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≪Original≫ Frequency Characteristics of Anodic Oxide Films: Effects of Anodization·Valtage

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Abstract

Effects of anodization voltage on frequency characteristics of anodic oxide films on tantalum were analyzed based on the following impedance equations:

$$\frac{1}{C_f}=\frac{\ln\ \omega\tau_w+P\ln\frac{\tau_w}{\tau_o}}{C_o(1+P)\ln\frac{\tau_w}{\tau_o}}$$

$$\tan\ \delta_f=\omega C_f R_f=\frac{\omega\tau_w\left(\frac{\pi}{2}-\tan^{-1}\omega\tau_o\right)+P\ln\frac{\tau_w}{\tau_o}}{\omega\tau_w\left(\ln\ \omega\tau_w+P\ln\frac{\tau_w}{\tau_o}\right)}$$

Here R_f, C_f and tan δ_f are equivalent series resistance in ohm, equivalent series capacitance in farad and dielectric loss of anodic oxide films respectively Parameters P, τ_o, τ_w and Co are defined as follows:

$$P=(d-w)/w$$

$$\tau_o=\kappa\rho_o$$

$$\tau_w=\kappa\rho_w$$

$$C_o=\kappa A/d$$

where d is the thickness of oxide film, w is the diffusion layer thickness, ρ_o is the resistivity of oxide film at the interface of metal and the oxide, ρ_w is the resistivity of oxide film at intrinsic region and A is the area of the film and $\kappa=0.0885\times10^{-12}\times$dielectric constant, (in farad/cm).

It was shown that dielectric loss and frequency dependence of equivalent series capacitance decrease as anodization voltage increases. This is a consequence of the fact that the thickness of diffusion layer increases a little with increasing anodization voltage whereas the total oxide thickness is proportional to the anodization voltage.

The ngative deviation of measured values from the relation, tan $\delta_f=0.682\ \Delta C_f$, was also discussed based on the impedance equations given above. Here ΔC_f is the change in capacitance between 0.1 and 1 KHZ

요 약

아노다이징 전압이 탄탈양극산화피막의 주파수 특성에 미치는 영향을 다음 임피단스 식을 이용하여 분석하였다.

$$\frac{1}{C_f}=\frac{\ln \omega\tau_w+P\ln\frac{\tau_w}{\tau_o}}{C_o(1+P)\ln\frac{\tau_w}{\tau_o}}$$

$$\tan\delta_f=\omega C_f R_f=\frac{\omega\tau_w\left(\frac{\pi}{2}-\tan^{-1}\omega\tau_o\right)+P\ln\frac{\tau_w}{\tau_o}}{\omega\tau_w\left(\ln\omega\tau_w+P\ln\frac{\tau_w}{\tau_o}\right)}$$

여기서 R_f, C_f, $\tan\delta_f$ 는 각각 양극산화피막의 등가직렬저항, 등가직렬용량, 유전손실이다. 파라메타 P, τ_o, τ_w, C_o 는 다음과 같이 정의된다.

$$P=(d-w)/w$$

$$\tau_o=\kappa\rho_o$$

$$\tau_w=\kappa\rho_w$$

$$C_o=\kappa A/d$$

여기서 d 는 양극산화피막의 두께, ω 는 확산층의 두께, ρ_o 는 금속과산화물의 계면에서의 산화물의 비저항, ρ_w 는 양극산화피막의 진성영역에서의 비저항, A 는 양극산화피막의 면적이며, $\kappa=0.0885\times10^{-12}\times$유전상수(in farad/cm).

등가직렬용량의 주파수에따른 변화와 유전손실은 아노다이징전압이 증가함에 따라 감소하였다. 이 현상은 산화피막의 확산층의 두께가 아노다이징전압이 증가함에 따라 약간 증가하는반면 선화피막 전체두께는 아노다이징전압에 비례하여 증가한다는 사실 때문이다.

실험측정치가 $\tan\delta_f=0.682\Delta C_f$ 관계식으로부터 負로 이탈하는것을 위의 임피단스 식에 바탕을 두고 검토하였다. 여기시 ΔC_f 는 0.1과 1KHZ 사이에서의 용량변화이다

1, Introduction

Anodic oxide films on valve metals are used as a dielectric of electrolytic capacitors. The anodic oxide films have interesting properties, namly, the reciprocal of the equivalent series capacitance being proportional to the logarithm of frequency and the equivalent series resistance being proportional to the reciprocal of frequency in audio frequency range. The first attempt to understand the above-mentioned properties was made by Young[1], who accounted for them by an exponential variation in conductivity through the film. Recently, Nishitani[2] derived the equations for equivalent series resistance and capacitance by assuming that the concentration profiles of metal ions and oxygen ions are the usual diffusion layer profile, and the distribution of restivity ρ is approximated as shown in Fig. 1. All the parameters in Nishitani's equations however could not be determined. It was, therefore, not possible to test the assumptions he made.

