

## Chemical processes accompanying the formation of modified ruthenium resistors and their functional properties\*

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The chemical processes of manufacturing thick-film ruthenium resistors, which are accompanied by an acid-base interaction between the inorganic components of the paste, were studied. The regularities of composition formation and consumer properties of the resistors were determined.

**Key words:** thick-film resistors, modifying additives, properties of resistors.

The introduction of some metals to resistive materials is widely used in thick-film microelectronics as a method for controlling their temperature coefficient of resistance (TCR).<sup>1,2</sup> The modifying effect exerted by these oxides on the properties of thick-film resistors (TFR) is due to at least three factors: influence of oxide as one of the components increasing the fraction of the phase with the metallic or semiconductor conductivity, influence of the modifier on the properties of a constant binder (CB) inducing a change in the parameters of the TFR, and influence of the additive on the properties of the current conducting phase (CCP) or the surface of its particles due to the formation of a chemical compound or a solid solution.<sup>3–5</sup>

The purpose of this work is to explain the effect of the most propagated modifying oxides on the specific surface resistance ( $\rho_s$ ) and TCR of thick-film resistors from the viewpoint of the chemical interaction in modified ruthenium pastes during their burn-in process.

### Experimental

Manufacturing, immobilization on the support by screen printing, and burn-in in an air atmosphere of ruthenium resistive pastes and electrophysical measurements of resistors (20 resistive films on one support of the VK 94-1 material and two parallel supports for each paste) were carried out using procedures presented previously.<sup>6,7</sup> The X-ray diffraction analysis (XRD) was carried out on a DRON-2 diffractometer (Cu cathode, Ni filter, velocity of detector turn 2 deg min<sup>-1</sup>). Lead ruthenate(IV) and

ruthenium dioxide were used as a current conducting phase, and lead-cadmium alumoborosilicate glass of the S-2 trade mark served as a CB.<sup>8</sup> The ruthenium CCP and CB were the products obtained simultaneously as one batch; *i.e.*, the specific surface area and granulometric composition of the pastes of all series were the same. The CCP to CB ratio in the inorganic compositions (IC) of the unmodified pastes was maintained constant: 35 : 65 (basis A) and 29 : 71 (basis B) for the samples based on lead ruthenate Pb<sub>2</sub>Ru<sub>2</sub>O<sub>6</sub> and ruthenium dioxide RuO<sub>2</sub>, respectively. The modifiers were introduced to replace the ruthenium compounds in the CCP in the amounts up to 10 wt.% (Table 1), except for the pastes of series 3 in which Nb<sub>2</sub>O<sub>5</sub> was introduced into the charge in amounts of 0.5, 1.0, 3.0, and 5.0 wt.%. Owing to this, in the samples of this series the CCP : CB ratio changed with an increase in the niobium(V) oxide content and was equal to 34.5 : 65.5, 34 : 66, 32 : 68, 30 : 70, and 25 : 75.

The data on the density ( $d$ ), coefficient of linear thermal expansion (CLTE), and resistivity ( $\rho$ ) of the initial inorganic components of the resistive pastes of which the first eight compounds are modifying oxides and their reaction products are presented in Table 2.

**Table 1.** Content of modifying oxides in the studied samples (wt.%)

Pastes based on Pb <sub>2</sub> Ru <sub>2</sub> O <sub>6</sub>		Pastes based on RuO <sub>2</sub>	
CCP	CB (recalculation)	CCP	CB (recalculation)
0.5	0.27	0.5	0.22
1.0	0.54	1.0	0.39
2.0	1.08	3.0	1.22
3.0	1.58	5.0	1.99
5.0	2.62	10.0	3.74
10.0	5.11		

\* Based on the materials of the XXI Mendeleev Congress on General and Applied Chemistry (September 9–13, 2019, St. Petersburg, Russia).

