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ELECTRON TUNNELING AND HOPPING POSSIBILITES IN RuO_2 THICK FILMS

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It is proposed in this paper that the temperature coefficient of resistivity (TCR) in thick film resistors arises from (i) the usual particle-to-particle conduction, (ii) electron tunneling, and (iii) the phonon-assisted hopping. Equations for activation energies are derived for the temperature minimum of the resistance with and without hopping. New equations for TCR are suggested. Some extensive calculations of TCR and activation energy have been made for RuO_2 thick film resistors, the results of which agree well with available experimental measurements.

1. INTRODUCTION

It is generally believed[1,2] that the conduction mechanism in thick film resistors is of two types: one is direct particle-to-particle contact and the other is quantum-mechanical tunneling. Fine metallic particles uniformly dispersed in a glassy medium, fired at a suitably high temperature and slowly cooled to room temperature can provide[3] a suitable situation for the above two mechanisms to occur at the same time. For the tunneling mechanism, however, there are two possibilities: (i) resonance-type tunneling which is today the most widely accepted[4] process for thick film phenomena and (ii) phonon-assisted hopping or electron hopping, first proposed by Mott[5] in his theory of amorphous semiconductors.

The theory of electronic conduction in thick film resistors using resonance-type tunneling has been developed by Pike[6] and Pike and Seager.[7] This theory has been recently applied[8-10] to many thick film resistors, but there are some instances[4,11] where deviations from this theory could be observed, especially when the percentage of the metallic particles in the glassy medium is rather low. The main objective of this paper is to emphasize that when the phonon-assisted hopping[9] is appropriately included along with the resonance-type tunneling, not only the earlier theory[6,7] can be improved, but also the physics of the situation can be more correctly described. We shall first develop here an equation for the temperature coefficient of resistivity (TCR) with hopping and then obtain equations for activation energy involving temperature minimum of resistance. We shall then make computer calculations of various TCR and activation energy curves and compare them directly with experimentally measured values of RuO_2 thick films.

2. THEORETICAL CONSIDERATIONS

In Figure 1 we show a typical electron path for particle-to-particle conduction, but for the tunneling mechanism we consider in Figure 2, an energy band diagram for the electron passing through the nonparticle or glassy region.

a) Metallic Conduction and Resonance Tunneling

If we consider only particle-to-particle conduction and simple resonance-type tunneling the total resistance of the film can be easily written. According to Pike and Seager[7] the

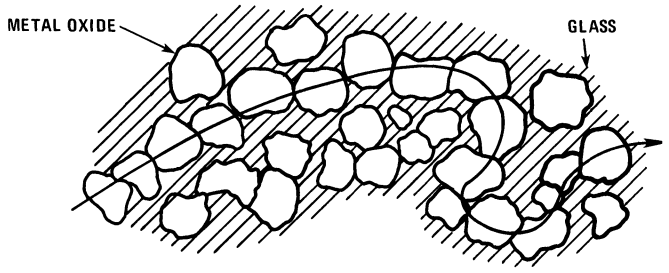

FIGURE 1 The particle to particle conduction in a thick film resistor.

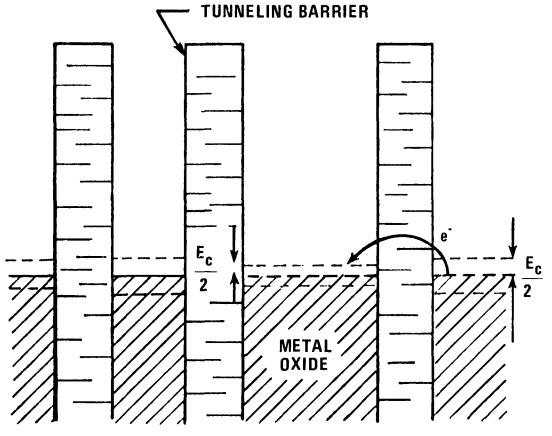

FIGURE 2 The tunneling mechanism of an electron in a thick film resistor. The resonance-type tunneling occurs when the width of the barrier is thin, such as the one in extreme left barrier. However, the phonon asisted hopping is possible when the width is wide enough, allowing many electron steps before tunneling out the barrier.

resistance in a series combination is given by

$$R = R_m + R_b \tag{1}$$

where

$$R_m = R_{mo}(1 + bT) \tag{2}$$

and

$$R_b = \frac{1}{2} R_{bo} \left(\frac{\sin aT}{aT}\right) \left[1 + \exp\left(\frac{E}{kT}\right)\right] \tag{3}$$