Using the same resistivity distribution as Nishitani suggested, the present authors[3] obtained the better impedance equations under conditions of $\omega\tau_w\gg1$ and $\ln(1+\omega^2\tau_o^2)\ll1$ as follows:

$$R_f=\left(\frac{\frac{\pi}{2}-\tan^{-1}\omega\tau_o}{\omega\tau_w}+\frac{P\ln\frac{\tau_w}{\tau_o}}{(\omega\tau_w)^2}\right)\times\left[\frac{\tau_w}{C_o(1+P)\ln\frac{\tau_w}{\tau_o}}\right] \tag{1}$$

$$\frac{1}{C_f}=\frac{\ln\omega\tau_w+P\ln\frac{\tau_w}{\tau_o}}{C_o(1+P)\ln\frac{\tau_w}{\tau_o}} \tag{2}$$

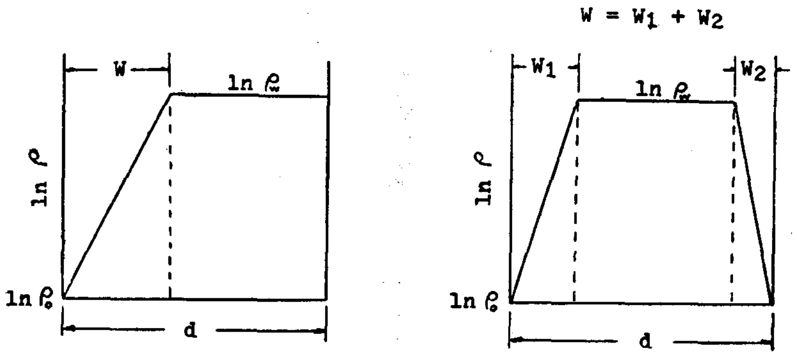

Fig. 1. The resistivity distribution in the andic oxide film.

and tan $\delta_f = \omega C_f R_f$

$$= \frac{\omega\,\tau_w\left(\frac{\pi}{2} - \tan^{-1}\omega\,\tau_o\right) + P\ln\frac{\tau_w}{\tau_o}}{\omega\,\tau_w\left(\ln\omega\,\tau_w + P\ln\frac{\tau_w}{\tau_o}\right)} \qquad (3)$$

Here R_f, C_f and tan δ_f denote properties of oxide films only whereas R_s, C_s, tanδ denote properties of oxide fillms with external resistance R_o, and ω is 2π times frequency, R and C are equivalent series capacitance, resectively. They are inter-related as given in Eqs. 4 to 6.

$$C_s = C_f \qquad (4)$$

$$R_s = R_f + R^o \qquad (5)$$

$$\tan\delta = \tan\delta_f + \omega\, C_f R_o \qquad (6)$$

Other parameters are defined in Fig. 1.

$$P = (d - w)/w$$

$$\tau_o = \kappa\rho_o$$

$$C_o = \kappa A/d$$

$$\tau_w = \kappa\rho_w$$

where A is the area of the films, and

$$\kappa = \varepsilon/(4\pi 9\times 10'') = 0.0885\times 10^{-12}\varepsilon \text{ farad/cm}$$

The dielectric constant ε is assumed constant throughout the film.

In our previous work[3] the equations were used to explain the change in impedance of anodic oxide films on tantalum when the films were heated. It was also shown that Nishitani's equations might hold only in a very limited frequency range.

In the present paper the equations are further discussed and used to explain the change in impedance of anodic oxide films on tantalum when tantalum was anodized at various voltages.

