MODEL OF ELECTRIC CONDUCTIVITY OF THICK-FILM RESISTORS
Part III. Temperature Dependence of Sheet Resistivity

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The model of electron transport based on phonon-assisted tunnelling of electrons, was used as a basis for working out the theory of temperature dependence of thick-film resistors (TFR). Tunnelling between localized impurity states in glass was assumed. The theory takes into account the effect of the activation energy, as well as that of the thermal expansion of the substrate. The contribution of the metallic type of conductivity ~~to~~ TFR resistivity is interpreted on the basis of the concept of overlapping wave functions of impurity d-states due to Ru admixtures in the glass. If the distances between impurities are smaller than the critical distance, a band of delocalized states arises which allows the metallic type of charge transport to take part in the process.

INTRODUCTION

The temperature dependence of sheet resistivity is one of the basic characteristics of thick-film resistors (TFR). During the last 15 - 20 years, a number of hypotheses aimed at interpreting the $R = R(T)$ relationship have been proposed [1 - 6]. Already the first analyses of the transport mechanisms involved [7] revealed how complex the problem actually was. The analyses resulted in the finding that none of the known charge transport mechanisms alone was capable of explaining the low values of the temperature coefficient of resistivity (*TCR*). The existence of a minimum on the $R = R(T)$ curves is usually explained by the presence of a phase with a metallic-type conductivity ($TCR > 0$), apart from a phase exhibiting temperature-activated conductivity [8 - 9]. Numerous authors assumed that the phase with the metallic type of conductivity comprised grains of the conductive component of the films ($Bi_2Ru_2O_7$, RuO_2). However, this hypothesis was cast doubt on in [10]. An exception is represented by study [11] in which its authors explain the change in the sign of *TCR* on the $R = R(T)$ curve by Mott's metal-insulant transition, similar to that occurring in some vanadium oxides. The low values of *TCR* require low activation energy values of the component having the non-metallic type of conductivity, whose effect prevails in the region of low temperatures. The indistinct temperature dependence of resistivity is characteristic of the tunnel mechanism of charge transport. In the frequently quoted study [1] the low activation energy values observed are ascribed to the energy required for transporting the electric charge (electron) between very small metallic grains. However, no significant relation between activation energy and grain size was reliably proved, which was contrary to the basic assumption of the theory. Another explanation [2, 12] is based on Mott's concept of variable range hopping [13]. In view of the low activation energy values established experimentally, the present author regards this mechanism as an unlikely one. Studies [14 - 17], which are based on different coefficients of linear thermal expansion of the film and of the substrate, have the common drawback of making use of the piezoresistivity theory which is unsuited for the TFR structure [24].

The model of electric charge transport in TFR, which is the subject of the present series of papers, is based on the evaluation of experimentally established frequency dependence of complex admittance [18]. Interpretation of the frequency dependence is based on the assumption of phonon-assisted tunnelling transport of charge carriers between localized impurity centers in glass.

THEORETICAL PART

In agreement with the concepts outlined in the previous papers [18 - 20, 24] let us assume that the transport mechanism responsible for $TCR < 0$ is based on phonon-assisted tunnelling within the narrow band of localized impurity states. According to theory [21 - 23], this mechanism corresponds to resistivity described by the equation

$$\rho \approx r_c^2 \exp(2r_c / \alpha + E_3 / kT) \qquad (1)$$

where α is Bohr's radius, r_c is the critical distance and E_3 is the activation energy of the narrow band width of the admixture states. The E_3 values of TFR vary over the range of hundredths to tenths of meV [11]. The low activation energy values are responsible for the fact that the resistivity values depend for the most part on the critical values of distances r_c of the impurities. This is why the thermal expansion of the substrate has to be included in the calculation of the course of the $R = R(T)$ relationship. With conventional TFR, the thickness of the substrate is always much greater than that of the film. For this reason, the expansion at the level parallel with the substrate surface is given by its linear thermal expansion coefficient α_s. In deriving the relationship for temperature dependence of resistivity we will start from the equation for piezoresistivity,

$$R = R_0 [1 + \Gamma(\delta r_c / r_{c0})] \qquad (2)$$

where Γ is the gauge factor and $\delta r_c / r_{c0}$ is the deformation. If $\alpha_s \approx \alpha_f$, where α_f is the coefficient of linear thermal expansion of the film, no correction for the meandrity of conductive paths in the conductive cluster is necessary. Let us substitute into Equation (2) from (1),

