

MODEL OF ELECTRIC CONDUCTIVITY OF THICK-FILM RESISTORS

I. PIEZORESISTIVITY

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On the basis of a model of electron transport in TFR (thick-film resistors), based on the tunnelling of electrons assisted by phonons between localized impurity states in glass, a simple theory of piezoresistivity has been worked out. From the relationship derived and from the experimental data, it is possible to obtain the concentration values of the impurity centres. Using the concepts of the mechanism involved in the formation of film macrostructure, an interpretation of the experimental course of $\ln N = f(v/v_c)$ was proposed.

1. INTRODUCTION

Thick-film resistors find wide application in hybrid integrated circuits and potentiometers. They are prepared from pastes applied by screen printing in suitable patterns onto insulating substrates. The pastes are composed of a conductive component (RuO_2 , $\text{Bi}_2\text{Ru}_2\text{O}_7$, etc.) and glass (usually a high-lead borosilicate one) and an organic lacquer carrier. Following the firing, during which the organic components burn out, the film comprises conductive particles surrounded by glass. The actual structure depends on the properties of the glass and the firing temperature [15]. With these materials, the mechanism of electric charge transfer has not yet been safely explained. There are several theories based on various concepts [1–7]. Most of them, attempting to explain the minimum on the temperature dependence of resistivity, consider a combination of two conductivity mechanisms exhibiting temperature coefficients of resistivity (TCR) of opposite signs. The positive TCR is ascribed to the metallic type of conductivity of the individual grains of the conductive component of the composite [2, 4]; however, this concept is disproved in [3] by the results of AC measurements. The choice of possible transport mechanisms characterized by their $\text{TCR} > 0$ is restricted by the requirement for a very low activation energy [1] which follows from the experimentally established very low TCR values, of the order of 10^{-4} K^{-1} . This requirement is best met by the concept of charge transfer between the individual conductive grains by tunnelling the current carriers through the glassy intergranular regions [5]. The activation energy associated with this process is attributed in [2] to charge transfer between small conductive grains; at the same time, the glass is assumed to contain impurities (traps), because the diffusion of Ru from the conductive particles in the course of firing is considered negligible [1, 2]. However, in that case it is no longer possible to explain the dependence of resistivity on the concentration of

the conductive component, nor the disagreement of the critical coefficients of the percolation theory with respect to the values found by computer modelling. An explanation was based on the assumption of diffusion of Ru ions into the glass in the course of firing and on the formation of a narrow band of localized impurity states distributed around Fermi level [7]. Direct evidence for tunnelling charge transfer assisted by phonons between localized impurity states in the glass may be considered to be presented by the results of measuring the frequency dependence of the components of admittance [6]. A fundamental problem is seen to be the frequently employed verification of theoretical concepts by comparing the experimental courses of the quite indistinct temperature dependence of resistivity. Particularly, fitting them by means of theoretical relationships using several unknown parameters can be regarded as highly questionable. An example for this is provided by study [4] in which series and parallel connections of resistances attributed to three transport mechanisms are combined: metallic conductivity of conductive grains, tunnelling and variable range hopping. The complexity of structure and a relatively small range of measurable phenomena have not so far allowed the theories to be explicitly proved nor disproved. This is why additional phenomena should be sought in order to elucidate the mechanism of conductivity of these complex composite materials. Piezoresistivity is one of these phenomena.

The sensitivity to deformation of thick-film resistors is studied for two reasons. One is associated with the requirement for elucidating the mechanism of electric conductivity mentioned above [5, 8–12], the other being aimed at applications in pressure and deformation sensors [14]. In the evaluation of experimental data, most of the studies published so far employ methods adequate for isotropic homogeneous materials. In the present model, use will be made, similarly to study [13], of the concept of a percolation network topology which corresponds well to the morphology of thick-film resistors with a quasihomo-

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geneous structure [7, 15]. The present author will attempt to interpret the experimental data in a more profound way on the basis of the concept of electron transport by activated tunnelling in glass (phonon-assisted tunnelling), [6, 7].

2. THEORETICAL

Derivation of the relationship for gauge factor Γ defined as a proportionality coefficient for the relative change in resistance and deformation $\epsilon = \delta r/r_0$:

$$\delta R/R_0 = \Gamma \delta r/r_0 \quad (1)$$

can be effected on the assumption that the transport of electrons takes place by tunnelling assisted by phonons within the narrow band of localized impurity states in the layers of glass between the conductive grains [6, 7]. For the resistance it then holds [16]:

$$\rho = \text{const} \times (\alpha r_c)^2 \exp(2\alpha r_c + \epsilon_3/kT), \quad (2)$$

where α^{-1} is Bohr's radius of impurity centre, r_c is the critical hopping (percolation) range and ϵ_3 is the activation energy, equal in its order of quantity to the width of the impurity band. The relationship between the critical hopping range r_c and the critical concentration of localized impurity states N is described by the equation

$$2r_c = \eta N^{-1/3}, \quad (3)$$

where $\eta = 1.78$ [16]. The expression for the gauge factor is obtained by developing equation (2) into Taylor series around r_{c0} for a non-deformed film:

$$\rho = \rho_0 + \rho_0 \left[(2 + \alpha r_{c0}) \delta r_c/r_{c0} + \right. \\ \left. + (2 + 2\alpha r_{c0} + (\alpha r_{c0})^2) (\delta_c/r_{c0})^2 + \dots \right] \quad (4)$$