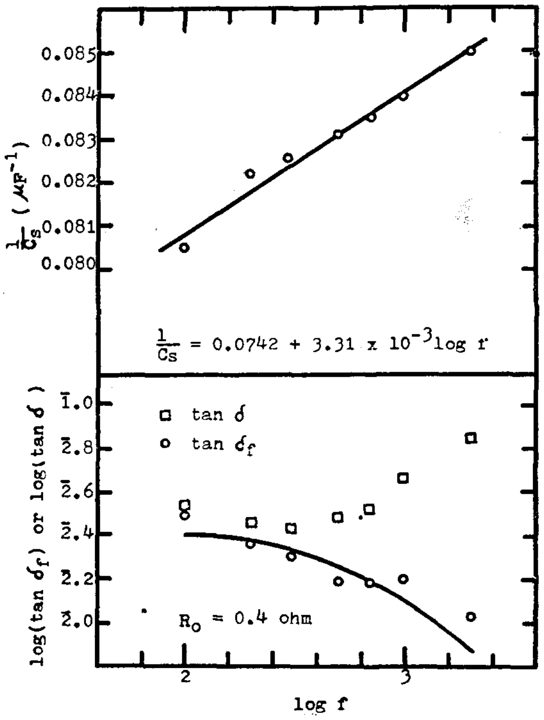

Fig. 2. Equivalent series capacitance and tanδ of a specimen anodized to 10 volts

2. Experimental Work

Specimens (2cm by 3cm) were made from Kawecki Berylco 0.0178mm thick tantalum foil of a capacitor grade. They were cut so that a 2mm tab was left attached to serve as the electrical contact. The pretreatment

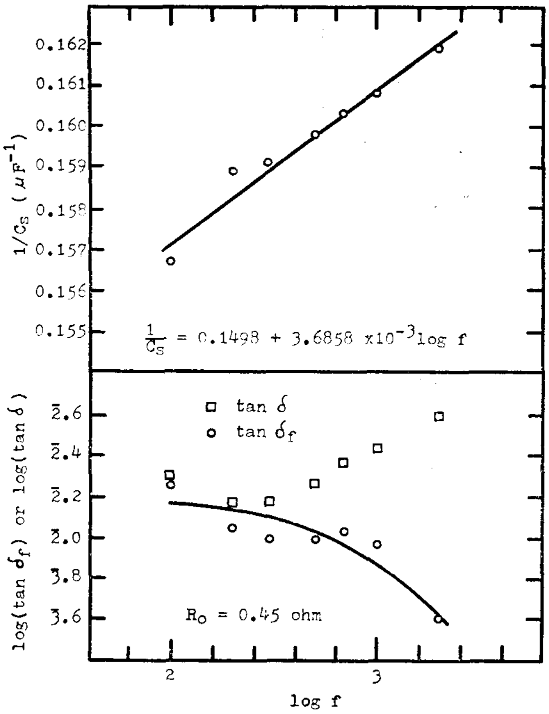

Fig. 3. Equivalent series capacitance and tan δ of a specimen anodized to 20 volts

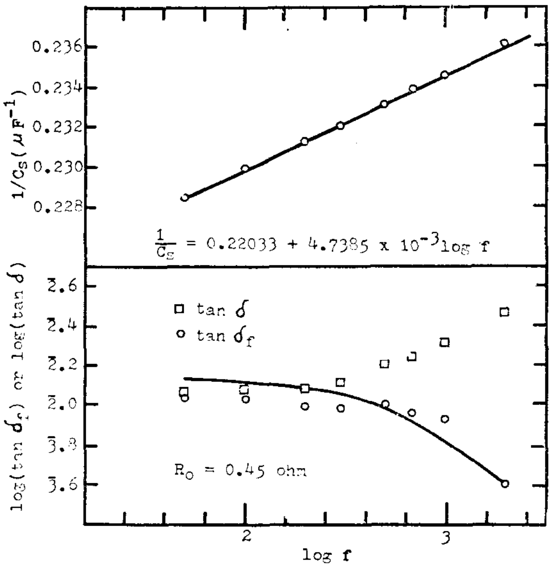

Fig. 4. Equivalent series capacitance and tan δ of a specimen anodized to 30 volts

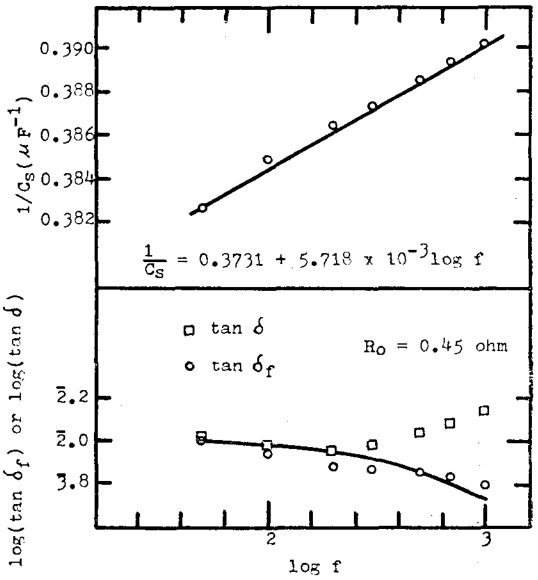

Fig. 5. Epuivalent series capacitance and tan δ of a specimen anodized to 50 volts