$$R_0 = A \exp(E_3 / kT),$$

and for deformation due to thermal expansion,

$$\delta r_c / r_c = \alpha_s T.$$

In the low temperature region where the transport mechanism with $TCR < 0$ prevails, the temperature dependence of resistivity is then defined by the equation

$$R(T) = A(1 + \Gamma\alpha_s T) \exp(E_3 / kT) \qquad (3)$$

If the coefficients of thermal expansion α_s and α_f differ significantly, the effective value of the thermal expansion coefficient has to be substituted into Equation (3) in place of α_s. In the case of films based on glasses currently employed in commercial pastes, the effective value of the thermal expansion coefficient differs from $\alpha_s = 6 \times 10^{-6}$ K^{-1} by less than 6 %. The courses of the relationship according to Equation (3) pass through a minimum.

EXPERIMENTAL PART

The compositions and the technology used in the preparation of samples were described in [24]. In the measurements, use was again made of model films which after firing comprised solely $Bi_2Ru_2O_7$ and a lead-silica-alumina glass (66 % PbO + 32.5 % SiO_2 + + 1.5 % Al_2O_3). The corundum substrate contained 96 % Al_2O_3. The temperature dependence of resistance over the temperature range of 85 to 400 K was measured in an evacuated metallic cryostat cooled with liquid nitrogen. The collection of thermocouple voltage and multimeter-measured resistance data was automatic, in a form suitable for computer processing.

The experimentally established temperature dependences of resistivity were used to determine, by means of Equation (3) and non-linear regression, the activation energy values E_3 and the $(\alpha_s\Gamma)$ products. We have restricted our calculations to the temperature range of 90 to 150 K, over which a very small effect of another transport mechanism with $TCR > 0$ was assumed. Figures 1 and 2 show examples of experimental points with the values calculated according to Equation (3), using the parameters established by the non-linear regres-

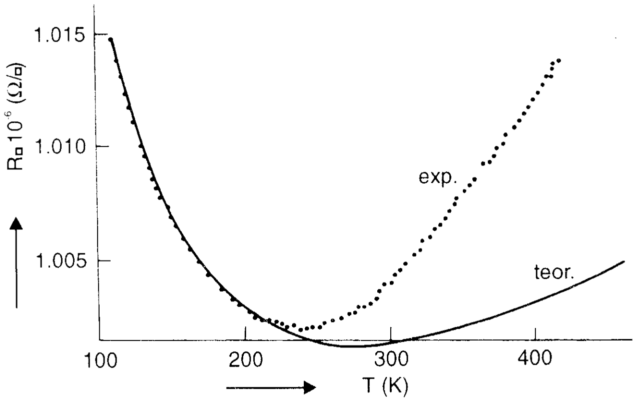

Figure 1. Temperature dependence of sheet resistivity of TFR for the composition with $v = 0.095$. The results are compared with the course obtained from non-linear regression

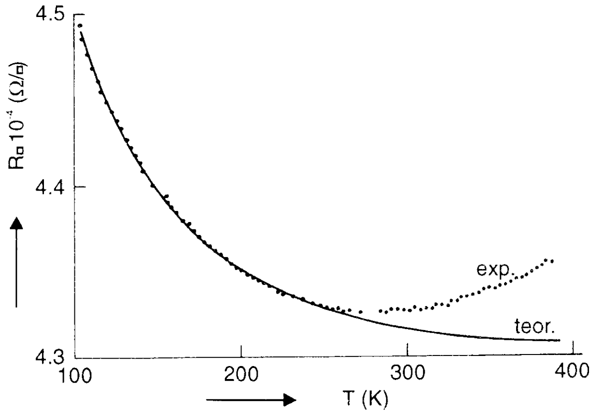

Figure 2. Temperature dependence of sheet resistivity of TFR for the composition with $v = 0.212$. The results are compared with the course obtained from non-linear regression