It can be easily shown that linearization of equation (4) (by neglecting the terms with relative elongation squared and cubed) results in an error of less than 1%. For the gauge factor it then holds that

$$\Gamma = 2 + 2\alpha r_{c0}. \quad (5)$$

From equations (3) and (5) one obtains the following equation for concentration N of localized states in the impurity band:

$$N = (1.78\alpha/(\Gamma - 2))^3 \quad (6)$$

which holds for the region of low concentrations of localized states N . A general analytical formula for resistivity at activated tunnelling was derived in [17] and has the following form:

$$\rho = \rho_p \exp(2\alpha r_c). \quad (7)$$

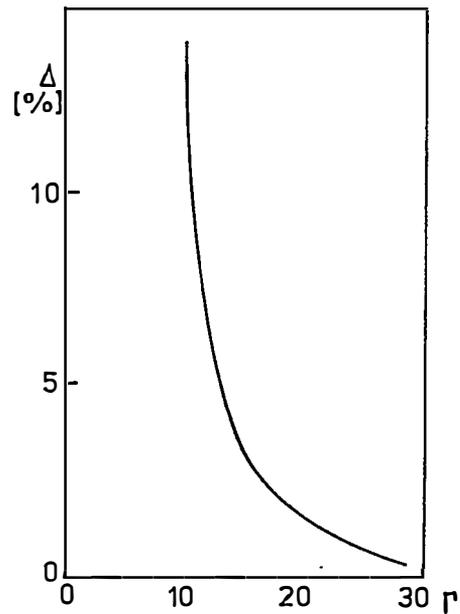


Fig. 1. Relative error involved in the determination of the concentration of impurity centres, calculated by means of approximative equation (6).

The pre-exponential factor is equal to

$$\rho_p = \text{const} \times \exp(\epsilon_3/kT) (2r_p/\eta)^6 H^{-1} \quad (8)$$

where $r_p = \alpha r_c$, and

$$H = 3 + 6r_p + 7r_p^2 + 2r_p^3 + 4r_p^4 - r_p^2 \exp(-2r_p).$$

Using a procedure similar to that employed in the derivation of formula (5), Γ can be found for any arbitrary concentration of N from the equation

$$\Gamma = 2 \left[3 + r_p - \frac{3r_p + 7r_p^2 + 3r_p^3 + 8r_p^4 + r_p^2 (r_p - 1) \exp(-2r_p)}{3 + 6r_p + 7r_p^2 + 2r_p^3 + 4r_p^4 - r_p^2 \exp(-2r_p)} \right]. \quad (9)$$

At low concentrations of N , equation (9) turns into equation (5), as can be shown by the limit for $N \rightarrow 0$ ($r_p \rightarrow \infty$). The bottom limit of parameter Γ can be estimated from the limit for $N \rightarrow 0$ ($r_p \rightarrow \infty$) which gives $\Gamma > 6$. This means that for the transport mechanism considered, $\Gamma > 6$. For the concentration of localized states in the impurity band it holds that

$$N = (\alpha\eta/2r_p)^3. \quad (10)$$

The error involved in the determination of concentration N , due to application of the approximative equation (6), increases with decreasing value of Γ (increasing concentration N), as indicated by Fig. 1.

From the topology of the conductive cluster skeleton it follows that the direction of jumps of electrons between the localized impurity centres is not generally identical with the vector of the macroscopic electric field. The conductive particles constitute a percolation network in the glass matrix. The paths of electrons in this lattice agree with the directions of the shortest connecting lines between the neighbouring conductive particles, forming the skeleton of the conductive cluster. Let us introduce a Cartesian coordinate system into the lattice. The angle between coordinate x of this system and i -th path of electron will be designated $\Theta_i \in (0, \pi)$ - Fig. 2. For relative elongation ϵ_i of path l_i it holds that [13]

$$\epsilon_i = \epsilon_x \cos^2 \Theta_i + \epsilon_y \sin^2 \Theta_i \cos^2 \Phi_i + \epsilon_z \sin^2 \Theta_i \sin^2 \Phi_i, \quad (11)$$

where $\epsilon_x, \epsilon_y, \epsilon_z$ are relative elongations in the directions of the individual ordinates, and Φ_i is the angle between projection l_i into plane y, z and coordinate y . The averaging via angle $\Phi_i \in \langle 0, 2\pi \rangle$ leads to the equation

$$\epsilon_i = \epsilon_x \cos^2 \Theta_i + 0.5 \sin^2 \Theta_i (\epsilon_y + \epsilon_z). \quad (12)$$

The macroscopic electric field is applied in the direction of ordinate x . First let us consider the case in which the macroscopic electric field and the external mechanical stress are parallel. Following simple rearrangement of equation (12) one obtains the following for deformation of the i -th path:

$$\epsilon_i = (1 + \text{tg}^2 \Theta_i)^{-1} [1 - 0.5(\mu_f + \mu_s) \text{tg}^2 \Theta_i] \epsilon_x, \quad (13)$$

where μ_f and μ_s are film and substrate Poisson ratios. On substituting into equation (1), one obtains the following expression for relative change in the resistance of i -th path:

$$\delta R_i / R_{i0} = \Gamma A_x(\Theta_i) \epsilon_x. \quad (14)$$

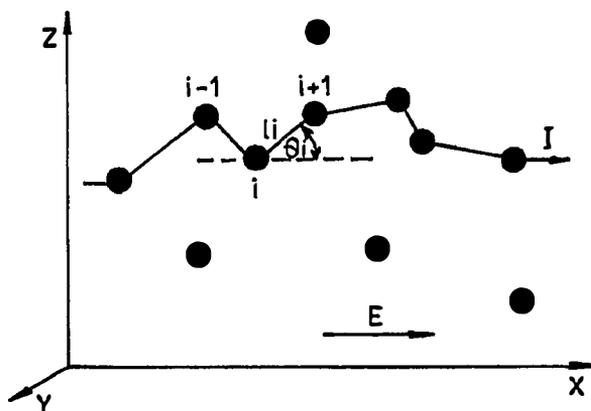


Fig. 2. Introduction of angle Θ_i between the direction of electron jumps (connecting lines between the closest conductive grains) and the vector of the external electric field.

