MODEL OF ELECTRIC CONDUCTIVITY OF THICK-FILM RESISTORS
IV. Voltage Dependence of Resistivity

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In the measurements, use was made of model films 15 ± μm in thickness, with the conductive component of $Bi_2Ru_2O_7$ dispersed in glass having the composition 66 % PbO + 32 % SiO_2 + 1.5 % Al_2O_3. The courses of the voltage dependence of resistivity are interpreted as the Poole-Frenkel phenomenon on isolated admixture centers in glass. The measurement on the isolated admixture centers was made possible by selecting samples having the concentration of the conductive component closely below the critical concentration (the percolation limit). As predicted, the charge transport proceeded by the hopping mechanism in the empty zone of delocalized states, which, according to an analysis of the results, lies by 0.76 ± 0.05 eV above the narrow impurity band [3, 10].

INTRODUCTION

Thick-film resistors (TFR), prepared by the firing of commercial pastes, show a very low voltage dependence. For example, for specimens with sheet resistivity, values of the voltage coefficient (*VCR*) ranging from 9 to 15 ppm cm V^{-1} are specified. *VCR* also decreases with the decreasing value of resistivity [1-2]. The low dependence of resistivity on electric field intensity corresponds to the concept of the prevailing mechanism of charge carrier transport which is assumed to proceed by phonon-assisted tunnelling within a narrow band of impurity states in the glass [3, 10]. The distances r between the atoms of admixtures in the glass increase with decreasing concentration of the conductive component in glass [3], thus causing the probability of tunnelling passages through the barrier between the localized centers to be exponentially reduced. In the case of samples whose concentration of the conductive component is closed to the percolation limit v_c the most part of the electric current is concentrated into the backbone of the conductive cluster. Further decreasing the concentration of the conductive components leads to an increase in the number of backbone sections [4] in which the distances between the admixtures exceed a certain critical value r_k. The tunnelling probability then becomes negligible compared to the probability of an electron becoming excited to a higher band. In this way the hopping mechanism of transport proceeding in the higher band with delocalized states will prevail [5]. It is therefore assumed that at concentrations close to the critical value v_c one can regard the backbone of a conductive cluster as a series connection of two types of resistances, namely the resistances composed of sections where the charge is transported by phonon-assisted tunnelling and those over sections taking place by the hopping mechanism. Unlike the tunnelling transport, the other mechanism can be expected to be distinctly voltage-dependent.

EXPERIMENTAL PART

The samples employed had the same composition as the films described in the previous parts of the present series of studies [3,4,9]. The content of the conductive component ($Bi_2Ru_2O_7$) in the paste corresponded to its concentration by volume v = 1.09 v_c in the fired film. The critical concentration (percolation limit), established by the standard method from the dependence of resistivity on the concentration of the conductive component, was v_c = 0.072. The dispersion of values of the ratio v/v_c, usual with samples having concentrations of the conductive component close to the critical one, allowed samples with concentrations just below the critical limit to be selected. In the weak electric field region, the planar resistivity was of the order of 10^{10} Ω/□. The samples were prepared from a model resistor paste which in its inorganic component contained solely a finely ground glass frit and the $Bi_2Ru_2O_7$ conductive pigment. The glass had the composition 66 % PbO + + 32.5 % SiO_2 + 1.5 % Al_2O_3. The specific surface areas of the powdered materials employed, determined by the Brunauer-Emmet-Teller (BET) method, amounted to 5 $m^2 g^{-1}$ for the conductive pigment, and 1.05 $m^2 g^{-1}$ for the frit. The lacquer component was based on ethyl-cellulose dissolved in terpineol. The resistor films were applied by screen printing onto corundum substrates containing 96 % Al_2O_3 and fired in a tunnel kiln at

850 °C with a holding period of 9 minutes at the highest temperature, using a total time of passage of 1 hour. The fired films were 15 ± 2 μm in thickness. The areas measured were 4 × 2mm in size, and provided with printed and fired AgPd contacts at the shorter sides. The voltage dependence of resistance was determined by measuring the current with the Tesla Brno BM 545 picoammeter, and the voltage with the Metra Blansko MT 100 voltmeter. The relative error in the sheet resistivity measurement ranged from 15 % on samples with resistances of the order of 10^{10} Ω, to 5 % on samples with resistances of the order of 10^{8} Ω. The stability of resistivity values in the course of measuring the voltage dependence was checked by measuring at an increasing and then at a decreasing voltage. The dependencies established were evaluated by linear regression. The correlation coefficient was within the interval of 0.980 to 0.998. The measurements were carried out at room temperature, in liquid nitrogen and in a temperature chamber over the temperature range of 298 to 378 K.