**Table 2.** Some properties of the used inorganic components and their reaction products

Compound	$d \cdot 10^3/\text{kg m}^{-3}$	CLTE $\cdot 10^6/\text{K}^{-1}$	$\rho/\text{Ohm m}$
Cu <sub>2</sub> O	6.0 <sup>9</sup>	0.9 <sup>10</sup>	0.9 <sup>11</sup>
CuO	6.45 <sup>9</sup>	$\alpha_a = 26.4; \alpha_b = -8.1;$ $\alpha_c = 9.4; \alpha_\beta = 16.6$ <sup>12</sup>	25–100 <sup>13</sup>
NiO	7.45 <sup>9</sup>	15.0 <sup>14</sup>	24.70 <sup>15</sup>
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	3.97 <sup>9</sup>	6.7 ( $\alpha$ ) and 5.0 ( $\alpha_\perp$ ) <sup>9</sup>	$3 \cdot 10^{14}$ (see Ref. 16)
Bi <sub>2</sub> O <sub>3</sub>	8.90 <sup>9</sup>	7.2–7.5 (monoclinic crystal system); 22 (cubic) <sup>9</sup>	$10^8$ – $10^{11}$ (see Ref. 16)
TiO <sub>2</sub>	3.84 <sup>9</sup>	8.19 <sup>14</sup>	$10^{13}$ (see Ref. 16)
Nb <sub>2</sub> O <sub>5</sub>	4.95 <sup>9</sup>	0.0 <sup>14</sup>	$10^4$ – $10^7$ (see Ref. 16)
$\alpha$ -WO <sub>3</sub>	7.16 <sup>9</sup>	8.9 <sup>17</sup>	$5 \cdot 10^3$ – $1 \cdot 10^5$ (see Ref. 16)
RuO <sub>2</sub>	$6.97 \pm 0.10$ <sup>9</sup>	10 ( $\alpha_a$ ) and –23 ( $\alpha_c$ ) <sup>18</sup>	$4 \cdot 10^{-5}$ (TCR $5000 \cdot 10^{-6} \text{ K}^{-1}$ ) <sup>5</sup>
Pb <sub>2</sub> Ru <sub>2</sub> O <sub>6</sub>	8.37	11.0 <sup>19</sup>	$2 \cdot 10^{-4}$ (see Ref. 5)
C-2	$4.737 \pm 0.007$ <sup>8</sup>	$7.02 \pm 0.03$ <sup>8</sup>	$1.5 \cdot 10^{10}$ (see Ref. 8))
PbWO <sub>4</sub>	8.28 <sup>20</sup>	12.7 ( $\alpha$ ) and 26.8 ( $\alpha_\perp$ ) <sup>21</sup>	$2 \cdot 10^6$ (800 °C) <sup>22</sup>
Pb <sub>1.5</sub> Nb <sub>2</sub> O <sub>6.5</sub> (Pb <sub>3</sub> Nb <sub>4</sub> O <sub>13</sub> )	6.766 <sup>23</sup>	—	$3.8 \cdot 10^{10}$ (see Ref. 24)
PbTiO <sub>3</sub>	7.30 <sup>25</sup>	–19.9 <sup>26</sup>	$9.2 \cdot 10^9$ (see Ref. 27)
$\alpha$ -SiO <sub>2</sub>	2.65 <sup>9</sup>	$\sim 0.6$ – $1.1$ <sup>28</sup>	$1 \cdot 10^{12}$ (see Ref. 14)
Phase with anortite structure PbAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	4.153 <sup>29</sup>	12.6 <sup>30</sup>	$1.4 \cdot 10^6$ (see Ref. 31)
PbO	9.51 <sup>9</sup>	25 <sup>32</sup>	$10^7$ (see Ref. 14)
B <sub>2</sub> O <sub>3</sub>	1.884 <sup>9</sup>	15 <sup>33</sup>	$4.5 \cdot 10^7$ (750 K) <sup>34</sup>

## Results and Discussion

The data of Table 3 were used for the evaluation of the acid-base interaction.

