

Studies on AC Dielectric Properties of Anodic Oxide Films on Superpurity Aluminium From Glycol-Borate Electrolyte

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AC dielectric properties such as resistance, capacitance, loss-tangent, dielectric constant of anodic aluminium oxide films have been studied. The effects of thickness, ageing period and temperature on these properties have been investigated in electrolytic capacitors in the frequency region 0.06-10.0 kHz. The hopping dispersion mechanism of charge carriers within the dielectric is due to two or more types of polarisations under ac current field. Real and imaginary parts of the complex dielectric constant alongwith ac conductivity have been deduced from the experimental values of capacitance and loss-tangent. The magnitude of the spreading factor has been presented under the studied conditions.

The applications of high quality dielectric oxide layers in thin film capacitors, resistors, optical devices etc. have made the frequency-dependence of dielectric properties a field of major consideration in the area of thin films¹⁻⁶. Various techniques, viz. plasma anodization, thermal oxidation, chemical vapour deposition and anodic polarisation have been employed for the production of uniform oxide layers of requisite character³⁻⁷. Different mechanisms—individual relaxation processes⁶ or the narrow distribution of these processes in conduction carriers⁸—have been put forth to explain the ac dielectric properties of the oxide bulk material. But no systematic study has been reported to predict the behaviour of anodic oxide films on superpurity aluminium, so far.

Birey⁶ in his work on thermally evaporated alumina films showed unambiguously that frequency relaxation mechanism of charge carriers explains the observed dielectric behaviour of alumina layers within the experimental frequency range 0.4-15 kHz. The statistical distribution of vacancies, defects or traps within these layers, alongwith film formation conditions, has a profound effect on the ac dielectric properties of highly resistive oxide films. Their dielectric properties depend considerably upon frequency below 1.0 kHz. The present investigation has, therefore, been undertaken to study the dependence of these properties upon frequency, temperature, ageing and thickness of the anodic aluminium oxide films.

Methods and Materials

Superpurity aluminium specimens of 2 cm² in area were prepared by the method described earlier⁷. The

anodization of the specimens was carried out at 303.15 K using 30% (wt/wt) solution of ammonium hydrogen borate in ethylene glycol under constant current conditions at 1.0 mA/cm² current density. Oxide films of different thicknesses, viz. 50, 125, 315, 625 and 1125 Å were prepared⁷, washed with distilled water, dried and placed in a desiccator. Capacitance, loss-factor and resistance of these electrolytic capacitors were measured as a function of frequency at a given temperature with an accuracy of ± 0.02 K in an electrolytic cell immersed in methanol maintained at constant temperature. An LCR bridge coupled with a low distortion audio oscillator-LDO 11 (UNITEC) was utilized for this purpose. In order to see the ageing effect on these properties specimens of 750 Å thickness were kept in a desiccator under high vacuum of the order of 10^{-6} torr for different time intervals (0 to 15 days) and the properties measured, similarly.

Results and Discussion

The plots of capacitance and loss-tangent of anodized specimens as a function of frequency on log-log scale are shown in Fig. 1. The variation in the region below and above 1.0 kHz, indicates that the two properties are proportional to the function f^{-n} having different magnitudes of n for different regions. Each curve has a separate magnitude of n . Figure 2 shows the dependence of resistance of oxide film on frequency. The resistance decreases sharply in the lower frequency region and gradually in the higher frequency region. The presence of minimum and a maximum in the intermediate region—which expands as thickness increases—shows the dependence of conduction carriers on the dielectric thickness. For dielectrics of lower thickness (50, 125, 315 Å) the behaviour is almost similar, which is expected as a result of some short circuit effects in these films. While studying the effect of ageing on dielectric properties of

