THE EFFECT OF FIRING TEMPERATURE ON THE
PROPERTIES OF MODEL THICK-FILM RESISTORS

I. Morphology and Microstructure of the Films

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On the basis of microscopical examinations and resistivity and Seebeck's
coefficient measurements, a model of the development of structure (morphology)
of thick-film resistors (TFR) during their firing has been suggested. The model
differs from those published so far particularly in that formation of a narrow
band of localised impurity states, resulting from diffusion of Ru from the
conductive grains, is considered instead of sintering of conductive grains in
the last stage of structural development.

INTRODUCTION

Perfect knowledge of the effect of technological conditions on the properties
of fired films is one of the prerequisites for continuing application of thick-film resistors
(TFR) in hybrid integrated circuits (HIC) in view of the increasing demands on their
parameters. The firing of the films is one of the decisive technological operations.
The present study is the first of a series of several papers in which the authors strive
to formulate a complex conception of the effect of firing parameters, particularly
its peak temperature, on the properties of thick-film resistors. The additional papers
will deal with the effect of firing temperature on the critical coefficients of the percola­
tion theory, the effect of repeated firing on the properties of model resistor films
and finally with the relationships between the parameters of the glass frit employed
and the behaviour of films in the course of firing.

Similarly to other types of thick layers, thick-film resistors are created by screen
printing on insulating, particularly alumina substrates and subsequent firing in
a tunnel kiln. After firing, the TFR represents an inequilibrial heterogeneous system
based on two essential inorganic components, namely the conductive pigment and
the glass. The initial pastes for screen printing also contain an organic vehicle. The
conductive component mostly consists of oxidic compounds of ruthenium, namely
RuO₂, or oxide compounds with cubic pyrochlor structure, particularly Bi₂Ru₂O₇
or Pb₂Ru₂O₆. The glass introduced into the paste in the form of a finely ground frit
belongs typically to the system of high-lead silicate or borosilicate glasses. The
inorganic component of commercial pastes used in the manufacture of HIC or
potentiometers further contains modifiers, i.e. oxides of metals which adjust the
course of the temperature dependence of sheet resistivity, or improve its long-term
stability.

The sheet resistivity of typical TFR depends on volume concentration of the
conductive component and varies over the range of 10 to 10⁷ Ohm⁻¹, which at
a film thickness of 15 µm corresponds to resistivities over the interval of 1.5 × 10⁻⁴ to
1.5 × 10² Ohm ⋅ m.
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The properties of TFR are closely associated with their structure (morphology), i.e. with the arrangement of conductive and insulating (glass) grains in the film, or conductive grains in the continuous glassy matrix. The literature describes essentially two different types of TFR morphology. The first type described in [1, 2] was found in films based on RuO₂ and is characteristic of segregation of conductive pigment particles at the grain boundaries of the substantially larger sintered glass particles. This type of arrangement of conductive particles is called segregated structure. Approximately homogeneous distribution of conductive particles in the glass matrix was observed in [3] with TFR based on ruthenates with a pyrochloir structure. This type of arrangement is called quasihomogeneous structure. In this type of morphology, the distribution of conductive particles throughout the glassy matrix is often approximated by sc lattice arrangement with the lattice parameter according to the equation [4]:

\[ s = \left( \frac{\pi}{6v} \right)^{1/3} \cdot d, \]

where \( v \) is the concentration of the conductive component by volume and \( d \) is the mean diameter of its grain. In addition to this, the two basic types of TFR structure can be combined with another type of segregation resulting from sedimentation of conductive grains towards the substrate [5]. The chemical reactions between the conductive component and glass, taking place during the firing, are discussed in [6]. According to this study, with the use of high-lead glasses and the Bi₂Ru₂O₇ conductive pigment, the firing reaction produces the mixed ruthenate Bi₂₋ₓPbxRu₂O₇₋₋₂ₓ, and decomposition of Bi₂Ru₂O₇ yields RuO₂, while the bismuth oxide enters the glass. In the case of systems based on RuO₂ it is assumed that firing brings about formation of Pb₂Ru₂O₆ particularly at the surface of conductive grains.

