

# Anodizing of Aluminum Coated with Silicon Oxide by a Sol-Gel Method

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Aluminum specimens were covered with SiO<sub>2</sub> film by a sol-gel coating and then anodized galvanostatically in a neutral borate solution. Time variations in the anode potential during anodizing were monitored, and the structure and dielectric properties of the anodic oxide films were examined by transmission electron microscopy, Rutherford backscattering spectroscopy, and electrochemical impedance measurements. It was found that anodizing of aluminum coated with SiO<sub>2</sub> films leads to the formation of anodic oxide films, which consist of an outer Al-Si composite oxide layer and an inner Al<sub>2</sub>O<sub>3</sub> layer, at the interface between the SiO<sub>2</sub> film and the metal substrate. The capacitance of anodic oxide films formed on specimens with a SiO<sub>2</sub> coating was about 20% larger than without a SiO<sub>2</sub> coating. In the film formation mechanism, the conversion of Al<sub>2</sub>O<sub>3</sub> to Al-Si composite oxide at the interface between the inner and outer layers is discussed in terms of inward transport of Si-bearing anions across the outer layer. © 2001 The Electrochemical Society. [DOI: 10.1149/1.1408633] All rights reserved.

Manuscript submitted January 9, 2001; revised manuscript received June 11, 2001. Available electronically October 9, 2001.

Barrier-type anodic oxide films formed on aluminum play an important role as dielectric films in aluminum electrolytic capacitors, and their physical and chemical properties determine the performance of the electrolytic capacitor. Recent development of mobile electronic devices, such as notebook computers and portable telephones, requires very small electrolytic capacitors with high electric capacitance. The electric capacitance, *C*, of the aluminum electrolytic capacitor is expressed by the following equation

$$C = \varepsilon_0 \varepsilon S / \delta$$
 [1]

where  $\varepsilon_0$  is the vacuum permittivity,  $\varepsilon$  the specific dielectric constant of the anodic oxide film, *S* the surface area, and  $\delta$  the film thickness. As the charge accumulated in the capacitor, *Q*, is expressed by the product of *C* and the applied voltage,  $V_{appl}$ , the following equation can be derived

$$Q = (\varepsilon_0 \varepsilon S / \delta) V_{\text{appl}}$$
[2]

 $V_{\rm appl}$  should be smaller than the formation potential of anodic oxide film,  $E_{\rm a}$ , since the application of  $V_{\rm appl}$  beyond  $E_{\rm a}$  leads to a breakdown of the anodic oxide film. Hence, the maximum accumulated charge,  $Q_{\rm max}$ , in an aluminum electrolytic capacitor is expressed by the following equation

$$Q_{\rm max} = (\varepsilon_0 \varepsilon S / \delta) E_{\rm a}$$
 [3]

The film thickness,  $\delta$ , is proportional to  $E_a$ , giving Eq. 4

$$E_{\rm a} = \delta/K$$
 [4]

where K is the film thickness per unit film-formation potential. Substitution of  $E_a$  with  $\delta/K$  into Eq. 3 gives Eq. 5<sup>1</sup>

$$Q_{\max} = \varepsilon \varepsilon_0 S / K$$
 [5]

It is obvious from Eq. 5 that larger values of *S* and  $\varepsilon_0$  and smaller values of *K* give larger  $Q_{\text{max}}$  values. Increases in *S* are achieved by electrochemical etching of the aluminum substrate before industrial anodization,<sup>2,3</sup> and many authors have investigated dc and ac etchings.

Another way to increase  $Q_{\max}$  is by increments in  $\varepsilon$  and decrements in K. These values, however, cannot be changed independently, since they are closely related to each other. Generally, materials with high  $\varepsilon$  have a relatively loose lattice-bonding and easily produce dipoles even in low electric fields. This strongly suggests that high- $\varepsilon$  materials are able to sustain only a low electric field, leading to a large K value. Table I indicates the value of  $\varepsilon$ , K, and  $\varepsilon/K$  for anodic oxide films formed on valve metals.<sup>4</sup> It is obvious from Table I that oxide films with higher  $\varepsilon$  values have higher K values. The value of  $\varepsilon/K$  is not constant, however, and differs from oxide film to oxide film. Titanium anodic oxide film has the largest  $\varepsilon/K$  value, and aluminum oxide film has the smallest one. Anodizing aluminum after hydrothermal<sup>5</sup> or thermal<sup>6</sup> treatment causes the formation of an anodic oxide film containing y-Al2O3 and leads to an increase in  $\varepsilon/K$ . The increase in  $\varepsilon/K$  is mainly due to a decrease in K, since the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-containing oxide film is able to sustain a high electric field. The formation of composite oxide films incorporating valve metal oxides in aluminum anodic oxide films would appear to be useful to increase  $\varepsilon/K$  because of the high  $\varepsilon/K$  values of valve metal oxides (see Table I).

