the anodic film and distribute to approximately an outer half of the inner layer. Almost similar depth profiles are obtained in the anodic film after annealing at 300 °C, but at the annealing temperature of 350 °C, the sputtering time for the outer layer is increased and the oxygen diffusion to the alloy film is obvious. These features at 350 °C are further enhanced after annealing at 400 °C. The alloy/anodic oxide interface of the specimens annealed at 350 and 400 °C is also not as sharp as those annealed at 250 °C and 300 °C. These findings are in agreement with the TEM observations (Fig. 4).

The elemental depth profiles of the anodic ZrO$_2$-WO$_3$ film formed on the silicon-free Zr$_{43}$W$_{57}$ change even at annealing temperature of 250 °C (Fig. 8). Unsharpened alloy/anodic oxide interface is obvious after annealing at 250 °C.

Precise composition of each layer in the anodic ZrO$_2$-WO$_3$-SiO$_2$ films was obtained by RBS analysis, as listed in Table I. The experimental spectra of the anodic films annealed at 250, 350 and 400 °C were replicated well by the simulated spectra obtained using the composition, thickness and density shown in Table I (Fig. 9a). The presence of phosphate anions is neglected in this simulation, because the concentration of phosphate anions in an anodic oxide film is usually ~ 5 at% or less and the atomic scattering factor of phosphorus is much lower than other metal atoms. In agreement with the TEM observation (Fig. 4a), the anodic film annealed at 250 °C is two layers, comprising an outer thin ZrO$_2$ layer free from tungsten and silicon species and an inner layer containing both tungsten and silicon species. The tungsten and silicon are slightly enriched in the inner mixed oxide layer compared with the alloy composition, because a part of zirconium oxidized is used to form an outer layer. The molar ratio of zirconium, tungsten and silicon atoms included in the whole anodic films can be calculated by using thicknesses, densities and compositions given by RBS. In addition, the charge calculated from the number of Zr$^{4+}$, W$^{6+}$ and Si$^{4+}$ ions in the anodic film annealed at 250 °C is in agreement with the charge passed during anodizing. Thus, the anodic film growth proceeds at high current efficiency close to 100% and thermal oxidation during annealing at 250 °C is negligible.
The anodic film formed on the Zr50W50.7. The formation of the layered outer thin layer free from tungsten and silicon species, as in the case of conductivity. species during film growth under the high electric field of anodic film is associated with the different mobilities of individual energy scale shown in Fig. 9b. The shift is associated with thickening of the outer ZrO2 layer, which is overlapped with tungsten yield, is reduced by increasing the annealing temperature to 400 °C, suggesting thinning of the anodic film. The yield of zirconium, which is divided to two layers with different compositions of the inner layer of the anodic film as well as alloy film. Such compositional change due to diffusion at elevated temperatures above 350 °C should hinder the proton conductivity.

### Discussions

The anodic film formed on the Zr37W47Si16 is two layers with an outer thin layer free from tungsten and silicon species, as in the case of the anodic film formed on the Zr50W50.7. The formation of the layered anodic film is associated with the different mobilities of individual species during film growth under the high electric field of \( \sim 5 \times 10^8 \) V m\(^{-1}\). Although the outer ZrO2 layer is crystallized after annealing at and above 215 °C (Figs. 4 and 5), the anodic films should be amorphous throughout the film thickness before annealing, as found for the film formed on Zr50W50.7. Amorphous anodic oxide is known to grow owing to the simultaneous migration of the anions toward the metal/film interface and cations toward the film/electrolyte interface by a cooperative mechanism so as to form film material both at the metal/film and at the film/electrolyte interfaces.16 A good correlation between the migration rates of cations and their single metal-oxygen bond energies has been reported.17-19 The cation species with lower metal-oxygen bond energies migrate faster toward the film/electrolyte interface. The metal-oxygen bond energies decrease in the following order: Si\(^{4+}\)-O (465 kJ mol\(^{-1}\)) > W\(^{6+}\)-O (407 kJ mol\(^{-1}\)) > Zr\(^{4+}\)-O (276 kJ mol\(^{-1}\)). The weakest Zr\(^{4+}\)-O bond strength results in the fastest migration of zirconium species, forming an outer thin ZrO2 layer free from tungsten and silicon species. In growing amorphous anodic alumina at high current efficiency, tungsten species migrate slower than aluminum species toward the film/electrolyte interface,20,21 while silicon species are immobile in various anodic oxides, including anodic aluminum oxide,22 titanium oxide,18, 23 niobium oxide24 and tantalum oxide.1 These facts imply the formation of an intermediate layer containing zirconium and tungsten species, but not silicon species, beneath the outer ZrO2 layer. However, the intermediate layer was not detected in the present anodic film formed on the Zr37W47Si16. In the present anodic film both the tungsten and silicon species are immobile or migrates at the same rate toward the film/electrolyte interface. Assuming that the both tungsten and silicon species are immobile, only the outer ZrO2 layer is formed at the film/electrolyte interface and the transport number of cations, estimated from the RBS result, is 0.07, which is much smaller than that estimated previously for amorphous anodic ZrO2.25 It is, therefore, more likely that both tungsten and silicon species are migrate at a similar rate toward the film/electrolyte interface.

Phosphorus species are incorporated in the anodic film and distribute approximately an outer half of the film thickness. Their distribution suggests their migration toward the alloy/anodic oxide interface at a rate slower than oxygen species.

The authors found previously that the anodic film formed on zirconium did not show proton conductivity.7 Thus, the outer ZrO2 layer should not be an efficient proton-conducting layer. In fact, the removal of the outer ZrO2 layer from the 180 nm-thick ZrO2-WO3 film formed on the Zr50W50 increased the proton conductivity by almost one order of magnitude.7 In the present study, the outer ZrO2 layer thickness and the proton conductivity is lost or deteriorated after annealing at 250 °C for the anodic ZrO2-WO3 film and at and above 350 °C for the anodic Zr37W47Si16.
Amorphous anodic ZrO$_2$-WO$_3$ nanofilms as well as ZrO$_2$-WO$_3$-SiO$_2$ nanofilms are a new class of proton-conducting electrolyte that has the efficient conductivity in the intermediate temperature range. The deterioration of proton conductivity of the anodic films is involved by a combination of alloy deposition by physical vapor deposition (PVD) and anodizing of the deposited material; such oxides show high thermal stability and strong Brønsted acidity and thermal tolerance can be fabricated readily by a combination of alloy deposition by physical vapor deposition (PVD) and anodizing of the deposited material; such oxides show high potential as efficient proton conductors. The current results strongly suggest that the anodic oxidation poses strong technique to design the proton conducting oxide membrane.

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