The development of structure during firing and the mechanisms involved are described in [7—9, 15]. The structure is assumed to develop in the following stages [9]:

1. Sintering of glass and wetting of conductive particles.
2. Rearrangement of conductive particles and formation of the conductive lattice.
3. Sintering of conductive particles in the presence of glass.
4. Growth of the larger conductive particles at the expense of the smaller ones (Ostwald ripening).

However, the sintering of conductive particles was not proved directly [7—9], being only indicated by the growth of conductive grains observed at high temperatures and after relatively long periods of time. The effect of the firing process on the properties of TFR was the subject of several additional studies [10—12]; however, a complex conception of the structure of TFR and their properties has still been lacking. Moreover, some conceptions of the structural development, e.g. those suggested in [7—9], and in particular the process of sintering of conductive grains, are in disagreement with the results of other measurements [13]. A new conception of the development of structure in the course of firing will therefore be suggested in the present and subsequent articles.

MATERIALS

To simplify the subject matter, use was made of specimens prepared from model resistor pastes containing only the glass frit and the conductive pigment in its inorganic component. The model films containing either Bi₂Ru₂O₇, with a surface
area (measured by the Brunauer—Emmet—Teller method, BET) of 5 m² g⁻¹, or RuO₂ with a BET surface area of 8.9 m² g⁻¹, were studied. Similarly, only one of the two glasses (A, B), whose composition and surface area are listed in Table I,

Table I

<table>
<thead>
<tr>
<th>Glass designation</th>
<th>Composition (wt. %)</th>
<th>Specific area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PbO</td>
<td>SiO₂</td>
</tr>
<tr>
<td>A</td>
<td>66</td>
<td>32.5</td>
</tr>
<tr>
<td>B</td>
<td>69</td>
<td>22</td>
</tr>
</tbody>
</table>

were used in the experimental films. After grinding, a part of glass A was air classified in the Multiplex-Zickzaacksichter 100 MR instrument made by Alpine Ausberg Co. The particle sizes of 3.5 and 10 µm were chosen as sorting limits. The classification produced 4 grain size fractions with BET surface areas of 2.24, 1.17, 0.78 and 0.51 m² g⁻¹ respectively. The value of specific area in brackets is given behind the letter A in the designation of the respective classified frit. The lacquer vehicle employed was based on ethylcellulose and terpineol. The type SA 305 08 substrates from TESLA Hradec Králové Concern Corporation contained 96% Al₂O₃. The specimens of films for resistivity and Seebeck's coefficient measurements were of rectangular shape 12 × 2 mm² in size and 15 to 30 µm in thickness according to the maximum temperature of the firing cycle. The firing of the films was carried out in a tunnel kiln with a soaking time of 9 minutes at the maximum temperature. The maximum firing temperatures were chosen from the range of 450 to 900 °C.

EXPERIMENTAL METHODS

The structure (morphology) of the films was studied by optical microscopy in reflected light and by scanning electron microscopy (SEM). Polished surfaces of the films were examined, in the case of SEM, after selective etching according to [16] to achieve suitable contrast between the conductive component and the glassy matrix. The dependence of porosity on firing temperature was evaluated quantitatively by the automatic image analyzer IBAS-SEM-IPS made by Opton Corporation, in combination with an optical microscope.

The DC resistivity was measured with the Metra MIT 291 multimeter at room temperature. The thermoelectric voltage as well as the voltage of Pt—PtRh10 thermocouples for the determination of the temperature difference were measured with the same multimeter with an accuracy better than 1 µV. A correction for thermoelectric voltage of the Pt leads was carried out in the calculation of Seebeck's coefficient αₜₘₜ.
EXPERIMENTAL RESULTS

In the present part, the results will be given of studying the morphology by optical and scanning electron microscopy, examination of the microstructure of crystalline components by X-ray diffraction and by area resistivity measurements at room temperature on specimens fired at various peak temperatures $t_v$ from the interval of 450 to 900 °C.