This equation can be simplified as has been further demonstrated by Pike and Seager.[7] Since $a \sim 5 - 10 \times 10^4/^\circ K$ for RuO_2 films, $aT \ll 1$ and activation energy $E \ll kT$ for the temperature range 0 to 600°K and $E \sim 1 - 10 \times 10^{-3}$ eV

$$R_b \simeq \frac{1}{2} R_{bo} \left(1 - \frac{1}{6} a^2 T^2\right) \left(2 + \frac{E}{kT}\right)$$
$$= R_{bo} \left(1 - \frac{1}{6} a^2 T^2\right) (1 + E/2kT) \tag{4}$$

In the above equations R_{mo} is the resistance of the metallic particles at the lower temperature, b is the temperature coefficient of resistance of this metal, a is a function of the barrier height,[7] and E is the activation energy (which is also equal to half the charging energy). Then the TCR which is defined as

$$\gamma = \frac{1}{R} \left(\frac{\partial R}{\partial T}\right) \tag{5}$$

can be obtained easily

$$\gamma = -\alpha' \left[\frac{a^2 T}{3} \left(1 + \frac{E}{4kT}\right) + \frac{E}{2kT^2}\right] + \frac{b}{(1 + bT)}$$
$$- \frac{\alpha' b}{(1 + bT)} \left(1 - \frac{a^2 T^2}{6}\right) \left(1 + \frac{E}{2kT}\right) \tag{6}$$

where

$$\alpha' = R_{bo} (R_b + R_m)^{-1} \tag{7}$$

Eq. (5) predicts a minimum value of R at certain temperature minimum T_m. We then get an activation energy equation with this T_m,

$$E = \frac{\dfrac{b}{(1 + bT_m)} \left[1 - \alpha' \left(1 - \dfrac{a^2 T_m}{6}\right) - \dfrac{\alpha' a^2 T_m}{3}\right]}{\dfrac{\alpha' a^2}{12\,K} + \dfrac{\alpha'}{2kT_m^2} + \dfrac{b\alpha' \left(1 - \dfrac{a^2 T_m^2}{6}\right)}{(1 + bT_m) 2kT_m}} \tag{8}$$

which can be reduced to

$$E = \frac{2k \left[\dfrac{6bT_m^2}{1 + bT_m} \left(\dfrac{1}{\alpha'} - 1\right) - 2a^2 T_m^3\right]}{\left[a^2 T_m^2 + 6 + \dfrac{6b}{(1 + bT_m)} \left(1 - a^2 \dfrac{T_m^2}{6}\right) T_m\right]} \tag{9}$$

In the present paper, α is different from α' and defined by

$$\alpha = R_b (R_b + R_m)^{-1} \tag{10}$$

In the Pike-Seager[7] work Eq. (6) was approximated (see their Eq. (10)) and the third term in the denominator of Eq. (9) (compare with their Eq. (12)) was neglected to a first approximation. Furthermore, no distinction was made between α' and α.

b) Metallic Conduction, Resonance Tunneling and Hopping

Mott[5] has shown that for electrons in a highly disordered system the dc conductivity (σ) has its contribution from thermally activated hopping. If we do not consider a very high temperature regime, then two possibilities exist: the weak field hopping and the strong field hopping.

For weak field hopping (i.e., when $eRF \ll kT$) the conductivity is given by

$$\sigma = 2e^2 R^2 \nu_p N(E_F) \exp\left(-2\alpha R - \frac{W}{kT}\right) \tag{11}$$

where

$$\text{W(hopping energy)} = \frac{1}{R_o^3 N(E_F)} \quad \text{for } \alpha R_o \gg 1 \text{ and}$$

$$= \frac{3}{4\pi R^3 N(E_F)} \quad \text{for } \alpha R_o \leqslant 1 \tag{12}$$

$$\text{R(hopping distance)} = \frac{3^{1/4}}{(2\pi\alpha N(E_F)RT)^{1/4}} \tag{13}$$

$$\nu_p \text{(hopping probability)} = \exp\left(-\frac{B}{T^{1/4}}\right) \tag{14}$$

$$\text{B(constant)} = 1.66 \left[\frac{\alpha_m^3}{kN(E_F)}\right]^{1/4} \tag{15}$$

where

$$\alpha_m = \frac{(2mW_o)^{1/2}}{\hbar}, \text{ and } W_o = E_c - E \tag{16}$$

In the above equations F is the field, R_o is the average nearest neighbor distance and $N(E_F)$ is the density of states (DOS) at the Fermi energy. For the sake of convenience the above expression may be written in a more compact form as

$$\sigma = A \exp\left(-\frac{B}{T^{1/4}}\right) \tag{17}$$

where

$$A = e^2 N(E_F)\,\bar{R}^2 \tag{18}$$

and

$$\bar{R}^2 = 3R/4 \tag{19}$$

Another approach based on the percolation theory[5] yields the same equation Eq. (17), but values for the two constants are different.

$$A = 0.022(C\alpha)\left(\frac{T_o}{T}\right)^{0.35} \tag{20}$$

and

$$B = (T_o)^{1/4} \tag{21}$$

where T_o and C are explicitly defined in Reference 5.