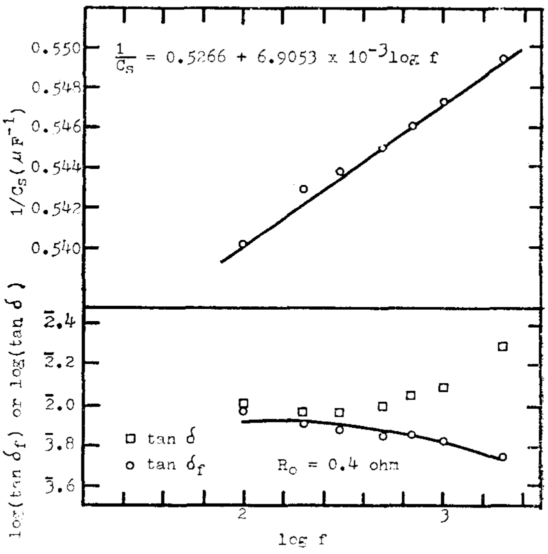

Fig. 6. Equivalent series capacitance and tan δ of a specimen anodized to 70 volts

consisted of degreasing by boiling in trichloroethylene, then air drying the specimens and after rinsing them with distilled water, immersing them in 1N nitric acid at 75°C for several minutes. This was followed by another rinse in distilled water, then absolute methanol, and finally drying them at 110°C for a few minutes.

The sample was anodized in a 0.1% phosphoric acid solution held at 90°C. The

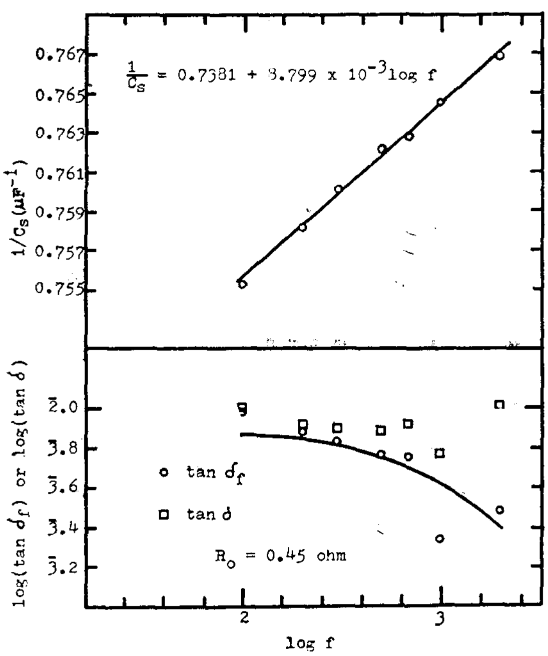

Fig. 7. Equivalent series capacitance and tan δ_f of a specimen anodized to 100 volts

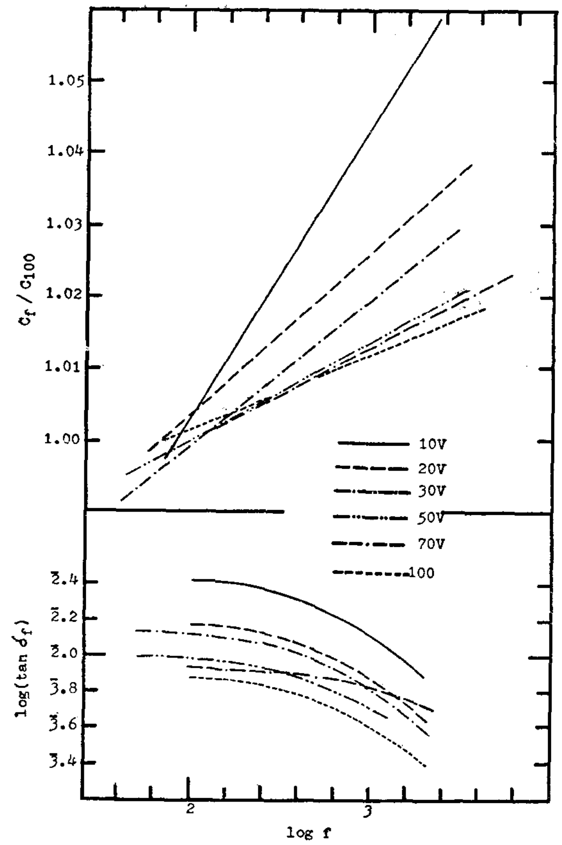

Fig. 8. Calculated equivalent series capacitance and tan δ_f of specimens anodized to voltages