Morphology of the films

The development of the morphology of films in the course of firing can be seen in Figs. 1 and 2 which are optical micrographs (magn. 500×) of films (glass + conductive component with volume concentration $v$): glass $A + Bi_2Ru_2O_7$ ($v = 0.1470$) and glass $B + RuO_2$ ($v = 0.1480$). On the micrographs the conductive component is white, glass is grey and the pores are black. Fig. 3 shows the effect of frit grain size on the structure of films based on $Bi_2Ru_2O_7$ ($v = 0.1802$) fired at peak temperatures of 600 and 850 °C respectively. All the four sorted fractions of glass frit $A$, dealt with in the paragraph on experimental materials, were used in the preparation of pastes for printing these films. A more detailed view of the TFR structure, particularly of the mutual movement (redistribution) of conductive grains in the course of firing is demonstrated by scanning electron micrographs (magn. 2500×) of the $B + RuO_2$ films ($v = 0.1481$) fired at several peak temperatures (Fig. 4).

The structure of crystalline components

X-ray diffraction on the fired films proved the formation of admixture bismuth-lead ruthenates [6] in films based on the $Bi_2Ru_2O_7$ conductive component, with both types of glass, $A$ and $B$. After firing, the combination of $Bi_2Ru_2O_7$ with glass $A$ showed a small amount of $RuO_2$ which, however, was not found in the combination with glass $B$. The amount of Pb entering the lattice of $Bi_2Ru_2O_6$ increases with firing temperature, as indicated by the dependence of the lattice parameter on firing temperature $t_v$ in Fig. 5. The value of the lattice parameter of $Bi_2Ru_2O_7$ is given

![Graph](image)

Fig. 5. Dependence of the lattice parameter of the pyrochloric structure of the conductive component in the $Bi_2Ru_2O_7$ films with glass $A$ on firing temperature.

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**Fig. 6.** Dependence of area resistivity on firing temperature of films a – Bi$_2$Ru$_2$O$_7$ with glass B ($v = 15.69$ vol. %), b – RuO$_2$ with glass A ($v = 13.68$ vol. %), c – RuO$_2$ with glass B ($v = 14.81$ vol. %).

**Fig. 7.** Area resistivity vs. firing temperature of Bi$_2$Ru$_2$O$_7$ films with sorted glass A particle size fractions; a – A(2.24), b – A(1.17), c – A(0.51).
as $a = 1.0288 \pm 0.00095 \text{ nm} \ [15]$, and $1.0299 \text{ nm} \ [14]$, and measurements on 8 different samples of the powdered compound $\text{Bi}_2\text{Ru}_2\text{O}_7$, carried out at our Institute, yielded the value $a = 1.0290 \pm 0.0002 \text{ nm} \ [17]$. For $\text{Pb}_2\text{Ru}_2\text{O}_6$, the same authors found $a = 1.0254 \text{ nm} \ [17]$, and $a = 1.0253 \pm 0.0002 \text{ nm} \ [18]$. Ruthenium oxide only was found in $\text{RuO}_2$-based films, and no formation of $\text{Pb}_2\text{Ru}_2\text{O}_6$ was observed contrary to the results of [6].

### Fig. 8. The effect of concentration of the $\text{Bi}_2\text{Ru}_2\text{O}_7$ conductive component on the course of dependence of area resistivity on firing temperature of films containing glass $A(0.51)$.

found $a = 1.0254 \text{ nm} \ [17]$, and $a = 1.0253 \pm 0.0002 \text{ nm} \ [18]$. Ruthenium oxide only was found in $\text{RuO}_2$-based films, and no formation of $\text{Pb}_2\text{Ru}_2\text{O}_6$ was observed contrary to the results of [6].