In previous investigations, the authors formed Al-Ti composite oxide films using a pore-filling method<sup>1</sup> and metal-oxide chemical vapor deposition (MOCVD)/anodizing<sup>7</sup> and found that the parallel capacitance of the Al-Ti composite oxide film is 40-60% higher than that of barrier-type anodic oxide films on aluminum. Mochitsuki *et al.* found an 80% increase in  $\varepsilon/K$  by forming Al-Ti composite oxide films using ion plating/anodizing.<sup>8</sup> With MOCVD and ion plating it is relatively difficult, however, to form a uniform dielectric film on the etched surface of aluminum foil, which is disadvanta-

Table I. Dielectric constant,	ε, Κ	value,	and	the	$\epsilon/K$	ratio	for
anodic oxide films on various	s meta	als.					

Oxide	K	З	$\epsilon/K$		
SiO <sub>2</sub>	0.4	3.5	9.0		
$Al_2O_3$	1.3	9.8	7.7		
$ZrO_2$	2.0	22-25	11-12.5		
Ta <sub>2</sub> O <sub>5</sub>	1.6	27.6	17.0		
Nb <sub>2</sub> O <sub>5</sub>	2.3	41.4	18.4		
TiO <sub>2</sub>	3.0	90.0	30.0		

K is the film thickness per unit potential (nm/V).

 $\varepsilon$  is the dielectric constant of oxide film.

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geous in industrial mass production. Sol-gel coatings have the advantage of providing a uniform coating on rough surfaces with high industrial productivity.<sup>9,10</sup>

Previously, the authors investigated the formation of Al-Zr composite oxides by sol-gel coating/anodizing and found that the  $\varepsilon/K$ value of composite oxide films is 20% higher than that of barriertype anodic oxide films on aluminum.<sup>11,12</sup> Lai reported a 50% increase in capacitance by forming anodic oxide films with sol-gel Nb<sub>2</sub>O<sub>5</sub> coating/anodizing.<sup>13</sup> Here, the increase in the apparent  $\varepsilon$ value was responsible for the increase in  $\varepsilon/K$ . Silicon oxide films have smaller values of  $\varepsilon$  and K than aluminum oxide films, but they have higher  $\varepsilon/K$  values (see Table I). The formation of Al-Si composite oxide films, therefore, may cause the increase in  $\varepsilon/K$ , mainly due to the decrease in K.

In the present investigation, the formation of Al-Si composite oxide films was attempted by sol-gel coating/anodizing, and the structure and the dielectric properties of the composite oxide films were examined as functions of the heating temperature of the  $SiO_2$  coating. Mechanisms of the formation of the composite oxide films on  $SiO_2$ -coated specimens during anodizing are discussed.

#### **Experimental**

Specimen.—Highly pure aluminum (99.99%) foil was used as specimens (2  $\times$  2 cm with handle). The specimens were electropolished in a perchloric acid/acetic acid mixture (78:22 v/v) at 28 V and 285  $\pm$  1 K for 1 min after ultrasonic degreasing in ethanol. The electropolished specimens were rinsed in distilled water and acetone before storage in a silica gel desiccator. The handle of specimens was shielded by a Shin-Etsu silicone coating to leave only the square part exposed.

Sol-gel coating .- Electropolished specimens were coated by SiO<sub>2</sub> films via a sol-gel dip-coating method. The sol for dip-coating was prepared in a N<sub>2</sub> atmosphere glove box, using the following procedure.<sup>9,10</sup> Reagent-grade pure tetraethoxysilane (TCL Co.) was first diluted with anhydrous ethanol while stirring. Then, nitric acid and distilled water were slowly added to the tetraethoxysilane solution while stirring at room temperature. The mixing molar ratio of tetraethoxysilane, anhydrous ethanol, distilled water, and nitric acid was 1:10:5.75:0.07.<sup>d</sup> The electropolished specimen was immersed in the sol and withdrawn from the sol at 1 mm/s in the glove box. After being taken out from the glove box, the specimen was dried in air for 300 s at room temperature. The dried specimens were heated in a furnace at 573 K for 1.8 ks under a flow of pure oxygen. This procedure was repeated two times. As the final step in the dipcoating (the second time) heating was carried out in pure oxygen for 30 min at  $T_{\rm h} = 573$ , 673, or 773 K. Flow charts of the dip-coating are given in Fig. 1.