For electronegativity (EN,  $\chi$ ) of elements we chose of ~20 known scales<sup>35,36</sup> the orbital<sup>37</sup> (as commonly recog-

nized) and refined<sup>35</sup> scales. The latter is the uniquely averaged scale based on the original EN scales obtained using the Mulliken–Vereshchagin, Allred–Rochow, and Pauling equations, which provides the absence of repetition of  $\chi$  for various elements and more precisely corresponds to the modern concepts on the chemical bond

**Table 3.** Acid-base properties and Gibbs energy for some simple and complex oxides

Compound	$\chi$				$C_c/C_m/C_i$ (%) <sup>41</sup>	$-G^\circ_{298}$	
	see Ref. 37	see Ref. 35	see Ref. 39	see Ref. 40		kcal mol <sup>-1</sup> (see Ref. 43)	kJ mol <sup>-1</sup> (see Ref. 44)
Cu <sub>2</sub> O	5.50	2.478	5.32	3.38	50.88/22.47/26.65	35.36	150.5
CuO	6.01	2.742	5.81	3.32	—	30.59	129.4
NiO	6.00	2.692	5.75	3.38	48.65/22.79/28.56	50.57	211.6
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	5.82	2.824	—	3.18	46.75/23.06/30.19	378.2	1582.0
Bi <sub>2</sub> O <sub>3</sub>	7.16	2.875	6.23	3.44	49.00/22.74/28.26	118.0	493.7
TiO <sub>2</sub>	6.25	2.825	5.81	3.12	40.15/24.08/35.76	212.55	943.9
Nb <sub>2</sub> O <sub>5</sub>	6.53	2.936	6.29	2.85	40.70/23.99/35.31	421.6	1764.1
$\alpha$ -WO <sub>3</sub>	6.72	3.031	6.59	2.98	42.13/23.76/34.12	182.63	763.9
RuO <sub>2</sub>	6.51	2.392	—	2.98	44.37/23.41/32.22	60.4	21.92 <sup>5</sup>
Pb <sub>2</sub> Ru <sub>2</sub> O <sub>6</sub>	6.31	2.804	—	—	—	—	57.69
S-2	6.25	2.66	—	—	—	—	—
PbTiO <sub>3</sub>	6.09	2.758	—	—	—	—	1061 ± 5.8 <sup>46</sup>
Pb <sub>1.5</sub> Nb <sub>2</sub> O <sub>6.5</sub>	6.33	2.852	—	—	—	—	220.2
PbWO <sub>4</sub>	6.44	2.906	—	—	—	243.9 <sup>47</sup>	—
$\alpha$ -SiO <sub>2</sub>	6.61	3.018	—	—	—	204.71	856.7
PbAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	6.20	2.888	—	—	—	—	469.0
PbO	5.88	2.656	5.42	3.57	47.12/23.01/29.87	45.16	188.2
B <sub>2</sub> O <sub>3</sub>	6.18	2.945	—	3.45	52.43/22.24/25.33	282.5	1194.3

nature. The generalized EN of simple and mixed oxides were calculated by the equation<sup>38</sup>

$$\chi(M_xMe_yA_aB_bC_cO_z) = \frac{x\chi_M + y\chi_{Me} + a\chi_A + b\chi_B + c\chi_C + z\chi_O}{x + y + a + b + c + z},$$

where  $\chi_M$ ,  $\chi_{Me}$ ,  $\chi_A$ ,  $\chi_B$ ,  $\chi_C$ , and  $\chi_O$  are the electronegativities of elements<sup>35,39</sup>;  $x$ ,  $y$ ,  $a$ ,  $b$ ,  $c$ , and  $z$  is the number of atoms M, Me, A, B, C, and O, respectively, in the molecule.

In addition, the generalized EN of the oxides,<sup>39,40</sup> degrees of covalence ( $C_c$ ) and metallicity ( $C_m$ ), ionic ( $C_i$ ) components of the element atom—oxygen (E—O) bond in the oxides,<sup>41</sup> and Gibbs energies ( $\Delta G^\circ$ ) of the acid-base interaction<sup>42</sup> are presented in Table 3.

The reproducibility of the properties of the CCP depending on the technological parameters was determined from the basis pastes A and B (Table 4). It follows from the results presented in Table 4 that the properties of the CCP ( $\rho_s$  and TCR) prepared from the basis pastes (five pastes are based on  $Pb_2Ru_2O_6$  and three pastes are based on  $RuO_2$ ) are reproduced within tolerances accepted in the electrotechnical area for thick-film resistive materials.