There is a considerable discussion in the literature about the value of B which supposedly varies from 1.78 to 2.48, but apparently not much is said about A. We will refer to these constants as Mott's A and B constants. In two dimension, however, Eq. (17) takes the form (which may be valid in some thin film studies)

$$\sigma = A \exp\left(-\frac{B}{T^{1/3}}\right) \tag{22}$$

where

$$B = \frac{3\alpha^2}{N(E_F)k} \tag{23}$$

For strong field hopping (i.e., when $eRF \gg kT$) the electron hops from higher to lower energy state without thermal activation. In this case the conductivity expression is shown to be

$$\sigma = A' \exp\left(-\frac{B}{T^{1/4}}\right) \tag{24}$$

where A' is another constant different from Mott's A and B coefficients.[5] We now denote the phonon-assisted (or hopping) resistance

$$R_p = \sigma^{-1}(l/S) \tag{25}$$

where l and S respectively represent the length and cross-sectional area of the film. Therefore the total effective resistance should read as

$$R = R_m + R_B \tag{26}$$

Two different situations of practical interest can now be discussed.

(i) Parallel connection mode: If the barrier resistance R_b and the hopping resistance R_p are considered in the parallel mode, the total effective barrier resistance will be

$$R_B = R_b R_p (R_b + R_p)^{-1} \tag{27}$$

giving a modified TCR equation

$$\gamma_m = \gamma\beta_o - \frac{\alpha'(1+2\beta)}{(1+\beta)^2}\left[\left(1 - \frac{a^2T^2}{6}\right)\frac{E}{2kT^2} + \left(1 + \frac{E}{2kT}\right)\frac{a^2T}{3}\right] - BT^{-5/4}\beta_1/4 \tag{28}$$

where

$$\beta_o = \frac{(1+\beta)}{(1-\alpha+\beta)} \tag{29}$$

$$\beta_1 = \frac{\alpha\beta}{(1+\beta)(1-\alpha+\beta)} \tag{30}$$

$$\beta = R_p/R_b \tag{31}$$

which gives, after some algebra, the activation energy

$$E = \frac{\dfrac{\alpha' a^2 T_m \beta_o}{3} - \dfrac{b\beta_o}{(1+bT_m)} + \dfrac{\alpha' b}{1+bT_m}\left(1 - \dfrac{a^2T_m^2}{6}\right)\beta_o + \dfrac{\alpha'(1+2\beta)}{(1+\beta)^2}\dfrac{a^2T_m}{3} + \dfrac{BT_m^{-5/2}\beta_1}{4}}{-\dfrac{\alpha' a^2\beta_o}{12k} - \dfrac{\beta_o\alpha'}{2kT_m^2} - \dfrac{\alpha'(1+2\beta)}{(1+\beta)^2}\dfrac{\left(1 - \dfrac{a^2T_m^2}{6}\right)}{2kT_m^2} - \dfrac{\alpha'(1+2\beta)}{(1+\beta)^2}\dfrac{a^2T_m}{6kT_m} - \dfrac{\alpha' b}{(1+bT_m)}\left(1 - \dfrac{a^2T_m^2}{6}\right)\dfrac{\beta_o}{2kT_m}} \tag{32}$$

In this equation E depends only on the value of T_m and not on T; furthermore, it is exact for samples with hopping in the weak field case.