The subscript at the correction factor A indicates the direction of deformation. The gauge factor Γ does not depend on angle Θ_i and the correction factor has the form

$$A_x(\Theta_i) = (1 + \text{tg}^2 \Theta_i)^{-1} \times [1 - 0.5(\mu_f + \mu_s) \text{tg}^2 \Theta_i], \quad (15)$$

and after simple rearrangement,

$$A_x(\Theta_i) = 0.5 \times [-\mu_f - \mu_s + (2 + \mu_f + \mu_s) \cos^2 \Theta_i]. \quad (16)$$

If the external voltage acts perpendicularly to the vector of the macroscopic electric field, the correction factor has the form

$$A_y(\Theta_i) = 0.5 [1 - \mu_f - (1 + 2\mu_s - \mu_f) \cos^2 \Theta_i]. \quad (17)$$

Let us replace the set of angles Θ_i by effective angle Θ_{ef} . This effective angle will be introduced by calculating the relative change in the resistance of the backbone of the conductive cluster, formed by series connections of R_i resistances of the individual paths l_i between the conductive grains:

$$\delta R / R_0 = \left(\delta \sum_{i=1}^n R_i \right) / R_0. \quad (18)$$

Differentiation and rearrangement yields

$$\delta R / R_0 = \left(\sum_{i=1}^n R_i \right)^{-1} \times \sum_{i=1}^n \{ (dR_i / dr_i) (r_i / R_i) (\delta r_i / r_i) R_i \}. \quad (19)$$

By introduction of the critical hopping range r_c , the corresponding resistance R_c , and taking into account the relationships

$$(r_c / R_c) (dR_c / dr_c) = \Gamma, \quad \delta r_i / r_i = A_j(\Theta_i) \epsilon_j,$$

$$\sum_{i=1}^n R_i = n R_c,$$

one obtains

$$(\delta R / R_0)_j = \Gamma \epsilon_j n^{-1} \sum_{i=1}^n A_j(\Theta_i). \quad (20)$$

The effective angle is introduced by the expression

$$A_j(\Theta_{ef}) = n^{-1} \sum_{i=1}^n A_j(\Theta_i), \quad (21)$$

so that it holds that

$$\Gamma_j = (\delta R / R_0) = \Gamma A_j(\Theta_{ef}) \epsilon_j. \quad (22)$$

Substitution of equations (16) or (17) for the correction factor gives the following expression for the effective angle:

$$\cos \theta_{ef} = \left(n^{-1} \sum_{i=1}^n \cos^2 \theta_i \right)^{1/2}. \quad (23)$$

The value of θ_{ef} for each sample can be obtained by measuring the piezoresistivity at both significant deformation directions, i.e. that parallel with, and that perpendicular to, the macroscopic electric field. The following holds from (22), (21), (16) and (17) for the ratios of measured values of uncorrected gauge factors:

$$\frac{\Gamma_y}{\Gamma_x} = \frac{1 - \mu_f - (1 + 2\mu_s - \mu_f) \cos^2 \theta_{ef}}{(2 + \mu_f + \mu_s) \cos^2 \theta_{ef} - \mu_s - \mu_f} \quad (24)$$

and for their difference it holds that

$$\Gamma_x - \Gamma_y = 0.5 (1 + \mu_s) (3 \cos^2 \theta_{ef} - 1) \Gamma. \quad (25)$$

3. SPECIMENS AND EXPERIMENTAL METHODS

To facilitate interpretation of experimental data, use was made of specimens prepared from model resistor pastes which, as their inorganic components, contained only a finely ground glass frit and the $\text{Bi}_2\text{Ru}_2\text{O}_7$ conductive pigment. The specific surface areas of the powdered materials, measured by the Brunauer-Emmet-Teller (BET) method, were $5 \text{ m}^2\text{g}^{-1}$ for $\text{Bi}_2\text{Ru}_2\text{O}_7$ and $1.05 \text{ m}^2\text{g}^{-1}$ for the glass, which had the composition 66% PbO , 32.5% SiO_2 and 1.5% Al_2O_3 . The lacquer component was based on ethylcellulose dissolved in terpineol. The resistor films were applied by screen printing onto substrates consisting of 96% Al_2O_3 , provided with AgPd electrodes. The specimens were fired in a tunnel kiln with a time of holding of 9 minutes at the highest temperature $t_{fr} = 800$ to 900°C . The thicknesses of the fired films were within the interval of 12 to $18 \mu\text{m}$.

Theoretical requirements made it necessary to measure at the same time the longitudinal and transverse piezoresistivity, and this is why the specimen shape

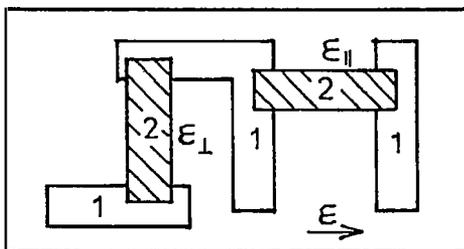


Fig. 3. The shape of the specimens employed (1 - electrode, 2 - resistor film).