The results obtained ( $\rho_s$  and TCR) allow one to normalize the properties of the modified thick-film resistors by samples of the basis pastes, which are burnt-in in one batch with them. This made it possible to evaluate the modifying effects of various additives.

The modified ruthenium resistive paste contains at least the CCP, CB, modifier, and temporal binder (TB). Since the object of the study is complicated, the chemical inter-

**Table 4.** Properties of the resistors manufactured from pastes of the basis composition

CCP	Content of CCP in IC (wt.%)	$\rho_s$ /kOhm m <sup>-2</sup>	TCR · 10 <sup>6</sup> /K <sup>-1</sup>	
			298–398 K	213–298 K
Basis A				
$Pb_2Ru_2O_6$	18	1390±43	-263±27	-295±31
	20	224±7	-65±15	-64±15
	23	63.2±1.9	-8±1	-2±1
	25	27.4±0.8	105±13	70±10
	30	11.6±0.3	177±17	154±16
	35	2.00±0.09	116±16	-83±27
	35	2.09±0.06	90±50	-100±60
	35	1.83±0.08	96±15	-95±18
	35	1.90±0.07	91±23	-91±24
	35	2.12±0.01	79±21	-91±18
	40	1.70±0.11	219±25	214±25
50	0.54±0.02	316±27	337±27	
Basis B				
$RuO_2$	29	0.54±0.01	169±27	7±19
	29	0.96±0.02	219±41	-51±17
	29	1.08±0.02	338±31	—

**Table 5.** Phase composition of the model systems  $Pb_2Ru_2O_6$ — $M_xO_y$  and  $RuO_2$ — $PbTiO_3$

Phase composition	
before thermal treatment	after thermal treatment
$Pb_2Ru_2O_6 + WO_3$	$RuO_2 + PbWO_4$
$Pb_2Ru_2O_6 + Nb_2O_5$	$RuO_2 + Pb_{1.5}Nb_2O_{6.5}$
$Pb_2Ru_2O_6 + TiO_2$	$RuO_2 + PbTiO_3$
$Pb_2Ru_2O_6 + SiO_2$	$RuO_2 +$ glass amorphous to X-rays
$Pb_2Ru_2O_6 + B_2O_3$	$RuO_2 +$ glass amorphous to X-rays
$Pb_2Ru_2O_6 + Al_2O_3$	$Pb_2Ru_2O_6 + Al_2O_3$
$Pb_2Ru_2O_6 + CuO$	$Pb_2Ru_2O_6 + CuO$
$Pb_2Ru_2O_6 + Cu_2O$	$Pb_2Ru_2O_6 + Cu_2O$
$Pb_2Ru_2O_6 + NiO$	$Pb_2Ru_2O_6 + NiO$
$Pb_2Ru_2O_6 + Bi_2O_3$	$Pb_{2-x}Bi_xRu_2O_7 + Bi_2O_3$
$PbTiO_3 + RuO_2$	$Pb_2Ru_2O_6 + TiO_2$

action and modifying effect of the additives were primarily studied on the model systems: the samples containing one and more components of the resistive paste along with the modifier.

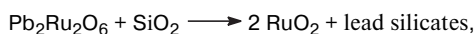
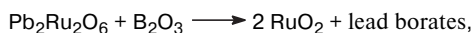
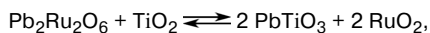
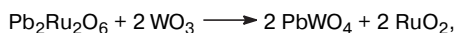
The phase compositions of the  $Pb_2Ru_2O_6$ — $M_xO_y$  (M is the modifier) and  $RuO_2$ — $PbTiO_3$  samples according to the XRD data before and after thermal treatment up to 1123 K (under the nonequilibrium conditions *via* the scheme of TFR burn-in) are shown in Table 5.<sup>48–52</sup>

The XRD patterns of the samples of the  $Pb_2Ru_2O_6$ — $Bi_2O_3$  system after calcination exhibit reflections of bismuth oxide and a phase with the pyrochlore structure. This pattern differs from that of  $Pb_2Ru_2O_6$  by the intensity of indices *hkl* 440 and 662. The intensity of these peaks increases after the thermal treatment with an increase in the  $Bi_2O_3$  content in the initial samples, and the XRD pattern becomes more similar to the XRD pattern of compound  $Bi_2Ru_2O_7$  (lead ruthenate and bismuth ruthenate are isostructural). This possibly indicates that the thermal treatment of the samples of this series completes by the formation of a solid solution  $Pb_{2-x}Bi_xRu_2O_7$  (Table 6).