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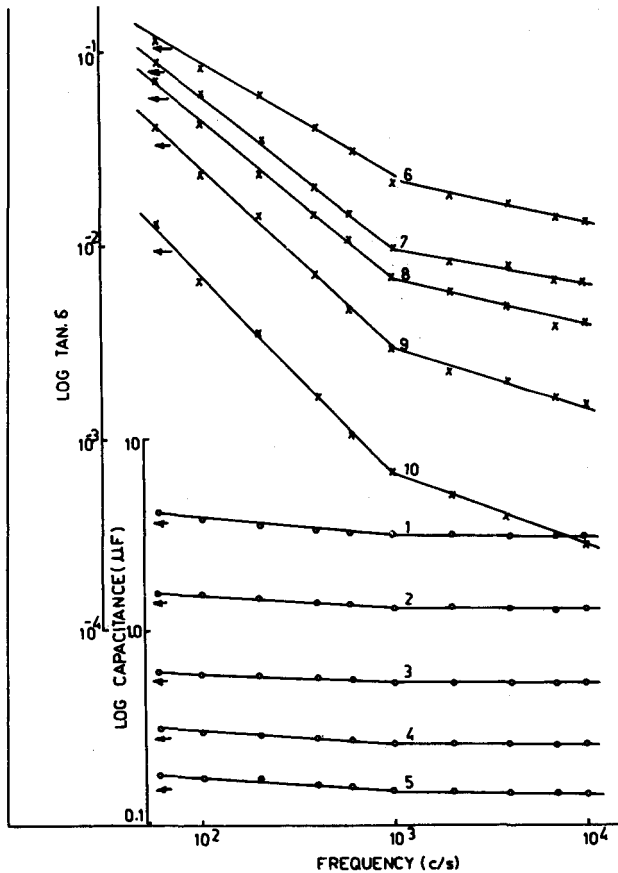


Fig. 1—Plots of log capacitance (o) and log ($\tan \delta$) (x) versus log (frequency) for aluminium oxide films of different thicknesses [1, 6 = 50; 2, 7 = 125; 3, 8 = 315; 4, 9 = 625; and 5, 10 = 1125 Å]

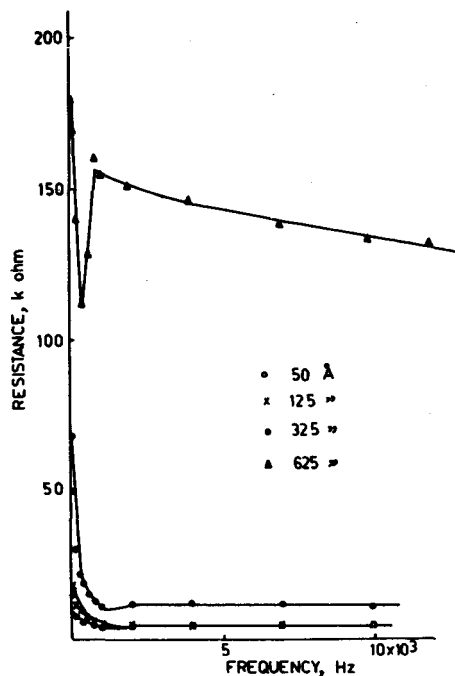


Fig. 2—Plots of resistance of oxide films of different thicknesses versus frequency

such capacitors the plots of capacitance and $\tan \delta$ versus ageing period for a given frequency are given in Fig. 3. The effect of temperature on capacitance and $\tan \delta$ (log-log scale) is shown in Fig. 4 for some chosen frequencies. The capacitance and $\tan \delta$ are proportional to T^n where T represent absolute temperature.

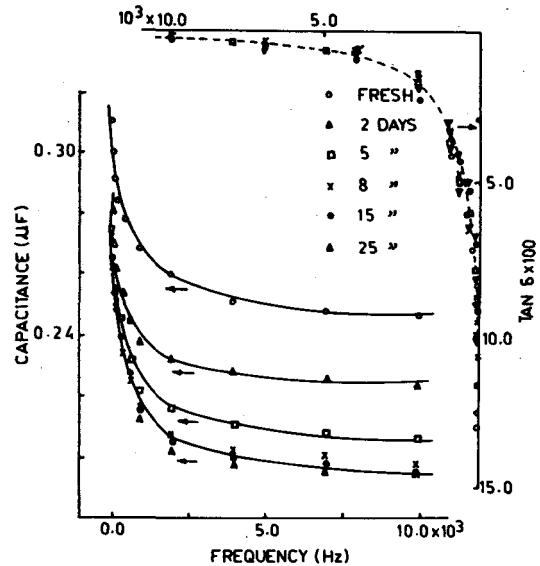


Fig. 3—Plots of capacitance (—) and $\tan \delta$ (---) versus frequency for aluminium oxide film of 750 Å thickness, aged for different time periods