**Area resistivity**

The dependence of area resistivity on peak temperature was studied for two main reasons. In the first place because it is the basic parameter of TFR and in the second the course of the $R(t_v)$ relationship was shown to supplement very suitably the
structural examination described above. The results of measuring the courses of $R(t_v)$ for three different systems of model TFR are plotted in Fig. 6. The shape of the dependence is essentially determined by processes taking place in the formation of the film structure, and the positions of the individual peaks on the ordinate of firing temperatures are closely associated with the properties of the glass. The actual shape of the dependence $R(t_v)$ is also affected by additional parameters, above all by the grain size of both components and the concentration of the conductive pigment. Fig. 7 demonstrates the influence of the glass frit grain size and Fig. 8 that of the concentration of the conductive components over the wide interval from 8.25 to 67.2 vol.% of Bi$_2$Ru$_2$O$_7$ with glass $A$ (0.51). Both parameters, as indicated by the diagrams, affect particularly the values of area resistivity at both extremes (minimum and maximum) and at the same time also influence the position of extremes along the firing temperature ordinate.

**DISCUSSION**

The mechanisms taking part in the development of the TFR structure considered on the basis of microscopic examinations and electrical measurements do not essentially differ from the concepts published earlier [7—9, 15] as regards the initial stages of firing. However, the present authors have a quite different idea of the final stage during which the structure of the resistor film is formed and which decisively influences the mechanism of charge transport in TFR. In the simplest way, this idea of the development of TFR structure can be described by the following steps:

a) sintering of glass,

b) wetting of the conductive particles with glass and their rearrangement under the effect of capillary forces,

c) diffusion of Ru from conductive particles into glass.

In Fig. 9 the individual mechanisms acting during the formation of the film structure are schematically adjoined to the individual sections of the dependence of area resistivity on firing temperature. A similar course is exhibited by the rela-

![Graph](image_url)

*Fig. 9. Schematic attribution of the mechanisms controlling the structural development of TFR to sections on the curve describing the dependence of area resistivity on firing temperature.*
tionship between the resistivity measured in the course of firing during the passage of the specimen through the kiln [15]. The division into the individual sections in Fig. 9 is only approximate, as the neighbouring mechanisms very likely overlap.

The development of structure in the course of firing begins by the burning out of the organic vehicle, which takes place virtually completely at temperatures of up to 450 °C. The course of the next two stages of structural development depends above all on the properties of the glass employed (viscosity, surface tension), grain sizes of the two components and to a lesser degree on the concentration of the conductive pigment.

a) Sintering of glass

The sintering of glass frit is effected by Newtonian viscous flow as shown e.g. in [7—9]. In the initial stages, the rate of sintering expressed as a time change in shrinkage, is given by equation [20]:

$$\frac{d}{dt} \left( \frac{A - L}{L_0} \right) = -\frac{3}{4} \gamma_{sv} \eta D^{-1},$$

where $A/L_0$ is the relative change in the distance between the centres of neighbouring particles, $\gamma_{sv}$ is the solid-vapour interfacial energy, $\eta$ is viscosity and $D$, is the mean diameter of the glassy particles. The films show shrinkage virtually in the direction of thickness, as the other two dimensions have been fixed by adhesion to the substrate since the initial stages of firing. The course of shrinkage is indicated by the initial part of the dependence of film thickness on firing temperature in Fig. 10. Comparison with the course of relationship between area resistivity and firing temperature (Fig. 9) shows a connection between the glass frit sintering and decreasing resistivity in region $A$. The sintering of glass is likewise well discernible on the micrographs. The process of sintering is virtually restricted to this region $A$. The sintering of glass and film shrinkage result in a compression of the conductive pigment grains and thus in reduced contact resistivity between them, in an increase in the density of conductive particles in the regions between the glass grains and thus in an increase in the electrical conductivity of the film. The granulometric composition of the glass grains remains virtually unchanged in this region and the conductive pigment is distributed among them or over their surface. In materials with mean glass particle size substantially larger then the mean size of conductive grains this stage of firing leads to a typical segregated structure, as defined in the introduction (Fig. 3). The resistivity value at the minimum of the area resistivity vs. firing temperature curve depends on the volume concentration of the conductive component as well as on the ratio of mean dimensions of the glass grains and the conductive ones. The larger the ratio, the smaller the resistivity of the film with a segregated structure [19], as also demonstrated by Fig. 7. According to equation (2), the grain size of the glass grains likewise affects the rate of sintering. This is why the position of area resistivity minimum shifts towards the higher firing temperatures with increasing mean glass grain diameter (with decreasing BET of the specific area). According to the present concept of the consequences of glass sintering, the conductance of electric current through a specimen is provided by direct contacts between the conductive grains. This is also in agreement with the sign of Seebeck's coefficient of films prepared at firing temperatures corresponding to the resistivity minimum, which is identical with the sign given for Bi$_2$Ru$_2$O$_7$ (Fig. 12). In studies [14, 21], the Seebeck's coefficient value of Bi$_2$Ru$_2$O$_7$ is given as $\alpha = -7 \mu V K^{-1}$. 

