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**ANALYTICAL STUDIES ON
THE ANODIC OXIDE FILMS BY MEANS
OF SECONDARY ION MASS SPECTROMETRY**

(陽極酸化皮膜の二次イオン質
量分析法による解析)

1979

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PREFACE

The work in this thesis was performed under the guidance of Professor Hideo Tamura at the Department of Applied Chemistry, Faculty of Engineering, Osaka University.

The object of this thesis is to describe the clarification of incorporation of impurity elements from the electrolytes or the metal substrate into anodic oxide films of tantalum and lead-antimony alloy and further, role of the incorporated impurity elements on the mechanism of growth. The author hopes that the secondary ion mass spectrometry presented in this thesis become one of a powerful tool on characterizing the anodic oxide films.

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INTRODUCTION

Anodic oxide films on metals are of great importance, they are utilized as protective coatings of metals and in technological devices such as capacitors and batteries.

On preparation of anodic oxide films, there are a variety of choices of the electrolytes, but many indications have been reported on that the composition of electrolytes have a large effect on anodic behaviors and natures of oxide films. It has also suggested that impurity elements in the metals have similar effects to that of the electrolytes. Incorporation of impurity elements from the electrolytes or the metal substrate seems to be responsible for the phenomena.

In order to elucidate these phenomena, it seems important to get knowledge on the incorporation.

Recently, the secondary ion mass spectrometry (SIMS) was effectively applied for analysis of the incorporation of phosphorus and fluorine in the anodic oxide films [1,2].

The object of this thesis is to investigate the incorporation behavior of impurity elements and the roles of them in the formation mechanism of anodic oxide films on tantalum and lead-antimony alloy, combining the electrochemical techniques with the SIMS. Since tantalum oxide films used as a capacitor are tight, the application of the SIMS technique for the analysis will not be difficult as suggested from the

published works, but no positive evidence on the effectiveness of the SIMS technique has been reported on porous films such as oxide films on lead-antimony alloy.

The contents of this thesis are composed of the following papers.

1. Incorporation of Electrolyte into Anodic Oxide Film on Tantalum
F. Arifuku, C. Iwakura, H. Yoneyama and H. Tamura
Denki Kagaku, 46, 19 (1978).
2. The Behavior of Incorporated Impurities in Tantalum Anodic Oxide Films at the Dielectric Breakdown
F. Arifuku, H. Yoneyama and H. Tamura
Electrochim. Acta, in contribution.
3. Migration of Incorporated Phosphorus in the Anodic Oxide Film Formation of Tantalum
F. Arifuku, H. yoneyama and H. Tamura
Electrochim. Acta, in contribution.
4. Distribution Profiles of Antimony as a Function of Depth of Corrosion Films of a Lead-Antimony Alloy
F. Arifuku, H. Yoneyama and H. Tamura
J. Appl. Electrochem., in press.
5. The Distribution of Antimony in the Oxide Layer Formed by Potentiostatic Oxidation of Pb-Sb Alloy
F. Arifuku, H. Yoneyama and H. Tamura
J. Appl. Electrochem., in press.

CHAPTER 1

INCORPORATION OF ELECTROLYTES INTO ANODIC OXIDE FILMS ON TANTALUM AND THE BEHAVIOR OF INCORPORATED IMPURITIES AT THE DIELECTRIC BREAKDOWN

1. INTRODUCTION

Insulating amorphous oxide films are usually formed on tantalum by anodic oxidation in almost all the aqueous electrolytes except for fluorides [3]. It was reported that anodic oxide films on tantalum had a " two-layer " structure [4] when they were formed in sulfuric acid, phosphoric acid and nonaqueous mixed solutions composed of ethylene glycol, $\text{Na}_2\text{B}_4\text{O}_7$ and small amount of H_2O . The two-layer structure of the film was supported by a radiotracer study [5] and infrared reflectance spectra [6] of the anodic oxide films.

It was also found that the electronic conductivity of the anodic oxide film depends strongly on the forming solution [7], which seemed to be related to the in-depth film composition.

The main purpose of this chapter was to elucidate by SIMS whether any other chemical species were incorporated from the electrolyte into the oxide film or not, and to investigate how incorporated elements behave on the dielectric breakdown.

2. EXPERIMENTAL

2.1. Preparation of samples

Commercially available tantalum sheets of 0.3 mm thickness and of 99.9 % purity were used in this study. The sheet was cut into rectangular pieces of three different sizes (7x10 mm, 11x15 mm and 12x20 mm). Edges of the pieces were polished mechanically with emery papers, and a tantalum wire (0.50 mm in dia.) was spot-welded onto one of the corners of the piece to make an electrical contact. Then only the portion of the tantalum wire was sealed in a glass tube. The spot-welded part was covered with an insulating oxide film prepared by oxidation in a flame. The electrodes were degreased with acetone, chemically polished for few seconds in a mixed acid solution (H_2SO_4 : HNO_3 : HF = 5 : 2 : 1.5 by volume), which was similar to that reported by Vermilyea [8], until the smooth surface was obtained, and finally washed with deionized water. After being dried in air with a blower, the insulating part of the electrodes was further covered with epoxy resin or Daifloil #200 (oligomer of trifluorochloroethylene) in order to prevent appreciable current leakage in the spot-welded part during anodic oxidation of the electrode. Immediately before use, the electrodes were dipped in HF solution for ten seconds, washed thoroughly in a stream of deionized water, and then subjected to anodic oxidation.

All the electrolytes were prepared by dissolving reagent grade chemicals into doubly distilled water.

Anodic oxidation of the tantalum electrode was carried out

up to a fixed potential under a constant current density.

To get information on behaviors of the incorporated elements at the dielectric breakdown, samples subjected to partial breakdown were prepared in the following manner. When the electrode reached a high oxidation potential in the forming solution and the breakdown commenced, the breakdown part of the film was noticed to change abruptly in the interference color. The oxidation current was forced to flow until approximately half the area of the electrode showed the color characteristics of the breakdown. The author will hereinafter describe the remaining part from the breakdown as "normal part".

The potential of the sample electrode in the anodizing solution was measured against a saturated calomel electrode (SCE). After anodization, sample oxide surfaces were thoroughly washed with a stream of deionized water for one or two hours to eliminate electrolyte components stuck to the surface.

2.2. Electrochemical measurements

The capacitance of the anodic oxide film was measured at 1 kHz in 0.5M H_2SO_4 by using a Wheatstone bridge assembly [9].

Current-potential curves were measured potentiostatically in 1M HClO_4 and current-time curves in the same solution at a fixed potential of -1.0 V vs. SCE.

All the measurements were carried out at 25 °C.

2.3. Secondary ion mass spectrometry

Measurements of in-depth profiles of impurities in the anodic oxide films on tantalum were carried out by using SIMS

(Hitachi, model IMA-2). Detailed descriptions for the IMA are found in articles already published [10-13].

As an impinging primary ion, Ar^+ was chosen. The acceleration voltage of the primary ion was set up at 10 kV, and that of the secondary ions at ± 3 kV. The sample current was adjusted so as to give $1.43 \times 10^{-4} \text{ A/cm}^2$ on a stainless steel sample holder with a diameter of the beam spot of 1/15 cm, except where the analysis was made for the breakdown films ($5.72 \times 10^{-4} \text{ A/cm}^2$, ϕ 1/30 cm). After the filament of the ion gun was kept under a discharged condition for about 1 hr, the primary ion beam was impinged onto the sample holder for about 0.5-1 hr so that fairly stable signals of secondary ions could be obtained, possibly by attainment of a constant temperature of the sample holder. The measurements were then conducted. The sample chamber was evacuated to approximately 10^{-7} Torr.

It is necessary in the in-depth analysis that the beam has the same intensity throughout the spot. To attain such a condition, impingement of the primary beam was conducted under an under-forcussing condition [11] and the suitability of the condition was confirmed in the in-depth analysis by checking an abrupt change in the signal intensity of Ta^+ at the tantalum-oxide interface of an anodic oxide film.

3. RESULTS AND DISCUSSION

3.1. Incorporation of impurity elements

After anodization of tantalum in various electrolytic solutions, impurities incorporated from electrolytes into the

oxide film were analyzed by IMA.

The solutions used were those of phosphoric acid, sulfuric acid, nitric acid, hydrochloric acid, boric acid, potassium fluoride, sodium chloride, lithium chloride, potassium chloride, sodium perchlorate, sodium borofluoride, sodium orthosilicate, sodium hydroxide, sodium sulfate, ammonium sulfate, nickel sulfate and sodium sulfite.

As expected, no incorporation of lithium, sodium and potassium ions was observed. Incorporation of nitrogen which was expected from the literature [14] was not observed in oxide films anodically prepared in 13.4, 6.7 and 3.4M HNO_3 . Incorporations of sulfur [4,5,14-17] and phosphorus [5,14,17,18] as constitutive elements of anions in the electrolytes were already reported. Recently in-depth profiles of the incorporated phosphorus and fluorine were successfully shown by Evans et al. [1,2] by means of IMA. No report is found for incorporation of chlorine, which will be revealed in the present study.

It was also found that any other elements constitutive of anions studied were not incorporated at all even when the concentration of the anions was chosen as high as possible.

Figure 1 shows in-depth profiles of ^{32}S and ^{16}O in oxide films which were formed by anodization up to 40 V in various concentrations of sulfuric acid. To obtain the data shown in Fig.1, negatively charged fragments of $^{32}\text{S}^-$ and $^{16}\text{O}^-$ were measured. The abscissa indicates the sputtering time or the time from the start of the bombardment with the Ar^+ primary ion. This corresponds approximately to the depth from the sample surface since the primary ion beam was fairly uniform. Though the

relation of the sputtering time to the depth was not directly measured, the sputter rate was supposed to be a few $\text{\AA}/\text{sec}$. The oxide film is judged to be sputtered out at time t_2 at which an abrupt change was observed in the signal intensity of oxygen ions. Figure 1 shows that the amount of incorporated sulfur and relative depth of the incorporation t_1 are increased with an increase of concentration of sulfuric acid. The incorporation was, however, restricted in the outer layer of the tantalum oxide film and the depth of the incorporation was only the half of the film thickness at the largest. This observation is in agreement with the results obtained by radiotracer [5] and by electrochemical studies [4,5]. Figure 1 clearly shows that the amount of incorporation is proportional to concentration of sulfuric acid

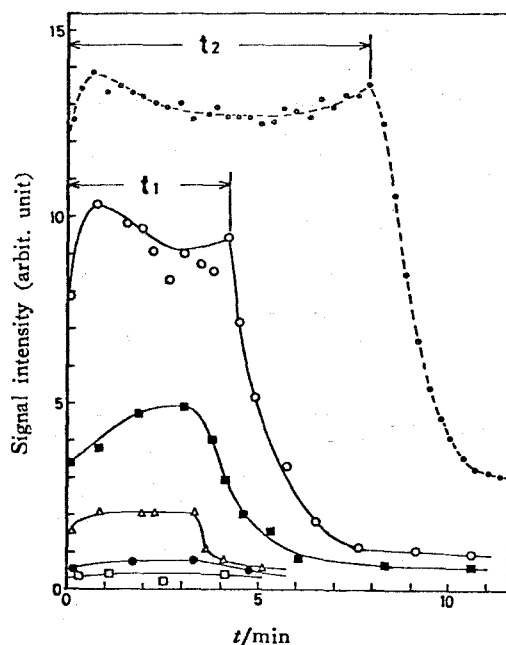


Fig. 1 Sulfur concentration profiles in anodic oxide films formed on tantalum at $0.2 \text{ mA}/\text{cm}^2$ in various concentration of sulfuric acid

Concentration of sulfuric acid :
 $\square$: 0.05 M, $\bullet$: 0.5 M, $\triangle$, $\blacksquare$: 6 M, $\circ$: 9 M
 -----Typical oxygen profile (9 M H_2SO_4)

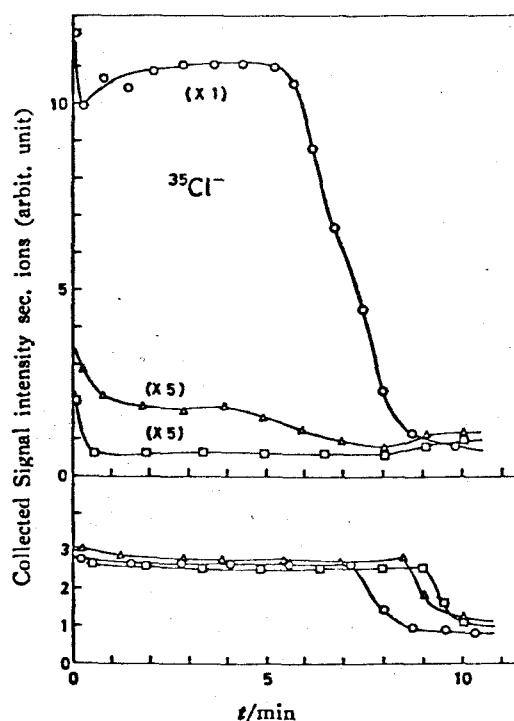


Fig. 2 Chlorine concentration profiles and collected secondary ions in anodic oxide films formed at $0.2 \text{ mA}/\text{cm}^2$ in hydrochloric acid

Concentration of hydrochloric acid :
 $\square$: 1.3 M, $\triangle$: 3.9 M $\circ$: 11.7 M

of the electrolyte.