(ii) Series connection mode: If, however, we choose to have a series-connection mode for R_b and R_p instead of a parallel-connection mode as discussed previously, we will find

$$R = R_m + R_b + R_p \tag{33}$$

which gives

$$\gamma_m = \gamma\beta_o - BT^{-5/4}\beta_1 D/4 \tag{34}$$

where

$$D = \frac{1-\alpha+\beta}{(1+\alpha\beta)(1+\beta)} \tag{35}$$

This now leads us to

$$E = \frac{\dfrac{b}{(1+bT_m)}\left[1-\alpha'\left(1-\dfrac{a^2T_m^2}{6}\right)\right] - \dfrac{\alpha' a^2 T_m}{3} - C}{\dfrac{\alpha' a^2}{12k} + \dfrac{\alpha'}{2kT_m^2} + \dfrac{b\alpha'}{1+bT_m}\dfrac{\left(1-\dfrac{a^2T_m^2}{6}\right)}{2kT_m}} \tag{36}$$

The significance and usefulness of these derivations may be realized when we apply them to the experiments made for RuO_2 thick films by us[11] as well as those done by others.[12–15] In the above equation C is defined by

$$C = \left(\frac{\beta_1}{\beta_o}\right)(DBT^{-5/4}/4) \tag{37}$$

3. COMPUTATION OF γ_m AND E FOR RuO_2 THICK FILM RESISTORS

In this section we will present our results of computations for RuO_2 thick film resistors. The range of the parameters α, β, and E studied in this investigation is given in Table I.

TABLE I
Data used in the calculation of resonance and hopping plots

α	β	E
0.5	0.5	1.0×10^{-3} eV
0.6	0.6	1.4
0.7	0.7	1.8
0.8	0.8	2.2
0.9	0.9	2.6

Note: The relation between α' and α may be expressed[11] as $\alpha = \alpha'\left[\left(1-\dfrac{a^2T^2}{6}\right)\left(1+\dfrac{E}{2kT}\right)\right]$

The value b for the temperature coefficient of resistance of Ru was considered to be $5 \times 10^{-4}/^{\circ}K$.

(a) Resonance Part

For resonance tunneling, we have calculated γ and E using Eqs. (5) and (8). For the sake of comparisons we have also used the Pike-Seager equations. All these results are plotted in Figures 3 and 4. Some small difference was observed between the two sets of γ in Figure 5, but the general trends of the curves were the same. The activation energy E from the Pike-Seager equation turned out to be 10% at low temperature, but 70% at high temperature – larger than those calculated from present equations. In the absence of hopping a most likely value of $\alpha \simeq 0.7$ has been suggested by Pike and Seager.[7] With this value of α and finding out T_m experimentally, it is possible to obtain the activation energy E of the film (the energy range 1.0 to 2.6×10^{-3} eV was investigated for this purpose).

(b) Hopping Part

We next consider calculations with hopping as pointed out earlier. For several sets of values of α and β we calculated γ_m for parallel and series connection modes in the energy range 1 to 2.6×10^{-3} eV. We only show here two such sets in Figures 5 and 6. The activation energies E were obtained likewise, these are shown in Figures 7 and 8. These energies do not depend on any particular value of E, but are strong functions of α and β. It is seen