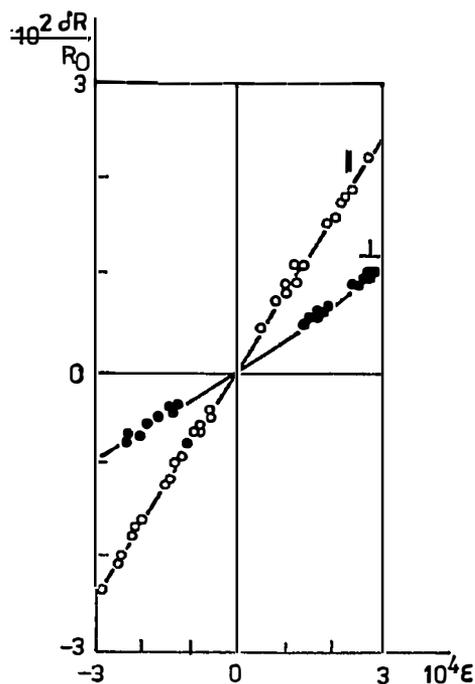


Fig. 4. An example of a measuring result uncorrected for θ_{ef} .

Table I

Measuring method	$t_{fr}^\circ\text{C}$	v_c	$-t$
Piezoresistivity	800	0.079	3.48
	850	0.074	3.54
	900	0.071	3.61
Admittance components	850	0.072	3.55
	880*	0.099	3.60

*The specimens were fired in another kiln under different conditions.

shown in Fig. 3 was chosen. The measurements were carried out by the three-point bending method [9] and the mean deformation was calculated according to [18]. The resistance was measured by the MIT290 multimeter (Metra Blansko) with an accuracy of 0.03%. An example of uncorrected measurement is given in Fig. 4. Poisson modulus of the substrate (containing 96% Al_2O_3) was $\mu = 0.22$ [10, 20]. No information on Poisson modulus of the resistor layer was available. For glasses in the PbO-SiO_2 system, the value specified is $\mu = 0.225$ [19], and so it was decided to put $\mu_f = \mu_s$ without incurring any great error, similarly as it was done in [20].

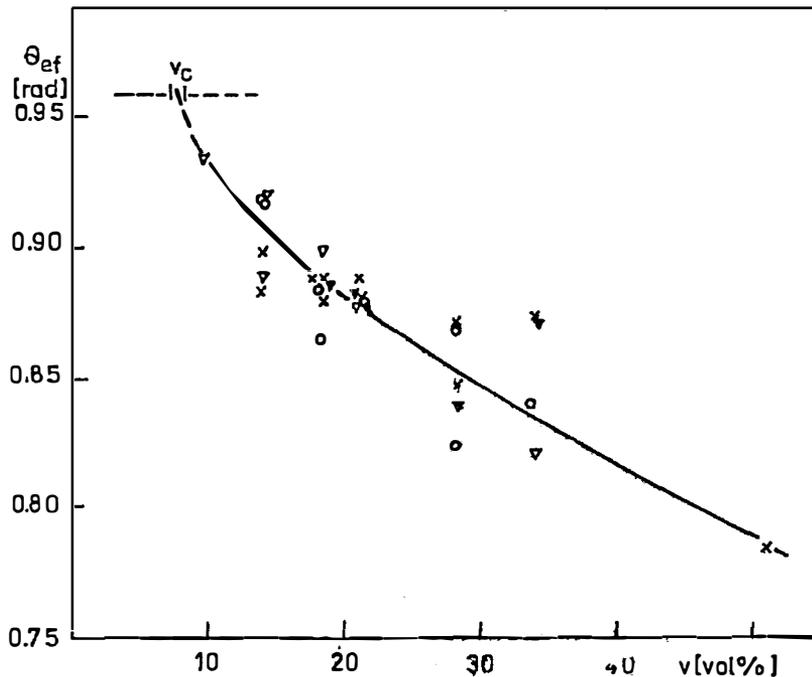


Fig. 5. Effective angle Θ_{ef} vs. concentration of the conductive component by volume for various firing temperatures: \times - 800° C, \circ - 850° C, \bullet - 900° C.

The concentrations of localized states in the impurity band, calculated by means of equation (6) from the results of piezoresistivity measurements, were compared with the concentrations established by measuring the frequency dependence of the admittance components, using the method described in [6]. Table I lists, for all of the specimen series employed, a survey of critical parameters defined by the following equation in the percolation theory:

$$R = A(v - v_c)^{-t}, \quad (1)$$

where R is planar resistivity, v the concentration of the conductive component in percent by volume, v_c is its critical value (percolation limit) and t is the critical exponent.

4. EXPERIMENTAL RESULTS

The uncorrected values of gauge factors Γ_x and Γ_y (the subscript indicates the direction of deformation, in both cases the electric field was oriented in the direction of ordinate x) were obtained by measuring piezoresistivity at two mutual orientations of external electric field and deformation, given by the shape of the specimen according to Fig. 3, and using the definition equation (1). On the assumption that $\mu_f = \mu_s$, the ratio Γ_x/Γ_y was used to calculate, for each specimen, the effective angle Θ_{ef} from equation (24). The values of Γ , adjusted by means of corrections (16) or (17), are regarded as material parameters which,

according to our concept, depend solely on the concentration N of localized impurity states and on the value of their Bohr radius, α^{-1} . The dependence of Θ_{ef} on the concentration of the conductive component by volume, is plotted in Fig. 5 for all three series of specimens fired at various temperatures. The mean values of gauge factor Γ were calculated for the individual concentrations of the conductive component, using the respective experimental values and corrections (16) and (17). Fig. 6 shows the plot of the gauge factor vs. the standardized concentration of the conductive component.

