LOW FREQUENCY CHARACTERISTICS OF TiO$_2$(RUTILE)–GLASS THICK FILMS

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(Received June 4, 1975; in final form December 2, 1976)

An analysis is made of the low-frequency characteristics of the permittivity $\varepsilon'$ and of tan $\delta$ of a thick-film insulator containing rutile grains bonded with an amorphous glass. The appearance of dielectric relaxation associated with a maximum of tan $\delta$, as well as characteristic Debye dispersions of the electric permittivity is observed. The relaxation time does not depend on the rutile concentration in the dielectric. An equivalent circuit describing the behaviour of a capacitor with such an insulator in the low frequency range is suggested. The experimental results are shown to be consistent with an analysis based on the assumption that a titanium ion relaxation process occurs in the rutile grains. In normal ambient conditions the influence of this kind of polarization disappears at frequencies higher than $10^2$ Hz; $\varepsilon'$ and tan $\delta$ then change insignificantly and the value of tan $\delta$ is conditioned by the hopping mechanism of conductivity in the glass and in rutile.

1. INTRODUCTION

Thick-film capacitors, where electrodes are made of a conducting paste Pd–Ag, and an insulating paste containing a mixture of boro-silicon glass and rutile powders have been shown to be usable at frequencies above $10^2$ Hz.

The most promising results were obtained by Borek, Licznierski and Rzasza after the printed and baked capacitors were protected with a silicone varnish. By using an insulator which obtained 90% of TiO$_2$ (rutile) and 10% of glass (by weight) and by choosing the dielectric thickness and the surface area of the electrodes, capacitors of values 15 pF to 600 pF, with tan $\delta < 20 \times 10^{-4}$ and with temperature coefficient of $\varepsilon' \sim -300$ ppm°C$^{-1}$ have been obtained. The field strength for insulation breakdown was about 20 V/1 $\mu$m. In difficult working conditions the changes were smaller than $\pm 1\%$ for 1000 hours.

Further investigations discussed in this paper showed that the electric properties of these capacitors deteriorate at very low frequencies. Dielectric loss increases and maxima of tan $\delta$ and dispersions of electric permittivity characterising the Debye relaxation process have been observed. The causes of these phenomena were investigated and results are presented below.

2. EXPERIMENTS

For the experiments presented in this paper, capacitors printed on a substrate of aluminium ceramic were prepared. The area of the electrodes was 1 cm$^2$ and the dielectric was 100 $\mu$m thick. An attempt has been made to evaluate the influence of TiO$_2$ grain concentration in the amorphous glass$^\dagger$ and the effect of electrode type on the low frequency characteristics of the capacitor.

In a first group of capacitors used for the experiment the insulator was made of pure glass or contained 60%, 90% and 95% of TiO$_2$ (by weight), and the electrodes were made of a conductive paste Pd–Ag. In a second group of capacitors the electrodes were made from various conductive pastes: Ag, Pd–Ag, Pt–Au, whilst the dielectric contained 90% of TiO$_2$ and 10% of glass.

The capacity and tan $\delta$ of capacitors prepared in this way were measured with a Scheiber$^2$ bridge in the frequency range of $10^{-9}$ Hz to $10^2$ Hz and with a

$^\dagger$The structure of the dielectric films was tested by X-ray diffraction. It was found that crystal indirect phases do not appear in the baking process. The dielectric consists only of an amorphous glass and polycrystalline rutile. The diameters of rutile grains did not exceed 6 $\mu$m.
Schering bridge in the higher frequency range. The temperature dependence of capacity and tan δ have been determined in the range 300 K to 420 K.

2.1. Results of Experiments

It has been stated that the maxima of tan δ and dielectric constant dispersion appear at temperature of 300 K and at a frequency of about $10^{-2}$ Hz (Figure 1) in all the capacitors with the insulator containing rutile grains. The dispersion and the maximum of tan δ moved with increasing temperature towards higher frequencies (Figure 2). The fact that maxima of tan δ appear at the same frequencies, independently of the molar composition of the dielectric, is a result characteristic of the experiment. At other ambient temperatures also, the position of the maxima of tan δ did not depend on insulation composition. The only influences exerted by the insulation composition were on the $\epsilon'$ and tan δ values which increased with increase of rutile concentration. It has been shown (Figure 3) that the type of electrodes used also had no basic influence upon the positions of the maxima of tan δ. On the other hand, the type of material used for electrodes, affected the frequency characteristics of $\epsilon'$ and tan δ below the range in which the maxima of tan δ appear.
The values $\tau_0$ and $W_m$ were determined from the plots shown in Figure 4. Further information is also given by the frequency characteristics of the insulator conductivity (Figure 5) which was calculated and plotted using the results shown in Figure 1. Within the frequency range investigated these characteristics are described by the relation:

$$\delta(\omega) = A \cdot \omega^n + B \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}$$  \hspace{1cm} (2)

where: $A$ and $B$ are constants

$$n \approx 1$$

The change in conductivity characteristics at the higher frequencies is consistent with the theory of the hopping mechanism of conductivity.\(^5\)