Anodizing.—The specimen coated with SiO<sub>2</sub> film was anodized in 0.5 M H<sub>3</sub>BO<sub>3</sub>/0.05 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> solution (pH 7.4) at  $T_a$ = 293 K with a constant current of  $i_a = 10$  A/m<sup>2</sup>, and the change in the anode potential (*vs.* Ag/AgCl sat. KCl) with time ( $E_a$  *vs.*  $t_a$ curve) was monitored by a digital multimeter connected to a PC system. Electropolished specimens without a SiO<sub>2</sub> layer were also anodized under the same conditions to elucidate the effect of the SiO<sub>2</sub> films on anodic oxide film formation.

*Electrochemical impedance spectroscopy.*—Specimens anodized to different  $E_a$  values were immersed in 0.5 M H<sub>3</sub>BO<sub>3</sub>/0.05 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> solution (pH 7.4) at 293 K, and impedance measurements were carried out by applying 10 mV of sinusoidal alternating voltage in the 0.01 Hz to 50 kHz range with a frequency-response analyzer (FRA) (NF S-5720B). Details of the procedure have been described elsewhere.<sup>14</sup>



Figure 1. Flow chart for the preparation of the coated film from sol solution.

*Film characterization.*—Encapsulated specimens were first trimmed and then sliced into 30 nm thick sections, using an ultramicrotome (Reichert-Nissei Ultra Cuts E) with a diamond knife (Diatome, Ltd., Diatome Ultra). Slices of the vertical section of the specimens were then examined under a transmission electron microscope (Hitachi H-700H) at 200 kV and analyzed with an energy-dispersive X-ray analyzer (Noruman 623M-3SST) equipped with another TEM (JEOL JEM-2000ES).

Anodic oxide films were also analyzed by Rutherford backscattering spectroscopy (High Voltage Engineering 1.7 MV Tandetron) using 2.0 MeV of a He<sup>2+</sup> ion beam supplied by a Van de Graff accelerator. The He<sup>2+</sup> ion beam angle was normal to the specimen surface, and the detector angle was 170° to the incident direction. The chemical composition of the anodic oxide films was determined using the RUMP program.<sup>15</sup>

### Results

SiO<sub>2</sub> film coated by the sol-gel method.—Figure 2 shows the TEM images of vertical cross sections of specimens covered with  $SiO_2$  films by a sol-gel method at  $T_h = (a)$  573, (b) 673, and (c) 773 K. All the films have uniform thickness, and the thickness of the  $SiO_2$  films is 430, 260, and 230 nm at  $T_h = 573$ , 673, and 773 K, decreasing with increasing  $T_{\rm h}$ . The cracks observed in the SiO<sub>2</sub> films in Fig. 2b and c are due to stress originating during slicing of the sample with a microtome. Figure 3a shows the Rutherford backscattering (RBS) spectrum obtained for the specimen coated with  $SiO_2$  at  $T_h = 773$  K (see Fig. 2c, and Fig. 3b) shows the concentration depth profile of Si, Al, and O simulated from the RBS spectrum. It can be seen from Fig. 3b that the coated film has about 200 nm thickness, consisting of an outer SiO<sub>2</sub> layer and an inner Al<sub>2</sub>O<sub>3</sub> or Al-Si mixed oxide layer. The inner oxide layer may be formed by thermal oxidation of the metal substrate and/or interdiffusion of Si<sup>4+</sup> and Al<sup>3+</sup> during heating. The film thickness estimated by RBS analysis is lower than that obtained from (TEM, see Fig. 2c), and this may be due to a porous structure of the  $SiO_2$  film.

Anodic oxide films formed on aluminum with SiO<sub>2</sub> coating.—Figure 4 shows  $E_a$  vs.  $t_a$  curves for specimens coated with SiO<sub>2</sub>-coating at  $T_h = 573$ , 673, and 773 K. In Fig. 4, the  $E_a$  vs.  $t_a$  curve for electropolished specimens without SiO<sub>2</sub> is also indicated as a chained curve, a straight line starting from zero. Specimens coated with SiO<sub>2</sub> show a 2-3 V jump in  $E_a$  at the very initial stage, and the  $E_a$  jump is almost independent of  $T_h$ . After the initial stage,

<sup>&</sup>lt;sup>d</sup> A clear and stable sol, with a viscosity of 2.0 mPa s and no turbidity, was prepared. The viscosity of the sol was almost unchanged, even after aging at room temperature for 1 week.



Figure 2. TEMs of vertical cross sections of specimens coated with  $SiO_2$  by the sol-gel method at  $T_h = 573$ -773 K. Procedure for the coating as in Fig. 1.

 $E_a$  increases linearly with  $t_a$  up to  $E_a = 300$  V. The slope of  $E_a vs.$  $t_a$  curves for specimens with SiO<sub>2</sub> coating is much steeper than that without SiO<sub>2</sub> coating, and is slightly steeper with higher  $T_h$ . All the specimens with SiO<sub>2</sub> coating show flatter slopes on the  $E_a vs. t_a$ curves above  $E_a = 300$  V, where gas evolution was observed on the surface of the specimen.