The validity of the theoretical assumptions can be verified by means of the established differences between the transverse and the longitudinal gauge factors, which according to the present theory, should correspond to equation (25), in contrast to the expression

$$\Gamma_y - \Gamma_x = 2(1 + \mu) \quad (2)$$

derived in [21] for a homogeneous isotropic material exhibiting conductivity in the zone of delocalized states. In studies [5, 10, 11], equation (27) was applied to the results of measuring piezoresistivity of thick-film resistors. The experimental values of $\Gamma_y - \Gamma_x$ plotted in Fig. 7 in terms of v/v_c are compared with the course of relationship (25) calculated by substituting the experimental values of Γ and Θ_{ef} . The course established in this way corresponds well to the theory being submitted.

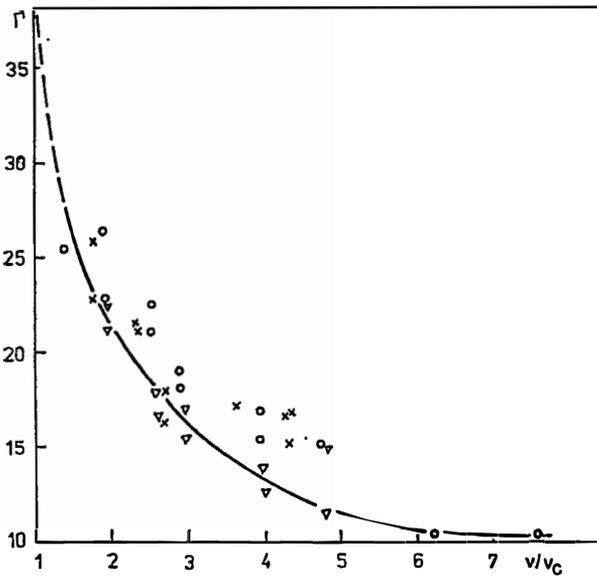


Fig. 6. Experimentally established course of the dependence of gauge factor Γ on standardized concentration of the conductive component (for designation of points refer to Fig. 5).

By means of equations (6) and (10), concentrations N of localized states in the impurity zone were calculated. The results were supplemented with the values obtained by evaluating the frequency dependence of the admittance components. The respective measuring and evaluating methods, based on theory [22] are described in the present author's study [6]. The very satisfactory agreement of the experimental relationships with the theory, demonstrated in [6], provides justification of the assumption on charge transport by tunnelling, assisted by phonons, between the impurity localized states in glass. From the expression for frequency dependence of complex conductivity, $\sigma^*(\omega)$,

$$\sigma^*(\omega) - \sigma(0) \sim \omega^s \tag{3}$$

the values of exponent s were determined (Fig. 8). It holds that

$$s = 1 - \lambda(\alpha r_c)^{-1}. \tag{4}$$

In [6] it was found that $\lambda \approx 1.4$, and Bohr's radius $\alpha^{-1} = 0.46$ nm was calculated for relative permittivity of the glass employed, equal to 8.6 and for the effective mass of the electron equal to the mass of a free electron.

The method allows concentration N to be established particularly in the region of subcritical concentrations of the conductive component ($v < v_c$). The resultant dependence of the concentration of localized states in the impurity band on the concentration of the conductive component by volume, standardized

with respect to its critical value, is plotted in Fig. 9 for top firing temperatures of 800–900°C.

5. DISCUSSION

Similarly to the study by Winkler and Steenwoorden [13], the topology of the conductive cluster skeleton has a key role in the processing of experimental data in the present author's theory. The effect of the distribution of conductive grains in the glass matrix is expressed quantitatively by the effective value of angle Θ between the direction of electron jumps and the vector of the external electric field. Using computer modelling, the value of $\Theta = 0.995 \pm 0.021$ rad was found for the critical concentration of the conductive phase, $v = v_c$ (for the cluster backbone). The results of computer modelling will be described in detail in the second part of the present study. Fig. 5 in-

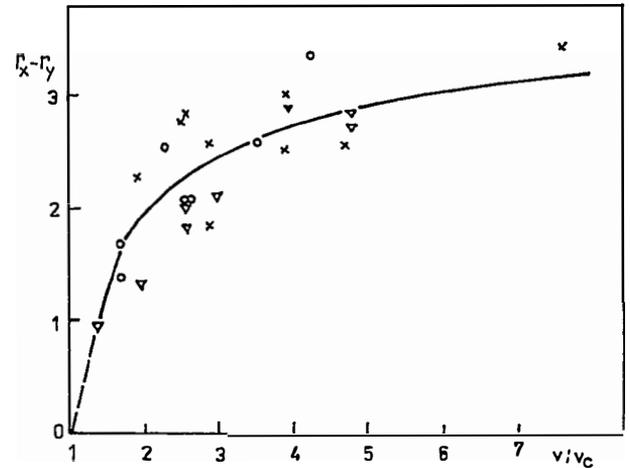


Fig. 7. The difference between longitudinal and transverse gauge factor vs. standardized concentration of the conductive component (for designation of points refer to Fig. 5).

