LOW FREQUENCY CHARACTERISTICS OF TiO_2 (RUTILE)–GLASS THICK FILMS

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An analysis is made of the low-frequency characteristics of the permittivity ϵ' 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; ϵ' 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,¹ 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, Licznarski and Rzasz 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 $\tan \delta < 20 \cdot 10^{-4}$ and with temperature coefficient of $\epsilon' \sim -300 \text{ ppm}^\circ\text{C}^{-1}$ have been obtained. The field strength for insulation breakdown was about 20 V/ μm . 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 $100 \mu\text{m}$ thick. An attempt has been made to evaluate the influence of TiO_2 grain concentration in the amorphous glass[†] 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 Scheiber² bridge in the frequency range of 10^{-3} Hz to 10^2 Hz and with a

[†]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 $6 \mu\text{m}$.

Schering bridge in the higher frequency range. The temperature dependence of capacity and $\tan \delta$ have been determined in the range 300 K to 420 K.

2.1. Results of Experiments

It has been stated that the maxima of $\tan \delta$ 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 $\tan \delta$ moved with increasing temperature towards higher frequencies (Figure 2). The fact that maxima of $\tan \delta$

FIGURE 1 Dispersion of the dielectric constant ϵ' (a) and of the maximum $\tan \delta$ (b) in capacitors with electrodes of Pd-Ag at 295 K (parameter – concentration of TiO_2 in the insulation).

FIGURE 2 Low-Frequency characteristics of the dielectric constant ϵ' (a) and $\tan \delta$ (b) at various ambient temperatures (electrodes Pd-Ag, insulation 95% TiO_2 + 5% of glass).

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 $\tan \delta$ did not depend on insulation composition. The only influences exerted by the insulation composition were on the ϵ' and $\tan \delta$ 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 $\tan \delta$. On the other hand, the type of material used for electrodes, affected the frequency characteristics of ϵ' and $\tan \delta$ below the range in which the maxima of $\tan \delta$ appear.

FIGURE 3 Low-Frequency characteristics of the dielectric constant ϵ' (a) and $\tan \delta$ (b) of the insulation 90% TiO₂ + 10% of glass at 333 K (parameter – type of electrode).

3. DISCUSSION

The low-frequency characteristics of ϵ' 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, τ , for all investigated compositions is given by the relation:

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

where:

$$\begin{aligned} \tau_0 &= 3.10^{-10} \text{ s} \\ W_m &= 0.65 \text{ eV} \end{aligned}$$

The values τ_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:

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

where: A and B are constants

$$n \cong 1$$

The change in conductivity characteristics at the higher frequencies is consistent with the theory of the hopping mechanism of conductivity.³

3.1. Equivalent Circuit of the Thick-Film Dielectric

An equivalent electric circuit model of a thick-film capacitor with a TiO₂ (rutile) + glass insulation, is

FIGURE 4 Temperature characteristics of relaxation time τ for various insulating materials.

FIGURE 5 Frequency characteristics of insulation conductivity, δ (parameter – concentration of rutile grains in the insulation).

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_∞ , 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 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:

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

FIGURE 6 Electric equivalent model of a thick film capacitor with an insulation of TiO_2 (rutile) + glass.

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

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 ϵ' , ϵ'' and conductivity $\delta(\omega)$ may be shown to be:

$$\epsilon' = \frac{\epsilon_s \cdot \epsilon_\infty}{\epsilon_s d_1 + \epsilon_\infty d_2} \cdot d \quad (5)$$

$$\epsilon'' = \left\{ \frac{A_r}{d_1 [(\epsilon_\infty d_2 / \epsilon_s d_1) + 1]^2} + \frac{A_s}{d_2 [(\epsilon_s d_1 / \epsilon_\infty d_2) + 1]^2} \right\} \frac{\omega^{n-1} \cdot d}{\epsilon_0} \quad (6)$$

$$\delta(\omega) = \epsilon_0 \epsilon'' \cdot \omega \quad (7)$$

where:

- $\epsilon_s, \epsilon_\infty$ — 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 Eq.'s (5) and (6) are approximations taking

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

and

$$\tan^2 \delta_2 = \frac{1}{(\omega R_s \cdot C_s)^2}$$

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 $A_s = 10 A_r$, $\epsilon_s = 8.5$; $\epsilon_\infty = 100$; $n = 1$; $f = 1$ 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 ω , it may be assumed that a good fit is obtained at other values of ω due to the parallel nature of the $\delta(\omega)$ curves on Figure 5.

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

FIGURE 7 Variation in conductivity, δ , of the insulation with rutile concentration.