### 3. DISCUSSION

The low-frequency characteristics of $\varepsilon'$ and $\tan \delta$ obtained for the insulators containing rutile grains that were investigated show that the dielectric relaxation process is of the Debye type. The mean relaxation time, $\tau$, for all investigated compositions is given by the relation:

$$\tau = \tau_0 \exp \frac{W_m}{kT}$$  \hspace{1cm} (1)

where:

$$\tau_0 = 3.10^{-10} s$$

$$W_m = 0.65 \ eV$$

### 3.1. Equivalent Circuit of the Thick-Film Dielectric

An equivalent electric circuit model of a thick-film capacitor with a TiO$_2$ (rutile) + glass insulation, is

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**FIGURE 3** Low-Frequency characteristics of the dielectric constant $\varepsilon'$ (a) and $\tan \delta$ (b) of the insulation 90% TiO$_2$ + 10% of glass at 333 K (parameter — type of electrode).

**FIGURE 4** Temperature characteristics of relaxation time $\tau$ for various insulating materials.
proposed which describes the frequency characteristics of this capacitor in the range $10^{-3}$ Hz to $10^{-6}$ Hz. This model is shown in Figure 6. The elements $R_1$, $C\infty$, $C_r$ and $R_r$ represent the properties of rutile, while the elements $R_s$ and $C_s$ represent those of the glass. It has been assumed that a relaxation process associated with microscopic phenomena in the volume of the rutile grain is responsible for the appearance of maxima of tan $\delta$ of the insulators tested.

In the proposed model, the relaxation time constant is represented by the elements $R_r$ and $C_r$. The resistances $R_1$ and $R_s$ represent the losses caused by the conduction mechanism. For frequencies above $10^2$ Hz (Figure 5), the values $R_1$ and $R_s$ are governed by hopping conductivity:

$$\frac{1}{R_1} = A_r \omega^n \cdot \frac{s}{d_1} \quad (3)$$

$$\frac{1}{R_s} = A_s \omega^n \cdot \frac{s}{d_2} \quad (4)$$

where:

- $d_1$, $d_2$ – equivalent thickness of rutile and glass films
- $s$ – electrode surface
- $A_r$, $A_s$ – constants

The characteristics presented in Figure 5 can be analysed in two frequency ranges. In the lower range (below $10^2$ Hz), dielectric relaxation phenomena dominate thus, in the model shown in Figure 6, the elements $R_s$ and $R_1$ may be neglected. In the upper range, however (above $10^2$ Hz), the influence of relaxation may be ignored and in the model shown in Figure 6 $R_r$ and $C_r$ can be neglected.

3.2. Results of Analysis of the Equivalent Circuit

The behaviour of the system in the upper frequency range, i.e. above $10^2$ Hz is most easily analysed. In this range (in the model presented in Figure 6) the influence of elements $R_r$, $C_r$ may be ignored, thus the equivalent circuit is reduced to the typical Maxwell-Wagner model for which $\varepsilon'$, $\varepsilon''$ and conductivity $\sigma(\omega)$ may be shown to be:

$$\varepsilon' = \frac{\varepsilon_s \cdot \varepsilon\infty}{\varepsilon_s d_1 + \varepsilon\infty d_2} \cdot d \quad (5)$$

$$\varepsilon'' = \left( \frac{A_r}{d_1 ([\varepsilon\infty d_2 / \varepsilon_s d_1] + 1)^2} + \frac{A_s}{d_2 ([\varepsilon_s d_1 / \varepsilon\infty d_2] + 1)^2} \right) \omega^{n-1} \cdot \frac{d}{\varepsilon_0} \quad (6)$$
\[ \delta(\omega) = \varepsilon_0 \varepsilon'' \cdot \omega \]  
(7)

where:

- \( \varepsilon_0, \varepsilon_\infty \) — high frequency electric permittivity of glass and rutile
- \( d_1, d_2 \) — thickness of rutile and glass layers
- \( d = d_1 + d_2 \) — total thickness of the insulation

In fact, Eqs. (5) and (6) are approximations taking

\[ \tan^2 \delta_1 = \frac{1}{(\omega R_1 \cdot C_\infty)^2} \]

and

\[ \tan^2 \delta_2 = \frac{1}{(\omega R_s \cdot C_2)^2} \]

as small compared to 1.