Figure 5 shows TEM images of the vertical cross sections of specimens anodized up to  $E_a = (a) 100$ , (b) 200, (c) 300, and (d) 400 V after SiO<sub>2</sub> coating at  $T_h = 773$  K. All the films show two layers at the interface between the SiO<sub>2</sub> layer and the metal sub-

strate: an outer dark layer and an inner somewhat darker layer. There is no SiO<sub>2</sub> layer on the specimens anodized up to  $E_a = 400$  V. Both the inner and outer layers increase with  $t_a$  (or  $E_a$ ), while the SiO<sub>2</sub> layer decreases with  $E_a$ . The disappearance of the SiO<sub>2</sub> layer at  $E_a = 400$  V is a result of decrease in its thickness with  $E_a$ . The outer dark layer in Fig. 5c shows a fine texture, the size of which is several nanometers. This could be due to mixing of fine particles of SiO<sub>2</sub> with Al<sub>2</sub>O<sub>3</sub>. The texture can be observed in the outer layer of all specimens, and the clear texture is possible only for thin slices of specimens with good focusing at TEM observation.



**Figure 3.** (a) RBS spectrum and (b) the concentration depth profiles of Si, Al, and O for SiO<sub>2</sub>-coated specimens with  $T_{\rm h} = 773$  K.

**Figure 4.** Change in anode potential,  $E_a$ , with time,  $t_a$ , during anodizing in 0.5 MH<sub>3</sub>BO<sub>3</sub>/0.05 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> solution at 293 K and 10 A/m<sup>2</sup> for specimens coated with SiO<sub>2</sub> at different  $T_h$ .

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Figure 5. TEMs of vertical cross sections of specimens anodized up to  $E_a = (a)$  100, (b) 200, (c) 300, and (d) 400 V after SiO<sub>2</sub> coating at  $T_h = 773$  K. Conditions of anodizing as in Fig. 4.

Figure 6 shows the TEM images of the vertical cross sections of  $E_a = 400$  V specimens with SiO<sub>2</sub> coating at (a) 573, (b) 673, and (c) 773 K. There are outer and inner layers on all the specimens, and the thickness of both layers decreases only slightly with increasing  $T_h$ . The  $T_h = 573$  K specimen shows a SiO<sub>2</sub> layer on the outer layer, but the  $T_h = 673$  K specimen shows no SiO<sub>2</sub> layer like the  $T_h = 773$  K specimen. In Fig. 6c ( $T_h = 773$  K), the positions examined by energy-dispersive X-ray (EDX) are indicated by the numbers 1-4, and the mole concentration of Si and Al at each position is shown in Table II. The values are similar to those at the other two positions of the oxide films. Both aluminum and Si are observed in the outer layer, whereas only Al is observed in the inner layer. The concentration of Al in the outer layer is lower at the more outer

parts, whereas the Si concentration decreases from the outer layer inward. The chemical composition of the outer layer at positions 1 and 3 can be estimated as  $AlSi_{3,3}O_{8,1}$  and  $AlSi_{0,4}O_{2,3}$ , assuming that the outer layer consists of Al-Si composite oxide. It is considered from Table II that the inner layer consists of alumina.

Figure 7a shows the RBS spectrum obtained for the  $E_a$  = 400 V specimen with SiO<sub>2</sub> coating at  $T_h$  = 773 K (Fig. 5d and 6c), and Fig. 7b shows the concentration depth-profile of Si, Al, and O, derived from the spectrum. Figure 7b shows that the Si concentration in the outer layer decreases with increasing the distance from the film surface, *X*, while the concentration of Al in this layer increases with *X*. This is consistent with the results of EDX (see Table II).



**Figure 6.** (a) TEMs of cross sections of specimens anodized up to  $E_a = 400$  V after SiO<sub>2</sub> coating at  $T_h =$  (a) 573, (b) 673, and (c) 773 K. Conditions of coating as in Fig. 1, and anodizing as in Fig. 4.

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Figure 8 shows time variation in the thickness of (a) the SiO<sub>2</sub> layer,  $\delta_{Si}$ , (b) the outer layer,  $\delta_c$ , and (c) the inner layer,  $\delta_a$ , during anodizing after SiO<sub>2</sub> coating with different  $T_h$ . The  $\delta_{Si}$  of all the specimens decreases linearly with  $t_a$ , and the slope of the  $\delta_{Si}$  vs.  $t_a$  curves decreases with  $T_h$ . The thickness of the outer layer,  $\delta_c$ , on all the specimens coated with SiO<sub>2</sub> increases linearly with  $t_a$  at  $t_a < 300$  s, and beyond this period the rate of increase in  $\delta_c$  decreases on the specimens with  $T_h = 673$  and 773 K. The slope of the  $\delta_c$  vs.  $t_a$  curves at the initial stage increases slightly with increasing  $T_h$ . The  $\delta_a$  of all SiO<sub>2</sub>-coated specimens increases with  $t_a$ , and the rate of increase in  $\delta_a$  decreases with  $t_a$ . The slope of the SiO<sub>2</sub>-coated specimens is much flatter than that of the specimen without SiO<sub>2</sub> coating (see chained curve in Fig. 8c), and it becomes slightly flatter with higher  $T_h$ .



