

# ABOUT THE INFLUENCE OF SiO<sub>2</sub> ON THE TEMPERATURE BEHAVIOUR OF RUTHENATE BASED THICK FILM RESISTORS

I. STORBECK and M. WOLF

*Zentralinstitut für Festkörperphysik und Werkstofforschung der AdW der DDR, Dresden*<sup>†</sup>

Substituting glass by SiO<sub>2</sub> in thick film resistors results in a small increase of  $R_{\square}$ , a decrease of  $dR_{\square}/dT$  and an increase of  $d^2R_{\square}/dT^2$  (at room temperature). From these experimental results it follows that substituting glass by SiO<sub>2</sub> leads to an increase in the resistance of the tunnel barrier, determining the resistivity of the TFRs. The other microscopic quantities, like charging energy and  $HTC_p$  of ruthenate, are estimated using the model of Pike and Seager, the generalization of which (necessary in order to take into account the influence of the strain dependence of  $R_{\square}$  and  $R_{\square}(T)$  in a correct way) is derived.

**Key words:** Thick film resistors; Temp. coeff. of resistance (TCR) ·

## 1. INTRODUCTION

It is well known, especially from patent literature, that there are a lot of ingredients (e.g. Bi<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, RuO<sub>2</sub>), by means of which the TCR of ruthenium based TFRs can be changed in a defined manner<sup>1</sup>. In spite of this experimental experience little is known as regards the influence of such TCR-modifiers on the conduction mechanism in these TFRs.

This contribution presents the results of investigations concerning the temperature behaviour of ruthenate based TFRs, in which glass was substituted by SiO<sub>2</sub>. Estimations show, that the dependence of the TCR on the SiO<sub>2</sub> content is not connected with the change of the coefficient of thermal expansion of the thick film (Section 1). In Section 2 the model of Pike and Seager<sup>2</sup> is generalized, in order to take into account strain effects, by which the temperature behaviour of any TFR is largely determined<sup>3</sup>. The comparison of the expressions obtained with the experimental results shows that with increasing content of SiO<sub>2</sub> the resistance of the tunnel barrier increases. Moreover, assuming the ratio of barrier resistance to total resistance of barrier and grain in series for the SiO<sub>2</sub> free case, it is possible to estimate all the other microscopic parameters determining the electrical conduction. The results are in reasonable agreement with the values given in<sup>2</sup> (Section 3).

## 1) EXPERIMENTAL RESULTS

The TFRs under study have been prepared by well known thick film technology. They consist of (i) a BiPb-ruthenate – for all resistors the same powders from the same batch have been used, and the volume fraction of this phase was the same in each sample, (ii) a glass frit, which, for some samples, was partially substituted by different amounts of SiO<sub>2</sub>. The results of the electrical measurements can be summarized as follows:

<sup>†</sup>DDR – 8027 Dresden, Postfach

With increasing  $v_{\text{SiO}_2}$  from 0 vol% to 13 vol%,  $R_{\square}$  increased by about a factor 2 from  $8 \text{ k}\Omega/\square$  to  $17 \text{ k}\Omega/\square$ , whereas the TCR decreased from  $80 \cdot \text{ppmK}^{-1}$  to  $-58 \cdot \text{ppmK}^{-1}$ . The  $v_{\text{SiO}_2}$  dependence of the parameters  $a_1$ ,  $a_2$  determined from the phenomenological equation:-

$$R_{\square}(T) = R(T_0) (1 + a_1\vartheta + a_2\vartheta^2), \vartheta = T - T_0, T_0 = 300 \text{ K} \quad (1)$$

is shown in Figure 1. It transpires that with increasing  $v_{\text{SiO}_2}$ ,  $a_1$  decreases, whereas  $a_2$  increases. The decrease of  $a_1$  leads to the behaviour of the TCR described above. It is well known that the  $R_{\square}$  of TFRs depends on strain  $\epsilon$ . This leads to the following approximate expression for the influence of the coefficient of thermal expansion of the film  $\alpha_f$  on the measured TCR<sup>3</sup>:-

$$\text{TCR} = \rho^{-1} \cdot \partial\rho/\partial T + \rho^{-1} \cdot \partial\rho/\partial\epsilon \cdot (2\alpha_s + \alpha_f) \quad (2)$$