voltage was increased by maintaining a constant formation current density of 0.5mA/cm^2 until a predetermined voltage was reached. The sample was then held at the formation voltage for 1 1/2hr.

Capacitance and dielectric loss measurements were made with a GR Model 1608-A impedance bridge with a GR 1310-B oscillator and a GR 1230-A tunable detector.

The bias voltage was not supplied. The measuring electrolyte was 30% sulfuric acid solution at room temperature.

3. Results and Discussion

The impedances of samples anodized at 10, 20, 30, 50, 70 and 100 volts are given in Table 1. These are plotted in Figs. 2 to 7 and analyzed with used Eqs. 2 and 3. The calculated results are summerized in Fig. 8. Before discussing experimental results in detail, it is explained how to evaluate the parameters in Eqs. 2 to 3. It can be seen from Eq. 2 that the plots of $1/C_f$ against $\log f$ are linear of which the slope is equivalent to

$$\frac{1}{C_o(1+P)\log\frac{\tau_w}{\tau_o}}(=\mathrm{SLP}) \qquad (7)$$

and the value of $1/C_f=0$ at $\log f=0$ is equivalent to

$$\frac{\log 2\pi\,\tau_w+P\log\frac{\tau_w}{\tau_o}}{C_o(1+P)\log\frac{\tau_w}{\tau_o}}(=\mathrm{ITC}) \qquad (8)$$

Hence we obtain,

$$\mathrm{ITC/SLP}=M=\log 2\pi\,\tau_w+P\log\frac{\tau_w}{\tau_o} \qquad (9)$$

Substitution of Eq. 9 into Eq. 3 gives us the expression of tan δ_f in terms of τ_w or $P\log\frac{\tau_w}{\tau_o}$ and τ_o as follows:

$$\tan\delta_f=\frac{\frac{\pi}{2}-\tan^{-1}\omega\,\tau_o}{\ln 10(M+\log f)}+\frac{P\log\frac{\tau_w}{\tau_o}}{\omega\,\tau_w(M+\log f)} \qquad (10)$$

where, from Eq. 9

$$\tau_w=\frac{1}{2\pi}10^{\left(M-P\log\frac{\tau_w}{\tau_o}\right)} \qquad (11)$$