This model illustrates the behaviour of the capacitors tested in the frequency range of 10^{-3} Hz to 10 Hz.⁸ The determination of $\omega \tan \delta_{\max}$ 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 $\delta \tan \delta / \delta \omega = 0$. The variation of $\omega \tan \delta_{\max}$ with rutile concentration, is given by Eq. (8):

$$\begin{aligned} & \left(1 + \frac{C_\infty}{C_s}\right) \omega^6 + \frac{1}{\tau^2} \left(1 - 2 \frac{C_r}{C_s} + \frac{C_r}{C_\infty}\right) \omega^4 - \frac{1}{\tau^4} \\ & \left(4 + \frac{C_r}{C_s} + 2 \frac{C_r}{C_\infty} + 3 \frac{C_r^2}{C_s C_\infty}\right) \omega^2 - \frac{1}{\tau^6} \\ & \left(2 + \frac{C_r}{C_s} + \frac{C_r}{C_\infty} + \frac{C_r^2}{C_s C_\infty}\right) = 0 \end{aligned} \quad (8)$$

where:

$\tau = R_r C_r$ — time constant of the relaxation term in the rutile grain volume

$\omega = \omega \tan \delta_{\max}$

C_∞, 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:

$$C_\infty = \frac{\epsilon_0 \cdot \epsilon_\infty \cdot s}{d_1}; \quad C_s = \frac{\epsilon_0 \cdot \epsilon_s \cdot s}{d_2};$$

$$C_r = \frac{\epsilon_0 \cdot \epsilon_r \cdot s}{d_1} \dagger$$

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

†The values ϵ_∞ and ϵ_s used were obtained from measurements of capacitors filled completely with rutile and glass; and $\epsilon_r / \epsilon_\infty = 0.48$.

TABLE I
 $\omega \tan \delta_{\max}$ as a function of rutile and glass proportion (vol.)
 in the insulation

Composition of the dielectric /volumetric/	Parameters of the equivalent circuit	$\omega \tan \delta_{\max}$
20% TiO_2 + 80% Glass		$\frac{1,457}{\tau}$
60% TiO_2 + 40% Glass		$\frac{1,450}{\tau}$
90% TiO_2 + 10% Glass		$\frac{1,430}{\tau}$
95% TiO_2 + 5% Glass		$\frac{1,410}{\tau}$

Similar effects have been observed in crystalline glasses $\text{P}_2\text{O}_5\text{--Fe}_2\text{O}_3$ by Hansen⁴ who explained them by the hopping resonance theory. Kinser⁵ attributed the same effects to the Maxwell–Wagner–Sillars polarization mechanism. These phenomena in rutile are well explained by the model proposed by Kojkov,⁶ 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, Kojkov⁷ proved that the barrier has a form such as that assumed for titanium ions leaving a lattice site for an interstitial

one. At constant temperature the concentration of the defects is:⁶

$$N = 2N_0 \exp \left(- \frac{W_1 - W_m}{kT} \right) \quad (9)$$

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.

$$N_2 = N_3 = N_0 \exp \left(- \frac{W_1 - W_m}{kT} \right) \quad (10)$$

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 ϵ_r' and ϵ_r'' 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 :

$$\frac{dN_2}{dt} = -N_2 P_{21} + N_0 P_{12} + N_3 P_{32} - N_2 P_{23} \quad (11)$$

$$\frac{dN_3}{dt} = -N_3 P_{31} + N_0 P_{13} + N_2 P_{23} + N_3 P_{32} \quad (12)$$

where: P_{ij} – is the probability of ion transition from i into j positions.

FIGURE 8 Model of a potential barrier of an interstitial ion with two equilibrium positions (a) without an electric field and (b) with an electric field.

But at $E = 0$

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

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

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

$$\frac{dN_2}{dt} = -N_2P_{21} + N_0P_{12} \quad (13)$$

$$\frac{dN_3}{dt} = -N_3P_{31} + N_0P_{13} \quad (14)$$

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

Then:

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

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

where:

ν – is the frequency of thermal vibrations of the dipole (vacancy-interstitial ion)

E – 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:

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

where:

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

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.

REFERENCES

1. R. Borek, B. Licznarski and B. Rzasa, *Microelectronics and Reliability*, **11**, pp. 511–523, 1972.
2. D. J. Scheiber, *Journal of Research*, **65c**, No. 1, p. 23, 1961.
3. N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, Clarendon Press, Oxford, 1971.
4. K. W. Hansen, *J. Electrochem. Soc.*, **112**, No. 10, pp. 994–996, 1965.
5. D. L. Kinser, *J. Electrochem. Soc.*, **117**, No. 4, pp. 546–548, 1970.
6. S. N. Kojkov, W. J. Kunin, A. N. Cykin, *Fizika Twierdogo Tiela, Solid State Physics*, **3**, No. 2, 1961, pp. 651–657.
7. S. N. Kojkov, M. N. Rozowa, *Fizika Twierdogo Tiela, Solid State Physics*, **7**, No. 9, 1965, pp. 2678–2682.
8. B. Licznarski, K. Nitsch and B. Rzasa, *Archiwum Elektrotechniki*, to be published in **2**, 77.