**Figure 7.** (a) RBS spectrum and (b) concentration depth profiles of Si, Al, and O in depth for specimens anodized up to  $E_a = 400$  V after SiO<sub>2</sub> coating at  $T_h = 573$  K. Conditions of anodizing as in Fig. 4.



**Figure 8.** Changes in the thickness of the SiO<sub>2</sub>-coated layer,  $\delta_{Si}$  (Fig. 9a), the outer Al-Si composite oxide layer,  $\delta_c$  (Fig. 9b), and of the inner Al<sub>2</sub>O<sub>3</sub> layer,  $\delta_a$  (Fig. 8b), with  $t_a$  during anodizing after SiO<sub>2</sub> coating with different  $T_b$ . Conditions of anodizing as in Fig. 4.

Here, it must be noted that on all the SiO<sub>2</sub>-coated specimens, the rate of increase in  $\delta_c$  during anodizing is higher than that of the decrease in  $\delta_{Si}$ .

Dielectric properties of anodic oxide films formed after SiO<sub>2</sub> coating.—Figure 9 shows the impedance Bode diagrams for specimens anodized up to  $E_a = 100, 200, 300, and 400 \text{ V}$  after SiO<sub>2</sub> coating at  $T_h = 773 \text{ K}$ .  $E_a = 0 \text{ V}$  represents the specimen without anodizing after SiO<sub>2</sub> coating. The log |Z| vs. log f curve for all specimens is divided into three regions: a horizontal straight line in the low-frequency region, a straight line with a slope of -1 in the middle-frequency region. The impedance, |Z|, in the low and high frequency does not depend on  $E_a$  and is about 10<sup>3</sup> and 10<sup>-1</sup> $\Omega$  m<sup>-2</sup>. The log |Z| vs. log f curve for SiO<sub>2</sub>-coated specimens ( $E_a = 0 \text{ V}$ ) is located in a much lower frequency region than that for electropolished specimens with heating at 823 K for 3 h.<sup>6</sup> The straight line in the middle-frequency region shifts to the high-



**Figure 9.** Bode diagram obtained for specimens anodized up to  $E_a = 0$ , 100, 200, 300, and 400 V after SiO<sub>2</sub> coating with  $T_h = 773$  K. Conditions of coating as in Fig. 1, and anodizing as in Fig. 4.

frequency direction with increasing  $E_a$ . The phase shift,  $\theta$ , for all specimens changes from 0° through -90 to 0° with increasing *f*, and the curve shifts to the higher frequency direction as  $E_a$  increases.

The impedance data in Fig. 9 may correspond to the equivalent electric circuit inserted in Fig. 9.<sup>e</sup> The symbols  $C_p$ ,  $R_p$ , and  $R_{soln}$  in the insert represent parallel capacitance of the film, the parallel resistance of the film, and the solution resistance, respectively. Figure 9 implies that  $C_p$  decreases with increasing  $E_a$ , and that  $R_p$  and  $R_{soln}$  do not depend on  $E_a$ . The specimens with  $T_h = 573$  and 673 K showed Bode diagrams similar to Fig. 9, suggesting similar equivalent electric circuits to that in Fig. 9. The values of  $R_p$  and  $R_{soln}$  did not depend on  $T_h$  and  $E_a$ , and only the  $C_p$  value changed with the parameters.<sup>f</sup>

The relationship between the reciprocal of the parallel capacitance,  $1/C_p$ , and anode potential,  $E_a$ , for specimens with and without SiO<sub>2</sub> coating is shown in Fig. 10. The  $1/C_p$  for the specimen is proportional to  $E_a$ . The specimens coated by SiO<sub>2</sub> show a flatter slope than those without SiO<sub>2</sub> coating, and this is more pronounced with increasing  $T_h$ . Consequently, the capacitance of anodic oxide film formed after SiO<sub>2</sub> coating is at most about 20% higher than without SiO<sub>2</sub> coating.



**Figure 10.** Change in the reciprocal capacitance,  $1/C_p$ , with anode potential,  $E_a$ , obtained for SiO<sub>2</sub>-coated specimens with different  $T_h$ . Conditions of anodizing as in Fig. 4.