Table 1. Impedances of specimens anodized to various anodization voltages

Anod. Voltage	f(c/s)	$C_s(\mu F)$	$\tan\delta$	$\tan\delta_f$	$1/C_s$	1/f	R_f	R_o
10	100	12.430	0.03450	0.0314	0.0805	0.0100	4.0174	0.4
	200	12.160	0.02900	0.0229	0.0822	0.0050	1.4978	
	300	12.120	0.02700	0.0179	0.0825	0.0033	0.7818	
	500	12.040	0.03065	0.0155	0.0831	0.0020	0.3103	
	700	11.980	0.03640	0.0153	0.0835	0.0014	0.2908	
	1000	11.910	0.04600	0.0161	0.0840	0.0010	0.2147	
	2000	11.770	0.07000	0.0108	0.0850	0.0005	0.0733	
20	100	6.381	0.02000	0.0182	0.1567	0.0100	4.5384	0.45
	200	6.295	0.01480	0.0112	0.1589	0.0050	1.4209	
	300	6.284	0.01500	0.0097	0.1591	0.0033	0.8164	
	500	6.258	0.01850	0.0097	0.1598	0.0020	0.4910	
	700	6.240	0.02310	0.0107	0.1603	0.0014	0.3917	
	1000	6.219	0.02700	0.0094	0.1608	0.0010	0.2410	
	2000	6.176	0.03900	0.0041	0.1619	0.0005	0.0525	
30	50	4.379	0.01150	0.0109	0.2284	0.0200	7.9094	0.45
	100	4.349	0.01190	0.0106	0.2299	0.0100	3.9049	
	200	4.325	0.01200	0.0096	0.2312	0.0050	1.7579	
	300	4.310	0.01290	0.0093	0.2320	0.0033	1.1379	
	500	4.292	0.01590	0.0098	0.2330	0.0020	0.7292	
	700	4.278	0.01750	0.0090	0.2338	0.0014	0.4801	
	1000	4.264	0.02050	0.0084	0.2345	0.0010	0.3152	
	2000	4.236	0.02800	0.0040	0.2361	0.0005	0.0760	
50	50	2.614	0.01025	0.0099	0.3826	0.0200	12.0316	0.45
	100	2.599	0.00940	0.0087	0.3848	0.0100	5.3063	
	200	2.588	0.00900	0.0075	0.3864	0.0050	2,3174	
	300	2.582	0.00945	0.0073	0.3873	0.0033	1.4917	
	500	2.574	0.01070	0.0071	0.3885	0.0020	0.8732	
	700	2.568	0.01190	0.0068	0.3894	0.0014	0.6036	
	1000	2.563	0.01350	0.0063	0.3902	0.0010	0.3883	
70	100	1.851	0.01030	0.0097	0.5402	0.0100	8.3563	0.4
	200	1.842	0.00940	0.0082	0.5429	0.0050	3.5610	
	300	1.839	0.00930	0.0076	0.5438	0.0033	2.1829	
	500	1.835	0.01000	0.0071	0.5450	0.0020	1.2347	
	700	1.831	0.01120	0.0072	0.5461	0.0014	0.8908	
	1000	1.827	0.01250	0.0068	0.5473	0.0010	0.5889	
	2000	1.820	0.01700	0.0056	0.5495	0.0005	0.2433	
100	100	1.324	0.01020	0.0098	0.7553	0.0100	11.8112	0.45
	200	1.319	0.00840	0.0077	0.7582	0.0050	4.6179	
	300	1.315	0.00798	0.0069	0.7605	0.0033	2.7694	
	500	1.312	0.00775	0.0059	0.7622	0.0020	1.4303	
	700	1.311	0.00840	0.0058	0.7628	0.0014	1.0068	
	1000	1.308	0.00585	000022	0.7645	0.0010	0.2618	
	2000	1.304	0.01040	0.0030	0.7669	0.0005	0.1847	

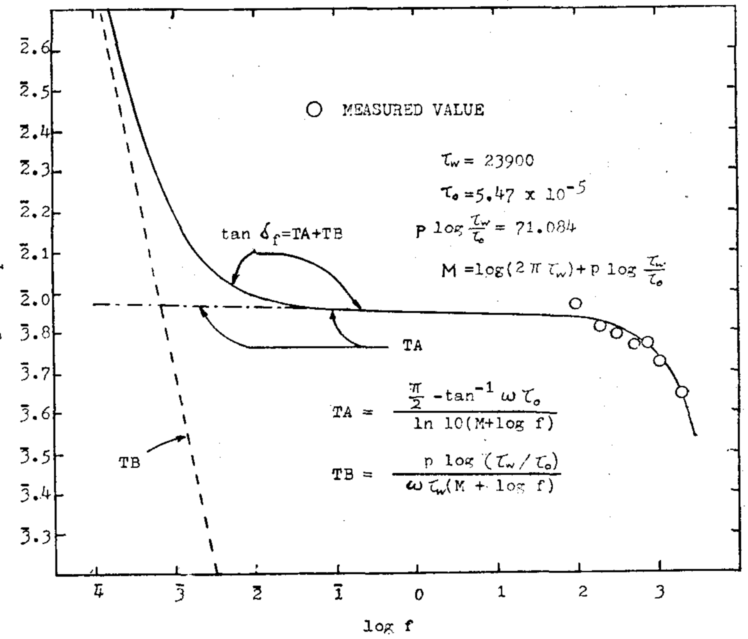

Fig. 9. Dependence of dielectric loss on frequency. It was calculated for the film anodized to 70 volts.

In principle, τ_o and $P \log \frac{\tau_w}{\tau_o}$ can be obtained by the best curve fitting of the values of $\tan\delta_f$ against frequency, since M can be evaluated from the experimental results of $1/C_f$ vs. $\log f$. Once $P \log \frac{\tau_w}{\tau_o}$ is obtained, τ_w can be evaluated using Eq. 11.