Figure 2 shows in-depth profiles of ^{35}Cl in oxide films formed at 40 V in hydrochloric acid, together with simultaneously measured secondary ion profiles collected at the β -slit of the mass spectrometer. The secondary ions collected at the β -slit give a measure of the amount of the total secondary ions. The figure shows that the amount of incorporated chlorine depends strongly on the concentration of the forming solution, but the in-depth distribution profile of chlorine differs from the case of phosphorus in the point that chlorine is distributed throughout the oxide film. The secondary ion profiles collected at the β -slit indicate that the sputtered-out time of the oxide films became short with an increase of the concentration of HCl. The decrease of the sputtered-out time of the films with an increase of the concentration of the incorporated impurities was also observed in the case of the film formed in phosphoric acid and sulfuric acid. This phenomenon will be discussed in section, 3.3.

Figure 3 gives the in-depth profiles of fluorine as well as oxygen in the films formed by pre-anodization up to 10 V in 0.05M H_2SO_4 and then by reanodization in 4M NaBF_4 . Boron ions could not be detected in these films by IMA. The figure, therefore, shows that only fluorine was incorporated into the oxide on the reanodization and was gradually accumulated at the metal-oxide interface. Similar results to those in Fig.3 were also reported on the samples which was reanodized in a 3M KF solution [1]. It is evident from Fig.3 that borofluoride ion dissociated into boron cation and fluorine anion at the oxide-solution interface under a high electric field. It is speculated from the in-depth

profiles of incorporated fluorine and chlorine that the sizes of the both anions play an important role in incorporation profiles of them.

3.2 Sulfur incorporation

The influence of forming current density on the depth of the sulfur incorporation was investigated with films formed in 9M H_2SO_4 up to 40 V. In Fig.4 the ratio of the time required for the incorporated layer to be sputtered out t_1 (see Fig.1) to that for total length of the film t_2 is plotted as a function of the forming current density. The ratio t_1/t_2 can not directly be connected to the ratio of the film thickness corresponding to the incorporated layer to the total film thickness, because the sputter rate was different between the layers with and without incorporated sulfur, as will be described in section, 3.3. If the correction for the difference between the sputter rate of

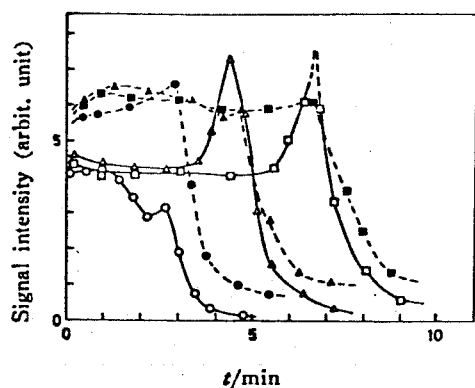


Fig. 3 Fluorine concentration profiles in reanodization films at 0.2 mA/cm^2

○, ● : 10V in 0.05M H_2SO_4 + 10V in 4M NaBF_4
 △, ▲ : 10V in 0.05M H_2SO_4 + 20V in 4M NaBF_4
 □, ■ : 10V in 0.05M H_2SO_4 + 30V in 4M NaBF_4
 Open symbols represent data of signal intensity of F^- and filled symbols those of O^-

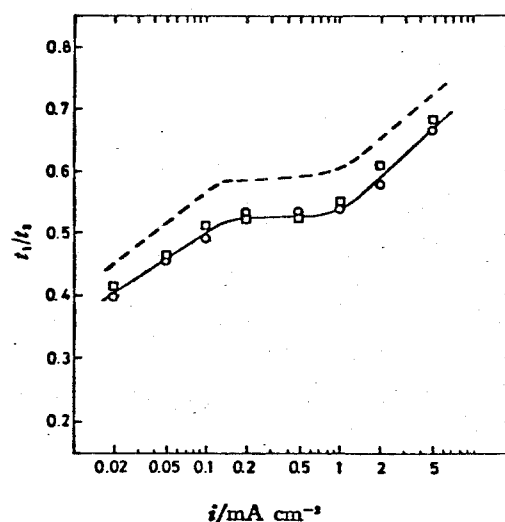


Fig. 4 t_1/t_2 ratio as a function of current density for formation at 40 V in 9 M H_2SO_4

○ : t_1 taken from $m/e=32$ ($^{16}\text{S}^-$ and $^{18}\text{O}_2^-$)
 □ : t_2 taken from $m/e=34$ ($^{16}\text{S}^-$)

the incorporated layer and that of the non-incorporated layer is made, the dotted curve in the figure was obtained. The results in Fig.4 clearly show the forming current density affects the incorporated depth of impurity. This results implies that the incorporation depth increased with an increase of the field strength, although the distribution of the field strength may not be uniform: the field strength in the incorporated layer is rather high compared with that in the non-incorporated layer [18]

3.3. Influence of incorporated sulfur on film properties

The forming potential attained was higher in 9M H_2SO_4 than in 0.5M H_2SO_4 when the same quantity of electric charge was passed with the same current density, as was already reported by Young [15] and Draper [16].

Figure 5 shows a typical example obtained in this study. When the film thickness was determined by a usual manner from capacitance data for the films formed in the same condition as in Fig.5, it was larger when the films were prepared in 9M H_2SO_4 by about 20 % than those prepared in 0.5M H_2SO_4 . When the films were formed at a fixed forming potential of 40 V, the film thickness was the same

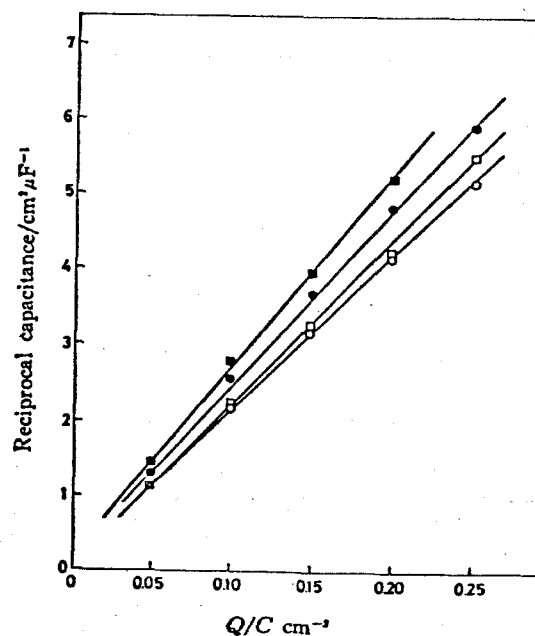


Fig. 5 Reciprocal capacitance vs. charge passed for anodization of tantalum in sulfuric acid

- : 0.5 M H_2SO_4 , 0.2 mA/cm²
- : 9 M H_2SO_4 , 0.2 mA/cm²
- : 0.5 M H_2SO_4 , 1.0 mA/cm²
- : 9 M H_2SO_4 , 1.0 mA/cm²

regardless of the concentration of sulfuric acid, so far as the current density used was not different, as reported by Draper [16]. This means that the film thickness is unequivocally determined by the forming potential. As already reported on the film prepared in 0.5 vol % H_2SO_4 [19], a linear relation was established between the forming potential and the time required for the film to be sputtered out by Ar^+ (sputtered-out time). Therefore, it was expected that measurements of the sputtered-out time would give a measure of the film thickness which was anticipated from capacitance data. However, the use of different forming solutions leads to the appreciable differences in sputtered-out time of the films. Typical data are presented in Table 1.

Table 1 Comparison of sputtered-out time for films formed at 40 V under four different conditions

Current density (mA/cm ²)	Forming solution	Sputtered-out time (min)	Relative differences based on the value obtained in 0.5 M H_2SO_4
0.2	0.5 M H_2SO_4	10.43	-13.0%
	9.0 M H_2SO_4	9.07	
1.0	0.5 M H_2SO_4	9.82	-14.8%
	9.0 M H_2SO_4	8.37	

It is evident that the sputtered-out time for the film formed in 9M H_2SO_4 is shorter than that in 0.5M H_2SO_4 , in spite of the same forming voltages (40 V). The similar trend to this phenomenon was also observed for the films formed with the same quantity of charge in the different forming solutions. In this case, film thickness determined from capacitance data was larger for the film formed in 9M H_2SO_4 by about 20 % than that in 0.5M H_2SO_4 , as described above. However, the sputtered-out time for the film formed in 9M H_2SO_4 was larger only by 5-10 % than that

in 0.5M H_2SO_4 . These results suggested that the sputter rate for the film formed in 9M H_2SO_4 was higher than that in 0.5M H_2SO_4 . Since sulfur incorporation was considered to be restricted in the outer region of the film (see Fig.1), there must be difference in the sputter rate between the films with and without appreciable sulfur incorporation.

Besides the change in physical properties of the film by the incorporation, the incorporation also brings a change in electrochemical properties of the film [7]. Figure 6 shows the variation of current at -1.0 V vs. SCE as a function of cathodic polarization time for two kinds of films. The difference

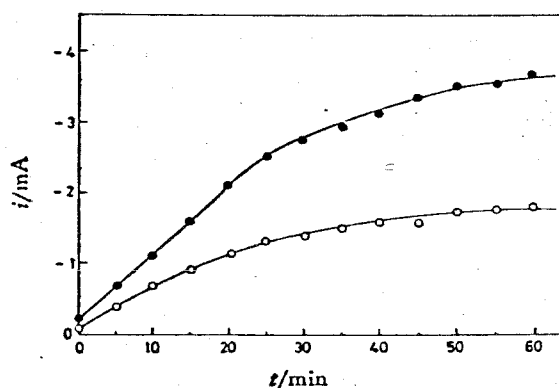


Fig. 6 Variation of current at -1.0 V vs. SCE as a function of electrolysis time for films formed up to 40 V at 0.2 mA/cm²

Concentration of sulfuric acid :
○ : 0.5M, ● : 9M

in the cathodic current behavior suggests that an electrochemical nature of the film is also largely influenced by incorporation of sulfur, although the electrochemical reaction caused by the cathodic current is ambiguous at the Ta_2O_5 electrode.