sion method. The calculated values of parameter ($\alpha_s\Gamma$) were employed in calculating the coefficient of linear thermal expansion of the substrate in such a way that they were compared with the values of gauge factor Γ_P obtained from piezoresistivity measurements [24]. The values of α_s, calculated for the temperature interval of 90 to 150 K, are listed in Table I together with the other parameters found for the various volume concentrations v of the conductive component. As the course of the temperature dependence of α_s in the low temperature region was unknown, we attempted to compare the mean value established, $\alpha_s = (2.7 \pm 0.7) \times 10^{-6}\ K^{-1}$, with the extrapolated dependence of $\alpha_s(T)$. This dependence was measured on samples of the conventional substrates over the temperature range of 297 to 1297 K (Table II). The course plotted in Figure 3 was calculated by means of the standard parabolic interpolation formula from the mean experimentally established values listed in Table II. The result in Figure 3 shows that the value of α_s calculated from the regression parameter ($\alpha_s\Gamma$) is in a relatively good agreement with the course of $\alpha_s(T)$.

Table I. Parameters of Equation (3), experimental values of gauge factor Γ_P and substrate thermal expansion coefficients α_s calculated from the parameter $\alpha_s\Gamma$

v/v_c	E_3 (eV)	$\alpha_s\Gamma \times 10^5$	Γ_P	$\alpha_s \times 10^5$ (90-150K)
1.16	0.450	8.66	32.0	2.7
1.33	0.375	8.45	28.1	3.0
1.38	0.345	6.25	25.2	2.5
1.59	0.295	7.59	24.5	3.1
1.89	0.263	4.38	21.7	2.0
1.89	0.234	4.76	21.7	2.2
2.04	0.188	3.49	21.4	1.6
2.12	0.215	6.92	19.1	3.4
2.63	0.135	5.04	17.8	2.8
2.88	0.071	7.60	17.9	4.2
2.94	0.103	4.82	17.7	2.7
3.17	0.055	2.48	15.6	1.8

Table II. Experimental values of substrate linear thermal expansion coefficient

T (K)	$\alpha_s \times 10^6$ (K^{-1})
297 - 397	5.93
297 - 597	6.61
297 - 897	7.45
297 - 1297	8.03

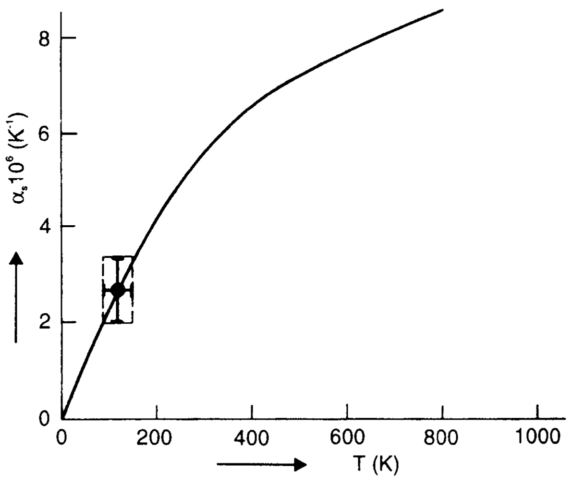

Figure 3. Temperature dependence of the substrate thermal expansion coefficient α_s. The values were taken from Table II in comparison with the mean value of α_s from Table I

DISCUSSION

The E_3 and ($\alpha_s\Gamma$) parameters established are important for assessing the plausibility of the theory. The values of product ($\alpha_s\Gamma$), obtained from piezoresistivity measurements, yield a reasonable value of the thermal expansion coefficient of the substrate for the temperature range of 90 to 150 K. The calculated activation energies E_3 are of the same order of magnitude as the values published in study [11].

The different courses of the theoretical and experimental relationships $R = R(T)$, shown in Figures 1 and 2, allow an additional type of transport to be considered, namely one of the metallic type. The interpretation assuming a contribution of the metallic-type conductivity to the film resistivity is significantly supported by the dependence of activation energy E_3 on the concentration of localized impurity states N. The N concentrations were calculated from the experimental values of piezoresistivity by the method described in [24]. The relationship

$$E_3 = E_{30} - aN^{1/3} \qquad (4)$$

is plotted in Figure 4. The parameters established for Equation (4) were $E_{30} = 0.97 \times 10^{-3}$eV and $a = 3.33 \times$ $\times\ 10^{-12}$ eVm, and correspond to a critical concentration of admixture centers $N_k = 2.4 \times 10^{25}\ m^{-3}$. For the critical distance of admixture centers, the theory provides the value [21 - 23]

$$r_c = 0.89\ N^{-1/3} \tag{5}$$

The insulant-metal transition in our formulas then corresponds to a critical distance of admixture states of r_c = 3 nm. It is assumed that at this distance the overlap of the d-state wave functions of admixtures in glass, namely Ru, is adequate for creating a band of delocalized states. Within this band, transport of free electrons characterized by $TCR > 0$ takes place. The narrow band is responsible for the high effective mass of charge carriers exhibiting the corresponding high resistivity.