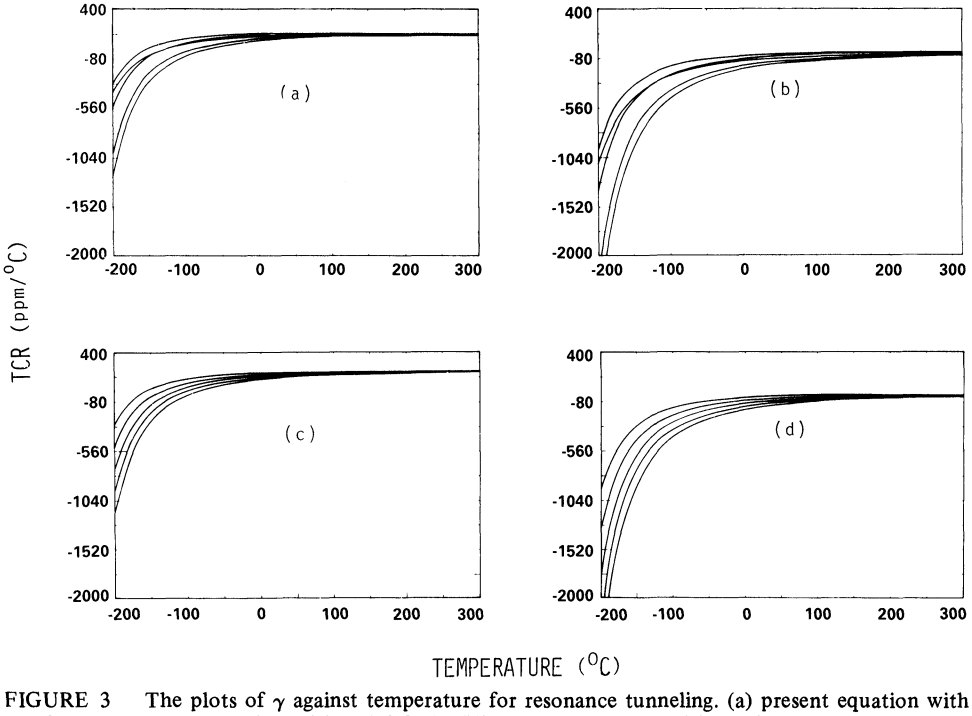

FIGURE 3 The plots of γ against temperature for resonance tunneling. (a) present equation with $\alpha = 0.5$, (b) present equation with $\alpha = 0.9$, (c) Pike-Seager equation with $\alpha = 0.5$ and (d) Pike-Seager equation with $\alpha = 0.9$. The plots are made for the energies 1.0, 1.4, 1.8, 2.2, 2.6×10^{-3} eV. The top plot in each of the figures refers to the lowest energy and the bottom one to the highest energy.

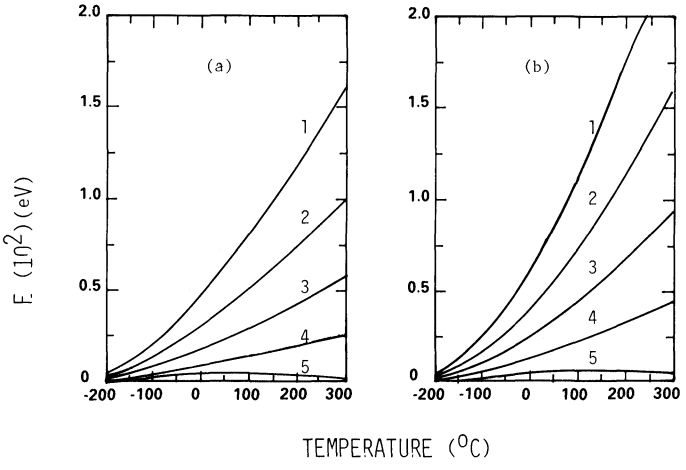

FIGURE 4 The plots of activation energies against temperature minimum at various values of α (= 0.5, 0.6, 0.7, 0.8, 0.9) for the (a) present equation, (b) Pike-Seager equation. Curves 1 through 5 go in the increasing order of α.

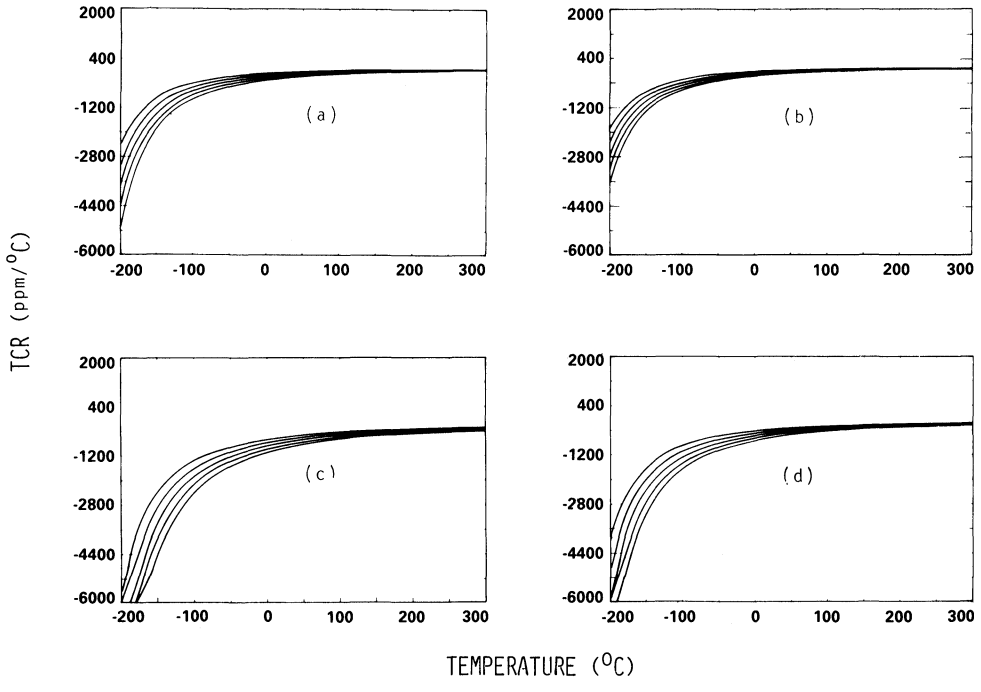

FIGURE 5 The plots of γ_m against temperature at various energies (1, 1.4, 1.8, 2.2, 2.6 $\times$ 10^{-3} eV)

(a): parallel mode with $\alpha = 0.6$ and $\beta = 0.5$
(b): series mode with $\alpha = 0.6$ and $\beta = 0.5$
(c): parallel mode with $\alpha = 0.9$ and $\beta = 0.5$
(d): series mode with $\alpha = 0.9$ and $\beta = 0.5$

The top curve in each of the figures refers to the lowest energy and bottom one the highest energy.