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b) Wetting of conductive particles and their rearrangement

The viscosity of the glass melt decreases with increasing temperature to such a degree that in the relatively short time of firing the surface of conductive grains is wetted and moreover, the capillary forces drive the glass melt between the conductive grains, thus changing their arrangement in the film [22]. The height \( h \) to which the liquid phase penetrates between the solid particles is given for the time-independent contact angle \( \Theta \) by equation (3) according to [23]:

\[
h^2 = \frac{\gamma_{LV}}{2\eta} \cos \Theta \cdot t
\]

where \( r \) is the capillary radius,
\( \gamma_{LV} \) is the solid-liquid interfacial energy.

The mechanism of wetting the surface of conductive particles with glass melt and the effects of capillary forces are responsible for the transition from the segregated structure to a quasihomogeneous one. On the micrographs, this development shows best on specimens with larger glass grains in the paste (Figs. 1 through 4). In agreement with equation (3) a better homogeneity of conductive particle distribution is achieved by firing at the same temperature with films of lower viscosity. According to their definitions, the segregated and quasihomogeneous structures are limit cases of the TFR structure. However, morphology of a number of fired films represents a transition between these limit cases and is characteristic particularly of glass regions free of conductive pigment and resulting from the larger glass grains in the paste. This type of structure will be called intermediate structure. With many films, this intermediate structure persists up to relatively high firing temperatures (Figs. 1 and 3), in dependence on the glass frit grain size distribution and the parameters of the glass. Deviations from an ideal distribution of conductive particles in the glassy

Fig. 10. Relative film thicknesses and volume percent of pores vs. the firing temperature of films; a – Bi₂Ru₂O₇ with glass A, b – glass A free from the conductive component.
matrix of the film forming the intermediate structure affect the concentration dependence of resistivity, particularly the value of critical concentration, the percolation limit [25].

Fig. 11. Viscosity of glasses A and B vs. temperature [27].

The percolation limit is that concentration of conductive particles at which the opposite sides of the specimen become conductively connected.

The stage of structural development discussed in this paragraph is often accompanied by liberation of gases from the melt and formation of bubbles, as seen in the diagram in Fig. 10 and the micrographs in Figs. 1 and 2. The liberation of gases, the ascent of bubbles towards the layer surface and their growth due to joining of smaller pores and an increase in gas pressure inside the bubble, all take place with decreasing glass viscosity at rising temperature of firing. The growth of bubbles results in an increase in the film volume, which means an increase in thickness, as demonstrated by Fig. 10. The similarity of the courses of the pore content (Fig. 10) and area resistivity (Figs. 6 through 8) on firing temperature is due to the fact that the formation and growth of pores depends above all on the viscosity of the glass just as on the wetting of the surface of conductive particles. The presence of pores in the film cannot cause the resistivity to increase by several orders as a result of change in the geometrical factor in the expression for resistivity. For the sake of illustration, Fig. 13 shows an example of pore distribution. The individual micrographs taken at one and the same point of the specimen were obtained during gradual diminishing of the film thickness by grinding.
c) Diffusion of Ru from conductive particles into glass

In contrast to studies [7 through 9, 15, 23] the present authors do not consider sintering of conductive particles as a necessary prerequisite for the conductivity of TFR with a quasihomogeneous or intermediate structure, for the following reasons:

1. In the studies quoted, no evidence was presented for the sintering of conductive particles during the firing of TFR; conversely, in [9] it is concluded that no direct evidence by microscopic methods is possible owing to the small dimensions of the conductive particles.