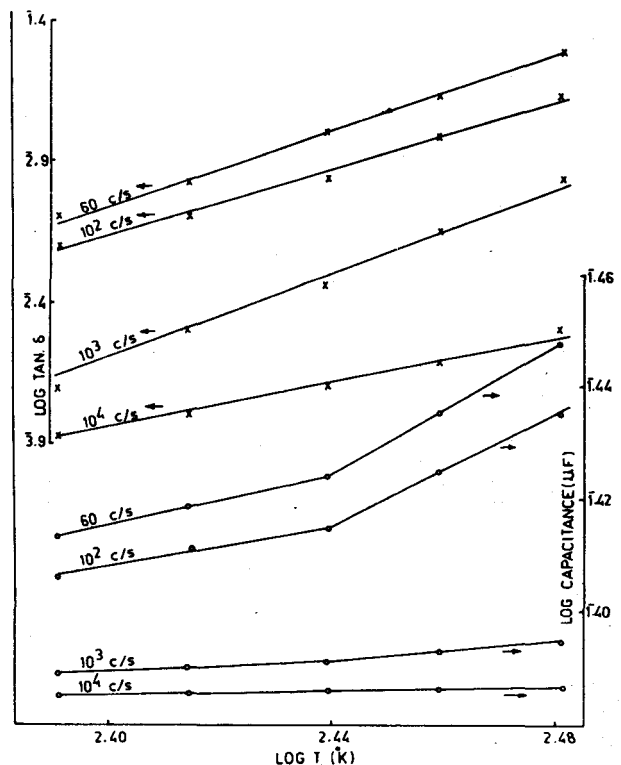


Fig. 4—Plots of log (capacitance) (o) and log ($\tan \delta$) (x) versus log (T) at different frequencies for oxide films of 730 Å thickness

For real dielectrics there exist two types of polarisations (i) an electronic process which has quick response and (ii) a process which is associated with the release of trapped charges whose response spreads over a finite time, with the applied field. The flow of current as a slow polarisation effect, in case of unit field is defined by response function α as shown in Eq. (1),

$$\alpha(t) = \frac{\epsilon_0(\epsilon_s - \epsilon_\infty)}{\tau} \cdot \exp(-t/\tau) \quad \dots(1)$$

where ϵ is the permittivity of free space (8.85×10^{-14} F/cm); ϵ_s and ϵ_∞ are static and high frequency dielectric constants, respectively; τ is the characteristic time constant and t is the response time of the current carriers in the field. This response generates a complex polarisation, according to which, the complex dielectric constant (ϵ^*) is given by Eq. (2)

$$\epsilon^* = \epsilon' - j\epsilon'' \quad \dots(2)$$

In Eq. (2) $\epsilon' (=C/C_0)$ is a real part of the complex dielectric constant in which C and C_0 are the capacitance and geometrical capacitance of the dielectric medium, respectively. C_0 can further be defined as $C_0 = \epsilon_0 A/d$, A and d are the area and thickness of the dielectric film respectively. The imaginary part of ϵ^* can be shown as $\epsilon'' = \epsilon' \tan \delta$ in which $\tan \delta$ is the dielectric loss-factor. Besides these two parameters, viz. ϵ' and ϵ'' of the dielectric medium, the electrical conductivity has also been derived using the Eq. (3)

$$\sigma_{ac} = \omega \epsilon_0 \epsilon'' \quad \dots(3)$$

In Eq. (3) $\omega = 2\pi f$ where f is an applied frequency.

Dielectric parameters for oxide films of different thicknesses at 298.15 K are calculated from the data given in Fig. 1. The real and imaginary parts of the complex dielectric constant decrease with rise in frequency. At high frequencies (≈ 10 kHz) the magnitude of ϵ' for aluminium oxide films varies from 8.4 to 9.8. The plots of ϵ' and ϵ'' versus frequency for a fresh film of 1125 Å thickness, shown in Fig. 5, indicate two dispersion regions in the given dielectric film, one above and the other below 1.0 kHz. The real dielectric constant at higher frequencies approaches to a bulk-like magnitude of aluminium oxide films, similar to that reported in literature^{6,8}. Similar plots are obtained for a sample of given thickness when aged for different time periods, at different temperatures over the studied frequency range. The decrease of ϵ' with increasing frequency may be attributed to the fact that anodized samples possess vacancies and defects or traps which increase with the increasing thickness of the dielectric⁷. The abnormal decrease in ϵ'' may be due to the presence of such layers which have high dielectric constants near oxide/electrolyte interface,

for all thicknesses of the films. AC conductivity of such dielectrics vary with changes in the defects in this dielectric region.