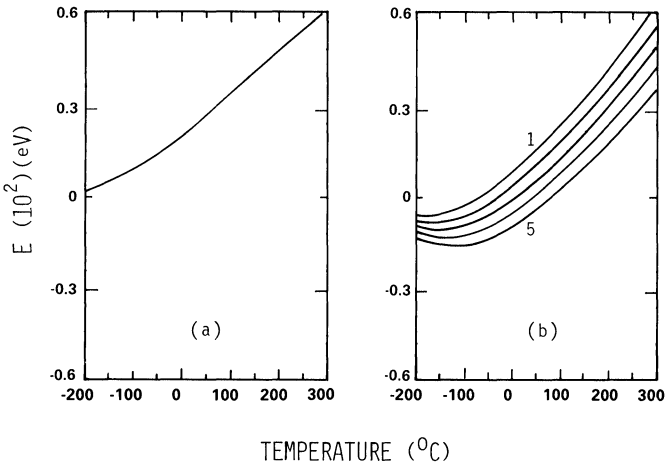

FIGURE 6 The plots of activation energies against temperature minimum for

(a): parallel mode with α = 0.6 and β = 05, 0.6, 0.7, 0.8 and 0.9
(b): series mode with α = 0.6 and β = 0.5, 0.6, 0.7, 0.8 and 0.9.

Please note that the curves for different β's were the same within the plotting scale. Curve 1 to 5 means β increasing from 0.5 to 0.9.

from Figures 7(a) and 8(a), for the parallel mode, E changes noticeably with α, but is rather insensitive to the change of β. However, for the series mode, E is sensitive to both α and β. This is quite contrary to what we have seen for resonance tunneling as displayed in Figures 4(a) and 4(b).

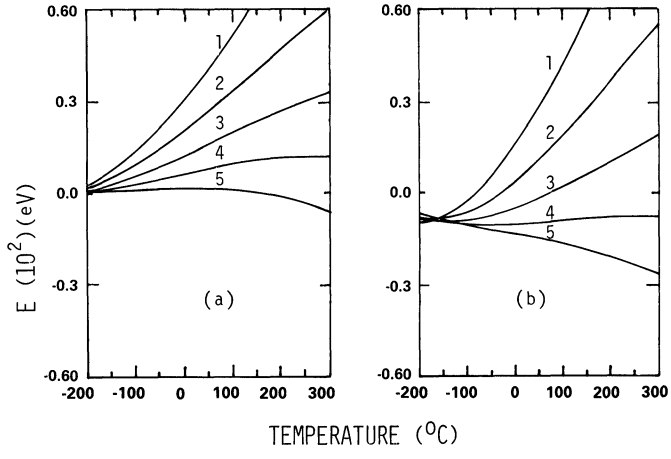

FIGURE 7 The plots of activation energies against temperature minimum for

(a): parallel mode with β = 0.6 and α = 0.5, 0.6, 0.7, 0.8 and 0.9
(b): series mode with β = 0.6 and α = 0.5, 0.6, 0.7, 0.8 and 0.9

Here curve 1 to 5 means increasing order of α.