#### Discussion

Dielectric properties of anodic oxide films after SiO<sub>2</sub> coating.—Figure 11 shows the  $E_a$  dependence of the thickness of the outer Al-Si composite oxide layer,  $\delta_c$ , and the inner Al<sub>2</sub>O<sub>3</sub> layer,  $\delta_a$ , obtained from specimens with SiO<sub>2</sub> coating at  $T_h = (a)$  573, (b) 673, and (c) 773 K (see Fig. 8). The chained curves in Fig. 11 represent the  $E_a$  dependence of the thickness of anodic oxide films formed on aluminum without SiO<sub>2</sub> film. Both  $\delta_c$  and  $\delta_a$  of all the specimens are proportional to  $E_a$ . The slope of  $(\delta_c + \delta_c)$  vs.  $E_a$ curve for the specimens with SiO2 coating is much flatter than without SiO<sub>2</sub> coating and decreases only slightly with increasing  $T_{\rm h}$ . The anode potential is sustained by both the inner and the outer layer of the anodic oxide films formed on the specimen with SiO<sub>2</sub> coating. Hence, the average electric field across the anodic oxide films  $(\delta_c + \delta_c)$  can be calculated to be 0.93, 1.03, and 1.08  $\times$  10<sup>9</sup> V/m at T<sub>h</sub> = 573, 673, and 773 K. These values are considerably larger than the value for anodic oxide films formed on aluminum without SiO<sub>2</sub> coating,  $0.67 \times 10^9$  V/m (see chained curves in Fig. 11). This is because the outer Al-Si composite oxide layer is able to sustain a high potential. Assuming that the K value across the inner layer is  $K_a = 1.5 \text{ nm/V}$  (=1/(0.67)  $\times$  10<sup>9</sup>) m/V), the K value of the outer layer,  $K_c$ , can be estimated using the following equation

$$K_{\rm c} = \delta_{\rm c} / [E_{\rm a} - (\delta_{\rm a} / K_{\rm a})]$$
<sup>[6]</sup>

The  $K_c$  of all the SiO<sub>2</sub>-coated specimens is in the range of 0.7-0.9 nm/V, decreasing with  $E_a$  and much smaller than the 1.5 nm/V for anodic oxide films on aluminum without SiO<sub>2</sub> coating, as shown in Fig. 12. The decrease in  $K_c$  with  $T_h$  may be correlated with the fact that the thickness of the coated SiO<sub>2</sub> film before anodizing decreases with  $T_h$ . The outer layer of the SiO<sub>2</sub>-coated specimens is formed by

<sup>&</sup>lt;sup>e</sup> Here, the authors adopted the simplest equivalent circuit. As shown in Fig. 5 or 6, the anodic oxide films formed after SiO<sub>2</sub> coating generally consist of three layers: an SiO<sub>2</sub> layer, an Al-Si composite oxide layer, and an Al<sub>2</sub>O<sub>3</sub> layer, and this could lead to more complicated equivalent circuits. The authors cannot explain the impedance response in Fig. 9, but this behavior has been also obtained in a previous investigation.<sup>11,12</sup>

<sup>&</sup>lt;sup>f</sup> The authors are not able to explain the independence of  $R_p$  with  $E_a$ . However, this has also been observed for specimens anodized in a neutral borate solution after thermal treatment and for specimens anodized in a neutral boric acid solution up to high anodic potentials.<sup>16</sup> Defects in the structure of the oxide films could be an explanation for the phenomenon.



**Figure 11.** Change in the thickness of the outer Al-Si composite oxide layer,  $\delta_c$ , and the inner Al<sub>2</sub>O<sub>3</sub> layer,  $\delta_a$ , with  $E_a$ , obtained for SiO<sub>2</sub>-coated specimens with different  $T_h$ . Condition of anodizing as in Fig. 4, and the chained curve for electropolished specimen without SiO<sub>2</sub> coating.

the conversion of  $SiO_2$  film during anodizing, as discussed in the following section. Lower heating temperature in the sol-gel coating allows more organic compounds to remain in the SiO<sub>2</sub> film, and this may lead to the formation of the outer layer with a higher  $K_c$  value.