There can be the case that the contribution of the second term in Eq. 10 is negligible as compared with that of the first term within the measured frequency range as shown in Fig. 9 where the calculation was made using data for the film anodized to 70V. In this case the measured data are fitted to Eq. 12 given below to obtain the value of τ_o

$$\tan\delta_f = \frac{\frac{\pi}{2} - \tan^{-1}\omega\tau_o}{\ln 10(M + \log f)} \qquad (12)$$

The values of $P \log \frac{\tau_w}{\tau_o}$ and hence τ_w and P cannot be uniquely determined. This is the case for the experimental results shown in Fig. 2 to 7.

However, τ_w can be estimated from the resistivity of the anodic oxide films, which has been reported to be of the order of 10^{16} ohm cm[4]. Therefore, τ_w is calculated to be 23900. It is not unreasonable to assume that τ_w is insensitive to the thickness of oxide films. Setting $\tau_w = 23900$ and using the value of τ_o obtained already, other parameters were calculated and tabulated in Table 2. It is noted that Fig. 9 is comparable to Fig. 5 of ref. 7. A calculation was made for the case of $\tau_w = 30$ which is equivalent to the resistivity of oxide film being 1.23×10^{13} ohm cm. The calculated results are summerized in Table 2.

It is noted that the value of $P \log \frac{\tau_w}{\tau_o}$ is very insensitive to a change in τ_w, and other parameters also not very sensitive to a change in τ_w. It is also note worthy that the diffusion layer thickness approaches a constant value as the oxide thickness decreases as shown in Fig. 10. Even for different values

Table 2. Values of parameters defining the resistivity distribution of anodic oxide films

Anod. voltage (V)	τ_o $\times10^4$	τ_w	$\log\frac{\tau_w}{\tau_o}$	$P\log\frac{\tau_w}{\tau_o}$	P	$(1/C_o)\times10^3$ (μF^{-1})	d(Å)	w
10	1.649	30	5.26	20.081	3.82	83.8	204.5	42.5
		23900	18.792	17.180	0.914	119.2	290.5	151.8
20	1.694	30	5.25	38.378	7.32	159.6	389	46.75
		23900	18.765	35.477	1.891	199.8	488	168.2
30	1.700	30	5.25	44.223	8.43	234.4	572	60.3
		23900	18.761	41.321	2.202	284.5	694	217
50	1.450	30	5.32	62.975	11.86	391	954	74.2
		23900	18.920	60.074	3.175	452	1102	264
70	0.547	30	5.74	73.985	12.9	551.5	1343	96.6
		23900	19.895	71.084	3.573	628	1533	335.5
100	1.428	30	5.45	81.609	15.32	783	1910	117
		23900	18.936	78.708	4.157	858	2094	406.5

$\varepsilon=27.6$ and $A=12\text{cm}^2$ were used in calculation

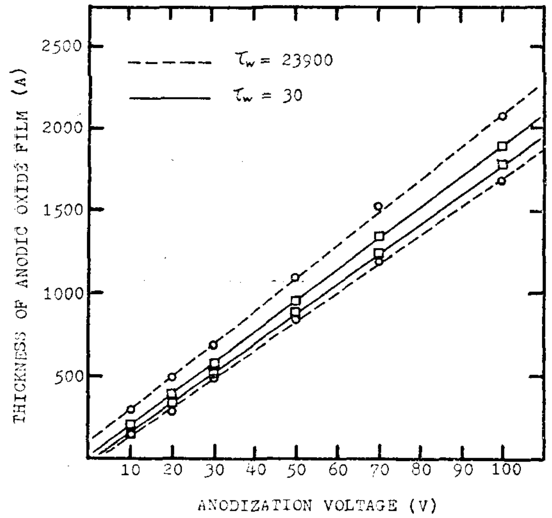

Fig. 10 Dependence of d and w on anodization voltage. The roughness factors of the oxide film is assumed to be unity. The diffusion layer thickness is the vertical distance between the upper line and the lower line.

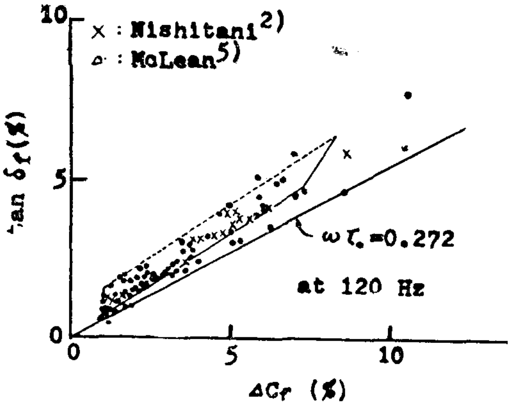

Fig. 11. Plots of $\tan\delta_f$ *vs* ΔC_f

of τ_w, the resistivity gradients at the limit thickness are the same, the resistivity change being appoximately in one order of magnitude per 8 Å distance, and the change in the depth of the diffusion layer being less sensitive to the anodization voltage than the thickness of the intrinsic region.