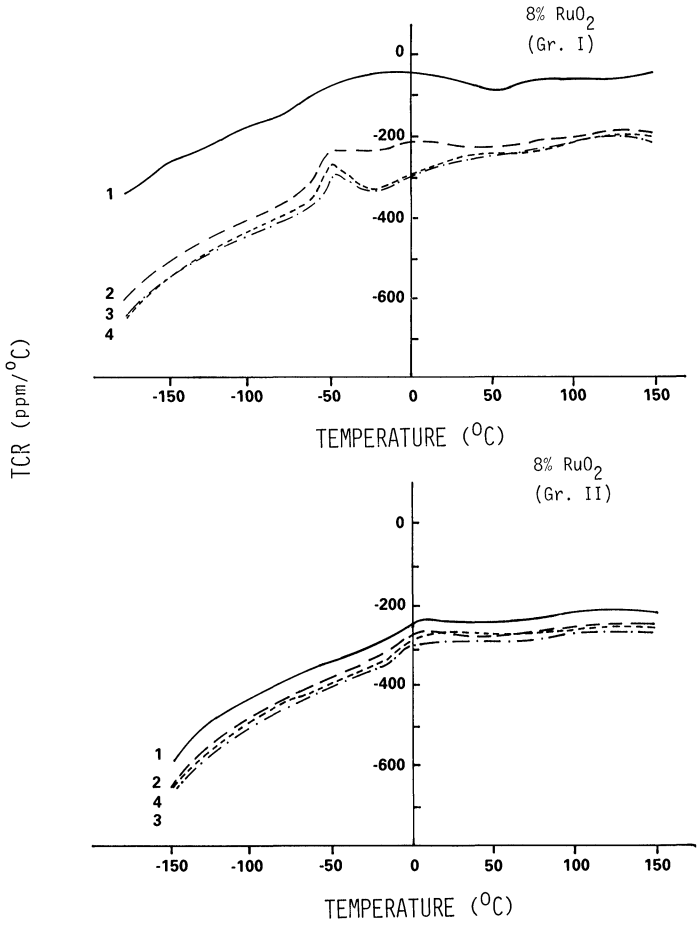

FIGURE 8 The experimental plots of α for 8% RuO_2 films as measured by Schaffer and Sergent.[12] The dimension[2] of the films were (1) 20 mil. X 20 mil., (2) 40 mil. X 40 mil., (3) 60 mil. X 60 mil., (4) 80 mil. X 80 mil. Group I and Group II represent particle size of 3.1 and 2.2 μ respectively.

Comparison with Experimental Results

We now examine the above results of TCR in the light of several recent experimental measurements.[11–15] In Figures 9 and 10 are shown some results for RuO_2 thick films as measured by Schaffer and Sergent[12] and Chen and Smith.[13] The later experiment of Chen et al.[15] has the same result as their earlier work[13] for resistance and TCR but the range of temperature has been extended. While experimental details of these measurements can be found in these referenced papers, the highlights of these measurements may be summarized here. These films were made of a resistive ink which consists of RuO_2 conductor particles, a glassy binder and an organic liquid. To prepare a resistor, the ink was first screen printed on ceramic substrates and then fired on a belt furnace usually around 800°C. By this process, the organic binder was evaporated but the RuO_2 particles were fused into the substrate through the glassy background.

We do not have actual experimental data for the activation energies and therefore no direct comparison can be made with the calculated plots of Figures 4 and 6. However,

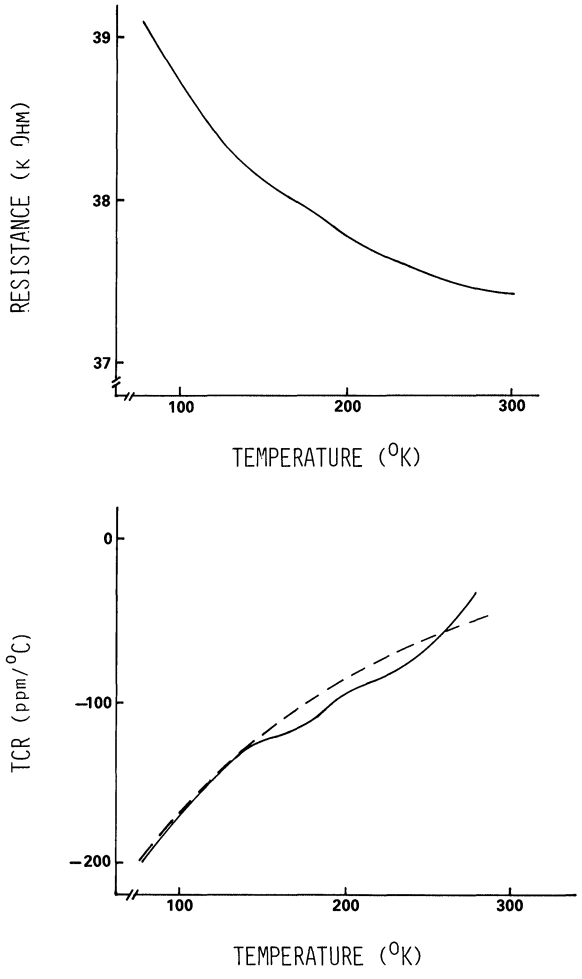

FIGURE 9 The experimental resistance and TCR data for RuO_2 films as reported by Chen and Smith.[13] The dimensions of the films were 100 mil. x 200 mil. and 0.5 mil. thick.