2. The low critical concentrations of the conductive phase (low values of the conduction threshold), found with TFRs of quasihomogeneous or intermediate structures [25] would require arrangement of the conductive particles in chains, and this is in disagreement with the effects of the mechanism discussed in article b).

3. The change in the sign of Seebeck's coefficient (Fig. 12) indicates a change in the decisive conductivity mechanism.

4. The results of measurements of the frequency dependence of complex conductivity components agree very well with the theory based on the assumption of transport within the narrow band of localized states near the Fermi level [13].

In the suggested model of the development of TFR structure the basic idea is therefore that at higher firing temperatures there is a non-negligible diffusion of Ru from the surface of conductive grains into the glassy matrix, and thus localized impurity states are formed in the disarranged structure of glass, which allows transport of electrons by phonon-assisted tunnelling [13]. RuO₂ is not a glass-forming oxide,

Fig. 12. Absolute Seebeck's coefficient vs. firing temperature of Bi₂Ru₂O₇ films with glasses A and B.

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and dissolves therefore very little in glasses [9, 26]. The creation of concentration of localized states satisfactory for transport of electrons by the mechanism mentioned results from the small distances between the conductive grains.

CONCLUSION

As follows from the account given above, the development of the structure of TFR in the course of film firing can be described to take place in the following three steps:

1. The sintering of glass.
2. The wetting of conductive particles with glass melt and their spreading by capillary forces.
3. Diffusion of Ru into glass and formation of a narrow band of localized impurity states.

The mechanisms given in points 1 and 2 agree essentially with the literature [7—9], but the present model shows a basic difference from the results of the quoted studies at point 3, describing the last stage of structural formation in most TFR films: according to the suggested conception, formation of a band of localized levels by diffusion of Ru into glass, instead of the earlier assumed sintering of conductive particles into chains. Our model is supported by the results of measuring Seebeck’s coefficient and the frequency dependences of impedance components [13].

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References

Cílem práce bylo vypracování modelu vývoje struktury modelových tlustovrství rezistorů během jejich vypalu. Použité modelové pasty, na rozdíl od komerčních, neobsahovaly ve své anorganické složce kromě vodivého pigmentu a mělty skleněné frity žádné modifikující oxidy ani další dopenty. Vliv teploty vypalu v tunelové peci byl sledován v intervalu vrcholových teplot od 450 do 900 °C s výdělkem 9 min. na maximální teplotě. Byly studovány pasty s kombinacemi vodivé složky Bi₂Ru₂O₇ nebo RuO₂ se sklem A nebo B, jejichž složení a BET měrný povrch uvádí tab. I. Část výsledků byla získána studiem v právě připravených se skelnou fritou složených, která byla po měření tloušťky na 4 granulometrické frakce.

Návrh modelu je podložen mikroskopickými vyšetřeními optickým i elektronovým rastrovým mikroskopem a měřením plošných resistivit a Seebeckova koeficientu. Z výsledků experimentů vyplýnulo, že vývoj struktury lze rozdělit do:

1. sintrovaní skla;
2. směsání vodivých částic sklovinou a jejich rozdružování kapilárními silami;
3. difúze Ru do skla a vzniku úzkého pásu lokalizovatelných příměsových stavů.

Uvedené výsledky se od vývoje publikovaných prací [7 až 9, 15, 24] zásadně liší v bodě 3 tím, že se předpokládá místo dříve uváděného sintrovaní vodivých částic vznik pásu příměsových hladin. Náš model je podpořen zejména výsledky měření Seebeckova koeficientu a dříve publikovanými kmitotovými závislostmi složek impedance [13].