McLean[5)] found from his impedance measurements of solid tantalum capacitors that the capacitance variation depends on $\tan\delta_f$ as shown in Fig. 11. In this Fig. $\tan\delta_f$ is plotted against the change in capacitance between 0.1 and 1 KHZ, ΔC_f. He obtained the following relation from the least square analysis of the data in Fig. 11:

$$\tan\delta_f=0.0028+0.642\Delta C_f \qquad (13)$$

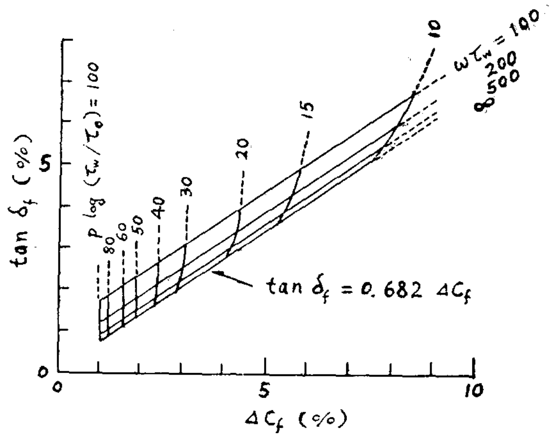

Fig. 12. Plots of tanδ_f *vs* ΔC_f(after Nishitani[2])

The theoretical basis of Eq. 13 was obtained by him from Eq. 14 derived by Young[1], and Winkel, *et al*[6]

$$\frac{1}{C_f}\frac{\partial C_f}{\partial \ln\omega} = -\frac{2}{\pi}\tan\delta_f$$

Setting $\frac{\partial C_f}{C_f} = \Delta C_f$ and $\partial \ln\omega = \Delta\ln\omega$ in the frequency range of 0.1 to 1 KHz, McLean obtained[5]

$$\tan\delta_f = 0.682\ \Delta C_f \tag{15}$$

Eq. 15 is in remarkably good agreement with the empirical Eq. 13. Similary, Nishitani[2] obtained Eq. 16

$$\frac{\tan\delta_f}{\Delta C_f} = 0.682 + \frac{P\log\frac{\tau_w}{\tau_o}}{\omega\,\tau_w} \tag{16}$$

Using Eq. 16, he could account for the positive deviation of expermimental data from the relation of Eq. 15 as shown in Fig. 12.

Starting from Eqs. 2 and 3, the following relation can be derived:

$$\frac{\tan\delta_f}{\Delta C} = 0.682 + \frac{P\log\frac{\tau_w}{\tau_o}}{\omega\tau_w} - \frac{1}{2.303}\tan^{-1}\omega\tau_o \tag{17}$$

Therefore, the negative deviation from the Eq. 15 may be attributted to the last term of Eq. 17. The lowest limit of the slope in the relation of tan δ_f vs ΔC_f in Fig. 11 can be obtained for the case of $\omega\tau_o = 0.272$ with a negligible value of the second term of Eq. 17. If $f = 120$Hz is assumed, τ_o is then evaluated to be 3.62×10^{-4} sec, which may be expected in the light of the values of τ_o in Table 2.

4. Conclusions

1) The frequency dependence of equivalent series capacitance and dielectric loss of anodic oxide films decrease with increasing anodization voltage, namely, with increasing oxide thickness.

2) The thickness of the diffusion layer increases a little with increasing anodization voltage whereas the total oxide thickness is proportional to the anodization voltage.

3) The resistivity gradient at the diffusion layer of anodic oxide films is insensitive to the resistivity value of intrinsic range and does not exceed the change in resistivity of one order of magnitude per 8 Å distance.

4) The negative deviation of measured values from the relation, tan $\delta_f = 0.682\ \Delta C_f$, can be attributed to the last term of the following relation:

$$\frac{\tan\delta_f}{\Delta C_f} = 0.682 + \frac{P\log\frac{\tau_w}{\tau_o}}{\omega\tau_w} - \frac{1}{2.303}\tan^{-1}\omega\tau_o$$

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