recent experimental work of Chen et al.[15] indicates a value for $T_m = 280°K$, where resistance is minimum for their RuO_2 film. If we take this value of T_m to calculate the activation energies we find, for $\alpha = 0.6$, $E = 3.0 \times 10^{-3}$ eV from Eq. (5) and $E = 4.2 \times 10^{-3}$ eV from Pike-Seager equation. It would seem quite appropriate to quote the values which Pike and Seager[7] found in their work with RuO_2 films determined from their measured values of T_m. These values range from 1.5 to 3.8×10^{-3} eV, which are in good agreement within our calculated numbers as observed from Figures 4 and 6. When hopping is present energy curves show much less dependence on temperature. One way to test whether or not hopping plays any meaningful part in the electronic conduction in thick film resistors is to measure E vs. temperature curves. A steeper slope of these curves, i.e., $\left(\frac{\partial E}{\partial T}\right)_T$, would indicate a possibility of only a resonance-type tunneling. The negative energy curves (curve numbered 5) in Figures 7(a) and 7(b) indicate a situation for a particular combination of the data α and β, which may not exist in an actual thick film resistor.

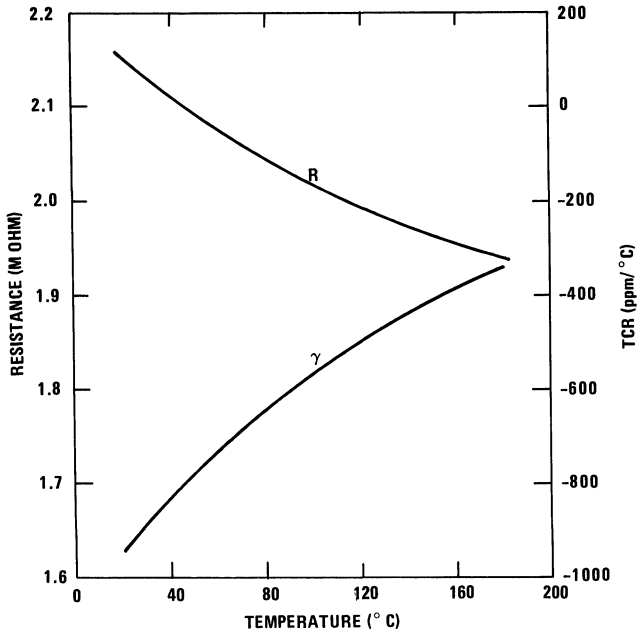

FIGURE 10 The present experimental plots of resistance and TCR for 11 μ thick RuO_2 films (with 2% RuO_2 and 0.3 μ particle size) in the 20–200 °C range. Note the high resistance and large γ in this film.

That is to say, it is not possible to have a thick film with arbitrary values of α and β.

Of the two sets of experimental[12,13] data, only in Figure 8 is the percentage of RuO_2 known[12] (8%). Presumably in Fig. 9 the percentage of RuO_2 should be about 20% by volume, which is calculated from the data of Chen et al.[15] of the resistance equal to 10 kΩ/sq., and the conductivity – percentage plot of Angus and Gainsbury (see Ref. 2 Vol. II). These two sets of plots seem to agree with our calculated plots in Figure 3(a) or 3(c) obtained without hopping. The general trend including the magnitude agree within 5% for α = 0.6. We, however, cannot find any physical reason for the presence of small humps observed around −50°C in Gr. I and around 0°C in Gr. II films in Figure 8. We believe these could very well arise from the experimental error[12] in the measurement or some artifact in plotting the data.

To find results to be compared with the plots of Figure 5, one must experiment with very small-percentage (less than 2%) of RuO_2 in the films. Our own experimentation with small-percentage RuO_2 thick films has been in the limited range of 25 to 200°C. In this range as is evident from Figure 10, the TCR has a slowly increasing trend, but stays negative all the way. We indeed observed such results (−942 to −250 ppm/°C). Detailed experimental work for the whole range of temperature is currently in progress for RuO_2 thick films. Further measurement on activation energy and barrier height will supplement this work. These results will be reported separately.

4. CONCLUSION

This paper calculates, for the first time, the TCR and the activation energy of RuO_2 thick film resistors with hopping. A comparison is then made with three sets of recent experi-

mental measurements. The results of the present investigation along with the experimental data, indicate that the hopping is important when the percentage of RuO_2 in the glassy matrix is rather low in the 2 - 5% range. When the percentage of RuO_2 is high the two well known mechanisms, i.e., particle-to-particle conduction and electron tunneling are sufficient to explain the observed TCR in those films. The present suggestion with regard to the TCR equation and activation energy takes one more step beyond the well known Pike-Seager theory, and helps us to understand the available experimental results better.

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