As shown in Fig. 10 and 11, both the 1/Cp and  $(\delta_c + \delta_a)$  values are proportional to  $E_a$ . Hence, the apparent dielectric constant,  $\varepsilon_{app}$ , of anodic oxide films formed on SiO<sub>2</sub>-coated specimens can be calculated using Eq. 1. Table III shows the change in the apparent dielectric constant,  $\varepsilon_{app}$ , with heating temperature,  $T_h$ , in SiO<sub>2</sub> coating. The dielectric constant of anodic oxide films formed on specimens without SiO<sub>2</sub> coating is also plotted. The  $\varepsilon_{app}$  of the anodic oxide films formed after SiO<sub>2</sub> coating is much smaller than that without SiO<sub>2</sub> coating, due to the formation of the composite oxide layer with a small dielectric constant. The slight decrease in  $\varepsilon_{app}$ with increasing  $T_h$  can be explained in terms of a larger  $\delta_c$  to  $\delta_a$  ratio for the anodic oxide films formed after the SiO<sub>2</sub> coating at higher  $T_h$ . The dielectric constant of the outer composite oxide layer itself cannot be obtained from the impedance measurements, since the



**Figure 12.** Relationship between  $K_c$  and the anode potential,  $E_a$ , obtained for sol-gel coated/anodized specimens with different  $T_h$ . Conditions of anodizing as in Fig. 4. Chained line indicates the  $K_c$ - $E_a$  relationship for specimen without SiO<sub>2</sub> coating.

Bode diagram for the specimen anodized after the  $SiO_2$  coating corresponds to an equivalent circuit of a uniform layer structure (see Fig. 9).

Consequently, the appreciable increase in parallel capacitance of anodic oxide films by coating with  $SiO_2$  before anodizing is due to the formation of the Al-Si composite oxide layer with a low  $K_c$  value.

Formation mechanism of anodic oxide films after  $SiO_2$  coating.—The important experimental facts on the film-formation mechanism during anodizing are the following

1. For SiO<sub>2</sub>-coated specimens the anode potential,  $E_a$ , increases linearly with time,  $t_a$ , after a jump of 2-3 V at the very initial stage of anodizing, and the slope of the  $E_a$  vs.  $t_a$  curves is much steeper than for the specimen without SiO<sub>2</sub> coating (see Fig. 4).

2. For anodic oxide films with an outer Al-Si composite oxide layer and the metal substrate during anodizing (see Fig. 5), the concentration of Si decreases inward through the outer layer, while the Al concentration increases (see Fig. 7 and Table II).

3. During anodizing, the thickness of the inner  $(\delta_a)$  and outer layers  $(\delta_c)$  increase, while the thickness of the SiO<sub>2</sub> layer,  $\delta_{Si}$ , decreases. The rate of increase in  $\delta_c$  is appreciably larger than the rate of decrease in  $\delta_{Si}$  (see Fig. 8).

Figure 13 shows a schematic model of the formation of the anodic oxide film during anodizing after  $SiO_2$  coating. It is assumed that the  $SiO_2$  layer has a network structure of micropores and cracks which may have been formed by the evaporation of organic compounds during heating of the sol precursor film. During the heattreatment, a thin thermal aluminum oxide film is formed at the interface between the  $SiO_2$  layer and metal substrate. The thermal

Table III. Change in the apparent dielectric constant,  $\varepsilon_{app}$ , with heat-treatment temperature,  $T_{\rm h}$ , for specimens anodized up to  $E_{\rm a} = 400$  V after SiO<sub>2</sub> coating.





Figure 13. Schematic illustration of the formation of the anodic oxide film during anodizing after SiO<sub>2</sub> coating.

oxide film may convert partly to an Al-Si mixed oxide by the interdiffusion of  $Al^{3+}$  and  $Si^{4+}$  during heating.

Water and electrolyte penetrates into the micropore network in SiO<sub>2</sub> film when dipping the SiO<sub>2</sub>-coated specimen in anodizing solution prior to anodizing. The small jump in  $E_a$  at the very initial stage of anodizing is due to the thermal oxide layer formed during anodizing.<sup>6</sup> The increase in  $E_a$  after the initial jump corresponds to the growth of an anodic oxide film with double-layer structure, an inner Al<sub>2</sub>O<sub>3</sub> layer, and an outer Al-Si composite oxide layer. During anodizing after SiO<sub>2</sub> coating,  $O^{2-}$  ions dissociated from water at the bottom of the SiO<sub>2</sub> layer transport inward across the anodic oxide film to form Al<sub>2</sub>O<sub>3</sub> at the interface between the inner Al<sub>2</sub>O<sub>3</sub> layer and metal substrate. Aluminum ions transport outward to form the composite oxide layer by filling the micropores with Al<sub>2</sub>O<sub>3</sub> at the interface between the outer composite oxide layer and the SiO<sub>2</sub> layer.

In addition to the formation of oxide at the two interfaces, a conversion of  $Al_2O_3$  to composite oxide may occur at the interface between the outer and inner layers due to the inward transport of  $SiO_4^{4-}$  or  $SiO_3^{2-}$  ions under the electric field across the composite oxide layer. This causes the lower concentrations of Si and the higher concentrations of Al deeper in the outer layer. The inward transport of Si-bearing anions may also result in the rate of increase in the outer layer.