RESULTS

The established experimental courses of the dependence of resistivity on voltage (Figure 1) conform to the concept of thermal ionization of localized impurity states assisted by the electric field (Poole-Frenkel's phenomenon). In the evaluation of experimental data, use was made of the equation [6]

$$R = B \exp(E_2/2kT) \exp(-\beta F^{1/2}/2kT), \quad (1)$$

where for Poole-Frenkel's coefficient it holds that

$$\beta = (e^3/\pi æ)^{1/2}. \quad (2)$$

In Equation (1), F is intensity of the local electric field and æ is the permittivity of glass. In principle, in the case of the isolated center, reduction of the Coulomb-type barrier by interaction with the electric field is involved. Equation (1) holds in the one-dimensional case of reducing the barrier height in the direction of the local field. The centers can be regarded as isolated ones if the intensity of the local field is greater than F_0 [7],

$$F_0 = (kT/\beta)^{1/2}. \quad (3)$$

In our case, for intensity of the local electric field it represents the condition $F > 9.10^5$ V m^{-1}. Lower values of resistances of bonds with the tunnelling mechanism prevailing cause the electric field to concentrate in the backbone sections containing voltage-dependent resistances. In the first approach it will be assumed that they are under full effect of the electric field, and that the local field intensity F is proportional to the external field intensity ε,

$$F = K \varepsilon. \quad (4)$$

The qualitative agreement of the experimental courses with Equation (1) is demonstrated by Figure 1 in

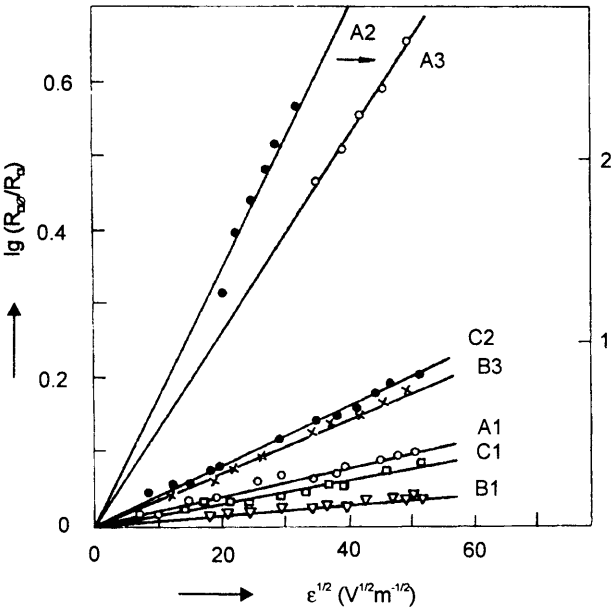

Figure 1. Examples of voltage dependence of resistivity of various samples of the series with v = 1.09 v_c on substrates designated A, B and C

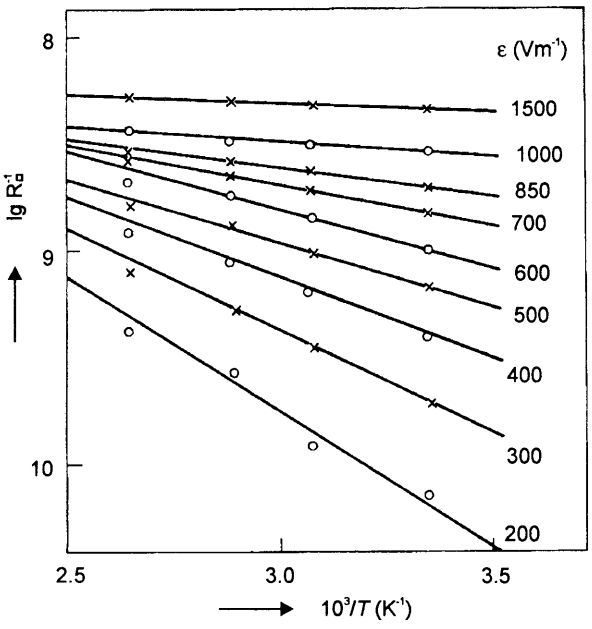

Figure 2. Temperature dependence of resistivity of sample A2 measured at various voltages.

which R_0 is the resistance value extrapolated to F = 0.

Quantitative comparison is impossible due to the already mentioned unknown intensity F of the local fields. The temperature dependence of conductivity A2, measured at several values of the external electric field intensity, is plotted in Figure 2 while Figure 3 shows the activation energy of hopping conductivity in terms of the external electric field intensity,

$$E_2 = E_{2o} - \beta_2 \varepsilon^{1/2}. \quad (5)$$

Using linear regression, the value of activation energy $E_{2o} = 0.76 \pm 0.07$ eV was determined. Coefficient β_2 includes the relation between the local electric field and the external one.