Obr. 1. Odleštěné povrchy vrstev Bi₂Ru₂O₇, se sklem A zralých při různých vrcholových teplotách, v = 14,70 obj. %, a - 600 °C, b - 700 °C, c - 900 °C.
Obr. 2. Odleštěné povrchy vrstev RuO₂ se sklem B zralých při různých vrcholových teplotách, v = 14,80 obj. %, a - 500 °C, b - 600 °C, c - 800 °C.
Obr. 3. Vliv zralosti zralého povrchu A (různým měrným povrchem) na morfologii vrstev s vodivou složkou Bi₂Ru₂O₇, v = 18,02 obj. %, tv = 600 °C; a - 2,24 m²/g, b - 0,78 m²/g, c - 0,51 m²/g, tₜ = 850 °C; d - 2,24 m²/g, e - 0,78 m²/g, f - 0,51 m²/g.
Obr. 4. Mikroskopické z rastrového elektronového mikroskopu vrstev RuO₂ se sklem B zralých při různých vrcholových teplotách; v = 14,81 obj. %, a - 550 °C, b - 600 °C, c - 700 °C.
Obr. 5. Závislost měřicího parametru pyrochlorové struktury vodivé složky vrstev Bi₂Ru₂O₇, se sklem A na teplotě výpravy.
Obr. 6. Závislost plošné resistivity na teplotě výpravy vrstev a - Bi₂Ru₂O₇, se sklem B (v = 15,69 obj. %), b - RuO₂ se sklem A (v = 13,68 obj. %), c - RuO₂ se sklem B (v = 14,81 obj. %).
Obr. 7. Závislost plošné resistivity na teplotě výpravy vrstev Bi₂Ru₂O₇, se sklem A, a - A(2,24), b - A(1,17), c - A(0,51).
Obr. 8. Vliv koncentrace vodivé složky Bi₂Ru₂O₇ na přiškodnou závislost plošné resistivity na teplotě výpravy vrstev se sklem A, (v = 0,51).
Obr. 9. Schématické přířazení mechanizmů řídících vývoji struktury TFR úseku na křivce závislosti plošné resistivity na teplotě výpravy.
Obr. 10. Relativní tloušťky vrstev a objemové procento půr proti teplotě výpravy vrstev; a - Bi₂Ru₂O₇, se sklem A, b - sklo A bez vodivé složky.
Obr. 11. Závislost vodivosti skel A a B na teplotě [27].
Obr. 12. Závislost absolutního Seebeckova koef. na teplotě výpravy vrstev Bi₂Ru₂O₇, se skly A a B.
Obr. 13. Mikroskopické snímky vrstvy Bi₂Ru₂O₇, se sklem A(0,51), tv = 700 °C, v = 18,02 obj. % postupně odrůžované z původní tloušťky 46,7 µm - na tl. 35 µm - b, 11,7 µm - c a 6,8 µm - d.
ВЛИЯНИЕ ТЕМПЕРАТУРЫ ОБЖИГА НА СВОЙСТВА МОДЕЛЬНЫХ ТОЛСТОПЛЕНОЧНЫХ РЕЗИСТОРОВ

I. Морфология и микроструктура слоев

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Целью предлагаемой работы является разработка развития структуры модельных толстопленочных резисторов в течение их обжига. Применяемые модельные пасты, в отличие от паст, находящихся в продаже, не содержат в своем неорганическом компоненте, кроме проводящего пигмента и молотой стеклянной фритты, никакие модифицирующие оксиды и никакие дальнейшие добавки. Влияние температуры обжига в туннельной печи исследованы в интервале пиковых температур в пределах от 450 до 900 °С с выдержкой 9 мин. на максимальной температуре. Исследовали пасты с комбинациями проводящего компонента Bi2Ru2O7 или RuO2 со стеклом A или B, состав и BET удельная поверхность, которые приводятся в табл. 1. Часть результатов получали, исследуя слои, изготовленные с помощью стеклянной фритты составом A, которую после помощи разделили в четыре гранулометрические фракции.