3.4. Dependency of breakdown voltage on concentration of electrolytes

The relation between the breakdown voltage and the concentration of the electrolytic solutions, measured in the relatively high concentration of sulfuric acid, phosphoric acid and hydrochloric acid, were indicated in Fig.7. The breakdown

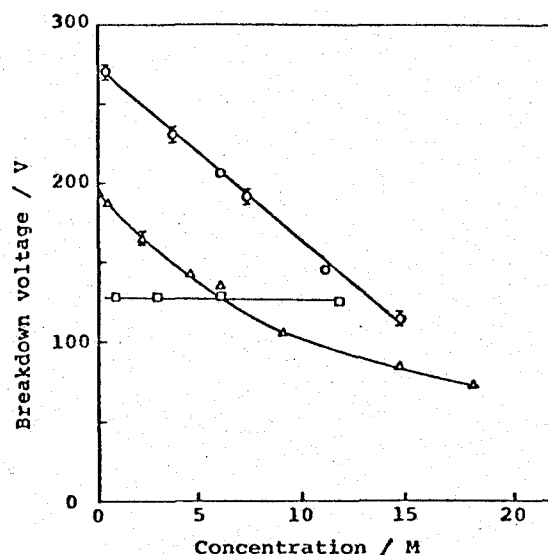


Fig.7. Dependence of the breakdown voltage of tantalum oxide films on the electrolyte concentrations.

O: H₃PO₄ , Δ: H₂SO₄ , □: HCl

voltage adopted in this study were the electrode potentials at which the emission of sparks and/or local gas evolutions commenced at 0.2 mA/cm^2 . In the limited high concentrations of the electrolyte used, the dependency of the breakdown voltage V_{bd} on the concentration was different among the kind of electrolyte, and a simple rule [20,21] applicable to a variety kinds of electrolytes was not established. As indicated in Fig.7, the following relations seem to be established between the concentration of electrolytes C and V_{bd} ; a linear decrease in V_{bd} with an increase in C and $C^{1/2}$ for phosphoric acid and sulfuric acid, respectively, and no effect of C on V_{bd} for hydrochloric acid.

3.5 Behavior of the incorporated impurity elements at the breakdown

Typical in-depth profiles of incorporated impurities in the normal and breakdown parts of oxide films formed in three

electrolytic solutions are shown in Figs.8 to 10. In these figures, the intensity of the incorporated elements is represented by a relative scale to that of secondary ions which were collected at the β -slit of IMA. The secondary ions collected at the β -slit can be used as a measure of the total secondary ions originated from the samples [22]. The change in the signal intensity of the secondary ions with sputtering time will be attributable to a change in sputter rate and/or secondary ion yield of the film. The relative intensity of the incorporated elements is, therefore, thought to show the intensity corrected for fluctuation in the amount of ions produced during the sputtering period.

Figure 8 shows for the incorporated sulfur. The film was formed in 9M H_2SO_4 . When the breakdown occurs, the incorporated sulfur seemed to be decreased near the surface region even on

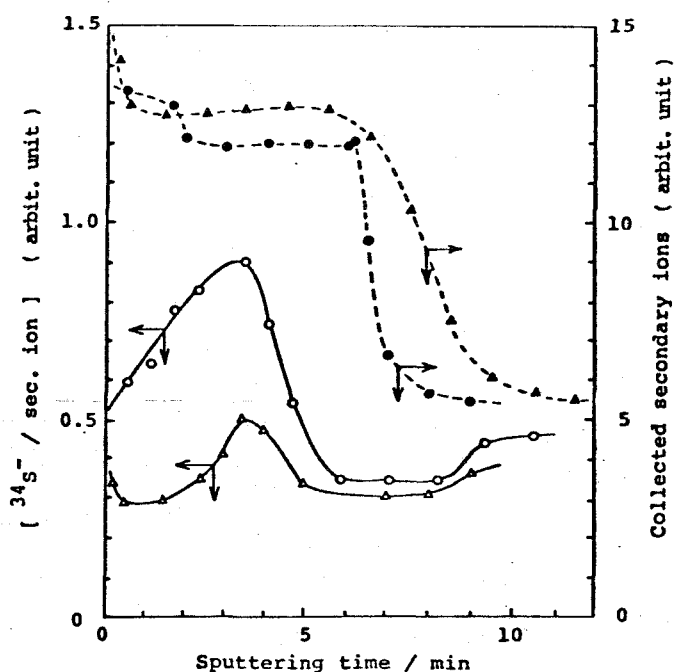


Fig.8. In-depth profiles of incorporated sulfur in tantalum oxide films anodized in 9M H_2SO_4 up to the dielectric breakdown voltage.

○, ●: normal part
 △, ▲: breakdown part

the normal part of the film, and at the breakdown part, the decrease is pronounced. This result suggests that the normal part of the film may not have the "normal properties" which a film having no history of the breakdown has, as suggested by Wood et al [23].

Fig.9 shows for phosphorus incorporated in the film prepared in 7.3M H_3PO_4 . The phosphorus profile at the normal part of the breakdown oxide film was almost consistent with that of the ordinary film [1,2]. It is obvious at the partially breakdown part positioned between the normal and the breakdown parts, that phosphorus became rich in the film surface region. Furthermore, the trend became more appreciable at the breakdown part, and, in addition, a decrease in the content of phosphorus is suggested in the interior of the film. A slight decrease in

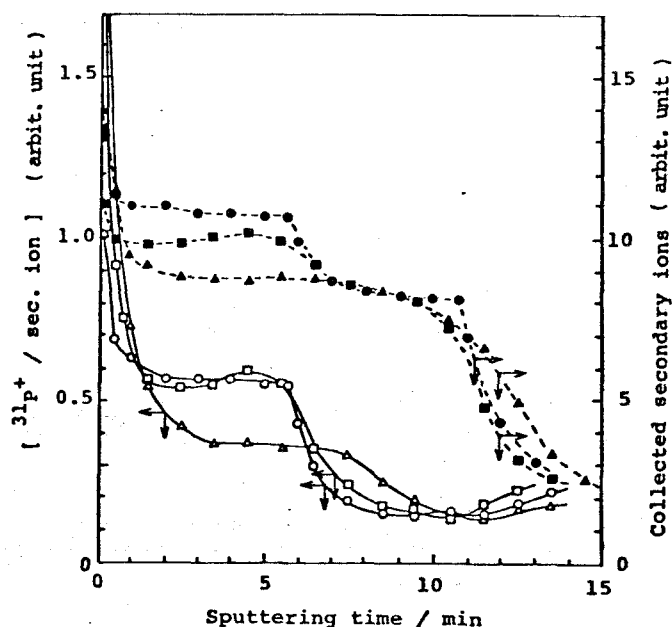


Fig.9. In-depth profiles of incorporated phosphorus in tantalum oxide films anodized in 7.3M H_3PO_4 up to the dielectric breakdown voltage.

- , ●: normal part
- , ■: partially breakdown part
- △, ▲: breakdown part

phosphorus content was occasionally observed in the surface region of the " normal part " of the film. However, almost the same profile of phosphorus as in Fig.9 was obtained even at the breakdown part of the film having such an anomalous " normal part ".

The in-depth profiles of the secondary ions and $^{35}\text{Cl}^-$ are shown in Fig.10(a), the secondary ions and $^{16}\text{O}^-$ in Fig.10(b), and signal intensity ratios of $[^{35}\text{Cl}^-/\text{sec. ions}]$ and $[^{16}\text{O}^-/\text{sec. ions}]$ in Fig.10(c) for tantalum oxide films anodized in 11.7M HCl up to the breakdown voltage. It is found that when the breakdown occurs, both chlorine and oxygen were intruded into the

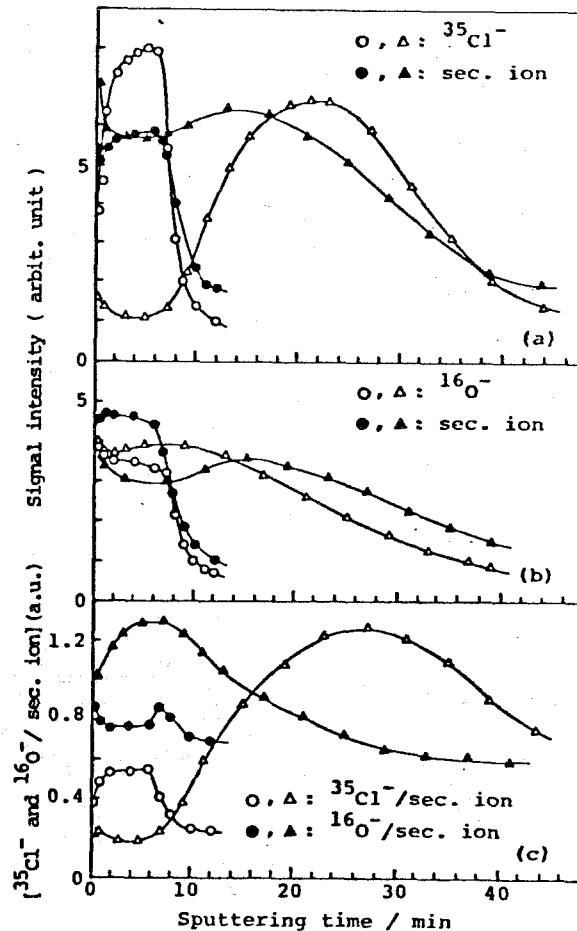


Fig.10. In-depth profiles of incorporated chlorine and of oxygen in tantalum oxide films anodized in 11.7M HCl up to the dielectric breakdown voltage. (a) $^{35}\text{Cl}^-$, (b) $^{16}\text{O}^-$ and (c) $[^{35}\text{Cl}^-/\text{sec. ion}]$ and $[^{16}\text{O}^-/\text{sec. ion}]$
 $\circ, \bullet$: normal part, $\triangle, \blacktriangle$: breakdown part

interior and the tendency for the intrusion was high for chlorine.

The results shown in Figs.8 to 10 show that distribution profiles of the incorporated impurities dramatically changes on the breakdown of the film. However, the trend of the change is quite different among the incorporated impurities. The removal was suggested for sulfur, while the intrusion into the substrate metal for chlorine. In the case of phosphorus, the behavior was complicated, and the surface enrichment accompanied with a decrease in the content in the film body was suggested.

A plausible explanation to the difference in the behaviors of the incorporated impurities on the breakdown is as follows. Sulfur and phosphorus are incorporated in the film in a form of oxyanions [14,24], while chlorine as a chlorine anion. When the breakdown commences, the ionization of the film takes place, and the incorporated chlorine is forced to move toward the metal substrate. On the other hand, the oxyanions of sulfur and possibly of phosphorus were broken down by the ionization under a high electric field to give positive charges, and then the resulting species having the positive charge migrate toward the solution side. Anyway, it seems difficult to imagine that the incorporated anionic species are stable on the breakdown.

CHAPTER 2

MIGRATION OF INCORPORATED PHOSPHORUS IN THE ANODIC OXIDE FILM FORMATION OF TANTALUM

1. INTRODUCTION

In order to clarify the growth mechanism of the anodic oxide film on tantalum formed in various electrolytic solutions, the transport numbers of constitutive ions of the anodic oxide film, i.e. those of tantalum and oxygen ions, were studied by many investigators [1,5,25-30]. Davies et al. [26,27], Whitton [28] and Pringle [30] used radioactive rare gas elements as immobile mass markers, and obtained 0.26-0.31, 0.28 and 0.243, respectively for the transport number of tantalum ions. On the other hand, when phosphorus which is incorporated in the anodic oxide film formed in phosphoric acid solution was used as a mass marker, relatively high values of ~0.5, 0.51-0.56 and 0.46 were obtained for the transport numbers by Randall et al. [5], Dell'Oca et al. [29] and Pawel et al. [1], respectively. Such difference in the transport numbers obtained may be attributed to mobility of the incorporated phosphorus under a high electric field. The immobility is essential for a marker to be used. A condition of the immobility will be satisfied when the marker has no charge. The incorporated phosphorus was suggested, however, to exist as oxyanions in the oxide film [14,24]. Therefore, the primary

purpose of this chapter was to investigate whether or not the incorporated phosphorus is mobile.

2. EXPERIMENTAL

2.1. Preparation of samples

The preparation procedure of samples was described in the previous chapter. A very thin marker layer was formed in 6M H_3PO_4 by galvanostatically oxidizing the sample by 1 V. The anodic oxidation was carried out galvanostatically in 0.5M H_2SO_4 up to a desired potential.