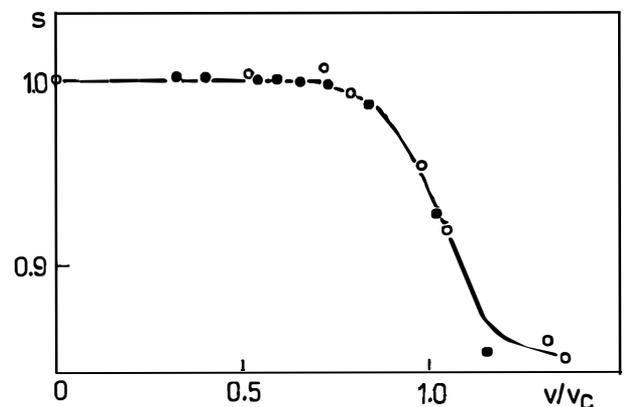


Fig. 8. Exponent s from equation (28) plotted in terms of the concentration of the conductive component, for various firing temperatures: \circ – 850°C, \bullet – 880°C.

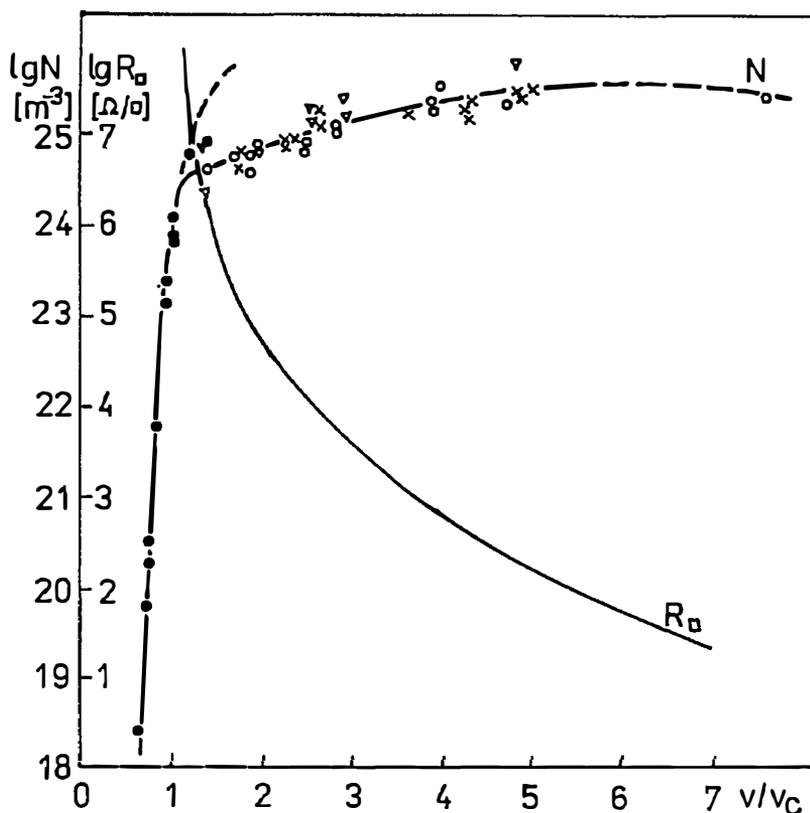


Fig. 9. Concentration of localized impurity states vs. standardized concentration of the conductive component by volume, in comparison with the course of planar resistivity: for designation of points, refer to Fig. 5. Results obtained from measurements of frequency dependence - ●

indicates that extrapolation of the experimental course to $v = v_c$ (for the backbone of the conductive cluster) yields a very satisfactory agreement with this value. The decrease of the value of the effective angle with increasing concentration of the conductive component is ascribed to the increasing share of conductive paths acting parallel with the cluster backbone.

Inclusion of corrections for the Θ_i angles leads to substantially higher gauge factor values compared to those published so far in the literature, with the exception of [13], namely $\Gamma = 3$ to 15. According to [17], the higher Γ values correspond to the concept of phonon-assisted tunnelling of electrons, because the condition $\Gamma > 6$ follows from the corresponding equation (9) for the gauge factor.

The concentration of impurity levels (Fig. 9) was determined in two ways: from the results of measuring the frequency dependence of the complex conductivity components in the concentration range of the conductive component lower than, or approximately equal to, the critical concentration, as well as from the gauge factor values of specimens with $v > v_c$. Both methods supplement one the other, and the

dependences on the concentration of the conductive phase, standardized with respect to the critical one, are linked well together.

Interpretation of the $\ln N = f(v/v_c)$ relationship is made difficult by the complexity of the film structures, combined with inhomogeneities in the distribution of conductive particles in the glassy matrix, as well as by the course of concentration of the localized impurity states between them. To be able to seek an explanation for the experimental data under such conditions, it is necessary to introduce a number of various approximations. In our attempt at interpretation we will use the mechanisms controlling the development of the TFR structure as a basis [15]:

1. In the course of firing the films, wetting of the conductive grains by the glass melt occurs, and their redistribution results from the effect of capillary forces [15, 25].
2. Diffusion of Ru into the glass from the surface of conductive grains is responsible for creating a narrow band of localized impurity states in which transport of electrons takes place [15].

One additional result of computer experiments will be utilized in deriving the approximative relationships. A great number of random structure simulations showed that the ratio of the mean distance L of the centres of conductive particles in the backbone to the reciprocal third root of the number n of generated particles is constant. On the simplifying assumption of spherical conductive particles of identical sizes, d in diameter, it holds that $v = \pi n d^3 / 6$, and thus

$$L/L_c = (v_c/v)^{1/3}; \quad (5)$$

hereafter, subscript c will designate quantities pertaining to the respective percolation limit. In first approximation, diffusion of Ru into the glass can be described, similarly as in [23], by the equation

$$N = N_0 \exp(-x^2/4D\tau), \quad (6)$$

where x is the distance from the surface of the conductive particle, D is the coefficient of diffusion, and τ is time. According to the theory of activated tunnelling, the critical concentration of impurity centres corresponds to the maximum hopping distance over the conductivity path, i.e. to the distance of impurity atoms at the middle between the surfaces of neighbouring conductive particles ($x = \delta/2$). Then it holds that

$$\ln N = \ln N_c + \gamma \left[1 - (\delta/\delta_c)^2 \right], \quad (7)$$

where $\gamma = \delta_c^2 / 16D\tau$.