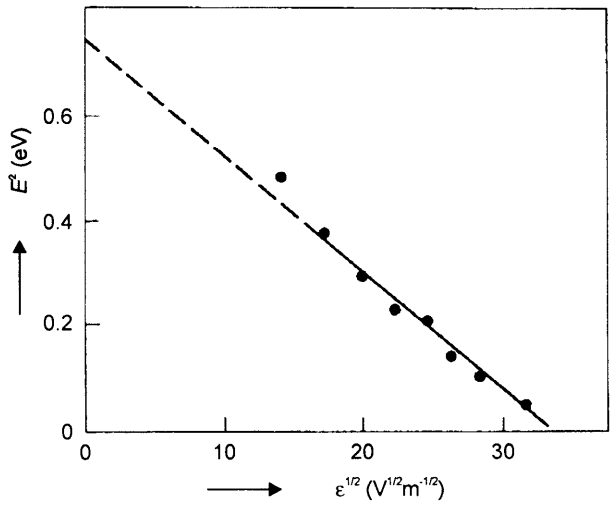

Figure 3. Activation energy of hopping conductivity E_2 of sample A2 vs. intensity of external electric field ε.

DISCUSSION

Activation energy E_{2O} is assumed to represent the distance of the narrow band of localized admixture states from the mobility edge, or from the higher unoccupied band with delocalized states. The relatively high value of activation energy E_{2o} causes the probability of the impurities becoming ionized to decrease rapidly, in terms of decreasing temperature, down to a negligible value at the temperature of liquid nitrogen. The measurements carried out at temperature LN_2 show a satisfactory agreement with the theoretical course derived for Fowler-Nordheim's tunnelling through the barrier separating two neighbouring admixture centers ($r > r_c$), whose form is modified by an electric field of intensity F [6]:

$$R = B\, F \exp(-\Phi/F), \quad (6)$$

where

$$\Phi = \frac{8\pi\,(2m^*)^{1/2}}{3eh} E_{20}^{3/3}, \quad (7)$$

m^* is the effective mass of the charge carriers, and h is Planck's constant.

The results of the measurements are plotted in Figure 4, again on the assumption of a proportionality between the intensities of local and external electric fields.

A comparison of the slopes of straight lines in Figures 3 and 4 with the respective constants β_2 and Φ enumerated for æ = 8, $E_{2o} = 0.76$ eV and $m^* = m_o$, gives for proportionality coefficient K the value of $1.3 \cdot 10^6$ from the dependence of activation energy on electric field

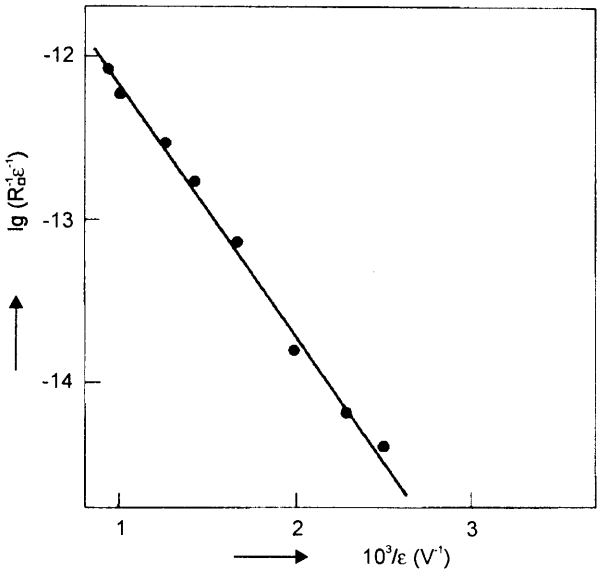

Figure 4. Example of Fowler-Nordheim's tunnelling [6] measured at temperature LN_2 on sample A2.

intensity, and the value of 7.1×10^5 from the F-N tunnelling. The satisfactory agreement of the two values shows that the assumption [4] is justified. At $K > 10^5$, our experiments give a local electric field intensity $F > > 10^7 - 10^8$ V m^{-1}, so that condition (3) is well satisfied and the localized centers can be regarded as isolated ones. The high values of proportionality coefficient K in Equation (4) are associated with the small number of bonds between the conductive grains containing impurities with distance $r > r_k$. Moreover, according to the concept of diffusion profile between the conductive grains [8], the sections with distances of impurities $r > r_k$ represent only fractions of distances between grains. More than a half of the backbone length is composed of diameters of conductive grains [8]. Further decreasing the concentration of the conductive component below the v_c value will increase the number of backbone sections of the conductive cluster with $r > r_k$, thus reducing the value of local electric field intensity and increasing the number

of series resistances with a high resistivity. This is why the distinct voltage dependence of type (1) resistance can only be observed on samples with a concentration of the conductive component approximately equal to the critical one.