2.2. Determination of in-depth position of the marker layer in the oxide film

Figure 11 shows typical in-depth profiles of $^{31}\text{P}^+$ and the secondary ions collected at the β -slit of the mass spectrometer

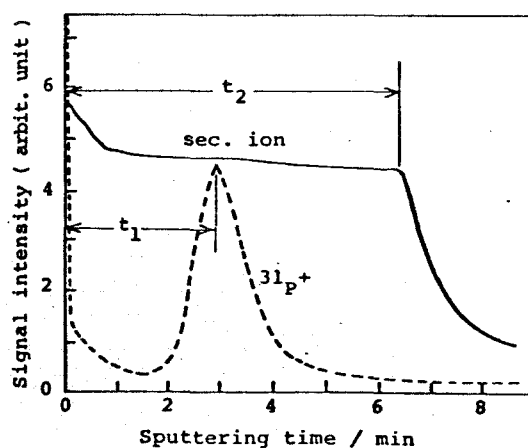


Fig.11. Typical in-depth profiles of $^{31}\text{P}^+$ and the collected secondary ion profiles for an anodic oxide film of tantalum formed initially at 1.0 mA/cm^2 to 1 V in 6M H_3PO_4 and then to 39V in 0.5M H_2SO_4 .

of IMA for a tantalum anodic oxide film containing the phosphorus marker layer. The secondary ions collected at the β -slit give a measure of the total secondary ions [31]. The time required for the oxide film to be sputtered out is assigned t_2 (min) and that for the incorporated phosphorus to give the highest intensity t_1 (min).

If assumptions are made; (1) the incorporated phosphorus is immobile, (2) the peak top of the $^{31}\text{P}^+$ profile give the center of the marker layer, and (3) the sputter rate is constant throughout in-depth direction of the oxide film, then the transport number of tantalum ions t_{Ta} is given by the following equation [1,30] for an oxide film formed in such a manner that firstly the oxide film was formed in 0.5M H_2SO_4 up to v_1 V, then by additional v V in 6M H_3PO_4 and finally again in 0.5M H_2SO_4 by additional v_2 V.

$$t_{\text{Ta}} = \frac{t_1}{t_2 \times \frac{v/2 + v_2}{v_1 + v + v_2}} \quad (1)$$

3. RESULTS AND DISCUSSION

In this study, the in-depth position of the marker layer is required in a relative scale to the total film thickness, and the absolute value of total film thickness is not important. Therefore, all the thickness were given in terms of the tantalum formation voltage. When t_{Ta} was determined for anodic oxide films formed at 0.2 mA/cm^2 , by formally employing the eq.(1), the results given in Table 2 were obtained. It is recognized in

Table 2 Typical variation of in-depth position of the peak top of the marker layer in the oxide films formed at 0.2 mA/cm^2

Initial anodization voltage in $0.5\text{M H}_2\text{SO}_4$ (v_1)	Marker layer anodization voltage in $6\text{M H}_3\text{PO}_4$ (v)	Reanodization voltage in $0.5\text{M H}_2\text{SO}_4$ (v_2)	Apparent t_{Ta} determined by eq(1)
-	1.0	9.0	0.108
-	1.0	19.0	0.350
-	1.0	29.0	0.387
-	1.0	39.0	0.411
-	1.0	49.0	0.428
-	1.0	69.0	0.438
9.5	1.0	9.5	0.130
14.5	1.0	14.5	0.252
19.5	1.0	19.5	0.330
24.5	1.0	24.5	0.330
9.5	1.0	34.5	0.405
9.5	1.0	59.5	0.419

this table that t_{Ta} obtained seems to depend on the formation voltage. The same was true for the oxide films formed at different current densities, (Fig.12). Furthermore it was recognized in Fig.12 that t_{Ta} increased with an increase in the formation current density. When the oxide film formation was made at a fixed current density up to a desired potential, and

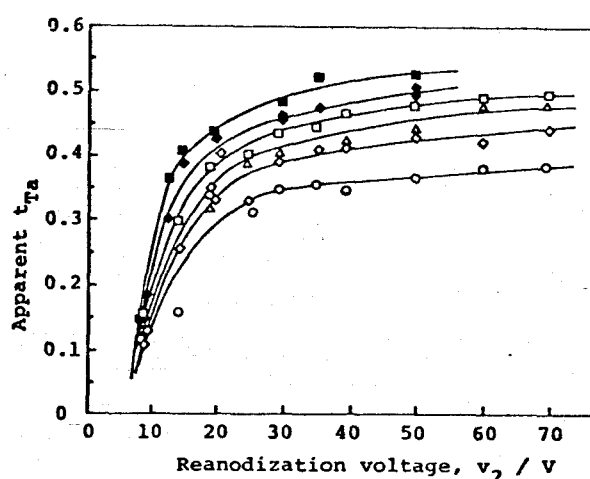


Fig.12. Apparent t_{Ta} as a function of the reanodization voltage.

○ : 0.05 mA/cm^2 ◆ : 0.2 mA/cm^2
 ◇ : 0.2 mA/cm^2 ■ : 1.0 mA/cm^2
 △ : 0.6 mA/cm^2
 □ : 1.0 mA/cm^2

then by maintaining the final forming potential for 1.5 hr, the prepared film gave a different t_{Ta} from that of the oxide film prepared only by the galvanostatic oxidation. The result is also given in Fig.12. During maintaining at the constant potential, the film continues to grow (several tens of $\text{\AA}$) with an exponential decay. The observation that t_{Ta} increased by 0.05-0.07 during this additional film formation will give an evidence to throw a doubt on immobility of the incorporated phosphorus as the mass marker.

Figure 13, obtained from the results in Fig.12, shows the position of the peak top of the marker layer, d in V of the oxide film thickness measured from the oxide-solution interface as a function of the forming voltage. It is observed that the position of the marker layer was proportional to the reanodization voltage, v_2 . The extrapolation of the relation to $d = 0$, however,

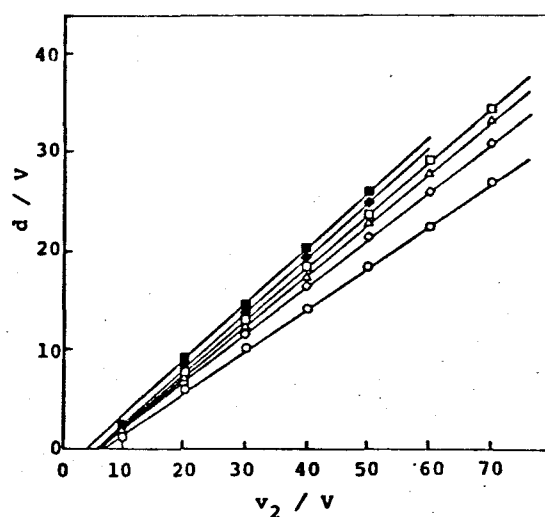


Fig.13. Position of peak top of the incorporated phosphorus as a function of reanodization voltage.

○ : 0.05 mA/cm² ◆ : 0.2 mA/cm²
 ◇ : 0.2 mA/cm² ■ : 1.0 mA/cm²
 △ : 0.6 mA/cm²
 □ : 1.0 mA/cm²

does not give the intersection point at zero volt, but 4 to 6 V of reanodization voltage depending on the forming current density. This result indicates that the oxide growth preferentially proceeded under the marker layer in the initial period of the reanodization (4-6 V). It is obvious that a dramatic change in t_{Ta} with v_2 , observed in a low anodization voltage region (see Fig.12), reflects this effect.

The analyses of Figs.12 and 13 were carried out under the assumption that the film has a constant sputter rate throughout the entire film thickness. This assumption may draw some criticisms, but seems to be fairly reasonable by the following reasons. It is noticed in Fig.11 that during the initial sputtering period, a relatively large signal intensity of secondary ions was obtained, followed by a constant intensity. One possible cause giving the high intensity may be adsorbed oxygen on the surface of the anodic oxide film [31]. The other will be due to a large sputter rate in the surface region of the film, which may be related to some structure difference in the inner and outer layers [4-6,29,32]. If it is assumed that the latter case is valid, then the correction of the film thickness is possible by integrating the area giving the excess intensity in the surface region. One will find, however, that this correction brings about only a few % of alteration of the position of incorporated phosphorus.

It is obvious that the slopes of the linear lines in Fig.13 depends on the current density used in the anodic oxidation. By inserting v_2 and d into t_2 and t_1 of eq.(1) respectively, with assumption of a constant sputter rate throughout the entire film

thickness, then one can obtain apparent t_{Ta} for individual current density used. As suggested in Fig.12, the apparent t_{Ta} values determined in this way was high for high current density, and the value for the 1 mA/cm^2 case was found to be in good agreement with ones reported by other investigators [1,5,29]. If t_{Ta} is assumed to be constant regardless of the oxidation current density used, however, then only one linear relation should be obtained between v_2 and d . Almost all the t_{Ta} values published to date have been obtained for the films anodized at 1 mA/cm^2 . Therefore, we are not sure whether or not t_{Ta} is varied with anodic oxidation current density. If the assumption is made, however, that t_{Ta} is invariable, then the difference in the slopes of the lines in Fig.13 must reflect that the incorporated phosphorus is mobile and the migration rate of it varies with the oxidation current density. A high migration rate is expectable under a high field strength across the film caused by a high current density used, which will bring about a large value of the apparent t_{Ta} . The incorporated phosphorus is possibly a large oxyanion bearing an electric charge [14,24], and hence must be mobile under a high electric field. The dependency of the apparent t_{Ta} on the anodic oxidation current density observed is explainable in this way.

It is possible to estimate the degree of migration of the incorporated phosphorus as a function of the oxidation current density, with assumption that t_{Ta} is invariable with the current density used. If the most recent value obtained by Pringle [30] was used as t_{Ta} , then the results given in Fig.14 was obtained. The results show that an increase in the forming current density

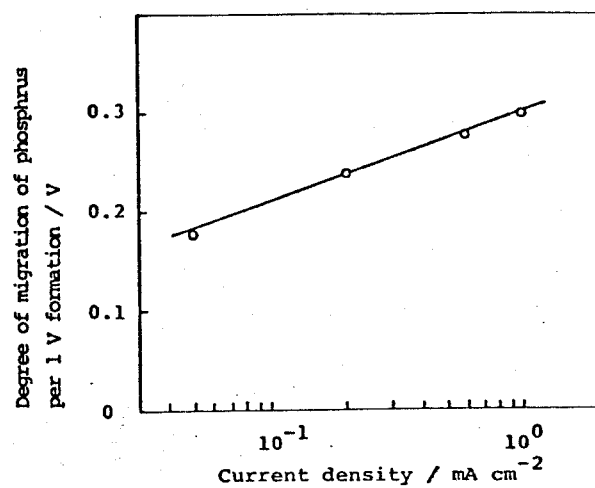


Fig.14. Migration of incorporated phosphorus in oxide films.

by twenty times makes the migration degree of the incorporated phosphorus near to double.

CHAPTER 3

DISTRIBUTION PROFILES OF ANTIMONY AS A FUNCTION OF DEPTH OF CORROSION FILMS OF A LEAD-ANTIMONY ALLOY

1. INTRODUCTION

Lead-antimony alloys have been widely used as the grid material of lead-acid batteries. Antimony in the alloy is anodically dissolved from the grid even below the equilibrium $\text{PbSO}_4/\text{PbO}_2$ potential [33,34]. Fortunately, however, the dissolved antimony has been recognized to play beneficial roles in the positive plate performance. In order to elucidate the beneficial roles of antimony, it seems helpful to have information on distribution profiles of dissolved antimony as well as on transference behavior of it. The transference behavior of dissolved antimony in electrolytes during charge-discharge cycles was studied by Dawson et al. [35,36] by means of tracer techniques, but the distribution of antimony as a function of depth of the active material and the corrosion film has not yet been reported.

Several studies on secondary ion mass spectrometry in in-depth mode [2,33-39] have shown that the technique used there is useful for analyzing a specified element as a function of depth of samples.

Therefore, the author aimed to obtain distribution profiles

of antimony as a function of depth of corrosion films of lead-antimony alloy.