In the first approximation, let us take all distances of centres of conductive particles in the cluster backbone equal to their mean value L , i.e. $\delta = L - d$. On substituting into (32) and while taking into account (30), one obtains

$$\ln N = \ln N_c + \gamma \left[1 - \left(\frac{(v_c/v)^{1/3} - a}{1 - a} \right)^2 \right] \quad (8)$$

where $a = d/L_c$. A comparison of the experimental values of concentrations N found in region $v/v_c < 1$ with equation (33) yields $\gamma = 1.6$ and $a = 0.88$.

In the case of diffusion between two conductive particles, equation (31) can only be used in an approximative way for low critical concentrations N . This is why equation (33) should be regarded as an approximation of the course of the relationship $N = f(v/v_c)$, applicable for the region of low concentrations of the impurity centres.

The initial large increments in concentration N with increasing values of v/v_c in the region where the backbone of the conductive cluster is formed ($v < v_c$) decreases dramatically above the critical concentration ($v > v_c$). The reason for this can be seen in the redistribution of conductive particles in the course of firing due to the effects of capillary forces which, at

an increasing concentration of the conductive component, are responsible for the slower growth of distances between the surfaces of neighbouring conductive particles than would correspond to the growth of their concentration. The increase in the proportion of the conductive component leads to an ever more homogeneous distribution of the conductive grains in the glassy matrix [15].

The second reason of the slow increase in concentration N , calculated from piezoresistivity measurements in the $v > v_c$ region, is the fact that with a conductive path composed of series connections of many sections with diverse values of resistance R_i , and thus also of Γ_i , the most significant part will be played by sections exhibiting the highest resistances, i.e. the lowest concentrations N , because the following equation holds for the effective gauge factor of a conductive path:

$$\Gamma_{\text{ef}} = \frac{\sum_i^n R_i \Gamma_i}{\sum_i^n R_i}. \quad (9)$$

On the opposite, the resultant gauge factor of the systems of parallel conductive paths is close to Γ_{ef} from equation (34) showing the lowest resistance, i.e. the lowest gauge factor. On considering this path as the backbone of a conductive cluster, one can point out that calculation according to equations (5) or (9) will yield the critical concentration of localized impurity states in the backbone of the conductive cluster, with the exception of the highest values of N : these are the values of concentration of the impurities at which delocalization occurs in the band of impurity states, as a result of the insulant-metal transition [26].

Fig. 9, and namely the comparison of the courses of the $\ln N = f(v/v_c)$ and $\ln R = f_1(v/v_c)$ relationships shows that the relatively rapid decrease of the resistivity of films with increasing concentration of the conductive component does not correspond to the increase in concentration of impurity centres in the glass over the $v > v_c$ region. It is logical to assume that this decrease of resistivity is in particular associated with an increase in the number of conductive paths acting in parallel with the backbone of the conductive cluster, as is known from computer modelling.

6. CONCLUSION

The results of measuring piezoresistivity of thick resistor films containing the $\text{Bi}_2\text{Ru}_2\text{O}_3$ conductive component are interpreted on the basis of the concept of transport by activated tunnelling through narrow band of localized impurity states in the glass [6, 7]. The formula derived for the gauge factor allows the critical concentrations of impurity centres, considered in the theory of phonon-assisted tunnelling of electrons, to be determined [16, 17]. The evaluation of experimental data takes into account the topology of

the conductive cluster skeleton by introducing the effective angle between the direction of electron jumps and the vector of the external electric field. The simple approximations based on the concept of the formation of film macrostructure, published earlier [15] allow the experimental courses of the $\ln N = f(v/v_c)$ relationship to be interpreted by means of a curve composed of two branches. The first branch corresponds to the region of subcritical concentrations of the conductive component, v/v_c , within which the backbone of the conductive cluster is formed, while the other branch describes the slow increase in N with increasing concentration $v > v_c$ in the region of redistribution of conductive particles, taking place in the course of firing. The experimental data for the $v < v_c$ region were obtained by measuring the frequency dependence of the admittance components, while those for the $v > v_c$ region were determined by piezoresistivity measurements. The results obtained appear to provide evidence bearing out the validity of the concept of electron transport mechanism in TFR, published earlier [6, 7] as well as of that involved in the formation of the film macrostructure [15].