CONCLUSION

The present paper is the fourth part of a series of studies [3, 4, 9] aimed at contributing to the elucidation of the charge transport mechanism in the composite systems of thick-film resistors. All of the studies were based on measurements of model films of simple composition. The measurements of voltage dependence of sheet resistivity of samples with a volume concentration of the conductive component close to the critical one (percolation limit) are supplemented with experimental results and theories published in the previous papers (frequency dependence of the components of complex admittance [10], piezoresistivity [3], temperature dependence of resistivity [9] and a computer model of the backbone of conductive cluster TFR [4]). The measurements were carried out on samples with the real concentration of the conductive components closely below the critical one. This allowed the Poole-Frenkel phenomenon to be studied on isolated admixture centers. From the dependence of activation energy of hopping conductivity E_2, measured at various applied voltages, the difference in energies between a narrow band of localized admixtures [3] and the closest narrow band of delocalized states was found to amount to $E_{20} = 0.76 \pm 0.07$ *eV*. This result can be regarded as a valid contribution to the knowledge of the energy band model of glass in TFR, alloyed by Ru impurity by diffusion from conductive grains in the course of firing [8]. To the author's knowledge, no such measurements have so far been carried out and interpreted. In the paper to follow, the results published so far will be synthesized into a proposed model of charge transport in thick-film resistors.

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MODEL ELEKTRICKÉ VODIVOSTI TLUSTOVRSTVÝCH RESISTORŮ

IV. Napěťová závislost resistivity

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Tlustovrstvé resistory (TFR), připravené výpalem komerčních past, jsou velmi málo napěťově závislé. Slabá závislost resistivity na intensitě elektrického pole odpovídá představě o převládajícím mechanismu transportu nosičů náboje, který probíhá tunelováním za asistence fononů v úzkém pásu příměsových stavů ve skle [3, 10]. U vzorků s koncentrací vodivé složky blízké kritické hodnotě v_C, je elektrický proud převážně soustředěn do páteře vodivého klasteru a při dalším poklesu koncentrace vodivé složky se pravděpodobnost tunelování stává zanedbatelnou vedle pravděpodobnosti excitace elektronu do vyššího pásu. Takto u vzorků s koncentrací vodivé složky těsně pod kritickou převládne hopping mechanismus transportu, založený na excitaci nosičů proudu do vyššího pásu s delokalizovanými stavy [5].

Při měření byly použity modelové vrstvy s vodivou složkou $Bi_2Ru_2O_7$ rozptýlenou ve skle o složení 66 % PbO + 32.5 % SiO_2 + 1.5% Al_2O_3. Vzorky byly připraveny standardní tlustovrstvou technologií s výpalem v tunelové peci s maximální teplotou 850 °C. Tloušťka vrstev byla 15 ± 2μm.

Experimentální průběhy napěťových závislostí resistivity vyhovují představě o termické ionizaci izolovaných lokalizovaných příměsových stavů za asistence elektrického pole (Poole - Frenkelův jev). Pro vyhodnocení experimentálních dat jsme použili vztah (1) [6]. F je intensita lokálního elektrického pole, která je podle našeho předpokladu úměrná intensitě vnějšího elektrického pole (4). Rozbor výsledků měření ukazuje, že podmínka $F > F_0$ (3) pro to, abychom příměsová centra mohli považovat ze isolovaná, je dobře splněna. Měřením závislosti resistivity na napětí při několika teplotách (obr.2) byla nalezena závislost aktivační energie hopping konduktivity na přiloženém napětí. Vyhodnocením metodou lineární regrese byla podle vztahu (5) získána hodnota E_{20} = 0.76 ± 0.07, kterou interpretujeme jako energii, kterou musí elektron v úzkém příměsovém pásu získat, aby přešel do vyššího prázdného pásu delokalizovaných stavů. Při dostatečně nízkých teplotách, např. při teplotě kapalného dusíku, je již pravděpodobnost excitace elektronu do vyššího pásu zanedbatelná a pozorujeme pouze tunelování nosičů náboje mezi příměsemi ve skle, které je silně ovlivňováno elektrickým polem, které deformuje potenciální bariéry mezi isolovanými příměsovými centry (Fowlerovo-Nordheimovo tunelování) - obr.4.

Tyto výsledky považujeme za příspěvek k poznání energetického pásového modelu skla v TFR, legovaného příměsí Ru difuzí z vodivých zrn během výpalu vrstvy [8]. Pokud je nám známo, nebyla dosud tato měření provedena a interpretována. V následujícím článku budou dosud publikované výsledky [3,4,9] syntetizovány do návrhu modelu transportu náboje v tlustovrstvých resistorech.