Figure 7 presents the theoretical curve of \( \delta(d_1/d_2) \) calculated from Eqs. (6) and (7), assuming that \( A_s = 10 A_r, \varepsilon_s = 8.5; \varepsilon_\infty = 100; n = 1; f = 1 \text{kHz} \). The experimental values obtained from measurements are marked with points.

As Eqs. (6) and (7) give a good fit to plotted values of \( \delta(d_1/d_2) \) at fixed \( \omega \), it may be assumed that a good fit is obtained at other values of \( \omega \) due to the parallel nature of the \( \delta(\omega) \) curves on Figure 5.

The values of \( \varepsilon' \) and \( \tan \delta \) were calculated from the model in Figure 6 with \( R_1 \) and \( R_s \) neglected.

This model illustrates the behaviour of the capacitors tested in the frequency range of \( 10^{-3} \text{ Hz to 10 Hz} \). The determination of \( \omega \tan \delta_{\text{max}} \) i.e. the frequency at which the maxima of \( \tan \delta \) will appear was the most important task. This value was calculated from the relation \( \delta(\omega) = 0 \). The variation of \( \omega \tan \delta_{\text{max}} \) with rutile concentration, is given by Eq. (8):

\[
(1 + \frac{C_\infty}{C_s}) \omega^4 + \frac{1}{\tau^6} (1 - 2 \frac{C_r}{C_s} + \frac{C_r}{C_\infty}) \omega^2 - \frac{1}{\tau^4}
\]

\[
(4 + \frac{C_r}{C_s} + \frac{2C_r}{C_\infty} + \frac{3C_r^2}{C_sC_\infty}) \omega^2 - \frac{1}{\tau^4}
\]

\[
(2 + \frac{C_r}{C_s} + \frac{C_r}{C_\infty} + \frac{C_r^2}{C_sC_\infty}) = 0
\]

where:

- \( \tau = R_sC_r \) — time constant of the relaxation term in the rutile grain volume
- \( \omega = \omega \tan \delta_{\text{max}} \)
- \( C_\infty, C_s, C_r \) — value of capacitance calculated from the equivalent circuit (shown in Figure 6) for various volumetric proportions of the rutile and glass layers:

\[
C_\infty = \frac{\varepsilon_0 \cdot \varepsilon_\infty \cdot s}{d_1}; \quad C_s = \frac{\varepsilon_0 \cdot \varepsilon_s \cdot s}{d_2}; \quad C_r = \frac{\varepsilon_0 \cdot \varepsilon_r \cdot s}{d_1}
\]

The values of \( \omega \tan \delta_{\text{max}} \) and the parameters of the equivalent circuit calculated for insulators with various volumetric proportions of rutile and glass content, and relaxation time \( \tau = 16 \text{ sec.} \) (see Eq. 1) are given in Table I. From this table it follows that differences between theoretical and experimental values of \( \omega \tan \delta_{\text{max}} \) are about 3% which is insignificant.

3.3. Microscopic Model for Dielectric Relaxation in Rutile Grains

The low-frequency relaxation mechanism has not been completely explained by other researchers.

\[ \varepsilon_r \] The values \( \varepsilon_\infty \) and \( \varepsilon_s \) used were obtained from measurements of capacitors filled completely with rutile and glass; and \( \varepsilon_r / \varepsilon_\infty = 0.48 \).
TABLE I

| Composition of the dielectric (volumetric) | Parameters of the equivalent circuit | $\omega_{\tan \delta_{max}}$ |
|------------------------------------------|--------------------------------------|---------------------------|
| 20% TiO$_2$ + 80% Glass                 | $C_e = 427 \, \mu F$                 | $4.45 \times 10^{-2}$    |
|                                          | $R_r = 7.8 \times 10^6 \, \Omega$   |                           |
|                                          | $C_s = 95 \, \mu F$                 |                           |
| 60% TiO$_2$ + 40% Glass                 | $C_e = 25 \, \mu F$                 | $4.50 \times 10^{-2}$    |
|                                          | $R_r = 3.5 \times 10^6 \, \Omega$   |                           |
|                                          | $C_s = 280 \, \mu F$                |                           |
| 90% TiO$_2$ + 10% Glass                 | $C_e = 950 \, \mu F$                | $4.50 \times 10^{-2}$   |
|                                          | $R_r = 3.5 \times 10^6 \, \Omega$   |                           |
|                                          | $C_s = 750 \, \mu F$                |                           |
| 95% TiO$_2$ + 5% Glass                  | $C_e = 30 \, \mu F$                 | $4.40 \times 10^{-2}$   |
|                                          | $R_r = 3.5 \times 10^6 \, \Omega$   |                           |
|                                          | $C_s = 1500 \, \mu F$               |                           |