**Table 6.** Ratio of intensities  $I_{440}/I_{444}$ , and  $I_{622}/I_{444}$  on the XRD patterns of the samples of the  $Pb_2Ru_2O_6$ — $Bi_2O_3$  system

Initial composition of samples before thermal treatment (wt.%)			Ratio of intensities indices of phase with pyrochlore structure after thermal treatment	
$Pb_2Ru_2O_6$	$Bi_2O_3$	$Bi_2Ru_2O_7$	$I_{440}/I_{444}$	$I_{622}/I_{444}$
100	0	0	3.0	2.9
90	10	0	3.0	3.0
80	20	0	3.4	3.2
60	40	0	3.5	3.4
50	50	0	4.3	3.8
0	0	100	4.5	4.1

Thus, the obtained results can be described by the following equations:



whereas no interaction was found for the cases of  $\text{Pb}_2\text{Ru}_2\text{O}_6 + \text{Al}_2\text{O}_3$  (CuO, NiO).

The presented equations show (see Table 3) that the modifying oxide with the  $\chi$  value

– higher than that of  $\text{RuO}_2$  ( $\text{WO}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$ ) displaces the latter from lead ruthenate to form its salt;

– close to  $\chi$  for  $\text{RuO}_2$  ( $\text{TiO}_2$ ,  $\text{SiO}_2$ ) participates in the reversible interaction in which  $\text{RuO}_2$  displaces this oxide from its compound;

– lower than that of  $\text{RuO}_2$  but higher than  $\chi$  of PbO does not interact with lead ruthenate;

– close to  $\chi$  for PbO ( $\text{Bi}_2\text{O}_3$ ) is incorporated into the structure of lead ruthenate to form a solid solution.

Modifying oxide  $\text{Al}_2\text{O}_3$  falls out of the presented regularities as more acidic than  $\text{RuO}_2$ . It is most likely that the interaction in the  $\text{Pb}_2\text{Ru}_2\text{O}_6$ – $\text{Al}_2\text{O}_3$  system occurs at higher temperatures.<sup>53</sup>

In addition, it is noteworthy that the interaction in the samples proceeds from left to right if the difference in the  $\chi$  values for the compounds at the left is higher than that for those at the right. A comparison of the differences in the  $\chi$  values in the exchange solid state reactions described earlier<sup>54,55</sup> also provides a similar conclusion with some exceptions.

The modifiers behave in different manners toward the CB (Table 7).

Remarkably, the interaction between the modifier and CB with the formation of a lead salt is observed when  $\chi$  of the modifier is higher than  $\chi$  of  $\text{SiO}_2$  and glass S-2. The exceptions are the S-2– $\text{Bi}_2\text{O}_3$  samples, which correspond to these conditions; however, no interaction was found in them.

The introduction of the modifiers into glass S-2 changes its properties. The resistance of the modified samples increases with an increase in the concentration of the additives, reaches extreme values, and decreases, which is characteristic of the considered oxides and was shown for examples of glasses with other compositions (Fig. 1).<sup>56–58</sup>

The phase compositions of the modified resistors are predetermined by the chemical nature of the modifying additive and are presented in Table 8 (according to the XRD data).