Предложенная модель основывается на микроскопическом исследовании, проводимом с помощью оптического и электронного сканирующего микроскопа и на измерении поверхностного удельного сопротивления и коэффициента Сеебека. Из результатов экспериментов следует, что развитие структуры можно подразделить в три этапа:
1. спекание стекла,
2. смещивание проводящих частиц стекломассой и их разделение капиллярными силами,
3. диффузия Ru в стекло и образование узкой полосы локализованных примесных состояний.

Приводимые результаты принципиально отличаются в 3 пункте от до сих пор опубликованных работ [7—9, 15, 24] в том смысле, что вместо ранее приводимого спекания проводящих частиц учитывается образование полосы примесных уровней. Предложаемый нами модели доказывается именно результатами измерения коэффициента Сеебека и ранее опубликованными частотными зависимостями компонентов импеданса [19].

Рис. 1. Отполированные поверхности слоев Bi2Ru2O7 со стеклом A, обжигаемых при разных пиковых температурах, v = 14,70 % по объему: a — 600 °С, b — 700 °С, c — 900 °С.

Рис. 2. Отполированные поверхности слоев RuO2 со стеклом B, обжигаемых при разных пиковых температурах, v = 14,80 % по объему: a — 500 °С, b — 600 °С, c — 800 °С.

Рис. 3. Влияние размера зерна стеклянной фритты A (с разной удельной поверхностью) на морфологию слоев с проводящим компонентом Bi2Ru2O7, v = 18,02 % по объему, tυ = 600 °С; a — 2,24 м²/с, b — 0,78 м²/с, c — 0,51 м²/с.

Рис. 4. Микросъемка из сканирующего электронного микроскопа слоев RuO2 со стеклом B, обжигаемых при разных пиковых температурах, v = 14,81 % по объему: a — 550 °С, b — 600 °С, c — 700 °С.

Рис. 5. Зависимость решеточного параметра пиroteхнологической структуры проводящего компонента слоев Bi2Ru2O7 со стеклом A от температуры обжига.

Рис. 6. Зависимость поверхностного удельного сопротивления от температуры обжига слоев a — Bi2Ru2O7 со стеклом B (v = 15,89 % по объему), b — RuO2 со стеклом A (v = 13,88 % по объему), c — RuO2 со стеклом B (v = 14,81 % по объему).

Рис. 7. Зависимость поверхностного удельного сопротивления от температуры обжига слоев Bi2Ru2O7 с разведенными фракциями стекла A; a — A(2,24), b — A(1,17), c — A(0,51).

Рис. 8. Влияние концентрации проводящего компонента Bi2Ru2O7 на ход зависимости поверхностного удельного сопротивления от температуры обжига слоев со стеклом A (0,51).
SPEVNÔVANIE KERAMIKY NA BÁZE Si₃N₄ POUŽITÍM SiC VISKROV sa ukazuje ako jedna z možností pripravy vyspelej keramiky s vysokou lomovou húčvnomástoťou. V práci japonských autorov K. UENA a S. SODEOKA (Yogyo-Kyokai-Shi, 94 (1986) 981) sa uvádza, že keramika s obsahom 15% SiC viskrov má koeficient lomovej húčvnomástoťou $K_{IC} = 7.2 \, \text{MN} \, \text{m}^{-3/2}$, príčom keramika na báze číšteho Si₃N₄ dosahuje maximálnych hodnôt $K_{IC} = 6.3 \, \text{MN} \, \text{m}^{-3/4}$. Mikroskopické pozorovania naznačujú, že šírenie trhlin v takjeto dvojkomponentnej keramike je často zabraľované viskrami a trhliny sú presmerované do medzi-vrstvy medzi matricou a viskrami. Tento odklon trhlin je možné prisúdiť existencii napiťí spôsobených rozdielnom tepelnom roztažaní matrix a viskrov.

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