( $\alpha_s$  - thermal expansion coefficient of substrate,  $\rho(T, \epsilon)$ -resistivity, dependent on the strain  $\epsilon$  and the temperature of TFR). If  $\text{SiO}_2$  would simply replace the glass and no change of conduction mechanism would occur (as one could imagine, because the volume fraction of ruthenate was not varied), from (2) the change of TCR per vol%  $\text{SiO}_2$  would follow as:-

$$\Delta\text{TCR}/v_{\text{SiO}_2} = -\rho^{-1} \cdot \partial\rho/\partial\epsilon \cdot (\alpha_{\text{gl}} - \alpha_{\text{SiO}_2}). \quad (3)$$

Here  $\rho^{-1} \cdot \partial\rho/\partial\epsilon$  can be approximated by the value of the gauge factor  $\text{GF} \approx 15 \dots 20$ .  $\alpha_{\text{SiO}_2}$  is approximately  $10^{-7} \cdot \text{K}^{-1}$  and can be neglected compared with  $\alpha_{\text{gl}} \approx 6 \cdot \text{ppmK}^{-1}$ . According to (3) this gives a contribution of about  $-1 \cdot \text{ppm K}^{-1}/\text{vol}\%\text{SiO}_2$ , which is at least one order of magnitude too small to explain the experimental value of about  $-21 \text{ ppm K}^{-1}/\text{vol}\%\text{SiO}_2$ . Thus one has to conclude, that substituting glass by  $\text{SiO}_2$  in Bi-

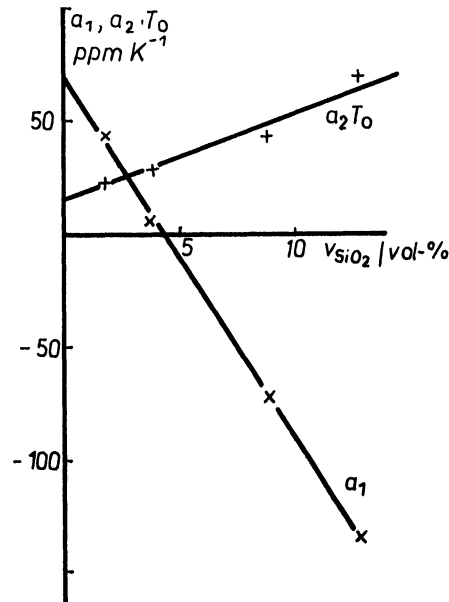


FIGURE 1 Dependence of  $a_1$ ,  $a_2$  on  $v_{\text{SiO}_2}$  for Bi-Pb-ruthenate resistors.

Pb-ruthenate TFRs (i) leads to a change of the electrical conduction mechanism, (ii) the change of the thermoelastic properties of TFRs makes a contribution to the change of TCR which can be neglected in the following model.

## 2) THEORETICAL MODEL

Pike and Seager developed a model, in which  $a_1$ ,  $a_2$  (see Eq. 1) are determined by the microscopic parameters governing the electrical conduction in TFRs. The shortcoming of their considerations is that they neglected the influence of  $\epsilon$  on TCR and  $a_1$ ,  $a_2$ , respectively, whereas in a later publication<sup>3</sup> it has been shown that the TCR is determined to a large extent by such strain effects. Thus, in the following discussion their model has to be generalized. Further, the physical reasons for the assumptions that need to be made will be given. The widely accepted model for a TFR consists of a network of current carrying chains, each built up from a microresistor  $r_0$ <sup>4</sup>. Hence  $R$  is given by

$$R = r_0(T, \epsilon, v_{\text{SiO}_2}, v) \cdot l/mn \quad (4)$$

As a change of  $T$  or  $\epsilon$  is a small disturbance for the TFR,  $l$ ,  $m$ ,  $n$  do not depend on  $T$  or  $\epsilon$ . Therefore  $r_0$  does not depend only on  $T$  and  $\epsilon$ , but also on the volume fraction of the metal-like phase  $v$  and  $v_{\text{SiO}_2}$ , otherwise the TCR would not depend on  $v$  (or  $R_{\square}$ , respectively) and the content of the TCR modifier, in contradiction to the experimental results. Following Pike and Seager (for further experimental evidence cf.<sup>5,6</sup>) it is assumed, that the microresistor  $r_0$  itself consists of a tunnel barrier  $r_b$  and a contribution from the grain  $r_g$ :-

$$r_0(T, \epsilon, v_{\text{SiO}_2}) = r_b(T, \epsilon, v_{\text{SiO}_2}) + r_g(T) \quad (5)$$