2. EXPERIMENTAL

2.1. Preparation of samples

Antimonial lead plates (4.92 wt % Sb) of a circular form (16 mm dia, 2 mm thick) were used in the present study as the test electrodes. After mechanical polishing with a plane, the electrode was subjected to electropolishing in a mixed solution of CH_3COOH and HClO_4 (7 : 3) at 9 V for 10 min at room temperature. The electropolishing did not give a surface of metallic luster but that covered with a black film. By wiping with a wetted tissue paper, however, the black film was easily removed off, and a brilliant surface of metallic luster was obtained. Then the specimen was mounted in a Teflon electrode holder, by which the position exposed to the electrolyte was decreased to 0.95 cm^2 . Before measurements, the electrode was cathodically polarized at -1.2 V for 30 min in 5M H_2SO_4 .

The electrolytic solution used in this study was 5M H_2SO_4 which was prepared from reagent grade H_2SO_4 and doubly distilled water, and was pre-purified by electrolysis. A mercurous sulfate electrode in this solution was used as the reference electrode, and the potentials cited in this chapter are referred to this electrode. Nitrogen gas was bubbled into the solution for de-aeration and agitation of the solution, just prior to and sometimes during the measurements.

All the experiments were carried out at 25 °C.

2.2. Ion microprobe mass analysis

The sample current of IMA was adjusted so as to give 4×10^{-4} A/cm² on a stainless steel sample holder with diameter of the beam spot of 0.40 mm.

2.3. Standard samples for in-depth analysis

It is desirable to get information on the content of antimony in the corrosion film from secondary ion signal intensities of antimonial species. For this purpose, relations between antimony contents and signal intensities must be obtained in advance by using standard samples containing known amount of antimony. The preparation of the standard samples was as follows; lead dioxide, and a mixture of lead sulfate and lead dioxide (80 : 20 wt %) were mixed with antimony oxides in various weight ratios, and the resulting mixtures were stirred in a wetted condition for 30 min, followed by drying under reduced pressure. Afterwards these were again mixed in an agate mortar for 30 min, and then pressed in a tablet from with 1.6 ton/cm².

In order to get a rough estimate on the thickness of the corrosion films from the sputtering time, the sputter rates were obtained for thin Pb, α -PbO₂ and β -PbO₂ films. These films were prepared on Pt by electrodeposition [40,41].

3. RESULTS AND DISCUSSION

3.1. Establishment of calibration curves

Figure 15 shows a negative secondary ion spectrum of an anodic corrosion film of the lead-antimony alloy. Though a

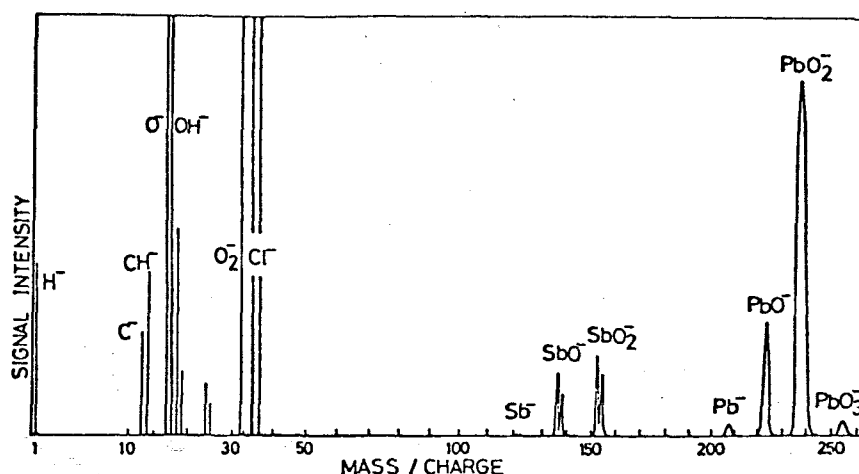


Fig.15. Negative secondary ion spectrum of an oxide film of the lead-antimony alloy.

variety of ionic fragments were produced by the ion bombardment onto the specimen, the highest intensities of the secondary ion signals were obtained at $^{121}\text{SbO}_2^-$ and $^{208}\text{PbO}_2^-$ for antimony and lead species, respectively. It was found that the relative sensitivity of secondary ions of antimony and lead were extremely higher for negative ions than for positive ions. From the results, signal profiles of SbO_2^- and PbO_2^- were chosen to get information on the distribution profiles of antimony in corrosion films of the antimonial lead.

In order to compensate effects introduced by variation of the primary ion intensity with time, it is desirable to use the ratio of signal intensity of SbO_2^- to that of PbO_2^- , I_{rel} , as a measure of the antimony content. Then this ratio was obtained for a variety of standard samples, and results are given in Fig.16. The open circles of Fig.16 concerns with samples composed of PbO_2 and Sb_2O_3 , and the triangular symbols with PbO_2 samples mixed with Sb_2O_5 . A linear relation was found to establish between the content of Sb and I_{rel} irrespective of the valence state of antimony. Therefore, I_{rel} can be used as a

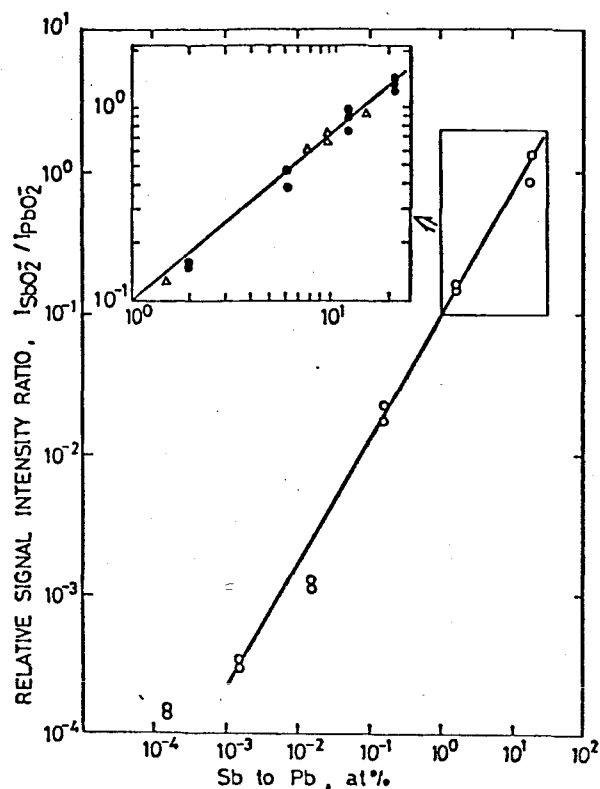


Fig.16. Ratio of signal intensity of $^{121}\text{SbO}_2^-$ to that of $^{208}\text{PbO}_2^-$, I_{rel} , obtained on pressed disc samples containing known amount of antimony as a function of atomic ratio of Sb to Pb.

calibration curve for analysis of antimony content in lead dioxide films.

In corrosion films, not only PbO_2 but also PbSO_4 may coexist. It is desirable, therefore, to examine the applicability of the calibration curve obtained to mixed phases of PbO_2 and PbSO_4 . Results obtained for pressed mixtures of 80 wt % PbSO_4 and 20 wt % PbO_2 containing various amount of Sb_2O_3 , are also plotted in the figure with closed circles, and it was found that almost the same relation as observed for PbO_2 discs hold also in this case. These results show that the content of antimony in the corrosion films can be determined by measuring I_{rel} .

3.2. Sputter rate of Pb, α -PbO₂ and β -PbO₂

If the current efficiency for deposition of Pb [42] and β -PbO₂ [43,44] is assumed to be 100 %, and if the deposited lead film to be non-porous [42], then it is possible to estimate the film thickness, d , from the quantity of electricity used in the deposition. When the film is sputtered out by Ar⁺ beam by the amount corresponding to the film thickness, the signal intensity of PbO₂⁻ sharply fell down, by which the time when the film is sputtered out, t , can be known. The average sputter rates, which is determined as values of d/t are given in Table 3.

As shown in Table 3, the sputter rate of the electrodeposited Pb was larger than that of the electrodeposited PbO₂. The mass sputtered per unit area per unit time, ng/sec cm², is also given in this table, which was need not to employ the assumption that the porosity of electrodeposited film was zero. Since oxides resist sputtering in a significant extent compared to the corresponding metals [45], it is thought that the difference in the sputter rates between Pb and PbO₂ is reasonable.

Table 3 Sputter rate of samples formed by electroplating on Pt

	Preparation condition of samples			Sputter rate	
	Current density (mA/cm ²)	Charge passed (C)	Film thickness (μ m)	(nm/sec)	(ng/sec cm ²)
Pb	10	4.2	5.8	3.8	43
	5	2.6	5.8	3.7	42
α -PbO ₂	1	0.57	1.19	0.90	8.4
	0.5	0.49	1.19	1.01	9.5
β -PbO ₂	2	1.15	2.38	0.95	8.9
	1	1.15	2.38	1.05	9.8
	0.5	0.58	1.19	1.23	11.5

3.3. In-depth analysis of antimony in the corrosion film formed by means of multi-triangular voltammetry

For preparation of samples, the lead-antimony electrode was anodized in 5M H_2SO_4 with a potential sweep method at 1 mV/sec for 50 times in the potential range between 0.90 and 1.65 V, and then held at 1.60 V for 30 min (sample 1), 1.38 V for 30 min (sample 2) or 1.12 V for 15 min (sample 3). At the respective potential selected, the followings were believed to have taken place, and confirmed by X-ray diffraction analysis on the prepared samples. The oxygen evolution accompanied with complete oxidation of the film to $\beta\text{-PbO}_2$ for the sample 1, complete oxidation to $\beta\text{-PbO}_2$ for sample 2 and reduction of $\beta\text{-PbO}_2$ to PbSO_4 for the sample 3. Each sample was rinsed with de-ionized water for a few seconds and then dried under reduced pressure (in a few torr).

Figure 17 shows typical signal intensity profiles of SbO_2^- , O^- and PbO_2^- as a function of sputtering time for sample 1.

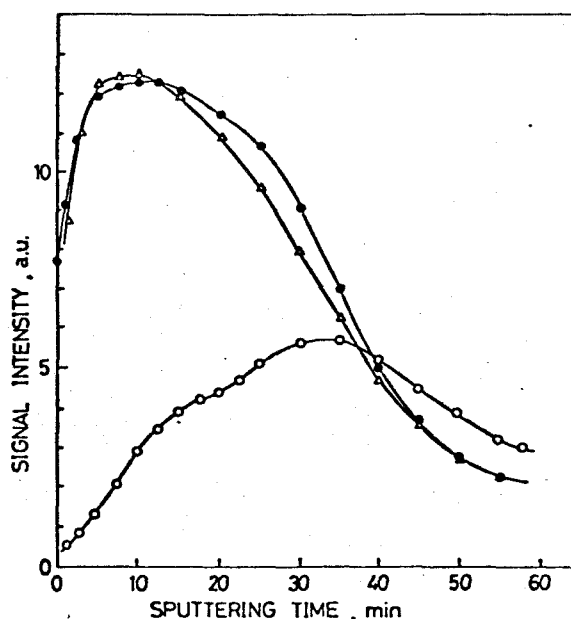


Fig.17. In-depth profiles of $^{121}\text{SbO}_2^-$ (O), $^{208}\text{PbO}_2^-$ (Δ) and $^{16}\text{O}^-$ ($\bullet$) in a corrosion film on the Pb-Sb alloy. See text for the preparation of the film.

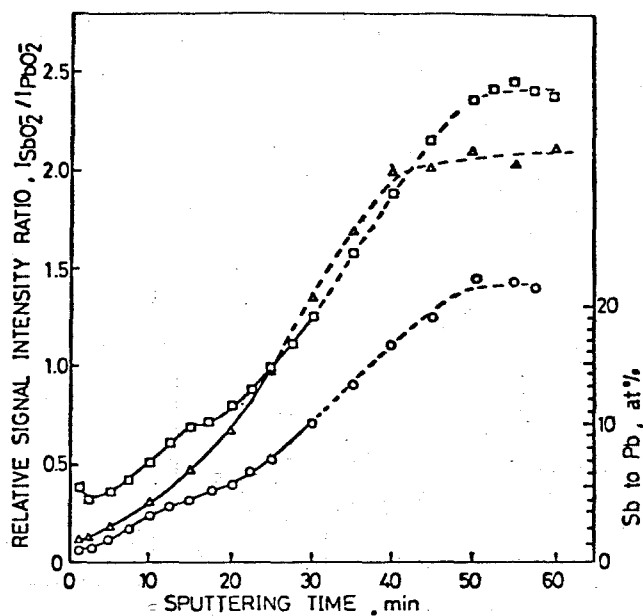


Fig.18. I_{rel} as a function of sputtering time for samples prepared at different final polarization potential;
 ○: 1.60 V, △: 1.38 V, □: 1.12 V.
 The solid lines show the regions of the corrosion layer.