Similar effects have been observed in crystalline glasses P$_2$O$_5$–Fe$_2$O$_3$ by Hansen, who explained them by the hopping resonance theory. Kinser attributed the same effects to the Maxwell–Wagner–Sillars polarization mechanism. These phenomena in rutile are well explained by the model proposed by Kojkov, who assumed that a thermally excited titanium ion may pass from a lattice site into an interstitial position. If however the bond between the vacancy and the ion is strong, such that the ion is not able to move freely in the lattice, the potential barrier for the ion has the shape shown in Figure 8a. By analysis of the rutile lattice, Kojkov proved that the barrier has a form such as that assumed for titanium ions leaving a lattice site for an interstitial.

At constant temperature the concentration of the defects is:

$$N = 2N_0 \exp \left( - \frac{W_1 - W_m}{kT} \right)$$

where: $N_0$ = total number of titanium ions in a volumetric unit of the lattice.

$W_m$ and $W_1$ are defined as shown in Figure 8a. This is equivalent to the forming of $N$ dipoles (vacancy-interstitial ion) in a volumetric unit. In the absence of an electric field we may assume that the number of ions in position 2 and 3 (Figure 8a) is the same.

$$N_2 = N_3 = N_0 \exp \left( - \frac{W_1 - W_m}{kT} \right)$$

This situation will change when an electric field is applied. The form of the barriers is shown in Figure 8b. By virtue of this barrier model the relaxation time of dipoles (vacancy-interstitial ion) was calculated and the relations for $\varepsilon''$ and $\varepsilon'''$ of the rutile grain were given. After the electric field is applied the concentration of ions in positions 2 and 3 will change in time $t$:

$$\frac{dN_2}{dt} = -N_2P_{12} + N_0P_{12} + N_3P_{32} - N_2P_{23}$$

$$\frac{dN_3}{dt} = -N_3P_{31} + N_0P_{13} + N_2P_{23} + N_3P_{32}$$

where $P_{ij}$ is the probability of ion transition from $i$ into $j$ positions.
But at $E = 0$

$$P_{23} = P_{21}P_{13} = P_{31}P_{12} = \frac{\nu}{2} \exp \left( -\frac{W_1 + W_m}{kT} \right)$$

$$\leq P_{12} = P_{13} = \frac{\nu}{2} \exp \left( -\frac{W_m}{kT} \right)$$

Hence the Eqs. (11) and (12) can be simplified:

$$\frac{dN_2}{dt} = -N_2P_{21} + N_0P_{12} \tag{13}$$

$$\frac{dN_3}{dt} = -N_3P_{31} + N_0P_{13} \tag{14}$$

It is assumed that the increase or decrease in potential barrier (Figure 8b) $e b E, e(d-b)E$ is considerably smaller than $kT$.

Then:

$$P_{21}^+, P_{31}^- \approx \nu \exp \left( -\frac{W_m}{kT} \right) \left( 1 \pm \frac{ebE}{kT} \right) \tag{15}$$

$$P_{12}^+, P_{13}^- \approx \nu \exp \left( -\frac{W_m}{kT} \right) \left( 1 \pm \frac{e(d-b)E}{kT} \right) \tag{16}$$

where:

- $\nu$ is the frequency of thermal vibrations of the dipole (vacancy-interstitial ion)
- $E$ is the internal electric field in rutile grain

After substitution of Eqs. (15) and (16) for Eqs. (13) and (14) and combining Eqs. (13) and (14) to give $d(N_3 - N_2)/dt$, we obtain:

$$N_3 - N_2 \approx -\frac{edE}{kT} N \left[ 1 - \exp \left( -\frac{t}{\tau} \right) \right] \tag{17}$$

where:

$$\tau = \nu^{-1} \exp \left( \frac{W_m}{kT} \right) \tag{18}$$

From the analysis presented the following conclusions may be drawn:

1) In rutile grains a Debye relaxation of vacancy-interstitial ion dipoles appears;

2) The activation energy of the relaxation time is equal to $W_m$ (see Figure 8).

According to Kojkov the value of this energy should be in the limits 0.5 eV to 1 eV. The authors obtained a value for $W_m$ in the range 0.6 to 0.7 eV.

In summary the results obtained are consistent with both the assumptions of the authors and as the interpretation of these phenomena proposed by Kojkov.

4. CONCLUSIONS

Rutile — glass dielectrics, which have been applied in thick-film techniques are characterized by specific properties in the very low frequency range, namely by an ion-relaxation process, causing a considerable increase of dielectric losses. In the high frequency range $\tan \delta$ of this insulation is very small, its value being determined by a hopping conductivity mechanism.

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