(The factor  $v$  has been dropped, because in the case considered  $v = \text{const.}$ )  $r_g$  should not depend on  $v_{\text{SiO}_2}$ , as reactions between the ruthenate and  $\text{SiO}_2$  are negligible. Thus, there remains the possibility that the electrical properties of the barrier are influenced by substituting glass by  $\text{SiO}_2$ . Comparing the electrical conduction in a metal grain and a tunnel barrier, it is reasonable to assume, that only  $r_b$  depends on  $\epsilon$ .  $r_b$  is determined by tunneling and depends therefore in an exponential way on the barrier thickness. Thus:-

$$r_b(T, \epsilon, v_{\text{SiO}_2}) = r_{b,0}(T, v_{\text{SiO}_2}) \cdot \exp \epsilon s_0 \quad (6)$$

should hold qualitatively, where  $s_0$  is determined by the barrier height and the thickness for  $\epsilon = 0$ . By means of equations (6) and (1) it is possible to replace  $r_0^{-1} \cdot \partial r_0 / \partial \epsilon$  by the experimentally available gauge factor  $GF = R^{-1} \cdot dR/d\epsilon$ . Taking this into account and taking the derivative of (4) with respect to  $T$  ( $\epsilon = \alpha_s T$ ) for  $a_1$ ,  $a_2$ , the following equations are obtained:-

$$a_1 = -\alpha \left( \frac{E}{2kT_0^2} + \frac{a^2 T_0}{3} \right) + (1 - \alpha)b + 3GF \alpha_s \quad (7)$$

$$T_0 a_2 = +\alpha \left( \frac{E}{2kT_0^2} - \frac{a^2 T_0}{6} \right) - 6 GF \alpha_s T_0 \left( \frac{E}{2kT_0^2} + \frac{a^2 T_0}{3} \right) \quad (8)$$

The notation follows Pike and Seager; E - charging energy, a - describes T dependence of tunnel barrier,  $\alpha = r_b/(r_b + r_g)$ , b - temperature coefficient of resistivity of metal-like grains. With regard to equations (7) and (8) the following comments can be made:-

- i) the change of  $\alpha_f$  with varying  $v_{SiO_2}$  has been neglected (cf. Section 1). Also, the difference between  $\alpha_f$  and  $\alpha_s$  can be neglected.
- ii) The second term in (8) is due to the derivative  $\partial^2 r_o / \partial T \partial \epsilon$ .
- iii) The derivative  $\partial^2 r_o / \partial \epsilon^2$  has been neglected, because (in spite of (Eq. 6)) up to now no non-linear behaviour of  $R_{\square}$  with respect to  $\epsilon$  has been observed.
- iv) The factors 3 and 6, respectively, arise because a change of T leads to strain components in three directions, and each of these contributes to the change of  $R_{\square}^7$ .

With regard to the other terms the reader is referred to reference (2).

### 3) ANALYSIS OF EXPERIMENTS AND DISCUSSION

The model developed in the preceding section enables a very detailed discussion to be made as regards the influence of  $SiO_2$  on the electrical conduction in the TFRs.

Firstly, it should be noted that within the investigated series the same ruthenate powder has always been used. Thus, and because chemical reactions between ruthenate and  $SiO_2$  are negligible, E and b in equations (7), (8) cannot depend on  $v_{SiO_2}$  (E is given by  $E = e^2 / 2\pi\epsilon\epsilon_0 d^2$ , d - diameter of ruthenate grains). GF values are obtained from experiment and depend weakly on  $R_{\square}$  and  $v_{SiO_2}$ , respectively. Thus, substituting glass by  $SiO_2$  leads to a change of  $\alpha$  and/or a. Secondly, it has to be emphasized that a change of 'a' alone cannot explain the experiments: according to equations (7), (8) in that case  $a_1$  as well as  $a_2$  should both increase or decrease, whereas with increasing  $v_{SiO_2}$ ,  $a_1$  decreases and  $a_2$  increases (cf. Figure 1). Thus it follows from the dependence of  $a_1$  and  $a_2$  on  $v_{SiO_2}$  that  $\alpha = r_b/(r_b + r_g)$  increases with increasing  $v_{SiO_2}$ . By means of simple mathematics from equations (7) and (8) four equations (magnitude and slope for  $a_1$  and  $a_2$ ) follow for five variables: E, a, b,  $\alpha$  and its derivative with respect to  $v_{SiO_2}$ ; (GF is obtained by experiment,  $\alpha_s \approx 6.1 \text{ ppm} \cdot K^{-1}$ ,  $T_o = 300 \text{ K}$ ). Hence, assuming a reasonable value for  $\alpha(v_{SiO_2} = 0)^2$  and a = const. all the other parameters can be calculated. These results are given in the following table:

TABLE I  
Microscopic parameters, determining conduction in TFRs from dependence of  $R_{\square}(T)$  on  $v_{SiO_2}$

$\alpha(v_{SiO_2} = 0)$	E/k	a	b	$\alpha(8.8 \text{ vol}\%)$
0.8	27 K	$1.2 \cdot 10^{-3} K^{-1}$	$57 \cdot 10^{-6} K^{-1}$	1.15
0.6	53 K	$1.5 \cdot 10^{-3} K^{-1}$	$234 \cdot 10^{-6} K^{-1}$	0.76

It has to be emphasized, that the results for E, a, b follow from  $a_1, a_2, \alpha(v_{SiO_2} = 0)$  without any further assumptions. The agreement with the figures given in<sup>4</sup> is excellent. Because, by definition,  $\alpha < 1$ , the results for the case  $\alpha(v_{SiO_2} = 0) = 0.6$  are more acceptable.

### 4. CONCLUSION

Summarizing, the following can be concluded:-

- i) substituting glass by  $SiO_2$  results in an increase of the resistance of the tunnel barrier

ii) this explains, why  $a_1$  and  $a_2$  in equation (1) change in the opposite way. The different slopes in Figure 1 are determined mainly by E and b because GF depends weakly on  $R_{\square}$  or  $v_{\text{SiO}_2}$ .

iii) a change of the parameter, 'a', due to different resonance centres cannot be excluded, but is not observable because of the effects for the tunnel barrier

iv) the derived values for both 'a', and temperature coefficient of resistivity of the metal-like phase, b, agree with published estimations. The value of  $E/k = 53$  K corresponds to a mean grain size of  $0.04 \mu\text{m}$ , in rough agreement without BET measurements.

It should be remarked that it is not possible to explain the change of  $R_{\square}$  by that of  $\alpha$ , because the structure of the network (e.g. the numbers of chains and microresistors l, m, n) can be influenced by the SiO<sub>2</sub> content. For the investigation of the TCR,  $a_1$  and  $a_2$  this is unimportant, as these quantities do not depend on l, m, n.

All these conclusions are valid only for the ruthenate/glass system that has been studied. For other ruthenate glasses the situation may be quite different.

#### ACKNOWLEDGEMENT

We would like to thank all our colleagues, who helped these investigations by preparing special inks, firing samples and performing physical measurements. We are especially indebted to Dr. F. Müller for his critical remarks and helpful discussions.

#### REFERENCES

1. DE-OS 21 31 553, DE-AS 24 03 628, US 3553 109
2. G.E. Pike, C.H. Seager, "Electrical properties and conduction mechanism of ruthenium based thick-film (cermet) resistors", *J. Appl. Phys.* **48**, 5152 (1977).
3. I. Storbeck, M. Wolf, "On experimental data of the TCR of TFRs and their relation to theoretical models of conduction mechanism". *Electrocomp. Sci. and Technol.* in press
4. (a) W.H. de Jeu, R.W.J. Geuskens, G.H. Pike, "Conduction mechanism and  $f^{-1}$ -noise in thick-film resistors with  $\text{Pb}_3\text{Rh}_7\text{O}_{15}$  and  $\text{Pb}_1\text{Ru}_2\text{O}_7$ ", *J. Appl. Phys.* **52**, 4128 (1981).
4. (b) M. Prudenziati, A. Rizzi, P. Davoli and A. Mattei, "Tunnelling in thick-film (cermet) resistors and the minimum of resistance". *Nuovo Cim.* **2D**, 697 (1983).
5. M. Prudenziati, B. Morten, C. Martini, G. Bisio, "High frequency response and conduction mechanism in thick-film (cermet) resistors" in "Recent Devel. in Cond. Matter Phys." ed. by J.T. Devreese et al., Plenum Press, New York and London 1981 vol. **2**, p. 399.
6. M. Prudenziati, "Conduction mechanisms in thick-film resistors", *Proceedings 3rd European Microelectronics Conference*, Avignon, p. 1 (1983).
7. C. Canali, D. Malavasi, B. Morten, M. Prudenziati and A. Taroni, "Strain sensitivity in thick-film resistors", *IEEE Transact. on Comp., Hybrids and Manufact. Technol.* **CHMT-3**, 421 (1980).



**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