Figure 18 gives I_{rel} as a function of the sputtering time for this sample together with the results for the other two kinds of samples. It is noticed that I_{rel} gradually increased with the sputtering time, that is, with an increase in the depth of the corrosion film. The solid lines in the figure, the ends of which were equal to the sputtering time giving the maximum signal intensity of SbO_2^- , $I_{SbO_2^-}$, as shown in Fig.17, are believed to give information on the corrosion films by the following reasons, although beyond that point monotonic increases in I_{rel} were still noticed with sputtering time. First, it was found by microscopic observation during the sputtering that the substrate alloy surface appeared almost at the time when $I_{SbO_2^-}$ reached its maximum. Second, the signal intensity of PbO_2^- , $I_{PbO_2^-}$, was found to depend on the partial pressure of oxygen over the lead-antimony alloy, as Fig.19 shows. In the sputtering

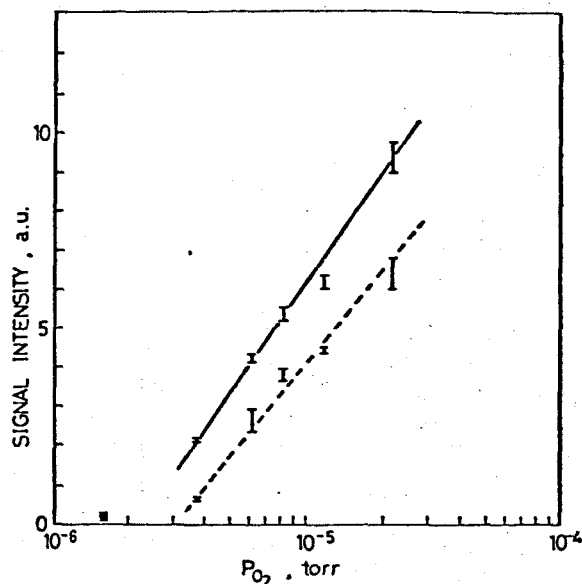


Fig.19. Signal intensity of $^{121}SbO_2^-$ and $^{208}PbO_2^-$ emerged from the Pb-Sb alloy (4.92 wt%) as a function of oxygen pressure over the sample surface.
 — : SbO_2^- (X1), - - - - : PbO_2^- (X10)

process for the corrosion film, neutral oxygen molecules as well as charged species must be produced from the oxide surface [31]. The maximum oxygen pressure over the sample surface will be attained when the Ar^+ beam reaches the substrate face, because the surface area of the crater in the corrosion film produced by sputtering is the largest at this point. Therefore at this stage the maximum $I_{SbO_2^-}$ will be obtained.

I_{rel} was converted into antimony content by using the calibration curve shown in Fig.16. The antimony content in the film at the film-substrate interface, was almost twice the antimony content in the substrate alloy, 8.81 at %. This result may indicate that dissolved antimony is accumulated in a corrosion film-substrate interface region [33].

If the solid lines in Fig.18 represent the distribution profiles of antimony in the sample films, then the author have to explain why the increasing trend in I_{rel} still continues after

the beam reached the substrate alloy. For this purpose, the author needs knowledges on morphorogy of the corrosion film. Presumably the corrosion film will not have the same thickness throughout the analyzing position. It has pores in it, and consists of aggregated particles of lead dioxide and sulfate [46, 47]. Furthermore, the substrate surface was not completely smooth. Therefore, it will be expectable that when the Ar^+ beam reached the top of the substrate, some position of the film still remains on the substrate. Further continuation of sputtering will then sputter the remaining film and the substrate. It can be noticed in Fig.19 that $I_{\text{SbO}_2^-}$ is much higher than $I_{\text{PbO}_2^-}$ when the substrate alloy is sputtered. Therefore, the contribution of the secondary ions from the substrate alloy must became prominent when the sputtering proceeds from the top of the substrate to its interior. After the corrosion film is completely sputtered out, eventually no change will occur in I_{rel} .

The above mentioned arguments closely relates also to resolution of the primary ion beam of IMA. The information on the beam resolution was obtained from the in-depth analysis of O^- and Ta^+ for an anodic film on tantalum. The in-depth profiles of O^- obtained is presented in Fig.20. By comparing the time giving a gradual signal drop, t_1 , to that required for sputtering out the film, t_2 , it was recognized that such a beam resolution as usually utilized in the in-depth analysis was attained in the present study.

The results presented in Fig.18 shows that the antimony content monotonically decreased in the film from the interior to the outer portion, independently of the final polarization

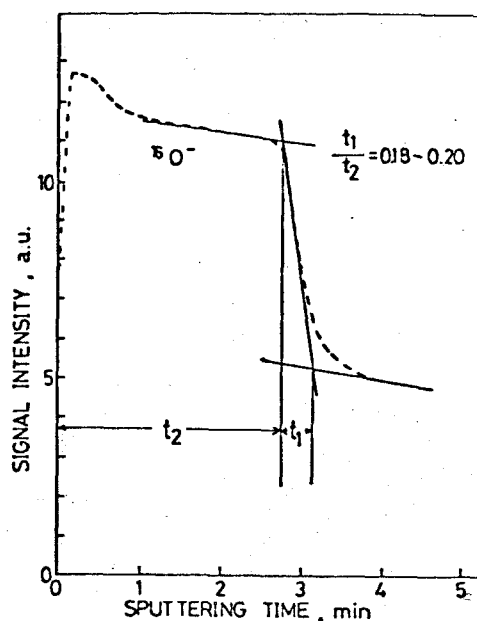


Fig.20. Intensity profile of the secondary ion $^{16}\text{O}^-$ as a function of the depth of an anodic oxide film on tantalum (50 nm thick).

potential chosen in the preparation of samples. Judging from the results on the sputter rates shown in Table 3, the thickness of the samples was around $1.8\ \mu\text{m}$. According to a model proposed by Dawson et al. on antimony transference in charge-discharge cycles [36], a large part of dissolved antimony adsorbs on PbO_2 , and the adsorbed antimony is released into electrolyte during the discharge. If the results on distribution profile of antimony reflect such an antimony transference, then the profile should greatly be different between the sample 1 and 3. However, the results did not satisfy this expectation.

The main cause responsible for this contradiction seemed to lie in that the samples were little washed before measurements of SIMS. The washing for only a few seconds will not remove completely the electrolyte held in pores of the corrosion film, so that antimony dissolved in this portion of electrolyte also contributes the distribution profiles obtained.

In order to test whether this view is valid or not, washing of the samples in an ultrasonic bath was tried for a fixed period of time before being mounted on a sample holder for the secondary ion mass spectrometry. The results obtained on these samples (Fig.21), however, showed that the washing for 60 min both in doubly distilled water and in 5M H_2SO_4 gave almost the same distribution profiles as in the case of 6 min washing and that the distribution profiles were eventually not influenced by the washing. Therefore, it is concluded that the corrosion films prepared by the potential sweep polarization at 1 mV/sec in the potential range between 0.90 and 1.65 V contained dissolved antimony which was tightly fixed to the corrosion film. This conclusion may be at least partly connected to the suggestion made by Richie et al. [48] that dissolved Sb^{5+} ions might occupy vacant Pb^{4+} octahedral sites in the PbO_2 lattice and also to formation of lead metaantimonate [49].

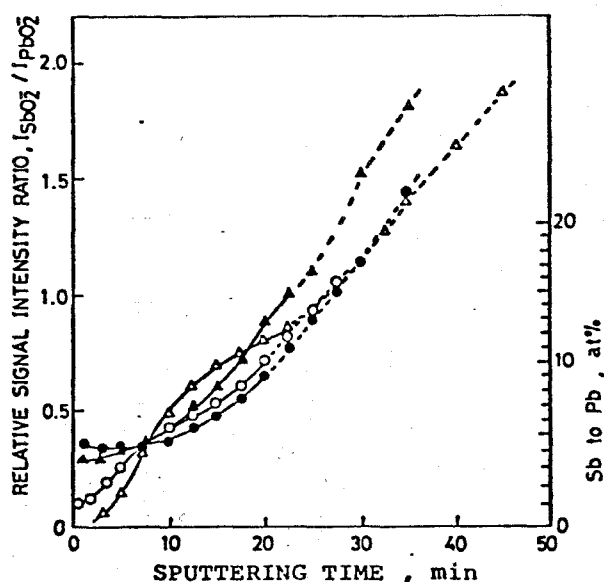


Fig.21. Effect of washing in an ultrasonic bath on distribution profiles of antimony in the film. The sample was prepared in the same manner as that in Fig.16.

O: 6 min in H_2O Δ : 6 min in 5M H_2SO_4
 ●: 60 min in H_2O $\blacktriangle$: 60 min in 5M H_2SO_4

CHAPTER 4

THE DISTRIBUTION OF ANTIMONY IN THE OXIDE LAYER FORMED BY POTENTIOSTATIC OXIDATION OF Pb-Sb ALLOY

1. INTRODUCTION

In a previous chapter, the author investigated the macroscopic distribution profiles of antimony in oxide films on a lead-antimony alloy, and revealed that the distribution profile was almost the same independent of the final polarization potential chosen for preparation of the films; the films were prepared by multi-triangular potential sweeps. The results obtained, however, showed that it was impossible to get information on the dissolution behavior of antimony from the well-grown oxide films of the alloy.

In this chapter, the distribution of antimony as a function of depth was obtained for films formed during the initial stages of potentiostatic oxidation of a lead-antimony alloy. In the potentiostatic oxidation of the alloy, lead dioxide crystals will be formed in several successive steps such as dissolution of the alloy, nucleation, two or three dimensional growth of the crystals [50-54]. Fortunately, one can distinguish these steps from the shape of the current-time curves obtained during the oxidation period. In this chapter, therefore, the main objective

was to correlate the distribution profiles with the individual step of the potentiostatic oxidation. Although it was already revealed [34,55] that the content of antimony in the alloy influences the dissolution behavior of antimony as well as the oxidation behavior of lead, the present study was conducted on an alloy of fixed antimony content.

2. EXPERIMENTAL

The preparation of lead-antimony electrodes was described in the previous chapter. During potentiostatic oxidation of the alloy, current-time curves were recorded, and the charge passed was evaluated from these transients. Samples prepared by potentiostatic oxidation were washed with distilled water for several seconds and then subjected to the in-depth analysis of antimony by using an ion microanalyzer. A mercurous sulfate electrode in 5M H_2SO_4 was used as the reference electrode.

3. RESULTS

The current-time curves for the Pb-Sb alloy in 5M H_2SO_4 obtained during potentiostatic oxidation are shown in Fig.22. These curves are similar to those obtained in 4.5M H_2SO_4 by Sharpe [55].