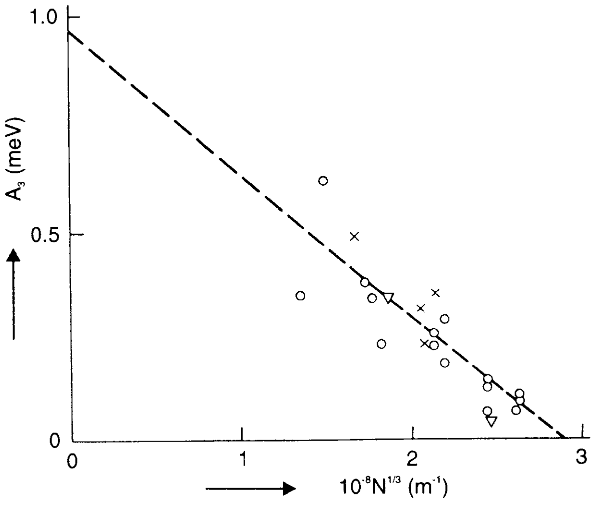

Figure 4. Activation energy E_3 vs. the critical concentration of impurity states according to Equation (4)

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MODEL ELEKTRICKÉ VODIVOSTI TLUSTOVRSTVÝCH RESISTORŮ

Část 3. Teplotní závislost plošné resistivity

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Na bázi modelu transportu elektronů v tlusto-vrstvých resistorech, založeném na tunelování elektronů za asistence fononů mezi příměsovými stavy ve skle [18-20, 24], je navržena teorie teplotní závislosti resistivity $R(T)$. V oblasti dostatečně nízkých teplot je průběh teplotní závislosti popsán vztahem (3), který vedle aktivační energie E_3 zahrnuje vliv teplotní roztažnosti substrátu. Aktivační energie E_3 charakterizuje rozptyl energií příměsových stavů v jejich úzkém pásu. Koeficient lineární teplotní roztažnosti substrátu α_s ovlivňuje průběh $R(T)$ prostřednictvím piezoresistivity [24]. Měření teplotních závislostí byla realizována na vzorcích modelových složení vrstev s vodivou složkou $Bi_2Ru_2Ob_7$ a sklem o složení 66 % PbO, 32,5 % SiO_2, 1,5 % Al_2O_3. Hodnoty parametrů z rovnice (3) byly vypočteny z dat nízkoteplotní části experimentálního průběhu $R(T)$ metodou nelineární regrese. Hodnoty parametru $\alpha_s\Gamma$ byly spolu s hodnotami gauge faktoru Γ_p, které byly nalezeny vyhodnocením měření piezoresistivity [24], použity k výpočtu koeficientu lineární teplotní roztažnosti substrátu α_s pro oblast teplot 90 - 150 K. Střední hodnota α_s(90 - 150 K) dobře koreluje s extrapolovaným průběhem teplotní závislosti koeficientu teplotní roztažnosti substrátu (obrázek 3), nalezené standardní kvadratickou interpolací naměřených hodnot (tabulka II). Porovnání experimentálních závislostí $R(T)$ s průběhy podle rovnice (3) (obrázky 1 a 2) ukazují na vliv dalšího mechanismu transportu, který je kovového charakteru s TCR>0. Interpretace tohoto mechanismu vychází z představy o vzniku příměsového pásu. Podle předpokladu pás vzniká v průběhu výpalu vrstev difúzí Ru z vodivých zrn do skla [19,20]. Předpokládá se, že v oblastech s vyšší koncentrací příměsových stavů dochází k překrývání vlnových funkcí d-stavů atomů Ru a k jejich delokalizaci, jak ukazuje závislost aktivační energie E_3 na kritické koncentraci příměsí (obrázek 4).