**Table 7.** Phase composition of the model samples CB– $\text{M}_x\text{O}_y$  (up to 10 wt.%  $\text{M}_x\text{O}_y$ ) according to the XRD data

Sample	Phase composition	
	before thermal treatment	after thermal treatment
1	CuO	Glass amorphous to X-rays
2 <sup>a</sup>	NiO	The same
3 <sup>b</sup>	NiO	NiO
4	$\text{Bi}_2\text{O}_3$	Glass amorphous to X-rays
5	$\text{Al}_2\text{O}_3$	Phase with anortite structure
6 <sup>c</sup>	$\text{TiO}_2$	$\text{TiO}_2 + \text{PbTiO}_3 +$ phase with $\alpha$ -quartz structure
7 <sup>d</sup>	$\text{Nb}_2\text{O}_5$	Glass amorphous to X-rays
8 <sup>e</sup>	$\text{Nb}_2\text{O}_5$	$\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$

<sup>a</sup> Up to 1 wt.% NiO were introduced into the sample.

<sup>b</sup> More than 1 wt.% NiO were introduced into the sample.

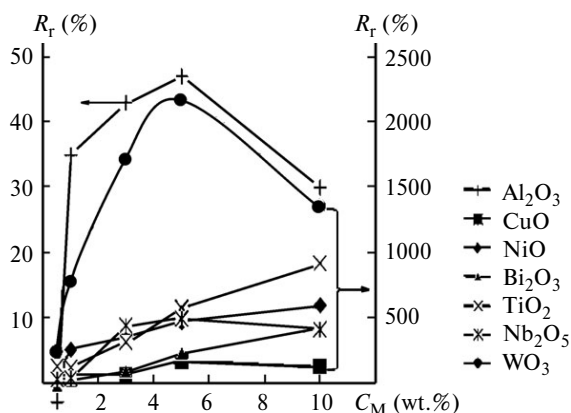
<sup>c</sup> Charge of S-2 with the  $\text{TiO}_2$  additive is sensitive to the thermal treatment conditions.

<sup>d</sup> Up to 3 wt.%  $\text{Nb}_2\text{O}_5$  were introduced into the sample.

<sup>e</sup> More than 3 wt.%  $\text{Nb}_2\text{O}_5$  were introduced into the sample.

Under the chosen thermal treatment conditions, glass S-2 reacts with lead ruthenate to form up to 30% ruthenate dioxide in the CCP. The introduction of oxide additives into this system controls the amount of formed  $\text{RuO}_2$ . The oxide with pronounced acidic properties, for example,  $\text{Nb}_2\text{O}_5$ , reacting with  $\text{Pb}_2\text{Ru}_2\text{O}_6$  in the model system decreases the amount of formed  $\text{RuO}_2$  in the pastes as if stabilizing the initial CCP, whereas the basic oxide, for example, CuO, with does not react with lead ruthenate in the model system, in the pastes favors an almost complete transformation of  $\text{Pb}_2\text{Ru}_2\text{O}_6$  into  $\text{RuO}_2$  (see Table 8).

Thus, the modification of the resistive pastes  $\text{Pb}_2\text{Ru}_2\text{O}_6$ –S-2–CB by the oxides considered controls the amount of ruthenium dioxide formed in the TFR, introduces the semiconductor or dielectric crystalline phase (directly or as a reaction product) into the film, and



**Fig. 1.** Relative change in the resistance of glass S-2 ( $R_r = [(R_m - R)/R] \cdot 100\%$ ) upon the introduction of modifying oxides ( $C_M$  is the modifier content).

**Table 8.** Phase composition of the modified resistors containing up to 10 wt.%  $M_xO_y$ 

Sample	Phase composition	
	before thermal treatment	after thermal treatment
1	CuO + $Pb_2Ru_2O_6$	$RuO_2$ + $Pb_2Ru_2O_6$ (traces)
2	$Bi_2O_3$ + $Pb_2Ru_2O_6$	$RuO_2$ + $Pb_{2-x}Bi_xRu_2O_7$
3 <sup>a</sup>	NiO + $Pb_2Ru_2O_6$	$RuO_2$ + $Pb_2Ru_2O_6$
4 <sup>b</sup>	NiO + $Pb_2Ru_2O_6$	$RuO_2$ + $Pb_2Ru_2O_6$ + NiO
5	$Al_2O_3$ + $Pb_2Ru_2O_6$	$RuO_2$ + $Pb_2Ru_2O_6$ + $Al_2O_3$ + + phase with anortite structure
6	$TiO_2$ + $Pb_2Ru_2O_6$	$RuO_2$ + $Pb_2Ru_2O_6$ + $TiO_2$ + + $PbTiO_3$ + $\alpha$ -quartz
7	$Nb_2O_5$ + $Pb_2Ru_2O_6$	$RuO_2$ + $Pb_2Ru_2O_6$ + + $Pb_{1.5}Nb_2O_{6.5}$
8	$WO_3$ + $Pb_2Ru_2O_6$	$RuO_2$ + $Pb_2Ru_2O_6$ + $PbWO_4$