The in-depth analysis of the resulting films show that the film thickness was almost constant and independent of the charge passed if the film was prepared at potentials less positive than 1.5 V. However, if the oxidation was carried out more positive

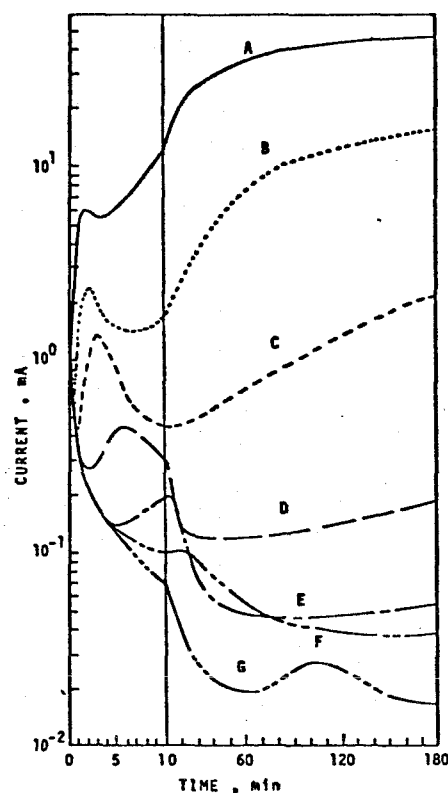


Fig.22. Current-time curves during potentiostatic oxidation of Pb-Sb alloy in 5M H_2SO_4 for 3 hr. A : 1.65 V, B : 1.60 V, C : 1.55V, D : 1.50 V, E : 1.45 V, F : 1.40 V, G : 1.30 V

to this potential, the film thickness was proportional to the charge passed. These results are given in Fig.23. The abscissa of this figure is a measure of the film thickness. On the basis of the results shown in Fig.23, the author tentatively classified the oxidation film prepared at various potentials into two groups and denoted here as the (A) and (B) groups. The film prepared at potentials less than 1.5 V belong to the (A) group, and those prepared at potentials more positive than 1.55V belong to the (B) group. The classification into these two groups was already suggested by Sharpe [55]. The results in Fig.23 seemed to be in agreement with those obtained by weight loss experiments during potentiostatic oxidation [56].

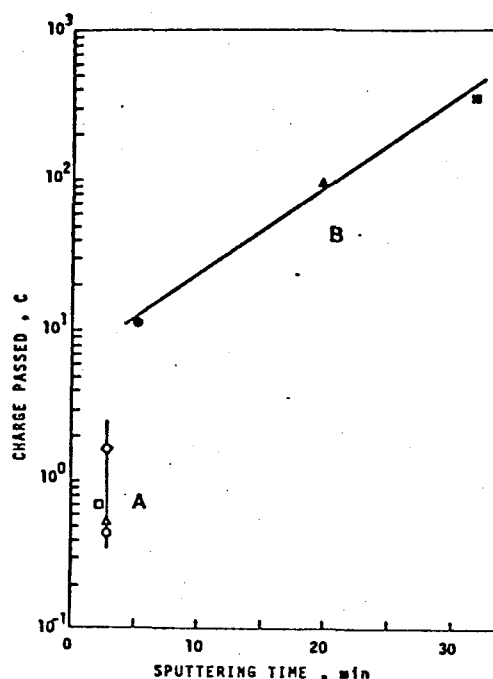


Fig.23. Relation between charge consumed in preparation of oxide film and time required for sputtering out the prepared film.
 ○: 1.30V, △: 1.40V, □: 1.45V, ◇: 1.50V
 ●: 1.55V, ▲: 1.60V, ■: 1.65V

Figures 24 and 25 show signal intensity ratios I_{rel} (SbO_2^- to PbO_2^-) as a function of sputtering time, for the two groups of films. The solid lines in the figures show the regions where a corrosion layer is observed (see the previous chapter). It is seen by comparing Fig.24 with Fig.25 that the distribution profiles are quite different for the (A) and for the (B) group. The relation between I_{rel} and sputtering time (i.e. film thickness) shows a distinct minimum for the (A) group, but a simple increasing trend for the (B) group. Furthermore, I_{rel} is larger for the (A) than for the (B).

In the previous paper, I_{rel} was converted into antimony content in the film by using a calibration curve between I_{rel} and antimony content. When this calibration curve was applied to the present results, however, very high antimony contents were

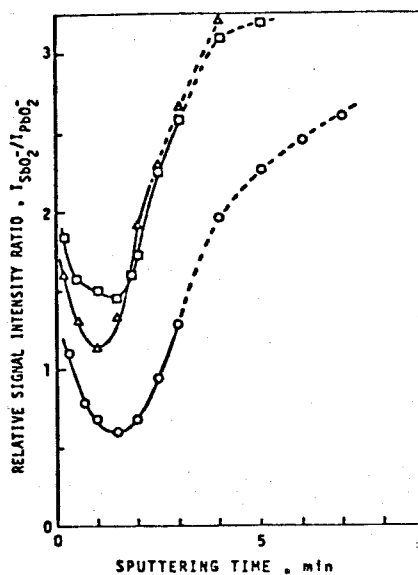


Fig.24. In-depth profiles of relative signal intensity ratio, $I_{\text{SbO}_2^-}/I_{\text{PbO}_2^-}$, as a function of sputtering time for films obtained by potentiostatic oxidation.
 O: 1.30 V, Δ: 1.45 V, □: 1.50 V
 The solid lines show the regions of the corrosion layer.

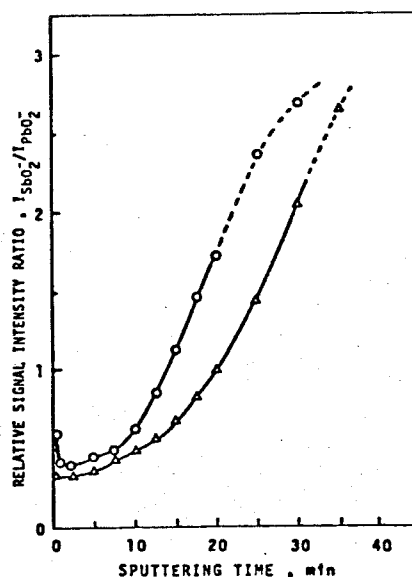


Fig.25. In-depth profiles of relative signal intensity ratio, $I_{\text{SbO}_2^-}/I_{\text{PbO}_2^-}$, as a function of sputtering time for films obtained by potentiostatic oxidation.
 O: 1.60 V, Δ: 1.65 V

obtained. The author therefore feel that the nature of the oxide film is different. In view of this, I_{rel} is used throughout this chapter only as a measure of the relative antimony contents in the corrosion film.

In order to study the dissolution behavior of antimony in the initial stages of the anodic oxidation of the alloy, distribution profiles for antimony were obtained for samples prepared by stopping the oxidation at the times shown with arrows in the current-time curve in Fig.26. The phenomenon occurring in the each oxidation step has already been studied by other investigators [51-53]. The films prepared at 1.5 and 1.6 V were chosen as representatives of the (A) and (B) groups, respectively, and the results are given in Figs.27 and 28. The following may be noted in Fig.27. (a) step 1; I_{rel} decreased linearly from the alloy substate to the surface of the film. (b) steps 2 to 4; I_{rel} shows plateaus and the location of the plateau moves towards the interior with further oxidation. In the surface region,

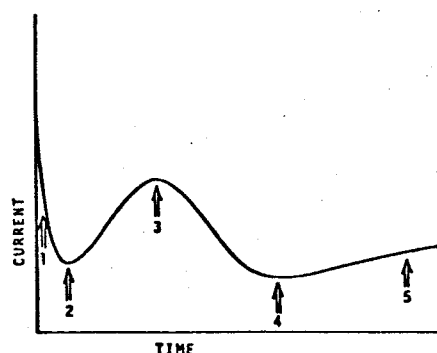


Fig.26. Schematic representation of the current-time curve for anodic oxidation under a potentiostatic control. The arrows indicate five oxidation steps at which specimens were prepared.

I_{rel} increased linearly with depth. (c) step 5; the dependency of I_{rel} on the depth becomes less defined, and I_{rel} began to show only a slight increase with depth. In Fig.28, slightly different results are noticed for steps 2 and 3. Almost linear dependencies on the depth are seen during stages in the oxidation.

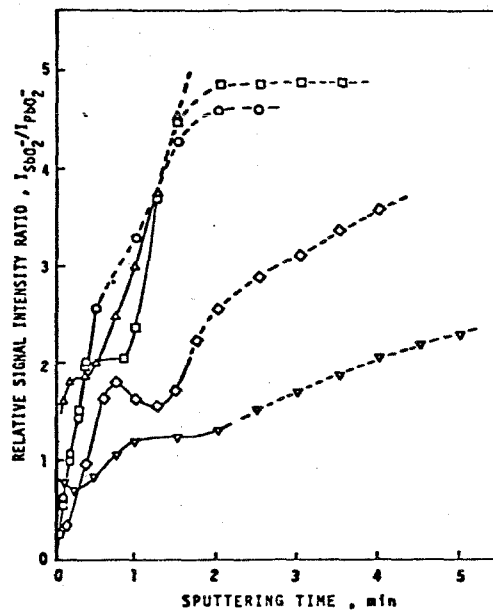


Fig.27. In-depth profiles of relative signal intensity ratio, $I_{SbO_2^-}/I_{PbO_2^-}$, as a function of sputtering time for films formed at oxidation steps denoted in Fig.26 for the 1.5 V oxidation case.
O: 1 , Δ: 2 , □: 3 , ◇: 4 , ▽: 5

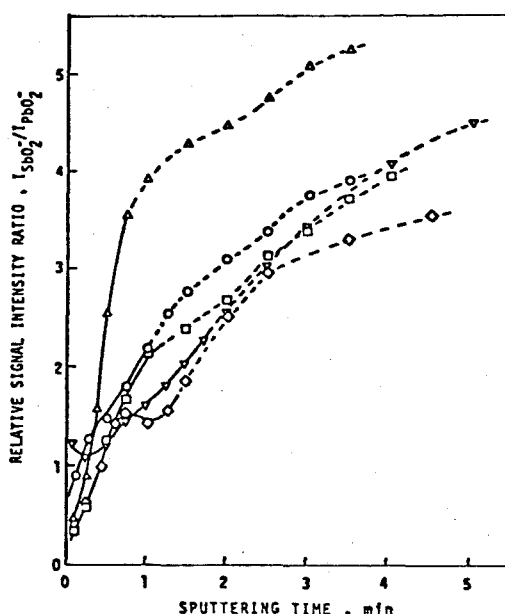


Fig.28. In-depth profiles of relative signal intensity ratio, $I_{SbO_2^-}/I_{PbO_2^-}$, as a function of sputtering time for films formed at oxidation steps denoted in Fig.26 for the 1.6 V oxidation case.

o: 1 , Δ: 2 , □: 3 , ◇: 4 , ▽: 5

4. DISCUSSION

When the oxidation is promoted, the profiles change from the top to the last profiles. In order to understand such changes, it seems appropriate to assume the existence of at least three electrochemical processes in the course of dissolution of antimony into the electrolyte;

- (1) ionization of antimony at the alloy-film interface. At this interface, the ionization of lead also occurs.
- (2) migration of antimony in the film.
- (3) dissolution of antimony from the oxide film region into the bulk electrolyte.

The author have no definite images on the processes 2 and 3, but the profiles obtained seems to be understandable of the existence of those processes are temporarily assumed. If the relative rate constant of the individual process is denoted as k_1 , k_2 and k_3 , the each profile in Fig.29 will be obtained depending on the relative magnitude of the hypothetical rate constants, which are also given in the figure.

The step 1 concerns with dissolution and precipitation of lead, and the profile obtained suggests that the rate of dissolution into the electrolyte bulk, k_3 , is larger than the dissolution rate of antimony from the alloy, k_1 . This trend holds for films prepared at both 1.5 and 1.6 V. During steps 2 and 3 the oxidation proceeds (i.e. nucleation and two and three dimensional growth of PbO_2 crystals occur), k_3 becomes relatively small compared to k_1 and k_2 the bulk migration rate constant. In the film prepared at 1.5 V the accumulation of antimony in the film takes place, and I_{rel} becomes independent

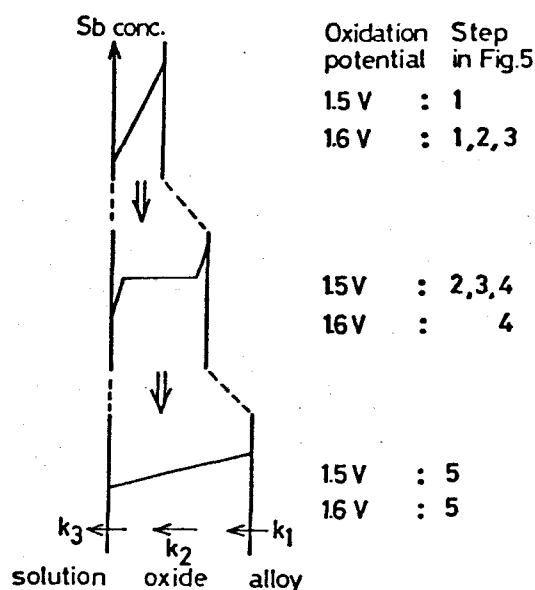


Fig.29. Classification of obtained profiles into three schematic representations.

of charge. The decrease of k_3 compared to k_1 and k_2 may reflect the situation that dissolved antimony strongly interacts with oxidized lead.