Considering the formation of the Si-bearing anions, it is well known that anodic oxide films on aluminum contain electrolyte anions from anodizing solutions, and that the electrolyte anions transport inward or outward across anodic oxide films during anodizing. Phosphate ions transport inward, and chromate and molybdate ions transport outward.<sup>17-20</sup> Borate ions move little in either direction.<sup>21-23</sup> The outward transport is due to the formation of cations, like  $CrO_2^{2^+}$ , under a high electric field across the oxide, and the inward transport is due to the formation of anions, like  $PO_3^-$ . The formation of cations or anions under the electric field depends on whether the affinity of metal ions with oxygen ions is stronger or weaker than that of aluminum ions with oxygen ions. P(V) with a strong affinity to  $O^{2^-}$  forms anions, and Cr(VI) with a weak affinity to  $O^{2^-}$  forms cations. B(III) does not form either cations or anions, since its affinity is similar to that of Al(III).

In the outer Al-Si composite oxide layer, Si forms a network structure with oxygen ions, and under an electric field the incorporation of  $Al_2O_3$  may break the network structure locally by the following reaction

 $SiO_2 + Al_2O_3 = SiO_3^{2-} + 2AlO^+$ 

These reactions occur in a molten slag at high temperatures with no electric field.<sup>24</sup> The network structure of silicon dioxide and  $P_2O_5$  tends to break up to form anions when  $Al_2O_3$ , MgO, and CaO are mixed with SiO<sub>2</sub> and  $P_2O_5$ . This is due to the covalent bonding characteristics of SiO<sub>2</sub> and  $P_2O_5$ , which cause a strong affinity with  $O^{2^-}$ .

The steeper slope of  $E_a vs. t_a$  curves for the SiO<sub>2</sub>-coated specimen can be explained by the following. The growth of the inner and outer layers is a result of the transport of  $O^{2-}$  and  $Al^{3+}$  ions. Assuming that the transport number of  $Al^{3+}$  ions remains around 0.4 during anodizing,<sup>25</sup> the growth rate of the outer layer would be much higher than that of the inner layer. This is because the formation of the outer layer consumes electric charge only for repairing cracks and voids in the SiO<sub>2</sub> film. Hence, the total growth rate of the inner and outer layer is much higher than the growth rate of anodic oxide films on specimens without SiO<sub>2</sub> in galvanostatic anodizing. This leads to the steeper slope of the  $E_a vs. t_a$  curve on specimens with SiO<sub>2</sub>. The ability of the outer layer to sustain a higher potential also plays a role in this phenomenon.

Only slight dependence of the growth of anodic oxide films on specimens with SiO<sub>2</sub> on heating temperature,  $T_h$ , at the final stage of the sol-gel method is difficult to explain. One could expect an appreciable difference in the structure of SiO<sub>2</sub> films coated at different  $T_h$  because of the difference in the SiO<sub>2</sub> film thickness (see Fig. 2). Differences in the micropore network structure and chemical composition of SiO<sub>2</sub> may also give rise to a compensatory effect on the conversion of the inner Al<sub>2</sub>O<sub>3</sub> layer to the outer Al-Si composite layer, leading to the only slight dependence of the anodic oxide film growth.

#### Conclusion

Aluminum was anodized in a neutral borate solution after  $SiO_2$  coating by sol-gel processing to examine the dielectric properties and formation mechanism of the anodic oxide films. The following conclusions may be drawn.

1. Anodizing of aluminum coated with  $SiO_2$  films by sol-gel dip-coating leads to the formation of oxide films which consist of an outer Al-Si composite oxide layer and an inner  $Al_2O_3$  layer at the interface between the  $SiO_2$  layer and the metal substrate.

2. The outer and inner layers grow during anodizing, while the  $SiO_2$  layer becomes thinner. The rate of increase in the outer layer thickness is higher than that of the decrease in the  $SiO_2$  film. This behavior can be explained by the conversion of  $Al_2O_3$  to Al-Si composite oxide at the interface between the inner and outer layers due to the inward transport of Si-bearing anions across the outer layer.

3. The capacitance of anodic oxide films formed on specimens with  $SiO_2$  coating is about 20% larger than that without  $SiO_2$  layer. This is due to the formation of the Al-Si composite oxide layer, which can sustain a higher electric field than  $Al_2O_3$ .

### Acknowledgments

The authors thank S. Toda, K. Nishinaka, and Y. Ohisa, Muroran Institute of Technology, for assistance with the experiments on the sol-gel coating, and Professor Emeritus S. Yamaguchi at Tohoku University for the RBS measurement. The work was financially supported by the Light Metal Education Foundation of Japan, and the Ministry of Education, Science, Sports and Culture, Japan, with a Grant-in-Aid for Scientific Research. A part of this work was carried out under the Visiting Researcher's Program of the Institute for Materials Research, Tohoku University.

Hokkaido University assisted in meeting the publication costs of this article.

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