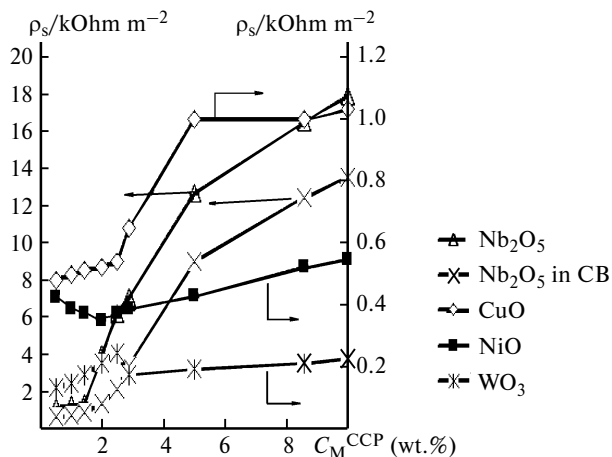
<sup>a</sup> In the films containing up to 2 wt.% NiO in the CCP.

<sup>b</sup> In the films containing 2–10 wt.% NiO in the CCP.

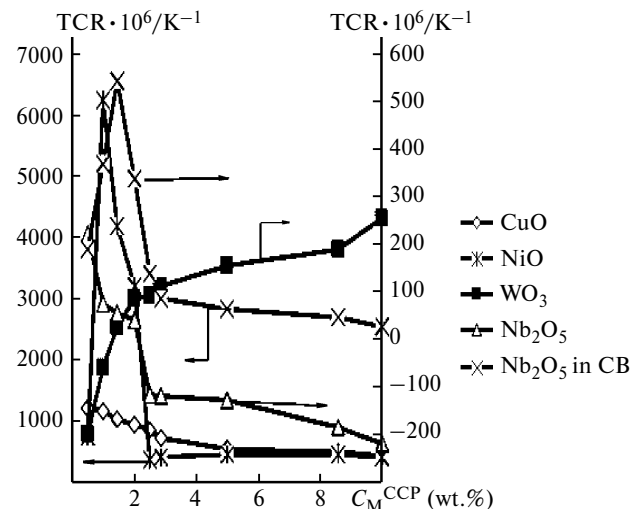
changes the composition of CB (due to the dissolution of the modifier and binding of a portion of lead oxide or other oxides during chemical interaction and doping).

The properties of the modified thick films based on  $Pb_2Ru_2O_6$  are presented in Figs 2 and 3. The modifiers can be divided into three groups by the character of action on  $\rho_s$  and TCR: oxides that increase  $\rho_s$  and transform the TCR values of the TFR from the range of positive values to the range of negative values:  $Al_2O_3$ ,  $TiO_2$ , and  $Nb_2O_5$ ; oxides that decrease  $\rho_s$  and increase the positive values of TCR of the TFR; and oxides that almost do not change  $\rho_s$  and TCR:  $Bi_2O_3$  and  $WO_3$ .

In the studied samples, NiO remains after annealing in the bulk of the resistive films as an individual phase (see Table 8). Nickel(II) oxide is a semiconductor. It is most



**Fig. 2.** Surface resistance of the resistors vs amount of the introduced modifier (here and in Fig. 3,  $C_M^{CCP}$  is the modifier content in the CCP).