The effect of ageing on σ_{ac} , ϵ' and ϵ'' has been studied and these parameters are calculated from the data in Fig. 3. The observed time dependence of C is due to variation of oxide bulk thickness, in addition to a change in the dielectric constant to some extent. It is noticed that both ϵ' and ϵ'' decrease at a given frequency with increase in ageing period at room temperature for a sample of 750 Å thickness. An increase in the film thickness with ageing can be explained on the basis of oxygen untrapped in the film on the electrode, resulting in oxidation of metal and the structural reorganisation thereon. This type of behaviour may be expected due to the formation of lower hydroxide, i.e. $AlO(OH)_2$ together with higher oxides. Decrease in conductivity, which is proportional to the dielectric loss-factor, also indicates subsequent film growth on ageing (Fig. 3).

The change in these dielectric properties with frequency and then temperature dependence have been calculated from the data in Fig. 4. The temperature dependence exhibits higher dispersion in lower frequency region as compared to that in higher frequency region. At high frequency the loss-tangent and capacitance show relatively less variation, thereby providing yet another support for the observed character of the carriers. These studies reveal that there are two types of dispersion processes of carriers, at least in these two distinct regions in each film. The deviation of the plots of ϵ'' versus ϵ' for a film of 1125 Å thickness (Fig. 6) from its curvature (convex) also confirms the presence of more than one relaxation time as defined by the Debye⁹ relation. This may be due to different sets of polarisations in different frequency regions. The modified form of Debye relation, when

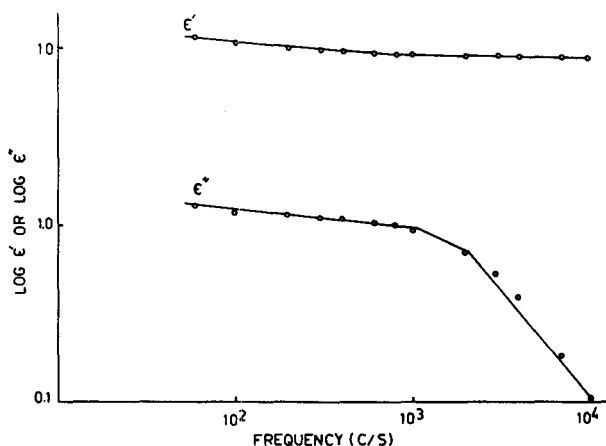


Fig. 5—Plots of $\log(\epsilon')$ and $\log(\epsilon'')$ versus $\log(f)$ for aluminium oxide film of 1125 Å thickness

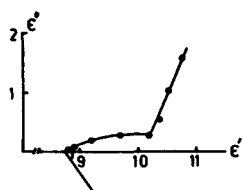


Fig. 6—Plot of imaginary dielectric constant versus real dielectric constant at different frequencies for 1125 Å thick aluminium oxide film

material has a spread of relaxation times, is given by Cole and Cole¹⁰ in the form of Eq. (4)

$$\epsilon' - i\epsilon'' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 - (i\omega\bar{\tau})^{1-k}} \quad \dots(4)$$

Table I—Values of Spreading Parameter (*k*) for Films of Different Thicknesses at Different Ageing Periods and Temperatures

Thickness (Å)	50	125	315	625	1125
<i>k</i>	0.159	0.253	0.441	0.533	0.712
Ageing period (days)	0	2	5	8	15
<i>k</i>	0.533	0.567	0.578	0.583	0.595
Temp (K)	246.0	259.7	274.4	288.4	302.8
<i>k</i>	0.633	0.622	0.600	0.567	0.533

In Eq. (4) $\bar{\tau}$ is the mean relaxation time and *k* (fractional number) is a spreading factor of the actual relaxation times above the mean value of $\bar{\tau}$. The magnitude of *k* has been worked out by extrapolating the curvature to the ϵ' -axis and finally measuring θ —the angle between the radius and the ϵ' -axis (in radians). The values of *k* thus obtained for samples of different thicknesses and under different conditions are given in Table I. The spreading factor *k* increases with increase in ageing period, oxide thickness and decrease in temperature.

Acknowledgement

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