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MODEL ELEKTRICKÉ VODIVOSTI TLUSTOVRSŤVÝCH RESISTORŮ

I. Piezoresistivita

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Článek je prvním ze série prací, jejichž cílem má být vypracování modelu elektrické vodivosti tlustovrstvých resistorů (TFR). Tato první část se zabývá piezoresistivitou, t.j. změnami rezistancí vrstev způsobenými jejich deformací. Uvádí se teorie piezoresistivity založená na hypotéze o transportu nosičů proudu tunelováním za asistence fononů mezi lokalizovanými příměsovými stavy ve skle. Tato představa vyplynula z rozboru výsledku měření kmitočtových závislostí složek admitance a byla dříve publikována v [6]. Vypracovaná teorie bere v úvahu vliv topologie vodivého klasteru (rozložení vodivých částic ve skleněné matici), podobně jako práce [13], který však kvantifikuje odlišným způsobem zavedením efektivního úhlu Θ_{ef} . Efektivní úhel je určitou střední hodnotou úhlů mezi lokálními směry toku nosičů náboje a vektorem vnějšího elektrického pole (23), která vyplynula z teorie piezoresistivity. Zvolený tvar vzorku z obr. 3 umožňuje Θ_{ef} experimentálně nalézt z rovnice (24) a měření piezoresistivity ve dvou vzájemných orientacích směru deformace a vektoru vnějšího elektrického pole. Při znalosti efektivního úhlu můžeme z experimentálních hodnot Γ_x , Γ_y nalézt gauge faktor Γ korigovaný na úhly Θ_i (obr. 2). Podle naší teorie závisí tato korigovaná hodnota Γ pouze na koncentraci příměsových stavů a jejich Bohrově poloměru. Za nejdůležitější výsledek považujeme právě možnost vypočítat z experimentálních hodnot Γ s pomocí vztahů (6) resp. (10) kritickou koncentraci N příměsových center v oblastech skla mezi vodivými zrny. Konečně jsou na základě představ o tvorbě makrostruktury vrstev [15] nalezeny aproximace

průběhu dvou větví závislosti $\lg N = f(v/v_c)$ – obr. 9, které dobře prokládají experimentální body. Závislost koncentrace příměsových center na normovaném obsahu vodivé fáze v/v_c nalezená vyhodnocením měření piezoresistivity je, zejména v oblasti podkritických koncentrací vodivé složky ($v < v_c$), doplněna s pomocí vztahů (28) a (29) výsledky měření kmitočtových závislostí složek admitance. Obě měření se dobře doplňují. Výsledky považujeme za potvrzení výše uvedené představy o mechanismu transportu náboje v TFR, dříve uvažovaném v našich pracích [6, 7].

Obr. 1. Relativní chyba určení koncentrace příměsových center daná použitím aproximačního vztahu (6).

Obr. 2. Zavedení úhlu Θ ; mezi směrem přeskoků elektronů (spojnice nejbližších vodivých zrn) a vektorem vnějšího elektrického pole.

Obr. 3. Použitý tvar vzorku (1 – elektroda, 2 – odporová vrstva).

Obr. 4. Příklad výsledku měření nekorigovaného na Θ_{ef} .

Obr. 5. Závislost efektivního úhlu Θ_{ef} na objemové koncentraci vodivé složky – různé teploty výpalu: \times – 800°C, \circ – 850°C, \bullet – 900°C.

Obr. 6. Experimentální průběh závislosti gauge factoru Γ na normované koncentraci vodivé složky (označení bodů viz obr. 5.).

Obr. 7. Závislost rozdílu podélného a příčného gauge factoru na normované koncentraci vodivé složky (označení bodů viz obr. 5.).

Obr. 8. Exponent s ze vztahu (28) vyneseny v závislosti na koncentraci vodivé složky – různé teploty výpalu: \circ – 850°C, \bullet – 880°C.

Obr. 9. Závislost koncentrace lokalizovaných příměsových stavů na normované objemové koncentraci vodivé složky v porovnání s průběhem plošné resistivity – označení bodů viz obr. 5., \bullet – z měření kmitočtových závislostí.

Konference

6. INTERNATIONAL WORKSHOP ON GLASSES AND CERAMICS FROM GELS

proběhl ve dnech 6.–11. října 1991 ve španělském městě Seville. Tato pracovní setkání předních odborníků pracujících v oblasti sol-gel metody se konají pravidelně v dvouletých intervalech. Předcházející setkání proběhlo v roce 1989 v Rio de Janeiro. Na setkání v Seville bylo předneseno 21 přehledových referátů, 43 příspěvkových referátů a asi 140 posterů. Referáty i postery byly podle obsahu rozděleny do šesti sekcí a ty na další subsekcce. Jednotlivé sekce a subsekcce pokrývaly následující okruhy otázek:

- A. Základy sol-gel procesu (subsekcce: chemie sol-gel procesu a prekursorů; metody pro charakterizaci vlastností gelů; struktura gelů; krystalizace gelů).
- B. Principy příprav materiálu sol-gel metodou (subsekcce: příprava solů a gelů; aerogely a xerogely).
- C. Materiály získané na základě sol-gel procesu (subsekcce: příprava vláken; ochranné povlaky a tenké filmy; skla, keramika, prášky a kompozitní materiály).

- D. Vlastnosti gelů a materiálů získaných sol-gel metodou (subsekcce: optické a elektrooptické vlastnosti; elektrické vlastnosti; reologické a mechanické vlastnosti).
- E. Použití materiálů získaných na základě sol-gel metody (subsekcce: supravodivé materiály; katalyzátory; chemické sensory, elektronická keramika).
- F. Perspektivy sol-gel procesu (subsekcce: příprava netradičních skel sol-gel metodou; diskuse o nových možnostech sol-gel procesu).

Mezi příspěvky byly čteněji zastoupeny referáty a postery zabývající se gely a skly s nelineárními optickými vlastnostmi, přípravou keramických prášků a ORMOCERU, vlastnostmi a využitím aerogelů. V sekci C byly uvedeny rovněž dva postery pracovníků Ústavu skelných a keramických materiálů ČSAV.

Předsedou organizačního výboru setkání byl prof. L. Esquivias (Universita Cádiz). Tato universita již vydala sborník abstraktů prací přihlášených na setkání. Vybrané referáty a postery budou zveřejněny ve zvláštním výtisku Journal of Non-Crystalline Solids.

V. Matějec