In the case of the film prepared at 1.6 V, however, the situation is different. The distribution profiles are understandable if k_1 and k_3 are larger than k_2 . Certainly k_1 is expected to be larger at high this applied potential. With the film formed at 1.5 V, k_3 was thought to be the smallest as described above. Therefore, the question arises as to why k_3 is now large. A plausible answer to this question may be as follows. According to the current-time traces in Fig.22, the lower the oxidation potential, the longer time is required to reach step 2. The charge passed before the current-time traces show step 2 to be reached was also high for the lower oxidation potentials as shown in Table 4. The formation of Pb^{4+} must pass through Pb^{2+} , Pb^{2+} is more stable at the 1.5 V oxidation than the 1.6 V case. Therefore, in the former case, there is more chance for the formation of complex Pb(II) oxides containing antimony for example as lead metaantimonate [49]. k_3 then refers to the dissolution of antimony from the complexed oxides. At 1.6 V, the life of the Pb^{2+} may be too short for the complexed oxides to be formed, so that dissolved antimony behaves freely as if there is no interaction with PbO_2 crystals; k_3 would then be large.

The significance of the appearance of the plateau in the

Table 4 Charge passed up to the oxidation step 2 in the Current-time curves of Fig.22

Applied potential (V)	1.30	1.40	1.45	1.50	1.55	1.60	1.65
Charge passed (C)	0.15	0.16	0.05	0.07	0.05	0.03	0.02

I_{rel} - charge curves during step 4, observed at both 1.5 and 1.6 V, will be different from that in the steps 2 and 3. In step 4, the alloy has just become completely covered by lateral overlaps of three dimensionally grown PbO_2 crystals. If antimony is anodically dissolved underneath the PbO_2 crystals in the course of the steps 3 to 4, it cannot directly dissolve into the electrolyte. The PbO_2 crystals blocks the dissolution into the electrolyte. Thus k_3 decreased, and antimony accumulation in the films causing the appearance of the plateau.

During step 5, the oxidation is leading to a thick film. In this process, the migration of antimony is the lowest of the three steps. Therefore a monotonic gradient of antimony appears.

Hence, the distribution profiles in Fig.25 seems to be reasonable. The results shown in Fig.24, however, are quite different from those expected during step 5 of the oxidation at 1.5 V. If k_3 is small and antimony will accumulate in the film surface region and the observed profiles will be observed. At present the author can give no definite explanation to the observed behavior, but the profiles may be caused because the removal of antimony only occurs from dense oxide films when the film growth continues. According to current-time traces of Fig.22, the charge passed in the 3 hr oxidation was dependent on the potential chosen, but the film thickness was not greatly different when the potential was below 1.5 V (as judged from the in-depth analysis of the films). This phenomenon implies that the film formation was complicated in the early stages of the 3 hr oxidation. At the 1 hr the current fell down to an almost constant value. Further polarization only leads to oxygen

evolution and rearrangement of the ionic configuration of the film, which brings about the accumulation of antimony in the surface region.

It is well known that the presence of antimony in the electrolyte influences the morphology of PbO_2 crystals [48,57]. Antimony must have some role in the crystalization step (steps 2 and 3). According to the distribution profiles obtained during these steps, more antimony is retained in the oxide films prepared at 1.5 V than that at 1.6 V. In the former oxides, the plateau appeared. Therefore, the effects of antimony will be more evident during the oxidation at 1.5 V than 1.6 V.

CONCLUSION

The author carried out the studies on the anodic oxide films of tantalum and lead-antimony alloy by employing the SIMS technique. The results obtained are summarized as follows.

1. Sulfur, chlorine, fluorine and phosphorus were incorporated from the electrolytes into the tantalum oxide films during the anodization. The incorporation depth of sulfur was dependent on the forming current density. The sputter of the film was influenced by the degree of incorporation of sulfur.
2. The impurity elements incorporated in the tantalum anodic oxide films changed their distribution profiles at the dielectric breakdown, reflecting the nature of these ions.
3. The incorporated phosphorus as a mass marker in the tantalum anodic oxide film is mobile and the migration rate of it is high for a high oxidation current density.
4. In-depth distribution profiles of dissolved antimony were analyzed for the corrosion films prepared by multi-triangular potential scans of the Pb-Sb alloy in 5M H_2SO_4 . A monotonically increasing trend in the content from the surface of the corrosion film to the lead alloy substrate was found independently of the final polarization potential chosen in the potential scan.
5. In the potentiostatic oxidation of Pb-Sb alloy in 5M H_2SO_4 , the effects of potential was grouped into two classes; the case of more negative than 1.5 V and of more positive than this

potential. Antimony dissolved from the alloy was retained in the oxide film in the steps of nucleation and two and three dimensional growth of PbO_2 for the case of the 1.5 V oxidation, and for 1.6 V the retention was observed in the lateral overlaps of three dimensional centers of PbO_2 . It is suggested that the dissolved antimony affect the nucleation of the lead oxide formation in the moderate charging of the positive plates of lead-acid batteries.

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REFERENCES

- 1) R. E. Pawel, J. P. Pemsler and C. A. Evans, Jr., J. Electrochem. Soc., 119, 24 (1972).
- 2) C. A. Evans, Jr. and J. P. Pemsler, Anal. Chem., 42, 1060 (1970).
- 3) L. Young, " Anodic Oxide Films ", Academic Press, New York (1961).
- 4) D. A. Vermilyea, Acta Met., 2, 482 (1954).
- 5) J. J. Randall, Jr., W. J. Bernard and R. R. Wilkinson, Electrochim. Acta, 10, 183 (1965).
- 6) H. Kihara-Morishita, T. Takeda and T. Takamura, Denki Kagaku 39, 417 (1971).
- 7) D. A. Vermilyea, J. Electrochem. Soc., 112, 1232 (1965).
- 8) D. A. Vermilyea, Acta Met., 1, 282 (1953).
- 9) H. Yoneyama and H. Tamura, Bull. Chem. Soc. Japan, 45, 3048 (1972).
- 10) I. Omura, Bunko Kenkyu, 19, 251 (1970).
- 11) H. Tamura, S. Yamamoto and T. Kondo, Shinku, 14, 42 (1971).
- 12) H. Tamura, Nippon Kinzoku Gakkai Kaiho, 11, 813 (1972).
- 13) H. Tamura, T. Kondo and T. Hirano, " Proc. 6th Intern. Conf. on X-ray Optics and Microanalysis " Eds. G. Shinoda, K. Kohra and T. Ishinokawa, Univ. of Tokyo Press, Tokyo (1972) p423.
- 14) G. Amsel, C. Cherki, G. Feuillade and J. P. Nadai, J. Phys. Chem. Solids, 30, 2117 (1969).

- 15) L. Young, Proc. Roy. Soc. (London), A258, 496 (1960).
- 16) P. H. G. Draper, Electrochim. Acta, 8, 847 (1963).
- 17) P. H. G. Draper, Acta Met., 11, 1061 (1963).
- 18) C. J. Dell'Oca and L. Young, J. Electrochem. Soc., 117, 1548 (1970).
- 19) H. Yoneyama, K. Ochi and H. Tamura, J. Appl. Electrochem., 6, 283 (1976).
- 20) S. Toshima, I. Uchida and K. Suzuki, Denki Kagaku, 38, 676 (1970); *ibid*, 38, 681 (1970).
- 21) D. A. Vermilyea, "Advances in Electrochem. and Electrochemical Engineering", Vol.3, Chap.4, Interscience Publications, New York (1963).
- 22) H. Tamura, T. Kondo, I. Kanomata, K. Nakamura and Y. Nakajima, Japan. J. Appl. Phys., Suppl.2, Part 1 (1974) p379.
- 23) G. C. Wood and C. Pearson, Corrosion Sci., 7, 119 (1967).
- 24) T. Takamura and H. Kihara-Morishita, Denki Kagaku, 43, 219 (1975).
- 25) J. A. Davies, J. P. S. Pringle, R. L. Graham and F. Brown, J. Electrochem. Soc., 109, 999 (1962).
- 26) J. A. Davies and B. Domeij, *ibid*, 110, 849 (1963).
- 27) J. A. Davies, B. Domeij, J. P. S. Pringle and F. Brown, *ibid*, 112, 675 (1965).
- 28) J. L. Whitton, *ibid*, 115, 58 (1968).
- 29) C. J. Dell'Oca and L. Young, *ibid*, 117, 1545 (1970).
- 30) J. P. S. Pringle, *ibid*, 120, 398 (1973).
- 31) C. A. Andersen, Intern. J. Mass Spectrometry Ion Phys., 2, 61 (1969); *ibid*, 3, 412 (1970).
- 32) D. M. Cheseldine, J. Electrochem. Soc., 111, 1128 (1964).

- 33) J. Burbank, J. Electrochem. Soc., 104, 693 (1957).
- 34) T. F. Sharpe, *ibid*, 124, 168 (1977).
- 35) J. L. Dawson, J. Wilkinson and M. I. Gillibrand, J. Inorg. Nucl. Chem., 32, 501 (1970).
- 36) J. L. Dawson, M. I. Gillibrand and J. Wilkinson, Power Sources, 3, 1 (1970).
- 37) H. W. Werner and H. A. M. de Grefte, Vac. Tech., 17, 37 (1968).
- 38) A. Benninghoven, Z. Phys., 230, 403 (1970).
- 39) J. M. Morabito and R. K. Lewis, Anal. Chem., 45, 869 (1973).
- 40) F. C. Mathers, " Metal Finishing Guidebook ", Metals and Plastics Publications Inc., New Jersey (1963) p332.
- 41) S. Ikari, S. Yoshizawa and S. Okano, Denki Kagaku, 27, 552 (1959).
- 42) A. K. Graham, " Electroplating Engineering Handbook ", 3rd ed., Reinhold Publishing Company, New York (1971) p246.
- 43) W. Mindt, J. Electrochem. Soc., 116, 1076 (1969).
- 44) L. W. Higley, W. M. Dressel and E. R. Cole, Report RI 8111 (1976) Bureau of Mines, Washinton DC, USA.
- 45) R. Kelly and N. Q. Lam, " Ion Surface Interaction- Sputtering and Related Phenomena ", Gordon and Breach Sci. Publishers, London, New York, Paris (1973) p37.
- 46) J. J. Lander, J. Electrochem. Soc., 103, 1 (1956).
- 47) D. Pavlov and N. Iordanov, *ibid*, 117, 1103 (1970).
- 48) E. J. Ritchie and J. Burbank, *ibid*, 117, 299 (1970).
- 49) D. E. Swets, *ibid*, 120, 925 (1973).
- 50) P. Ruetschi and R. T. Angstadt, *ibid*, 111, 1323 (1964).

- 51) P. Casson, N. A. Hampson and K. Peters, J. Electroanal. Chem., 83, 87 (1977).
- 52) P. Casson, N. A. Hampson and K. Peters, J. Electrochem. Soc., 124, 1655 (1977).
- 53) E. M. L. Valeriotte and L. D. Gallop, ibid, 124, 370 (1977).
- 54) E. M. L. Valeriotte and L. D. Gallop, ibid, 124, 280 (1977).
- 55) T. F. Sharpe, ibid, 122, 845 (1975).
- 56) J. J. Lander, ibid, 98, 213 (1951).
- 57) J. Burbank, ibid, 111, 1112 (1964).