**Fig. 3.** Dependences of the TCR of the resistors on the amount of the introduced modifier.

likely that this explains the decrease in  $\rho_s$  and the increase in the TCR of the TFR modified by this oxide in the range of the additive content 2.0–2.5 wt.% in the TFR (see Figs 2 and 3). After annealing of the pastes, aluminum(III), titanium(IV), niobium(V), and tungsten(VI) oxides form new crystalline phases with the properties of semiconductor or dielectric ( $\alpha$ -quartz, phase with the anortite structure,  $PbTiO_3$ ,  $Pb_{1.5}Nb_2O_{6.5}$ , and  $PbWO_4$ ), increasing the fraction of the semiconductor component of the TFR (see Table 8). The character of the influence of the listed oxides on the properties of the modified resistive thick film is independent of the method of introduction of the corresponding modifier into the paste, since the same reaction product is always formed. For instance,  $Pb_{1.5}Nb_2O_{6.5}$  is formed in the TFR with the additive  $Nb_2O_5$  or glass S-2, and modified by  $Nb_2O_5$  (curve of  $Nb_2O_5$  in the CB). At the same time, the absolute values of the electrophysical parameters of the TFR are predetermined by the concentration of the formed compound (see Figs 2 and 3).

As shown above, the effect of the basic oxides controlling the properties of the CB induces the accumulation of the CCP with a higher (than that of lead ruthenate, initial CCP) conductivity:  $RuO_2$ .<sup>59</sup> As a consequence, in the modified TFR the TCR increases (in the range of positive temperatures) and  $\rho_s$  decreases, and the higher the amount of formed  $RuO_2$ , the stronger the decrease in  $\rho_s$  (see Figs 2 and 3).

Thus, the properties of the thick-film resistors are determined by several processes leading to an increase in or compensation of their conductivity. If the former predominate (formation of significant amounts of  $RuO_2$ , appearance of different-valence ions of the same metal in the CB, increase in the volume fraction of the CCP, doping of the CB, etc.), then the conductivity of the thick film increases with an increase in the amount of the modifier

introduced into the paste. For instance, this is observed for the modification of the pastes based on lead ruthenate by copper(II) oxide. If the mechanisms of controlling the properties of the CCP are balanced, then the introduction of the modifier exerts no effect on the electrophysical parameters of the modified thick films as it takes place in the pastes based on lead ruthenate and tungsten(IV) oxide. If the latter predominate (decrease in the RuO<sub>2</sub> content, concentration of additional semiconductor and dielectric phases, decrease in the volume fraction of the CCP, etc.), then the conductivity of the film decreases with an increase in the content of the additive in the paste as, for example, for the modification of the pastes based on lead ruthenate and niobium(V) oxide. The properties of the CCP are predetermined by their phase composition, which are determined, in turn, by the chemical properties of the modifiers and resistive paste as a whole.

Thus, the burn-in of the modified ruthenium resistive pastes and formation of thick-film resistors are accompanied by a complex of physicochemical processes, including chemical reactions occurred between the CCP and CB due to which their phase compositions and electrophysical properties (electrical conductivity, TCR, dielectric and other properties) change.

The main criteria determining the character of occurrence of the chemical reactions in the thick-film resistive materials are the acid-base properties of the modifiers and CB, namely, their strength toward ruthenium dioxide as an acid. If the acidic properties of the modifier and/or CB are manifested stronger than those of RuO<sub>2</sub>, the latter is displaced from its compounds in the composition of the resistors (in our case, from lead ruthenate). In addition, the introduction of a stronger base than lead(II) oxide into the resistive paste results in the formation of a compound of this base with RuO<sub>2</sub> due to the reaction with lead ruthenate. The new phase composition of the thick-film resistive films is thus formed. The processes of CB doping are completed with a change in its composition and properties. All these processes form the surface electrical resistivity and TCR of the thick-film resistive films.

In addition, the studies performed make it possible to select (if practically necessary) the components indifferent to each other for the preparation of resistive pastes, i.e., characterized by acid-base properties equal in strength.

The obtained results will be useful for the prediction of the phase composition and functional properties of the new modified ruthenium resistive materials.

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Received September 10, 2019;  
in revised form October 28, 2019;  
accepted April 14, 2020